ANTHROPOGENIC CLIMATE CHANGE HAS DRIVEN LAKE SUPERIOR PRODUCTIVITY BEYOND THE RANGE OF HOLOCENE VARIABILITY:

An Organic and Stable Isotopic Study of Human Impacts on a Pristine Biogeochemical System

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ABSTRACT

Recent studies have noted that changes in Lake Superior's physical, chemical and biological processes are apparent – including a warming of the surface waters at a rate twice as great as the surrounding airshed in the last 20 years. These changes are often difficult to perceive as cause for concern when not placed within a historical context. In this study, bulk C and N elemental abundance and stable isotope analysis of sediments from three piston and corresponding gravity cores, representing a record of lake-wide paleoproductivity trends spanning the Holocene, allows for the historical comparison with recent (1800 A.D. to present) productivity trends. Overall, Lake Superior experiences a slow, steady increase in productivity consistent with the concept of 'natural' eutrophication, which is characterized by gradual increases in TOC and TON, as well as the steady ^{13}C-enrichment of bulk sedimentary organic carbon and ^{15}N-enrichment of bulk sedimentary organic nitrogen compositions.

Over the last 200 years bulk concentrations and stable isotope compositions of carbon and nitrogen from eight sediment multicores sampled at high resolution indicate that the Lake Superior basin has undergone productivity changes in the last two centuries (1800 to present) which are unique in the context of the Holocene. Overall, lake-wide sedimentary bulk organic proxy data show increasing primary production between 1900 and present, as indicated by an ~2‰ increase in $\delta^{13}C_{org}$. The most recent increases in productivity are likely a response to increasing water temperatures and longer stratified periods reported in Lake Superior.

Down-core variations in the δ^{13}C composition of algal-derived short-chain *n*-alkanes do not exhibit the same trend as that observed for bulk sedimentary organic matter ($\delta^{13}C_{org}$). The δ^{13}C of bulk sedimentary organic matter shows systematic ^{13}C-enrichment over the last ~9000 years, while the δ^{13}C values of aquatic derived *n*-alkanes exhibit a systematic ^{13}C-depletion to present-day. Down-core variation in δ^{13}C values of *n*-alkanes likely reflect multiple isotope effects associated with carbon partitioning and fractionation associated with the biosynthesis of *n*-alkanes.

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PREFACE

Lacustrine Sediments

Lakes constitute approximately 2.8% of Earth's land surface area (Downing, 2006), yet they serve as critical resources for society by providing water for drinking, hygiene, industry, power generation, and recreation (Williamson et al., 2008). Lakes are also hot spots of biodiversity and are often sensitive indicators of environmental changes, both regional and global. The interconnectedness of lakes to their surrounding environments - the habitats they provide and biodiversity they hold, along with society's heavy reliance on their resources makes managing any resultant effects of environmental change important. In order to assess any potential impacts, it is essential to know how lakes have responded to past changes. This is primarily accomplished through the reconstruction of paleolimnological trends (i.e. production in the water column, changes in terrigenous and aquatic input over time, as well as precipitation and wind patterns) using lake sediment core records. This is especially useful in systems where historical records are lacking.

Sediment core records contain a wealth of knowledge about the environments from which they are taken. Moreover, lakes, being intimately tied to their surrounding environments and, in general, having higher primary productivity and sedimentation rates than oceans, make it that much more likely they will capture environmental changes within their subaqueous sedimentary record. According to Meyers (1997) we are able to deduce much about past ecosystems and environments in which sedimentary OM was created and deposited by looking at the elemental abundances and isotopic compositions of bulk OM, as well as those of specific molecules contained within sediments. Meyers (1997) also points out that, although much (over 90%, Eadie et al., 1984) of the OM delivered and produced within a lake is modified after its formation, through early degradation and diagenesis, once it has been sedimented (buried below the oxic-anoxic interface within sediments) the effects of remineralization and any subsequent alterations of compounds slow, allowing for the retention of paleolimnological information for analysis.

Sedimentary Organic Geochemical Proxies

Organic matter within lake sediments originates from two main sources, aquatic/autochthonous and terrigenous/allochthonous production. The biochemical compositions (e.g. lipids, carbohydrates, proteins) of these two sources vary, but differences are not always distinctive enough to identify source signatures within the complex mixture of sedimentary components. Traditional approaches for tracing inputs of OM to lake sediments have included elemental analysis of bulk sediments as well as bulk carbon and nitrogen stable isotope compositions. Evaluations involving isotope composition and abundances of molecular biomarker compounds, specifically lipids, have been used to further disentangle sources of OM in lake sediments. Generally speaking, approaches that have used multiple techniques have been the most successful in unraveling the identity of sources of OM.

