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A PALEOCLIMATIC STUDY OF THE MIDWESTERN UNITED STATES FROM
THE STABLE ISOTOPE RECORDS IN LAKE SEDIMENTS

by

Norman Alan Lovan

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Geology

Western Michigan University
Kalamazoo, Michigan
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A PALEOCLIMATIC STUDY OF THE MIDWESTERN UNITED STATES FROM THE STABLE ISOTOPE RECORDS IN LAKE SEDIMENTS

Norman Alan Lovan, Ph.D.

Western Michigan University, 1998

Stable isotope records from both the organic and inorganic components of lake sediments have been obtained from radiocarbon dated cores raised from Ladd Lake in Ohio and Lake Winnebago in Wisconsin. The hydrogen (δD) and carbon ($\delta^{13}C$) isotope records extracted from sediment bulk organic matter and the oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) taken from calcium carbonate provide a unique means to obtain a continuous fine resolution record of environmental change on a regional scale. Sediment organic matter was concentrated by successive digestion in HCl followed by HF:HCl using a newly developed microwave acid digestion procedure. Hydrogen was extracted using a newly developed pyrolysis technique that provides a simple and reliable method for collecting hydrogen isotopic data from sediment organic matter with an overall reproducibility of better than 3%. Carbon to nitrogen ratios (C/N) were used to constrain the organic carbon data. Oxygen and carbon were extracted from sediment carbonate material using the septum phosphoric technique of Krishnamurthy et al. (1997).

The isotopic hydrogen and carbon record from Ladd Lake indicate rapid transitions between cool and warm phases over a 22,000 calendar year period. These

data suggest that the so-called Mid-Holocene warm phase from ~8.5ka BP to 3ka BP (thousand calendar years before present) experienced oscillatory cooling periods throughout this ~6ka year interval. This may result from changes in relative dominance of precipitating air masses or changes in the seasonality (longer summers-shorter winters, etc.). In a world first, by combining the oxygen isotope ratio ($\delta^{18}\text{O}$) of calcium carbonate and the hydrogen isotope ratio (δD) of coexisting organic matter from the Lake Winnebago core, an inferred paleotemperature record was generated. These results show that during the Mid-Holocene warm period ~6-2ka BP, the spring-summer lake temperatures were as much as 6-10⁰ C higher than present. This might result from changes in the length of season's i.e., longer summers and shorter winters. The isotopic records from both lakes show evidence for cooler temperatures around 8ka and 2ka BP and significant climatic instability during this interval. Evidence for cooler temperatures in the Midwestern United States at 8ka BP is in agreement with recent observations from ice core studies and may thus have been a global event.

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Na chorayam na cha raja harayam
Na bhratru bhajyam na cha hara karee
Vyaye kruthe vardhathi yeva nityam
Vidya dhanam sarva dhanat pradhanam

ancient Sanskrit verse

Neither can it be stolen by thieves, nor confiscated by Kings
Neither can it be divided amongst brothers nor does it any harm
It grows more as more is spent
Wealth of knowledge is the greatest among all wealth's

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CHAPTER I

INTRODUCTION

Isotope Studies and Harold Urey

The use of stable isotopes in geologic and other disciplinary studies had its beginning in 1931 with the work of Harold C. Urey at the University of Chicago. From suggestions by his colleagues that naturally occurring isotopes of hydrogen may exist, Urey predicted on a theoretical basis that there should exist a difference in the vapor pressures of the isotopes of hydrogen (Faure, 1986). Using spectroscopic methods, Urey was able to detect an isotope having a mass nearly twice the mass of hydrogen in the residual volume of gas produced by evaporating approximately 6 liters of liquid hydrogen. Urey named this new isotope "deuterium" (Murphy, 1964). Interestingly, the specific causal reason for the existence of isotopes was not known until 1932 when Chadwick established the existence of neutrons in the atomic nuclei. Harold Urey was awarded the Nobel Prize for chemistry in 1934 for his discovery of deuterium.

Subsequent to these early studies and as a consequence of World War II, Urey became involved in developing methods for the separation of ^{235}U by gaseous diffusion.

Once the war ended, however, Urey re-focused his knowledge of isotopic fractionation to the possibility that natural processes could fractionate stable oxygen isotopes and that such fractionation might occur in marine carbonates. Urey further suggested that the

extent of fractionation is temperature dependent. It was from these ideas that a method of measuring the depositional temperature of marine skeletal calcium carbonate was developed. The resulting oxygen isotope method became a very useful proxy for global paleotemperature studies and gave rise to the branch of isotope geology that deals with the fractionation of the stable isotopes by naturally occurring physical and chemical processes. While this dissertation focuses primarily on the use of hydrogen as a paleoclimate proxy and is augmented by the study of isotopic ratios of oxygen and carbon, all such studies are owing to Urey's research and insight into the isotopic fractionation of elemental species.

Isotopic Fractionation

Each elemental species is composed of atoms having a unique number of protons that define the element and denote its atomic number. Soddy (1913) introduced the term isotope in suggesting that the place occupied by a particular element in the periodic table could accommodate more than one kind of atom. Later, isotopes came to be defined as atoms having the same number of protons but differing in their number of neutrons (Chadwick, 1932). Therefore, isotopes of a given elemental species differ in their atomic weights and in their nuclear properties which, in turn, lead to slight variations in their physical and chemical properties. The total number of different nuclides currently known to exist is close to 1700 (Faure, 1986). Thus, more than 1000 isotopes are formed as variants from the 92 naturally occurring elements. Furthermore, the isotopes of any element may be characterized as either radioactive or stable. Radioactive isotopes are

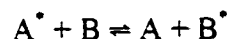
unstable and decay to a stable state via energy loss through release of α , β or γ particles and by electron capture. Stable isotopes do not undergo radioactive decay and only about 287 occur naturally from the near 1700 known nuclides.

The thermodynamic properties of a given molecule are largely dependent on the nuclear mass. Studies relative to the thermodynamic properties and fractionation characteristics of isotopic molecules report that the energy of a molecule within a chemical system can be described by its electronic energy plus the translational, rotational, and vibrational components (Urey, 1947; Bigeleisen, 1952, 1965; Bigeleisen and Mayer, 1947; Broecker and Oversby, 1971). Molecules containing different isotopes of an element in equivalent positions have different energies because of the differences in their vibrational components that are mass dependent. Consequently, isotope fractionation results from slight variations in the chemical and physical properties due and proportional to the mass differences between the isotopes of a given atomic species.

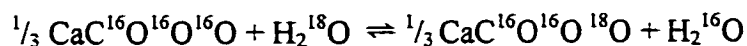
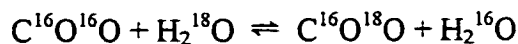
Faure (1986) describes the fractionation of stable isotopes by noting that the energy of a molecule decreases with decreasing temperature, and at absolute zero it assumes a certain finite value called the zero-point energy which is greater than the minimum value by $\frac{1}{2} h\nu$, where h is Planck's constant and ν is the vibration frequency. Furthermore, the vibration frequency of a molecule is inversely proportional to the square root of its mass. It follows, therefore, that a given molecule (i.e. a water molecule H_2O), which contains the lighter of two isotopes (hydrogen vs. deuterium) will have a higher vibration frequency and thus a higher zero-point energy. Consequently, bonds that form

between molecules possessing the lighter isotope are more easily broken and cause it to be more reactive than the similar molecule containing the heavier isotope. Isotopic fractionation, therefore, describes a phenomena wherein two isotopes of an element partition between two phases or substances and lead to a difference in the isotopic ratios (heavy isotope/light isotope) between these systems.

In natural systems, isotopic fractionation results from two main processes being equilibrium exchange reactions and kinetic (rate dependant) physical-chemical processes (Hoefs, 1980). Among chemical reactions, there are exchange reactions occurring at equilibrium conditions that involve only the redistribution of isotopic species between differing molecules without any change in the chemical system. A generic representation is shown in the simplified formula below wherein the asterisk indicates the heavier of the isotopic species. An example would be exchange of hydrogen between hydrogen-bearing



clay and organic matter in soils or organic rich lake sediment. In nature such reactions are numerous. The following are two examples involving the oxygen isotope exchange between water and carbon dioxide and between calcium carbonate and water.



Kinetic fractionation, unlike equilibrium reactions, occurs in irreversible processes that result mainly from differences in the reaction rates of isotopic molecules. The biochemical process of photosynthesis and the process of gaseous diffusion are examples that lead to kinetic fractionation. Similarly, other physical-chemical processes that result in isotopic (kinetic) fractionation include melting and crystallization, evaporation and condensation, adsorption and desorption, and diffusion of ions or molecules due to temperature or concentration gradients. For all of these chemical reactions and physical processes alike, it is the mass differences between the isotopes of a given element that effect the slight variations in the chemical and physical properties, which results in isotopic fractionation.

The Fractionation Factor (α)

The isotopic fractionation factor alpha (α) is similar to the concept of the chemical equilibrium constant but refers to isotopic equilibrium conditions between two phases and is similarly temperature dependant. As an illustration, consider the chemical reaction where $A + B \rightleftharpoons B + C$. Chemical equilibrium at a given temperature would be defined by the equation $K_{eq} = [B] [C] / [A] [B]$ or the product of the activities of the products over the product the activities of the reactants. Isotopic equilibrium or the fractionation factor at a given temperature is termed alpha (α). Alpha (α) is defined as the ratio of the heavy to the light isotope in a molecule of one phase divided by the ratio of the heavy to the light isotope in the same molecular species but in a different phase and

is written as follows:

$$\alpha_{A-B} = R_A / R_B$$

where R denotes the ratio of heavy isotope over the lighter isotope (D/H, $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$ etc.) in phases A and B respectively. To illustrate, consider the evaporative process in which the water molecule A in the liquid phase changes state to the water molecule B in the vapor phase or $A_{\text{liquid}} \rightleftharpoons B_{\text{vapor}}$. If in this change of state process our interest is in the isotopes of hydrogen, alpha would be defined as $^2\alpha = (\text{D/H})_{\text{liquid}} / (\text{D/H})_{\text{vapor}}$. Similarly, should our interest have been in the isotopes of oxygen, alpha would be written as the following: $^{18}\alpha = (^{18}\text{O}/^{16}\text{O})_{\text{liquid}} / (^{18}\text{O}/^{16}\text{O})_{\text{vapor}}$. The temperature dependence of alpha is of monumental importance when it is realized that the fractionation factor of any given system generally approaches unity at increasing temperatures. As a result, isotopic fractionation in nature is interpretable in terms of environmental temperature, and consequently, environmental change.

The Delta Notation (δ)

Delta notation is a means of expressing alpha (α) such that the small decimal changes in alpha can be easily scaled larger to magnify the differences in absolute isotopic ratios. The results are expressed as δ -notation in units per mil (‰) and are derived as follows:

$$\delta\text{‰} = [\alpha - 1] 10^3$$

$$\text{where } \alpha_{A-B} = R_A / R_B$$

$$\text{by substitution } \delta\text{‰} = [(R_A / R_B) - 1] 10^3$$

where R denotes the ratio of heavy over light isotopes of any element such as D/H, $^{18}\text{O}/^{16}\text{O}$ etc., and A and B are the respective phases or molecules. In practice, however, it is easier to measure the isotopic ratios relative to two substances rather than the absolute ratio. Thus the isotopic ratios are typically compared with respect to an international standard and are given by the following expression:

$$\delta\text{‰} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] 10^3$$

where R denotes the ratio of heavy over light isotopes of any element such as D/H, $^{18}\text{O}/^{16}\text{O}$ etc., both in the sample and the standard, respectively. The relationship between α and δ can be further illuminated by consideration of the reaction $A \rightleftharpoons B$ where A and B are individual phases or molecules of the same elemental species. Alpha, defined above as $\alpha = R_B / R_A$ may be re-defined in relation to the two phases or molecules by substituting δ values for A and B as follows:

$$\delta_A = [(R_A / R_{\text{std}}) - 1] 10^3$$

$$\delta_B = [(R_B / R_{\text{std}}) - 1] 10^3$$

by re-arrangement,

$$R_A/R_{\text{std}} = \delta_A/10^3 + 1 \text{ and } R_B / R_{\text{std}} = \delta_B/10^3 + 1$$

thus,

$$\alpha_{(A-B)} = R_B / R_A = (R_B/R_{\text{std}}) / (R_A/R_{\text{std}})$$

substitution yields $\alpha_{(A-B)} = (1000 + \delta_A) / (1000 + \delta_B)$

As will be shown in subsequent sections and chapters, this expression of α is very useful for establishing isotopic relations between differing phases or molecules.

The International Standards

The δ values of any given sample are reported with respect to internationally accepted standards. These standards are used to make inter-laboratory comparisons and provide common reference platforms from which δ values are interpreted. Preparation, calibration and distribution of acceptable standards are overseen by the International Atomic Energy Agency (IAEA) of the National Institute of Standards and Technology. Their preparation and cross calibration is discussed by Blattner and Hulston (1978), Gonfiantini (1978) and Coplen, et al (1982, 1983). The isotopic studies undertaken in this project include hydrogen, oxygen and carbon from the various sedimentary components that were analyzed.

There are several accepted standards available for reporting hydrogen and oxygen isotopic values. These are known as SMOW (Standard Mean Ocean Water), V-SMOW (Vienna-SMOW), NBS-1 (National Bureau of Standards-1), SLAP (Standard Light Antarctic Precipitation) and GISP (Greenland Ice Sheet Precipitation). SMOW, the primary international standard for oxygen and hydrogen, was originally prepared by Craig (1961) and possessed a value corresponding to a hypothetical water whose oxygen and hydrogen isotope ratios represent the mean isotopic ratio of all ocean waters (Craig 1961,

Epstein and Mayeda 1953, Horibe and Kobayabawa 1960). The reference value for SMOW is arbitrarily set at 0‰. Due to limited availability, however, the original SMOW standard has been replaced by Vienna SMOW (V-SMOW) which was artificially prepared by Craig (1966) at the request of IAEA. V-SMOW was prepared by distilling water collected from the Pacific Ocean at 0° latitude and 180° longitude. Its ^{18}O content is essentially identical to Craig's, 1961, SMOW standard which had been defined with respect to the existing NBS-1 water standard (Gathiersburg, MD, U.S.A.) as follows:

$$(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}} = 1.008 (^{18}\text{O}/^{16}\text{O})_{\text{NBS-1}}$$

$$(\text{D}/\text{H})_{\text{SMOW}} = 1.050(\text{D}/\text{H})_{\text{NBS-1}}$$

Craig (1961a) evaluated the isotope ratio of SMOW and found the following relationships:

$$(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}} = (1993.4 \pm 2.5) 10^{-6}$$

$$(\text{D}/\text{H})_{\text{SMOW}} = (158 \pm 2.0) 10^{-6}$$

The absolute values for V-SMOW have been evaluated and may be found in Baertschi 1976, Haegman, et al 1970, De wit, et al 1980. It has been agreed that for all practical purposes SMOW and V-SMOW are identical (Gonfiantini 1978) and the accepted practice is to report hydrogen and oxygen δ values as SMOW, even though it is V-SMOW that is available to laboratories through the IAEA.

In most laboratories, secondary reference standards are routinely prepared for day to day isotopic studies. These samples are frequently calibrated against the international

standards such as SMOW, PDB, NBS-1 and NBS-19 etc. The hydrogen and oxygen data presented in the present study were prepared from distilled waters taken from the distillation plant in the Institute for Water Sciences Stable Isotope Laboratory (IWS at Western Michigan University, Department of Geology) on various dates and designated LAB-1, LAB-5 and LAB-6. These reference waters were calibrated against SMOW and stored in airtight bottles. The final conversion with respect to SMOW was achieved using the following relation:

$$\delta_{\text{sample-SMOW}} = \delta_1 + \delta_2 + \delta_1\delta_2 \cdot 10^{-3}$$

where, $\delta_1 = \delta_{\text{sample-LAB}}$

and $\delta_2 = \delta_{\text{LAB-SMOW}}$

Each lab standard was repeatedly calibrated for its hydrogen and oxygen δ values. Calibration of LAB-1 with respect to SMOW resulted in mean δ values of $-65.7 \pm 1.5\text{‰}$ for hydrogen and $-10.4 \pm 0.1\text{‰}$ for oxygen. Similar results were obtained for the secondary LAB-5 and LAB-6 reference standards (as would be expected since their origin was from the same distillation facility). A detailed discussion of the calibration and comparison for laboratory standards used by the IWS Stable Isotope Laboratory at Western Michigan University (Department of Geology), i.e. LAB-1 with other international standards such as SLAP and GISP, is found in Machavaram (1993).

The standard used for carbon is the PDB (Peedee Belemnite) standard developed at the University of Chicago. The Peedee Belemnite is a Cretaceous Belemnite

(*Belemnitella Americana*) from the Peedee Formation of South Carolina. In actual practice, a working lab standard is compared to PDB in a manner similar to that previously discussed for hydrogen. The IWS Stable Isotope Laboratory at Western Michigan University converts to PDB values using the NBS-19 standard. Other standards are available for use in isotopic carbon analysis and include the Solenhofen limestone (NBS-20), Graphite (NBS-21), Petroleum Standard (NBS-22) and others. Carbon isotopes are normally analyzed as CO₂ gas using mass spectrometers equipped with double collectors (Craig, 1957). As a result, oxygen from the CO₂ molecule may also be analyzed using the PDB standard in addition to the SMOW and other standards sometimes used during analysis of water samples. There are many papers available discussing isotopic geology of carbon and its analysis, only a few are mentioned here (Schwarcz, 1969; Degens, 1969; Hoefs, 1980; Deines, 1980).

The study of stable isotope geochemistry and light element isotopic fractionation had a major breakthrough after the invention of the double inlet mass spectrometer by Neir in 1947. This instrument allowed the measurement of minute differences in isotopic abundance via the use of a double inlet and a double collector system by offering a means for precise comparison of a sample with a standard. With its use Harold Urey and his associates at the University of Chicago began a detailed study of natural isotope abundance of lighter elements which led to an understanding that water molecules could vary in isotopic composition. These pioneering studies gave way to related studies of the isotopic effects on phase equilibria, reaction rates and transport processes involving isotopic water species and laid the foundation for the quantitative understanding of natural

abundance variations of light element isotopes in nature.

Studies of the fractionation of hydrogen, oxygen, carbon, nitrogen and sulfur have provided information in a large variety of geological environments. The elemental group whose isotopes are especially susceptible to natural isotope fractionation includes the most abundant elements in the Earth. These comprise the light element isotopes of hydrogen, carbon, nitrogen, oxygen and sulfur. The natural abundance for some of the more frequently analyzed of these isotopes is tabulated in Table 1.

Table 1

Natural Isotopic Abundance of the Stable Isotopes of Hydrogen, Carbon, Nitrogen and Oxygen (After Faure, 1986; Lederer et al., 1967)

Isotope Species	% Isotopic Abundance
H	99.9852
D	0.0148
^{12}C	98.8900
^{13}C	1.1100
^{14}N	99.6300
^{15}N	0.3700
^{16}O	99.7590
^{17}O	0.0370
^{18}O	0.2040

Fractionation of Oxygen and Hydrogen in the Hydrologic Cycle

Oxygen is the most abundant chemical element in the crust of the Earth and combines with hydrogen to form water (H_2O). Oxygen has three stable isotopes and hydrogen has two stable isotopes. As a result, ordinary water molecules have nine different isotopic configurations whose mass differences are reflected by these isotopic combinations: H_2^{16}O (18), H_2^{17}O (19), H_2^{18}O (20), HD^{16}O (19), HD^{17}O (20), HD^{18}O (21), D_2^{16}O (20), D_2^{17}O (21), D_2^{18}O (22). The vapor pressures of these different isotopic combinations are inversely proportional to their respective masses. Thus, provided equilibrium between the vapor and liquid is maintained, the fractionation factor (α) at any given temperature is the ratio of the vapor pressures.

Mechanistic processes that induce fractionation of the water molecule include evaporation and precipitation. Because H_2^{16}O has a significantly higher vapor pressure than D_2^{18}O , when water vapor is formed by evaporation of liquid water the vapor is enriched in ^{16}O and H while the remaining liquid is enriched in ^{18}O and D. Conversely, during subsequent condensation the liquid phase becomes similarly enriched in heavier isotopes. Consequently, the isotopic composition of water in nature is intimately related to the hydrologic cycle, wherein the source of all fresh water is the low latitude oceans.

Craig and Gordon (1965) found that the isotopic fractionation factors for evaporation of water under equilibrium conditions at 25°C are 1.0092 and 1.074 for ^{18}O and D, respectively. However, the $\delta^{18}\text{O}$ values for water vapor in the North Pacific and North Atlantic Oceans were found significantly more depleted than predicted by

equilibrium values. Thus, the isotopic composition of the water vapor over the oceans was shown to not conform to predictions based on evaporation alone but requires additional explanations related to kinetic effects (Craig and Gordon, 1965).

When water evaporates from the surface of the ocean, a moist air mass containing this water vapor is formed that is depleted in ^{18}O and D relative to the ocean. Subsequently, when raindrops form in a cloud by condensation of that water vapor, the liquid phase is enriched in ^{18}O and D. The isotopic composition of the first raindrops is similar to that of the parent ocean water. However, the continuing preferential removal of ^{18}O and D during precipitation results in the further depletion of vapor in the moist air mass. Thus the $\delta^{18}\text{O}$ and δD values of water vapor in an air mass will become progressively more negative as rain, snow or hail precipitate from it. This process of condensation of water in equilibrium with water vapor and its subsequent removal from a cloud can be viewed as a “Rayleigh Distillation” (Dansgaard, 1965). Therefore, the isotopic distribution during rainout can be expressed as:

$$R = R_0 f^{(\alpha-1)},$$

where R is the isotopic ratio of the remaining vapor, R_0 is the isotopic ratio of the vapor before condensation begins, f is the fraction of vapor remaining, and α is the temperature dependant isotope fractionation factor $R_{\text{liquid}}/R_{\text{vapor}}$. Using the equation for α , the Rayleigh equation may be converted into δ -notation as follows:

$$\alpha = R / R_0 = f^{(\alpha-1)},$$

$$1000 + \delta^{18}\text{O} / 1000 + \delta^{18}\text{O}_0 = f^{(\alpha-1)},$$

$$\delta^{18}\text{O} = (1000 + \delta^{18}\text{O}_0) f^{(\alpha-1)} - 1000$$

$$\delta^{18}\text{O}_0 = [(1000 + \delta^{18}\text{O}) / f^{(\alpha-1)}] - 1000$$

The $\delta^{18}\text{O}$ value is the remaining vapor and, $\delta^{18}\text{O}_0$ is the isotopic ratio of the vapor before condensation begins. The fractionation of the oxygen isotopes during condensation of water from vapor at 25°C according to the Rayleigh distillation model ($^{18}\alpha = 1.0092$ at 25°C) is shown in Figure 1. The diagram shows that the $\delta^{18}\text{O}$ value of the remaining vapor is depleted as condensation progresses. The $\delta^{18}\text{O}$ of the liquid that is in equilibrium with the vapor at any given instant is calculated using a rearrangement of the equation for α as follows:

$$^{18}\alpha = R_{\text{liquid}}/R_{\text{vapor}} = 1000 + \delta^{18}\text{O}_{\text{liquid}} / 1000 + \delta^{18}\text{O}_{\text{vapor}}$$

$$\delta^{18}\text{O}_{\text{liquid}} = ^{18}\alpha [1000 + \delta^{18}\text{O}_{\text{vapor}}] - 1000$$

The evolution of the isotopic composition of atmospheric precipitation from the oceanic reservoir to the ice sheets at the poles can be explained by viewing the precipitation process using a simple Rayleigh model at liquid-vapor equilibrium. Secondary processes, however, such as addition of secondary moisture sources (Machavaram and Krishnamurthy, 1994), evaporation of the condensate during rainout and the physical nature of co-existing condensate phases (ice, liquid and vapor) also affect the isotopic signature of precipitation in a given region. Some modified Rayleigh models have been reported which consider these secondary processes (Gat, 1980; Gedzelman and

Arnold, 1994; Ciais and Jouzel, 1994). That aside, the result of isotopic fractionation during evaporation of water from the oceans and subsequent condensation of vapor in clouds is that fresh water is generally depleted in ^{18}O and D compared to sea water.

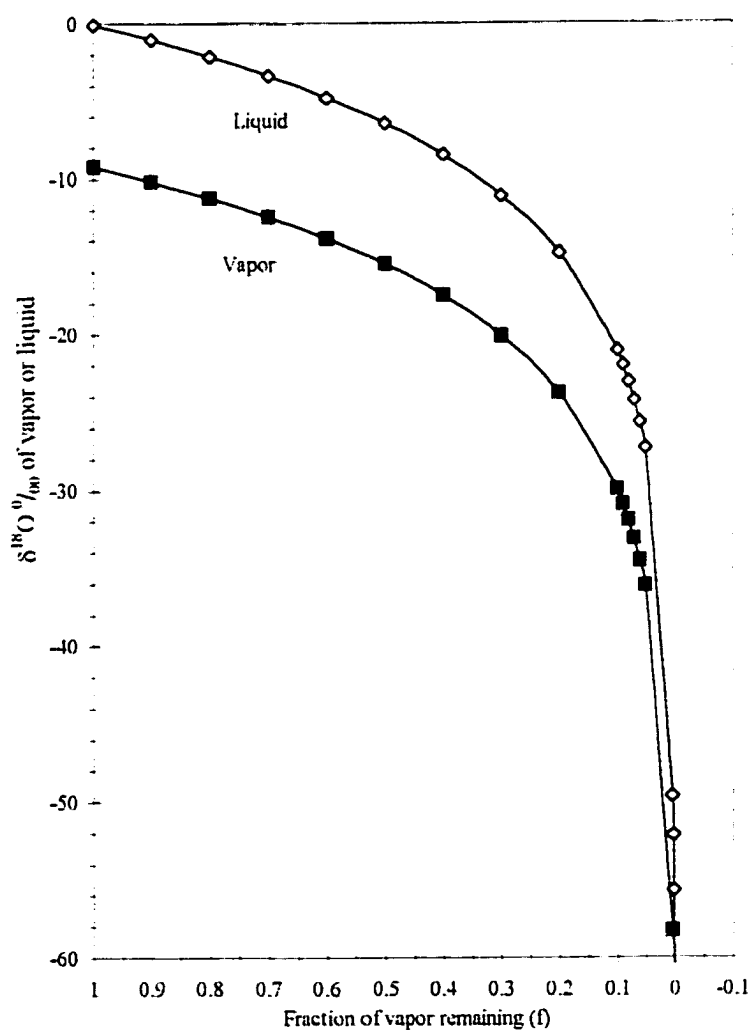


Figure 1. Fractionation of Oxygen Isotopes During Condensation of Water From Water Vapor at 25°C via Rayleigh Distillation.

Many processes act on the precipitating air mass during transit that cause local and regional effects. When superimposed on the water molecule during air mass transit,

these processes affect the stable isotopic distribution in precipitation. These causal effects must be considered when interpreting the isotopic ratios in the precipitation that recharge fresh water systems and the resultant climatic signal imparted to the various proxy recorders. It can be shown that as a marine water vapor parcel enters the continent and undergoes increased loss of vapor by continuous condensation, the vapor becomes increasingly depleted in the heavier isotopic species with increasing distance from the coast. Subsequent condensates from that transitory air mass will become progressively depleted in their δD and $\delta^{18}O$, as it moves further away from the original oceanic source.

This is known as the “continental effect”. Further, because alpha (α) is temperature dependent, in any given region the isotopic ratios in precipitation exhibit a positive linear correlation with the mean annual surface air temperature of that region. Known as the “temperature effect”, Dansgaard (1964) demonstrated this relationship between the $\delta^{18}O$ values of average annual precipitation and average annual air temperature by analysis of a large number of meteoric water samples from various global stations. Regression of his data shows the relationship is expressed as follows:

$$\delta^{18}O_{\text{mean}}\text{‰} = 0.695T_a - 13.6$$

where $\delta^{18}O_{\text{mean}}$ is the mean annual isotope ratio for oxygen in precipitation expressed in per mil notation and T_a is the mean annual surface air temperature expressed in degrees Celsius. Dansgaard found that a simple Rayleigh process could explain this effect where the fractionation factor governing the condensation was calculated by taking surface air

temperature. Thus, the relationship between the $\delta^{18}\text{O}$ and the air temperature reflects the fact that the isotope fractionation factor increases with decreasing temperature.

The more rain that falls during a single event or over a unit time (i.e. month) tends to deplete the vapor source causing the isotopic ratios to become more negative with subsequent precipitation. Termed the “amount effect”, this is predominantly observed in tropical regions and in the mid-latitudes during summer months. The effect becomes negligible in polar areas where the temperature effect predominates. The “altitude effect” results from the orographic ascent of the air mass and the resultant expansion and cooling that causes condensation. The progressive rainout of the heavy isotopes during the air mass ascent effects a negative correlation with increasing altitude (Freidman and Smith, 1970; Dincer, et al., 1970; Moser and Stichler, 1971). Similarly, as an air mass moves to higher geographic latitudes, the δD and $\delta^{18}\text{O}$ values become more negative as the temperature drops. This is termed the “latitude effect”.

The importance of these various fractionation effects and processes is that understanding them allows quantification of regional hydrologic and atmospheric factors that influence the climate–isotope relationship for precipitation. This in turn allows extrapolation of climatic information from proxy indicators.

The δD - $\delta^{18}\text{O}$ Relationship

On the basis of a large number of analyses of meteoric waters collected from a global network of stations, Craig (1961) showed that the $\delta^{18}\text{O}$ and δD values of meteoric

water are linearly related by the following equation:

$$\delta D = 8 \delta^{18}O + 10$$

Called the Meteoric Water Line (MWL), the relation was defined through regression of the weighted-average isotopic composition for all the precipitation samples obtained. The only meteoric water samples that do not fit this relationship are from closed basins where excessive evaporation occurs. This latter non-equilibrium process typically results in a slope between 5 and 6 and is referred to as the "evaporation line" (Gat, 1971; Stewart, 1975). The meteoric water line may be regarded as the locus of the isotopic composition of worldwide fresh water bodies. The intercept of 10 stems from the fact that evaporation over the ocean is in fact a non-equilibrium (kinetic) process favoring lighter isotopes to heavier ones during oceanic evaporation. This being the case, the initial water vapor formed over the ocean would have an initial isotopic composition of -80‰ for δD and -10‰ for $\delta^{18}O$ under equilibrium conditions at 20°C. The 10 per mil value in the above equation represents an excess of deuterium relative to ^{18}O .

The d -excess Parameter

In order to relate the available information on the δD - $\delta^{18}O$ relationship of any water sample to that of Meteoric Water Line, Dansgaard (1964) rearranged the MWL equation substituting the d -parameter for the 10‰ intercept as follows:

$$d = \delta D - 8\delta^{18}O$$

Subsequent to this, Merlivat and Jouzel (1979) showed a linear correlation of the d -parameter value to relative humidity over the oceanic surface. The d -value has little significance when the slopes are less than 8 or for waters that are subjected to non-equilibrium processes (Yurtsever and Gat, 1981). Where the slopes are close to 8, however, the d -parameter provides useful geophysical information. In these instances, the d -parameter can be used as a valuable tool for understanding the source flux of precipitation in a given region and quantifying secondary sources of importance (Machavaram and Krishnamurthy, 1995).

Fractionation in the Carbon Reservoir

Carbon, which is one of the most abundant elements in the universe occurring naturally as both diamond and graphite, is the basis for the existence of life on Earth. In reduced form, carbon is found in organic compounds and coal. In the oxidized state, carbon occurs primarily as carbon dioxide (CO_2), carbonate ions in aqueous solution and as carbonate minerals. Having two stable isotopes (see Table 1), carbon is fractionated by a variety of natural processes including photosynthesis in green plants and inorganic exchange reactions. In general terms, the fractionation of carbon during photosynthesis leads to enrichment of ^{12}C in the organic compound, whereas inorganic exchange reactions (i.e. CO_2 gas and aqueous carbonate species) tend to enrich carbonates in ^{13}C . The fractionation of oxygen in the carbonate-water system also results from an isotope exchange reaction between calcium carbonate and water related to the above aqueous carbonate system. This will be discussed in a subsequent section. The differences

exhibited by isotopic carbon species follow the principles discussed previously, that is, fractionation is primarily caused by kinetic and mass dependent chemical differences of the isotopes.

Fractionation in Organic Carbon Reservoirs

Fractionation in organic carbon reservoirs typically results from kinetic differences in the isotopic species. Kinetic differences result in differences in properties such as diffusion velocity and rates of vaporization. For $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$, the ratio of diffusion flux would be predictable since the diffusion coefficient (D) is inversely proportional to the square root of the molecular weight. The fractionation factor alpha (α) would be written as the alpha of diffusion and thus the square root of the respective masses (M). The masses of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ are 44 and 45 and alpha would be written as follows:

$$\alpha = (D_{44} / D_{45})^{1/2} = (M_{45} / M_{44})^{1/2} = 1.010$$

Lighter isotopes thus diffuse faster than their heavier counterparts. Similarly, the vapor pressure of isotopic compounds decreases with increasing isotopic mass creating a tendency for compounds with lighter isotopes to evaporate more quickly.

Fractionation in Inorganic Carbon Reservoirs

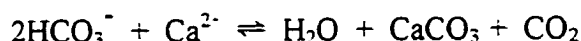
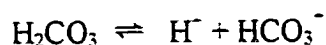
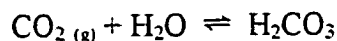
Purely chemical differences, on the other hand, result principally from differences in the vibration frequencies of isotopic molecules. As the electronic structure is not changed by isotopic substitution, identical bonds are formed between the isotopic species.

However, because the vibration energy levels are mass dependent, changes through isotopic substitution will alter the vibrational frequency. This leads to a small fractionation due to the fact that bonds formed with lighter isotopes are thus more easily broken than bonds involving the heavier isotope.

Fractionation in Calcium Carbonate (CaCO₃)

Carbon

In natural water environments, equilibrium involving carbon can be represented by the following three reactions:



The dissolved carbonate species that are present in ground water are derived chiefly from soil zone CO₂ and carbonate aquifer material. Dissolved inorganic carbon (DIC) in lacustrine environments, however, is controlled by the DIC of waters that recharge the lake, CO₂ exchange between the atmosphere and water, and photosynthesis and respiration of the organic matter in the lake.

The isotopic composition ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of calcium carbonate precipitated from aqueous solutions is controlled by the properties of the system that have an effect on the abundance of carbonate and bicarbonate ions in the system (Deines et al., 1974). For

carbon the controlling factors include (a) the $\delta^{13}\text{C}$ of the CO_2 gas in equilibrium with carbonate and bicarbonate ions in solution; (b) fractionation of carbon isotopes between CO_2 gas, the carbonate and bicarbonate ions in the solution, and solid calcium carbonate; (c) the temperature of isotopic equilibrium; and (d) the pH and P_{CO_2} of the system (Deines et al., 1974; Deuser and Degens, 1967, Emrich et al., 1970; Vogel et al., 1970).

When CO_2 dissolves in water to form carbonic acid and its ions, isotopic exchange reactions enrich HCO_3^- in ^{13}C relative to the CO_2 . Subsequently, when CaCO_3 precipitates from solution, the solid phase is further enriched and the resulting fractionation of carbon isotopes in the carbonate relative to the $\text{CO}_{2(g)}$ varies with temperature in accordance with the following equation (Deines et al., 1974; Faure, 1991):

$$10^3 \ln \alpha_{\text{Carbonate Species} - \text{CO}_2} = [(A \times 10^6) / T^2] + B$$

$$\text{where } \alpha = R_{\text{Carbonate Species}} / R_{\text{CO}_2}$$

$$\text{and } R = ^{13}\text{C}/^{12}\text{C}$$

The values for A and B are constants in the above equation and are shown in Table 2. As an illustration, using the HCO_3^- values from Table 2, calculation of $\alpha_{\text{HCO}_3^- - \text{CO}_2}$ at 20° and 25°C shows fractionation-values of 1.0082 and 1.0077, respectively. Thus, the use of carbon isotopes in paleotemperature studies is limited due to the very small differences in their associated fractionation factors.

The fractionation factors for the carbon isotopes in the carbonate system were reported by Emrich et al., 1970. Using the equation for alpha as follows:

$$\alpha_{\text{Carbonate} - \text{CO}_2} = \delta^{13}\text{C}_{\text{calcite}} + 1000 / \delta^{13}\text{C}_{\text{CO}_2} + 1000$$

and a $\delta^{13}\text{C}$ value of -7‰ for the CO_2 gas, it can be shown that the calcium carbonate is enriched in ^{13}C by about 10‰ when precipitated in isotopic and chemical equilibrium at 20°C ($\alpha_{\text{Carbonate} - \text{CO}_2}$ at 20°C = 1.0103).

Table 2

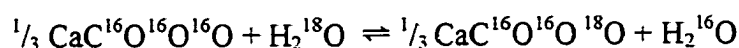
Constants Related to Fractionation Values of Carbon Isotopes Between Aqueous Carbonate Ions and Calcium Carbonate Relative to Carbon Dioxide Gas
(After Deines et al., 1974)

Carbonate Species	A	B	$\alpha^{20^\circ\text{C}}$
H_2CO_3	0.0063	-0.91	0.9991
HCO_3^-	1.099	-4.54	1.0082
CO_3^{2-}	-0.87	-3.4	1.0067
$\text{CaCO}_{3(s)}$	1.194	-3.63	1.0103

Oxygen

The oxygen isotopic signal ($\delta^{18}\text{O}$) of calcium carbonate is determined by the $\delta^{18}\text{O}$ of the water and the water temperature during carbonate precipitation. Typically, calcium carbonate (calcite and aragonite) is enriched in ^{18}O compared to the water from which they precipitate. The paleotemperature scale, suggested by Urey (1947) and developed

by Epstein et al. (1951, 1953) is based on these facts when biogenic calcite precipitates from water under equilibrium conditions. The difference results from an isotope exchange reaction between calcium carbonate and water written as follows:



If calcite precipitates are formed in isotopic equilibrium conditions, the $\delta^{18}\text{O}$ of the water from which calcite precipitated can be determined from the experimentally derived calcite-water fractionation equation (Friedman and O'Neil, 1977)

$$10^3 \ln \alpha_{\text{Calcite-Water}} = [(2.78 \times 10^6)/T^2] - 2.89$$

where T is in degrees Kelvin and the calculation of alpha require that $\delta^{18}\text{O}$ for both calcite and water be reported with respect to SMOW. In their application of $\delta^{18}\text{O}$ of calcite tests in paleoclimate studies, Epstein et al. (1953) derived a relevant equation for the relationship between the temperature of water and the δ values of calcite and water. This was modified by Craig (1965) and written:

$$t^\circ\text{C} = 19.9 - 4.2(\delta_{\text{C}} - \delta_{\text{W}}) + 0.13(\delta_{\text{C}} - \delta_{\text{W}})^2$$

where δ_{C} is the $\delta^{18}\text{O}$ of CO_2 obtained from reacting calcium carbonate with 100% H_3PO_4 at 25°C and δ_{W} is the $\delta^{18}\text{O}$ of the water and both δ -values are based on the same standard.

The isotopic fractionation factor for the calcite-water system was worked out by O'Neil and Epstein (1964) and has a value of 1.0286 at 25°C . If the δ value of sea water is taken

to be zero, from the equation $\alpha_{\text{Carbonate-water}} = \delta^{13}\text{C}_{\text{calcite}} + 1000 / \delta^{13}\text{C}_{\text{water}} + 1000$, it can be shown that the $\delta^{18}\text{O}$ value of calcite is +28.6‰ (SMOW) relative to water when isotopic equilibrium is established at 25°C. It is customary, however, to express the $\delta^{18}\text{O}$ of carbonate using the PDB standard.

In lacustrine settings, such as those in this study, the oxygen isotope ratio of the environmental water is determined largely by the waters recharging the lake. As fresh water lakes typically exhibit negative $\delta^{18}\text{O}$ values, the $\delta^{18}\text{O}$ of carbonates from these lakes are generally depleted in comparison to marine carbonates. The tremendous variation in the $\delta^{18}\text{O}$ value of meteoric waters generally precludes accurate paleotemperature determinations from freshwater carbonates (Fritz et al., 1975). Thus, the $\delta^{18}\text{O}$ of calcite often provides information regarding the $\delta^{18}\text{O}$ of the environmental water rather than the temperature of precipitation.

The accuracy of the paleotemperature determination is limited by several prerequisite conditions. First, the $\delta^{18}\text{O}$ of the water with which the calcium carbonate equilibrated must be known. The concurrent variations in the temperature and isotopic variation of the water can sometimes be resolved by analysis of benthic shell material from deep-water lakes. In such cases, the bottom temperatures may remain near constant and permit estimates of the $\delta^{18}\text{O}$ of the water from the $\delta^{18}\text{O}$ of bottom dwelling mollusks or ostracodes (Lister, 1988). One very imaginative attempt at paleotemperature estimates involves combining the $\delta^{18}\text{O}$ of marl carbonate and δD from the bulk organic fraction from sediment matter (Chapter III and Lovan et al., 1998 in review). This technique

translates the δD of the sediment organic matter to the $\delta^{18}O$ of the lake water. Then using the $\delta^{18}O$ of the marl in combination with the inferred $\delta^{18}O$ of the water, an $\alpha_{\text{Calcite-Water}}$ is calculated and translated to an inferred temperature using the Friedman and O'Neil (1977) equation noted above. A second limiting factor is that some carbonates are precipitated under non-equilibrium conditions (the so-called vital effects). In these cases, the $\delta^{18}O$ value of the carbonate is not a function of the temperature or the $\delta^{18}O$ of the water alone. Other factors may include seasonality of shell growth (Xia et al., 1997a & 1997b) or the habitat during the life cycle of an organism. Finally, the mineral composition must be both unaltered and known (Lowenstam, 1961; Horibe and Oba, 1972). The post-depositional alteration of carbonate material makes difficult the proof that the isotopic composition of oxygen has remained unchanged.

Fractionation in Reduced Carbon Reservoirs

Photosynthesis and Carbon Fractionation

Photosynthesis is a complex process wherein atmospheric carbon dioxide is incorporated into green plants. The process begins with diffusion of CO_2 gas from the atmosphere across the walls of leaf cells and its subsequent dissolution into the plant cytoplasm. Through the action of enzymes, the cytoplasmic $^{12}CO_2$ is preferentially converted into acids containing 3 carbon atoms for C_3 plants (the Calvin cycle) or acids with four carbon atoms in C_4 plants (the Hatch-Slack cycle). During the enzymatic reactions ^{12}C is preferentially removed from the dissolved CO_2 of the cytoplasm to form

the various 3 or 4 carbon acids. The remaining dissolved CO_2 in the cytoplasm becomes enriched in ^{13}C and further fractionation becomes inhibited unless the residual carbon dioxide is removed (Farquhar et al., 1989). Respiration of enriched CO_2 , presumably from the cytoplasm, through the roots of vascular plants and their leaves during dark periods has been observed (Keeling, 1958, 1961; Abelson and Hoering, 1961). The final step in the fractionation of carbon by both C_3 and C_4 plants occurs during the synthesis of various organic compounds from the phosphoglyceric acid.

If modeled in more specific terms, the first fractionation described for C_3 plants asserts a diffusion, $(M_1/M_2)^{1/2}$, of atmospheric CO_2 across the leaf wall and dissolution into the cytoplasm as ribulose 1:5 diphosphate (RUDP) or $\text{CH}_2\text{OPO}_3\text{-CO-(CHOH)}_2\text{-CH}_2\text{OPO}_3$. This diffusive fractionation results in a $\sim 4.4\text{‰}$ shift in the $\delta^{13}\text{C}$ value (Farquhar, 1989). C_3 plants fix carbon by carboxylation of RUDP forming 3-phosphoglyceric acid (PGA) or $\text{CO}_2\text{-COH}_3\text{-CH}_2\text{OPO}_3$. The enzyme related fractionation shows a depletion of $\sim 27\text{‰}$ (Farquhar et al., 1989) in C_3 plants. In C_4 plants, CO_2 diffuses into the leaf where it dissolves and is converted to HCO_3^- . Further dissolution forms phosphoenolpyruvate (PEP) or $\text{CH}_2\text{-CPO}_3\text{-CO}_2$ which exhibits an $\sim 5.7\text{‰}$ discrimination against $\text{H}^{13}\text{CO}_3^-$. Carbon dioxide is then released into the bundle sheath and re-fixed by RUDP. This subsequently transforms to PGA.

C_3 (i.e. higher vascular plants, most grasses, trees, wheat, rice) and C_4 plants (i.e. corn, cactus, tropical grasses, sugarcane, sorghum, arid area shrubs) have mean $\delta^{13}\text{C}$ values around $-25 \pm 5\text{‰}$ and $-14 \pm 2\text{‰}$, respectively. Aquatic plants fix CO_2 by the normal

C₃ pathways with diffusion taking place in the aqueous phase (Farquhar et al., 1989). When disequilibrium conditions exist (i.e. during high productivity) a depletion of the CO₂ available for plant photosynthesis can result and bicarbonate is used as the carbon source. This leads to more enriched $\delta^{13}\text{C}$ values. Measured $\delta^{13}\text{C}$ values for aquatic plants range between -11 and -39‰. Smith and Epstein (1971) subdivided photosynthetic plants into two large categories based on their $\delta^{13}\text{C}$ values. Most terrestrial plants range from -24 to -34‰, while the $\delta^{13}\text{C}$ of aquatic plants, tropical grasses, corn, and desert and salt marsh plants vary from -6 to -19‰. An intermediate group is formed by algae and lichen with $\delta^{13}\text{C}$ values from -12 to -23‰. Organic matter in Holocene sediment has $\delta^{13}\text{C}$ values ranging from -10‰ to -30‰ (Eckelman et al., 1962, Shultz and Calder, 1976; Meyers et al., 1884; Meyers and Eadie, 1993; Krishnamurthy et al, 1995).

Francey and Farquhar (1982) and Farquhar et al. (1989) modeled the physical and enzymatic basis of carbon isotope discrimination during photosynthesis. This model equation, in its simplest form, is given by:

$$\delta^{13}\text{C}_p = \delta^{13}\text{C}_{\text{air}} - a - (b - a) (C_i / C_a)$$

where $\delta^{13}\text{C}_p$ is the isotope ratio of the fixed carbon (photosynthate); $\delta^{13}\text{C}_{\text{air}}$ is the isotope ratio the source (i.e. atmospheric carbon); a is the fractionation due to diffusion of CO₂ in the leaf (4.4‰); b is the fractionation due to fixation of CO₂ via enzyme action (~27‰ for C₃ plants); C_i is the concentration of CO₂ in the leaf intercellular space; C_a is the concentration of CO₂ in the atmosphere.

Cellulose, Hydrogen and Alpha

Plants are extremely complex chemical systems. Early efforts to examine the temporal isotopic variations in natural systems demonstrated the dependence of the D/H ratio in plant total hydrogen on the δD in associated environmental waters (Smith and Epstein, 1970; Schiegl and Vogel, 1970; Libby and Pandolfi, 1974; Scheigl, 1974). Problems associated with plant chemical heterogeneity were eliminated with the analysis of a single chemical substance (cellulose) common to all plants (Epstein et al., 1976).

Cellulose is complex carbohydrate having the elemental composition of carbon, hydrogen and oxygen (CHO). Cellulose hydrogen consists of two types. Hydrogen bound to carbon is non-exchangeable, while hydrogen bound to oxygen readily exchanges with ambient water sources (Mann, 1971; Epstein et al., 1976). Examination of non-exchangeable hydrogen in plant cellulose (Epstein et al., 1976) made possible the use of biogenic-hydrogen as a proxy indicator to environmental change. This was a consequence of the fact that carbon bound hydrogen in plant cellulose had remained unchanged since its biosynthesis from meteoric waters. The δD of cellulose extracted from plants after removal of non-exchangeable hydrogen has been shown to be a reasonable proxy of the δD for the environmental water in which they grew (White et al., 1994; Yapp and Epstein, 1982; Buhay et al., 1996). This technique has been applied by various workers, particularly in regard to the analysis of cellulose extracted from tree rings (Ramesh et al., 1985; Edwards et al., 1985; Edwards and Fritz, 1986; Epstein and Krishnamurthy, 1990; Epstein, 1995; Lipp et al., 1996). Studies using the cellulose fraction of organic matter

taken from lake sediments have also been undertaken (Edwards and McAndrews, 1989; Edwards and Elgood, 1992).

The quantitative relationship between the δD of plant cellulose and ambient water has been worked out extensively (Yapp and Epstein, 1982; Edwards and Fritz, 1986; White et al., 1994; Buhay et al., 1996). Collectively, these works consider in detail the role of leaf water evaporation controlled by ambient humidity. Their models of the water to cellulose evolution consider the equilibrium, kinetic and biochemical fractionation of hydrogen. The δD -water relationship is in the form of

$$(1000 + \delta D_{\text{cellulose}})/(1000 + \delta D_{\text{water}}) = {}^D\alpha_n {}^D\alpha_e {}^D\alpha_k - {}^D\alpha_n ({}^D\alpha_e {}^D\alpha_k - 1)h$$

where $\delta D_{\text{cellulose}}$ is the measured δD of the non-exchangeable hydrogen in the cellulose and δD_{water} is the δD of the source water, while ${}^D\alpha_n$ is the net biochemical fractionation factor, ${}^D\alpha_e$ and ${}^D\alpha_k$ are the equilibrium and kinetic hydrogen isotope fractionation factors between the liquid and vapor phases, and h is the relative humidity.

For aquatic plants, such as in this dissertation study, negligible effects due to humidity changes can be assumed as a consequence of their submersion in water. Thus, the relative humidity (h) from the above model will approach unity ($h \approx 1$). This reduces the fractionation to ${}^D\alpha_n$, the biochemical fractionation, which has a value of 0.9530 (Edwards and Fritz, 1986). Rewritten as

$${}^D\alpha_n = (1000 + \delta D_{\text{cellulose}})/(1000 + \delta D_{\text{water}})$$

cellulose is thus shown to be depleted in δD by about 47‰ with respect to the δD of the water utilized by the plants.

Stable Isotopes as Proxy Recorders in Lake Sediment

Proxy recorders provide an indirect means of assessing environmental information where direct measurement of temperature, chemical and other records is not possible. Except when historical data exist, proxy recorders are the only acceptable means for retrieval of paleoenvironmental information. In fact, the only reliable long term climatic information available today is the recorded temperature and precipitation data for the past 100 years (Jones et al., 1986). The principle isotopic tools currently employed in continental paleo-climatic and environmental studies are the δD , $\delta^{18}O$ and $\delta^{13}C$ found variably in cellulose (primarily of trees), ground water, ice cores, and carbonate materials found in cave, soil and lacustrine environments. Temporal variations in the isotopic signatures from tree ring studies are limited to hundreds, perhaps thousands, of years. While cave studies offer longer temporal records, only studies of lake sediments offer the potential for fine resolution analysis of continental paleoenvironmental change. McKenzie (1985) described lakes as natural “beakers” in which geochemical processes can be effectively studied. Lakes are much quicker to respond to environmental change and offer a more rapid sedimentation rates than oceanic basins. Further, because of their smaller size, temporal changes in lacustrine geochemical signals are amplified. The standard proxy indicators commonly employed in the paleoclimatic study of lake-sediments are pollen analysis, micro-faunal analysis and stable isotope analysis of the various

sedimentary components. The isotopic tools currently used in paleoclimate studies using lake sediments are the stable isotopes of carbon and oxygen ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) found in the sediment constituents.

Carbon

The carbon isotopic signature in lake sediment has two components, the inorganic and the organic fraction. Calcium carbonate is the primary inorganic component and can be precipitated either biogenically or inorganically as lake marl. If isotopic equilibrium with the lake water is established, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the calcium carbonate can be interpreted in terms of environmental changes (Abell, 1982; Dean and Stuiver, 1993; Fritz et al., 1975; Schelske & Hoddell, 1991; Drummond, 1995). To understand the lakes' carbon chemistry both the organic and inorganic carbon sources and depositional mechanisms need be understood.