Bulk Organic Matter Proxies – There are a variety of commonly used bulk organic matter proxies that are used in paleolimnological reconstructions. Each is discussed below along with their respective application(s) and any potential complications that may arise in their interpretation. In general, bulk organic matter proxies are best used in conjunction with one another when reconstructing past trends within lake systems.

Total Organic Carbon

The abundance of OM held within lacustrine sediments is often inferred from the concentration of total organic carbon (TOC); measured as a bulk quantity and expressed as the percentage by weight of sediment that consists of organic carbon (%TOC). A general estimate of OM content within the sediment is determined as twice the concentration of TOC (Killops and Killops, 2005). The value obtained from analysis is representative of the fraction of OM that escaped remineralization during sedimentation;

higher content generally indicates higher production for an otherwise steady state system. TOC concentrations are influenced by both the initial production of biomass and any subsequent degree of degradation (Meyers, 2003). Therefore, direct TOC measurements, alone, do not take into account the different origins of OM, delivery routes, depositional processes, and amount of preservation. The interactions between these various factors make it difficult to separate each of their effects; however, it is possible when jointly assessed with other paleolimnological proxies.

Changes occurring within the rates of OM delivery to lake sediments can be determined from organic carbon mass accumulation rates (MARs). MARs are especially useful as measures of delivery and preservation of OM, as they take into account changes in sedimentation rate that are not easily deduced from TOC values alone. MAR values are calculated as mass of TOC per unit of lake bottom area, per unit of time, typically expressed in units of mg cm^{-2} y^{-1}.

Ratio of Carbon and Nitrogen (C:N)

Sedimentary C:N ratios are generally reliable indicators of OM source and are used to further distinguish the origins of sedimentary OM between aquatic and terrigenous production. Due to the inherent structure of cellular compounds, the C:N ratio of protein rich algae (typically 4-10) and protein poor vascular land plants (+20) differs; changes in C:N ratios therefore indicate changes in source material delivered to lake sediments (Meyers, 1997). The differences in C:N ratios of aquatic and terrigneous source material typically survive water column mineralization and diagenesis within sediments, as it is assumed they occur at the same rates for both carbon and nitrogen. The ratio can sometimes be misleading, especially in sediments having low OM concentrations (TOC <0.3%) and high inorganic nitrogen concentrations (Meyers, 2003). C:N ratios are used best as relative indicators of changes over time, rather than for quantification. Especially when coupled with other proxy data (i.e. $\delta^{13}C_{org}$), C:N ratios can reveal temporal changes in OM sources.

Stable Isotopes of Carbon and Nitrogen ($\delta^{13}C_{org}$ and $\delta^{15}N$)

Measuring the stable isotope composition of OM is a widely utilized method employed to examine sources of OM, assess past productivity, and identify changes in the availability of nutrients in surface waters (Meyers 1997; 2003). Isotopes, atoms of an element that contain the same number of protons but differ in the number of neutrons, can be easily distinguished as they differ in mass (Kendall and Caldwell, 1998). Due to the kinetics and thermodynamics of chemical reactions, heavier isotopes require larger activation energies for reactions to occur (measured as kinetic isotope effects). Thus, in environmental systems lighter isotopes are preferentially incorporated into and removed from compounds; this is conventionally known as kinetic isotope fractionation (Freeman, 2001; Kendall and Caldwell, 1998; Hayes, 1993). Subsequently, the degree to which any produced compounds differ in isotope composition from their source material becomes a function of the pathway the chemical reaction follows and constraints due to the isotope composition of the source material (Hayes, 1993).

The stable carbon isotope composition ($\delta^{13}C_{org}$) of OM in lake sediments is especially useful in determining past productivity trends. Values are expressed in conventional delta notation relative to a standard, Vienna Pee Dee Belemnite (VPDB) and reported in units of parts per thousand (‰):

$$\delta^{13}C = [(^{13}C/^{12}C_{sample})/(^{13}C/^{12}C_{reference})-1]x10^3$$

Isotopic fractionation can and does occur during carbon fixation (i.e. production in the water column) due to variations in the concentration of aqueous CO_2; this fractionation is then reflected in the $\delta^{13}C$ of primary photosynthate (Fogel and Cifuentes, 1993; Goericke et al., 1994). Essentially, ^{12}C is more energetically favorable than ^{13}C in the assimilation of CO_2 during photosynthesis. As photosynthesis increases, reserves of ^{12}C within the water column become depleted and discrimination of ^{13}C is reduced. Therefore, in the absence of other factors, e.g. changes in pH, temperature, nutrient availability, growth rate, and community composition (see: Beardall et al., 1982; Takahashi et al., 1990; Fogel and Cifuentes, 1993; Hinga et al., 1994; and Laws et al., 1995), any increase in productivity will yield an increase in the $\delta^{13}C$ of OM that is produced in the lake and subsequently buried in its sediment. Terrigenous productivity and source identification gathered from $\delta^{13}C_{org}$ is based on the difference in isotope composition of C_3 (trees, shrubs and cold season grasses) and C_4 (tropical and temperate grasses) plants. In general, $\delta^{13}C_{org}$ values of -27‰ and of -14‰ are seen for C_3 and C_4 plants, respectively (O'Leary, 1981).

The $\delta^{13}C$ found in atmospheric CO_2 is widely acknowledged to be influenced by the historic and continued burning of fossil fuels, called the Suess Effect (Gruber et al., 1999; Verburg, 2007). Thus, $\delta^{13}C$ analysis requires a correction factor to interpret data from OM produced between 1700 A.D. and present (Verburg, 2007).

In addition to $\delta^{13}C_{org}$, stable nitrogen isotope compositions ($\delta^{15}N$) can also be used to identify sources of OM to lakes and reconstruct past productivity. Values of $\delta^{15}N$ are expressed in delta notation as relative to air and reported in units of parts per thousand (‰):

$$\delta^{15}N = [(^{15}N/^{14}N_{sample})/(^{15}N/^{14}N_{air})-1]x10^3$$

The interpretation of $\delta^{15}N$ is generally more complicated than $\delta^{13}C$, due to the myriad reactions involved in the assimilation of nitrogen. Yet, it can provide valuable insight when combined with additional proxies (Talbot, 2001). The fundamental difference in the availability of inorganic nitrogen reservoirs available to plants in water and those on land is what makes the application of $\delta^{15}N$ values to identify OM sources possible (Meyers, 2003). The isotopic difference between these sources of nitrogen is roughly preserved in the $\delta^{15}N$ values in lake sediments. $\delta^{15}N$ values of OM from algae are typically +8.5‰, whereas the $\delta^{15}N$ values for land plants are +0.5‰, as presented by Peterson and Howarth (1987). The interpretation of these values can be complicated by various factors. Shifts in biotic assemblage, source deliveries (agricultural runoff and human sewage), and biogeochemical cycling each introduce complications (Meyers, 2003; Talbot, 2001).

Molecular Biomarker Proxies – Bulk proxies represent the whole mixture of OM components, and while biomarker proxies represent a smaller fraction of this total mixture, they have the ability to convey important details of individual sources and diagenetic pathways not readily ascertained from bulk OM proxies alone.

Hydrocarbon Biomarkers

N-alkanes, linear aliphatic hydrocarbons, are lipid biomarkers of particular interest as they are the most refractory of the lipid classes. They are the predominant component of epicuticular waxy coatings of plants and can be a robust recorder of the origins of OM in lake sediments, while constituting less than a percent of sediment OM. There are two principal sources of hydrocarbons to lake sediments; organisms that live within a lake (autochthonous/aquatic production) and those that live around it (allochthonous/terrigenous production). Each source produces a distinctive set of hydrocarbons, so their characteristic molecules serve as proxies for the source and delivery of OM. Lacustrine paleoproductivity is reflected in the abundances of the odd sequenced, lower numbered *n*-alkanes; C_{15}, C_{17}, and $C_{19.}$ Vascular land plants produce large proportions of C_{27}, C_{29}, and C_{31} *n*-alkanes in their epicuticular waxy coatings. The relative abundances of both short and long chained *n*-alkanes found in lake sediments therefore reflect the proportion of OM produced within and around a lake (Meyers, 2003).

N-alkane biomarkers are not immune to paleolimnetic changes and diagenetic alterations. Studies have shown that short chain aquatic *n*-alkanes are preferentially degraded in the water column, relative to their long chain homologs (see: Meyers, 1993 and references therein). Thus, preferential degradation of algal components ultimately biases the lipid record of OM sources retained in sediments. Sediment grain size also influences the concentration of *n*-alkanes held within sediments. For the most part, *n*-alkanes and total extractable lipid concentrations decrease with decreasing particle size; an exception to this is seen with clay-sized particles, owing to their larger surface area per unit volume and sorptive capacities (Thompson and Eglinton, 1978). Thompson and Eglinton (1978) also show that in finer-grain-sized sediments *n*-alkanes tend to have more microbial reworking than in coarser sediment, due to each sizes respective sinking rate and exposure time in the water column. On the other hand, terrigenous biomarkers have to be considered in terms of both the areas of erosion that supply them and the selectivity and rates of transfer and deposition by transport processes.