The main sources of organic carbon in a lake are the submerged plants such as macrophytes and plankton, etc. Terrestrial vegetation supplied to a lake is typically plant debris transported to the lake via stream input and runoff. In theory, the $\delta^{13}\text{C}$ of organic carbon can be dictated by water temperature, atmospheric CO_2 concentration, lake productivity and contribution from terrestrial sources. The influence of temperature on $\delta^{13}\text{C}$ of lake organic materials would manifest itself through temperature dependent fractionation during photosynthesis. Significant temperature effects, unfortunately, have been documented in only a few cases involving marine plankton and seemed to produce

divergent results. Jasper and Hayes (1990) and Rau et al. (1991) have argued that atmospheric CO₂ is a determinant of the ultimate isotopic carbon ratio of sedimentary organic matter. There exists a need to further explore evidence that atmospheric CO₂ can influence the $\delta^{13}\text{C}$ of lake organic matter. The effects of lake productivity on the $\delta^{13}\text{C}$ of lake organic matter has been addressed in numerous studies such as those by McKenzie (1985), Hollander and Mckenzie (1991) and Schelske and Hoddel (1991). When a lake goes into a state of enhanced photosynthesis, the production zone is depleted in dissolved CO₂ leaving the lakes carbon pool enriched in ^{13}C . Therefore, an increase or decrease of productivity in a stratified lake should be reflected by like increase or decrease in the $\delta^{13}\text{C}$ of both the inorganic and the organic carbon that is produced in the surface water and subsequently sedimented. There is a general indication that most parameters affecting the isotopic distribution of lacustrine organic matter remain relatively constant and change only if the environmental conditions are altered to a significant degree (Harkansson, 1985; Stuiver, 1970; Dean and Stuiver, 1993; Talbot and Johannessen, 1992).

Oxygen

The oxygen isotope composition of a lake is subject to variation in temperature, moisture provenance and the processes acting on the lake (i.e. evaporation). Variation in the $\delta^{18}\text{O}$ of lacustrine carbonates should reflect some combination of change in the isotopic composition of the lake or change in the temperature of calcite precipitation. Xia et al. (1996) found that the relationship between $\delta^{18}\text{O}$ of the ostracode shells and the

culture water shows a clear and consistent temperature dependence of oxygen isotope fractionation during biogenic calcification in controlled experiments. Further, it was noted that the $\delta^{18}\text{O}$ in ostracode shells were well defined by the $\delta^{18}\text{O}$ of the water from which the shells are formed. Showing near parallel linear regression to $\delta^{18}\text{O}$ of water and ostracode calcite, Xia et al. (1996) found the 15°C regression line is shifted upward by approximately 2‰ compared to the 25°C regression line. A similar 2‰ difference would be expected from inorganic carbonate given a temperature difference of 10°C.

Many lacustrine carbonates show a strong temporal covariance in their isotopic carbon and oxygen compositions. The strongest covariance is seen in closed systems and lakes with long residence times and probably reflects the isotopic evolution of the lake water versus the recharge rate (Talbot, 1990; Talbot and Kelts, 1990; McKenzie and Hollander, 1993). Lack of covariance has been reported in lakes where residence time is short and open lake conditions are evident (McKenzie and Hollander, 1993; Wolfe et al., 1996). Additionally, Smith et al. (1997) show poor covariance and negative excursions in $\delta^{18}\text{O}$ of carbonate during drought periods when ground water recharge provided the dominant isotopic signal.

Hydrogen

The proxy indicators for extracting paleoenvironmental information from organic bearing sediments have largely been restricted to successful efforts in the development of a reliable and documentable technique for data acquisition. Oxygen isotopic studies using

the cellulose fraction of terrestrial and lacustrine organic matter have been undertaken with notable success. Burk and Stuiver (1981) modeled $\delta^{18}\text{O}$ in wood cellulose accounting for source water $\delta^{18}\text{O}$, biochemical fractionation, and humidity- and temperature-dependent isotopic enrichment via evapotranspiration. Edwards et al. (1985) and Edwards and Fritz (1986) modeled both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ using only the input water δD and $\delta^{18}\text{O}$ and relative humidity as variables (see previous discussion Hydrogen, Cellulose and Alpha). Although initially applied to wood cellulose studies, Edwards and Fritz (1988), Edwards and McAndrews (1989) and Edwards and Elgood (1992) latter reinforced their findings with oxygen isotopic studies in lake sediment and lake sediment cellulose. However, attempts to obtain useful hydrogen isotope data from aquatic plant cellulose have shown only limited success, possibly owing to species dependent variability in biochemical fractionation effects between the source water and photosynthetic aquatic species (Stiller and Nissenbaum, 1980, Sternberg et al., 1984a, 1984b; Sternberg, 1988; Edwards, 1993).

In general, the use of hydrogen as an isotopic proxy in lacustrine studies has been slow in development, as there is no single established and perfected technique available for the extraction of hydrogen from the organic matter in sediment. Recently, it has been suggested that the δD of “bulk organic matter” extracted from sediments may also serve as a proxy of the δD of environmental water (Krishnamurthy et al., 1995). In a pilot study using a radiometrically dated sediment core from Austin Lake in Michigan, Krishnamurthy et al. (1995) sought to investigate and establish the suitability of δD from

the insoluble organic residue of lake sediment as a paleoclimatic indicator. Hydrogen was extracted from bulk sediment organic matter using a protocol developed by Krishnamurthy and Epstein (1991) for analysis of organic material from cherts. Without close attention to the analytical procedures, organic matter in sediment was concentrated by acid digestion in HCl followed by HF:HCl. Krishnamurthy et al. (1995) demonstrated the feasibility of using D/H ratios in lake organic matter as a viable paleoclimatic proxy while using the $\delta^{13}\text{C}$ and C/N ratio to shed light on the depositional environment of the lake studied. A brief discussion of the Austin Lake study will be presented in Chapter 3 in conjunction with data from this present study. With that in mind, the apparent success in using the Krishnamurthy and Epstein (1991) protocol for sample preparation and hydrogen extraction in the Austin Lake pilot study necessitated confirmation that the D/H ratio of the bulk organic matter from lake sediment is reliable as a proxy of climatic history.

Objectives of This Study

The primary objectives of this study are threefold:

1. Demonstrate the potential of D/H ratios in lake organic matter as a useful proxy for paleoclimate study. This project extends the research begun by Krishnamurthy et al. (1995) by analysis of new cores acquired from lake systems in Ohio and Wisconsin.
2. Develop a technique for the extraction of hydrogen from organic rich sediment that yields repeatability in the δD . This dissertation project stems from a need to refine and further document the hydrogen extraction technique initiated in the pilot

study undertaken by Krishnamurthy et al. (1995). As will be shown, the refinement of their initial procedure required the addressing of questions concerning the exchangeable versus non-exchangeable hydrogen in the HF:HCl "organic rich" residues.

3. Generate a continent-based regional paleoclimate record covering the Pleistocene-Holocene period using stable isotope records taken from bulk organic matter in lake sediment. Stable isotope analysis ($\delta^{13}\text{C}$, δD) of acid-resistant (HCl and HF-HCl) sediment residues are prepared from radiometrically dated sediment cores. The carbon/nitrogen (C/N) ratio of these residues is determined in order to constrain the interpretation of the stable-carbon isotope ratios in the sediment organic fraction. Additionally, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO_2 evolved from carbonate bearing sediment found within these cores is analyzed to further augment the interpretation of the paleo-environmental status for one of the two lakes reviewed.

The basis for an environmental interpretation of the hydrogen isotopic distribution of lacustrine organic matter stems from the assumption that the organic matter in lake-sediments is made primarily of the photosynthesizing aquatic plants that grew in the lake. As the source of hydrogen for these plants was the local meteoric water recharging the lake, the δD of lake organic matter should reflect the δD of local meteoric water via the δD of the lake. Since the δD of local meteoric water is directly related to climatic factors, the δD of lake-organic material should be interpretable in terms of climatic changes. Similarly, the $\delta^{13}\text{C}$ of the sediment organic carbon component will yield data relative to the environmental status of the lake such as lake productivity and lake chemistry (i.e. CO_2

exchange).

For the purpose of this study, the residual organic matter remaining after successive acid digestion of the parent sediment sample can be defined as “kerogen” having a predominant and concentrated elemental composition of carbon, hydrogen, nitrogen and oxygen (CHNO). Schoell (1984) demonstrated that for kerogen extracted from rock (residual organic materials of C,H,N,O elemental composition) all carbon bound hydrogen is non-exchangeable at low temperatures ($\leq 130^{\circ}\text{C}$) while the fraction of oxygen and nitrogen bound hydrogen (non-carbon bonded hydrogen) of the organic matter is available for isotopic exchange with ambient water hydrogen. Carbon-bonded hydrogen, on the other hand, exhibited isotopic exchange with ambient water hydrogen at higher temperatures. Below 170°C , however, the isotopic integrity of carbon-bonded hydrogen in kerogen is preserved over geologic time (Schoell, 1981 in Shimmelmann, 1991; Schoell, 1984). With few exceptions, the studies of δD in residual sediment organic materials of C,H,N,O elemental composition use bulk hydrogen and principally do not address the influence of exchangeable and non-exchangeable hydrogen on the bulk δD value.

Study Area

Samples used in this study came from radiometrically dated lacustrine cores raised from Ladd Lake in northwestern Ohio, Lake Winnebago in east central Wisconsin and Austin Lake in southwestern Michigan. Figure 2 shows the location of Ladd Lake, Lake

Winnebago and Austin Lake within the study area. Additionally, Mediterranean sapropel samples were incorporated into this study and provided insight to bulk sediment organic residues from marine sources having low organic carbon content (1 to 7%). The dotted line on Figure 2 represents the maximum extent of the Wisconsin Ice Sheet (Flint, 1957).

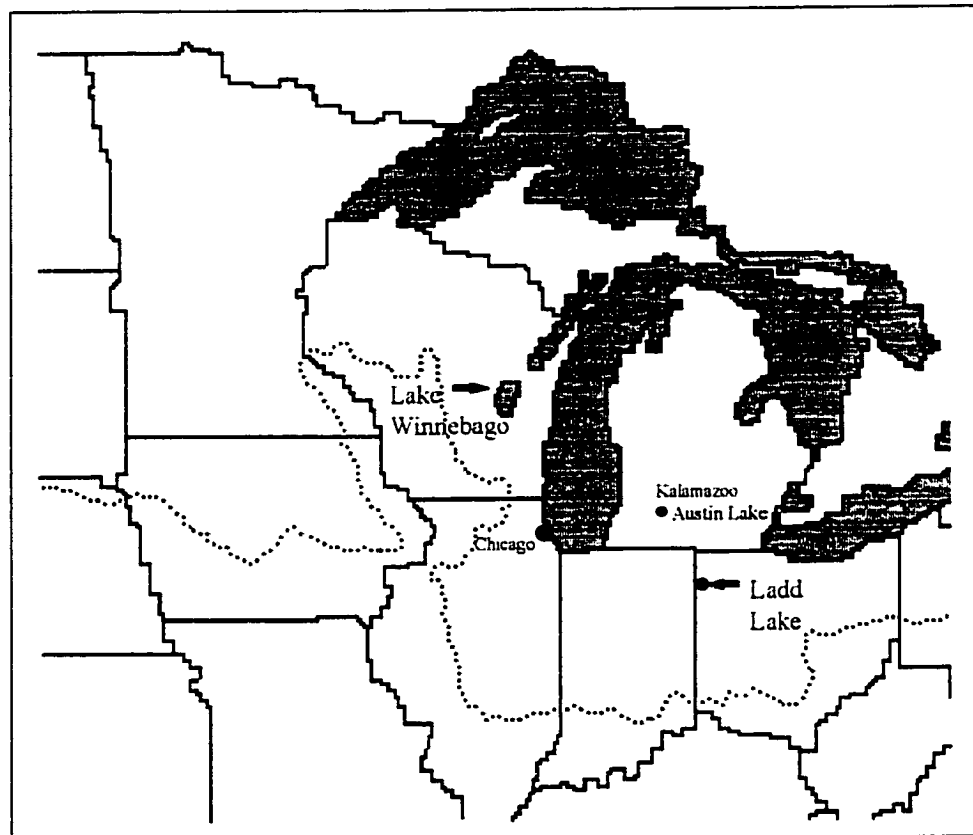


Figure 2. Study Area Showing the Mid-Western United States and the Location of Ladd Lake in Northwestern Ohio, Lake Winnebago in East Central Wisconsin and Austin Lake in Southwestern Michigan. The dotted line indicates the maximum extent of the Wisconsin ice sheet as indicated by Flint, 1957.

Many if not most of the Midwestern lakes were formed in glacial drift as kettle or pro-glacial lakes related to the last glacial advance of the specific area. Murphy and Wilkinson (1980) described Midwestern lakes as dimictic hard-water systems wherein low magnesium calcite has accumulated throughout the Holocene. Groundwater recharging such lakes typically emanates from carbonated rich glacial drift, which in turn may often be underlain by carbonate bedrock and carbonate bedrock aquifers. Consequently, waters recharging marl lakes from groundwater sources are very often enriched in calcium and bicarbonate.

Core and Sample Acquisition

The initial stage of this project required collecting various lacustrine cores. Sediment sub-samples were then prepared for isotopic analysis. The general criteria for acquisition of the required sediment core were that each core be of lacustrine origin, possess a distinctly post glacial interval and, preferably, have been radiometrically dated to establish sediment chronology. Three sediment cores were acquired through the University of Minnesota's Limnologic Research Center. Under their supervision and guidance, each of the 3 cores was sub-sampled for stable isotopic analysis. Two of these cores, one each from Ladd and Fudger Lakes in Ohio, had undergone pollen analysis (Shane, 1991). The third core, from Lime Lake in Michigan, showed evidence of large-scale slump features rendering only the upper 1 to 2 meters as viable with regard to a paleoclimate study. Only the 12-meter length Ladd Lake core had been radiocarbon dated and thus it became the initial focus of this research. Both the Fudger and Lime

Lake cores were archived for future study. Subsampling and other information relative to the Fudger Lake and Lime Lake cores may be found in the appendix.

Ladd Lake is located in Defiance County, NW Ohio, at coordinates 41° 24' 0" N; 84° 45' 45" W. Surface elevation is at 249 m above sea level and the lake can be found on the Butler, East Quad, USGS 7.5-minute series map. The 12 meter Ladd Lake core was raised November 13, 1986 using a 5 cm. diameter Wright-Livingston piston sampler from an anchored plywood platform lashed to two canoes. Coring was done after locating the deepest spot of the lake by using sounding gear consisting of a line and perforated metal plate. Depth sounding indicated a mid-lake depth of 950 cm. Only one core was raised and the water depth at core point was ~9 m. With the water surface considered 0 cm the top of core starts at 930 cm, and the base of core at 2132 cm. The last drive (bottom) of the Ladd Lake core (2092-2132 cm) was grey clay with sand from 2122 to 2132. This may represent pre-lake sediment or bedrock.

Sub-sampling of the Ladd Lake core took place at the University of Minnesota Limnologic Research Center and Western Michigan Universities Stable Isotope Laboratory. Ladd Lake sediment samples were extracted from their respective core by using a newly washed and modified plastic 3, 6 and/or 10cc syringe. Modification by blunt cutting the syringe resulted in a "coring device" that provided a convenient method for extracting the sediment sample by coring the sediment core with the syringe tube and extruding the sample using the syringe plunger. Approximately 3 to 5 grams of sediment were collected at each sampled interval. Individual samples were collected at a 4 to 5 cm interval, then placed into separate, new, sterile pre-labeled 20ml vials. Vials were labeled

alphanumerically for sample identification by using the abbreviations LL for Ladd Lake and the subsequent numbers indicating the core depth in centimeters. Collectively, approximately 300 samples were removed from the Ladd Lake core and 137 of these were used in this research.

As work in the experimental phase progressed, additional samples were incorporated into this study. These included Mediterranean sapropel samples, sediment samples from a core raised from Lake Winnebago, Wisconsin and selective Austin Lake samples (Krishnamurthy et al., 1995). Fifteen sapropel samples were provided by Dr. Phillip Meyers, University of Michigan, which he selected from archived Mediterranean sapropel samples that were raised in 1995 during their ongoing Ocean Drilling Program. These samples were used both in the development of the hydrogen extraction technique and for subsequent stable isotope analysis related to their origin (the latter will appear in a peer reviewed manuscript currently in preparation). Twenty-five additional samples, consisting of non-sapropel “background” samples, were also provided.

Lake Winnebago is located at coordinates 44° 09' N; 88° 10' W and occupies portions of Calumet, Fond du Lac and Winnebago Counties in central-eastern Wisconsin. Workers from Lawrence University, Appleton, Wisconsin, raised several vibracore from the north-central portion of Lake Winnebago during the summer of 1995. Sixty sediment samples from core LW7 and 43 mollusk shells collected from core LW8 were extracted and provided (obtained through Dr. G. L. Smith) for stable isotope study. Each core was approximately 3 meters in length. Each of the sixty sediment samples was extracted using a newly acid washed plastic utensil then individually placed into separate new, acid-

washed and pre-labeled 20ml vials. Vials were labeled LW7-9, LW7-20, etc. with LW7 indicating Lake Winnebago vibracore 7 and subsequent numbers designating the core's sample interval depth in centimeters. The forty-three shell samples were collected from core intervals between 87 and 131 cm by processing 1 cm slices of the core using a modification of the techniques of Forester (1988) and Smith (1993) and reported in Smith (1997). Each represented the picked, washed, sand-to-gravel size fraction of the bulk sediment sample from a designated cm-interval. In addition to the hydrogen study performed on the acid resistant sediment organic material, samples from core LW7 were analyzed for stable isotope ratios in both organic carbon ($\delta^{13}\text{C}$) from the carbonate free residue and inorganic carbon and oxygen ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of the marl carbonate (see subsequent Chapters).

Sediment Chronology

Six radiocarbon dates were obtained from bulk sediment organic matter in samples collected from select intervals over the length of the Ladd Lake core. Table 3 shows the results of these radiocarbon dates. Dates were generated by the Illinois State Geological Survey for the University of Minnesota Limnologic Research Center (UMLRC). Sample pretreatment included use of acid to remove carbonates and KOH to remove humics. UMLRC analysis included percent organic matter, carbonate and siliceous residue determinations (reported as % of dry weight). These were done at 8-cm intervals by the loss-on-ignition (LOI) method of Dean (1974). Pollen sample analysis was performed by Dr. Linda C. K. Shane. The top 11 meters of this 12-meter core were

reported as Holocene in Shane, Linda C. K., Vegetation History of Western Ohio, Final Report on 1990 Grant from The Ohio Department of Natural Resources, September 15, 1991. Individual samples from the Ladd Lake core were fitted to ages obtained from sedimentation rates based on ^{14}C dates. Conversion of radiocarbon dates to calendar years using the techniques of Bard et al. (1993), and Stuiver and Becker (1993) was performed and used in plots relating to the data interpretation presented in Chapter III.

Six Radiocarbon dates were obtained for the Lake Winnebago samples from the CO_2 gas evolved from sediment organic matter by combustion of the carbonate free organic fraction. AMS dating analysis was performed for Western Michigan University at Purdue University's Prime Laboratory for rare isotope measurement and is shown in Table 3. Dates for individual samples were estimated by using a linear sedimentation rate between radiocarbon dated intervals. Based on the chronology determined, the extrapolated surface age of the topmost sample is ~1300 years B.P. This result is most likely due to the loss of the first few centimeters during core recovery. A living clam sample collected from the lake's sediment surface in 1993 gave a "modern" radiocarbon age suggesting very little hard water effect even though the Lake Winnebago water chemistry is strongly influenced by recharge from the carbonate rich local groundwater. This absence of 'hard-water effect' might be due to rapid equilibration of the dissolved inorganic carbon with atmospheric carbon dioxide in this shallow ($\leq 6\text{m}$) lake. Data for samples that were separated by less than 140 years (i.e. twice the standard deviation reported for the radiocarbon dates) were averaged and converted to calendar years based on the methods of Bard et al. (1993) and Stuiver and Becker (1993).

The oldest date of 14.6 kyr for the Ladd Lake core and 12.1 kyr for the Lake Winnebago core is consistent with geological observations in both areas that these lakes formed at the termination of the last glacial period in response to the melting and retreating ice mass.

Table 3

Radiocarbon Dates From the Ladd Lake, Ohio and Lake Winnebago, Wisconsin Cores

Ladd Lake Core		Lake Winnebago Core LW7	
Depth (cm)	^{14}C Date (yr. BP)	Depth (cm)	^{14}C Date (yr. BP)
1194-1200	300 ± 70	1	$1,320 \pm 70$
1451-1459	$3,860 \pm 70$	58	$2,410 \pm 70$
1807-1815	$5,750 \pm 100$	100	$4,950 \pm 70$
2004-2010	$10,140 \pm 120$	127	$7,250 \pm 80$
2045-2051	$11,750 \pm 180$	151	$10,400 \pm 90$
2100-2108	$14,680 \pm 310$	271	$12,050 \pm 90$

Stable Isotopic Analysis

Isotopic analyses presented in this dissertation were obtained from various sedimentary components of samples taken primarily from Midwestern United States lacustrine cores. The principal focus of this project was the stable hydrogen isotopes in

sediment organic matter. Auxiliary studies include the analysis of stable isotopes of carbon and oxygen from marl carbonate and shell material, as well as the organic carbon from the carbonate free insoluble sediment residues. The isotopic analysis in each case was accomplished using a Micromass-Optima isotope ratio mass spectrometer. All isotopic ratio data are expressed in the delta notation per mil where:

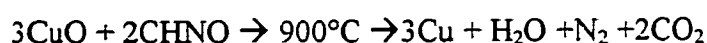
$$\delta\text{‰} = [(R_{\text{sample}} / R_{\text{standard}}) - 1] \times 10^3$$

where R is $^{18}\text{O}/^{16}\text{O}$, D/H, $^{13}\text{C}/^{12}\text{C}$ etc.

Carbon isotope ratios are reported relative to the PDB (Pee Dee Belemnite) Standard. Hydrogen isotopic ratios are reported relative to SMOW (Standard Mean Ocean Water). Oxygen isotopic ratios are variously reported relative to both the PDB Standard and SMOW. Precision for both carbon and oxygen is $\pm 0.1\text{‰}$ and for hydrogen, it is $\pm 2\text{‰}$.

Carbon is always analyzed as CO_2 gas. Inorganic carbon, such as that in carbonate materials, is usually reacted with 100% phosphoric acid at 25°C . Organic carbon compounds are oxidized to CO_2 at 900°C to 1000°C . In this study, the inorganic carbon from marl-rich sediment was analyzed using the septum-phosphoric technique developed by Krishnamurthy et al. (1997). Analysis of organic carbon ($\delta^{13}\text{C}$) is accomplished by combustion of carbonate free sediment samples (insoluble HCl residue) in the presence of CuO at 900°C for 3 hours. This combustion protocol is also used for the isotopic analysis of hydrogen from sediment organic matter. The latter, however, requires the further concentration of the sediment organic matter to remove any

potentially hydrogen-bearing inorganic phase (i.e. silicate minerals) present in the residual material. A general protocol for this was initially developed by Krishnamurthy and Epstein (1991) and subsequently used by Krishnamurthy et al. (1995) in their Austin Lake study (Kalamazoo, Michigan). The carbonate free residues are re-digested in an HF:HCl solution. In this procedure, the sediment organic matter (the insoluble HF:HCl-residues) from each sample is combusted in the presence of CuO in the same manner as the organic carbon from the carbonate free residues. The controlling reaction for both these processes is as follows:

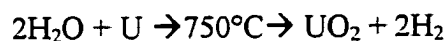


Sediment organic residues (both HCl and HF:HCl insoluble residues) have an elemental composition of carbon, hydrogen, nitrogen and oxygen (CHNO). Their gaseous CO₂, H₂O and N₂ combustion by-products are cryogenically separated and may be individually collected and measured. Carbon and Nitrogen yields were recorded for the carbonate free residue (HCl-residue) and the HF:HCl residues. These data were used in calculating the carbon/nitrogen (C/N) ratios for both residual materials, which are discussed later. The C/N ratios of the carbonate free fraction were used to constrain the interpretation of the organic carbon data. The δ¹³C of the CO₂ gas were determined for both residual materials.

Hydrogen yields were determined only for the HF:HCl-residue and used for calculation of the atomic hydrogen to carbon (H/C) ratio. Hydrogen gas was generated by passing the combustion water over uranium metal heated to 750°C. Gaseous H₂ was

subsequently collected then transferred to the mass spectrometer for measurement of δD .

This procedure for water reduction was first reported by Bigeleisen et al., 1952, and is described by the following reaction:



Given the recent global environmental awareness, other potentially less dangerous metals are frequently used for deuterium analysis. Thus, in some laboratories, water is quantitatively reduced under vacuum using zinc heated to $450^\circ C$ (Freidman, 1953; Coleman, et al, 1980) or chromium heated to $750^\circ C$ (Gehre, et al, 1996). The present study uses uranium for reduction of water in all its hydrogen isotopic analyses.

CHAPTER II

DEVELOPMENT OF A HYDROGEN EXTRACTION TECHNIQUE

Methodology

Ultimately, the development and use of this hydrogen extraction technique is intended for the analysis of the deuterium/hydrogen (D/H) ratios of organic matter in sediments. Hydrogen isotope ratios are measured using an isotope-ratio mass spectrometer and gaseous hydrogen. Thus, a prime focus of this and any hydrogen extraction technique is to first isolate the hydrogen-bearing fraction that can then be converted into hydrogen gas. For the purpose of this study, this fraction is the residual organic matter remaining after successive acid digestion (HCl followed by HF:HCl) of the parent sediment sample. This insoluble residue, termed “kerogen” or “HF:HCl residue”, can be defined as having a predominant elemental composition of carbon, hydrogen, nitrogen and oxygen (CHNO). Once extracted from the sediment the organic residue can be oxidized to form water by combustion. Gaseous hydrogen is then routinely generated by reducing the water (H₂O) using uranium metal heated to 750°C or metallic zinc heated to 450°C. Additionally, Gehre et al. (1996) demonstrated that chromium heated to 750°C is also an efficient reducing agent. This study uses heated uranium metal for hydrogen conversion in all instances.

Following the collection of suitable lacustrine core and sediment sample

preparation, the experimental plan used in developing a hydrogen extraction technique was to first establish a reference data set of δD , $\delta^{13}C$, C/N, H/C and % organic carbon from the acid resistant residues described in subsequent sections. Once this base data set was established, experiments pertaining to the exchangeable hydrogen attached to the residual organic molecule and removal of the exchangeable hydrogen were designed.

Sample Preparation

Acid Digestion Procedure

Successive acid-digestion of the parent sediment sample(s) was necessary for the removal of any inorganic-hydrogen bearing materials from the sediment organic matter. Acid resistant sediment organic residues were initially prepared for hydrogen extraction based on the protocol established by Krishnamurthy and Epstein (1991) and subsequently used by Krishnamurthy et al. (1995) in their Austin Lake study (Kalamazoo, Michigan). Unprocessed (raw) sediment samples were dried as necessary then powdered using an agate mortar and pestle. Aliquots of each unprocessed, dried and crushed sample were set aside for analysis of inorganic carbon and oxygen via the 100% H_3PO_4 digestion technique (Lake Winnebago samples only) using the modified septum digestion technique developed by Krishnamurthy et al. (1997) for isotopic studies of carbonates. The remaining unprocessed sample was digested in concentrated HCl (38%) to remove carbonates prior to digestion with

HF:HCl [mixed as a 1:1 (v:v) solution from concentrated HF (48%) and HCl (38%)] to remove silicates.

Initially, the conventional HF:HCl digestion procedure was followed, wherein samples were digested while kept in a ~60°C water bath to speed the reaction. This technique required a mean cumulative HF:HCl processing time of ~2700 minutes in acid. The total time required to process an individual sediment sample through both the HCl and HF:HCl digestions and into its residual organic matter for isotopic analysis ranged from 7 to 10 days. A faster process was desired. For this, a newly developed HF:HCl microwave digestion procedure was adopted that much improved the efficiency of the HF:HCl procedure. The specific details of the HCl and HF:HCl digestion procedures are discussed below.

HCl Digestion

The standard procedure for analysis of organic matter in sediment is to prepare a carbonate free sediment residue by digesting the “raw” sediment in hydrochloric acid (HCl). In this study, carbonate removal was accomplished by placing dried and powdered unprocessed sediment samples in 15ml acid resistant centrifuge tubes with approximately 9 ml of concentrated HCl. Each sample tube was mixed thoroughly by stirring with a glass rod, then capped and kept in a constant temperature water bath at ~60°C. Spent HCl was replenished at 3 and 5 hour intervals by first centrifuging each tube, then pouring off the supernatant and replenishing each tube with ~ 9ml of fresh HCl. Samples were again stirred and capped before returning them to the 60°C water

bath. Typically, 2 to 3 cycles of 3 to 5 hours of HCl-digestion were used (cycled until no reaction could be observed). Each sample was then rinsed to near pH neutral (using laboratory-distilled water of pH 6) and freeze-dried. Aliquots of each dried HCl-residue were separated for organic carbon studies ($\delta^{13}\text{C}$, percent organic carbon and C/N) and archive storage. The remaining fraction of HCl-residue was used in the subsequent HF:HCl digestion.

HF:HCl Digestion

The HF:HCl digestion procedure is designed to concentrate the sediment organic matter by removing silicates and any remaining hydrogen bearing inorganic components from the carbonate-free HCl-residue. Both the conventional and a newly developed microwave digestion procedure were used to remove silicates and further concentrate the sediment organic remains. The conventional HF:HCl digestion and hydrogen extraction methods (Krishnamurthy et al., 1995) were used in the initial stage of this research involving a pilot group of 42 sediment samples. These 42 samples were selected over the 12-meter length of the Ladd Lake core and corresponded, where possible, to intervals of pollen analysis (Shane, 1991 and Shane and Anderson, 1993).

Dried and powdered HCl-residues were placed in 15ml acid (HF) resistant centrifuge tubes and approximately 9 ml of the concentrated HF:HCl solution was added, then mixed thoroughly using a nalgene stirring rod and capped. The sample-tubes were kept in a constant-temperature water bath at $\sim 60^{\circ}\text{C}$ for variable duration

ranging from hours to days, then centrifuged and the supernatant decanted. The HF:HCl residues were then rinsed to near pH neutral and freeze dried, as before. After processing the initial 20 samples through one HF:HCl digestion cycle the process was modified by first determining the dry weight of the powdered HCl-residues before placing them into the 15ml acid (HF) resistant centrifuge tubes. Weights were measured using a Metler balance, model AE 240, which yield accurate results to 0.02 mg. Now, each sample was processed through an HF:HCl digestion cycle and weighed before being re-processed in consecutive HF:HCl digestion cycles. This technique was followed until successive freeze-dry weights of the HF:HCl residues reached a near constant weight (defined as exhibition of less than 10% change in successive freeze-dry weights following each HF:HCl digestion cycle). The rationale for this method was to determine the point that inorganic material in each residue became essentially irreducible. The initial 20 samples and the remaining 22 pilot group samples were processed in this manner until less than 10% change in weights occurred as described above. Due to lack of an initial dry weight for the first 20 samples, their overall mass reduction could not accurately be determined. The remaining 22 samples, however, exhibited a mean of 82% mass reduction during the residual organic concentration process. Table 4 shows the results for all 42 pilot samples. The sample number, centrifuge tube number (given to identify grouping, i.e. first 20 or last 22 samples), and the initial and final weights of the residues are shown adjacent to their overall percent reduction in sample weight through the digestion procedure along with the cumulative time in HF:HCl for each sample. Using this conventional digestion

procedure, the cumulative time required to achieve an irreducible concentration weight ranged from 1658 minutes to 7527 minutes in the HF:HCl solution.

Table 4

Summary Weight Change During Successive HF:HCl Digestion of Pilot Group Samples From Ladd Lake Are Shown With the Cumulative Time in Acid

Sample Number	Tube Number	Initial Wt. HCl residue (grams)	Final Wt. HF:HCl residue (grams)	% Wt. Reduction	Cumulative Minutes in HF:HCl
LL934	1	0.12533	0.00396	96.84%	2084
LL1078	2	0.20711	0.02428	88.28%	6511
LL1024	3	0.09906	0.01489	84.97%	2084
LL1054	4	0.08205	0.01994	75.70%	1826
LL1134	5	0.13726	0.02596	81.09%	1826
LL1190	6	0.06035	0.03055	49.38%	2084
LL1204	7	0.03103	0.03069	1.10%	1658
LL1234	8	0.10256	0.0302	70.55%	1786
LL1250	9	0.05197	0.04927	5.20%	1658
LL1266	10	0.03107	0.02698	13.16%	1658
LL1366	11	0.06319	0.04322	31.60%	2026
LL1435	12	0.07605	0.03296	56.66%	2026
LL1449	13	0.07207	0.05157	28.44%	2026
LL1463	14	0.00952	-0.00596	162.61%	2026

Table 4 - Continued

Sample Number	Tube Number	Initial Wt. HCl residue (grams)	Final Wt. HF:HCl residue (grams)	% Wt. Reduction	Cumulative Minutes in HF:HCl
LL1467	15	0.03285	0.01927	41.34%	2026
LL1515	16	-0.00883	-0.01907	-115.97%	2026
LL1551	17	0.01095	-0.00359	132.79%	2115
LL1559	18	0.04144	0.02455	40.76%	2115
LL1651	19	-0.03071	-0.0425	-38.39%	2115
LL1699	20	-0.04526	-0.06455	-42.62%	2115
LL1735	21	0.17715	0.03548	79.97%	2652
LL1767	22	0.20559	0.05158	74.91%	2652
LL1791	23	0.23775	0.05366	77.43%	2652
LL1807	24	0.32748	0.03726	88.62%	2967
LL1819	25	0.23055	0.03818	83.44%	2652
LL1823	26	0.16176	0.02178	86.54%	2652
LL1867	27	0.18913	0.02140	88.69%	2407
LL1899	28	0.19348	0.05815	69.95%	2407
LL1923	29	0.27829	0.06756	75.72%	2407
LL1951	30	0.37378	0.03750	89.97%	2722
LL1975	31	0.32240	0.07786	75.85%	2407

Table 4 – Continued

Sample Number	Tube Number	Initial Wt. HCl residue (grams)	Final Wt. HF:HCl residue (grams)	% Wt. Reduction	Cumulative Minutes in HF:HCl
LL1984	32	0.25184	0.05883	76.64%	2407
LL2004	33	0.27035	0.08322	69.22%	2655
LL2028	34	0.23252	0.04910	78.88%	2655
LL2042	35	0.21692	0.04102	81.09%	2655
LL2056	36	0.28476	0.03798	86.66%	2655
LL2060	37	0.26230	0.03477	86.74%	2665
LL2084	38	0.35068	0.05292	84.91%	2665
LL2098	39	1.30905	Stepwise	Stepwise	7527
LL2108	40	0.66223	0.07237	89.07%	2967
LL2111	41	0.67857	0.06008	91.15%	2960
LL2115	42	0.76455	0.05908	92.27%	7527

Overall, the time required to process an individual sediment sample from its “raw” parent state into its residual organic matter for isotopic analysis ranged from 7 to 10 laboratory days. A faster, more time efficient, method was desired. This led to developing an alternative method for the speeding the HF:HCl sediment digestion process. This newly developed procedure is discussed in the following section. The

isotopic analysis of the 42 Ladd Lake pilot samples is reported in subsequent sections of this manuscript, which follow the acid digestion procedures.

HF:HCl Microwave Digestion Procedure

The microwave digestion procedure uses a programmable microwave unit (CEM Corporation, MDS-2000 unit) having the capability of monitoring both pressure and temperature within a control digestion vessel. This “microwave sample preparation system” was originally designed for laboratory use in digesting, dissolving, hydrolyzing and drying a wide range of materials. In the past, it had been used primarily for rapid preparation of samples for analysis by atomic absorption, inductively coupled plasma emission spectroscopy and gas or liquid chromatography. The MDS-2000 unit delivers ~630 watts of microwave energy at a frequency of 2450 MHz at full power with the percent power being programmable in 1% increments. Compounds such as water and other polar liquids absorb microwave energy rapidly. When confined in the sealed beaker system, the rapid heating and elevated pressures cause the sample to digest or dissolve in a short time.

In the general protocol dried and weighed HCl-residues are placed into acid resistant Teflon (CEM®) beakers. Approximately 9ml of the concentrated HF:HCl solution were uniformly added to each beaker. Each beaker was sealed and mounted within the microwave unit on a direct drive rotary tray (capacity for 12 sample beakers). The microwave unit may be programmed to maintain either a specified temperature or a set pressure within the control digestion vessel where both are

monitored simultaneously. After initial experimentation, the best results were experienced by using full power and processing the sample(s) for 60 minutes at 120°C resulting in a sustained pressure of ~35 psi. Once processed the digestion vessels were allowed to cool (~ 30 minutes) until reaching manageable temperatures (35 to 50°C). The beaker contents (acid plus samples) were subsequently transferred to HF resistant centrifuge tubes, then centrifuged and the supernatant decanted. Next, samples were rinsed with distilled water and centrifuged repeatedly until the decanted liquid attained a near pH neutral condition. Once achieved, the HF:HCl residues were freeze-dried and stored in appropriately labeled vials.

Ninety-five additional Ladd Lake samples and 60 Lake Winnebago samples were processed using this microwave digestion technique. Table 5 shows a comparison of the statistical summaries for both the conventional and microwave HF:HCl digestion procedures. What initially required a mean of 2656 cumulative minutes (44.26 hours) in HF:HCl was reduced to 60 total minutes of microwave HF:HCl digestion followed by approximately 30 minutes for cool down. Similar overall mass reductions were exhibited in each procedure. Both the Ladd Lake Pilot Group series and the Ladd Lake microwave samples show a mean reduction in mass of 82%. Lake Winnebago samples exhibited a mean mass reduction of 85%. Although statistically unsubstantiated, digestion efficiency seemed to be enhanced when HCl-residues of less than 600mg were used. Indeed, the MDS-2000 operations manual cautioned against using samples larger than 500mg. In testing this advice, however, larger initial sample residues sometimes resulted in the formation of solids (perhaps

CaF, presumably due to HF reaction with “poorly processed” carbonate free samples). Much of this was rectified by use of samples smaller than 600 mg and meticulous

Table 5
Statistical Summary and Comparison of the Conventional and Microwave HF:HCl Digestion Techniques

Digestion Process:	\bar{x}	N	Parameters Max.	Min.
Conventional Process:				
Ladd Lake Pilot Group				
Minutes in Acid	2656	42	7527	1658
% Mass Reduction	82%	22	70%	92%
Microwave Process:				
Ladd Lake				
Minutes in Acid	60	95	N/A	N/A
% Mass Reduction	82%	95	59%	98%
Lake Winnebago				
Minutes in Acid	60	95	N/A	N/A
% Mass Reduction	85%	60	75%	93%

attention to the HCl digestion phase, rinse and freeze dry procedures. Empirical observation during continued utilization of the microwave unit suggested that a strict

adherence to using small initial samples (<600mg) resulted in less variation (greater uniformity) in the quality of the generated HF:HCl residues. Figure 3 further supports that the microwave digestion procedure was more efficient. The data shown is a plot of the % organic carbon in the HCl residue vs. the % organic carbon in the HF:HCl

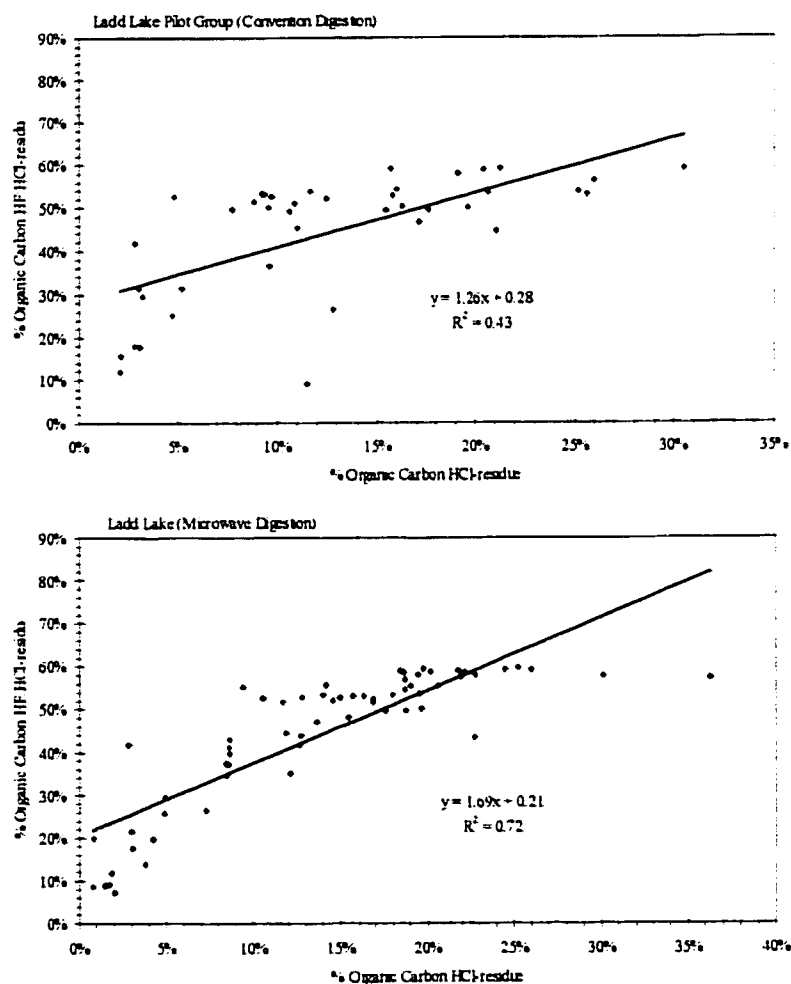


Figure 3. Regression of % Organic Carbon From the HCl and HF:HCL-Residues of Conventionally and Microwave Digested Ladd Lake Samples.

residue for both the Ladd Lake Pilot Group (conventional digestion) and the Ladd Lake samples digested using the microwave procedure. Obvious scatter in the conventionally digested samples is reduced in the microwave-digested samples. The increase of slope quantitatively demonstrates the higher efficiency in concentrating the organic matter by the HF:HCl microwave procedure. This observation is supported by the R^2 value from regression of the microwave group ($R^2 = 0.72$) which shows a significantly improved correlation over that of the conventionally processed samples ($R^2 = 0.43$).

Overall, both the conventional and microwave digestion processes resulted in the concentration of the organic remains initially contained in the bulk sediment. The microwave procedure, however, offered a much-improved efficiency in both time-use and the organic concentration. Using this method, each sample was then prepared for combustion and isotopic analysis of δD .

Experimental Phase Isotopic Analysis

Ladd Lake Pilot Group

As previously discussed, the Ladd Lake pilot group samples corresponded to intervals of pollen analysis over the length of the 12-meter core. These samples were digested using the conventional process until less than 10% change in successive freeze-dried sample weights was realized. Isotopic analysis of the HCl and the HF:HCl-residues was accomplished by combusting each sample in the presence of

CuO, then cryogenically separating the gaseous CO₂, H₂O and N₂ combustion by-products. The controlling reaction for this process is as follows:



Carbon and nitrogen yields were recorded for the carbonate free residue (HCl-residue) and the HF:HCl residues. These data were used in calculating the carbon/nitrogen (C/N) ratios and percent organic carbon for both residual materials. The C/N ratios of the carbonate free fraction were used to constrain the interpretation of the organic carbon data. Literary reference to the percent organic carbon typically addresses the carbonate free component (HCl-residue). The percent organic carbon of the HF:HCl residue was monitored in this study to ascertain if additional information could be obtained after further residual organic concentration during the acid digestion procedures. The $\delta^{13}\text{C}$ of the CO₂ gas was determined for both residual materials. Hydrogen yields and the hydrogen to carbon ratio (H/C), however, were determined only for the HF:HCl-residue. Passing the water over uranium metal heated to 750°C generated hydrogen gas that was subsequently collected then transferred to the mass spectrometer for measurement of δD . Both $\delta^{13}\text{C}$ and δD were analyzed using a Micromass-Optima isotope-ratio mass spectrometer. All isotopic ratio data are reported in standard delta notation in per mil values as follows:

$$\delta\text{‰} = [(\text{R}_{\text{sample}} / \text{R}_{\text{standard}}) - 1] 10^3$$

where R is ¹⁸O/¹⁶O, D/H, ¹³C/¹²C etc.

Carbon isotope ratios are reported relative to the international standard PDB. Hydrogen isotopic ratios are reported relative to SMOW.

As this methodology development is focused on the extraction of hydrogen from sediment bulk organic matter, discussion of the isotopic carbon and nitrogen results will be postponed to Chapter III. The δD of the Pilot Group samples extracted via the conventional techniques will be shown in subsequent sections of this chapter in conjunction with the newly developed hydrogen extraction procedure.

Isotopic Analysis During Stepwise Digestion

To evaluate the effects of acid digestion on the δD of the HF:HCl residue, a single sample was selected based on availability for successive combustion experiments. Sample number LL2098 was digested using the conventional acid digestion technique and an aliquot of sample LL2098 was removed for isotopic analysis following each successive freeze dry cycle of the HF:HCl procedure. A total of six digestion cycles were performed.

Table 6 relates the findings for the δD , $\delta^{13}C$ and H/C ratio analysis through each step. Also included in Table 6 are the cumulative minutes in HF:HCl and the percent organic carbon in both the HCl and HF:HCl residues. The HCl residue exhibited a δD of -90‰ with an H/C ratio of 1.980. The organic carbon content in the HCl residue was low at only 2.83 percent. As shown, there was a general decrease in

Table 6

Details of δD and $\delta^{13}C$ Analysis for a Single Sample Through Each Step Using the Conventional Acid Digestion Procedure

Stepwise Analysis of Sample LL2098					
Residue Analyzed	δD	Cumulative Acid Time (minutes)	H/C	$\delta^{13}C$	% Organic Carbon
HCl	-90‰		1.980	-28.55‰	2.83
HF#1	-102‰	1504	1.069	-28.87‰	11.27
HF#2	-100‰	2645	0.918	-28.64‰	16.16
HF#3	-101‰	2690	0.834	-28.47‰	20.00
HF#4	-122‰	7300	0.352*	-28.41‰	23.37
HF#4 Repeat.	-104‰	7300	0.801	-28.45‰	25.23
HF#5	-108‰	7387	0.756	-28.37‰	32.36
HF#5 Repeat.	-109‰	7387	0.858	-28.81‰	31.86
HF#6	-112‰	7547	0.710	-28.70‰	30.75
HF-residue mean	-107‰		0.787	-28.59‰	

*loss of hydrogen suspected

both the δD value and the H/C ratio following successive HF:HCl acid digestions. The decline in H/C ratio may be related to continued loss of hydrogen bearing

inorganic materials in the insoluble residues. The δD values of the HF:HCl residues exhibit a range from -100‰ to -122‰. This general negative trend in δD during successive digestion cycles may be related to isotopic exchange between the residual matter and the liquid fractions used during the digestion and rinse procedures. Alternatively, the range in δD values may reflect poor precision using the conventional extraction technique. The one outlier at $\delta D = -122‰$ is considered flawed as the H/C ratio suggests an aberrant loss of hydrogen, perhaps during sample handling.

The mean $\delta^{13}C$ value of the HF:HCl residues (-28.59‰) is virtually identical to the organic carbon (-28.55‰) value from the HCl-residue. These $\delta^{13}C$ values are well within the accepted 0.1‰ precision for carbon isotopic ratios. The percent organic carbon in the residue generally increases with each digestion cycle but seems to plateau after 4 digestion cycles. These lines of evidence lend support to the observation that the molecular carbon structure of the insoluble organic residue suffers little, if any, degradation during the acid digestion procedures.

Exchangeable Hydrogen Experiments

Whereas previous studies using D/H of plant materials suggest that it is only the non-exchangeable hydrogen in cellulose that is a potential climate proxy, Krishnamurthy et al. (1995) argue that either the HF:HCl insoluble residue reasonably approximates the cellulose non-exchangeable hydrogen or that the D/H of HF:HCl residue itself may be a new climate proxy, behaving much like cellulose. To address

the issue of non-exchangeable hydrogen in the HF:HCl residue four samples from the Ladd Lake pilot series were selected (again on a quantity/availability basis) for repeated experimentation. Two of the samples were selected from among those having the most positive δD values (-118‰ and -119‰) and two from those having the most negative values (-140‰ and -146‰). All four of these HF:HCl residues had organic carbon contents greater than 50% whereas their corresponding HCl residue organic carbon content ranged from ~11 to 21%.

To determine if hydrogen exchange indeed occurs an experiment was designed wherein weighed aliquots of each sample were placed in 6mm Vycor (quartz-nickel glass) boats to which 0.2cc of deuterium enriched water ($\delta D = +64$ ‰) was added. Sample boats were placed within 9mm Vycor tubes and CuO was added. The 9mm tube was then necked using a torch with an oxygen-natural gas flame and the sample plus enriched water was allowed to equilibrate for 24 hours at room conditions. Once equilibrated each sample was freeze-dried while on the vacuum line, then sealed and combusted at 900°C for 3 hours. The results of isotopic analysis, shown in Table 7, exhibit isotopic values from 19 to 39‰ higher (more positive) than their respective parent (original/non-spiked) δD values. This clearly suggested that isotopic exchange had occurred between the HF:HCl residues and the water.

As it is the non-exchangeable hydrogen that offers the potential proxy indicator, a second experiment was then needed to evaluate the potential for driving off exchanged hydrogen. Using the same four samples, aliquots of each were first

spiked, equilibrated and freeze dried, as before, then pyrolyzed (heated while in vacuum) at 150°C for 2 hours prior to sealing and combustion. To accomplish this, a cylindrical ceramic (porcelain) furnace was constructed having a 3.5-inch internal diameter and fitted with sheet aluminum housing. The heating mechanism was constructed of two semi-circular ceramic plates that housed a series of coiled heating elements that occupied linear grooves along the interior wall of the furnace. Quartz-wool insulation was placed between the metal housing and ceramic surfaces. Temperature regulation was accomplished by using an Omega™ temperature controller wired to the furnace coil and a thermocouple. The base of the furnace sat on a ceramic plate covered with quartz wool and all were positioned on an adjustable accordion stand (support jack). The necked 9mm sample tubes were evacuated on the extraction line with the furnace positioned beneath the sample and its height adjusted to encase the sample. The thermocouple wire was then placed inside the furnace and quartz-wool was used to seal the upper furnace opening for heat retention. The furnace was then turned on, brought to the designated temperature and held at constant temperature for the desired time. Table 7 shows the results. In each case, the isotopic ratios of the spiked and pyrolyzed samples were driven in a negative direction compared to the values from the initial spike experiment. The resultant δD from this experiment approached that of the original HF:HCl residue used in the Pilot Group. This pre-heating process seemed to drive off water that became adsorbed and possibly exchanged with the HF:HCl residue. If exchange was occurring, the

exchanged deuterium was preferentially being removed by pyrolysis of each sample prior to combustion.

Table 7
Exchangeable Hydrogen in HF:HCl-Residues

Sample ID	Pilot Group Original δD	Spiked (+64‰ Wtr.) δD	Spike & Pyrolyzed 2 hours at 150°C δD
LL1366	-119‰	-99‰	-112‰
LL1767	-118‰	-99‰	-118‰
LL1923	-146‰	-107‰	-121‰
LL1975	-140‰	-111‰	-124‰

This phenomenon of deuterium loss through pre-heating was further explored by individually subjecting non-spiked aliquots of each of the previous four samples to 2, 5, 12 and 24 hours of pyrolysis at 150°C. Each sample was then sealed and combusted and the δD of the evolved water determined. The purpose, in this case, was to determine whether the δD values of the HF:HCl residues would stabilize by removal of ambient waters that were either adsorbed onto or exchanged with the residual organic matter during sample preparation and storage. If so, it was hoped that stable and repeatable isotopic ratios from each residue could be achieved by pre-heating the sample. Table 8 and Figure 4 show the results of these four pre-heating

experiments. The change in the δD from the original ($\Delta\delta D$) is also shown in the table. This value represents the difference in the δD -value of the original Pilot Group sample and the respective δD of the sample pyrolyzed at 150°C for the indicated time ($\Delta\delta D = \delta D_{\text{original}} - \delta D_{\text{P150}}$). Three of the samples show an initial positive shift in their

Table 8

Pyrolysis of HF:HCl Residues at 150°C for Variable Duration Prior to Combustion and Determining the Isotopic Ratios

Pyrolysis Duration (hrs.)	Sample ID	δD	$\Delta\delta D$ ($\delta D_{\text{original}} - \delta D_{\text{P150}}$)	H/C
Original	LL1366	-119‰	---	0.80
2 hrs	LL1366	-110‰	9‰	0.84
5 hrs	LL1366	-116‰	3‰	0.81
12 hrs	LL1366	-124‰	-5‰	0.79
24 hrs	LL1366	-127‰	-8‰	0.85
Original	LL1767	-118‰	---	0.76
2 hrs	LL1767	-126‰	-8‰	0.90
5 hrs	LL1767	-130‰	-12‰	0.89
12 hrs	LL1767	-133‰	-15‰	0.91
24 hrs	LL1767	-135‰	-17‰	0.87
Original	LL1923	-146‰	---	0.92
2 hrs	LL1923	-141‰	5‰	0.81

Table 8 – Continued

Pyrolysis Duration (hrs.)	Sample ID	δD	$\Delta \delta D$ ($\delta D_{\text{original}} - \delta D_{P150}$)	H/C
5 hrs	LL1923	-150‰	-4‰	0.74
12 hrs	LL1923	-151‰	-5‰	0.74
24 hrs	LL1923	Lost H ₂	Lost H ₂	Lost H ₂
Original	LL1975	-140‰	---	0.93
2 hrs	LL1975	-133‰	7‰	0.82
5 hrs	LL1975	-138‰	2‰	0.80
12 hrs	LL1975	-142‰	-2‰	0.81
24 hrs	LL1975	-145‰	-5‰	0.81

δD value after only two hours of pyrolysis but all four samples exhibit deuterium loss (more negative δD values) at more than two hours of pyrolysis at 150°C. Figure 4 graphically demonstrates that after approximately 5 hours of pre-heating the D/H ratios in each sample begin to plateau and seem to approach a stabilized value by 12 hours of pyrolysis at 150°C. In each sample, the δD shows no more than a 3‰ difference in their final analyses.

From this initial series of experiments it became evident that hydrogen exchange had indeed occurred but that stable δD values may be obtainable through

pre-heating of the HF:HCl residue prior to combustion and isotopic analysis. Further exploration of this finding was needed, however, to quantify the hydrogen release pattern from the HF:HCl residues. To address this issue, samples of both low and high percent organic content were selected and spiked with either deuterium enriched or

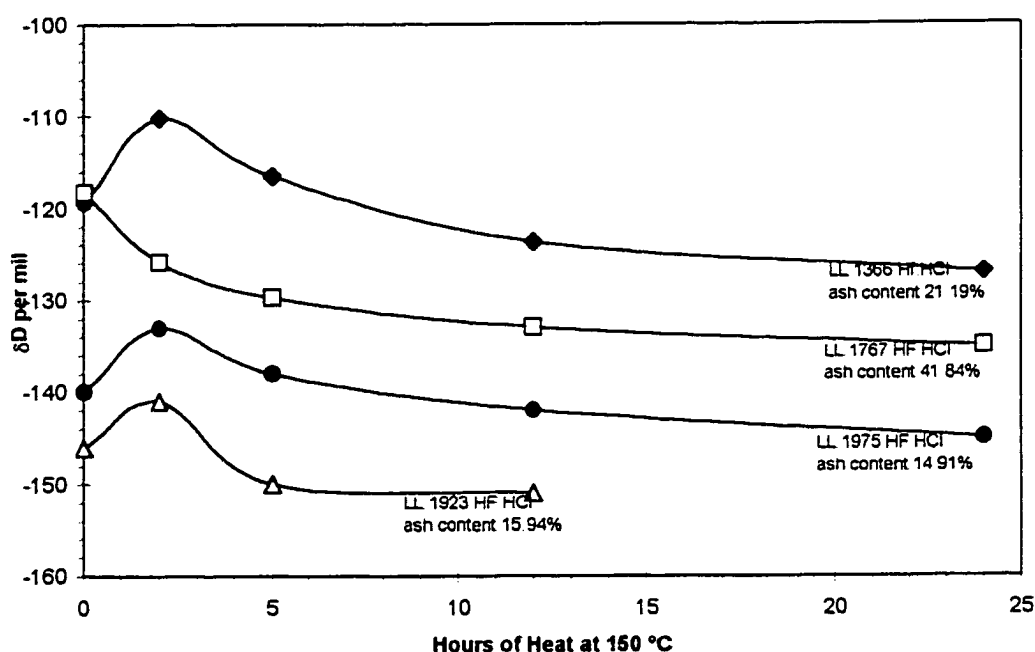


Figure 4. Pyrolysis of HF:HCl Residues at 150°C for Variable Duration Prior to Combustion and Determining the Isotopic Ratios.

depleted waters in the manner previously described. Sapropel samples were now incorporated into the study, as they are known to be sediments of low bulk organic content. After equilibration and freeze drying, each sample was individually evacuated then heated from room temperature (~20°C) to 150°C and held at constant temperature for 30 minutes while trapping any pyrolysis water in liquid nitrogen. The

trapped water was subsequently transferred, passed over heated uranium metal, the hydrogen collected and the δD determined. Using this methodology, the pyrolysis temperature was stepped in 50°C increments then held constant for 30 minutes through interval steps over the 150° to 350°C range. Pyrolyzed waters were collected during each step and their D/H ratios were determined where yields permitted. When hydrogen yields were too small for measurement (accurate measurements of δD require that $> 10 \mu\text{mols H}_2$ be collected to transfer to the mass spectrometer), successive yields were combined until their cumulative yields were sufficiently large. After collection of the final pyrolysis water from the 350°C step, the sample tubes were sealed and combusted at 900°C for 3 hours. The δD of the water from combustion was measured and recorded as the 350° to 900°C fraction.

Hydrogen yields from each stepped temperature increment are tabulated in Table 9. Sample identification is indicated alpha-numerically. The abbreviations LL for Ladd Lake, AL for Austin Lake and SAP for Mediterranean sapropel samples describe the sample provenance. The numbers adjacent to Ladd Lake and Austin Lake samples represent core depth (cm) and the numbers adjacent to sapropel samples designate a cross-referenced ID to the sapropel sample. All of these samples were spiked HF:HCl residues and the δD of the spiked water is shown in parenthesis adjacent to the sample identification number.

The data shown in Table 9 are plotted in Figures 5 and 6 as hydrogen released in micro-mols per milligram vs. pyrolysis temperature ($\mu\text{mols/mg}$ vs. T°C).

Comparison of Figures 5 and 6 demonstrate release pattern differences in samples having low versus high organic carbon content. The sapropel HF:HCl-residues

Table 9

Hydrogen Yields of Pyrolysis Water Released From Lake Sediment and Sapropel HF:HCl-Residues During Stepped Temperature Pyrolysis

Sample ID And Spike Value (%)	Pyrolysis Temperature (°C)					Combusted Fraction
	150°	200°	250°	300°	350°	350°-900°C
	Hydrogen Yield (μmols/mg)					
LL1923(+64)	0.84	0.93	2.05	1.50	2.08	7.10
LL1763-67(+64)	1.00	0.73	0.81	1.60	1.81	9.39
AL27(-290)	1.04	1.20	1.23	1.21	1.05	10.39
SAP4(+64)	1.90	0.72	0.63	1.20	0.37	0.39
SAP7(+64)	1.65	0.62	0.79	1.16	0.53	0.20
SAP6(-290)	1.35	0.62	0.53	0.63	0.77	0.59
SAP6(+64)	1.26	0.64	0.57	0.59	0.89	0.30
SAP15(+64)	1.23	0.53	0.61	1.40	0.27	0.12

(Figure 5) all have measured percent organic carbon contents from 2 to 7% in their respective HF:HCl residues. These low organic content samples have markedly higher

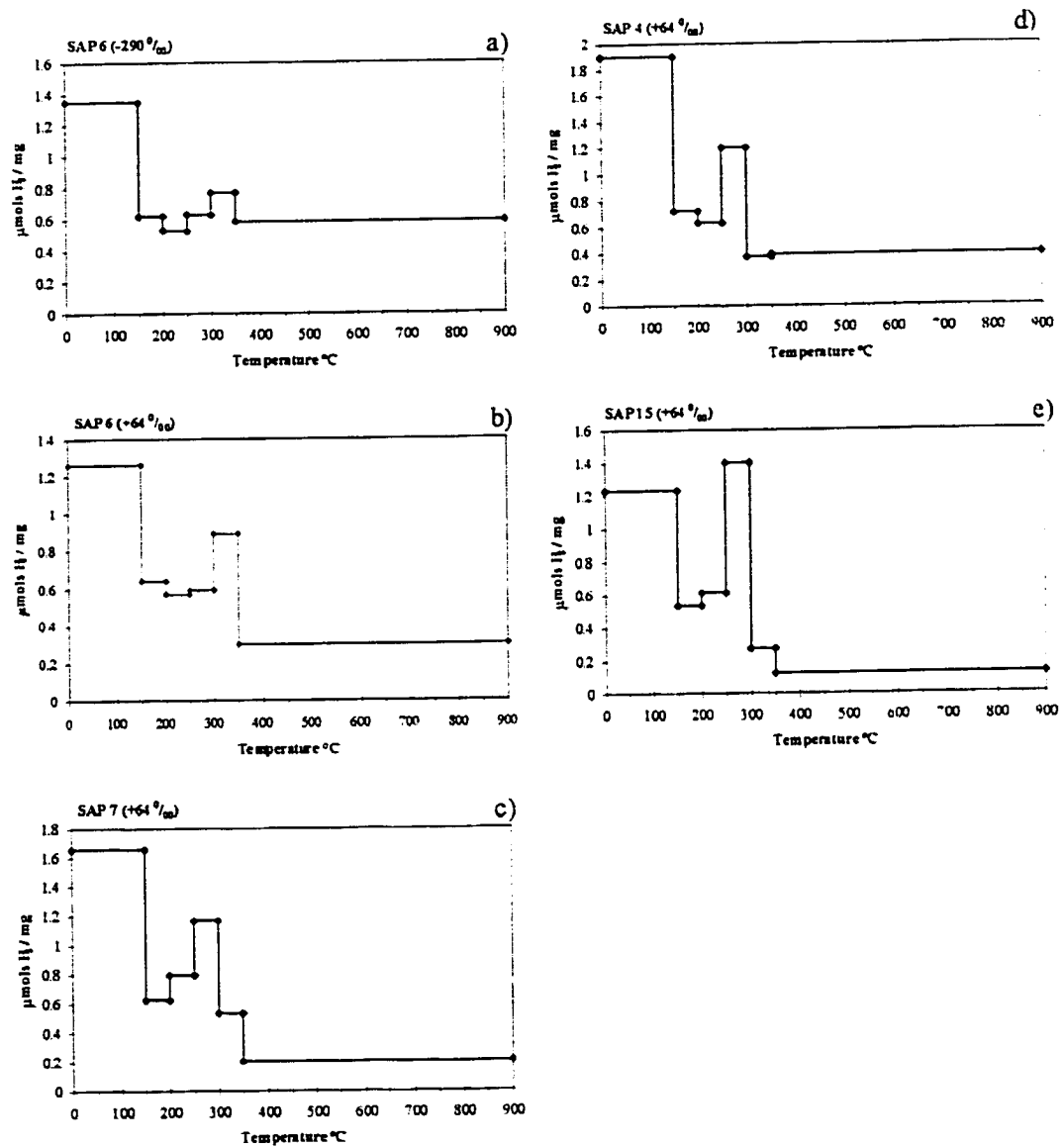


Figure 5. Hydrogen Release Pattern of Sapropels During Pyrolysis.

release of water (hydrogen) during the early pyrolysis phase (below 350°C) when compared to the release pattern of lake sediment HF:HCl residues in Figure 6.

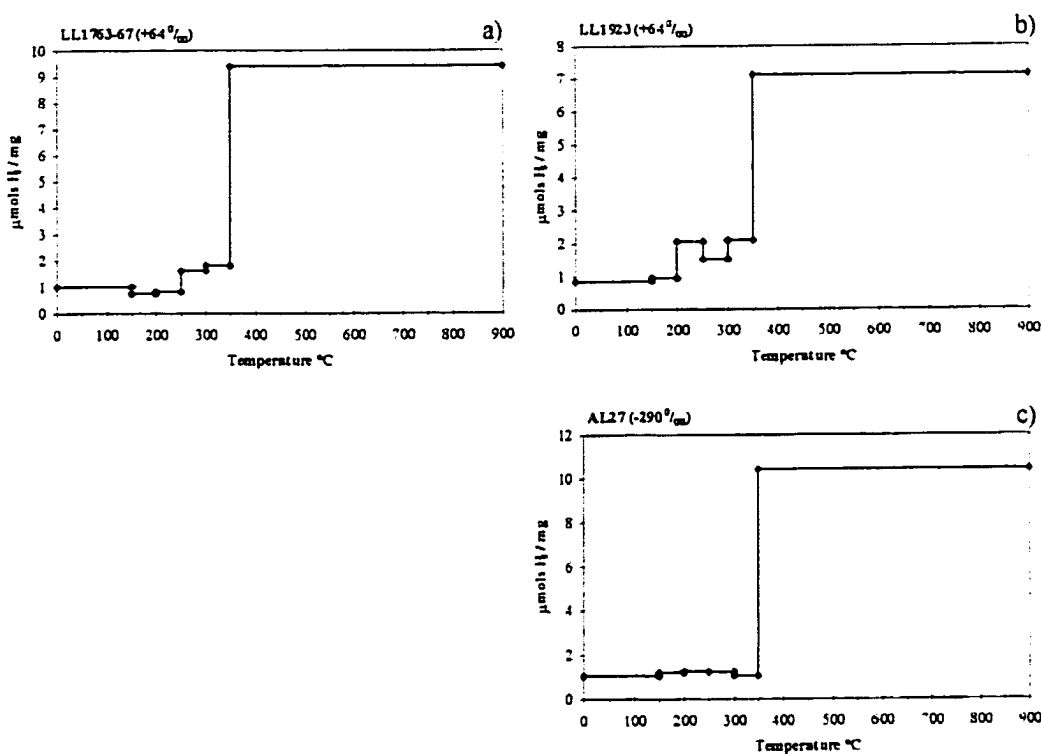


Figure 6. Hydrogen Release Pattern of Lake Organic Matter During Pyrolysis.

The bimodal release-pattern exhibited by the sapropels (Figure 5) suggests that inorganic materials within these low organic carbon content residues, such as residual clays, may account for much of the released pyrolysis waters and hydrogen exchange below 350 $^{\circ}\text{C}$. The high organic carbon content lake samples (all >50% organic carbon in their HF:HCl residues), shown in Figure 6, release most of their water during the 350 $^{\circ}$ to 900 $^{\circ}\text{C}$ combustion segment.

The percent of the total hydrogen released during pyrolysis and combustion is quantified in Table 10. Sapropels (in this case HF:HCl residues with less than 10% organic carbon content) release greater than 90% of their pyrolysis water below

350°C. Lake sediment samples (in this case, the HF:HCl residues have an organic carbon content of ~50%) show very limited release of water during the lower temperature pyrolysis. These higher organic content residues give up 50% or more of their hydrogen in the 350° to 900°C fraction. As a result, the δD signal of the 350° to

Table 10

Percent Hydrogen Released During Each Stepped
Temperature Pyrolysis Increment

Sample Identification and Spike Value (‰)							
SAP7 (+64)	SAP4 (+64)	SAP6 (+64)	SAP6 (-290)	SAP15 (+64)	LL1923 (+64)	LL1763-67 (+64)	
Percent organic Carbon in the HF:HCl residue							
2.4	5.4	7.8	7.8	1.2	52.9	40.7	
T°C	Percent Hydrogen Released During Incremental Pyrolysis						
25°C	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
150°C	33.3%	36.5%	29.7%	30.1%	29.6%	5.8%	6.5%
200°C	12.5%	13.7%	15.1%	13.9%	12.7%	6.4%	4.7%
250°C	16.0%	12.1%	13.3%	11.8%	14.6%	14.2%	5.3%
300°C	23.3%	23.0%	13.8%	14.0%	33.7%	10.4%	10.4%
350°C	10.8%	7.3%	21.0%	17.2%	6.6%	14.3%	11.8%
900°C	4.1%	7.4%	7.1%	13.1%	2.8%	48.9%	61.3%

900°C increment from the low organic carbon content sapropels represents only a small fraction of the bulk hydrogen signal from its insoluble residue. But given the fact that each residue contained less than 10% organic carbon, it may be argued that the exchanged hydrogen was removed during pre-heating with removal of pyrolysis water associated with the inorganic fraction. A similar argument can be made for the higher organic content samples. The δD of the 350° to 900°C fraction from lake sediment residues represents generally more than 50% of the bulk hydrogen signal from their insoluble residue.

Table 11 and Figures 7 and 8 show the δD of the water released during each stepped temperature pyrolysis increment and the final 350° to 900°C combustion interval. Additionally, for the purpose of comparison, Table 11 also includes the δD of the parent (original) HF:HCl residue of each sample. These values were taken from the pilot series of each group and their δD values reflect the bulk hydrogen signal with no pyrolysis or spike. With respect to these experiments, each sample showed the effects of the “spike water” in the δD of pyrolysis water captured during preheating below 350°C. The δD of the combusted fraction (350°-900°C) for each sample was consistently driven toward their respective parent values. For the sapropels, the bimodal release pattern below 350°C and the minimal water (hydrogen yield) released in the combustion fraction (350°-900°C) often made difficult the δD measurement for during each increment step for these low organic content samples. Similar “yield” problems were encountered for δD measurement with the high organic content

Table 11

The δD of Pyrolysis Water in Lake Sediment and Mediterranean HF:HCl-Residues
During Stepped Temperature Pyrolysis

Sample ID And Spike Value (‰)	Pyrolysis Temperature (°C)						Combusted Fraction
	Original δD (‰)	150° δD (‰)	200° δD (‰)	250° δD (‰)	300° δD (‰)	350° δD (‰)	350°-900°C δD (‰)
LL1923(+64)	-146	Tstm	Tstm	-54	Tstm	-103	-135
LL1763-67(+64)	-120	Tstm	+62	Tstm	+2	-63	-128
AL27(-290)	-94	-118	-95	-74	-67	-75	Lost gas
SAP4(+64)	-117	-86	Tstm	-85	Tstm	-139	Tstm
SAP7(+64)	-128	-94	Tstm	-93	Tstm	-149	Tstm
SAP6(-290)	-118	-94	-92	-84	-88	-82	-131
SAP6(+64)	-118	+49	+24	-15	-58	-55	-118
SAP15(+64)	-102	-46	-29	-69	-115	-125	-127

tstm = too small to measure

samples but only at temperatures below 350°C. The isotopic analysis of the pyrolysis water from both high and low organic content samples indicated that either exchanged or adsorbed hydrogen is preferentially removed by release of pyrolysis water during

incremental temperature steps. This was evidenced by the δD of the pyrolysis waters captured below 350°C, which all showed values that are “spike affected” when

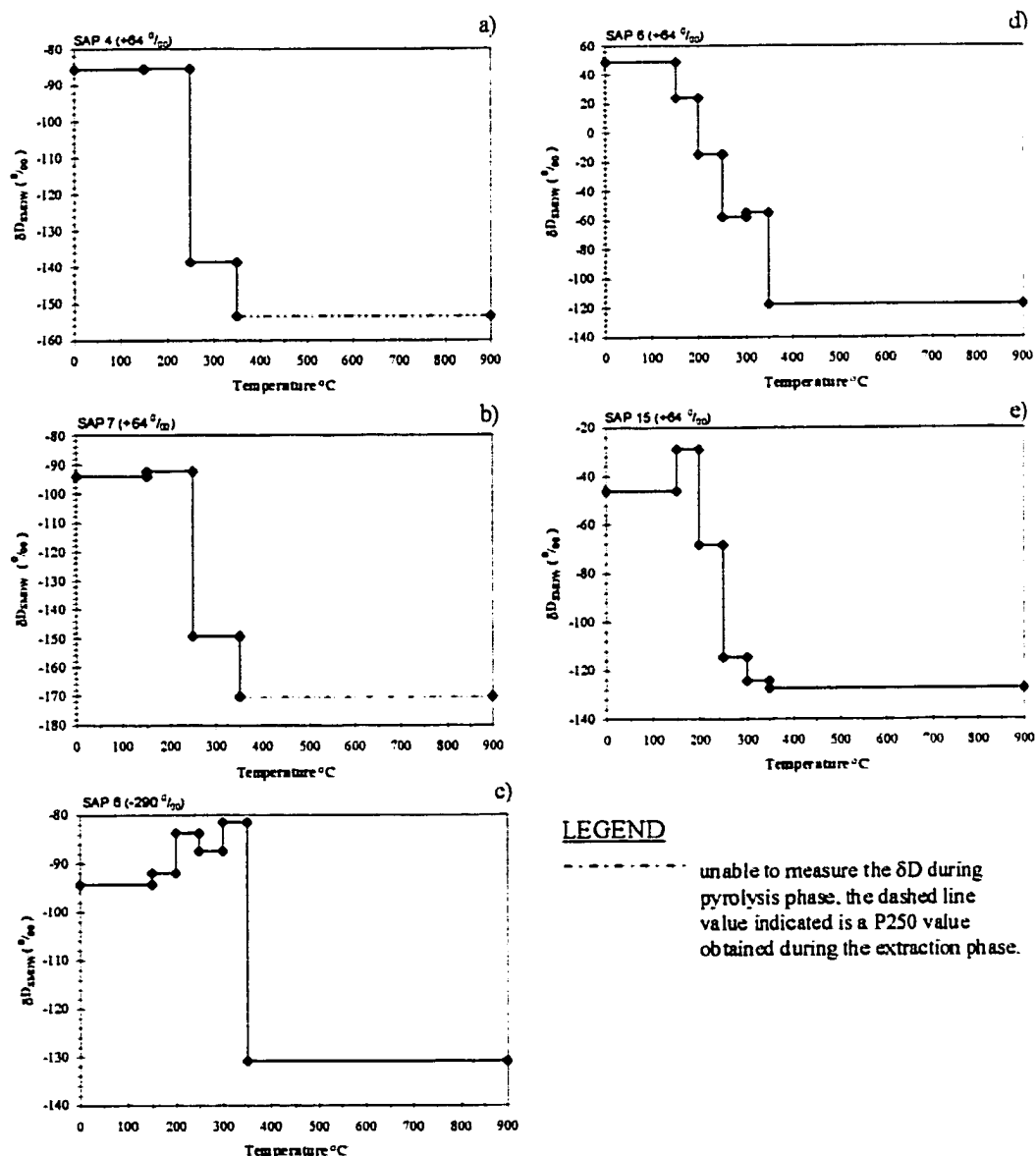


Figure 7. δD of Pyrolysis Water in Sapropel HF:HCl-Residues During Stepped Temperature Pyrolysis.

compared to the δD of the original or “parent” value. On the other hand, the δD for all the combustion fractions (350°-900°C) showed isotopic values that approximate

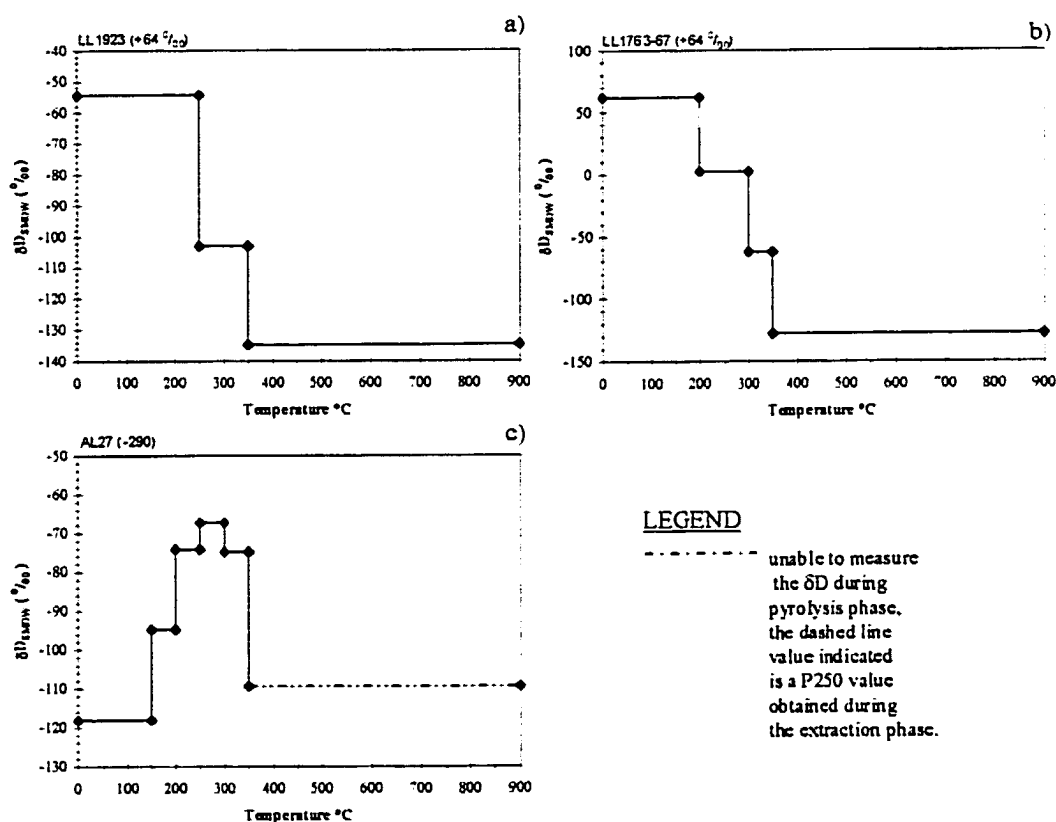


Figure 8. δD of Pyrolysis Water in Lake Sediment HF:HCl-Residues During Stepped Temperature Pyrolysis.

the “original” value. These results were typical despite the fact that the organic content of the insoluble residue seemed to control the release pattern of the pyrolyzed waters. In both high and low organic content residues, the adsorbed or exchanged hydrogen was largely driven off in the 150°-350°C preheating process. Support for these observations are shown in the Table 11 examples. Samples LL1763-67(+64),

SAP6(-290) and SAP15(+64) show δD values lower (more negative) post combustion δD values than their original δD -value. In the others, the δD of the combustion fraction equals or is only slightly more positive than the original δD value. It is not clear whether the hydrogen exchanged was between the organic matter itself with the spike water, or whether exchange of hydrogen was between waters adsorbed by the residual organic material. In either case, both the high and low organic content residues may (arguably) have retained some component of adsorbed/exchanged hydrogen in the 350° to 900°C fraction, but if so, it appears minor. Consequently, samples that are not “spike affected” by abnormally enriched or depleted waters during their preparation should potentially reflect isotopic values dominated by a largely non-exchangeable hydrogen signal.

Review and Discussion

Review of the experimental data clearly illustrates several important results. First, when equilibrated with enriched or depleted water, each sample showed effects of hydrogen exchange with its respective spike-water. To augment the Ladd Lake pilot samples shown in Table 4, two sapropel samples and an additional lake sample were subsequently spiked with deuterium enriched water having a δD of +64‰. Sapropel 4 and 7 had non-pyrolyzed and non-spiked (original) δD values of -117‰ and -128‰. After equilibration, freeze-drying and combustion per the initial experiments, the spiked sapropels exhibited δD values of -106‰ and -108‰,

respectively. Similarly, sample LL1763-67, spiked with the same enriched water, exhibited an original δD of -120‰ and a spiked δD of -90‰.

A second important observation is that adsorbed waters and possibly exchanged hydrogen may be systematically driven off by pre-heating the HF:HCl-residues while under vacuum prior to their combustion. Evidence of this was seen in the 150°C preheating of the spiked initial samples (Table 7), as well as during the incremental pyrolysis experiments. Preheating spiked samples for 2 hours at 150° drove the δD values in a negative direction. The δD of pyrolysis waters during incremental temperature pyrolysis showed that each sample exhibited an increasing loss of the adsorbed/exchanged spike-water with the larger proportion being removed at temperatures below 350°C. This later result is most notably observed by comparison of the two SAP6 samples, one spiked with -290‰ water and the other with +64‰ water (Table 11). As the pyrolysis temperature increased, the δD of the higher temperature fractions and the combusted 350°-900°C fraction were driven toward the “original” δD -value of the parent sample. In fact, every sample exhibited lower (more negative) D/H ratios in their final post-pyrolysis combusted fraction (350°C to 900°C) than was exhibited in the lower temperature pyrolysis-fractions (150°C to 350°C). It is arguable, however, as to whether “adsorbed/exchanged” hydrogen was present in the 350°C to 900°C fractions of these spiked samples.

In these initial pyrolysis experiments it is suggested that deuterium is preferentially released in pyrolysis water during preheating below 350°C. To assist the

confirmation of this phenomena, several samples were combusted at temperatures of 500°, 550°C, and 900°C after first equilibrating each with +64‰ spike water. Doing this allowed a reference point between the 350°C highest pyrolysis-temperature and the 900°C combustion-temperature. The results, given in Table 12, showed that the bulk hydrogen isotopic signal from each temperature fraction exhibited only a minor (~10‰) variation in δD values from the 500°C, 550°C, and 900°C fractions. These variations in the bulk δD from variable temperatures of combustion were small compared with the larger shifts in δD values from lower temperatures (150°-350°C) during the incremental pyrolysis of these same samples (compare to Table 8). Shifts in these later increments were sometimes greater than 100‰.

Table 12
Variable Temperature Combustion of HF:HCl Residues

Sample ID (Spike ‰)	900°C $\delta D_{\text{Original}}$ (‰)	Combustion Temperature		900°C δD (‰)
		500°C δD (‰)	550°C δD (‰)	
SAP4 (+64)	-117	-94	-96	-106
SAP7 (+64)	-128	-106	-98	-108
SAP7	-128		-123	
SAP12	-131		-121	
LL1975 (+64)	-140	-110	-113	-119

Interestingly, non-spiked aliquots of sapropels number 12 and 7 were also combusted at 550°C. Both samples exhibited only a slight positive shift from the δD value of their parent sample combusted at 900°C. In addition, the 550°C combustion-residue of SAP7 was re-evacuated, resealed and re-combusted at 900°C. This re-combusted sample had a δD of -142‰. This, in light of the pyrolysis experiments, suggests that the early water (and thus hydrogen) released during low temperature pyrolysis of spiked samples may be adsorbed waters and that exchanged hydrogen may be predominantly from waters attached to the organic residues.

The third significant observation is that the initial experiments seem to indicate the potential for stable D/H ratios after 5 to 12 hours of pyrolysis at 150°C (refer to Table 8 and Figure 4). In these experiments, the δD of the pyrolyzed and combusted HF:HCl samples maintained δD values within ~3‰. However, in experiments with pyrolysis to 350°C, low percent-organic-carbon-residues (sapropels) exhibited a significant early release of water (hydrogen) with yields too low for determination of D/H ratios in the higher temperature “combustion fractions” (350°C to 900°C). This occurred despite using samples as large as 110 mg (the typical lake sample aliquot used in combustion range from 5 to 10mg of HF:HCl residue). Thus, the questions relative to establishing a reliable pyrolysis extraction technique became twofold. First, could precision be documented for a pyrolysis-extraction technique? Secondly, can a uniformly applied single pyrolysis procedure (i.e. a single temperature and specified

pyrolysis duration) provide sufficient yield in the post-pyrolysis combustion fraction to measure the δD when percent organic carbon in the insoluble residue is low?

To examine these questions a pyrolysis temperature of 250°C was selected with duration of 60 minutes. The rationale for choosing this temperature and duration was that previous efforts had shown that pyrolysis at 150°C for 5 to 12 hours had resulted in near uniform δD values. Additionally, during subsequent incremental pyrolysis experiments to 350°C, cumulative preheating times were ~2 hours. As noted, this higher temperature and cumulative duration sometimes resulted in insufficient hydrogen yields for determination of the δD in the combusted fraction of samples having a low organic carbon content. The pyrolysis at 250°C for 60 minutes seemed a justifiable compromise.

To test the viability of this rationale, 15 sapropel samples were processed by preheating HF:HCl residues to 250°C and holding the temperature constant for 60 minutes before sealing the sample tube and combusting for δD analysis. The results are shown in Table 13. All but one of the sapropels gave sufficient yields for δD analysis of the combusted fraction (250°-900°C). Additionally, the δD of captured 250°C pyrolysis waters was measured for sapropel number 6 and 15 before these sample tubes were sealed and combusted for δD analysis of the 250°-900°C fraction. In this case, only sample SAP6 was spiked before preheating. Table 13 shows the δD of the captured 250°C pyrolysis waters and the subsequent combusted fraction (250°C to 900°C). The spiked SAP6 samples again showed the “adsorbed / exchanged”

enrichment effects with the deuterium enriched spike water in the 250°C fraction. Interestingly, both spiked samples showed isotopically similar δD values in their combusted fractions (-87‰ and -95‰) considering the vast difference (~200‰) between their respective spike water δD . SAP 15, with only 1.21% organic carbon in its HF:HCl residue, consistently released water yields that were too small to measure (tstm) δD in the post-pyrolysis combusted fraction.

Table 13

Hydrogen Isotopic Ratios of the Non-Pyrolyzed (Original) Sample are Compared to the δD After Pyrolysis at 250°C Before Combustion and the 250°C Pyrolysis-Waters and Subsequent Combustion Fraction

Sample ID Spike Value (‰)	Original δD (‰)	δD P250°C (‰)	Pyrolysis Water 250°C δD (‰)	Combusted Fraction 250°-900°C δD (‰)
SAP1	-99	-150		
SAP2	-143	-185		
SAP3	-115	-171		
SAP4	-117	-154		
SAP5	-124	-163		
SAP6	-118	-162		
SAP6(+64)	-118		+38	-87
SAP6(+252)	-118		+109	-95

Table 13 - Continued

Sample ID Spike Value (‰)	Original δD (‰)	δD P250°C (‰)	Pyrolysis Water 250°C δD (‰)	Combusted Fraction 250°-900°C δD (‰)
SAP7	-128	-170		
SAP8	-108	-166		
SAP9	-129	-161		
SAP10	-116	-156		
SAP11	-125	-152		
SAP12	-131	-165		
SAP13	-99	-138		
SAP14	-122	-167		
SAP15	-102	Tstm	-84	Tstm
AL7	-94	-127		
AL7(+64)	-94		+30	-121
AL27	-97	-109		
AL27(+64)	-97		+84	-73
AL27(+252)	-97		+143	-65

Tstm = too small to measure

Although higher in their percent organic content than the sapropels, two samples from Austin Lake, Michigan were also analyzed in the above manner. Aliquots of sample AL27 were separately spiked with +64‰ and +252‰ water, while, an aliquot of sample AL7 was spiked with +64‰. The results, also shown in Table 13, again showed the effects of their respective spike waters in the 250°C pyrolysis-water. The δD value of the 250°-900°C combusted-fraction in the AL7(+64) sample is -121‰ and quite similar to that of the 250°-900°C combusted-fraction in the AL7 at -127‰. Additionally, the magnitude of the 250°-900°C combusted-fraction in the AL27 spiked samples belies the magnitude of δD -value of their spike water. These values showed isotopically similar δD values in their combusted fractions (-73‰ and -65‰) considering the considerable difference (~200‰) between their respective spike water δD . Collectively, these experiments suggest that the δD values of the waters released during pyrolysis are primarily those adsorbed by the HF:HCl residue during the sample preparation prior to combustion. Additionally, there may be some indication of exchange between the organic residue and the process water used as the post-pyrolysis combustion δD values for HF:HCl residues were amplified by the use of spike equilibration. However, this exchange, if present, must be minor given the similarity of δD value in the 250°-900°C combusted-fraction of identical samples spiked with waters of vastly differing δD signatures.

Further testing was needed to determine whether the δD of 250°-900°C combusted fractions would yield results that offered stable and reproducible δD

values. Initially, two samples from those previously pyrolyzed at 150°C were selected. Sample LL1923 and LL1975 were each pyrolyzed at 250°C before being sealed and combusted for δD analysis. The results are shown in Table 14 as a comparison to the previous 150° pyrolysis for variable duration's. Similar δD values were obtained for

Table 14
Comparison of δD Values After Pyrolysis at 150° and 250°C

Sample ID Number	Original $\delta D_{\text{original}}$ (‰)	Pyrolysis at 150°C				Pyrolysis at 250°C
		2 hrs δD (‰)	5 hrs δD (‰)	12 hrs δD (‰)	24 hrs δD (‰)	1 hr. δD (‰)
LL1923	-146	-141	-150	-151		-153
LL1975	-140	-133	-138	-142	-145	-143

these samples at both the 5 to 12 hour pyrolysis at 150°C and the 1-hour at 250°C pyrolysis temperatures. Thus, it would appear that potential stable δD values may be obtainable using a pyrolysis extraction technique. Further, tests of precision in the reproducibility were now needed.

Analytical Precision

In any study, reproducibility in the δ -values of is of paramount concern. For illustration purposes let us consider the precision for the carbon data obtained in the

Ladd Lake Pilot Group series. The accepted precision for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ is $\pm 0.1\text{‰}$. With data reproducibility at such a fine resolution, variation of 2 and 3 per mil often signals a significant change in the environmental parameters affecting these isotopic ratios. In the Ladd Lake pilot group series, the $\delta^{13}\text{C}$ of the organic carbon in the HCl-residue range 6.6‰ (-26.2‰ to -32.8‰), while the $\delta^{13}\text{C}$ of the HF:HCl residues range by 6.3‰ (-27.7 to -34.0‰). In each scenario the range of $\delta^{13}\text{C}$ values are slightly above 6‰ . Data reproduced at $\pm 2.0\text{‰}$ for carbon data having this range would represent an unacceptable 30% or greater error in the reported values.

The accepted precision in reported δD values is $\pm 2.0\text{‰}$. The δD values of the Ladd Lake Pilot Group data show a range of 44‰ from maximum of -104‰ to a minimum of -146‰ . If the data are reproducible at $\pm 2.0\text{‰}$ there is a 4‰ difference between the maximum and minimum acceptable δD values, thus 4‰ of the 44‰ range in reported δD values would represent less than 10% error for these data. The error involved is thus somewhat dependent on the magnitude and range of the δ -values being considered. Table 15 shows a comparison of repeated δD values during the extraction phase for the Ladd Lake pilot series and the Sapropel pilot series. These samples were extracted using the conventional extraction method (per Krishnamurthy et al., 1995) and thus, were not pyrolyzed prior to combustion.

The difference in their repeat δD values range from a minimum of 1‰ to 19‰ . Comparisons of the change in δD ($|\Delta\delta\text{D}|$) value to their respective percent organic

Table 15

Extraction Phase Precision in Repeat Analysis of D/H Ratios
Using the Conventional Extraction Technique

HF:HCl Residue	Conventional Extraction Repeats:			% org. Carbon (HF-residue)
	1st run $\delta D(\text{‰})$	Repeat $\delta D(\text{‰})$	$ \Delta\delta D (\text{‰})$	
LL1024	-118	-117	1	55.66
LL1234	-112	-117	5	47.90
LL1435	-110	-113	3	41.85
LL1449	-117	-125	8	55.79
LL2111	-143	-134	9	35.03
LL2115	-121	-117	4	23.76
SAP2	-136	-143	7	3.12
SAP4	-115	-117	2	5.35
SAP7	-109	-128	19	2.41
SAP10	-119	-117	2	7.07
SAP14	-125	-122	3	5.2
SAP15	-97	-102	5	1.4

carbon seem to generally exhibit greater shifts with lower organic carbon content. Six of the 12 analyses show a standard deviation $\leq 2\text{‰}$ based on their paired analysis. The

remaining six pair generally seems to lack repeatability using the conventional extraction procedure.

To test precision in the δD value of the HF:HCl residue when each sample was pyrolyzed at 250°C for 1 hour, multiple analyses of various samples were performed. Table 16 shows the isotopic results. Sapropels again proved problematic. Low post-

Table 16

Multiple Analysis Test for Reproducibility Using the δD -P250
Hydrogen Extraction Technique of HF:HCl Residues

Sample ID Number (spike ‰)	δD -P250 Data (‰) Analysis Number				Std. Dev. σ (‰)	% Organic Carbon HF:HCl
	1	2	3	4		
	Date of Extraction (mm/yr.)					
	1/97	1/97	1/97	1/97		
SAP4	tstm	Tstm	Tstm	-154	N/A	5.17
SAP7	tstm	Tstm	-168	-173	± 2.5	2.43
AL7	-129	-125	-126	-128	± 1.6	51.36
LL1763-67	-131	-132	-131	-133	± 0.8	40.86
LL1763-67(+64)	-93	-93			± 0.0	40.86
LL1763-67(+252)	-101	-100			± 0.5	40.86

combustion hydrogen yields in the sapropel samples again rendered some individual samples as too small to measure (tstm) the δD value of the evolved water. In these cases, the collected hydrogen was combined with that of the next combusted sample until sufficient yield was available to measure the δD of the HF:HCl-residue. Consequently, the δD value for SAP4 represents the combined yields of all four samples analyzed. The δD value of the SAP7 reported as analysis number 3 is likewise from the combined yields of the first 3 analyses. Although still problematic, analysis of sapropel HF:HCl samples having low organic carbon contents was possible as is evidenced in the Table 13 results where 14 of the 15 sapropels gave measurable post-pyrolysis combustion yields. The two δD values obtained from SAP7 have an average of -170.5‰ . Each of the reported values differs from this mean value by $\pm 2.5\text{‰}$. Lake sediment samples, due to their higher percentage organic carbon content in their HF:HCl residues, consistently gave measurable yields from all the post 250°C pyrolysis combustion attempts. Analysis #1 through 4 of Austin Lake sample number 7 (AL7) resulted in a mean value of -127‰ . The standard deviation (σ) of these 4 samples is $\pm 1.6\text{‰}$. Four aliquots of Ladd Lake sample number 1763-67 (LL1763-67) were analyzed. Their mean δD was -131.5‰ with a σ -value of $\pm 0.5\text{‰}$. Two additional sets of two LL1763-67 samples were spiked respectively with $+64\text{‰}$ water and $+252\text{‰}$ water using the procedure previously described. After pyrolysis and combustion, both sample sets showed $<2\text{‰}$ variation in their δD values.

From these relatively few January 1997 analyses, it appeared that the protocol for hydrogen extraction using a pyrolysis temperature of 250°C for 60 minutes yielded reproducible δD values with a precision of better than $\pm 2\%$. Based on these findings and the results in the experimental phase, a generalization of an idealized hydrogen extraction procedure could now be summarized. Figure 9 shows a comprehensive flow chart for the hydrogen pyrolysis-extraction-procedure from the sediment sample acquisition through the δD -P250 analysis. Sediment samples were acquired and prepared for demineralization. Aliquots of dried and powdered samples were separated as needed for carbonate analysis. The remaining sample fraction was digested in HCl to remove carbonate material. After rinsing and freeze-drying, Aliquots of HCl residues were combusted for organic carbon analysis. HCl residues were then further demineralized using the microwave digestion procedure. An aliquot of each freeze dried HF:HCl residue was preheated while in vacuum at 250°C for one hour, and subsequently sealed, then combusted at 900°C for three hours in the presence of cupric oxide. Adsorbed water and exchangeable hydrogen either within the organic residue or attached to any remaining inorganic fraction was largely removed leaving primarily the non-exchangeable hydrogen to become a combustion by product. Water from the combusted sample was separated cryogenically and passed over uranium metal at 750°C. The resulting hydrogen was analyzed using an isotope-ratio mass spectrometer. The overall reproducibility of the δD values using the δD -P250 technique appeared better than 3%.

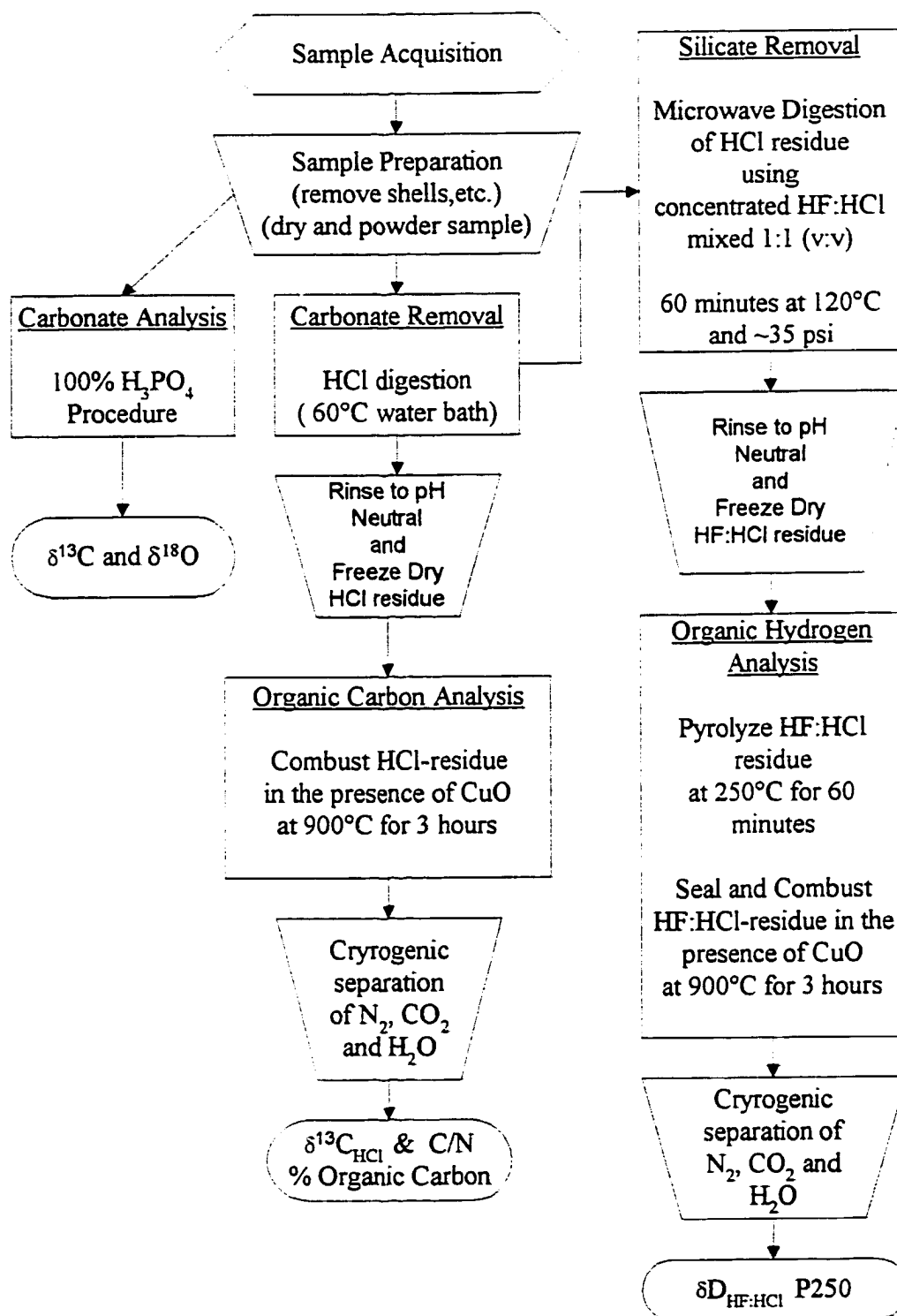


Figure 9. Comprehensive Flow Chart for the Hydrogen Extraction Procedure.

This being established, the Ladd Lake Pilot samples were processed via this technique. The D/H ratios of both the initial pilot series data and corresponding δD -P250 results for the 42 pilot group samples are shown in Figure 10 plotted with respect to ^{14}C years before present. This graphically compares the results of hydrogen

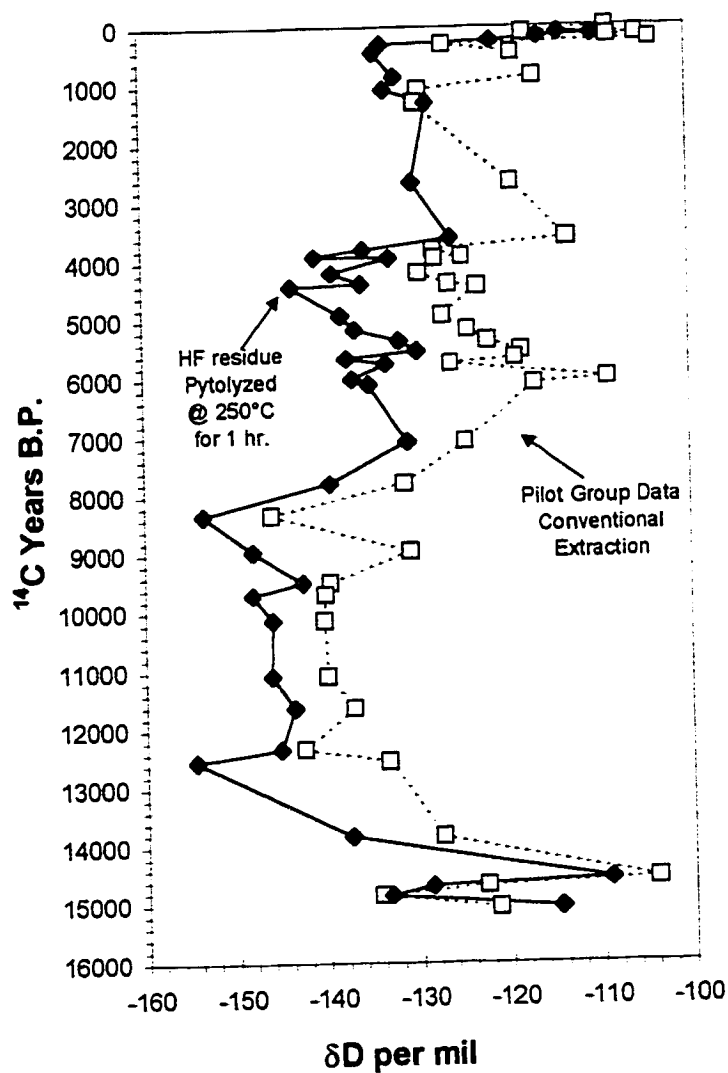


Figure 10. δD of Ladd Lake Pilot Group Samples Using Both the Conventional Extraction Technique and the δD -P250 Protocol.

isotopic ratios extracted from sediment organic matter using both the pre-heated (P250) and non-pyrolyzed conventional hydrogen extraction techniques. There is a remarkable similarity in the “curve-shape”, however, one need remember that only the pyrolyzed series exhibited acceptable precision. Figure 11 shows the δD values as a function of H/C ratio for both the Pilot Group series and the Ladd Lake δD_{P250} series data. Good correlation between δD_{P250} and H/C may be an indicator that hydrogen was contributed predominantly from the organic residue. When the H/C ratio increases the δD of the HF:HCl residue decreases (becomes more negative). If adsorbed/exchanged waters were contributing to the final δD signal, more positive values in the δD would be expected. This is due to the fact that waters used to process the samples are typically more enriched than the organic matter. As was seen from the pyrolysis experiments, the majority of the adsorbed waters were removed with the pre-heating of the sample residues and thus their contribution to the final δD signal is minimized. Further, the positive trend in δD with corresponding decrease in the H/C suggests that water was lost through fractionation processes. In addition to this, the good correlation ($R^2 = 0.63$) of the δD -P250 and H/C data may indicate that no serious modification of the non-exchangeable hydrogen within the organic carbon structure has occurred (i.e. through the sample preparation and pyrolysis extraction procedures). The poorer correlation for the conventionally extracted pilot series data ($R^2 = 0.23$) suggests that adsorbed waters/exchangeable hydrogen within the bulk δD signal of the HF:HCl-residue may account for the poorer precision exhibited by the

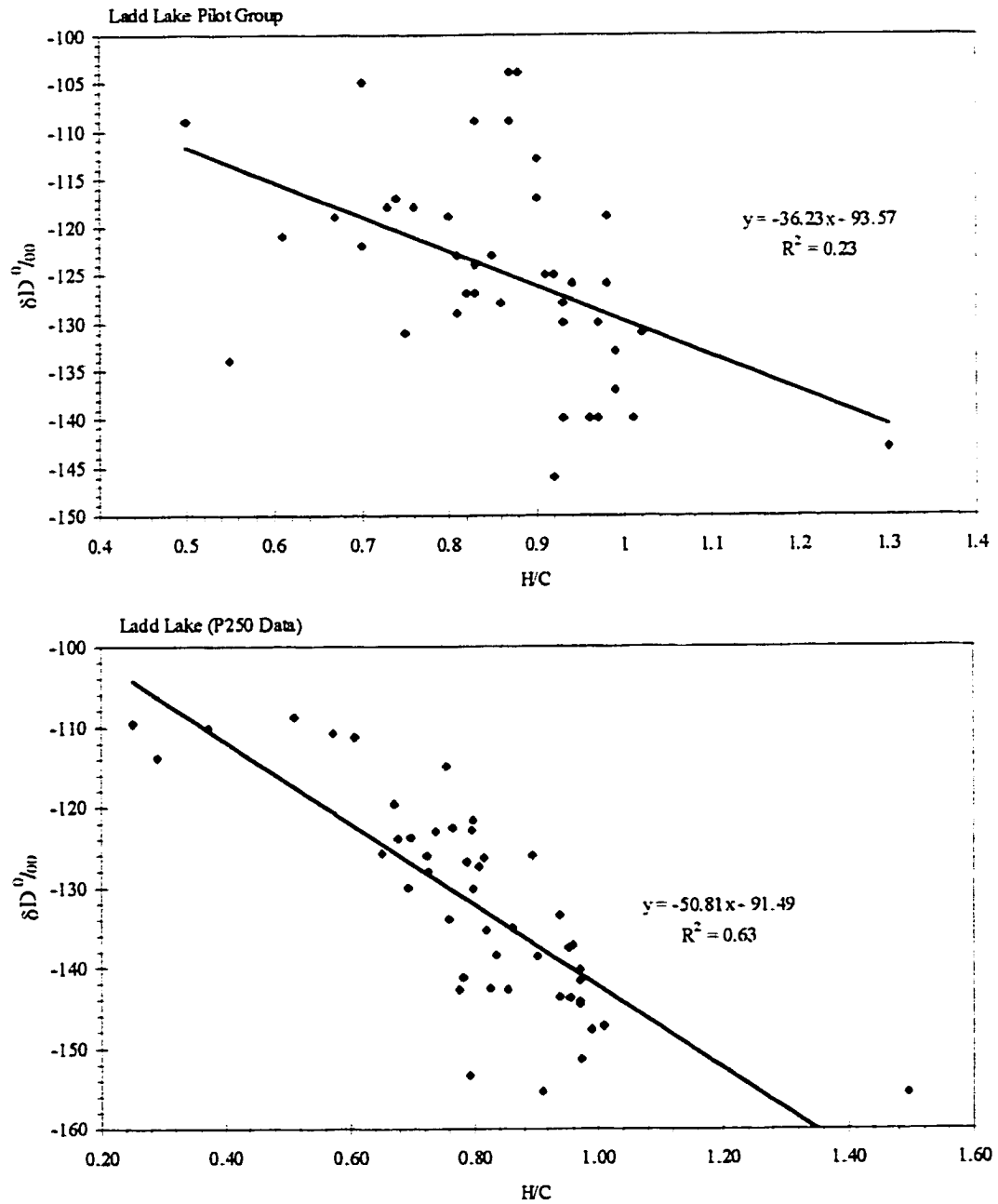


Figure 11. Regression Plot of H/C Ratio vs. δD for the Ladd Lake Pilot Group Extracted Using the Conventional Technique and the Ladd Lake Core Using the Pyrolysis Extraction Technique P250.

pilot series. Additionally, the early and bimodal release of water (hydrogen) in samples of low organic content may suggest that residual inorganic materials (i.e. hydrous clays) significantly contribute to hydrogen exchange within such HF:HCl residues. The pyrolysis experiments and the acceptable precision after the pre-heating of the P250 data group suggests a majority removal of any absorbed/exchanged hydrogen. The near mirror image of the isotopic ratio data in Figure 10 should not suggest that pyrolysis of the data need not be undertaken for analysis of hydrogen. In fact, it should be realized that significant contribution by adsorbed/exchanged hydrogen could radically affect the data outcome of δD values should a series of samples be processed in multiple labs using isotopically distinct waters during sample preparation.