The relative aquatic and terrigenous fluxes of OM to lake sediments are determined from the ratio of terrigenous to aquatic hydrocarbons (TAR_{HC}), shown below (adapted from Meyers, 1997):

$$TAR_{HC} = (C_{27}+C_{29}+C_{31})/[(C_{27}+C_{29}+C_{31})+(C_{15}+C_{17}+C_{19})]$$

By calculating the ratio in this manner the resulting year to year flux values are easier to compare as they will always lie between 0 and 1; values greater than 0.5 would represent a greater flux of terrigenous materials, while values less than 0.5 would represent a greater aquatic flux.

Compound-Specific Isotopes

Studying the stable carbon isotope composition of *n*-alkanes ($\delta^{13}C_{n\text{-alkane}}$) may reveal changes in particular sources of OM and act as an independent verification of changes in primary production and changes in the contribution of sources that are not readily conveyed by bulk organic matter proxies alone. Interpretation of compound specific isotopes requires some finesse, as isotope compositions of individual sedimentary hydrocarbons are determined by isotope effects associated with specific reactions of biosynthesis and diagenesis that are unique to the molecule.

Scope and Framework of this Study

The aim of this study is to reconstruct trends in primary productivity in Lake Superior over the last 10,000 years using bulk and molecular biomarker proxies of sedimentary OM. This will ultimately provide a historical context in which to assess any anthropogenically induced changes in the trophic state of Lake Superior that have transpired over the last 200 years (time of human habitation of the region).

Chapter 1: Introduces the methods of organic geochemical analysis and the development of age models used in the present study.

Chapter 2: Addresses changes in the trophic state of Lake Superior over the last 10,000 years using bulk OM proxies from three piston and corresponding gravity sediment cores; providing a contextual historic baseline in which to assess anthropogenic influences on the sedimentary geochemical record during the time of human habitation of the region (1700 A.D. to present).

Chapter 3: Provides a high resolution record of lake-wide paleoproductivity using bulk OM proxies from eight sediment multicores in order to assess changes in primary productivity over the last 200 years (the time of human habitation of the region) within Lake Superior.

Chapter 4: Focuses on the application and use of *n*-alkane biomarkers as indicators of OM source changes over the last 10,000 years within Lake Superior.

CHAPTER 1

Methodology and Age Modeling

1.1. METHODS

1.1.1. Sediment cores

Chapter 2: Three lake sediment cores were retrieved using a Kullenberg piston corer aboard the R/V Blue Heron from Lake Superior (Figure 1-1; latitude and longitude listed in Table 1-1); one in 2002 (**Split Rock – SR**), one in 2009 (**Keweenaw – KW**), and one in 2011 (**Isle Royale – IR**). Gravity cores were also taken as trigger cores corresponding to each of the three piston cores, providing a more complete sediment core record.

Chapter 3: Eight sediment multicores, designed to capture the sediment water interface, were collected aboard the R/V Blue Heron from each basin of Lake Superior (Figure 1-1; latitude and longitude listed in Table 1-2); one in 2003 (**BH03-3**), three in 2009 (**BH09-**2, **BH09-3**, **BH09-4**) and four in 2010 (**LG MC**, **IR MC**, **EM MC**, and **CM MC**).

Initial core description and splitting were performed at the National Lacustrine Core Repository (LacCore). Subsamples were taken from each multicore at 0.5 cm intervals to 10 cm and every 1 cm thereafter to depth and from each gravity and piston core at 10 cm intervals to the base of the core. Sediment samples were subsequently frozen and freeze-dried for geochemical analyses.

1.1.2. Elemental and stable isotopic analysis of carbon and nitrogen

1.1.2.1. Sample Preparation

Homogenized dry sediment samples of known weight (12-20 mg), were placed into silver (Ag) foil capsules in designated sample trays and 1 μL of nanopure filtered H_2O was dispensed into each sample capsule. Sample trays were then placed in a desiccator, sans desiccant, containing a 200 mL beaker of 12M HCl for 8 hours to