Based on these results, work was begun on the extraction phase for the remaining Ladd Lake and Lake Winnebago samples using the “ δD -P250” protocol (so termed because of the 250°C-pyrolysis temperature). During this extraction phase, several lake sediment samples from the Ladd Lake and Lake Winnebago cores were repeated, some randomly and a few due to apparent errant values. These initial extractions and repeated values are shown in Table 17.

With only one exception, each repeated value exhibited no more than a 3 per mil difference from their respective initial value. In hope of further strengthening the statistical basis for repeatability, several additional samples were extracted and analyzed for δD to be added to those already repeated. The initial δD -P250

extractions and precision tests took place from January through July and August of 1997. Table 18 shows the results and includes Table 17 repeated data as analysis #1

Table 17

Extraction Phase Precision in Repeat Analysis of D/H Ratios
Using the δD -P250 Extraction Technique

HF:HCl Residue	P-250 Extraction Repeats:			% org. Carbon (HF-residue)
	1st run $\delta D(\text{‰})$	Repeat $\delta D(\text{‰})$	$ \Delta\delta D $	
LL1851	-123	-123	0	57.45
LL2036	-123	-126	3	42.88
LL2068	-124	-124	0	41.80
LW7-19	-145	-143	2	43.98
LW7-82	-131	-131	0	29.71
LW7-261	-116	-124	8	56.81

and #2 for the purpose of comparison to these subsequent repeat analyses performed in January 1998. The month and year of each extraction are shown above each sample group. Five total aliquots of AL7 were analyzed and resulted in a standard deviation (σ) of $\pm 2.1\text{‰}$. Eight total aliquots of LL1763-67 resulted in a mean δD of was -135‰ . The original σ -value of $\pm 0.8\text{‰}$ for the initial 4 samples now became $\pm 3.8\text{‰}$. Interestingly, the σ -value of for the later four LL1763-67 analyses was $\pm 0.7\text{‰}$. This

might suggest that waters absorbed during sample storage had affected the ultimate δD of the HF:HCl residue. Two additional aliquots of LL2036 and LW7-19, plus three and four aliquots of LL2068 and LW7-261, respectively, were analyzed. The σ -value for each is shown in Table 18. The mean σ -value for all the repeat analyses shown in Table 18 is $\pm 2.3\text{‰}$ using the δD -P250 technique.

With the exception of LW7-261, which is a peat sample from the Lake Winnebago core, the σ -value for all these analyses were better than $\pm 4\text{‰}$. While this seems unacceptable, it may represent a reasonable %-error when associated with δD analysis of sediment organic matter over the length of any given sediment core. For the Ladd Lake core alone, the δD -P250 extraction phase data exhibited a range of 106‰ from -53‰ to -159‰ . The σ -value of $\pm 4\text{‰}$, if applied to the Ladd Lake

Table 18

Multiple Analysis Test for Reproducibility Using the δD -P250
Hydrogen Extraction Technique of HF:HCl Residues

Sample ID Number (spike ‰)	δD-P250 Data (‰)								Std. Dev. σ (‰)	% Organic Carbon HF:HCl
	1	2	3	4	5	6	7	8		
Date of Extraction (mm/yr.)										
	1/97	1/97	1/97	1/97	1/98	1/98	1/98	1/98		
SAP4	Tstm	Tstm	Tstm	-154					N/A	5.17
SAP7	Tstm	Tstm	-168	-173					±2.5	2.43

Table 18 - Continued

Sample ID Number (spike ‰)	δ D-P250 Data (‰) Analysis Number								Std. Dev. σ (‰)	% Organic Carbon HF:HCl
	1	2	3	4	5	6	7	8		
AL7	-129	-125	-126	-128	-123				± 2.1	51.36
LL1763-67	-131	-132	-131	-133	-139	-138	-140	-139	± 3.8	40.86
LL1763-67 (+64)	-93	-93							± 0.0	40.86
LL1763-67 (+252)	-101	-100							± 0.5	40.86
Date of Extraction (mm/yr.)										
	6/97	7/97	1/98	1/98	1/98					
LL1851	-123	-123							± 0	57.45
LL2036	-123	-126	-129	-132					± 3.4	42.88
LL2068	-124	-124	-132	-130	-132				± 3.6	41.80
Date of Extraction (mm/yr.)										
	5/97	5/97	1/98	1/98	1/98	1/98				
LW7-19	-145	-143	-142	-141					± 1.5	43.98
LW7-82	-131	-131							± 0	29.71
LW7-261	-116	-124	-138	-135	-132	-131			± 7.5	56.81
								$\bar{x}\sigma$	2.3	
N/A= not applicable										
tstm = too small to measure										

δD -P250-repeats of Table 18, equates to $\sim 7.5\%$ error $[(8\text{‰ deviation}/106\text{‰ range}) \times 100]$ for that data set. For the Lake Winnebago core, the δD -P250 extraction phase data exhibited a range of 21‰ from -124‰ to -145‰ . If the peat sample from this group is omitted, the Lake Winnebago data are well within the accepted precision for hydrogen data.

With the additional 1/98 repeat data, some interesting questions have arisen. First, are the data indeed repeatable? Table 18 data suggest that δD data extracted and repeated during any given continuous analytic session will yield repeatable δD -P250 values. This is supported by the similarity in the σ -value of for the two sets of four LL1763-67 residues analyzed in January of 1997 and 1998 (Table 18). If these changes were caused by adsorbed waters during storage, one could imply that the absolute values of the δD could potentially change, but the systematic shifts in the resultant δD analysis over a whole core length would remain essentially unchanged. The later being the more important as it is the relative temporal change in δD values over the core length that is of paleoclimatic interest. The second issue becomes, how will adsorbed waters during sample storage affect the ultimate repeatability of the δD using a pyrolysis extraction technique? As previously noted, with the exception of the peat sample (LW7-261) the individual σ -values all show better than $\pm 4\text{‰}$ precision and if the entire data set were considered the mean σ -value for all the repeat analyses were $\pm 2.3\text{‰}$.

To better understand these σ -value data, let us again consider the percent organic matter in the HF:HCl residue in comparison to that of the HCl residue. It was shown in Figure 3 that the microwave digestion procedure was more efficient than the conventional technique in concentrating the HF:HCl residue by noting that the increase of slope from regression of the HF:HCl % organic carbon with respect to the HCl % organic carbon. This quantitatively demonstrated the higher efficiency in concentrating the organic matter by the HF:HCl microwave procedure. The slope of the microwave digested Ladd Lake samples was 1.69. For comparison, Figure 12 shows the regression of % organic carbon for HF:HCl vs. HCl residues from the Lake Winnebago and sapropel samples. Lake Winnebago samples show a near 5-fold increase in the % organic carbon of the HF:HCl over the HCl residues. Though only four samples were used, the LW7-19 data shown in Table 18 exhibit better than the accepted precision for δD analysis. LW7-19 averaged 43% organic carbon in its four combusted HF:HCl residues and 8.6% organic carbon in its corresponding HCl fraction, which directly corresponds to the 5 fold increase in the concentration of the percent carbon from the MWD procedure. This is compared to the LW7-261 sample, a peat, which showed an average of 63% organic carbon in the HF:HCl residues and 55% in its HCl residue. Clearly, the concentration process for this peat material was less efficient than for the lake sediment. This was probably a function of the higher initial organic content of the raw material. However, the lack of precision in the LW7-261 peat sample may further imply that substantially more inorganic hydrogen bearing

remains undigested in this sample and offers problems in extracting precise δD information. Perhaps, the higher initial organic content even inhibited the HF reaction.

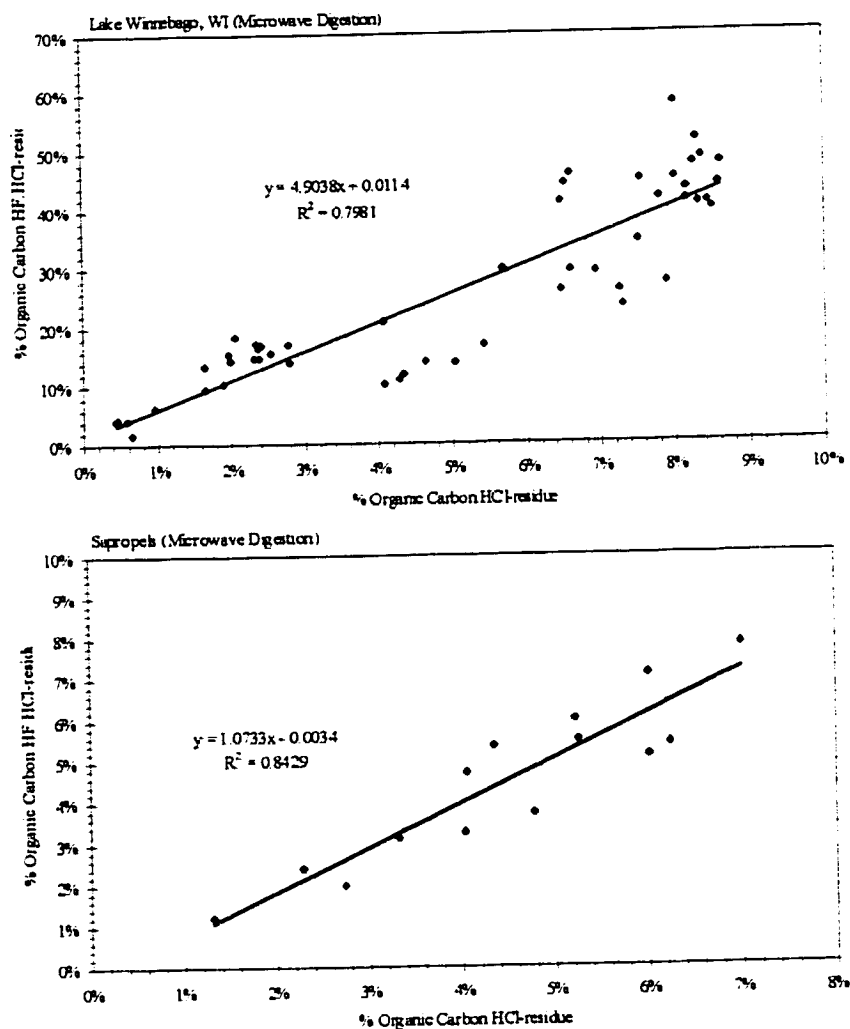


Figure 12. Regression of % Organic Carbon in the HCl and HF:HCL Residues of Lake Winnebago and Sapropels Samples.

The slope of the sapropel regression data shows only a minor increase in the concentration of the HF:HCl residue from the HCl residue. This is consistent with the earlier finding that a large fraction of the insoluble residue from sapropels appeared inorganic in that the bimodal release of pyrolysis waters at less than 350°C was reminiscent of water release patterns from clays. Another possibility is that the higher apparent inorganic content of sapropel residues may be from reaction precipitants formed during microwave digestion. Regardless of the origin of the materials, an inability to concentrate the organic fraction may manifest itself in the resultant imprecision of the δD analysis. Such may be the case with the Lake Winnebago peat sample.

While minor refinements to the microwave digestion technique and the pyrolysis extraction procedure may need future exploration, the advantages currently offered by these techniques are readily apparent. Comparisons of the conventional and microwave digestion processes show greater efficiency of time and residual organic concentration when the MWD procedure were followed. Further, the pyrolysis technique offers the only means currently available to remove adsorbed waters that otherwise would partially mask the δD signal of the insoluble organic matter. In doing so, the pyrolysis-hydrogen-extraction technique is the only method currently available that may provide uniformity in results and offer precision the δD reproducibility if samples are processed in competing labs using isotopically distinct processing waters.

This being established, the use of hydrogen extracted from sediment organic matter may now be fully explored as an environmental proxy.

CHAPTER III

RESULTS AND CONCLUSIONS

A Paleoclimatic Study of the Midwestern United States From the Stable Isotope Records in Lake Sediments

The late Pleistocene to Holocene climate record from ~15 thousand calendar years before present (ka BP) to the present shows dramatic oscillations between warm and cold intervals on time scales of decades to centuries (Dansgaard, W. et al., 1993; Mayewski, P.A. et al., 1993; Alley, R.B. et al., 1997; Stager, J.C. and Mayewski, P.A., 1997). Significant events for which evidence exists are the Bolling-Allerod warm phase, the Younger Dryas (YD) cold phase, the Mid-Holocene Warm (MHW) phase and the Little Ice Age. Debate still goes on regarding the global extent of these post-glacial climatic events. For instance, it is not settled beyond dispute as to whether the Little Ice Age or the Younger Dryas were experienced globally. Some recent work, however, suggests that evidence for the Younger Dryas may be preserved even in the loess deposits in China (Zhisheng, A. and Porter, S.C., 1997; Chen, F.H. et al., 1995).

In the Midwestern United States, there is evidence for the occurrence of significantly warmer climates during the middle part of the Holocene. This Mid-Holocene Warm interval is believed to have started anywhere between 8 to 6ka BP and lasted until 3 to 2ka BP (Krishnamurthy et al., 1995; Baker et al., 1992; Rea et al.,

1994; Coleman et al., 1990; Coleman et al., 1994; Dorale, et al., 1992; Chumbley et al., 1990). The wealth of data from this region unfortunately yields only qualitative information regarding temperature records, an exception being the $\delta^{18}\text{O}$ record of speleothems from a cave in Iowa (Dorale, et al., 1992). This later study suggested that the mean annual air-temperatures in the region were up to 4°C higher during the MHW. Similarly, in work using the $\delta^{18}\text{O}$ values of cellulose extracted from plant remains isolated from lake sediments, Edwards and Fritz (1986, 1988) have shown major temperature increases during the MHW in Canada.

In this current study, the organic matter extracted from lake sediments was analyzed for δD and $\delta^{13}\text{C}$ in two Midwestern United States lake cores. Carbon to nitrogen (C/N) ratios from the carbonate free sediment residues were used to constrain the interpretation of the organic carbon analysis. Hydrogen isotopic data were initially extracted using procedures followed by Krishnamurthy et al. (1995). A pilot study of 42 samples from the Ladd Lake core was processed via those techniques. Subsequently, the δD -P250 protocol (refer to Chapter II) was followed for the remaining analyses. Samples used in this study came from radiometrically dated lacustrine cores raised from Ladd Lake in northwestern Ohio and Lake Winnebago in east central Wisconsin. Figure 13 shows the location of Ladd Lake and Lake Winnebago within the study area. Pollen analysis of the Ladd Lake core was performed by Dr. Linda Shane (Shane, 1991, Shane and Anderson, 1993). Data provided by Dr. Shane are used to augment the interpretation based on the isotopic

analysis of the Ladd Lake organic matter. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the carbonate bearing sediment found within the Lake Winnebago core were also analyzed to further augment the interpretation of δD and $\delta^{13}\text{C}$ from its sediment organic residues. For the purpose of continuity in discussion, the results from the Ladd Lake and Lake Winnebago studies are presented separately, along with individualized interpretations allowed by their respective isotopic results.

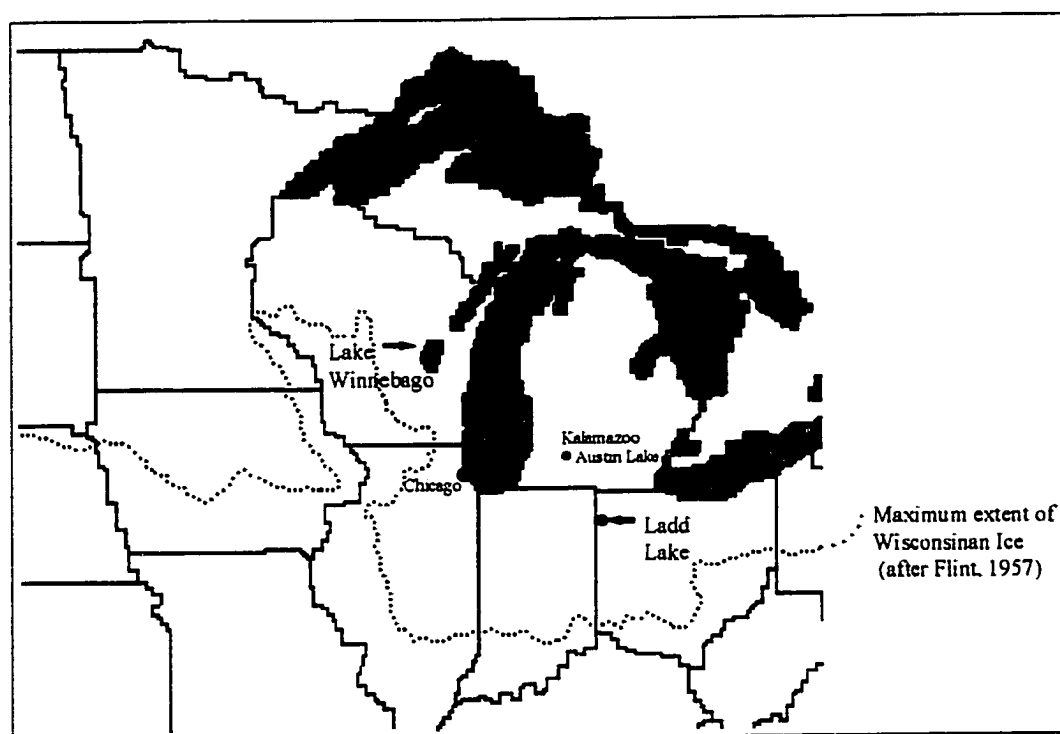


Figure 13. Map of the Midwestern United States Showing the Location of Lake Winnebago, Ladd and Austin Lakes.

A primary focus of this dissertation project was to generate a continent-based regional paleoclimate record covering the Pleistocene-Holocene period using stable

hydrogen isotope records taken from bulk organic matter in lake sediment. The basis for an environmental interpretation of the hydrogen isotopic distribution of lacustrine organic matter stems from the assumption that the organic matter in lake-sediments is made primarily of the photosynthesizing aquatic plants that grew in the lake. As the source of hydrogen for these plants was the local meteoric water recharging the lake, the δD of lake organic matter should reflect the δD of local meteoric water via the δD of the lake. Since the δD of local meteoric water is directly related to climatic factors, the δD of lake-organic material should be interpretable in terms of climatic changes.

A major influence on the hydrogen and oxygen isotopic composition of natural waters is exerted by the atmospheric part of the global water cycle. As noted in Chapter I, during evaporation, water vapor becomes preferentially enriched in the lighter isotopes of H and O, while the residual fluid becomes isotopically heavier. Similarly, during precipitation, rain and snow are enriched, leaving the remaining moisture depleted. Thus, the general trend of atmospheric precipitation is one where precipitation in equatorial regions is relatively isotopically heavy and becomes progressively depleted toward the poles. This global trend is a consequence of the fact that most of the evaporation occurs in the tropics and then is transported pole-ward to higher latitudes. Thus, examination of the geographic distribution of the δD and $\delta^{18}O$ of rainfall and the proxy indicators through which climatic patterns are revealed becomes important. In an initial attempt to check the calibration of the δD -values from lake organic matter to the known information regarding precipitation and mean

annual surface air temperature, the HF:HCl residues from four surface samples from four differing latitudes were analyzed. Table 19 shows the δD -P250 value along with the degrees latitude and regional provenance for these samples. Regression of these data (Figure 14) indicates $\sim 3\text{‰}$ depletion per degree latitude for the organic hydrogen

Table 19

δD -P250 Value, Degrees Latitude and Regional Provenance for Samples Used in Calibration of Surface Sediment Organic Matter in Lakes

Regional Provenance	Latitude	$\delta D_{\text{organic}}$
Ladd Lake, Ohio, USA	N41.0	-118‰
Austin Lake, MI, USA	N42.2	-122‰
Lake Winnebago, WI, USA	N44.0	-129‰
White Horse Lake, Antarctica	S66.0	-189‰

isotopic data with an R^2 value of 0.99. This is similar to the findings by Yurtsever (1975) for precipitation data where $\sim 0.5\text{‰}$ depletion per degree latitude for oxygen data. If multiplied by a coefficient of 8 (from $\delta D = 8.17 \delta^{18}O + 10.56$, Gat, 1981) these data show $\delta D = \sim 4\text{‰}$ depletion per degree latitude. Thus, it would appear there is a good correlation between the δD signal of these surface sediment samples and the mean δD of the meteoric precipitation via the lake.

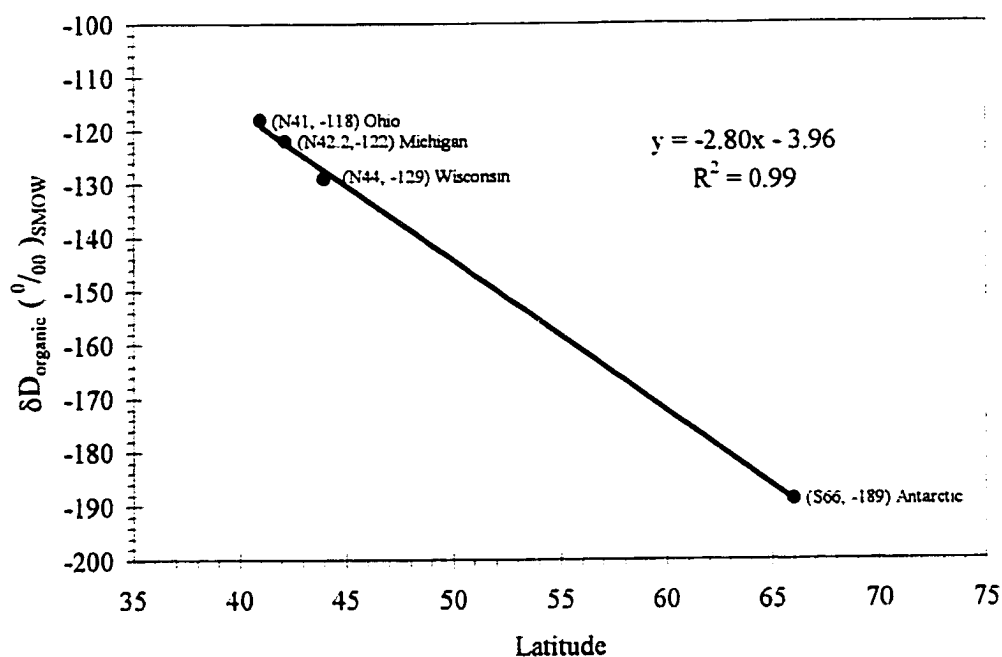


Figure 14. Regression of $\delta D_{\text{organic}}$ of Surface Samples From Lacustrine Cores at Four Different Latitudes.

Chronology

As discussed in Chapter I, six radiocarbon dates were obtained from bulk sediment organic matter in samples collected from select intervals over the length of the Ladd Lake core. These dates are all bulk sediment dates where the sampled interval span as much as 10 cm. Six radiocarbon dates were also obtained for the Lake Winnebago samples from the CO_2 gas evolved from sediment organic matter by combustion of the carbonate free organic fraction. Table 3 in Chapter I shows the results of these radiocarbon dates. Figures 15 and 16 show plots of the sedimentation rate (Depth in cm versus Years BP) for the Ladd Lake and Lake Winnebago cores,

respectively. Calendar years are designated using an open triangle and the radiocarbon years are denoted by a solid square in both plots.

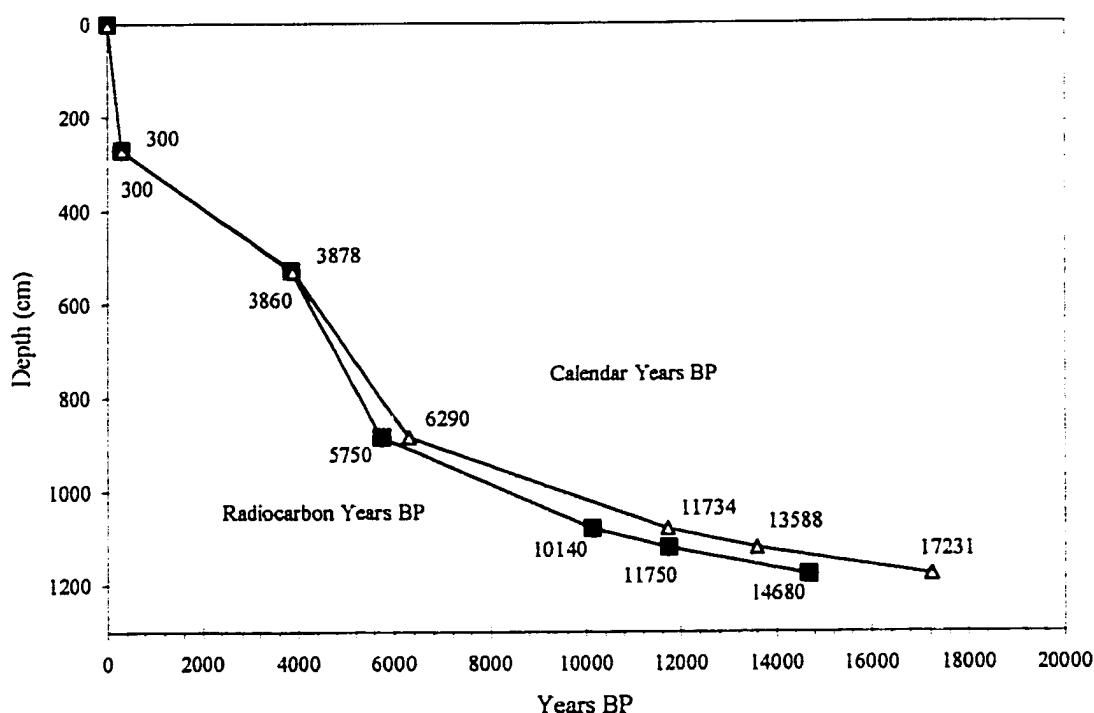


Figure 15. Plot Showing the Ladd Lake Sedimentation Rate as a Function of Depth in Centimeters (cm) per Years Before Present (Years BP).

Shane (personal communication) indicates that the date at 264-270 cm is taken just below the so-called European settlement horizon and dates to ~300 ^{14}C years BP. The dates from the 521-529 cm interval (3860 ^{14}C yrs.) and the 877-885 cm interval (5750 ^{14}C yrs.) are generally correct. However, it should be noted that the basal three dates from the Ladd Lake core are considered generally correct but are thought

potentially off by a few hundred years. The error arises due to hard water effects, slow sedimentation rates through these intervals and the several centimeter span of

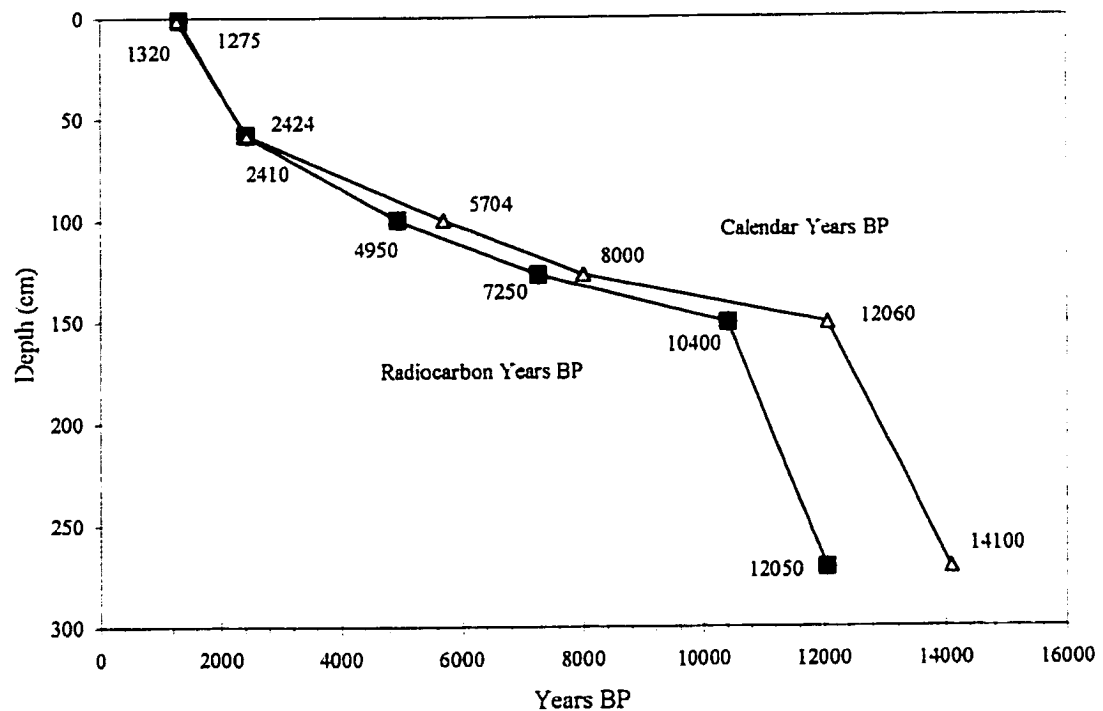


Figure 16. Plot Showing the Lake Winnebago Sedimentation Rate as a Function of Depth in Centimeters (cm) per Year Before-Present (Years BP).

bulk sample used for the radiocarbon analysis (Shane, personal communication). Dates assigned to intervals below the oldest radiocarbon interval were based on use of the previous up core sedimentation rate and should be used with a modest degree of caution. Similar problems in the Lake Winnebago core were avoided by analysis of CO₂ gas from organic matter extracted at a discrete depth interval. The oldest date of 14.6 thousand ¹⁴C years (kyr) for the Ladd Lake core and 12,050 years for the Lake Winnebago core is consistent with geological observations in both areas that these

lakes formed at the termination of the last glacial period in response to a melting and retreating ice mass.

The isotopic results of the Ladd Lake Pilot Group Study, shown in the following sections, are plotted versus radiocarbon years. Subsequent plots of the Ladd Lake and Lake Winnebago isotopic date are shown in relation to calendar years before present (Cal. Years BP). Conversion of radiocarbon dates to calendar years was accomplished for both cores by using the linear regression equation of Bard et al. (1993) where:

$$y = 1.24x - 840$$

Dates for individual samples were estimated by using a linear sedimentation rate between radiocarbon dated intervals after conversion to calendar years before present. Using the above equation, radiocarbon dates younger than ~ 700 years result in modern age determinations. For this reason, calendar dates for the uppermost portions of each core were extrapolated from a sedimentation rate from the next down-core radiocarbon dated interval. For the Ladd Lake Core this was accomplished using an interval sedimentation rate calculated from the 3878 Calendar year point to the 300 year radiocarbon date shown in Figure 15. Dates younger than 300 years were based on extrapolation to the surface. The extrapolated surface age of the topmost Lake Winnebago sample is ~1300 years BP based on the radiocarbon chronology determined. This result is most likely due to the loss of the first few centimeters during core recovery. A living clam sample, collected from the lake's

surface sediment, gave a "modern" radiocarbon age suggesting very little hard water effect. Dates for samples separated by less than 140 years (i.e. twice the standard deviation reported for the radiocarbon dates) were averaged before conversion to calendar years.

Review of Ladd Lake Pilot Group Isotopic Data

A pilot series of 42 samples from the Ladd Lake core were analyzed using the conventional techniques of Krishnamurthy and Epstein (1991) and subsequently used by Krishnamurthy et al. (1995) in their Austin Lake study (Kalamazoo, Michigan). The results of these data are presented, briefly, below as a review of the initial isotopic results mentioned above and in previous Chapters.

Analysis of the CO₂ yields from combustion of the HCl-residue indicates that percent organic carbon ranged from 2% to ~30% in these pilot-samples. Temporal variation in the organic carbon content of both the HCl and HF:HCl residues from the 42 pilot group samples are shown in Figure 17 plotted against ¹⁴C years before present. HCl residues are shown as open diamonds while HF:HCl residues are shown as circles. Literary reference to percent organic carbon data has historically been presented with respect to the HCl (carbonate free) residue. These data show a mid-core increase to roughly 25% percent organic carbon with the basal and surface portions of the core having as low as 2% organic carbon. The general scatter of the HCl-percent organic carbon data over the length of the core and the similarity in the

surface and basal percent organic content suggests that no diagenetic effects have altered the sediment mass. The further concentration of the sediment organic matter

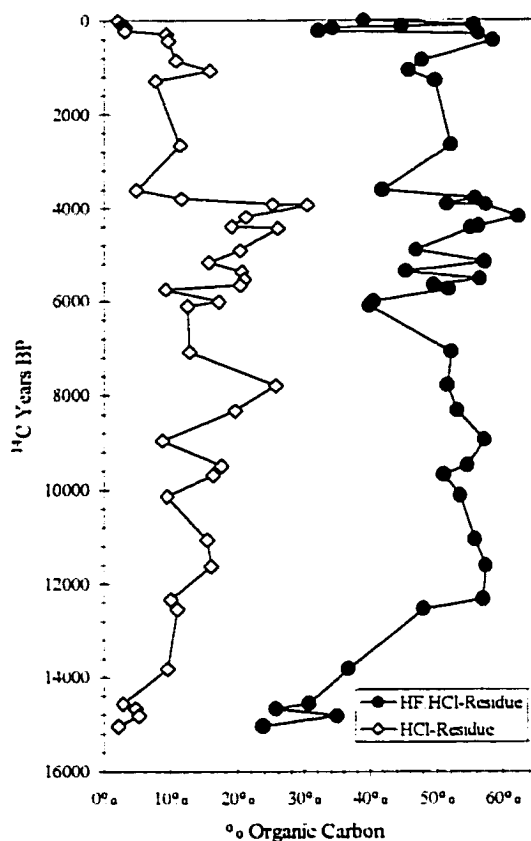


Figure 17. Percent Organic Carbon From the Ladd Lake Pilot Group Series.

during the HF:HCl digestion is graphically evidenced by the higher percent organic content of the HF:HCl residues. Figure 18 shows the atomic carbon to nitrogen (C/N) ratios and the $\delta^{13}\text{C}$ from both the HCl and the HF:HCl residues in the Ladd Lake pilot group series. The $\delta^{13}\text{C}$ of the organic carbon in the HCl-residues range from -26.2‰ to -32.8‰. These results are consistent with values reported in other mid-continent

studies. The $\delta^{13}\text{C}$ of the HF:HCl-residues closely mimic those of the organic carbon in the HCl-residues. This may indicate very little destruction of the organic carbon

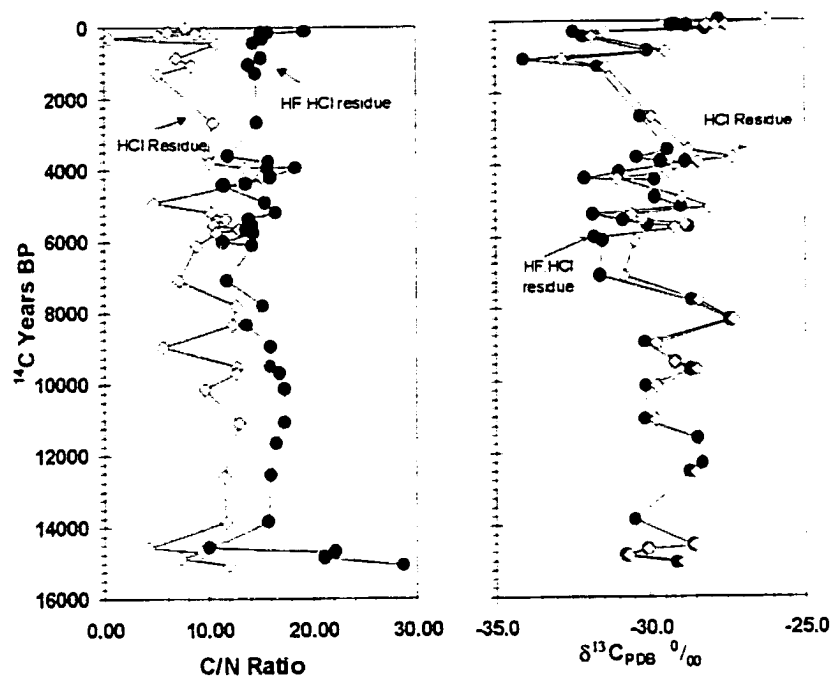


Figure 18. C/N and $\delta^{13}\text{C}$ vs. Age for Both HCl and HF:HCl-Residues From Ladd Lake Pilot Group Series.

during the successive acid digestions. The C/N ratios of the organic carbon in the HCl-residues range from 4.6 to 15.2 with a mean value of ~ 10 indicating lacustrine origins for the residual organic matter (Meyers and Ishiwatari, 1993). The general positive shift in the C/N ratios of the HF:HCl-residue is due to loss of nitrogen. One potential source for nitrogen in the residual organic matter is protein. These data may suggest that N_2 is lost from the protein portion of the organic matter during the successive acid digestions.

Figure 19 shows a plot of the absolute value of the change in the $\delta^{13}\text{C}$ ($|\Delta\delta^{13}\text{C}|$) calculated as $|\delta^{13}\text{C}_{\text{HCl}} - \delta^{13}\text{C}_{\text{HF:HCl}}|$ and the change in the C/N ratio calculated as

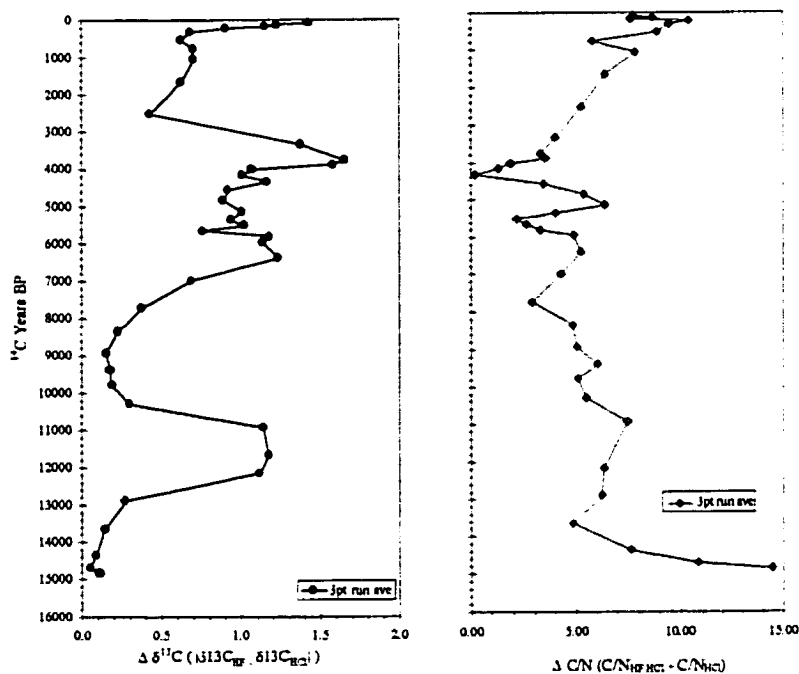


Figure 19. Plot of the Change in $\delta^{13}\text{C}$ and Change in C/N vs. Radiocarbon Years Before Present for the Ladd Lake HF:HCl and HCl Residues.

$\text{C/N}_{\text{HF}} - \text{C/N}_{\text{HCl}}$. Both are plotted versus radiocarbon years before the present. These data have been smoothed using a 3pt running average. It is interesting to note that the larger deviations between the $\delta^{13}\text{C}$ values occur mid-core where the organic content is generally highest. However, a regression of the change in the $\delta^{13}\text{C}$ with respect to the % organic carbon content showed no correlation for either the HF:HCl residues ($R^2 = 0.028$) or the HCl residues ($R^2 = 0.012$). Further, regression of the $\delta^{13}\text{C}$ vs. the % organic carbon within their respective residual organic materials (Figure 20) also

showed a lack of correlation. This may, perhaps, indicate that the $\delta^{13}\text{C}$ of the organic matter from Ladd Lake is not controlled by productivity in the lake. During periods of

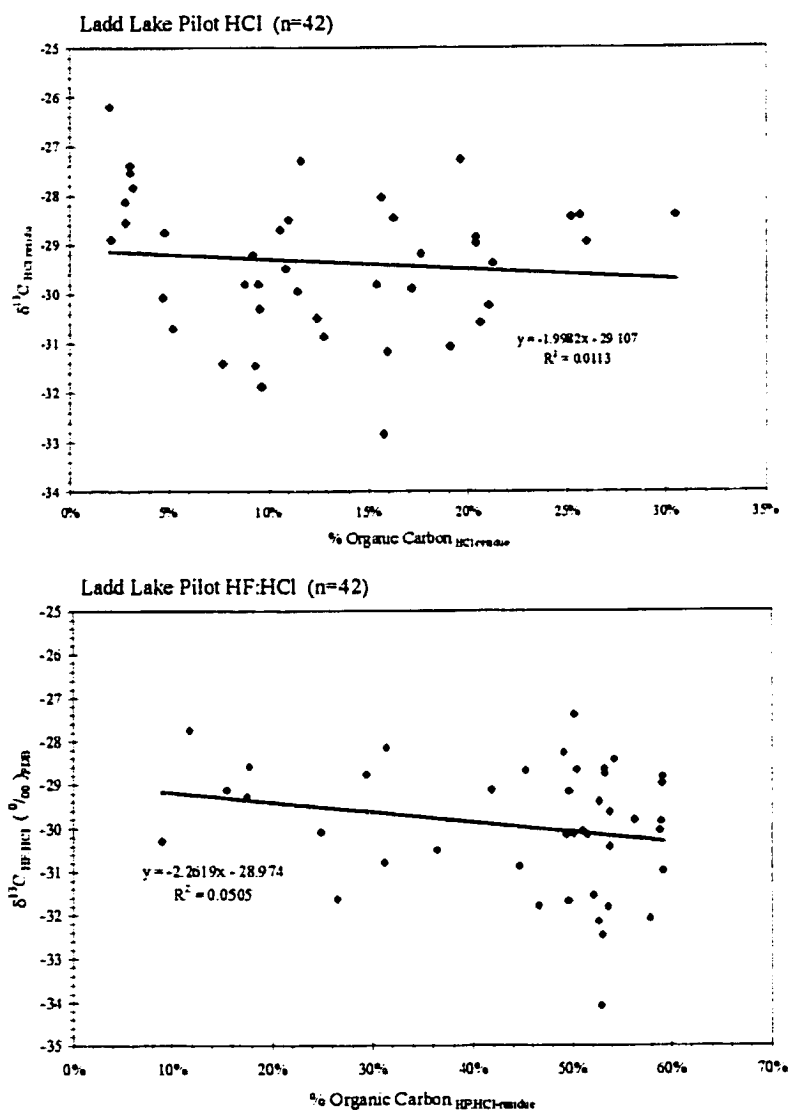


Figure 20. Regression of $\delta^{13}\text{C}$ vs. the % Organic Carbon for Both the HCL and HF:HCL Residual Organic Materials.

high productivity the $\delta^{13}\text{C}$ values of the organic carbon become more positive as a result of depleting the aqueous CO_2 and uptake of the isotopically heavier HCO_3^- . Thus, if high organic content were controlled by periods of high productivity, a positive covariance would be expected between the % organic carbon and the $\delta^{13}\text{C}$ signature. The change in the C/N, shown in Figure 19, appears on first impression to show larger shifts at the base and top of the core where the % organic content is lowest. More work, however, is needed to clarify the source and mechanisms for loss of the nitrogen and to understand the slight variance that exists between $\delta^{13}\text{C}$ values in the HCl and HF:HCl organic residues.

The δD results from the pilot group study were shown in Chapter II as a comparison to their δD -P250 data. These same data, shown here as Figure 21, exhibited conventionally extracted hydrogen isotopic values ranging from a maximum δD value of -104‰ to a minimum of -143‰ . Their corresponding δD -P250 values range from -109 to -154‰ . The absolute value change in the $\delta\text{D}_{\text{P250}}$ from the conventionally extracted δD -values range from a maximum difference of 28‰ to a minimum of 1‰ . As discussed previously, it is noteworthy that the data from both extraction techniques show a remarkable similarity in their curve shape and systematic shifts of their δD values. It must be remembered, however, that the pyrolyzed samples reflect a more accurate representation of the non-exchangeable hydrogen due to the removal of adsorbed/exchanged waters from the organic residue.

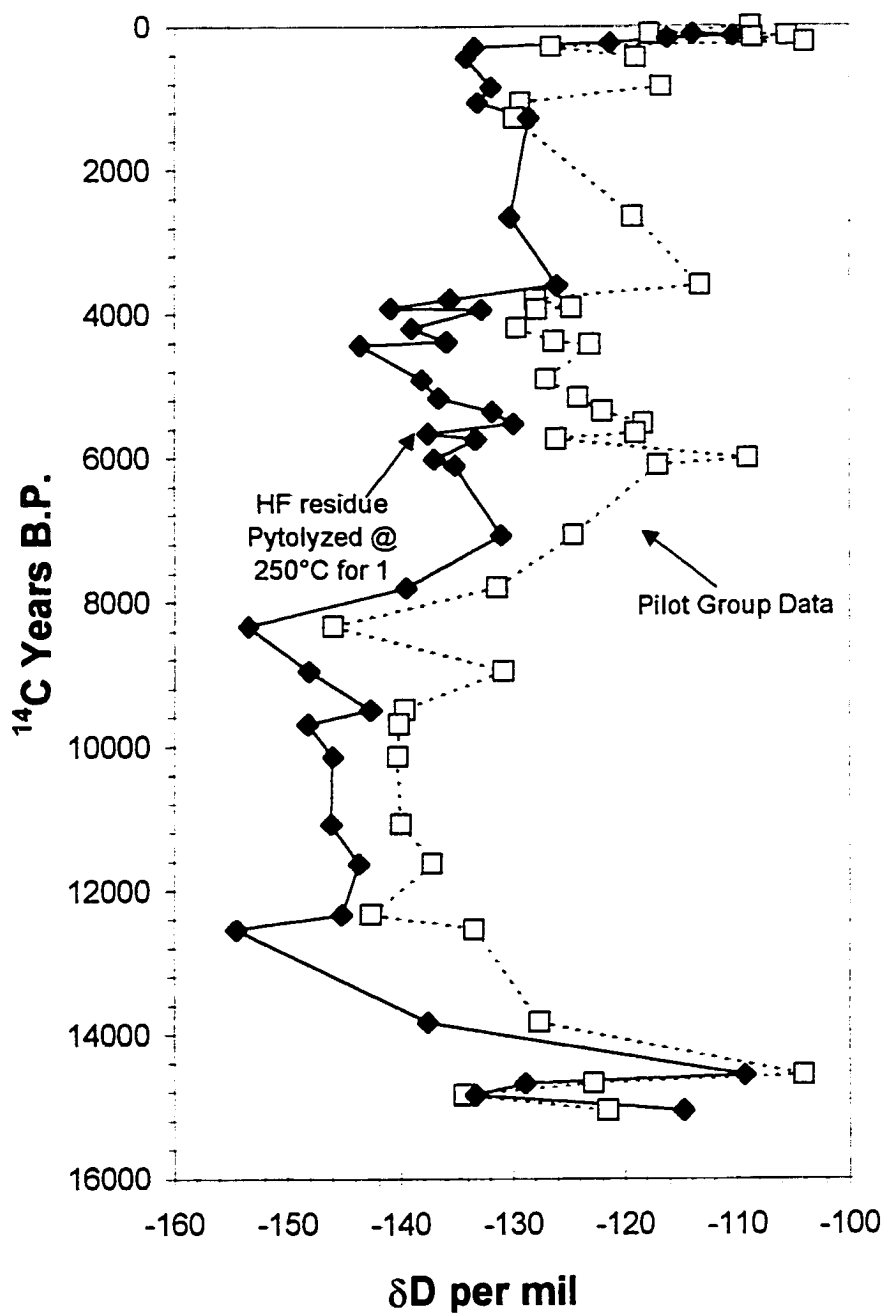


Figure 21. The δD of Ladd Lake Pilot Group Samples vs. Calendar Years Before Present Using Both the Conventional and δD -P250 Extraction Procedures.

Ladd Lake, Ohio

Review of Pollen Data

Ladd Lake is located on the outer edge of the Fort Wayne moraine. The predominant local landform is the lake plain formed by a series of pro-glacial lakes ancestral to Lake Erie that filled the Lake Erie basin. Very few modern lakes are present in northwestern Ohio and similar to most lakes present in this area, Ladd Lake was formed in response to glacial wasting. The oldest date of 14.6 thousand ^{14}C years (kyr) for the Ladd Lake core is consistent with geological observations in the lake formed at the termination of the last glacial period in response to a melting and retreating ice mass. The ice free date for Ladd Lake corresponds to ~14,500 to 14,000 radiocarbon years before the present (Shane, personal communication). This translates to ~17,140 to 16,520 calendar years before the present. Lewis et al. (1992) reported that the ice was out of Ohio and the Lake Erie Basin by 14,100 radiocarbon years. The various glacial levels of Lake Erie do not affect Ladd Lake directly as it is outside the maximum Erie basin of Lake Maumee.

Physiographic descriptions of the Ladd Lake area refer to it as the Till Plain located south of the Great Lakes (Shane and Anderson, 1993). Elevations are generally 300m or less. To the east, on the Allegheny Plateau (eastern and southern Ohio), elevations generally exceed 300m. These slight elevation differences play a role in the orographic cooling of eastward-moving air masses which leads to increased precipitation and seasonality differences between the Allegheny Plateau and the Till

Plains area (Climates of the States, 1985 in Shane and Anderson, 1993). The reported vegetation history of the Till Plains region shows an east-to-west gradient during glacial times (Shane and Anderson, 1993). Pollen records in the western Till Plains suggest a climatic reversal chronologically equivalent to the European Allerod/Younger Dryas at 12,000 to 10,000 radiocarbon years before present (Shane, 1987, 1989). The Holocene pollen record of the Ladd Lake core is dominated by oak with substantial and fluctuating amounts of elm, ash, hickory, beech, walnut, sycamore and hackberry (Shane, 1991). The pre-European vegetation is reported by Gordon (1965) as a Beech-Maple forest with abundant Elm-Ash forest nearby.

Table 20, adapted from the text of Shane's (1991) report, shows the general temporal findings from the pollen data interpretation with regard to temperature and rainfall estimates through the Late-Glacial and Holocene. The data are based on the mean annual data adapted from pollen transfer function and pollen analysis. The core depths shown correspond to Ladd Lake isotopic sample numbers adopted in this study. These data along with radiocarbon age, mean annual precipitation and the mean July and January temperatures are shown for the Late Glacial and Holocene intervals. Shane (1987, 1991) suggested that modern south to north gradients in the estimated climate parameters were not established until about 11,000 years ago, being several thousand years after the area was free of glacial ice (Shane, 1991; Shane, 1987). The relative accuracy of the transfer function temperature estimates is shown at the base of the table where historical records are recorded above the estimated values. Late Glacial January temperatures are shown as much as 10°C cooler than the

Holocene January temperatures. Mean July temperatures, however, indicate smaller differences in the same interval. This may suggest a greater seasonality difference during the Late Glacial where longer and colder winters were more prevalent.

Table 20

Ladd Lake, Ohio, Temperature and Rainfall Estimates Through the Late-Glacial and Holocene Based on Mean Annual Data From Pollen Transfer Function and Pollen Analysis Data (Adapted From Shane, 1991)

Time Period	Core Depth (cm)	¹⁴ C Date (Years BP)	Transfer Function Mean Annual Data		
			Mean Precip. (cm)	Mean July (T°C)	Mean January (T°C)
Late Glacial	2132-1965	ca. 14000 To 9800	80	20	-15
	2100-2050	>13000	78	21.5 - 22.5	-12 to -10
	2050-1965	ca. 13,000	83 - 70	22.5 - 20.5 To 22.5	-10 to -14.5 To -6
Holocene	1965-1720	Ca. 9,500 to ca. 5,000	85-65	23	-3
	1720-1190	Ca. 5,000 to ca. 200	85	23.5 to 24	-2
	1190-930	Post-European	85.7 Recorded 85.2 Estimated	22.5 Recorded 23.1 Estimated	-4.8 Recorded -3.4 Estimated

Figure 22 shows a plot of the mean annual precipitation and the mean July temperature from the pollen transfer function and pollen analysis data provided by Dr.

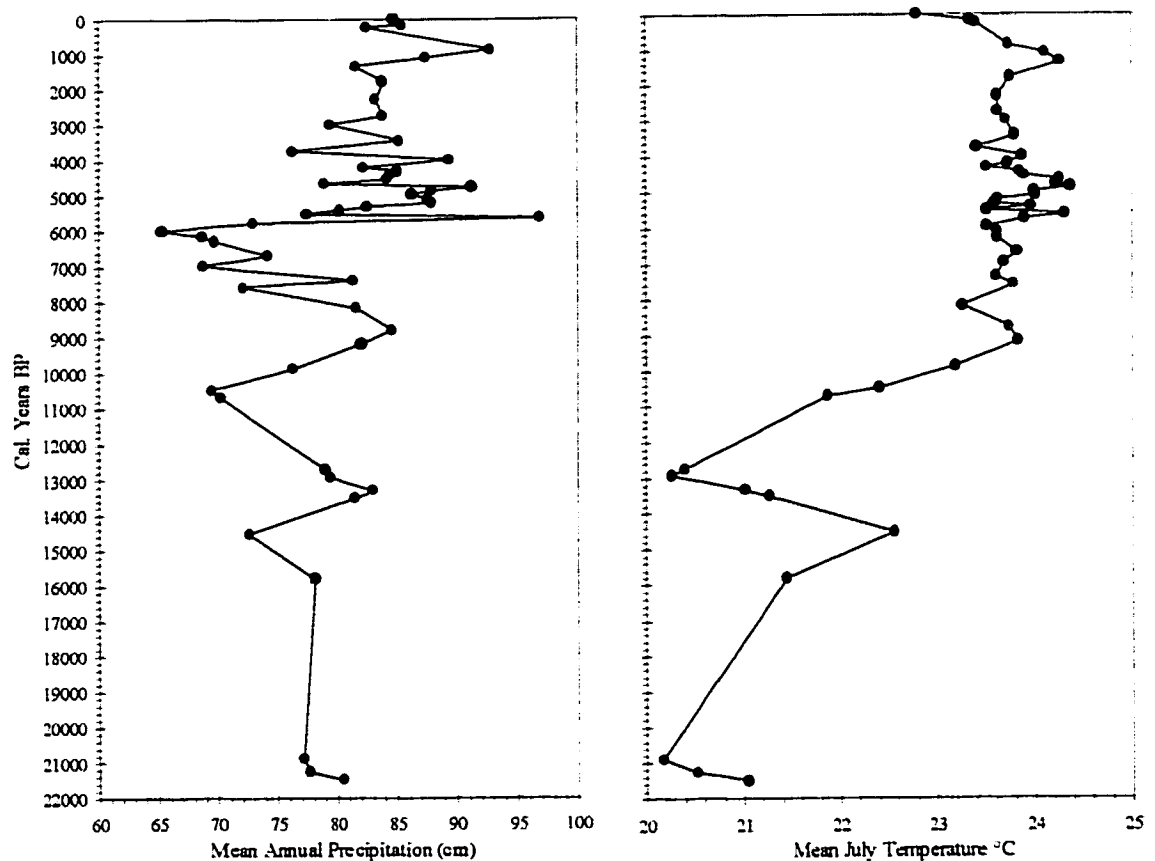


Figure 22. Mean Annual Precipitation and July Temperatures Based on Pollen Analysis and Transfer Function Data Provided by Dr. Linda Shane, University of Minnesota.

Linda Shane of the University of Minnesota Limnologic Research Center. These data have been adapted from their original form and plotted with respect to calendar years before present. The mean annual precipitation data indicate periods of drier conditions

8ka BP to 6ka BP during the early Mid-Holocene Warm. Drier conditions are also indicated at ~10.4ka BP and ~14.5ka BP. The mean July temperature data suggest a rather oscillatory but sustained Holocene Warm Phase from ~10ka BP to ~1.5ka BP.

Ladd Lake Isotopic Data

Hydrogen

The δD_{P250} vs. calendar years BP for the Ladd Lake core is shown in Figure 23. The diagram on the left is plotted as the raw data set while the opposite plot is shown after applying a 3 point running average for data smoothing. The rationale for smoothing is to filter out the relatively high frequency oscillations. Although, these oscillations may be real, their timing cannot be identified more realistically given the limited number of dates and the precision associated with the ^{14}C dating.

Because there is a positive correlation between the δD in precipitation and the mean surface temperature, systematic shifts in hydrogen isotopic values qualitatively suggest cool phases during negative excursions and warm phases during positive trends. Using this line of reasoning, Krishnamurthy et al. (1995) , indicated Southwestern Michigan experienced a mid-Holocene warming between 8500 and 2000 years before present. Additionally, the hydrogen isotope record of Austin Lake also provided evidence for intense cold conditions which peaked around 1200 years before present. Interestingly, evidence for a similar climatic shift from the Southern Hemisphere was reported by White et al. (1994).

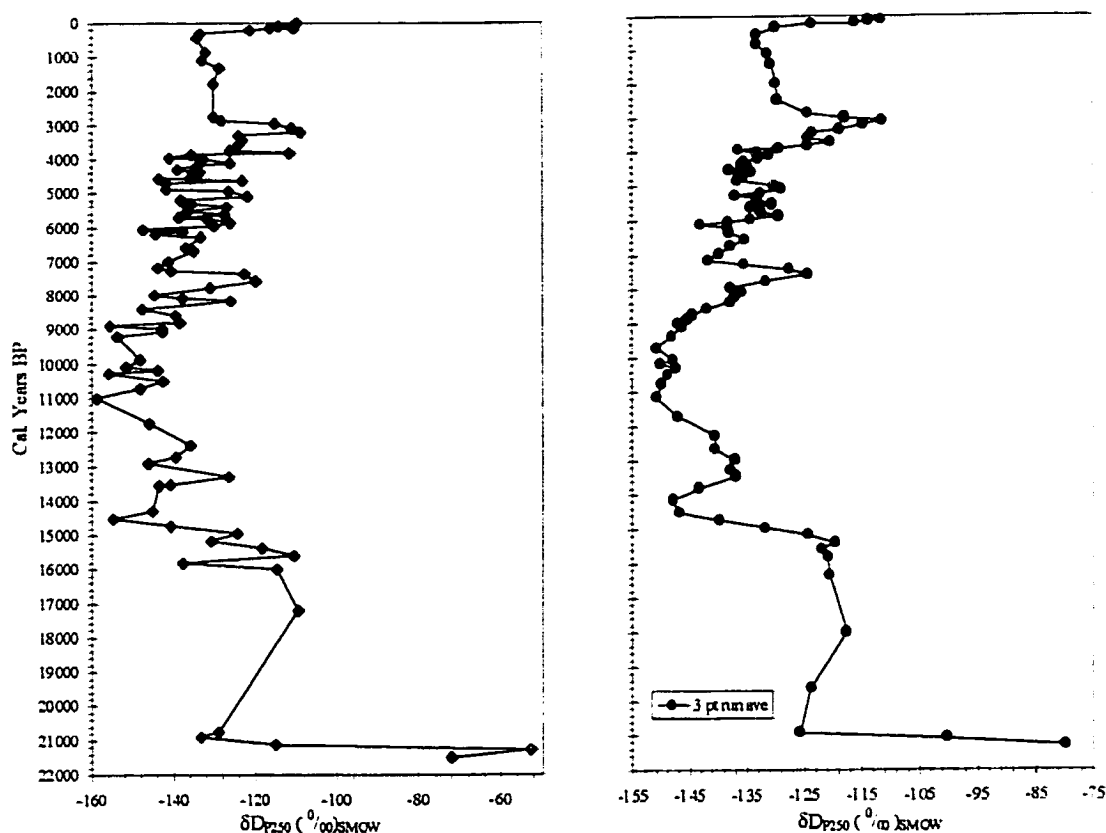


Figure 23. Comparison of Raw and Smoothed Ladd Lake δD -P250 Data Plotted With Respect to Calendar Years Before the Present.

Figure 24 again shows the smoothed δD -P250 data but with annotation of notable systematic shifts in the isotopic data. To the left of the isotopic data reported intervals of “warm” and “cool” phases are indicated from various regionally distinct areas along with calendar year (ka BP) and radiocarbon (k BP) chronologies. Table 21 shows the subdivisions of the hydrogen isotopic record in the Ladd Lake organic matter into 3 or (possibly 4) stages – on Figure 24) and inferred climatic conditions.

Also shown in Table 21 are the calendar years BP and the corresponding radiocarbon year BP for the intervals discussed.

The Ladd Lake data suggest a general agreement with the earlier work of Krishnamurthy et al. (1995) but indicate that the Mid-Holocene warming was well underway by 8500 calendar years before the present. As shown, the isotopic results may be subdivided into 3 or possibly four stages. With respect to the Mid-Holocene

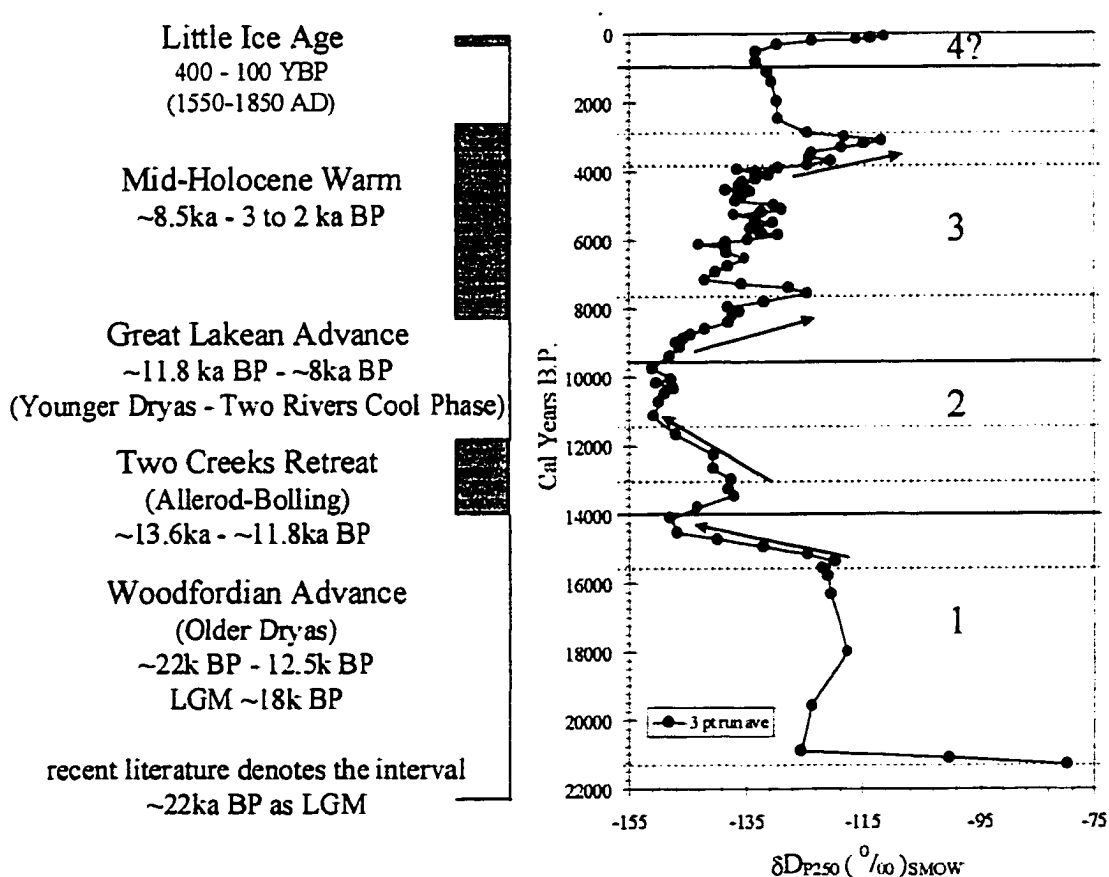


Figure 24. δD_{P250} vs. Calendar Years Before Present From Ladd Lake, Ohio.

Warm, the Ladd Lake data show an overall generally increasing trend in the δD from ~9.5ka BP to the present. This warming (Stage 3) reaches an isotopic maximum at approximately 3000 years BP. In contrast to the Austin Lake record, the Ladd Lake data also show intermittent oscillations between cool and warm intervals throughout the ~6000 year "MHW". Abrupt shifts between cooler and warmer phases are indicated throughout and after a rapid warming from ~4ka BP to ~3ka BP, a generally cooler phase is indicated from ~3000 years BP to roughly 300 years BP.

Table 21

Subdivisions of the Hydrogen Isotopic Record in the Ladd Lake Organic Matter Into 3 or Possibly 4 Stages With Inferred Climatic Conditions

Stage	^{14}C Thousand Years BP	Calendar Thousand Years BP	Avg. δD (‰)	Inferred Climate	Reported Designation
1	18.4 – 11.8	22 – 13.8	Woodfordian Glacial		
	18.4 – 17.6	22 – 21	-90	Cold Phase	LGM
	17.6 – 12.9	21 – 15.2	-122 \pm 2.5	Cool period	
	12.9 – 12.4	15.2 – 14.5	Rapid	Cooling	Transition
	12.4 – 11.8	14.5 – 13.8	-146 \pm 2.1	Cool period	
2	11.8 – 8.3	13.8 – 9.5	Transition to Holocene		
	11.8 – 11	13.8 – 12.8	-137 \pm 0.5	Warm Phase	Two Creeks
	11 – 9.8	12.8 – 11.3		Cooling	Transition

Table 21 – Continued

Stage	¹⁴ C Thousand Years BP	Calendar Thousand Years BP	Avg. δD (‰)	Inferred Climate	Reported Designation
	9.8 – 8.3	11.3 – 9.5	-149 ±1.3	Cold Phase	Great Lakean
3	8.3 - 0	9.5 – present	Inter glacial – M H W ?		
	8.3 – 6.8	9.5 - 7.6		Warming	Transition
	6.5 – 3.8	7.3 – 3.9	-135 ±3.4	Cooler period	
	3.8 – 3	3.9 – 3		Warming	Transition
	2.5 – 1	2.5 – 1	-130 ±0.5	Cooler period	
	1 – 0.3	1 – 0.3	-133	Cold	
	300 YBP- present	300 YBP- present		Warming	Transition

Prior to the MHW, the near 22,000 calendar year record shows evidence of the Woodfordian advance (22ka BP to 13.8ka BP) with the Last Glacial Maximum (LGM) at ~22ka BP. The subsequent Two Creeks warm phase, from ~13.8ka BP to ~12.8ka BP in the Ladd Lake isotopic record, is followed by a decreasing trend providing evidence of the Great Lakean Advance (~11.8ka to ~8ka BP). This latter cool phase contains what may comprise the Younger Dryas (~11 kyr to 10 kyr BP or 12.8ka to 11.6ka BP) and Two Rivers cool phases. Perhaps it should again be noted that the ice free date for Ladd Lake corresponds to ~14,500 to 14,000 ¹⁴C years BP

(~17,140 to 16,520 calendar years BP) the present. The various glacial levels of Lake Erie do not affect Ladd Lake directly as it is outside the maximum Erie basin of Lake Maumee, lying between the Wabash River and the Fort Wayne moraines. Dates older than the oldest ^{14}C date of 14.6 kyr BP (17.2k calendar years BP) for the Ladd Lake were assigned based on use of the previous up core sedimentation rate and should be used with a modest degree of caution.

Stage 1 of the Ladd Lake isotopic record corresponds to LGM and younger intervals of the Woodfordian Glacial. The two δD -values at the base of the core have a mean of -90‰. First impressions may be that these values are too positive in comparison to up core δD -values to reflect glacial conditions. Yapp and Epstein (1977), however, measured the δD from 40 radiocarbon dated trees collected from geographic regions spanning North America and covering the Late Glacial to Mid-Holocene. Their results showed that LGM cellulose δD -values were enriched by 19‰ in the ice free areas compared to modern waters. This positive bias was thought due to the lower ocean temperatures and smaller temperature gradients that existed between the ocean and ice-free continent. Warmer winters and cooler summers of the Glacial interval were considered compatible with this. The enriched value of the oceans and lower summer temperatures resulted in higher original vapor retention at higher latitudes than observed at present.

Subdivisions of the Ladd Lake Stages are indicated by the dotted line within each stage-interval. The LGM of Stage 1 was followed by an interval of stationary

isotopic values having a mean δD of $-122 \pm 2.5\text{‰}$ from $\sim 21\text{ka BP}$ to $\sim 15.2\text{ka BP}$. Yapp and Epstein (1977) show a temperature coefficient of $\sim 7\text{--}8\text{‰}$ per $^{\circ}\text{C}$ for the non-exchangeable hydrogen in cellulose. The temperature coefficient of δD in precipitation is similar at ~ 4 to 6‰ per degree C (Dansgaard, 1964). If these observations are extrapolated to the results from this study, the $\sim 32\text{‰}$ shift in the δD -values from the LGM to the 21ka to 15.2ka BP interval would correspond to a temperature variation ranging from 4.6 to 8°C using a 4 and 7‰ per degree C relationship. This magnitude of difference seems unlikely. Alternatively, changes in seasonality may have resulted in warmer summers with increased ablation of the ice sheet even if associated with cooler annual mean temperatures. The shift, however, perhaps is associated with a change in the air mass history as relates to the meteoric waters received by Ladd Lake through this time. As the oceans warmed from their lower LGM temperatures, a stronger gradient between the oceans and ice free continent may have developed leading to more depletion of the original vapor in the transitory air mass as it supplied meteoric precipitation to the Ladd Lake area.

The rapid decrease in the δD from 15.2ka to 14.5ka BP leads to a negative δD peak at $\sim 14.5\text{ka BP}$. This rapid shift may be related to a “trans-US wet event” during which time unusually wetter conditions were observed in the United States (Broecker, 1994). This wet period reportedly preceded a period when global ice caps reached a prominent maxima before going into a rapid retreat during the Two Creeks-Allerod/Bolling warm phase. The three δD values (from $\sim 14.5\text{--}13.8\text{ka}$) coincide with

this maxima and have a mean δD of $-146 \pm 2\text{‰}$. Using the 4 and 7‰ per degree C relationship the $\sim 24\text{‰}$ shift from 15.2ka BP to these peak δD values would correlate to a 3.4 – 6°C cooling.

Stage 2 of the Ladd Lake hydrogen results suggest that this area experienced a transitional period of a warmer then cooler phase between the Late Glacial and the Holocene (~ 13.8 ka BP to ~ 9.5 ca BP). Dansgaard et al (1971) noted similar findings from the $\delta^{18}\text{O}$ of a Greenland ice core. Here these intervals correspond well to the documented Two Creeks warm phase (retreat 13.8ka to 12.8ka BP) and the Great Lakean re-advance (cold phase) from ~ 11.3 ka to 9.5ka BP. The mean δD values during the peak of the Two Creeks “warm” is indicated as $-137 \pm 0.5\text{‰}$. There is a 12‰ depletion from this value to the mean δD during the peak of the Great Lakean . This corresponds to a 1.7 to 3°C cooling from the preceding warm phase.

The δD -values through the MHW interval range from a -148‰ minimum to a -109‰ . As previously noted, abrupt oscillations between warm and cool intervals occur and possess shifts in the δD values by as much as 32‰ (i.e. between 4ka BP and 3ka BP). A similar rapid positive shift occurred at from ~ 9.5 ka to 7.8ka BP. The reversal of these rapid positive swings occurs in even more abbreviated time intervals. Irrespective of these oscillations, the mean δD -value during the 7.3 to ~ 4 ka BP interval is -135 ± 3.4 and differs by $\sim 14\text{‰}$ from the mean cool phase value ($-149 \pm 1.3\text{‰}$) from 11.8 to 8ka BP. This would equate to an extrapolated ~ 2 to 3.5°C mean difference between these cool and warm phases. Although oscillations do occur

during the 7.3 to ~4ka BP interval, the shifts are not of great magnitude. The mean values during the cooler excursions at 3ka BP to ~300 YBP are very similar to those of the 7.3 to ~4ka BP interval.

Temperature changes deduced from the hydrogen isotope record through the MHW are perhaps a slight overestimate although they are within the range advocated by data from speleothems and pollen distribution. This is because interpreting the δD of sediment organic matter requires consideration be given to the possible atmospheric processes that could influence local precipitation, since ultimately it is the δD of local precipitation that is implied from the sediment record.

The δD of local precipitation is strongly influenced by the history of the air mass as well as temperature. At present, air masses in the Ladd Lake and other Midwestern areas originate principally from three potential sources. These include warm air masses from the Gulf of Mexico, maritime air masses from the Pacific and Atlantic, and cold dry air masses from the Canadian Arctic (Eichenlaub et al, 1990). Of these, the major rain-bearing air masses are those from the Gulf of Mexico, the maritime Atlantic and to some degree the Pacific. Drastic changes in the degree of relative dominance (or relative percent contribution) from these sources can influence the δD of the local precipitation. For this area of the Midwest, if there were an intensification of moisture transport from the Gulf of Mexico superimposed on the temperature increase during the mid-Holocene, heavier δD values could be produced. The results of stable isotope investigation of rain in Kalamazoo, Michigan, showed the

average summer δD of rain through 3 consecutive years in that region was -37‰ (Machavaram, 1997). Moreover, model calculations show that the rain derived from vapors originating from the Gulf of Mexico are isotopically the heaviest, ignoring the negligible thunderstorm fractions (Machavaram and Krishnamurthy, 1994). Therefore, if during the "mid-Holocene" warm phase (8-3ka BP), there was an intensification of vapor transport from the Gulf of Mexico, it could explain in part the δD increases in the Ladd Lake organic matter. Negative oscillations of the δD signal through the MHW interval could likewise be partially explained through shifts in the relative dominance of the respective air masses if, in addition to the Gulf moisture, a secondary air mass from the Pacific may also have contributed to the area precipitation. The latter would require that the westerlies were periodically much stronger as has recently been suggested (COHMAP, 1988).

Verification of these observations can be seen in the pollen studies and isotope studies of cave deposits from other Midwestern states. Dorale et al. (1992) used oxygen isotope ratios of speleothems from the Cold Water cave in northeast Iowa to provide evidence of a rapid warming by 3°C around 5900 years before present and a cooling by 4°C at 3600 years before present. Extensive palynological investigations indicate that prairie was dominant in central Iowa between 8-3kyr before present and that the climate was drier than the present during the same time interval (R.G. Baker, et al, 1992). Ladd Lake pollen data, Figure 22, show evidence that the interval from 8ka BP to 6ka BP may have been drier than the following 6ka BP to present. An

intensified Gulf of Mexico vapor transport can also account for the latter observations while an increase in the relative contribution from a Pacific air mass could account for the former. Baker et al. (1992) used similar arguments to show why prairie was dominant in parts of eastern Iowa while forest vegetation prevailed in some other areas. Assuming the temperature estimates based on Cold Water Cave in Iowa are valid (Dorale, 1992), a 3° increase in temperature during the warmer mid-Holocene in northwestern Ohio could be ascribed. The rest of the heavy isotope signal that occur during the positive δD excursions are probably the result of a dominating moisture transport from the Gulf of Mexico.

The Mid-Holocene Warm phase provides an excellent analog to modern weather phenomena wherein specific years have been marked by relatively mild winters with longer summers. It is arguable that the MHW was intermittently marked by longer summers and shorter winters resulting in, or caused by, a near constant high pressure ridge over the Midwestern United States, thus accounting for intensified Gulf of Mexico transport. Irrespective of the seasonality and circulation patterns, the δD signal of the Ladd Lake organic matter indicate that the Midwestern United States experienced significant temperature and/or environmental oscillations during the so-called Mid-Holocene Warm phase. This generally increasing trend occurring over the past ~8.5ka to 3ka BP interval was punctuated by intermittent rapid return to cooler periods.

Carbon

The hydrogen to carbon ratios of the δ D-P250 series and the conventionally extracted Pilot Group (the open squares) are shown in Figure 25. These data are shown in conjunction with the organic carbon content of both the HCl and HF:HCl residues analyzed and each are plotted against calendar years before present. As noted in the review of the pilot group series, there is a mid-core increase in percent organic carbon. This is again evident from these data. Further, the general scatter of the percent organic carbon data over the length of the core and the similarity in the surface and basal percent organic content suggests that no diagenetic effects have altered the sediment organic matter. The further concentration of the sediment organic matter during the HF:HCl digestion is graphically evidenced by its higher percent organic content compared to the HCl residues. Interestingly, the curve shape of the H/C ratios from the pyrolyzed samples (solid diamonds) somewhat mimics those of the percent organic carbon data. Regression of these data yields a positive correlation ($R^2 = 0.45$, $y = 0.98 + 0.35x$). Another note of interest is that visual comparison of the H/C ratios from the conventionally extracted Pilot series and the δ D-P250 series (solid diamonds) indicate greater differences may occur where the organic content of the residues are lower. This perhaps results from the greater water loss during the low temperature release of pyrolysis waters from samples having lower % organic content (i.e. a higher inorganic component in the insoluble residue).

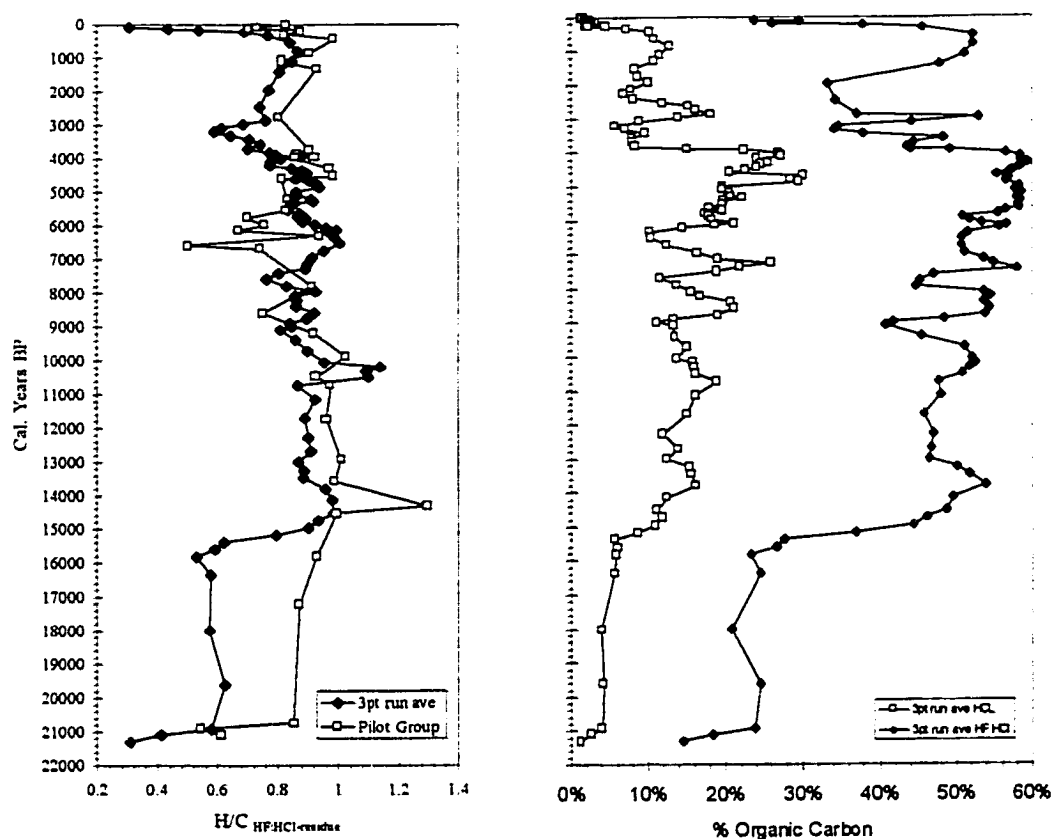


Figure 25. H/C Ratio of HF:HCl Residues From the Pilot Group and the δD -P250 Series Are Shown Beside the Percent Organic Carbon From the HCl and HF:HCl Residues.

Figure 26 shows the atomic carbon to nitrogen (C/N) ratios plotted versus calendar years BP from both the HCl and the HF:HCl residues for all the Ladd Lake samples. The C/N ratios of the organic carbon in the HCl-residues have a mean value of 10.7 indicating lacustrine origins for the residual organic matter. Again, the positive shift in the C/N ratios of the HF:HCl-residue is due to loss of nitrogen possibly from

the protein portion of the organic matter during the successive acid digestions. Future work is needed to clarify the source and mechanisms for this nitrogen loss.

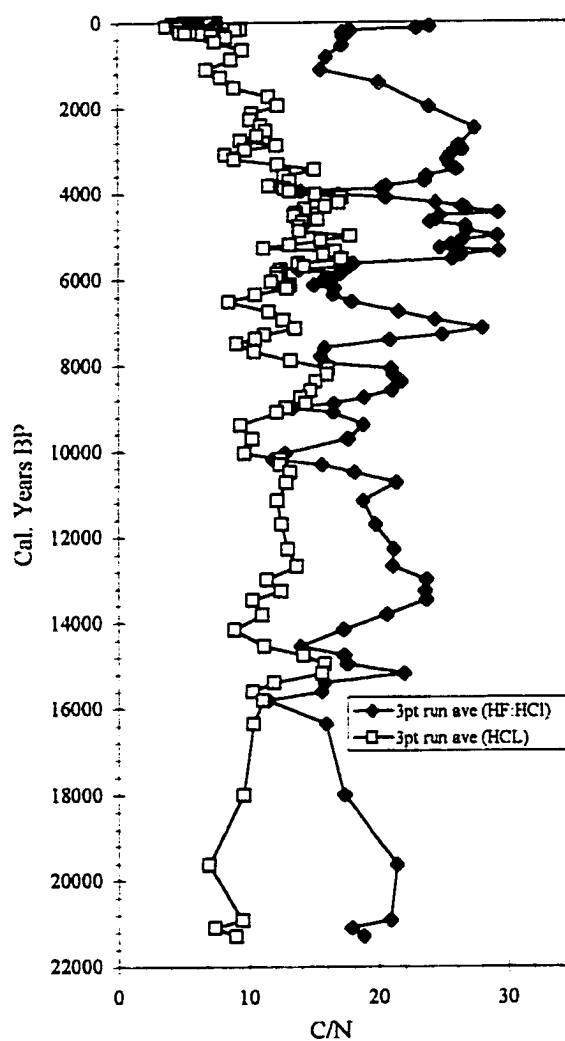


Figure 26. C/N vs. Calendar Age for Both HCl and HF:HCl-Residues From Ladd Lake Samples.

The $\delta^{13}\text{C}$ of the organic carbon in the HCl-residues are shown in Figure 27 plotted versus calendar years before the present. The data range from -25.4‰ to

-32.8‰, which is consistent with values reported in other mid-western studies. A regression of the $\delta^{13}\text{C}_{\text{HCl}}$ with respect to the % organic carbon content shows a lack of correlation ($R^2 = 0.055$, $n=137$). This may suggest that the $\delta^{13}\text{C}$ of the organic

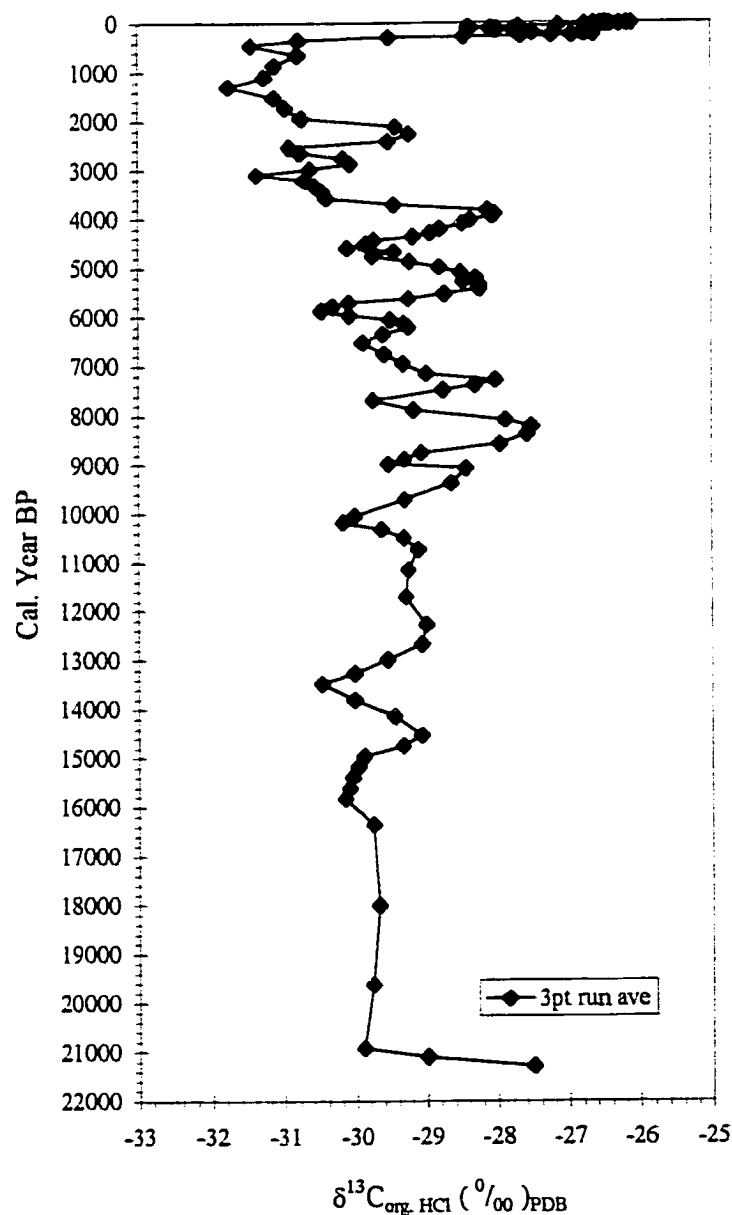


Figure 27. Plot of $\delta^{13}\text{C}_{\text{HCl}}$ vs. Calendar Years BP From Ladd Lake.

matter from Ladd Lake is not singularly controlled by productivity in the lake. It should be noted, however, that the $\delta^{13}\text{C}$ values are relatively uniform from ~22ka BP to ~15ka BP but vary sharply over short time intervals from 15ka BP to the present. Perhaps during this later period, productivity is influencing the $\delta^{13}\text{C}_{\text{organic}}$ signal while the whole core regression implies otherwise. If these rapid variations in the $\delta^{13}\text{C}$ organic signal do indicate changes in productivity, they occur intermittently over short time scales. The positive shifts would represent periods of increased productivity wherein the available CO_2 becomes depleted and photosynthesis continues while consuming the isotopically heavier bicarbonate. In the Austin Lake study (Krishnamurthy et al., 1995) the $\delta^{13}\text{C}$ values of the residual organic matter exhibited values ranging from -23 to -14 ‰ with an up core trend to increased δ values. The Austin Lake trend suggested a propensity towards continuous depletion of CO_2 perhaps via increasing lake productivity. In light of the δD record from Austin Lake, the carbon data indicated two periods of enhanced CO_2 abstraction which corresponded to intervals where climatic warming were indicated.

Figure 28 shows a comparison of the δD , $\delta^{13}\text{C}$ and the precipitation all plotted as the difference from the mean value vs. calendar years BP. The precipitation data are based on the mean annual values from Shane, 1991 and the isotopic data correspond directly to intervals used in the pollen transfer function data. The mean values are indicated on the vertical zero-line of each diagram. The annual precipitation

value over the length of the core was 80.76cm per year while the mean δD and $\delta^{13}C$ for these data are -130 and -29.1‰ , respectively.

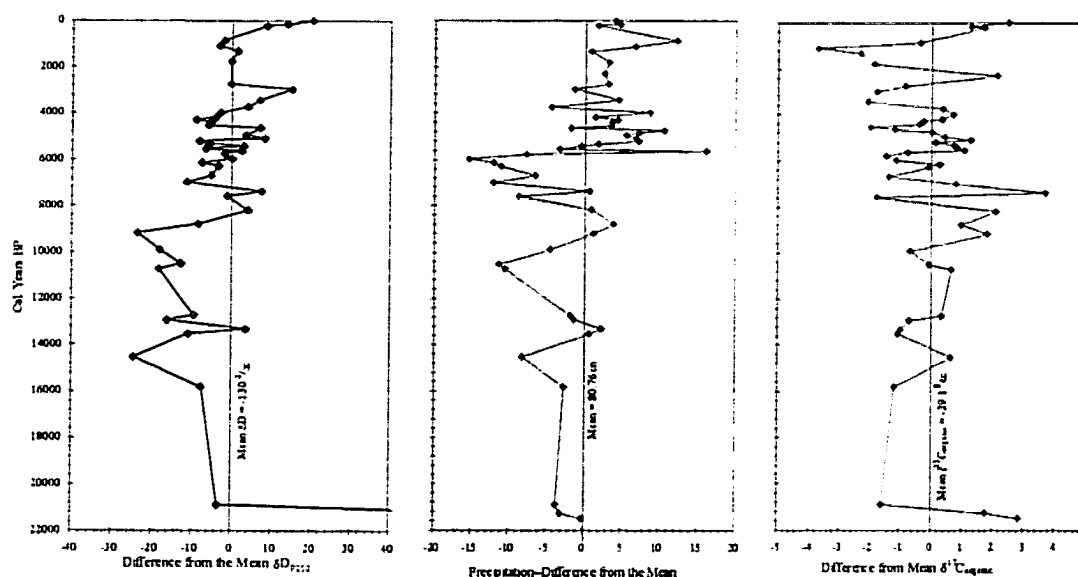


Figure 28. Comparison of the Difference From the Mean From δD , $\delta^{13}C$ and the Corresponding Mean Annual Precipitation From Ladd Lake.

Plotted in this manner the “pollen” precipitation data suggest that prior to 6000 years BP, Ladd Lake recorded conditions that were generally drier than normal with only short duration wet periods at ~ 13.2 ka BP and ~ 8.8 ka BP. The drier conditions indicated from ~ 8 ka BP to ~ 6 ka BP in the pollen data correspond to a generally more negative interval in the δD record. These negative δD excursions indicate periods where non-evaporative processes exhibited a greater influence on the lake water. Seasonality may be suggested wherein a greater relative proportion of winter precipitation was received by the lake, possibly due to longer winters-shorter

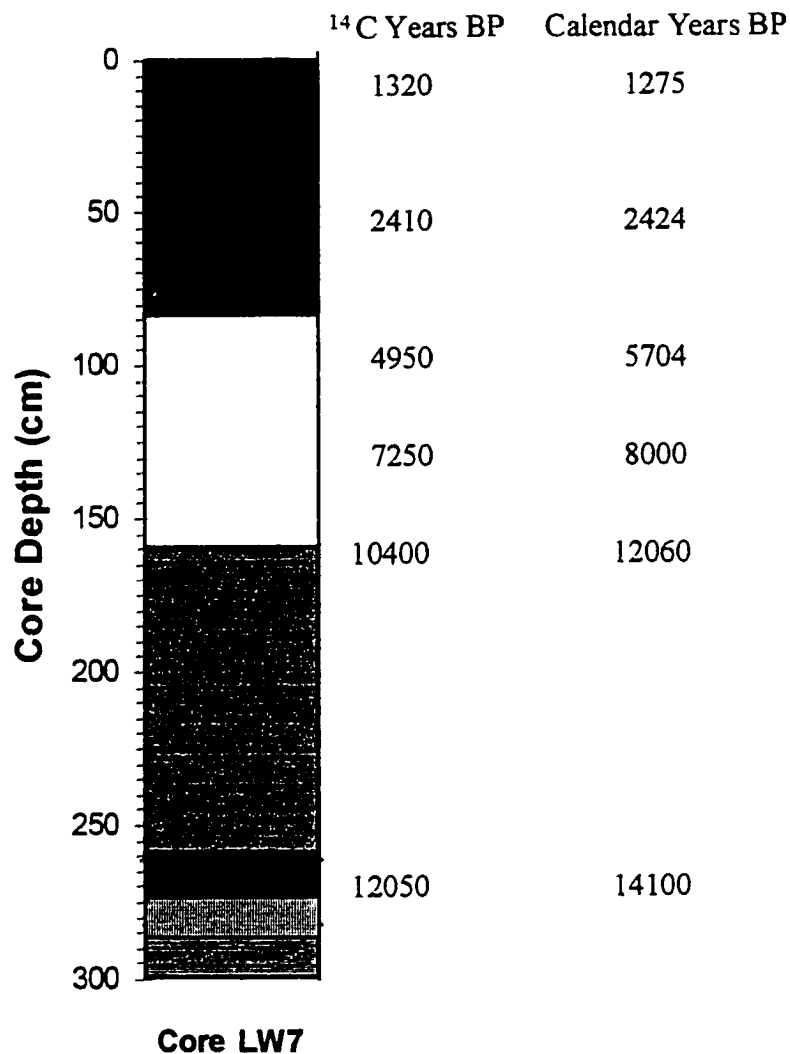
summers. However, even within this negative segment, the δD values exhibit a tendency toward and overall positive excursion of the δD values. In fact, after a rapid negative shift from ~8 to 7kaBP, the δD values up core from ~7ka BP generally trend in a positive direction with intermittent negative oscillations through the remainder of the Holocene. The greater precipitation indicated from ~6ka BP to the present by the pollen data is in keeping with a generally increasing dominance of Gulf moisture. This may be expressed in the δD signals generally positive trend up core from ~9ka BP. The negative excursions of the δD signal through this interval may result from periodic increased relative dominance of a secondary air mass from the Pacific.

The drier conditions indicated from ~15ka BP to 14ka BP and 12ka BP to 10ka BP by the precipitation data are seemingly supported by the isotopic results. The δD exhibits a concurrent negative trend, ruling out evaporative enrichment, and thus may be related to cooler periods during which the jet stream was pushed further south allowing drier arctic air masses to increase their regional dominance. If peak drier conditions at ~14.5ka BP and 10.5ka BP are indeed related to cooler periods during which the jet stream was pushed further south, an increase in the length of winter and the relative contribution of winter precipitation may be implied. The positive trend in δD and $\delta^{13}C$ from ~10ka to 7.5ka BP may signal a greater relative dominance of Gulf moisture with increased lake productivity.

Lake Winnebago, Wisconsin

The glacial and post-glacial history of Lake Winnebago and the Lake Winnebago basin has been reported by Weidman, 1911, Wielert, 1980, McKee & Laudon, 1972, McCartney & Michelson, 1982, McCartney, 1983, Thwaites, 1943, Need, 1985. This report documents the late Quaternary climatic and environmental change in Lake Winnebago based on the stable isotope records from the various sedimentary components in sediment cores samples. As noted in Chapter I, sixty sediment samples were taken from a core raised from Lake Winnebago during the summer of 1995 and provided for isotopic analysis. A diagrammatic representation of the stratigraphy, sampling intervals and ^{14}C dates obtained by Accelerator Mass Spectrometry on the organic fractions are shown in Figure 29 along with their corresponding calendar years before the present (BP).

Lake Winnebago is a 747 km² lake (45 km x 16.6 km), having an average and very uniform depth of 5.3 meters (Smith, 1997). The contemporary lake is a remnant of the larger glacial Lake Oshkosh that occupied the lake basin during the Two Rivers-Younger Dryas advance 13.6 to 11ka BP (Thwaites, 1943; McKee and Laudon, 1972; Smith, 1997). During the Two Rivers oscillation the Green Bay lobe of the Laurentide ice sheet re-advanced over Two Creeks-age (~14ka BP) forests to a position along the northern end of contemporary Lake Winnebago. Here, it deposited a low moraine that now forms the retaining dam of the lake and marks the terminal position of the last glacial re-advance in the area (Smith, 1997).



LEGEND

- Black Gytja (0 - 84 cm)
- Brown Silt (84 - 159 cm)
- Laminated Red Clay (159 - 259 cm)
- Marsh Peat (259 - 274 cm)
- Gray Silty Clay (274 - 287 cm)
- Reddish Clay (287 - 299.5 cm)

Figure 29. Schematic of the Stratigraphic Sequence in Lake Winnebago Showing the Radiocarbon Dates Obtained by Accelerator Mass Spectrometry on the Organic Fraction and Their Corresponding Calendar Years BP.

Glaciolacustrine sediments blanket the area north and west of Lake Winnebago and document the maximum extent of the lake basin during the early Holocene (Wisconsin Geological and Natural History Survey, 1976). Quaternary sediments beneath the lake, documented by coring efforts (refer to Figure 29), are composed of a reddish-gray to brown sandy clay till overlain by freshwater marsh peat, laminated lacustrine red clay, brown silts and black gyttja (Haase, 1996; Smith, 1997). The distinctive laminated red clay unit was deposited while the lake basin was occupied by the much larger glacial Lake Oshkosh (Weidman, 1911; Thwaites, 1943; McKee and Laudon, 1972). A 23 meter drop in lake-level, to near modern levels, has been documented by mapping the elevations of raised paleo-shorelines and outlets (Weidman, 1911; Thwaites, 1943).

Groundwater provides a major source of recharge to the lake. The lake is seasonally ice covered at which time the groundwaters charge the lake with dissolved solids (420 ppm in late winter) emanating from the carbonate bedrock (Olcott, 1966) and carbonate-rich glacial drift aquifers. With seasonal warming, dilution of the lake water occurs with the addition of snowmelt runoff and spring rains. Total dissolved solids are decreased in the late spring to a measured 190 ppm (Olcott, 1996) and isotopically lighter water is added. Olcott (1966) reports a seasonal variation in the pH of the lake water with winter pH values of 7.4 compared to summer pH values of 8.4 indicating that the lake is a HCO_3 dominated system.

Isotopic Results

The oxygen and carbon isotope ratios ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) of calcium carbonate in marl and the hydrogen and carbon isotope ratios (δD and $\delta^{13}\text{C}$) of the coexisting organic matter have been obtained from the Lake Winnebago samples. The calcium carbonate fraction was analyzed using a modified phosphoric acid technique with an analytical reproducibility of 0.1‰ (Krishnamurthy et al., 1997). The $\delta^{13}\text{C}$ from the carbonate-free HCl-residues, and δD from the HF:HCl residues extracted from sediment organic matter based on the protocol using the microwave digestion process and the δD -P250 procedure. Details of the sample preparation procedure for the $\delta^{13}\text{C}$ and δD measurements of lake organic matter were discussed in Chapter II. Overall reproducibility of the δD values is better than 3‰. Hydrogen isotopic data are reported with respect to SMOW. All carbon and oxygen isotopic data are reported with respect to the PDB standard unless otherwise noted.

Carbon isotope ratios for marl samples in Lake Winnebago exhibited a mean $\delta^{13}\text{C}$ of $-1.7 \pm 1\text{‰}$ while the mean $\delta^{18}\text{O}$ for marl was -8.6‰ with a range from -5.6 to -12.0‰ . This represents analysis of 58 samples from the 60 samples provided. The two peat samples from interval 261 and 271 were not analyzed for their $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of carbonate. The $\delta^{13}\text{C}_{\text{Organic}}$ ranged from -31.0 to -28.5‰ with a mean $\delta^{13}\text{C}$ value of -29.9‰ . These values are consistent with other reports for $\delta^{13}\text{C}$ of lacustrine organic carbon in the Midwest. The mean carbon to nitrogen ratio (C/N) exhibited a value of 10.9 ± 3 . This is clearly consistent with lacustrine origins. Hydrogen isotopic data

exhibited a range in δD_{P250} of 21‰ from -124‰ to -145‰. Comparisons of the % organic content and C/N ratios, etc., between the HCl and HF:HCl residues from the Lake Winnebago samples will not be presented here. Suffice it to say that these data showed similar shifts in values as did their analogous organic residues in the Ladd Lake core.

Because multiple isotopic analyses were performed, the Lake Winnebago data will be presented in sections related to the various data extractions. The marl carbon and oxygen isotopic data will be presented first with the $\delta^{13}C$ of the organic carbon woven into the discussion. This will be followed by a discussion of the δD results as they relate to a discussion of paleotemperature from the combined $\delta D_{Organic}$ and $\delta^{18}O_{Marl}$ in lacustrine sediment components.

Lake Winnebago Marl ($\delta^{18}O$ and $\delta^{13}C$) and Organic Carbon

In general, lakes respond quickly to environmental pressures. Because of the limited size of their reservoir, the isotopic signals resulting from environmental perturbations are amplified (McKenzie, 1985). Lake waters can exhibit a wide range of isotopic compositions. Influencing factors include the isotopic composition of the rainfall in the catchment area and its seasonality, the amount and temperature of evaporation, and the relative humidity. Covariance, or lack of covariance, between isotopic carbon and oxygen in sedimented carbonates can provide climatically important information on the hydrologic state of the lake. The occurrence of isotopic

covariance between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in authigenic carbonates has been reported to reflect the isotopic evolution of the lake water vs. recharge rate. The strongest covariance has been observed in closed systems or lakes with very long residence times and or excessive evaporation (Talbot, 1990; Talbot and Kelts, 1990). Lack of covariance or weak covariance has been observed in open systems with short residence times (McKenzie and Hollander, 1993; Wolfe et al., 1996). Additionally, Smith et al. (1997) showed poor covariance along with negative excursions in $\delta^{18}\text{O}$ of carbonate during drought periods when ground water recharge provided the dominant isotopic signal.

The carbon isotopic signature in lake sediment has two components, the inorganic and the organic fraction. The primary inorganic component is calcium carbonate which can be precipitated either biogenically as shells or inorganically as lake marl. The main sources of organic carbon in a lake are the submerged plants (i.e. macrophytes and plankton) living in the lake. As a result, the $\delta^{13}\text{C}$ of lake organic matter can be related to climatically induced changes in the trophic state of the lake. When a lake goes into a state of enhanced photosynthesis, the production zone is depleted in dissolved CO_2 leaving the lakes carbon pool enriched in ^{13}C . Therefore, an increase or decrease of productivity in a stratified lake should be reflected by like increase or decrease in the $\delta^{13}\text{C}$ of both the inorganic and the organic carbon that is produced in the surface water and subsequently sedimented.

The oxygen isotope ratio of calcium carbonate produced in a lake is determined by the oxygen isotope ratio of the lake itself as well as the temperature of precipitation. The oxygen isotope ratio of the environmental water in turn is determined by that of the waters recharging the lake. In almost all the cases the recharging waters are the local precipitation whose isotopic ratio bears a direct relationship with surface air temperature and more importantly, the history of the air mass that results in precipitation (Dansgaard, 1964). If isotopic equilibrium with the lake water is established, the $\delta^{18}\text{O}$ of the calcium carbonate can be interpreted in terms of environmental changes (Abell, 1982; Dean and Stuiver, 1993; Fritz et al., 1975; Schelske & Hoddell, 1991; Drummond, 1995).

The carbon and oxygen isotope ratios ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of calcium carbonate in marl have been obtained from the Lake Winnebago samples. Figure 30 shows the $\delta^{18}\text{O}_{\text{Marl}}$ conjunction with the $\delta^{13}\text{C}$ of both the marl carbonate and the carbon of the coexisting sediment organic matter. The $\delta^{13}\text{C}$ of the marl carbonate define a very narrow range ($-1.7 \pm 1\text{‰}$). When CO_2 dissolves in water to form carbonic acid and its ions, isotopic exchange reactions enrich HCO_3^- in ^{13}C relative to the CO_2 . Subsequently, when CaCO_3 precipitates from solution, the solid phase is further enriched. Using the equation for alpha ($\alpha_{\text{Calcite}-\text{CO}_2} = \delta^{13}\text{C}_{\text{calcite}} + 1000 / \delta^{13}\text{C}_{\text{CO}_2} + 1000$) and a $\delta^{13}\text{C}$ value of -7‰ for the CO_2 gas, it can be shown that the calcium carbonate is enriched in ^{13}C by about 10‰ when precipitated in isotopic and chemical equilibrium at 20°C ($\alpha_{\text{Calcite}-\text{CO}_2}$ at $20^\circ\text{C} = 1.0103$).

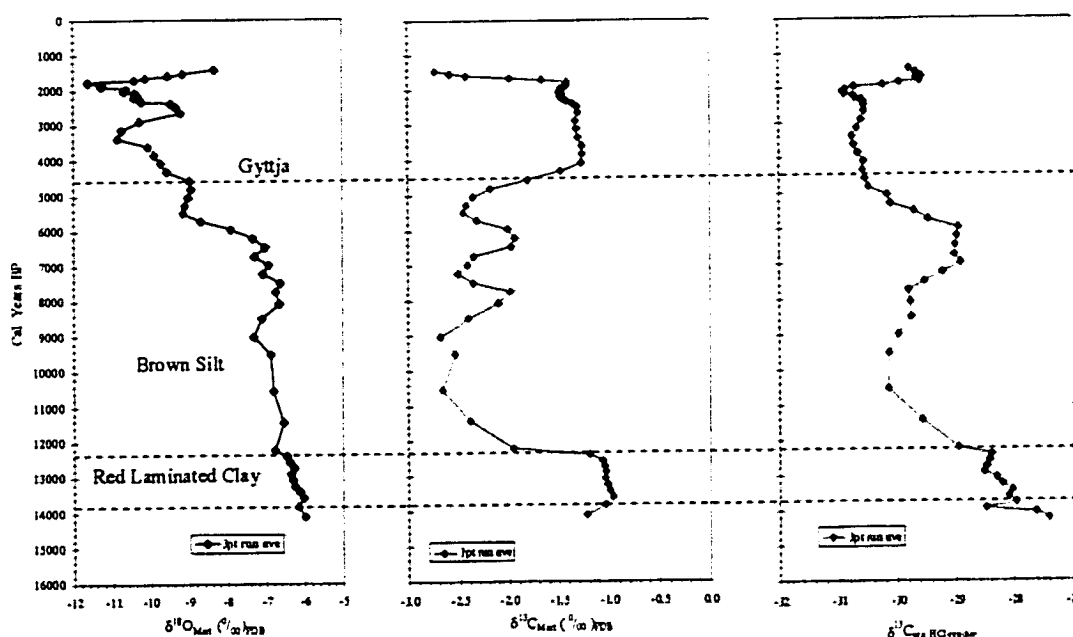


Figure 30. Plots of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ From Marl Carbonate and $\delta^{13}\text{C}$ of Organic Matter From Lake Winnebago.

The most isotopically enriched intervals are at the base of the core and correspond to the red laminated clay unit (~13.7ka BP to 12.2ka BP). The $\delta^{13}\text{C}$ -values range from -1 to -1.4‰ for the marl through this interval. The abrupt negative shift at ~12ka BP corresponds stratigraphically to the base of the brown silt. The $\delta^{13}\text{C}_{\text{Marl}}$ range from $\sim -3\text{‰}$ near the base of the silt (~12ka BP) then generally increase up core to the base of the black gyttja at ~4.4ka BP. At ~4.4ka BP the $\delta^{13}\text{C}_{\text{Marl}}$ values again increase rapidly to and stabilize at values near -1.5‰ up core to ~1.5ka BP. As one can see, it is interesting that a relationship exists between the isotopic values and the lithologic stratigraphy.

A plot of the % carbonate and % organic carbon with respect to calendar years before present is shown in Figure 31. Percent carbonate shows a generally decreasing trend up core from 151 cm corresponding to ~12.2ka BP. Below sample 151 is

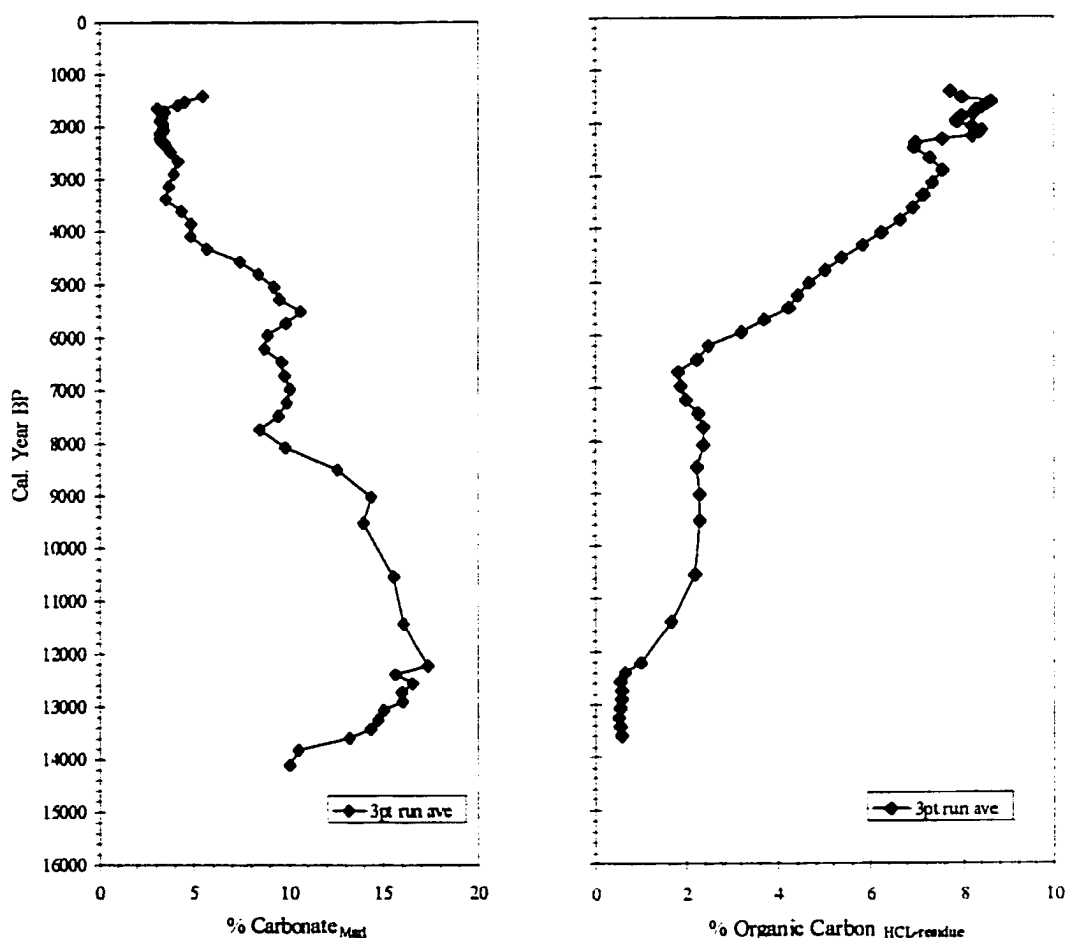


Figure 31. A Plot of % Carbonate and % Organic Carbon vs. Calendar Years Before Present From Lake Winnebago.

the laminated red clay of glacial Lake Oshkosh. Regression of the $\delta^{18}\text{O}_{\text{Marl}}$ vs $\delta^{13}\text{C}_{\text{Marl}}$ through this interval, shown in Figure 32, results in a positive isotopic covariance with

an $R^2 = 0.46$ ($r = 0.68$). This is interesting because regression of the whole core, Figure 33, shows no isotopic covariance in the $\delta^{18}\text{O}_{\text{Marl}}$ vs. $\delta^{13}\text{C}_{\text{Marl}}$ ($R^2 = 0.008$). Changes in the hydrologic state of the lake, perhaps from a closed system during Oshkosh time to an open system post-Oshkosh may be implied.

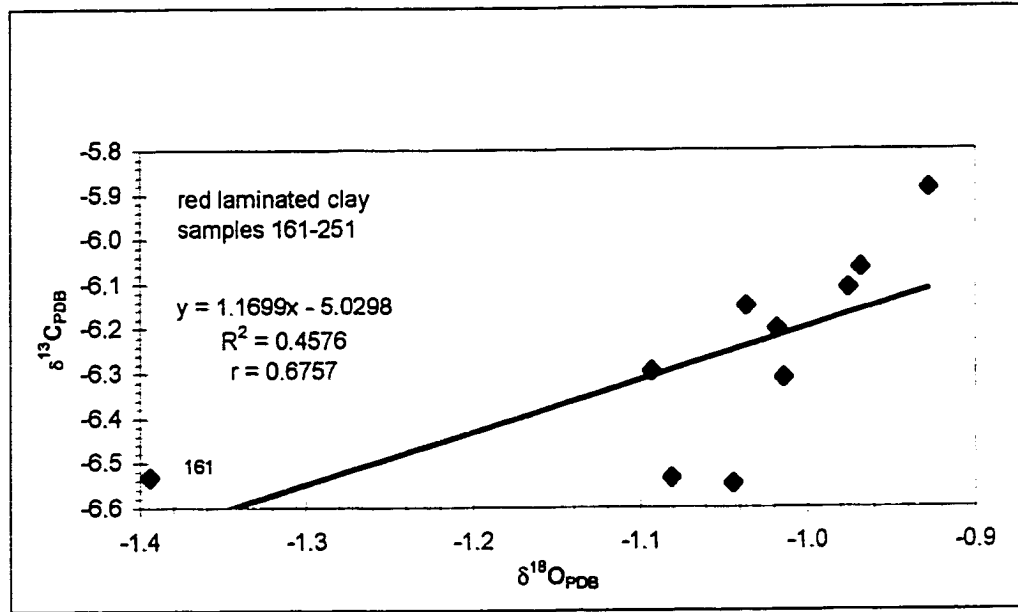


Figure 32. Regression of the $\delta^{18}\text{O}_{\text{Marl}}$ vs $\delta^{13}\text{C}_{\text{Marl}}$ Through the Red Laminated Clay Interval.

The general increase in percent carbonate from the sample at 251cm (13.7ka BP) to the sample just below sample 151cm (~12.2ka BP) coincides with the red laminated clay interval and the basins reported occupation by glacial Lake Oshkosh. As is indicated by a the positive correlation in the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, closed system conditions may have prevailed and probably were due to a blocked northward drainage by the Laurentide Ice Sheet. As the ice retreated, the lakes hydrologic state began

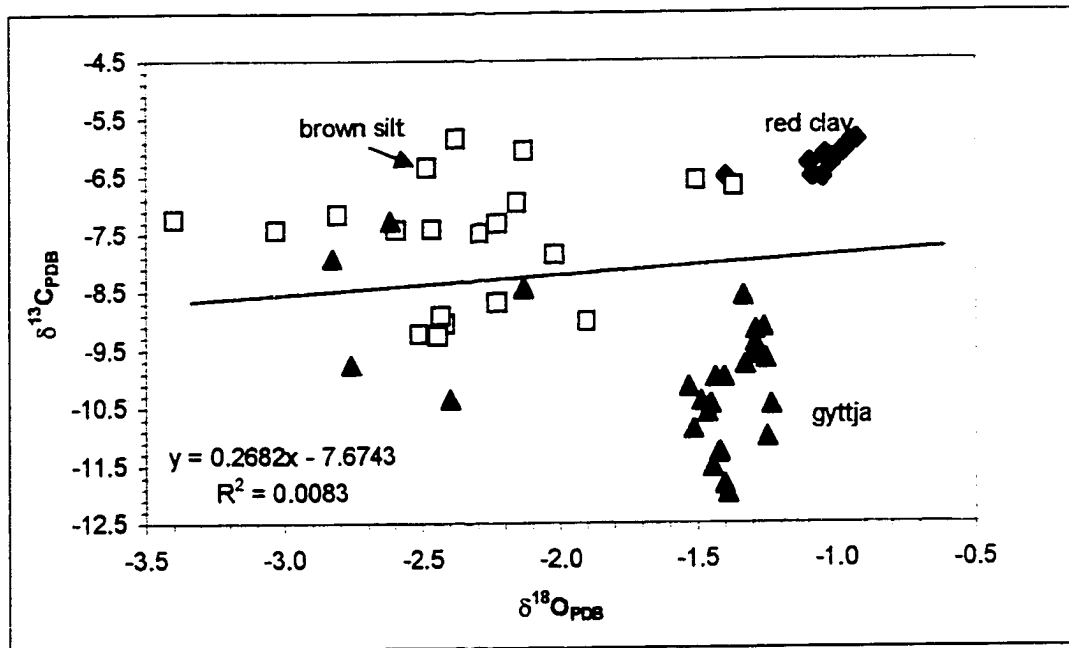


Figure 33. Regression of the $\delta^{18}O_{Marl}$ vs $\delta^{13}C_{Marl}$ in Core LW7 From Lake Winnebago.

to change. Figure 34 shows the regression of $\delta^{18}O_{Marl}$ vs. $\delta^{13}C_{Marl}$ in the brown silt and black gyttja intervals up core from the red laminated clay. These sediment units show weaker correlation with $R^2 = 0.01$ and 0.22 for the silt and gyttja intervals, respectively. More open system conditions may be implied for these upper stratigraphic units. If so, the decrease in the % carbonate and concurrent increase in % organic carbon at ~ 12.2 ka BP may be related to the decrease in lake elevation and volume which in turn is reflected in the stratigraphy of the lake. One could speculate that the general and stepped decrease in carbonate content up core from sample 151cm correlate with lake level changes during the stepped 23 meter drop in glacial Lake Oshkosh lake-levels. If so, the rapid shifts in the % carbonate from ~ 9 ka to 8ka

BP and ~5 to 4.2ka BP may correlate with changes to lower lake volume and residence times at ~8ka and 4.5ka that are reflected in the lack of isotopic covariance in these intervals.

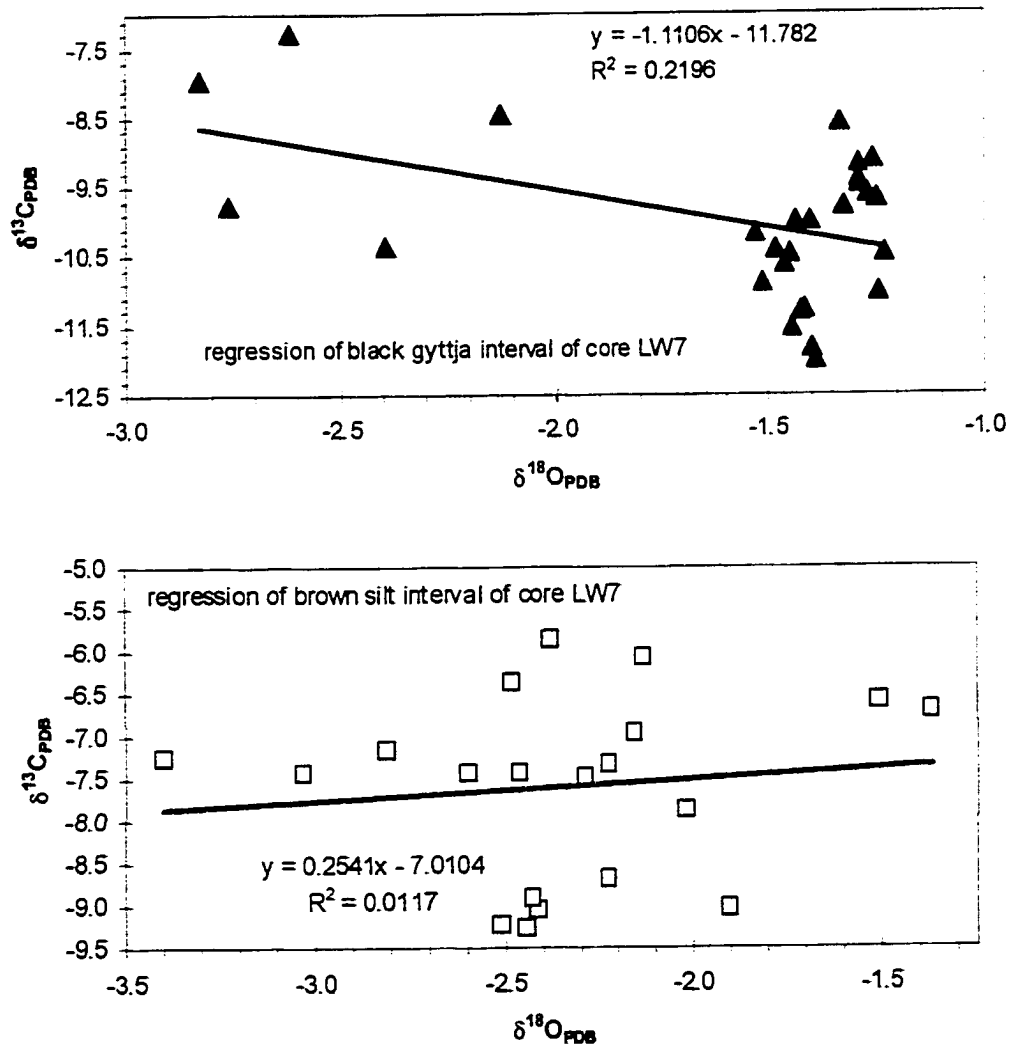


Figure 34. Regression Plots of $\delta^{18}\text{O}_{\text{Marl}}$ vs $\delta^{13}\text{C}_{\text{Marl}}$ in the Black Gytja and Brown Silt Intervals.

Figure 35 shows a regression of the % organic carbon and the % carbonate. There is a negative correlation with $R^2 = 0.8$. As a lake becomes more productive,

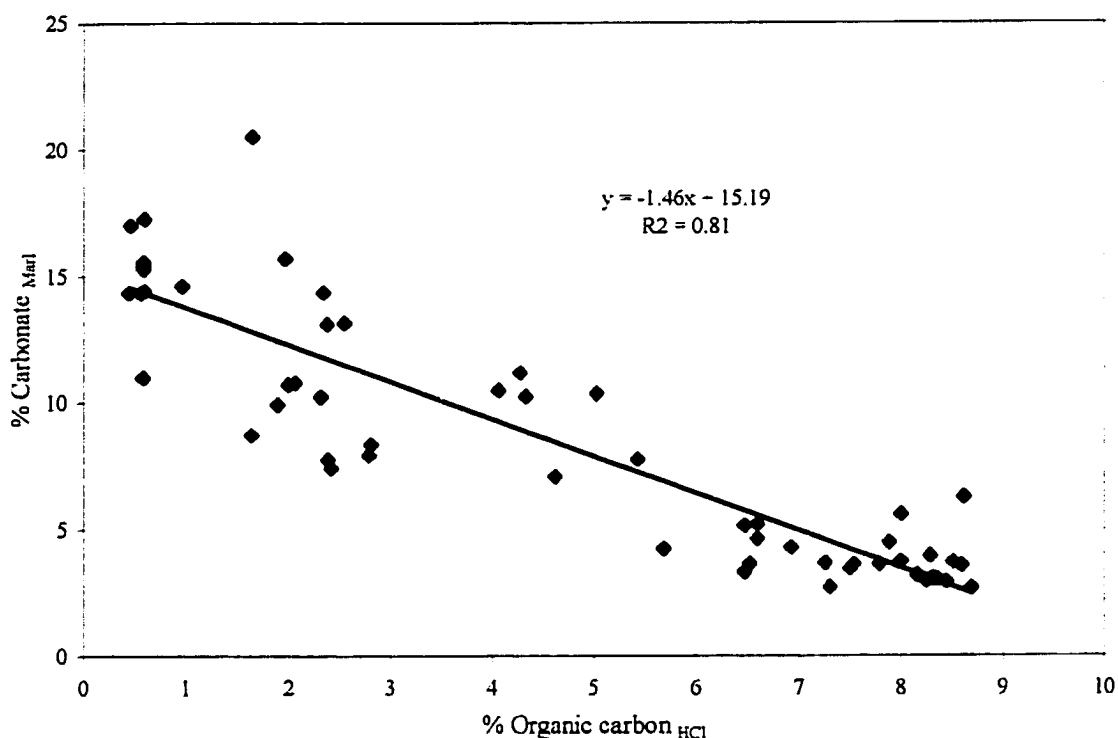


Figure 35. Regression of the % Organic Carbon in the HCL-Residue and the % Carbonate of the Marl From Lake Winnebago.

the photosynthetic activity increase depleting the available CO_2 . This biologically induced depletion often results in the supersaturation and subsequent carbonate precipitation. However, with high productivity, DIC reservoir is depleted and the volume of total carbonate precipitation is reduced. Thus, concurrent with the persistent up-core decrease in percent carbonate there is a sustained increasing trend in the organic carbon content (Figure 31). Periodic reduction of the lake volume

concurrent with climatic warming during the mid-Holocene may have increased the nutrient supply to the lake as the catchment area effectively grew in response to the lowering lake levels and decreasing surface area of the lake. With greater nutrient supply, the lake could become more productive. Thus the % organic carbon would increase at the expense of the carbonate.

Figure 36 shows the $\delta^{13}\text{C}$ vs. calendar years BP for both the inorganic (marl carbonate) and organic carbon from Lake Winnebago. The negative trends from ~12.2ka BP to ~9ka BP in both the $\delta^{13}\text{C}_{\text{Org}}$ and $\delta^{13}\text{C}_{\text{Marl}}$ may suggest a long period in which long winters and cooler summers dominated. The $\delta^{13}\text{C}$ of DIC in lake water is strongly dependent on the duration and magnitude of the summer and redox stratification in the lake. If summers were shorter a larger reserve of respiratory carbon dioxide could accumulate within the inversely stratified water column during winter ice over due to relatively higher levels of dissolved oxygen in the hypolimnic waters. Thus, if winters were longer, the greater DIC content would result in depleted $\delta^{13}\text{C}$ values relative to the $\delta^{13}\text{C}$ values of short winter-long summer. If the lack or covariance between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ through this interval indeed represent open lake conditions and shorter residence times, longer winters could allow for longer periods where groundwater provided the sole or dominant recharge to the lake.

The positive shift in the $\delta^{13}\text{C}_{\text{Marl}}$ at ~9ka to 8ka BP is mirrored by a lesser but positive shift in the $\delta^{13}\text{C}_{\text{org}}$. Concurrent is a rapid decrease in the % carbonate (see

Figure 31). Warmer and perhaps wetter conditions may be implied through the possible increased productivity during the early Holocene. The negative shift in $\delta^{13}\text{C}$

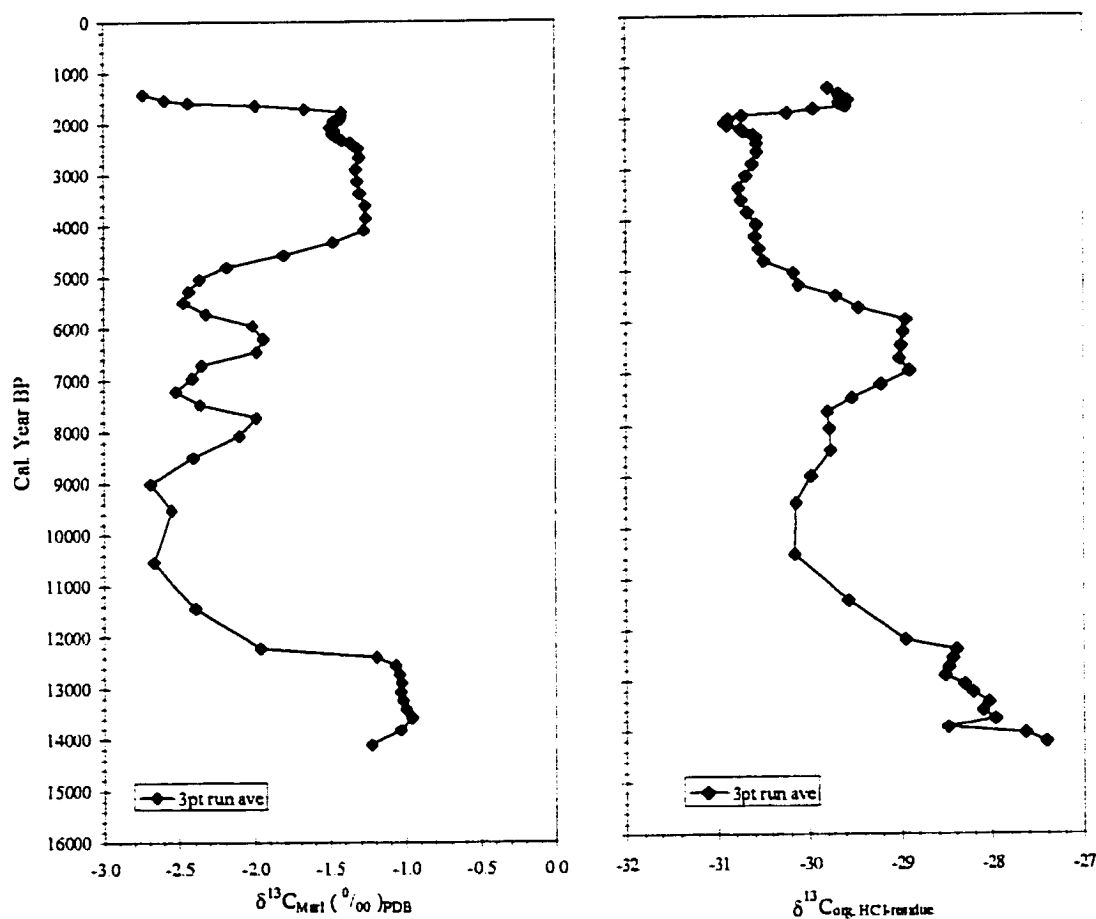


Figure 36. $\delta^{13}\text{C}$ vs. Calendar Years BP for Both the Inorganic (Marl Carbonate) and Organic Carbon From Lake Winnebago.

of the marl at ~8ka to 7ka BP is coincident with a rapid positive shift in the $\delta^{13}\text{C}$ of the organic carbon. As will be shown in subsequent sections, the δD from the Lake Winnebago organic matter show a similar rapid shift from ~8ka to 7ka BP as does the

inferred temperature. The later were interpreted to represent a possible shift in dominant recharge to the lake from summer precipitation to groundwater influx. Warmer temperatures and perhaps longer summers during the early Mid-Holocene Warm may have assisted greater lake productivity resulting in more positive $\delta^{13}\text{C}_{\text{org}}$ values.

In the Great Lakes region, the seasonal warming and cooling of a lakes surface water normally effects a spring and fall overturn, as well as periods of thermal stratification during the summer and winter intervals (Hough, 1958). Typically, lake water is stratified from the time the water warms above 4°C in the spring until it cools below 8°C in the fall. As the water warms, photosynthetic modification of the epilimnic $\delta^{13}\text{C}$ is often accompanied by seasonal $\delta^{18}\text{O}$ enrichment associated with a shift in predominant moisture source followed by partial evaporative enrichment later in the summer. DIC in the epilimnion becomes progressively heavier as long as the lake remains stratified. Thus an increase in the summer or annual average temperature causes a longer period of stratification and enriched $\delta^{13}\text{C}$. Likewise the longer summer results in enrichment of $\delta^{18}\text{O}$ through evaporation and an increase in the proportion of annual precipitation from the Gulf of Mexico occurring during the summer.

Recharge to the modern Lake Winnebago is dominated by groundwater sources via carbonate and carbonate rich glacial drift aquifers. Olcott (1966) reports that Lake Winnebago is typically saturated to supersaturated with CaCO_3 and that much of its ionic enrichment (i.e. Ca^{2+} , Mg^{2+} and HCO_3^- , etc) occurs during the winter

months when the lake is iced over. During this time the lake waters become both thermally stratified and dominated by the dissolved inorganic carbon (DIC) signal of the ground waters recharging the lake. The $\delta^{13}\text{C}$ of the lake waters would also take on a value reflective of the groundwater component with a $\delta^{13}\text{C}$ value near -10 ‰ to -11‰ being typical of groundwater in this area (Atekwana and Krishnamurthy, 1998).

Lake Winnebago, however, does not seem to follow the typical seasonal thermal stratification observed in most lakes in the Great Lakes region. Water temperatures in Lake Winnebago range seasonally from approximately 0 to 26°C (Olcott, 1966). Figure 37 shows Lake Winnebago water temperature data, provided by Dr. G. L. Smith. Temperatures were taken from 1 and 4 meter depths in Lake Winnebago during 1993-1994. Thermal stratification is evidenced during January, February, March and ending in April. No significant stratification is thought to take place from April through December. During these warm months, the broad and shallow Lake Winnebago is regularly wind-mixed and does not develop a persistent stratification. As a result, the wind-effected circulation continually mixes the lake waters and the DIC signal of the lake waters should quickly approach an isotopic equilibrium with the atmospheric CO_2 minimizing any reservoir effect from a groundwater dominated signal. Support for this idea is evidenced in a living clam sample collected from the lake's sediment surface in 1993. Radiocarbon dating gave a "modern" radiocarbon age suggesting very little hard water effect despite Lake Winnebago's water chemistry being strongly influenced by recharge from the carbonate rich local groundwater. This absence of 'hard-water effect' might be due

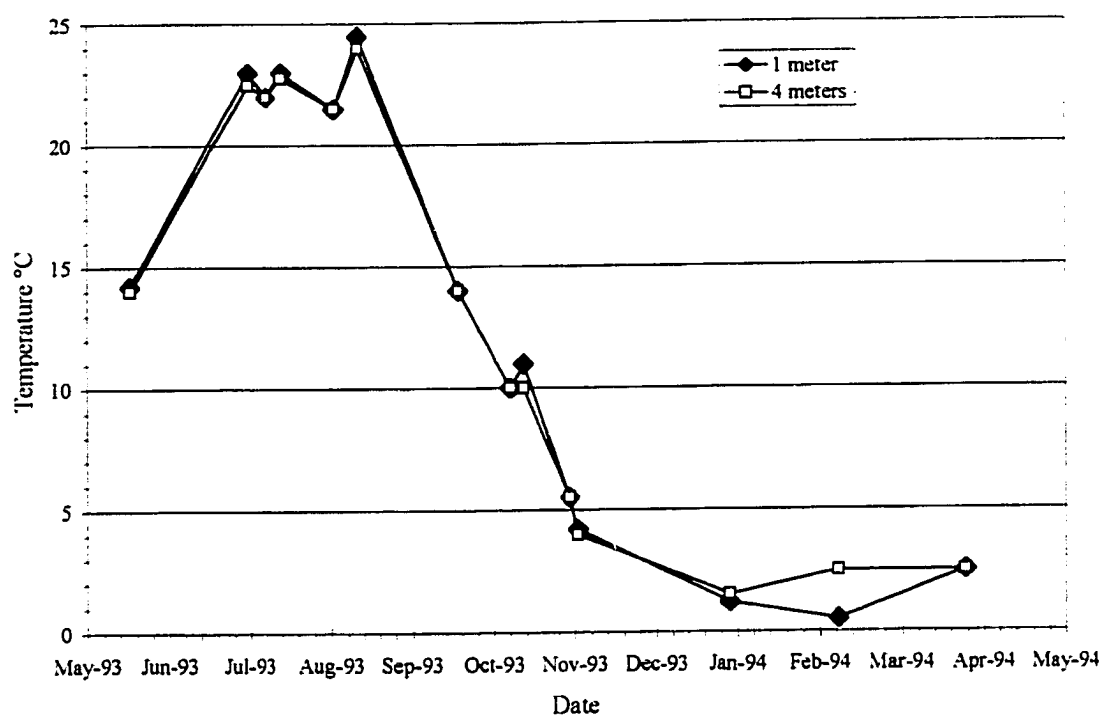


Figure 37. Water Temperatures From 1 and 4 Meter Depths Taken From Lake Winnebago During 1993-1994.

to rapid equilibration of the dissolved inorganic carbon with atmospheric carbon dioxide in this shallow ($\leq 6\text{m}$) lake. This hypothesis is supported by the fact that the down core $\delta^{13}\text{C}$ values of the calcium carbonate define a very narrow range ($-1.7 \pm 1\text{‰}$) that is within the range expected for calcium carbonate precipitating under conditions of equilibrium between dissolved inorganic carbon and atmospheric carbon dioxide (Emrich et al., 1970).

As a result the $\delta^{13}\text{C}$ reflected in the marl carbonates yield the expected enriched late summer value. The $\delta^{18}\text{O}$ of Lake Winnebago marl carbonates, however, yield

values that are non-covariant with the $\delta^{13}\text{C}$ values. These values suggest that the $\delta^{18}\text{O}$ signal of Lake Winnebago late summer waters are dominated still by the isotopic signal of recharging groundwater. The lack of a warm weather development of a persistent epilimnic layer due to the wind-mixed circulation perhaps prevents the “typical” epilimnic enrichment of $\delta^{18}\text{O}$ resulting in a non-covariant carbon-oxygen isotopic signal in the marl carbonates.

Dansgaard (1964) recognized that the oxygen isotopic composition of meteoric precipitation is correlative to the mean annual air temperature. Compositional differences between summer vs. winter precipitation and changes in the magnitude or duration of seasonal climatic patterns and dominant air mass combine to greatly effect the average isotopic composition of meteoric water influx as well as the $\delta^{13}\text{C}$ of dissolved inorganic carbon in lake water. Under normal conditions wherein Mid-Western lakes undergo seasonal bi-annual stratification, isotopic covariance of oxygen and carbon in marl carbonates has been observed. Interruption of this normally covariant condition may be explained by a circumstance wherein the oxygen isotopic signal of groundwater recharge to a lake dominates the lakes oxygen isotopic signal (Smith, et al., 1997). If augmented by the lack of persistent summer thermal stratification of the lakes water column, rapid equilibration between atmospheric CO_2 and DIC may occur. Indeed, given the narrow range of $-1.7 \pm 1\text{‰}$ for $\delta^{13}\text{C}_{\text{Marl}}$ over the length of the Lake Winnebago core, conditions of equilibrium between dissolved

inorganic carbon and atmospheric carbon dioxide may have been sustained throughout.

Paleotemperature From δD and $\delta^{18}O$ in Lacustrine Sediment Components

Reported here is a combined analysis of the oxygen and hydrogen isotope systematics in lake sediments. The combined $\delta^{18}O$ and δD isotopic records are used to evaluate quantitative temperature estimates during the late Pleistocene to Holocene period (14ka to 10ka BP-present). In doing so, these data provide for the first time, a technique that allows a continent based paleotemperature determination from the isotopic records in lake sediment.

Two types of isotope records are discussed here. The first is the $\delta^{18}O$ of the calcium carbonate fraction that exists in these sediments as marl. The second is the δD record of organic matter that coexisted with the marl. Calcium carbonate precipitation takes place in lakes either biogenically or inorganically when the waters are supersaturated with respect to calcite. In temperate regions, the effect is most pronounced during the summer months (typically April-September), when supersaturation is effected either through plants depleting the dissolved carbon by photosynthesis or by evaporation of water. The latter process is more likely in tropical regions although some evidence also exists for this in temperate lakes (Talbot, 1990; Drummond et al., 1995). One useful test to distinguish between the two processes is to test for a covariance between $\delta^{18}O$ and $\delta^{13}C$ of the calcium carbonate, a positive

correlation indicating calcium carbonate deposition via evaporation of water (Talbot, 1990). The organic fraction associated with the calcium carbonate component in the sediment results from the remains of vegetation that grew in the lake's euphotic zones. In temperate climates, production of organic matter production is also more vigorous during the growing season (May to September) and thus is coeval with carbonate generation.

The oxygen isotope data, presented in Figure 38, have been smoothed using a three point running average to filter the relatively high frequency oscillations. The rationale for the smoothing process is that while these oscillations may be real, their timing could not be identified more realistically given the limited number of dates and the precision associated with the ^{14}C dating. The $\delta^{18}\text{O}$ values, in Figure 38, exhibit a range of -6 to -12‰. These data show that there is a near-linear decreasing trend from the bottom of the core upwards. Moreover, the fluctuations within the trend are much more pronounced during the time interval of ~6ka BP to the present.

The oxygen isotope ratio of calcium carbonate produced in a lake is determined by the oxygen isotope ratio of the lake itself as well as the temperature of precipitation. The oxygen isotope ratio of the environmental water in turn is determined by that of the waters recharging the lake. In almost all the cases the recharging waters are the local precipitation whose isotopic ratio bears a direct relationship with surface air temperature and more importantly, the history of the air mass that results in precipitation (Dansgaard, 1964). The temperature effect on the isotope distribution in precipitation is opposite to the effect on the isotope distribution

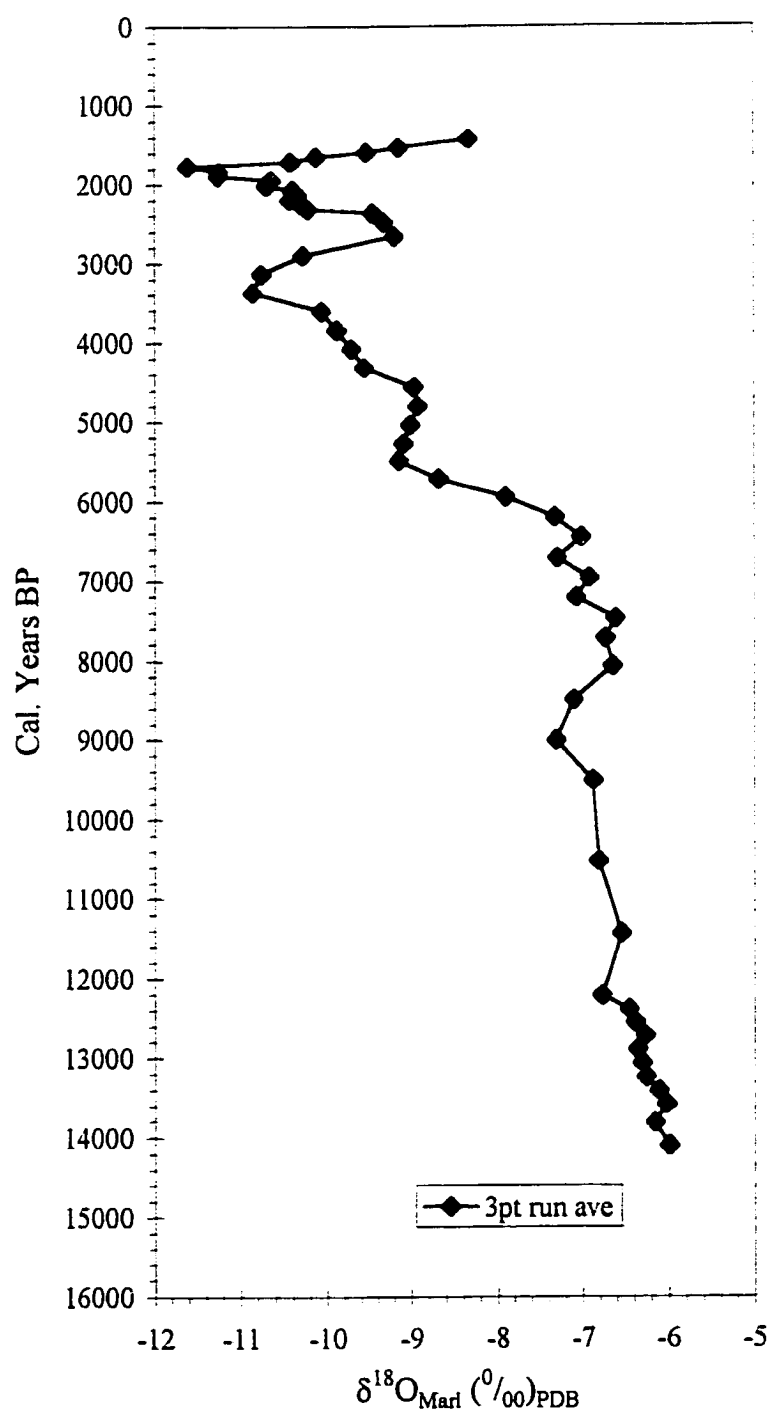


Figure 38. $\delta^{18}\text{O}$ of Marl Carbonate From Lake Winnebago Plotted vs. Calendar Years Before Present.

in the precipitating calcium carbonate. Similarly, the effect due to the history of the air mass is dependent upon the fraction of moisture that still remains in vapor-form at any given place, the higher this fraction the higher (more positive) the $\delta^{18}\text{O}$ of the precipitation. In the case of lakes such as Lake Winnebago that are more strongly influenced by groundwater recharge than surface runoff, the isotope ratio of the lake may reflect that of the local groundwater. The latter is almost always the mean isotope ratio of annual precipitation, taking into account fractional contributions of summer and winter precipitation (Gat, 1981). Thus, in an ideal case, the $\delta^{18}\text{O}$ of lacustrine calcium carbonate can be used to evaluate the $\delta^{18}\text{O}$ of the lake water or the temperature of carbonate precipitation if one of the variables is known or can be inferred.

The δD record obtained from the Lake Winnebago core, smoothed similar to the $\delta^{18}\text{O}$ record, is shown in Figure 39. Note that this record does not extend over the core's full length, as does the $\delta^{18}\text{O}$ record. This is due to the absence of extractable organic matter, sufficient enough to determine its δD , within the red laminated clay stratigraphic sequence (see Figure 29). Hence comparison is made for the section 0-159 cm of the core representing the past 9ka years.

The δD of plants, or more precisely the δD of cellulose extracted from plants after removal of non-exchangeable hydrogen, has been shown to be a reasonable proxy of the δD of the environmental water in which the plants grew (White et al., 1994; Yapp and Epstein, 1982; Buhay et al., 1996). The quantitative relationship between

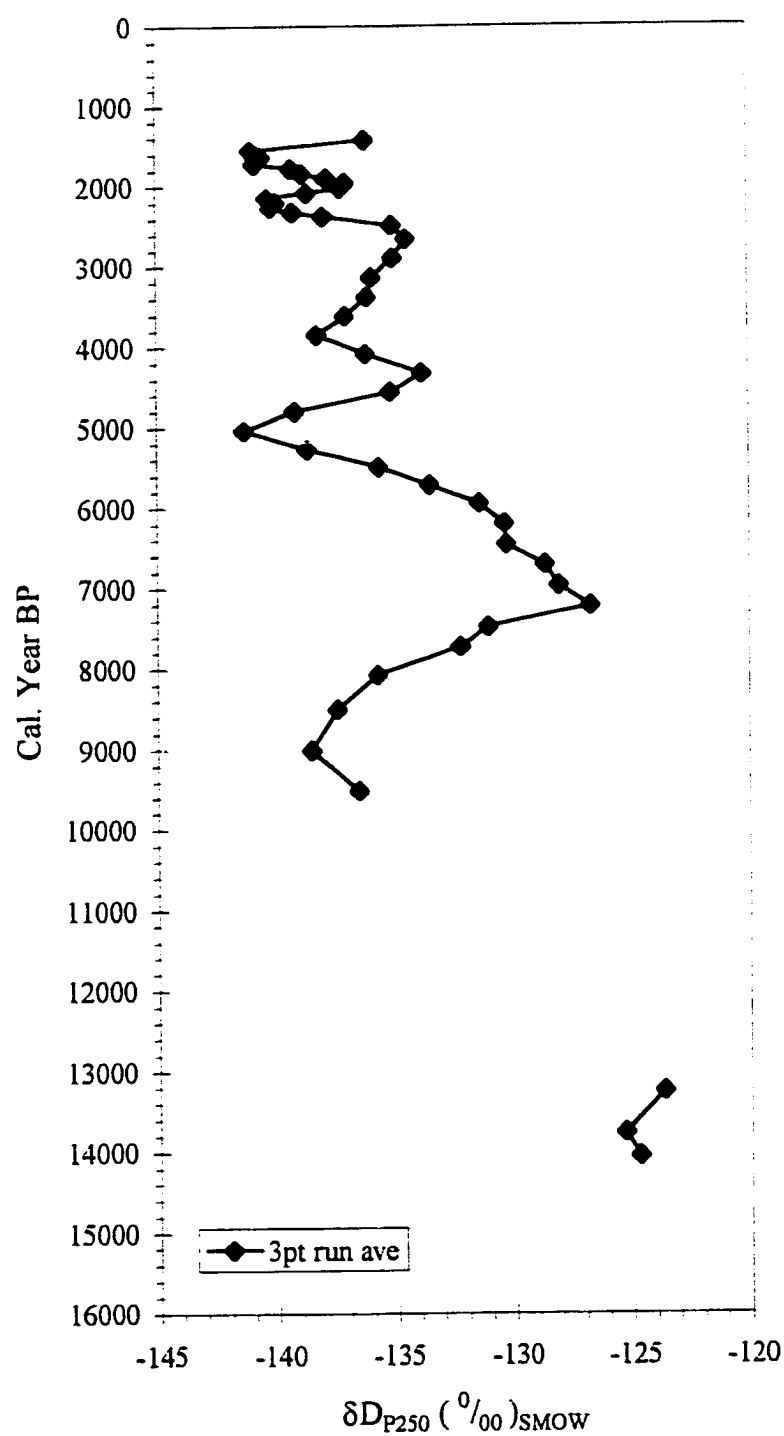


Figure 39. δD of Sediment Organic Matter From Lake Winnebago Plotted vs. Calendar Years Before Present.

the δD of plant cellulose and ambient water has been worked out extensively (Edwards and Fritz, 1986; White et al., 1994; Yapp and Epstein, 1982; Buhay et al., 1996). These works, discussed in Chapter I, consider in detail the role of leaf water evaporation controlled by ambient humidity. The δD -water relationship is in the following form:

$$(1000 + \delta D_{\text{cellulose}})/(1000 + \delta D_{\text{water}}) = {}^D\alpha_n {}^D\alpha_e {}^D\alpha_k - {}^D\alpha_n ({}^D\alpha_e {}^D\alpha_k - 1)h$$

where $\delta D_{\text{cellulose}}$ is the measured δD of the non-exchangeable hydrogen in the cellulose and δD_{water} is the δD of the source water, while ${}^D\alpha_n$ is the net biochemical fractionation factor, ${}^D\alpha_e$ and ${}^D\alpha_k$ are the equilibrium and kinetic hydrogen isotope fractionation factors between the liquid and vapor phases, and h is the relative humidity.

For aquatic plants, such as in this case, negligible effects due to humidity changes ($h \approx 1$) are assumed. This reduces the fractionation to ${}^D\alpha_n$, the biochemical fractionation, and has a value of 0.9530 (Edwards and Fritz, 1986). Cellulose is shown to be depleted in δD by about 47‰ with respect to the δD of the water utilized by plants. As previously discussed, it has been suggested that the δD of bulk organic matter extracted from sediments may also serve as a proxy of the δD of environmental water (Krishnamurthy et al., 1995). Although a quantitative relationship for bulk organic matter in sediment is lacking, reason suggests that it can be attempted by indirect methods through applying the logic followed for cellulose. The δD of the topmost sample (~1300 years BP) was -129‰. Using a measured δD of -55‰ for

the present day Lake Winnebago water, it can be seen that the δD of organic matter is depleted by about 78‰ as follows:

$$\alpha_n = (1000 + \delta D_{\text{organic matter}}) / (1000 + \delta D_{\text{water}})$$

$$\alpha_n = 1000 + (-129‰) / 1000 + (-55‰) = 0.922$$

$$\delta D_{\text{organic matter}} = 0.922(1000 + \delta D_{\text{water}}) - 1000 = -78‰$$

Implicit in this calibration procedure is the assumption that the isotopic ratio of the lake has not changed during the last seven hundred years or so. It is interesting to note that the depletion by 78‰ is higher than what was demonstrated for cellulose. One explanation for this is based on the technique developed for the determination of δD of organic matter in which the samples are preheated prior to combustion. Krishnamurthy and Machavaram (1997) showed that preheating cellulose resulted in an isotopic shift in the same direction as seen with the organic matter reported in Chapter II.

Thus, in what is believed to be a new approach, the δD of the organic matter is extracted from the same samples after measuring the $\delta^{18}O$ from the marl carbonate. The δD of the organic matter were then translated to the δD of the lake water in which the plants grew by using the above fractionation of 78‰ and assuming constancy of this value down core. The resulting δD of the lake water was then used to infer the $\delta^{18}O$ of the lake water by using the well-known relationship of the meteoric water line (Craig, 1961):

$$\delta D = 8 \delta^{18}O + 10$$

The “inferred” $\delta^{18}O$ of the lake is shown in Figure 40 which shows a range of -7 to -9‰. Measured $\delta^{18}O$ values from Lake Winnebago collected at the Jefferson Park outlet in April 1997 were -8‰. Although limited in number, $\delta^{18}O$ values for groundwater from this region are available and range in value from -9 to -11‰ (Krabbenhoft et al., 1990).

In the next step, the $\delta^{18}O$ of the carbonate fraction and the above-inferred $\delta^{18}O$ values of the lake through time can be combined to infer the temperature at which the calcium carbonate was precipitated. This makes use of the experimentally determined calcite-water fractionation equation (Friedman and O’Neil, 1977):

$$10^3 \ln \alpha_{\text{Calcite-Water}} = [(2.78 \times 10^6)/T^2] - 2.89$$

where T is in degrees Kelvin and the calculation of alpha require that $\delta^{18}O$ for both calcite and water be reported with respect to SMOW.

This inferred, smoothed temperature record is shown Figure 41. The surface temperature of 20.2°C is based on the measured average temperatures for the months September 1993 – April 1994 (provided by Dr. George Smith). The data from Figures 40 and 41 reveal interesting features regarding the paleotemperature of the region. The $\delta^{18}O_{\text{water}}$ does not show the expected positive correlation with temperature, i.e. warmer periods are not generally coincident with lighter $\delta^{18}O$ values. This rules out evaporative enrichment suggesting that the $\delta^{18}O_{\text{water}}$ was influenced by other factors.

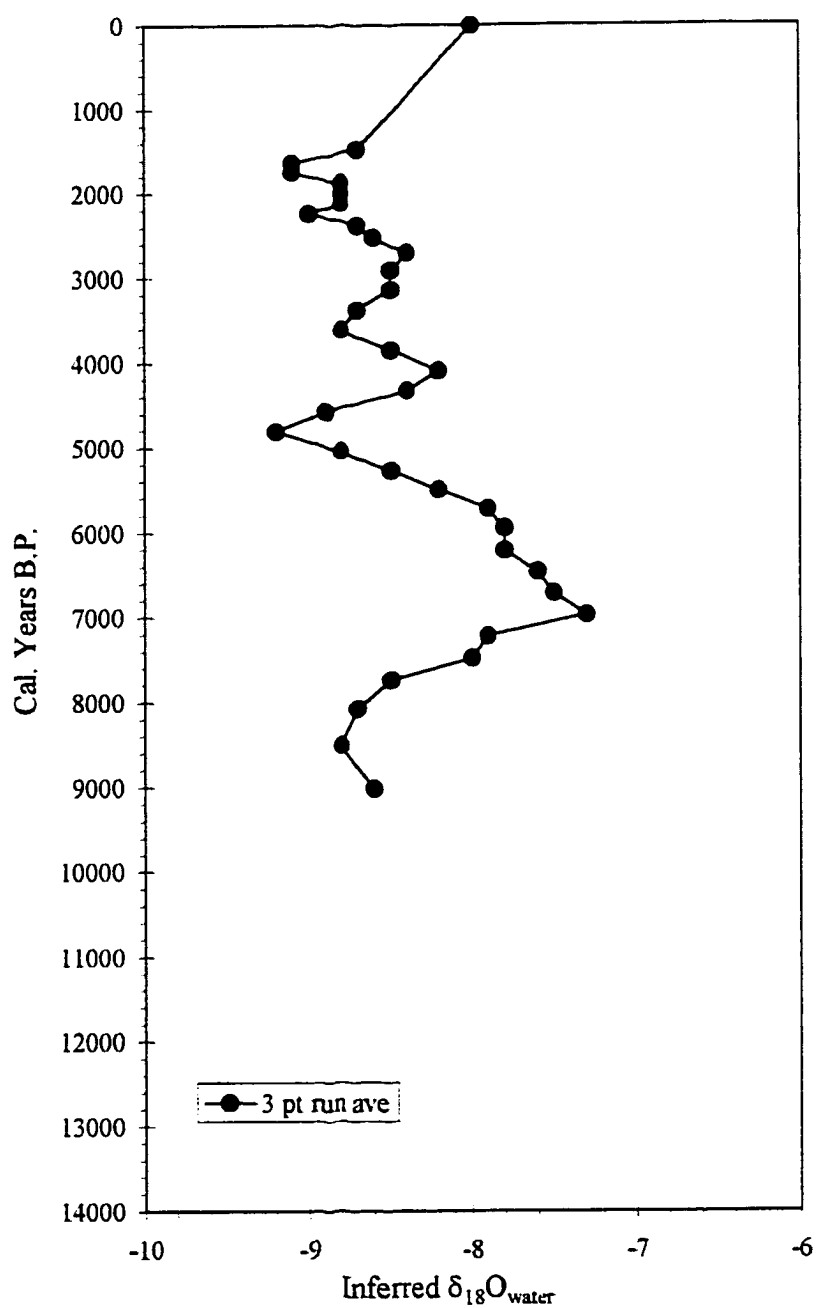


Figure 40. The Inferred $\delta^{18}\text{O}_{\text{water}}$ Translated From the δD of Sediment Organic Matter From Lake Winnebago Plotted vs. Calendar Years Before Present.

Three possible mechanisms are examined to explain this trend. First, as suggested in previous work from North America, lower $\delta^{18}\text{O}_{\text{water}}$ may indicate “open lake” conditions, i.e. higher inflow than outflow (Wolfe et al., 1996). This would necessitate

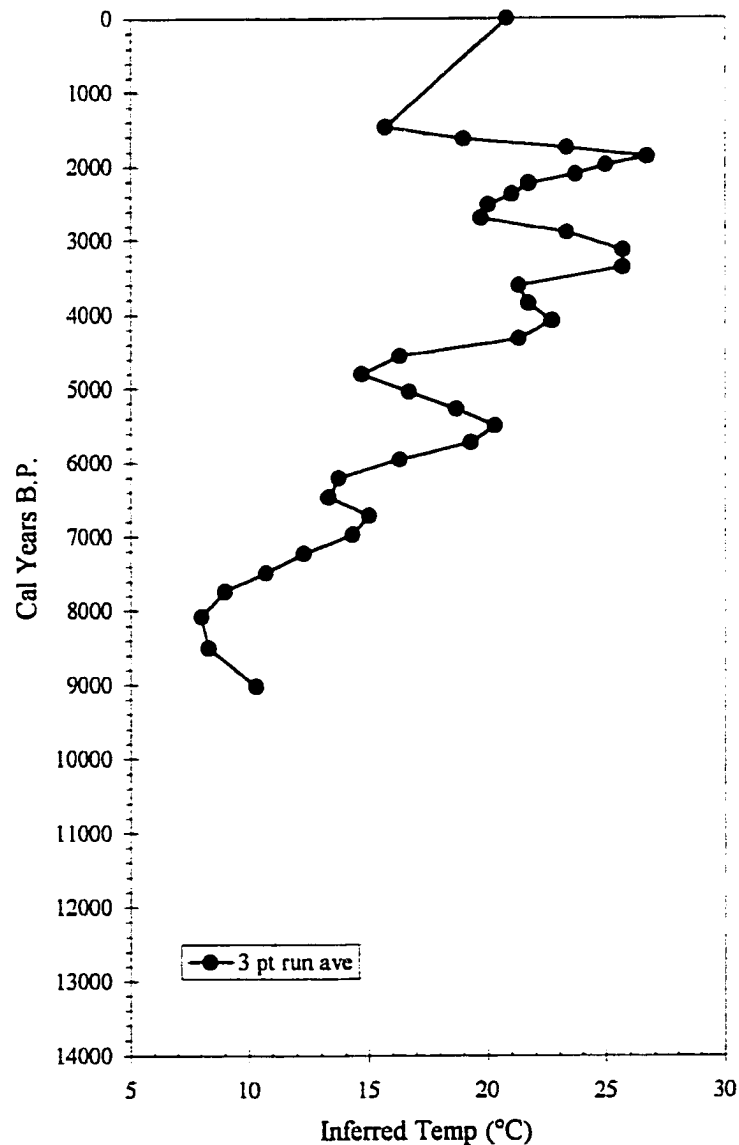


Figure 41. The Inferred Water Temperature From Lake Winnebago Plotted vs. Calendar Years Before Present.

an increasing trend in precipitation between 7-5ka BP. Though possible, this contradicts existing paleoclimate data from the region (Baker et al., 1992; Dorale et al., 1992; Chumbley et al., 1990). It is, however, consistent with Lake Winnebago ostracode data that supported a warm middle Holocene climate yet indicated low solute concentrations for Lake Winnebago (Smith, 1997). This is in agreement with pollen studies which suggest that the middle Holocene boundary between warm-dry and warm-moist conditions were located west and southwest of Lake Winnebago (Baker et al., 1992; Chumbley et al., 1990).

A second mechanism is that the lake's recharging process shifted from one derived primarily of summer precipitation (between 8-7ka BP) to one dominated by groundwater inflow. A similar mechanism has been suggested in a recent work from Minnesota (Smith et al., 1997). Since groundwater $\delta^{18}\text{O}$ represents an average of annual precipitation values, it is expected to be isotopically lighter compared to summer precipitation (Gat, 1981).

The third mechanism is related to the history of the air mass responsible for precipitation in the study area. Three major air masses operate in the Midwestern region today. These are: (1) Dry, warm Pacific, (2) Dry, cold Arctic and (3) Moist, Gulf of Mexico air masses. Of these, the Gulf air is the dominant precipitation bearing air mass. Everything remaining the same, the observed 2‰ shift in the $\delta^{18}\text{O}_{\text{water}}$ can be achieved by either reducing the fraction of vapor remaining at the study site by ~20% between 7-5 ka BP (see Chapter I, the Rayleigh equation) or secondly, in addition to the Gulf moisture a secondary air mass from the Pacific may also have contributed to

the area precipitation (Dansgaard, 1964). The former scenario would require that regions in the trajectory of the Gulf vapor (Southern and Southeastern U.S.) experienced higher rainfall during this time period. The latter would require that the westerlies were much stronger. More study is needed to fully investigate these scenarios; however, both processes appear to be reasonable (COHMAP, 1988).

Irrespective of the circulation patterns responsible for the $\delta^{18}\text{O}_{\text{water}}$, the inferred temperatures indicate that the Midwestern United States experienced significant temperature oscillations with a generally increasing trend occurring over the past 9ka BP. Further, this increasing trend is punctuated by intermittent return to cooler periods. During the so-called Mid-Holocene Warm phase (MHW, 6-4ka BP) the temperatures were the highest, except for a return to brief, cooler climates around 5 and 3ka BP. The overall variation in the water temperature during the MHW was as high as 10°C. Previous model calculations indicate that during the MHW, the summer temperatures were higher by 2-4°C (COHMAP, 1988). Evidence from cave deposits in Iowa suggests an increase in mean annual air temperature of 3°C (Dorale et al., 1992). Since marl precipitation occurs during the growing season of May-September, the temperatures estimated in this study indicate the water temperature during the growing season. The larger shift estimated for Lake Winnebago could easily be achieved by changes in seasonality, i.e. longer summers and shorter winters (warmer summers and/or winters).

Another interesting observation emerging from this study is the middle to late Holocene climatic instability in this region. The cooler temperatures indicated around

8ka BP have also been reported from many other parts of the world and may in fact represent a major global cooling event (Alley et al., 1997; Stager and Mayewski, 1997). However, the relatively widespread instability during the middle and later parts of the Holocene (6-2ka BP) contrasts with the Greenland Ice cores studies that hypothesized a climatically stable Holocene period (Dansgaard et al., 1993). More detailed study is required to demonstrate whether this variability was a regional or continental scale effect.

Discussion

Regional climates in the Midwestern United States are largely dictated by the interaction and relative dominance of the major air mass that circulates through the region. Three air masses are dominant in the Midwest at present; warm and dry air from the Pacific, maritime tropical from the Gulf of Mexico, cold and dry continental Arctic (Bryson, 1966; Machavaram and Krishnamurthy, 1994; Bradbury et. al., 1993; Baker et. al., 1992).

Baker et al. (1992) studied pollen profiles at 4 locations transecting Iowa, Minnesota and Wisconsin tying patterns of Holocene vegetation and environmental change in the Midwestern United States to the dominant air mass in a specific region. The vegetational boundary between prairie and forest was thought coincident with the regions dominant air mass. When warm, dry pacific air dominates, prairie vegetation is abundant, whereas, a dominant maritime tropical air mass (Gulf of Mexico) provides summer humidity and dominates where deciduous forest is present whereas a

continental arctic air mass supports conifer- hardwood forests (Bryson, 1966; Baker et. al., 1992). Isotopic studies of precipitation in Kalamazoo, Michigan, show conclusively that summer and winter precipitation in this portion of the Great Lakes region is dominated by Gulf of Mexico and Continental Arctic plus Atlantic air masses, respectively (Machavaram and Krishnamurthy, 1994). Additionally, Machavaram and Krishnamurthy (1994) used the greater winter d-excess values derived from the local meteoric water line to evidence the contribution of lake effect snow via Lake Michigan to the area precipitation.

The hydrogen isotope record of Austin Lake provided evidence for intense cold conditions which peaked around 2000 years before present (Krishnamurthy et al., 1995). Similar isotopic evidence was seen at both Ladd Lake and Lake Winnebago. In addition, there is evidence for a similar climatic shift from the southern hemisphere (White, et al, 1994). The prevalence of cold conditions may also account for (perhaps cause) the sharp rise in atmospheric methane production in high latitudes, as seen from measurements in Greenland ice cores (Brook, et al 1994). All this would suggest that perhaps the cold phase around 2000 years before present was global. The pilot work of Krishnamurthy et al. (1995) also indicated that Southwestern Michigan experienced a mid-Holocene warming between 8000 and 2000 years before present. These findings were consistent with observations made in pollen studies (R.G. Baker, et al, 1992) and isotope studies of cave deposits from other Midwestern states (Dorale et al., 1992). The warm, dry period lasting about 6000 years might have been responsible for the decrease in atmospheric methane concentration deduced from ice

cores in Greenland (Brook, et al, 1994). The Ladd Lake and Lake Winnebago data also recorded evidence of the MHW. However, the intermittent oscillatory nature of their δD records and inferred temperature data throughout the Holocene suggests greater climatic instability during this generally warmer phase. This (6-2ka BP) instability contrasts with the Greenland ice core studies that hypothesized a climatically stable Holocene period (Dansgaard et al., 1993). More detailed study is required to demonstrate whether this variability was a regional or continental scale effect.

CHAPTER IV

CONCLUSIONS

The primary objectives of this study were threefold:

1. Demonstrate the potential of D/H ratios in lake organic matter as a useful proxy for paleoclimate study.
2. Develop a technique for the extraction of hydrogen from organic rich sediment that yields repeatability in the measured δD values.
3. Generate a continent-based regional paleoclimate record covering the Pleistocene-Holocene period using stable isotope records taken from bulk organic matter in lake sediment.

Several useful techniques grew out of the efforts to achieve these primary objectives. These include a newly developed HF:HCl microwave digestion procedure to concentrate the organic fraction of lake sediments and a pyrolysis extraction technique for analysis of hydrogen isotope ratios in these organic residues. The microwave digestion technique offers a time efficient means to process sediment samples that results in organic concentrations that equal or surpass the organic concentration efficiency in previously used conventional procedures. The pyrolysis extraction technique (δD -P250) offers a refinement to the hydrogen extraction technique initiated in the pilot study undertaken by Krishnamurthy et al. (1995) by

addressing concerns related to adsorbed water and exchangeable/non-exchangeable hydrogen in the HF:HCl "organic rich" residues. Some of the salient results are as follows:

1. Individual samples are pyrolyzed at 250°C for ~60minutes, then sealed, combusted and analyzed for δD . Pre-heating the residual organic matter while under vacuum effects the removal of the majority portion of adsorbed/exchanged water from the HF:HCl-residue.
2. The resulting hydrogen isotopic data appear reproducible at better than 3‰ and offer what is thought to be a close approximation of the non-exchangeable hydrogen signal from these sediment bulk-organic residues.
3. The pyrolysis-hydrogen-extraction technique is the only method currently available that may provide uniformity in results and offer precision in the δD reproducibility if samples are processed in competing labs using isotopically distinct processing waters.

While a primary focus was to demonstrate the proxy potential of D/H ratios in lake organic matter, the stable isotope analyses included both the $\delta^{13}C$ and the δD of the acid-resistant (HCl and HF-HCl) sediment organic residues. Additionally, the $\delta^{13}C$ and $\delta^{18}O$ in CO_2 evolved from the coexisting sediment carbonate component was analyzed to augment the organic residue interpretation of the Lake Winnebago samples. In what is believed to be a new approach, the δD and $\delta^{18}O$ isotopic records from the Lake Winnebago core were combined and used to evaluate quantitative

temperature estimates during the late Pleistocene to Holocene period. Based on this research, the following conclusions can be drawn:

1. Stable isotopes of hydrogen from the bulk organic matter in lake sediments can be used as a paleoclimatic proxy.
2. Inferred paleotemperature data can be generated from a combined $\delta^{18}\text{O}_{\text{carbonate}} - \delta\text{D}_{\text{organic}}$ data set.

Ultimately, this project provided continent based information related to climate changes in the Midwestern United States during the Pleistocene-Holocene. Some of the salient observations are as follow:

1. Cool phases at approximately 2000 and 8000 years ago were evidenced in the lacustrine isotopic data from both Ladd Lake, Ohio and Lake Winnebago, Wisconsin. Cool phases noted at similar ages have been reported by means of data extracted from other proxy records in ice core and cave deposits suggest that these events may have been global.
2. The Ladd Lake hydrogen isotopic data and the inferred temperatures indicated by the Lake Winnebago data suggest that the Midwestern United States experienced significant temperature oscillations with a generally increasing trend occurring over the past 9ka BP punctuated by intermittent return to cooler periods.
3. The Mid-Holocene Warm phase from ~8500 years to ~2000 years before the present may not have been a stable climatic period. The Ladd Lake and Lake Winnebago data show relative instability during the middle and later parts of the Holocene (6-2ka BP). This contrasts with the Greenland Ice cores studies that

hypothesized a climatically stable Holocene period. More detailed study is required to demonstrate whether this variability was a regional or continental scale effect.

4. Initial attempts to calibrate the δD of lacustrine surface sediment organic matter to known information regarding precipitation and mean annual surface air temperature indicate a -3‰ per degree latitude for the δD from lake organic matter. This is similar to the findings of Yurtsever (1975) which indicated $\sim 4\text{‰}$ per degree latitude. Thus, it would appear there is a relatively good correlation between the δD signal of these surface sediment samples and the mean δD in precipitation via the lake. More work is needed in this calibration.

Appendix A

Ladd Lake Pilot Group HF:HCl Isotopic Results

Isotopic Results from HF:HCl Residues (Conventional Extraction)
Pilot Group Series - Ladd Lake, OH

Isotopic Data - HF:HCl residue combusted at 900°C in the presence of CuO.										
¹⁴ C	Core	HF:HCl Residue	C/N	sample	CO ₂	% organic				
YBP	Sample #	δD	H/C	δ ¹³ C _{HF:HCl}	(μmol)	Carbon _{HF:HCl}				
5	LL 934	-109	0.83	-27.7	11.45	4.48	145.82	39.07%		
107	LL 1024	-118	0.73	-29.1	19.32	2.89	133.99	55.66%		
141	LL 1054	-105	0.70	-29.3	15.93	9.18	341.91	44.71%		
168	LL 1078	-109	0.87	-28.8	15.19	9.41	269.22	34.35%		
232	LL 1134	-104	0.88	-28.2	15.21	11.12	298.04	32.18%		
295	LL 1190	-127	0.82	-32.5	15.30	6.08	285.43	56.36%		
437	LL 1204	-119	0.98	-32.2	14.37	6.46	315.05	58.55%		
850	LL 1234	-117	0.90	-30.1	15.19	5.50	219.47	47.90%		
1070	LL 1250	-129	0.81	-34.1	13.84	14.76	563.73	45.85%		
1290	LL 1266	-130	0.93	-31.7	14.63	4.68	194.05	49.78%		
2664	LL 1366	-119	0.80	-30.3	14.64	6.29	273.24	52.15%		
3613	LL 1435	-113	0.90	-29.4	11.95	4.28	149.22	41.85%		
3805	LL 1449	-128	0.86	-30.4	15.90	6.71	311.86	55.79%		
3924	LL 1463	-125	0.92	-29.6	15.72	4.65	199.30	51.45%		
3945	LL 1467	-128	0.86	-28.8	18.37	9.66	462.87	57.52%		
4200	LL 1515	-130	0.97	-31.0	16.08	4.12	213.73	62.28%		
4391	LL 1551	-126	0.98	-32.1	13.65	4.46	305.66	56.37%		

Isotopic Data - HF:HCl residue combusted at 900°C in the presence of CuO,									
¹⁴ C	Core	HF:HCl Residue	HF:HCl	Residue	C/N	sample	CO ₂	% organic	
YBP	Sample #	δD	H/C	δ ¹³ C _{HF:HCl}	C/N	(mg)	(μmol)	Carbon _{HF:HCl}	
4433	LL 1559	-123	0.81	-29.8	11.52	8.20	376.24	55.08%	
4922	LL 1651	-127	0.83	-29.8	15.50	7.40	289.32	46.94%	
5177	LL 1699	-124	0.83	-29.0	16.55	4.78	227.83	57.22%	
5368	LL 1735	-122	0.70	-31.8	13.85	9.93	374.86	45.32%	
5538	LL 1767	-118	0.76	-30.9	14.18	4.21	337.43	56.51%	
5665	LL 1791	-119	0.67	-30.1	13.62	8.01	330.44	49.52%	
5750	LL 1807	-126	0.94	-28.8	14.38	14.34	617.73	51.71%	
6017	LL 1819	-109	0.50	-31.8	11.46	7.61	256.70	40.49%	
6107	LL 1823	-117	0.74	-31.6	14.27	6.04	200.49	39.85%	
7087	LL 1867	-125	0.91	-31.6	11.76	6.06	263.35	52.17%	
7800	LL 1899	-131	0.75	-28.7	15.35	6.67	286.42	51.55%	
8335	LL 1923	-146	0.92	-27.4	13.71	8.41	371.17	52.98%	
8959	LL 1951	-131	1.02	-30.2	16.03	9.89	471.37	57.22%	
9494	LL 1975	-140	0.93	-29.2	15.98	7.87	357.92	54.60%	
9694	LL 1984	-140	0.97	-28.7	16.96	14.16	601.69	51.01%	
10140	LL 2004	-140	0.96	-30.1	17.34	13.25	590.90	53.54%	
11082	LL 2028	-140	1.01	-30.2	17.45	8.76	407.02	55.78%	
11632	LL 2042	-137	0.99	-28.4	16.58	9.04	433.18	57.52%	
12336	LL 2056	-143	1.30	-28.3	lost N	6.04	287.11	57.06%	
12549	LL 2060	-133	0.99	-28.7	16.07	14.23	569.92	48.08%	

Isotopic Data - HF:HCl residue combusted at 900°C in the presence of CuO.									
¹⁴ C	Core	HF:HCl Residue		sample		CO ₂	% organic		
YBP	Sample #	δD	H/C	δ ¹³ C _{HF:HCl}	C/N	(mg)	(μmol)	Carbon _{HF:HCl}	
13828 LL	2084	-128	0.93	-30.5	15.78	13.47	412.49	36.76%	
14573 LL	2098	-104	0.87	-28.6	10.04	7.49	191.88	30.75%	
14680 LL	2108	-123	0.85	-30.1	22.11	18.33	391.79	25.66%	
14840 LL	2111	-134	0.55	-30.8	21.05	6.84	199.60	35.03%	
15053 LL	2115	-121	0.61	-29.1	28.66	19.53	386.62	23.76%	

Appendix B

Ladd Lake Pilot Group HCl Isotopic Results

Isotopic Results from HCl Residues
Pilot Group Series - Ladd Lake, OH

Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.									
¹⁴ C	Core	HCl Residue	Δδ ¹³ C	sample	CO ₂	% organic			
YBP	Sample #	δ ¹³ C	C/N	HF - HCl	(mg)	(μmol)	Carbon _{HCl}		
5	LL 934	-26.2	7.78	1.54	38.01	64.43	2.03%		
107	LL 1024	-28.1	6.06	1.01	27.03	62.85	2.79%		
141	LL 1054	-27.5	9.64	1.75	12.08	30.69	3.05%		
168	LL 1078	-27.8	8.76	0.94	19.59	52.44	3.21%		
232	LL 1134	-27.4	5.17	0.77	26.39	66.74	3.04%		
295	LL 1190	-31.5	0.52	1.01	10.19	79.39	9.35%		
437	LL 1204	-31.9	10.80	0.27	18.12	146.20	9.69%		
850	LL 1234	-29.5	6.89	0.59	9.34	84.53	10.87%		
1070	LL 1250	-32.8	8.32	1.25	8.47	111.29	15.77%		
1290	LL 1266	-31.4	5.07	0.28	10.98	70.76	7.74%		
2664	LL 1366	-29.9	10.44	0.35	12.78	122.16	11.48%		
3613	LL 1435	-28.8	9.96	0.66	20.86	83.61	4.81%		
3805	LL 1449	-27.3	10.14	3.13	12.59	122.23	11.65%		
3924	LL 1463	-28.5	13.55	1.19	5.24	109.91	25.18%		
3945	LL 1467	-28.4	15.71	0.43	4.57	116.03	30.48%		
4200	LL 1515	-29.4	15.19	1.60	10.29	181.93	21.23%		
4391	LL 1551	-31.1	13.19	1.03	17.83	283.16	19.06%		

Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.									
¹⁴ C	Core	HCl Residue	Δδ ¹³ C	sample	CO ₂	% organic			
YBP	Sample #	δ ¹³ C	C/N	HF - HCl	(mg)	(μmol)	Carbon _{HCl}		
4433	LL 1559	-29.0	12.40	0.87	16.38	356.32	25.96%		
4922	LL 1651	-29.0	4.67	0.87	5.90	100.25	20.40%		
5177	LL 1699	-28.0	10.31	0.93	8.14	106.12	15.65%		
5368	LL 1735	-30.6	11.64	1.24	9.35	160.55	20.61%		
5538	LL 1767	-30.2	10.57	0.65	12.39	216.96	21.02%		
5665	LL 1791	-28.9	12.96	1.20	9.92	168.59	20.40%		
5750	LL 1807	-29.2	10.80	0.45	24.18	186.32	9.25%		
6017	LL 1819	-29.5	Lost	2.28	11.22	160.16	17.14%		
6107	LL 1823	-30.5	8.81	1.05	10.02	103.94	12.45%		
7087	LL 1867	-30.9	7.15	0.77	8.25	87.86	12.79%		
7800	LL 1899	-28.4	12.65	0.24	8.03	171.42	25.63%		
8335	LL 1923	-27.3	12.33	0.13	7.46	121.80	19.60%		
8959	LL 1951	-29.8	5.54	0.36	8.14	59.79	8.82%		
9494	LL 1975	-29.2	12.70	0.02	6.16	90.24	17.59%		
9694	LL 1984	-28.5	12.63	0.21	5.68	76.99	16.27%		
10140	LL 2004	-29.8	9.66	0.34	11.10	87.99	9.52%		
11082	LL 2028	-29.8	12.93	0.35	8.91	114.29	15.40%		
11632	LL 2042	-31.2	6.52	2.67	29.39	392.81	15.95%		
12336	LL 2056	-28.8	lost N	0.52	13.46	113.04	10.08%		
12549	LL 2060	-28.5	11.51	0.19	9.41	86.28	11.01%		

Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.									
¹⁴ C	Core	HCl Residue	Δδ ¹³ C	sample	CO ₂	% organic			
YBP	Sample #	δ ¹³ C	C/N	HF - HCl	(mg)	(μmol)	Carbon _{HCl}		
13828 LL	2084	-30.3	11.65	0.20	12.17	97.09	9.58%		
14573 LL	2098	-28.5	4.15	0.04	19.99	47.07	2.83%		
14680 LL	2108	-30.1	9.33	0.02	15.64	61.57	4.73%		
14840 LL	2111	-30.7	7.25	0.09	16.68	72.57	5.22%		
15053 LL	2115	-28.9	11.93	0.23	24.38	42.66	2.10%		

Appendix C

Ladd Lake δD -P250 Isotopic Results

Isotopic Results from HF-HCl Residues (δD_{P-250})
Ladd Lake, OH

		HF-HCl Residue-Pyrolyzed at 250°C for 1 hr, sealed and combusted w/CuO@900°C									
Calendar Years	¹⁴ C YBP	Core Sample #	δD_{P-250}	H/C	C/N	sample (mg)	N ₂ (μ mol)	CO ₂ (μ mol)	H ₂ (μ mol)	% organic Carbon	comments
5	5	LL 934	tstm	0.08	17.19	15.01	2.60	89.38	3.47	7.15%	tstm
7	7	LL 936	-110	0.25	19.42	18.40	4.67	181.44	22.87	11.84%	
9	9	LL 938	tstm	0.06	29.50	29.97	3.76	221.84	6.44	8.89%	tstm
107	107	LL 1024	-114	0.29	32.74	5.41	2.88	188.57	27.54	41.84%	
141	141	LL 1054	-110	0.37	19.59	11.77	4.39	172.08	32.21	17.55%	
168	168	LL 1078	-116	0.64	16.37	8.75	6.55	214.33	68.17	29.40%	
232	232	LL 1134	-121	0.60	17.31	7.15	5.40	186.91	56.50	31.38%	
295	295	LL 1190	-133	0.83	17.98	9.11	11.20	402.73	167.25	53.07%	
443	437	LL 1204	-134	0.87	16.50	8.07	10.73	354.16	154.51	52.68%	
871	850	LL 1234	-132	0.82	17.07	9.74	12.13	414.20	170.08	51.05%	
1100	1070	LL 1250	-133	0.91	14.45	8.87	13.53	391.00	177.16	52.92%	
1329	1290	LL 1266	-129	0.82	15.07	5.00	6.86	206.68	84.52	49.62%	
1786	1729	LL 1298	-130	0.70	30.71	11.79	6.58	403.85	140.35	41.12%	
2300	2224	LL 1334	tstm	0.10	15.23	14.11	3.50	106.51	5.32	9.06%	tstm
2757	2664	LL 1366	-130	0.80	25.80	8.12	6.88	355.15	141.96	52.51%	
2871	2774	LL 1374	-128	0.73	25.80	10.46	8.40	433.31	157.34	49.73%	
2986	2884	LL 1382	-115	0.76	26.43	13.38	11.98	633.32	239.45	56.82%	

HF-HCl Residue-Pyrolyzed at 250°C for 1 hr, sealed and combusted w/CuO@900°C											
Calendar Years	¹⁴ C YBP	Core Sample #	δD_{P-250}	H/C	C/N	sample (mg)	N ₂ (μ mol)	CO ₂ (μ mol)	H ₂ (μ mol)	% organic Carbon	comments
3100	2994	LL 1390	-111	0.57	26.55	16.29	6.58	349.22	100.40	25.74%	
3214	3104	LL 1398	-109	0.51	23.14	27.63	10.73	496.71	127.48	21.58%	
3329	3214	LL 1406	-124	0.68	26.21	11.19	9.80	513.64	174.33	55.10%	
3443	3324	LL 1414	-123	0.74	27.11	20.48	11.67	632.39	233.79	37.07%	
3557	3434	LL 1422	-124	0.70	24.74	9.99	8.86	438.58	153.09	52.70%	
3743	3613	LL 1435	-126	0.79	19.10	11.32	10.74	410.38	163.00	43.52%	
3857	3723	LL 1443	-111	0.61	26.64	15.51	8.40	447.28	136.11	34.62%	
3878	3805	LL 1449	-136	0.92	16.06	10.70	14.93	479.57	221.05	53.81%	
3958	3924	LL 1463	-141	0.86	18.01	9.89	13.53	487.55	209.72	59.18%	
3985	3945	LL 1467	-133	0.85	7.87	7.96	23.81	374.73	158.76	56.51%	
4118	4051	LL 1487	-126	0.73	24.92	9.35	9.33	465.01	168.67	59.70%	
4198	4115	LL 1499	-134	0.76	28.88	11.47	9.80	565.90	215.38	59.23%	
4305	4200	LL 1515	-139	0.84	19.29	6.56	8.40	323.85	136.11	59.26%	
4385	4263	LL 1527	-134	0.94	31.19	8.47	6.53	407.28	191.32	57.73%	
4411	4285	LL 1531	-135	0.86	29.96	14.49	11.67	698.95	301.74	57.91%	
4545	4391	LL 1551	-136	0.89	26.58	12.15	10.73	570.51	253.61	56.37%	
4598	4433	LL 1559	-144	0.90	17.58	11.13	14.93	525.18	235.20	56.65%	
4651	4476	LL 1567	-123	0.80	29.13	15.37	11.67	679.51	270.60	53.07%	
4705	4518	LL 1575	-142	1.02	25.10	6.32	6.38	320.29	163.00	60.84%	
4891	4667	LL 1603	-142	0.97	25.75	12.99	11.67	600.70	291.83	55.51%	

HF-HCl Residue-Pyrolyzed at 250°C for 1 hr, sealed and combusted w/CuO@900°C											
Calendar Years	¹⁴ C YBP	Core Sample #	δD_{P-250}	H/C	C/N	sample (mg)	N ₂ (μ mol)	CO ₂ (μ mol)	H ₂ (μ mol)	% organic Carbon	comments
4971	4731	LL 1615	-126	0.82	29.52	10.70	8.86	523.33	213.97	58.71%	
5105	4837	LL 1635	-122	0.80	32.34	8.59	6.53	422.24	168.67	59.01%	
5211	4922	LL 1651	-138	0.98	17.38	12.11	16.80	584.09	284.75	57.90%	
5291	4986	LL 1663	-137	0.96	27.06	11.47	10.26	555.49	266.35	58.14%	
5318	5007	LL 1667	-135	0.82	29.62	9.72	7.93	469.69	192.73	58.01%	
5425	5092	LL 1683	-127	0.79	31.29	14.22	11.20	700.67	276.26	59.15%	
5531	5177	LL 1699	-137	0.91	18.12	8.51	11.20	405.83	184.24	57.25%	
5638	5262	LL 1715	-127	0.81	27.71	11.16	9.80	543.03	219.63	58.41%	? N2 leak
5718	5325	LL 1727	-139	0.90	8.08	8.64	23.89	385.99	174.33	53.63%	
5771	5368	LL 1735	-132	0.88	17.05	7.02	9.33	318.18	140.56	54.41%	
5878	5453	LL 1751	-126	0.89	9.64	11.42	22.02	424.38	189.90	44.61%	? N2 leak
5985	5538	LL 1767	-130	0.87	17.61	4.69	6.27	220.78	96.19	56.51%	
6065	5601	LL 1779	-147	1.01	13.49	10.82	19.69	530.97	267.77	58.91%	? N2 leak
6145	5665	LL 1791	-138	1.00	17.82	12.06	15.40	549.03	274.84	54.65%	
6198	5708	LL 1799	-144	0.97	13.58	11.70	19.14	519.71	252.19	53.32%	? N2 leak
6290	5750	LL 1807	-133	0.94	18.41	14.16	14.93	549.76	259.27	46.61%	
6590	6017	LL 1819	-137	1.05	17.38	15.69	19.60	681.36	358.37	52.13%	
6690	6107	LL 1823	-135	1.02	17.78	13.01	16.34	580.73	296.08	53.59%	
6990	6374	LL 1835	-141	0.78	29.43	16.51	11.20	659.15	257.86	47.93%	
7190	6552	LL 1843	-144	0.94	25.65	9.19	8.86	454.73	213.69	59.40%	

HF-HCl Residue-Pyrolyzed at 250°C for 1 hr, sealed and combusted w/CuO@900°C

Calendar Years	¹⁴ C		Core Sample #	δD_{P-250}	H/C	C/N	sample		N ₂ (μ mol)	CO ₂ (μ mol)	H ₂ (μ mol)	% organic	
	YBP						(mg)					Carbon	comments
7290	6641	LL	1847	-140	0.97	29.04	10.19	8.40	487.68	236.62	57.45%		
7390	6731	LL	1851	-123	0.77	19.96	10.14	12.13	484.32	185.66	57.34%		
7490	6909	LL	1859	-120	0.67	13.44	14.19	11.67	313.57	105.53	26.53%		
7590	7087	LL	1867	-131	0.87	15.95	12.89	15.27	487.23	211.31	45.38%		
7990	7265	LL	1875	-145	0.97	18.94	13.06	14.93	565.64	274.84	51.99%		
8090	7354	LL	1879	-138	0.95	14.79	10.13	15.87	469.42	223.88	55.63%		
8190	7444	LL	1883	-126	0.65	28.99	13.40	10.26	595.10	194.15	53.31%		bad trace?rpt
8390	7622	LL	1891	-148	0.99	19.47	12.82	14.93	581.52	287.59	54.45%		
8590	7800	LL	1899	-140	0.94	16.64	10.51	14.00	465.93	219.63	53.22%		
8790	7978	LL	1907	-138	0.84	26.81	11.39	9.80	525.37	219.63	55.37%		
8890	8068	LL	1911	-155	0.91	12.98	7.69	13.07	339.21	154.51	52.95%		
8990	8157	LL	1915	-143	0.78	9.79	10.30	16.34	319.77	124.21	37.27%		
9090	8246	LL	1919	-143	0.86	17.07	16.98	14.47	493.87	211.14	34.92%		
9190	8335	LL	1923	-153	0.79	22.60	9.58	8.86	400.62	158.76	50.20%		
9890	8959	LL	1951	-148	0.93	16.61	11.56	14.93	496.18	230.96	51.53%		
10090	9137	LL	1959	-151	0.97	13.57	5.87	9.33	253.14	123.28	51.77%		
10190	9226	LL	1963	-144	0.95	8.10	9.04	24.74	400.76	191.32	53.22%		
10290	9315	LL	1967	-156	1.50	13.84	11.79	18.67	516.74	386.68	52.62%		
10490	9494	LL	1975	-143	0.83	24.87	9.53	7.93	394.36	163.00	49.68%		
10715	9694	LL	1984	-148	0.98	15.44	12.01	16.34	504.55	246.53	50.43%		

HF-HCl Residue-Pyrolyzed at 250°C for 1 hr, sealed and combusted w/CuO@900°C

Calendar Years	¹⁴ C		Core Sample #	δD _{p-250}	H/C	C/N	sample		N ₂ (μmol)	CO ₂ (μmol)	H ₂ (μmol)	% organic Carbon	comments
	YBP						(mg)						
11015	9962	LL	1996	-159	0.80	23.69	11.61	8.86	419.80	167.25	43.41%		
11734	10140	LL	2004	-146	1.00	17.14	15.71	19.14	656.18	327.23	50.14%		
12384	10650	LL	2017	-136	0.88	18.38	9.39	9.33	342.90	150.26	43.84%		
12734	10925	LL	2024	-139	0.83	27.90	10.62	7.46	416.44	172.91	47.07%		
12934	11082	LL	2028	-146	1.02	16.79	9.89	12.13	407.35	208.31	49.44%		
13334	11397	LL	2036	-126	0.75	26.09	14.31	9.80	511.14	192.73	42.88%		
13534	11554	LL	2040	-141	0.89	27.62	10.07	8.86	489.59	216.80	58.37%		
13584	11632	LL	2042	-144	1.02	17.11	10.24	13.53	463.03	235.20	54.28%		
14330	12336	LL	2056	-145	0.97	17.06	14.39	17.27	589.23	286.17	49.16%		
14543	12549	LL	2060	-154	0.95	17.50	14.73	15.87	555.23	264.93	45.25%		
14756	12762	LL	2064	-141	1.03	7.21	6.72	20.07	289.58	148.85	51.73%		
14969	12975	LL	2068	-124	0.82	27.17	15.29	9.80	532.36	218.22	41.80%	original	
15182	13188	LL	2072	-131	0.86	18.19	7.58	6.88	250.50	107.87	39.67%		
15395	13401	LL	2076	-118	0.71	20.38	10.80	6.52	265.73	93.86	29.54%		
15608	13615	LL	2080	-110	0.30	8.77	24.65	16.34	286.62	42.95	13.96%		
15821	13828	LL	2084	-138	0.77	17.47	13.44	11.67	407.68	157.34	36.41%		
16035	14041	LL	2088	-115	0.52	8.11	20.69	21.01	340.52	88.25	19.76%		
17231	14573	LL	2098	-109	0.45	22.13	27.88	9.33	413.01	91.99	17.78%		
20747	14680	LL	2108	-129	0.76	21.50	18.32	8.86	381.05	144.60	24.97%		
20907	14840	LL	2111	-133	0.67	20.42	10.29	6.55	267.44	89.65	31.20%		

HF-HCl Residue-Pyrolyzed at 250°C for 1 hr, sealed and combusted w/CuO@900°C										
Calendar Years	¹⁴ C YBP	Core Sample #	δD_{P-250}	H/C	C/N	sample (mg)	N ₂ (μ mol)	CO ₂ (μ mol)	H ₂ (μ mol)	% organic Carbon comments
21120	15053 LL	2115	-115	0.31	20.65	17.44	5.48	226.52	35.48	15.59%
21280	15213 LL	2118	-53	0.25	12.36	23.63	6.83	168.72	21.01	8.57% Sand -redo?
21493	15426 LL	2122	-72	0.36	23.21	10.11	3.61	167.47	30.35	19.89% used all HF

Appendix D
Ladd Lake HCl Isotopic Results

Isotopic Results from HCl Residues
Ladd Lake, OH

Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.									
Calendar	¹⁴ C	Core	HCl Residue	sample	N ₂	CO ₂	% organic		
YBP	YBP	Sample #	δ ¹³ C	C/N	(mg)	(μmol)	(μmol)	Carbon	comments
5	5	LL 934	-26.2	7.78	38.01	4.14	64.43	2.03%	
7	7	LL 936	-26.6	7.65	66.68	6.63	101.50	1.82%	
9	9	LL 938	-25.5	7.16	75.70	6.49	93.05	1.47%	
11	11	LL 940	-27.3	7.34	63.04	6.91	101.44	1.92%	
14	14	LL 942	-25.7	4.42	88.47	10.29	91.01	1.23%	
16	16	LL 944	-26.8	5.19	68.74	10.26	106.45	1.85%	
18	18	LL 946	-27.0	7.22	54.12	5.28	76.32	1.68%	
23	23	LL 950	-25.4	3.27	73.59	12.60	82.46	1.34%	
25	25	LL 952	-26.9	11.12	48.29	2.21	49.11	1.21%	
27	27	LL 954	-26.5	1.90	66.61	22.26	84.37	1.51%	nitrogen high ??
32	32	LL 958	-26.8	7.77	45.04	3.46	53.82	1.43%	
77	77	LL 998	-28.0	3.01	38.35	9.80	59.06	1.84%	
89	89	LL 1008	-28.2	7.66	35.71	4.47	68.51	2.29%	
91	91	LL 1010	-29.0	3.50	47.83	13.07	91.41	2.28%	
98	98	LL 1016	-28.0	4.73	43.87	9.08	85.88	2.34%	
100	100	LL 1018	-28.1	2.95	50.73	17.27	101.83	2.40%	
107	107	LL 1024	-28.1	6.06	27.03	5.19	62.85	2.79%	

Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.									
Calendar	¹⁴ C	Core	HCl Residue	sample	N ₂	CO ₂	Carbon		
YBP	YBP	Sample #	δ ¹³ C	(mg)	(μmol)	(μmol)		comments	
116	116	LL 1032	-27.9	45.47	6.29	78.07	2.05%		
123	123	LL 1038	-28.2	39.94	9.33	87.27	2.61%		
125	125	LL 1040	-27.1	56.21	13.62	87.21	1.85%		
130	130	LL 1044	-28.6	45.64	6.88	136.30	3.56%		
141	141	LL 1054	-27.5	12.08	1.59	30.69	3.05%		
168	168	LL 1078	-27.8	19.59	2.99	52.44	3.21%		
182	182	LL 1090	-27.5	61.77	7.10	122.79	2.37%		
218	218	LL 1122	-27.1	65.86	14.47	147.70	2.68%		
223	223	LL 1126	-25.7	39.57	4.88	57.13	1.72%		
232	232	LL 1134	-27.4	26.39	6.45	66.74	3.04%		
236	236	LL 1138	-26.8	57.93	14.47	98.93	2.04%		notes called LL1136
250	250	LL 1150	-26.6	56.81	3.70	65.56	1.38%		
259	259	LL 1158	-28.3	44.36	14.47	97.09	2.61%		
273	273	LL 1170	-28.1	38.73	3.46	50.80	1.57%		
291	291	LL 1186	-29.0	36.82	2.71	73.83	2.39%		
295	295	LL 1190	-31.5	10.19	76.11	79.39	9.35%		
443	437	LL 1204	-31.9	18.12	6.72	146.20	9.69%		
614	602	LL 1216	-31.0	20.73	9.33	204.77	11.79%		
871	850	LL 1234	-29.5	9.34	6.13	84.53	10.87%		
1100	1070	LL 1250	-32.8	8.47	6.69	111.29	15.77%		

Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.									
Calendar	¹⁴ C	Core	HCl Residue	sample	N ₂	CO ₂	% organic		
YBP	YBP	Sample #	δ ¹³ C	C/N	(mg)	(μmol)	Carbon	comments	
1329	1290	LL 1266	-31.4	5.07	10.98	6.97	70.76	7.74%	
1443	1400	LL 1274	-31.0	10.29	31.11	10.90	224.37	8.61%	
1786	1729	LL 1298	-31.0	11.40	14.80	4.68	106.62	8.60%	
1957	1894	LL 1310	-30.9	12.96	21.46	6.32	163.91	9.11%	
2071	2004	LL 1318	-30.3	12.31	17.76	7.46	183.73	12.35%	
2300	2224	LL 1334	-27.0	5.61	42.85	5.46	61.24	1.71%	
2414	2334	LL 1342	-30.4	12.51	24.14	5.06	126.68	6.26%	
2529	2444	LL 1350	-31.2	14.76	15.86	7.38	217.97	16.40%	
2643	2554	LL 1358	-31.1	6.78	18.98	14.93	202.53	12.73%	
2757	2664	LL 1366	-29.9	10.44	9.68	6.52	136.10	16.88%	
2871	2774	LL 1374	-29.4	11.05	16.18	11.53	254.67	18.78%	
2986	2884	LL 1382	-30.9	14.92	11.53	6.05	180.57	18.69%	
3100	2994	LL 1390	-31.6	3.24	18.58	11.67	75.54	4.85%	
3214	3104	LL 1398	-31.6	6.52	23.52	4.51	58.81	2.98%	
3329	3214	LL 1406	-28.9	16.98	23.52	5.46	185.26	9.40%	
3443	3324	LL 1414	-31.2	13.31	49.96	13.53	360.23	8.60%	
3557	3434	LL 1422	-31.3	14.85	17.19	5.12	152.10	10.56%	
3743	3613	LL 1435	-28.8	9.96	20.86	4.20	83.61	4.81%	
3857	3723	LL 1443	-28.3	14.50	32.31	7.93	229.94	8.49%	
3878	3805	LL 1449	-27.3	10.14	12.59	6.03	122.23	11.65%	

Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.									
Calendar	¹⁴ C	Core	HCl Residue	sample	N ₂	CO ₂	Carbon		
YBP	YBP	Sample #	δ ¹³ C	C/N	(mg)	(μmol)	(μmol)	% organic	comments
3958	3924	LL 1463	-28.5	13.55	5.24	4.06	109.91	25.18%	
3985	3945	LL 1467	-28.4	15.71	4.57	3.69	116.03	30.48%	
4118	4051	LL 1487	-28.2	16.01	10.38	6.86	219.59	25.24%	
4198	4115	LL 1499	-28.8	19.61	6.96	3.87	151.68	26.01%	
4305	4200	LL 1515	-29.4	15.19	10.29	5.99	181.93	21.23%	
4385	4263	LL 1527	-28.6	12.85	13.78	13.53	347.83	30.12%	
4411	4285	LL 1531	-29.5	14.82	15.21	9.80	290.31	22.78%	
4545	4391	LL 1551	-31.1	13.19	17.83	10.73	283.16	19.06%	
4598	4433	LL 1559	-29.0	12.40	16.38	14.37	356.32	25.96%	
4651	4476	LL 1567	-30.3	20.23	11.68	3.95	159.69	16.32%	can't find HCl res.
4705	4518	LL 1575							
4758	4561	LL 1583	-29.1	9.77	3.83	7.92	154.82	48.24%	
4891	4667	LL 1603	-29.9	11.46	20.46	15.40	352.85	20.58%	
4971	4731	LL 1615	-28.7	20.42	10.15	4.19	171.15	20.12%	
5105	4837	LL 1635	-27.8	21.48	7.32	2.63	112.90	18.41%	
5211	4922	LL 1651	-29.0	4.67	5.90	10.73	100.25	20.40%	
5291	4986	LL 1663	-28.1	13.19	8.77	6.33	167.00	22.72%	
5318	5007	LL 1667	-28.4	15.61	8.95	4.68	145.98	19.46%	
5425	5092	LL 1683	-28.3	21.30	11.27	5.43	231.26	24.49%	
5531	5177	LL 1699	-28.0	10.31	8.14	5.15	106.12	15.65%	

Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.									
Calendar	¹⁴ C	Core	HCl Residue	sample	N ₂ (μmol)	CO ₂ (μmol)	% organic	Carbon	comments
YBP	YBP	Sample #	δ ¹³ C	C/N	(mg)	(μmol)			
5638	5262	LL 1715	-29.9	19.70	10.57	4.19	165.11	18.64%	
5718	5325	LL 1727	-29.8	11.34	9.35	6.74	152.91	19.52%	
5771	5368	LL 1735	-30.6	11.64	9.35	6.90	160.55	20.61%	
5878	5453	LL 1751	-30.6	14.42	19.42	6.70	193.16	11.87%	
5985	5538	LL 1767	-30.2	10.57	12.39	10.26	216.96	21.02%	
6065	5601	LL 1779	-29.4	11.64	12.50	9.80	228.10	21.78%	
6145	5665	LL 1791	-28.9	12.96	9.92	6.51	168.59	20.40%	
6198	5708	LL 1799	-29.6	14.91	13.40	5.28	157.51	14.03%	
6290	5750	LL 1807	-29.2	10.80	24.18	8.63	186.32	9.25%	
6590	6017	LL 1819	-29.9	5.80	17.08	9.33	108.29	7.57%	repeat
6690	6107	LL 1823	-30.5	8.81	6.12	4.14	72.97	14.31%	
6990	6374	LL 1835	-28.3	19.98	27.56	8.92	356.46	15.43%	
7190	6552	LL 1843	-29.1	9.08	13.33	12.13	220.26	19.72%	
7290	6641	LL 1847	-29.5	11.46	18.62	14.93	342.30	21.94%	
7390	6731	LL 1851	-25.4	13.12	9.67	11.20	293.87	36.26%	
7490	6909	LL 1859	-30.0	6.99	21.90	9.53	133.26	7.26%	
7590	7087	LL 1867	-30.9	7.15	8.25	5.85	87.86	12.79%	
7990	7265	LL 1875	-28.4	17.05	19.14	6.86	233.77	14.57%	
8090	7354	LL 1879	-28.2	15.33	20.55	7.95	243.70	14.15%	
8190	7444	LL 1883	-27.0	15.89	15.60	7.38	234.63	17.95%	

Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.									
Calendar YBP	¹⁴ C		Core Sample #	HCl Residue $\delta^{13}\text{C}$	C/N	sample (mg)	N ₂ (μmol)	CO ₂ (μmol)	Carbon % organic comments
	YBP								
8390	7622	LL	1891	-27.3	16.80	12.25	5.71	191.79	18.68%
8590	7800	LL	1899	-28.4	12.65	8.03	6.72	171.42	25.63%
8790	7978	LL	1907	-28.1	14.64	18.84	10.26	300.46	19.03%
8890	8068	LL	1911	-30.6	14.41	25.88	9.61	276.95	12.77%
8990	8157	LL	1915	-29.2	13.84	22.86	5.82	161.14	8.41%
9090	8246	LL	1919	-28.9	10.29	25.16	12.42	255.72	12.13%
9190	8335	LL	1923	-27.3	12.33	7.46	4.94	121.80	19.60%
9890	8959	LL	1951	-29.8	5.54	8.14	5.40	59.79	8.82%
10090	9137	LL	1959	-30.8	12.90	27.21	14.93	385.20	16.89%
10190	9226	LL	1963	-29.4	10.48	11.61	7.26	152.24	15.65%
10290	9315	LL	1967	-30.3	14.02	17.87	7.99	224.09	14.96%
10490	9494	LL	1975	-29.2	12.70	6.16	3.55	90.24	17.59%
10715	9694	LL	1984	-28.5	12.63	5.68	3.05	76.99	16.27%
11015	9962	LL	1996	-29.6	13.22	23.32	16.80	444.12	22.73%
11734	10140	LL	2004	-29.6	10.77	11.10	4.08	87.99	9.52%
12384	10650	LL	2017	-28.6	13.50	22.30	8.83	238.36	12.76%
12734	10925	LL	2024	-28.8	14.54	25.85	10.18	296.08	13.67%
12934	11082	LL	2028	-29.8	12.93	8.91	4.42	114.29	15.40%
13334	11397	LL	2036	-30.1	6.53	40.39	22.41	292.55	8.64%
13534	11554	LL	2040	-30.2	17.84	26.15	13.62	485.89	22.17%

Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.									
Calendar	¹⁴ C	Core	HCl Residue	sample	N ₂	CO ₂	% organic		
YBP	YBP	Sample #	δ ¹³ C	(mg)	(μmol)	(μmol)	Carbon	comments	
13584	11632 LL	2042	-31.2	29.39	30.21	392.81	15.95%		
14330	12336 LL	2056	-28.7	31.17	15.87	276.27	10.58%		
14543	12549 LL	2060	-28.5	9.41	3.75	86.28	11.01%		
14756	12762 LL	2064	-30.0	22.62	8.40	221.44	11.68%		
14969	12975 LL	2068	-29.5	26.19	7.91	278.29	12.68%		
15182	13188 LL	2072	-30.2	22.83	5.04	166.16	8.69%		
15395	13401 LL	2076	-30.2	29.37	4.76	120.94	4.91%		
15608	13615 LL	2080	-29.8	38.37	9.41	121.45	3.78%		
15821	13828 LL	2084	-30.3	12.17	4.17	97.09	9.58%		
16035	14041 LL	2088	-30.4	44.02	5.20	157.45	4.27%		
17231	14573 LL	2098	-28.5	19.99	5.67	47.07	2.83%		
20747	14680 LL	2108	-30.1	15.64	3.30	61.57	4.73%		
20907	14840 LL	2111	-30.7	16.68	5.01	72.57	5.22%		
21120	15053 LL	2115	-28.9	24.38	1.79	42.66	2.10%		
21280	15213 LL	2118	-27.3	96.88	10.73	60.32	0.74%		
21493	15426 LL	2122	-26.2	111.76	3.18	77.02	0.82%		

Appendix E

Lake Winnebago δD -P250 Isotopic Results

Isotopic Results from HF:HCl Residues
Core LW7 - Lake Winnebago, WI

¹⁴ C Age (yr)	Core Sample #	sample Wt. (mg)	N ₂ (μmol)	CO ₂ (μmol)	H ₂ (μmol)	C/N ratio	H/C ratio	δD _{P-250} (‰)	% organic Carbon _{HF:HCl}	comments
1320	LW7-1	3.57	3.44	172.35	57.90	25.05	0.67	-129	57.95%	WMU ¹⁴ C
1492	LW7-10	13.66	7.46	520.10	184.24	34.85	0.71	-141	45.71%	
1549	LW7-13	15.12	10.73	598.39	223.88	27.88	0.75	-139	47.51%	
1607	LW7-16	No sample available								
1664	LW7-19	16.57	14.47	607.02	205.45	20.98	0.68	-143	43.98%	repeat
1722	LW7-22	9.82	6.72	396.47	127.01	29.52	0.64	-140	48.47%	
1779	LW7-25	8.73	6.66	375.12	123.75	28.16	0.66	-140	51.58%	
1836	LW7-28	13.52	8.86	486.49	164.42	27.44	0.68	-139	43.20%	
1894	LW7-31	7.96	6.16	313.83	113.00	25.49	0.72	-138	47.33%	
1951	LW7-34	10.27	6.72	383.16	139.16	28.53	0.73	-137	44.79%	
2008	LW7-37	13.20	8.40	458.09	177.16	27.28	0.77	-136	41.66%	
2066	LW7-40	15.09	8.86	511.01	191.32	28.83	0.75	-139	40.65%	
2123	LW7-43	15.01	8.86	496.77	187.07	28.03	0.75	-141	39.73%	
2180	LW7-46	20.75	13.07	707.45	274.84	27.07	0.78	-141	40.93%	
2238	LW7-49	14.81	8.86	508.04	201.23	28.66	0.79	-138	41.18%	
2295	LW7-52	17.33	11.67	649.00	253.61	27.82	0.78	-141	44.96%	
2353	LW7-55	12.36	8.40	454.27	178.58	27.05	0.79	-138	44.12%	

Isotopic Results from HF:HCl Residues
Core LW7 - Lake Winnebago, WI

¹⁴ C Age (yr)	Core Sample #	sample Wt. (mg)	N ₂ (μmol)	CO ₂ (μmol)	H ₂ (μmol)	C/N ratio	H/C ratio	δD _{P-250} (‰)	% organic Carbon HF:HCl	comments
2410	LW7-58	10.42	7.93	356.27	141.77	22.47	0.80	-134	41.05%	WMU ¹⁴ C
2592	LW7-61	16.10	6.63	364.51	120.48	27.48	0.66	-133	27.18%	
2774	LW7-64	12.21	5.88	348.76	93.86	29.68	0.54	-137	34.29%	
2955	LW7-67	12.62	5.32	244.38	71.44	22.98	0.58	-136	23.25%	
3137	LW7-70	12.23	5.57	263.42	82.65	23.65	0.63	-136	25.86%	
3319	LW7-73	10.25	5.51	248.00	87.32	22.50	0.70	-137	29.05%	
3501	LW7-76	10.33	5.23	252.68	92.92	24.15	0.74	-139	29.36%	
3683	LW7-79	9.32	3.94	200.62	64.90	25.43	0.65	-139	25.84%	
3865	LW7-82	10.36	4.76	256.44	70.67	26.96	0.55	-131	29.71%	original
4046	LW7-85	26.12	9.80	361.15	74.24	18.43	0.41	-131	16.60%	repeat
4228	LW7-88	12.06	3.38	137.49	18.67	20.31	0.27	-143	13.69%	
4410	LW7-91	10.99	leak	128.13	17.27	leak	0.27	-143	14.00%	
4592	LW7-94	37.86	11.20	372.02	40.15	16.61	0.22	-138	11.80%	repeat
4774	LW7-97	31.01	7.46	280.90	21.47	18.82	0.15	-135	10.87%	
4950	LW7-100	23.17	8.86	402.86	102.73	22.73	0.51	-134	20.87%	WMU ¹⁴ C
5206	LW7-103	15.31	4.06	216.57	36.88	26.70	0.34	-131	16.98%	

Isotopic Results from HF:HCl Residues
Core LW7 - Lake Winnebago, WI

Isotopic Data - HF:HCl Combustion in the presence of CuO after pyrolyzing 1 hr at 250°C										
¹⁴ C Age	Core	sample	N ₂	CO ₂	H ₂	C/N	H/C	δD _{P-250}	% organic	comments
(yr)	Sample #	Wt. (mg)	(μmol)	(μmol)	(μmol)	ratio	ratio	(‰)	Carbon _{HF:HCl}	
5463	LW7-106	18.97	4.98	219.86	30.35	22.07	0.28	-129	13.91%	
5719	LW7-109	18.89	5.34	162.00	11.20	15.16	0.14	-131	10.30%	
5976	LW7-112	12.23	3.22	145.13	22.41	22.56	0.31	-131	14.25%	
6232	LW7-115	14.42	2.71	161.01	12.41	29.69	0.15	-124	13.40%	
6488	LW7-118	13.31	4.11	202.92	47.16	24.67	0.46	-129	18.30%	
6745	LW7-121	17.91	4.06	217.42	40.62	26.80	0.37	-127	14.57%	
7001	LW7-124	15.24	4.22	212.48	42.95	25.15	0.40	-137	16.74%	repeat
7250	LW7-127	13.40	3.50	164.18	31.28	23.48	0.38	-133	14.71%	WMU ¹⁴ C
7635	LW7-130	17.97	6.74	257.03	55.56	19.06	0.43	-138	17.17%	
8019	LW7-133	18.63	11.67	237.26	43.89	10.17	0.37	-142	15.29%	
8404	LW7-136	13.02	1.47	168.72	34.08	57.31	0.40	-136	15.56%	
8788	LW7-139	12.45	1.47	169.78	31.28	57.67	0.37	-132	16.37%	
10400	LW7-151	9.68	1.59	76.20	3.69	23.93	0.10	tstm	9.45%	WMU ¹⁴ C
10538	LW7-161	16.11	3.89	85.56	2.04	11.00	0.05	tstm	6.38%	
10675	LW7-171	20.46	2.70	74.09	1.51	13.70	0.04	tstm	4.35%	
10813	LW7-181	22.56	3.08	79.56	2.80	12.93	0.07	tstm	4.23%	

Isotopic Results from HF:HCl Residues
Core LW7 - Lake Winnebago, WI

¹⁴ C Age (yr)	Isotopic Data - HF:HCl Combustion in the presence of CuO after pyrolyzing 1 hr at 250°C									
	Core	sample	N ₂ (μmol)	CO ₂ (μmol)	H ₂ (μmol)	C/N ratio	H/C ratio	δD _{P-250} (‰)	% organic	comments
	Sample #	Wt. (mg)						Carbon HF:HCl		
10950	LW7-191	40.98								
11088	LW7-201	53.71								
11225	LW7-211	60.03								
11363	LW7-221	55.51	2.21	194.62	1.96	44.07	0.02	tstm	4.21%	
11500	LW7-231	60.59								
11638	LW7-241	32.75								
11776	LW7-251	92.75								
11913	LW7-261	7.51	2.63	355.42	103.66	67.62	0.58	-124	56.81%	peat
12050	LW7-271	7.27	4.03	355.75	103.66	44.16	0.58	-125	58.74%	WMU ¹⁴ C
12188	LW7-281	47.97	6.49	402.80	33.15	31.02	0.16	-125	10.08%	
12325	LW7-291	67.45						tstm	1.57%	red clay till

Appendix F
Lake Winnebago HCl Isotopic Results

Isotopic Results from HCl Residues
Core LW7 - Lake Winnebago, WI

¹⁴ C Age (yr)	Core	Sample # depth (cm)	Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.							comments	
			sample (mg)	CO ₂ (μmol)	% organic Carbon	δ ¹³ C _{PDB} (‰)	C/N ratio	N ₂ (μmol)	CO ₂ (mg/μmol)		N ₂ (mg/μmol)
1320	LW7	1	42.97	286.55	8.01	-29.8	15.36	9.33	6.67	0.22	WMU ¹⁴ C
1492	LW7	10	16.95	93.12	6.60	-29.8	15.91	2.93	5.49	0.17	repeat
1549	LW7	13	19.01	136.43	8.62	-29.8	11.34	6.02	7.18	0.32	
1607	LW7	16	12.32	89.19	8.69	-29.4	5.91	7.54	7.24	0.61	none left
1664	LW7	19	25.61	183.35	8.59	-29.8	14.06	6.52	7.16	0.25	
1722	LW7	22	17.84	124.26	8.36	-29.5	12.15	5.11	6.97	0.29	
1779	LW7	25	17.22	118.90	8.29	-29.7	12.28	4.84	6.90	0.28	repeat
1836	LW7	28	23.86	162.29	8.17	-29.5	11.50	7.06	6.80	0.30	repeat
1894	LW7	31	19.24	132.28	8.25	-30.6	13.99	4.73	6.88	0.25	
1951	LW7	34	17.84	112.10	7.54	-30.6	12.11	4.63	6.28	0.26	
2008	LW7	37	28.21	183.02	7.79	-31.0	14.41	6.35	6.49	0.23	
2066	LW7	40	43.13	298.74	8.32	-31.1	13.92	10.73	6.93	0.25	repeat
2123	LW7	43	22.24	157.65	8.51	-30.7	11.99	6.58	7.09	0.30	
2180	LW7	46	33.29	234.10	8.44	-30.9	13.94	8.40	7.03	0.25	repeat
2238	LW7	49	24.70	167.87	8.16	-30.6	12.93	6.49	6.80	0.26	
2295	LW7	52	38.33	255.45	8.00	-30.6	15.21	8.40	6.66	0.22	repeat
2353	LW7	55	20.11	109.28	6.52	-30.6	10.39	5.26	5.43	0.26	

Isotopic Results from HCl Residues
Core LW7 - Lake Winnebago, WI

¹⁴ C Age (yr)	Core	Sample #	Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.										comments
			depth (cm)	sample (mg)	CO ₂ (μmol)	% organic Carbon	δ ¹³ C _{PDB} (‰)	C/N ratio	N ₂ (μmol)	CO ₂ (mg/μmol)	N ₂ (mg/μmol)		
												WMU ¹⁴ C	
2410	LW7	58	28.81	155.19	6.47	-30.6	11.81	6.57	5.39	0.23			
2592	LW7	61	27.86	182.96	7.88	-30.5	8.52	10.73	6.57	0.39			
2774	LW7	64	31.93	199.69	7.51	-30.5	7.75	12.89	6.25	0.40			
2955	LW7	67	41.81	254.33	7.30	-30.7	9.08	14.00	6.08	0.33			
3137	LW7	70	30.33	183.31	7.26	-30.8	8.97	10.22	6.04	0.34			
3319	LW7	73	45.52	262.70	6.93	-30.8	7.82	16.80	5.77	0.37			
3501	LW7	76	38.19	209.82	6.60	-30.7	8.99	11.68	5.49	0.31			
3683	LW7	79	29.65	159.76	6.47	-30.6	7.78	10.26	5.39	0.35		repeat	
3865	LW7	82	20.37	96.30	5.68	-30.5	11.03	4.36	4.73	0.21			
4046	LW7	85	32.99	149.01	5.42	-30.7	6.96	10.70	4.52	0.32			
4228	LW7	88	44.21	185.33	5.03	-30.5	9.03	10.26	4.19	0.23			
4410	LW7	91	30.26	116.53	4.62	-30.3	4.99	11.68	3.85	0.39			
4592	LW7	94	39.97	144.41	4.34	-29.8	5.95	12.13	3.61	0.30			
4774	LW7	97	38.39	136.85	4.28	-30.3	9.07	7.54	3.56	0.20			
4950	LW7	100	10.54	35.67	4.06	-29.0	11.83	1.51	3.38	0.14		WMU ¹⁴ C	
5206	LW7	103	25.16	58.41	2.79	-29.0	7.97	3.66	2.32	0.15			

Isotopic Results from HCl Residues
Core LW7 - Lake Winnebago, WI

¹⁴ C Age (yr)	Sample # Core	depth (cm)	Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.							comments
			sample (mg)	CO ₂ (μmol)	% organic Carbon	δ ¹³ C _{PDB} (‰)	C/N ratio	N ₂ (μmol)	CO ₂ (mg/μmol)	
5463	LW7	106	19.87	46.48	2.81	-28.8	12.80	1.82	2.34	0.09
5719	LW7	109	33.91	53.40	1.89	-29.1	8.42	3.17	1.57	0.09
5976	LW7	112	24.19	40.22	2.00	-29.1	12.00	1.68	1.66	0.07
6232	LW7	115	19.23	26.18	1.63	-28.8	10.91	1.20	1.36	0.06
6488	LW7	118	12.22	20.97	2.06	-28.8	10.45	1.00	1.72	0.08
6745	LW7	121	34.23	65.98	2.31	-30.0	12.03	2.74	1.93	0.08
7001	LW7	124	24.39	49.05	2.41	-29.8	10.32	2.38	2.01	0.10
7250	LW7	127	18.95	37.65	2.39	-29.6	7.71	2.44	1.99	0.13
7635	LW7	130	19.15	37.32	2.34	-29.9	10.22	1.73	1.95	0.09
8019	LW7	133	14.11	23.10	1.97	-29.7	9.42	1.23	1.64	0.09
8404	LW7	136	20.71	43.91	2.55	-30.3	15.73	1.40	2.12	0.07
8788	LW7	139	21.07	41.66	2.37	-30.4	16.99	1.23	1.98	0.06
10400	LW7	151	15.01	20.58	1.65	-29.8	12.31	0.84	1.37	0.06
10538	LW7	161	19.42	15.50	0.96	-28.5	15.50	0.72	0.80	0.04
10675	LW7	171	106.68	41.14	0.46	-28.5	7.91	2.60	0.39	0.02
10813	LW7	181	89.50	43.51	0.58	-28.1	8.74	2.49	0.49	0.03

repeat

WMU ¹⁴CWMU ¹⁴C

repeat

repeat

Isotopic Results from HCl Residues
Core LW7 - Lake Winnebago, WI

¹⁴ C Age (yr)	Core	Sample #	Isotopic Data - HCl residue combusted at 900°C in the presence of CuO.										comments
			depth (cm)	sample (mg)	CO ₂ (μmol)	% organic Carbon	δ ¹³ C _{PDB} (‰)	C/N ratio	N ₂ (μmol)	CO ₂ (mg/μmol)	N ₂ (mg/μmol)		
10950	LW7	191		93.49	46.09	0.59	-28.7	6.30	3.66	0.49	0.04	repeat	
11088	LW7	201		93.79	45.56	0.58	-28.7	4.78	4.76	0.49	0.05	repeat	
11225	LW7	211		78.51	38.17	0.58	-28.2	8.87	2.15	0.49	0.03	repeat	
11363	LW7	221		84.74	31.52	0.45	-28.0	8.17	1.93	0.37	0.01	repeat	
11500	LW7	231		98.53	45.95	0.56	-28.4	9.23	2.49	0.47	0.01	repeat	
11638	LW7	241		42.81	21.13	0.59	-27.7	4.33	2.44	0.49	0.03	repeat	
11776	LW7	251		74.77	36.07	0.58	-28.2	6.26	2.88	0.48	0.02	repeat	
11913	LW7	261		5.91	252.49	51.29	-28.0	25.79	4.90	42.72	0.83	peat-orig.	
12050	LW7	271		14.89	402.51	32.45	-29.2	18.39	10.95	27.03	0.74	WMU ¹⁴ C	
12188	LW7	281		19.07	64.86	4.08	-25.7	11.38	2.85	3.40	0.15	organic rich	
12325	LW7	291		31.46	16.98	0.65	-27.3	6.93	1.23	0.54	0.04	red clay	

Appendix G

Lake Winnebago Marl (H_3PO_4) Isotopic Results

Isotopic Results from Phosphoric Acid Digestion
Core LW7 - Lake Winnebago, WI

¹⁴ C Age (yr)	Core Sample #	Sample Wt. (mg)	CO ₂ (μmol)	% Carbonate	δ ¹³ C _{PDB} (‰)	δ ¹⁸ O _{PDB} (‰)	δ ¹⁸ O _{SMOW} (‰)	comments
1320±70	LW7-1	84.47	0.15	0.02	-2.8	-7.9	22.7	WMU ¹⁴ C
1492	LW7-10	132.38	0.19	0.01	-2.6	-7.3	23.4	
1549	LW7-13	77.09	0.15	0.02	-2.8	-9.8	20.8	
1607	LW7-16	185.2	0.15	0.01	-2.4	-10.4	20.2	
1664	LW7-19	78.48	0.15	0.02	-2.1	-8.4	22.2	
1722	LW7-22	87.02	0.19	0.02	-1.4	-11.5	19.0	
1779	LW7-25	85.65	0.15	0.02	-1.4	-11.3	19.2	
1836	LW7-28	59.37	0.19	0.03	-1.4	-12.0	18.5	
1894	LW7-31	70.36	0.15	0.02	-1.5	-10.5	20.1	
1951	LW7-34	61.54	0.19	0.03	-1.4	-11.3	19.2	
2008	LW7-37	57.78	0.19	0.03	-1.5	-10.2	20.4	
2066	LW7-40	72.96	0.15	0.02	-1.5	-10.6	19.9	
2123	LW7-43	87.75	0.19	0.02	-1.5	-10.4	20.1	
2180	LW7-46	73.78	0.15	0.02	-1.4	-10.0	20.6	
2238	LW7-49	63.79	0.19	0.03	-1.5	-10.9	19.6	
2295	LW7-52	54.08	0.15	0.03	-1.4	-10.0	20.6	
2353	LW7-55	83.55	0.19	0.02	-1.3	-9.8	20.8	

Isotopic Results from Phosphoric Acid Digestion
Core LW7 - Lake Winnebago, WI

¹⁴ C Age (yr)	Core Sample #	Sample Wt. (mg)	CO ₂ (μmol)	% Carbonate	δ ¹³ C _{PDB} (‰)	δ ¹⁸ O _{PDB} (‰)	δ ¹⁸ O _{SMOW} (‰)	comments
2410±70	LW7-58	83.03	0.19	0.02	-1.3	-8.6	22.0	WMU ¹⁴ C
2592	LW7-61	78.64	0.19	0.02	-1.3	-9.6	21.0	
2774	LW7-64	76.15	0.15	0.02	-1.3	-9.4	21.2	
2774	LW7-64	164.27	0.15	0.01	-1.3	-9.1	21.4	repeated
2955	LW7-67	117.36	0.15	0.01	-1.4	-11.8	18.7	
3137	LW7-70	107.41	0.19	0.02	-1.2	-11.0	19.5	
3319	LW7-73	127.75	0.15	0.01	-1.2	-9.7	20.9	
3501	LW7-76	89.75	0.19	0.02	-1.3	-9.5	21.1	
3683	LW7-79	100.35	0.15	0.01	-1.2	-10.5	20.1	
3865	LW7-82	110.77	0.19	0.02	-1.3	-9.2	21.4	
4046	LW7-85	173.02	0.15	0.01	-1.9	-9.0	21.6	
4228	LW7-88	117.97	0.19	0.02	-2.2	-8.7	21.9	
4410	LW7-91	138.98	0.15	0.01	-2.4	-9.1	21.5	
4592	LW7-94	195.69	0.19	0.01	-2.4	-9.3	21.3	
4774	LW7-97	138.98	0.19	0.01	-2.4	-8.9	21.7	
4950±70	LW7-100	144.71	0.19	0.01	-2.5	-9.2	21.3	WMU ¹⁴ C
5206	LW7-103	141.45	0.15	0.01	-2.0	-7.9	22.8	

Isotopic Results from Phosphoric Acid Digestion
Core LW7 - Lake Winnebago, WI

¹⁴ C Age (yr)	Core Sample #	Sample Wt. (mg)	CO ₂ (μmol)	% Carbonate	δ ¹³ C _{PDB} (‰)	δ ¹⁸ O _{PDB} (‰)	δ ¹⁸ O _{SMOW} (‰)	comments
5463	LW7-106	127.59	0.15	0.01	-1.5	-6.6	24.1	
5719	LW7-109	192.52	0.19	0.01	-2.3	-7.5	23.1	
5976	LW7-112	140.61	0.15	0.01	-2.2	-7.0	23.7	
6232	LW7-115	189.39	0.19	0.01	-2.6	-7.4	23.2	
6488	LW7-118	199.94	0.19	0.01	-2.5	-6.4	24.3	
6745	LW7-121	172.9	0.15	0.01	-2.5	-7.4	23.2	
7001	LW7-124	29.67	22.00	7.41	-2.1	-6.9	23.8	repeat
7250±80	LW7-127	37.16	28.80	7.75	-1.4	-6.7	24.0	WMU ¹⁴ C
7635	LW7-130	116.95	0.15	0.01	-2.8	-7.2	23.5	
8019	LW7-133	133.76	0.19	0.01	-3.0	-7.4	23.2	
8404	LW7-136	95.21	0.15	0.02	-2.2	-7.3	23.3	
8788	LW7-139	120.67	0.19	0.02	-2.4	-5.9	24.8	
10400±90	LW7-151	86.33	0.15	0.02	-3.4	-7.2	23.4	WMU ¹⁴ C
10538	LW7-161	159.91	0.19	0.01	-1.4	-6.5	24.1	
10675	LW7-171	97.72	0.15	0.02	-1.1	-6.5	24.1	
10813	LW7-181	140.8	0.19	0.01	-1.1	-6.3	24.4	
10950	LW7-191	118.75	0.15	0.01	-1.0	-6.3	24.4	

Isotopic Results from Phosphoric Acid Digestion
Core LW7 - Lake Winnebago, WI

¹⁴ C Age (yr)	Core Sample #	Sample Wt. (mg)	CO ₂ (μmol)	% Carbonate	δ ¹³ C _{PDB} (‰)	δ ¹⁸ O _{PDB} (‰)	δ ¹⁸ O _{SMOW} (‰)	comments
11088	LW7-201	98.91	0.19	0.02	-1.0	-6.2	24.5	
11225	LW7-211	154.03	0.15	0.01	-1.0	-6.5	24.1	
11363	LW7-221	64.12	0.19	0.03	-1.0	-6.2	24.5	
11500	LW7-231	103.29	0.15	0.01	-1.0	-6.1	24.6	
11638	LW7-241	89.28	0.19	0.02	-1.0	-6.1	24.6	
11776	LW7-251	104.76	0.15	0.01	-0.9	-5.9	24.8	
11913	LW7-261	123.94			Did Not Process			Peat
12050±90	LW7-271	135.83			Did Not Process			Peat WMU ¹⁴ C
12188	LW7-281	192.64	0.15	0.01	-1.2	-6.5	24.2	
12325	LW7-291	129.02	0.19	0.01	-1.5	-5.6	25.1	

Appendix H

Sapropel Isotopic Results

Sapropel Samples Provided by the University of Michigan-Ocean Drilling Program - Dr. Phillip Meyers
Mediterranean Coring Project

WMU Sample #	Leg	Hole	Core	University of Michigan-Identification Data				Sapropel Sample		
				Sec	Int	Sample	Bid	Rec	Date	Time
SAP 1	161	974B	3H	03	015-016	carbonate	010	30	050895	1103
SAP 2	161	974B	4H	05	027-028	carbonate	020	01	050895	1900
SAP 3	161	974B	4H	05	111-112	carbonate	020	02	050895	1900
SAP 4	161	974B	5H	02	046-047	carbonate	024	06	050895	2229
SAP 5	161	974B	5H	01	068-069	carbonate	023	17	050895	2156
SAP 6	161	974B	6H	05	005-006	carbonate	034	16	050995	0319
SAP 7	161	974B	6H	05	020-021	carbonate	034	23	050995	0319
SAP 8	161	974B	6H	07	062-063	carbonate	036	44	050995	0450
SAP 9	161	974B	6H	06	084-085	carbonate	037	01	050995	0537
SAP 10	161	974B	6H	05	134-135	carbonate	034	45	050995	0319
SAP 11	161	974B	7H	05	025-026	carbonate	042	19	050995	0736
SAP 12	161	974B	7H	05	097-098	carbonate	042	20	050995	0736
SAP 13	161	974B	7H	01	117-118	carbonate	042	18	050995	0736
SAP 14	161	974B	10H	04	060-061	carbonate	053	24	050995	1648
SAP 15	161	974B	16H	04	123-124	carbonate	062	42	050995	0450

Sapropel Samples Provided by the University of Michigan-Ocean Drilling Program - Dr. Phillip Meyers
Mediterranean Coring Project

WMU Sample #	Isotopic Data										
	Conventional Extraction					δD-P250 Extraction					
	HCL Residue C/N	δ ¹³ C _{HCL}	% C _{org}	HF:HCL Residue δ ¹³ C _{HF}	H/C	δD	1st HF % C _{org}	2nd HF % C _{org}	H/C	δD _{P250}	% C _{org}
SAP 1	7.12	-22.7	2.74%	-22.8	2.2	-99	1.88%	1.99%	0.3	-150	1.62%
SAP 2	11.65	-23.1	3.32%	-23.0	1.0	-143	2.96%	3.12%	0.3	-185	2.67%
SAP 3	11.06	-23.5	4.03%	-23.5	1.3	-115	2.97%	3.25%	0.7	-171	2.58%
SAP 4	9.85	-21.9	4.34%	-22.1	1.4	-117	4.45%	5.35%	0.3	-154	5.17%
SAP 5	8.11	-21.3	5.26%	-21.5	1.0	-124	4.86%	5.48%	0.6	-163	5.35%
SAP 6	14.62	-21.6	7.00%	-21.6	1.2	-118	7.76%	7.78%	0.7	-162	6.98%
SAP 7	9.22	-23.1	2.28%	-23.2	1.7	-128	1.91%	2.41%	0.3	-170	2.43%
SAP 8	14.96	-22.2	6.02%	-22.3	2.3	-108	9.85%	5.09%	0.6	-166	4.50%
SAP 9	11.57	-23.1	4.78%	-23.1	1.2	-129	3.46%	3.71%	0.6	-161	3.52%
SAP 10	11.38	-21.3	6.02%	-21.1	1.2	-116	7.80%	7.07%	0.6	-156	7.34%
SAP 11	9.70	-23.5	4.06%	-23.6	1.2	-125	3.92%	4.69%	0.3	-152	4.39%
SAP 12	13.96	-23.7	6.25%	-23.6	1.2	-131	4.50%	5.38%	0.4	-165	4.88%
SAP 13	17.41	-21.5	9.95%	-21.3	1.1	-99	24.31%	18.20%	0.4	-138	13.93%
SAP 14	14.47	-22.8	5.23%	-22.8	1.3	-122	6.12%	5.98%	0.3	-167	5.53%
SAP 15	5.85	-23.9	1.31%	-24.0	3.1	-102	1.00%	1.21%	0.2	tstm	1.14%

Appendix I

Acid Digestion Data From Conventional and Microwave Digestion Protocol

Conventionally Digested Ladd Lake Pilot Group Samples

WMU Sample Number		Time in Acid	HF:HCl Minutes	Number of HF:HCL treatments
LL	934	34 hrs 44 min	2084	4
LL	1024	108 hrs 31 min	6511	6
LL	1054	34 hrs 44 min	2084	4
LL	1078	30 hrs 26 min	1826	4
LL	1134	30 hrs 26 min	1826	4
LL	1190	34 hrs 44 min	2084	4
LL	1204	27 hrs 38 min	1658	2
LL	1234	29 hrs 46 min	1786	4
LL	1250	27 hrs 38 min	1658	2
LL	1266	27 hrs 38 min	1658	2
LL	1366	33 hrs 46 mins	2026	3
LL	1435	33 hrs 46 mins	2026	3
LL	1449	33 hrs 46 mins	2026	3
LL	1463	33 hrs 46 mins	2026	3
LL	1467	33 hrs 46 mins	2026	3
LL	1515	33 hrs 46 mins	2026	3
LL	1551	35 hrs 15 mins	2115	3
LL	1559	35 hrs 15 mins	2115	3
LL	1651	35 hrs 15 mins	2115	3
LL	1699	35 hrs 15 mins	2115	3
LL	1735	44 hrs 12 min	2652	2
LL	1767	44 hrs 12 min	2652	2
LL	1791	44 hrs 12 min	2652	2
LL	1807	49 hrs 27 min	2967	3
LL	1819	44 hrs 12 min	2652	2
LL	1823	44 hrs 12 min	2652	2
LL	1867	40 hrs 7 min	2407	2
LL	1899	40 hrs 7 min	2407	2
LL	1923	40 hrs 7 min	2407	2
LL	1951	45 hrs 22 min	2722	3
LL	1975	40 hrs 7 min	2407	2

WMU Sample Number		Time in Acid	HF:HCl Minutes	Number of HF:HCL treatments
LL	1984	40 hrs 7 min	2407	2
LL	2004	44 hrs 15 min	2655	2
LL	2028	44 hrs 15 min	2655	2
LL	2042	44 hrs 15 min	2655	2
LL	2056	44 hrs 15 min	2655	2
LL	2060	44 hrs 25 min	2665	2
LL	2084	44 hrs 25 min	2665	2
LL	2098	125 hrs 27 min	7527	6
LL	2108	49 hrs 27 min	2967	3
LL	2111	49 hrs 20 min	2960	3
LL	2115	122 hrs 47 min	7527	5
		mean	2660	2.88
		std. Dev.	1314	1.05
		range	1658 to 7527	2 to 6

HF:HCl Microwave Acid Digestion
Ladd Lake, OH

¹⁴ C Age YBP	Core Sample #	Raw sample Wt. (mg)	Acid Residue Wt. (mg)	% Wt. Reduction
5	LL 934	280.09	39.57	85.87
7	LL 936	358.51	18.64	94.80
9	LL 938	433.25	39.09	90.98
11	LL 940	337.31	51.05	84.87
14	LL 942	386.13	21.77	94.36
16	LL 944	318.64	25.16	92.10
18	LL 946	352.29	36.59	89.61
23	LL 950	252.01	15.58	93.82
25	LL 952	353.23	17.88	94.94
27	LL 954	354.46	42.66	87.96
32	LL 958	340.62	46.46	86.36
77	LL 998	109.38	2.06	98.12
89	LL 1008	315.63	54.43	82.76
91	LL 1010	453.48	41.03	90.95
98	LL 1016	397.63	31.99	91.95
100	LL 1018	356.82	58.19	83.69
107	LL 1024	88.66	2.35	97.35
116	LL 1032	386.47	56.93	85.27
123	LL 1038	306.91	31.87	89.62
125	LL 1040	384.61	41.21	89.29
130	LL 1044	386.59	41.43	89.28
141	LL 1054	164.53	13.49	91.80
168	LL 1078		Pilot Group	
182	LL 1090	453.54	49.96	88.98
218	LL 1122	343.03	39.27	88.55
223	LL 1126	399.65	39.92	90.01
232	LL 1134		Pilot Group	
236	LL 1138	361.72	29.56	91.83
250	LL 1150	482.43	48.71	89.90
259	LL 1158	404.79	39.24	90.31
273	LL 1170	416.13	39.46	90.52
291	LL 1186	363.36	35.26	90.30

¹⁴ C Age YBP	Core Sample #	Raw sample Wt. (mg)	Acid Residue Wt. (mg)	% Wt. Reduction
295	LL 1190		Pilot Group	
437	LL 1204		Pilot Group	
602	LL 1216	266.35	52.14	80.42
850	LL 1234		Pilot Group	
1070	LL 1250		Pilot Group	
1290	LL 1266		Pilot Group	
1400	LL 1274	374.74	77.36	79.36
1729	LL 1298	221.74	41.18	81.43
1894	LL 1310	323.63	46.58	85.61
2004	LL 1318	288.81	66.87	76.85
2224	LL 1334	492.41	54.96	88.84
2334	LL 1342	377.52	36.87	90.23
2444	LL 1350	172.11	32.12	81.34
2554	LL 1358	220.91	38.97	82.36
2664	LL 1366	74.84	15.99	78.63
2774	LL 1374	219.53	44.33	79.81
2884	LL 1382	107.61	29.18	72.88
2994	LL 1390	281.71	29.36	89.58
3104	LL 1398	381.12	28.08	92.63
3214	LL 1406	252.16	60.00	76.21
3324	LL 1414	313.84	62.17	80.19
3434	LL 1422	161.01	21.12	86.88
3613	LL 1435		Pilot Group	
3723	LL 1443	431.13	63.51	85.27
3805	LL 1449		Pilot Group	
3924	LL 1463		Pilot Group	
3945	LL 1467		Pilot Group	
4051	LL 1487	168.07	47.03	72.02
4115	LL 1499	167.25	62.73	62.49
4200	LL 1515		Pilot Group	
4263	LL 1527	128.14	37.92	70.41
4285	LL 1531	170.56	53.79	68.46
4391	LL 1551		Pilot Group	
4433	LL 1559		Pilot Group	
4476	LL 1567	104.89	24.87	76.29

¹⁴ C Age YBP	Core Sample #	Raw sample Wt. (mg)	Acid Residue Wt. (mg)	% Wt. Reduction
4518	LL 1575	36.18	7.09	80.40
4561	LL 1583	not enough HF for analysis		
4667	LL 1603	318.83	67.09	78.96
4731	LL 1615	155.35	43.77	71.82
4837	LL 1635	122.35	32.11	73.76
4922	LL 1651		Pilot Group	
4986	LL 1663	144.83	41.89	71.08
5007	LL 1667	163.99	43.94	73.21
5092	LL 1683	152.48	54.07	64.54
5177	LL 1699		Pilot Group	
5262	LL 1715	139.68	40.68	70.88
5325	LL 1727	154.83	28.59	81.53
5368	LL 1735		Pilot Group	
5453	LL 1751	203.38	42.03	79.33
5538	LL 1767		Pilot Group	
5601	LL 1779	202.58	40.52	80.00
5665	LL 1791		Pilot Group	
5708	LL 1799	210.14	41.06	80.46
5750	LL 1807		Pilot Group	
6017	LL 1819		Pilot Group	
6107	LL 1823		Pilot Group	
6374	LL 1835	367.53	102.75	72.04
6552	LL 1843	171.15	28.80	83.17
6641	LL 1847	200.97	41.18	79.51
6731	LL 1851	54.76	22.58	58.77
6909	LL 1859	350.67	67.68	80.70
7087	LL 1867	HF small - not enough HCl to cook down		
7265	LL 1875	270.78	47.20	82.57
7354	LL 1879	213.39	38.65	81.89
7444	LL 1883	174.93	54.08	69.08
7622	LL 1891	205.01	46.29	77.42
7800	LL 1899		Pilot Group	

¹⁴ C Age YBP	Core Sample #	Raw sample Wt. (mg)	Acid Residue Wt. (mg)	% Wt. Reduction
7978	LL 1907	144.19	43.03	70.16
8068	LL 1911	333.31	48.35	85.49
8157	LL 1915	384.36	54.58	85.80
8246	LL 1919	393.24	94.53	75.96
8335	LL 1923	53.38	11.95	77.61
8959	LL 1951		Pilot Group	
9137	LL 1959	266.13	58.29	78.10
9226	LL 1963	171.11	40.62	76.26
9315	LL 1967	199.33	47.06	76.39
9494	LL 1975	57.11	12.37	78.34
9694	LL 1984		Pilot Group	
9962	LL 1996	236.99	85.15	64.07
10140	LL 2004		Pilot Group	
10650	LL 2017	258.88	59.59	76.98
10925	LL 2024	233.05	63.46	72.77
11082	LL 2028		Pilot Group	
11397	LL 2036	264.98	56.67	78.61
11554	LL 2040	167.22	53.01	68.30
11632	LL 2042		Pilot Group	
12336	LL 2056		Pilot Group	
12549	LL 2060		Pilot Group	
12762	LL 2064	212.53	40.16	81.10
12975	LL 2068	223.67	60.42	72.99
13188	LL 2072	257.39	42.99	83.30
13401	LL 2076	250.52	33.36	86.68
13615	LL 2080	548.19	130.43	76.21
13828	LL 2084		Pilot Group	
14041	LL 2088	410.51	70.09	82.93
14573	LL 2098		Pilot Group	
14680	LL 2108		Pilot Group	
14840	LL 2111		Pilot Group	
15053	LL 2115		Pilot Group	
15213	LL 2118	577.53	44.74	92.25
15426	LL 2122	322.38	7.25	97.75

HF:HCl Microwave Acid Digestion
Core LW7 - Lake Winnebago, WI

¹⁴ C Age YBP	Core Sample #	Raw sample Wt. (mg)	Acid Residue Wt. (mg)	% Wt. Reduction
1320	LW7-1	61.61	4.61	92.52
1492	LW7-10	375.79	34.85	90.73
1549	LW7-13	183.67	24.81	86.49
1607	LW7-16	No sample remaining for digestion		
1664	LW7-19	240.94	51.67	78.55
1722	LW7-22	167.06	21.61	87.06
1779	LW7-25	213.55	30.44	85.75
1836	LW7-28	234.17	34.81	85.13
1894	LW7-31	142.22	16.50	88.40
1951	LW7-34	205.59	29.52	85.64
2008	LW7-37	300.31	44.91	85.05
2066	LW7-40	334.07	52.69	84.23
2123	LW7-43	353.79	56.06	84.15
2180	LW7-46	306.06	50.38	83.54
2238	LW7-49	292.77	47.01	83.94
2295	LW7-52	251.96	37.10	85.28
2353	LW7-55	266.41	34.94	86.88
2410	LW7-58	299.78	40.07	86.63
2592	LW7-61	305.74	51.26	83.23
2774	LW7-64	314.34	50.77	83.85
2955	LW7-67	331.67	59.41	82.09
3137	LW7-70	349.01	59.16	83.05
3319	LW7-73	305.08	48.93	83.96
3501	LW7-76	282.85	39.78	85.94
3683	LW7-79	297.86	44.76	84.97
3865	LW7-82	214.94	27.51	87.20
4046	LW7-85	340.78	68.41	79.93
4228	LW7-88	398.25	80.80	79.71
4410	LW7-91	353.84	62.64	82.30
4592	LW7-94	399.28	80.31	79.89
4774	LW7-97	346.53	65.48	81.10

HF:HCl Microwave Acid Digestion
Core LW7 - Lake Winnebago, WI

¹⁴ C Age YBP	Core Sample #	Raw sample Wt. (mg)	Acid Residue Wt. (mg)	% Wt. Reduction
4950	LW7-100	270.77	32.73	87.91
5206	LW7-103	266.72	24.99	90.63
5463	LW7-106	311.42	31.31	89.95
5719	LW7-109	352.33	42.49	87.94
5976	LW7-112	294.85	29.43	90.02
6232	LW7-115	350.75	39.58	88.72
6488	LW7-118	296.49	24.55	91.72
6745	LW7-121	403.51	47.36	88.26
7001	LW7-124	339.27	34.82	89.74
7250	LW7-127	414.23	53.86	87.00
7635	LW7-130	285.44	26.80	90.61
8019	LW7-133	299.67	30.72	89.75
8404	LW7-136	340.12	38.98	88.54
8788	LW7-139	363.39	44.92	87.64
10400	LW7-151	389.52	48.69	87.50
10538	LW7-161	296.28	37.30	87.41
10675	LW7-171	409.38	87.89	78.53
10813	LW7-181	384.73	73.83	80.81
10950	LW7-191	325.26	49.25	84.86
11088	LW7-201	420.43	72.81	82.68
11225	LW7-211	394.01	78.29	80.13
11363	LW7-221	352.76	67.99	80.73
11500	LW7-231	398.41	62.76	84.25
11638	LW7-241	300.67	34.95	88.38
11776	LW7-251	415.39	97.23	76.59
11913	LW7-261	85.31	38.97	54.32
12050	LW7-271	175.48	76.12	56.62
12188	LW7-281	396.31	97.83	75.31
12325	LW7-291	475.57	109.65	76.94

Appendix J
Archived Sample Collection

Fudger Lake, Ohio

Fudger Lake is located in Champaign County, west central Ohio. Geographically, Fudger Lake is located at 40° 06' N; 83° 32' W, at an elevation of 320 m and may be found on the Mechanicsberg Quad, USGS 7.5 minute series map. Fudger Lake is located on the inner edge of the Cable Moraine in central-western Ohio approximately 5 kilometers east-northeast of the town Mechanicsberg. The near 19 meter length core was raised by University of Minnesota personnel, from an anchored plywood platform lashed to two canoes via a 5-cm. diameter Wright-Livingston piston sampler. Coring was done after locating the deepest spot of the lake by using sounding gear consisting of a line and perforated metal plate. The single core was collected on 5-31-86 and 6-1-86 in ~700 cm deep water. Top to base of core was 670 to 2522 cm with the water surface designated as 0cm. No radiocarbon analysis was performed due to high carbonate content although one AMS date was taken at the core depth interval 2172 cm and resulted in an age of approximately 11,700 years (personal communication with Dr. Shane). Data provided by the University of Minnesota indicates that the cores length covered the Late Glacial and Holocene time frame with the top 13m of the Fudger Lake core reported as Holocene. A stable isotopic study of the Late Glacial section was completed and published. The Holocene interval is documented in a report on pollen analysis dated 9-15-91 by Dr. Linda C. K. Shane to the Ohio Department of Natural Resources titled "Vegetation History of Western Ohio".

The Fudger Lake core was the first to be sub-sampled for use in this dissertation research. Sub-sampling began July 3, 1995. A total of 432 sediment samples were extracted from the Fudger Lake core by sampling on a 4-cm interval. Dr. Linda Shane was present to oversee the initial subsampling, which took place in the stable isotope laboratory located in Rood Hall, Department of Geology, Western Michigan University, Kalamazoo, MI. Final samples were extracted from the Fudger Lake core on August 12, 1995.

Lime Lake, Michigan

Lime Lake, Kent County, Michigan, is located on the Sparta, MI Quad, USGS 7.5 minute series map about 3 miles NNE of Sparta townsite in the SW corner of section 33, Solon Township. Driving to this lake, one would go north from Kalamazoo, Michigan, or south from Grand Rapids on highway 131 to State Highway 57. Exiting west and traveling approximately 2 to 4 miles to Pine Island Drive then south approximately $\frac{3}{4}$ mile to Lime Lake Drive. Turning left on Lime Lake Drive to the Public Access.

The Lime Lake core was raised by University of Minnesota Limnologic Research Center (UMN-LRC) personnel on July 25, 1995 under the supervision of Dr. Linda Shane. Lime Lake is reportedly named for its abundant carbonate content (personal communication with Dr. Shane). The Department of Geology at Western Michigan University supplied the pontoon boat that was used as a coring platform during the raising of this core. After numerous technical problems were overcome,

including loosening the core barrel and support rig overboard, a 9-meter core was recovered. Due to slump features within the core, only the top few meters may be viable for paleoclimatic investigation. Samples were removed from the Lime Lake core at a 4cm resolution.

Samples were removed from the Fudger Lake core using newly washed razor and knife blade utensils. Samples were then individually placed into separate new, pre-labeled 20 ml vials, and stored in a refrigerated environment at $\sim 10^{\circ}\text{C}$. Sub-samples from the Lime Lake core were extracted August 11th and 12th at the UMN-LRC and samples from the Ladd Lake core were extracted beginning September 26th, 1995 and ending November 13th, 1995 in the stable isotope laboratory at Western Michigan University. Lime Lake sediment samples were extracted using a newly washed, modified-plastic 3, 6 and 10cc syringes. Each syringe was modified by blunt-cutting the needle-end. The resulting "coring device" provided a convenient method for extracting the sediment sample by coring the sediment core with the syringe tube and extruding the sample using the syringe plunger. Approximately 2cc of sediment were collected at each sample interval. Individual samples were then placed into separate new, sterile, pre-labeled 20ml vials. Vials were labeled alphanumerically using letter abbreviations and numbers to designate their core origin and depth. The abbreviations LL for Ladd Lake, FL for Fudger Lake and LM for Lime Lake were adopted and the subsequent numbers were assigned to designate both the core's sample number and interval depth in centimeters (i.e. LL-123 for Ladd Lake core with sample from the 123 cm interval depth). Collectively, approximately 871 samples were removed from

three UNM-LRC cores by extracting sediment material on a high-resolution interval of 4 to 5 cm. Samples from Lime and Fudger Lakes were archived for future work and are currently keep refrigerated in the Stable Isotope Laboratory on the 3rd floor of Rood Hall, Western Michigan University.

Appendix K

Notes on Observations Relative to the University of Minnesota-Limnologic Research Centers Sampling Protocol

Observations Related to the University of Minnesota-Limnologic Research Center
Core and Sampling Protocol

The general sediment core preparation procedure used by the UMN-LRC and followed in this instance was to raise the core using a Wright-Livingston Piston Sampler with a metal core string housing a plastic liner. The plastic liner is a 7cm diameter, 1/16th inch thick, polycarbon tube (polycarbonate). This tubing costs approximately \$5 to \$7 per linear foot. After the core is acquired, the liner is extruded from the metal core barrel while in the field and sawn, using a hacksaw, into meter long segments. The tubes are labeled as to up and the depth of the top and bottom. Plugs of floral foam are inserted into the ends to prevent sample loss. The core-segment ends are then capped with pre-fitted plastic caps (orange in color) and stored for later extrusion following transport to the LRC lab. At the Limnologic Research Center, the cores are opened and halved. Splitting the cores polycarbonate liner sheath is achieved by first mounting the meter long tube segment containing the core material on a frame built of several 2 by 4 inch wooden blocks joined by attaching 3 meter-sticks. This frame is built with aligned grooves carved at ½ the liner diameter depths into each 2x4 block such that each frame is thus designed to hold the two halves of a one-meter segment liner tube. Liner tubes are halved using a retractable exacto-style blade which is passed down the edge of the meter-stick mounting blocks to maintain a straight edge. For tougher material, a cast cutting saw was obtained from medical equipment suppliers and is permanently mounted upside down on a stationary platform designed to enable vertical adjustment of the saw blade. Once

properly positioned, the liner tube/mount assembly is passed by the cast cutting blade much in the fashion of a carpenter's table saw. If high organics are present and the core is "oozing", a metal "flashing" material is used to slice between the pre-cut liner halves. Two pieces of 1 meter length flashing are inserted simultaneously so that each split liner half will be capped by the respective flashing. Individual sediment core halves are then carefully transferred to similarly halved PVC tubes. Prior to transfer, each PVC half tube is covered with a sheet 18' wide heavy duty aluminum foil which is then covered with a sheet of 18' wide plastic wrap. The plastic wrap is obtained from the Sysco Corp. Houston, Texas, in 18" by 2000' rolls. The foil is purchased from Alcan Corporation. Each sediment core-segment is wrapped for storage in a refrigerated vault kept at 4 to 10°C. The halved segments are first marked to indicate the top, bottom, core depth segment interval and other pertinent information. One half of each segment is used for sampling and one half is archived as a reference. Prior to storage the archived half is photographed using a wall mounted Polaroid MP-3 land camera. Smear slides of each core segment are prepared and cured using ultraviolet light and Norland optical adhesive 61, lot 151 from Norland Products, Inc., New Brunswick, NJ 08902.

An email note to Norman Lovan on Sample Collection and Digestion from Dr. Linda Shane

If the HF:HCl mix is to remove carbonates and silicates, I may know some of your problem. We need to remove these in pollen processing too and use the following routine.

The sample is in a 15 ml polypropylene test tube. We heat (water bath at gentle boil) with ca 6 ml 10% HCl (v:v) for 10 to 20 minutes. On very rare occasions we repeat (one sample out of 200 or 300). Centrifuge down and pour off the supernatant into acid reaction bucket containing water and soda ash. This can be followed by a water rinse, if desired or if the samples will be left for several days.

Then we treat with HF. We put ca 6 ml of conc. ca. 48% HF into the sample tube and boil in water bath for 20 minutes. Then centrifuge and decant. Need lots of safety routines with this operation. Then we rinse 3-5 times with hot 10% HCl (put tubes in water bath for 1-2 minutes). The problem is that HF and silicates form colloids that do not break up readily, but will if mixed with hot HCl. The number of repetitions depends on how much clay is present. If there are lots, there are more colloid clumps to break up. At this point, I water-mount a small amount of sample on a slide and check it for remaining crystals and colloidal clumps that look like dirty gray clouds. About a third of the time we need to repeat the hot HF followed by hot HCl rinses routine. Again this is usually true in clay sediments. I should mention that

earlier we have screened the desegregated sediment through 160 um mesh. This removes larger sand grains and helps the later HF digestion out.

So there are several points here that might relate to your procedure:

(1) We always do the HCl BEFORE the HF because HF in the presence of carbonates forms an insoluble ppt of CaF that is a total nuisance in making decent pollen slides. Who knows how water of hydration works in this reaction. So, remove the carbonates first, and the issue goes away.

(2) In both HCl and HF reactions, heat is critical. A sample left in cold HCl needs several hours and in cold HF can take a week or more to digest.

(3) It is usually more chemical work to remove silicates, so we try to adjust the amount of treatment to the sample requirements. Also the HF behaves as if it has gone to completion when it hasn't. It needs replenishing whereas the HCl does not.

(4) The water presumably held in the colloidal clumps is likely high, so that may affect your weights.

Some information from the above may help speed your procedure. The steps I just described take about 2 to 3 hours to complete for a set of 8 samples. (Total pollen processing takes 8 to 12 hours for a set of 8.)

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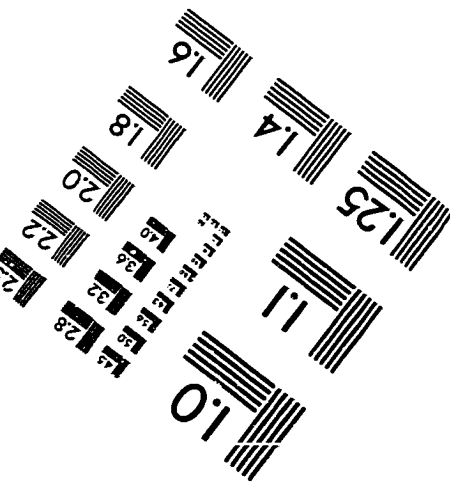
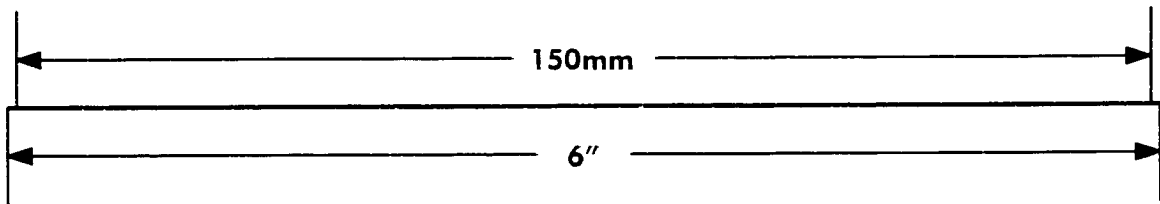
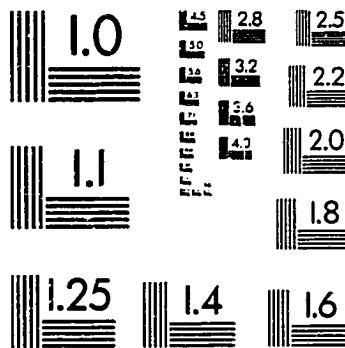
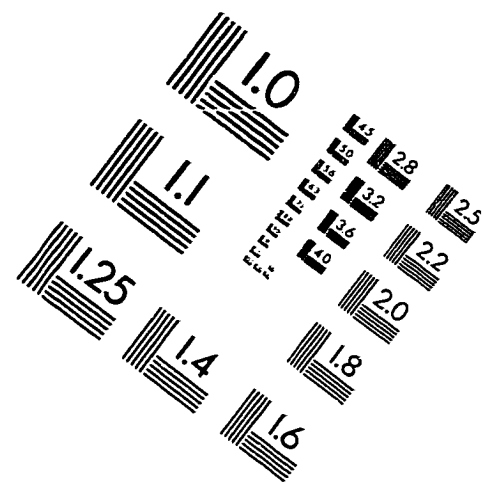
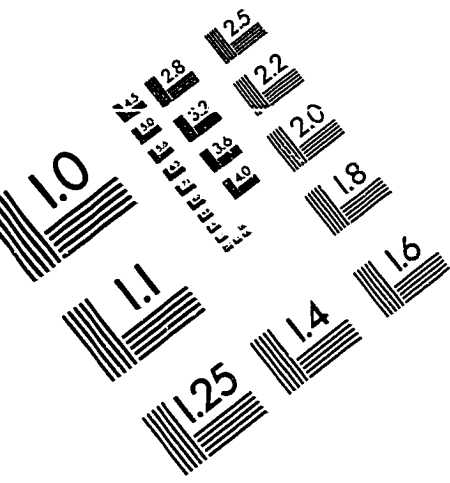
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IMAGE EVALUATION TEST TARGET (QA-3)



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