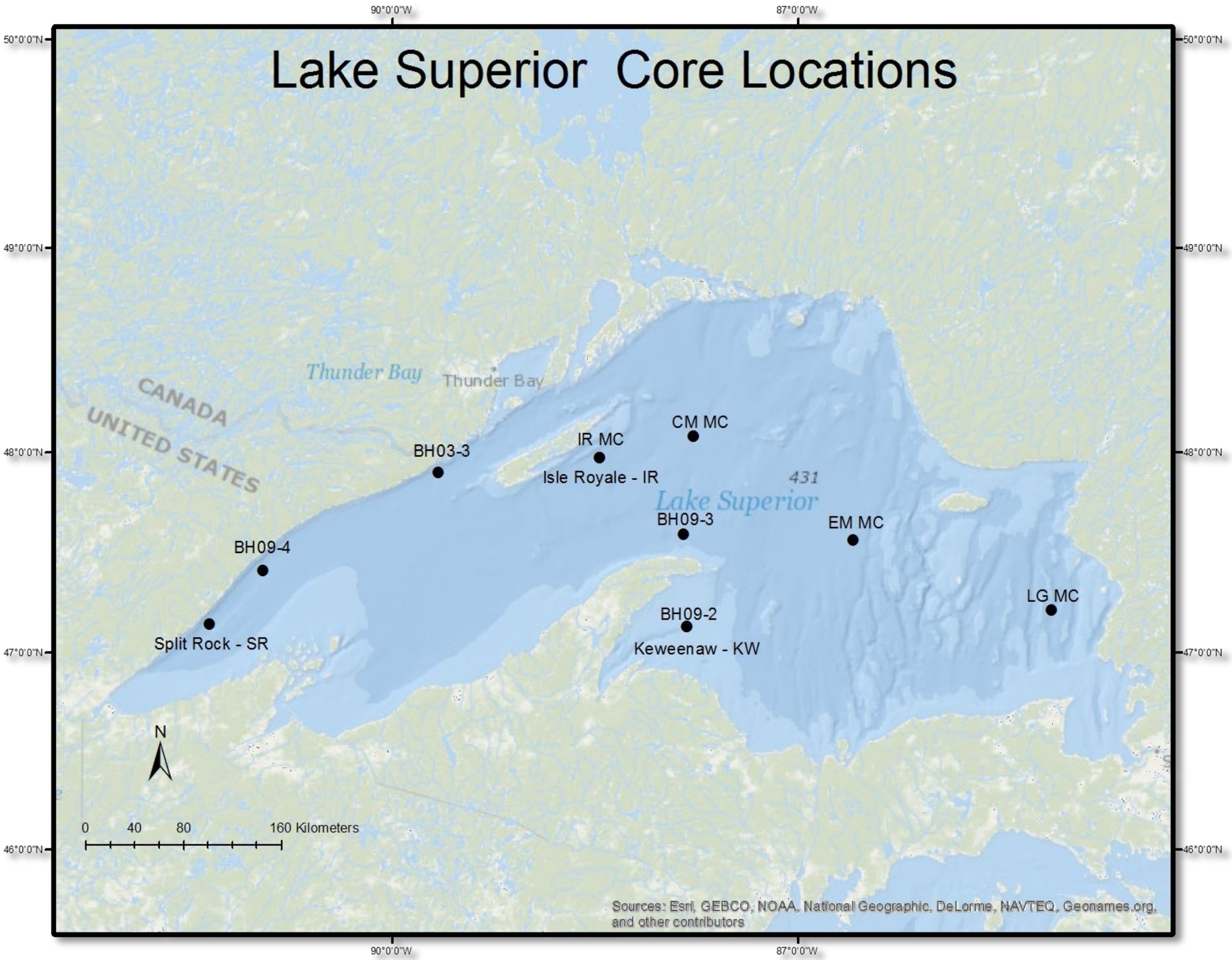


FIGURE 1-1. Locations of the three piston cores (**Split Rock – SR**, **Keweenaw – KW**, **Isle Royale – IR**) and eight sediment multicores (**BH03-3**, **BH09-2**, **BH09-3**, **BH09-4**, **LG MC**, **IR MC**, **EM MC**, **CM MC**), corresponding latitude and longitude are listed in Tables 1-1 and 1-2.

CORE	Year Taken	Degrees, Minutes, Seconds		Sedimentation Rate (mm/yr)	
		Latitude - N	Longitude - W	Current Study	Kemp et al. (1978)
Split Rock – SR	2002	47° 8' 25.8"	91° 21' 3"	0.63	0.89
Keweenaw – KW	2009	47° 7' 42"	87° 49' 15.6"	0.78	1.42
Isle Royale – IR	2011	47° 58' 24.8"	88° 28' 6.24"	0.47	0.28-0.50

TABLE 1-1. Data listed for the three piston sediment cores. The far right columns provide a comparison between calculated sedimentation rates from the current study and those from Kemp et al. (1978).

CORE	Year Taken	Degrees, Minutes, Seconds		MARS		Bioturbation Zone	
		Latitude - N	Longitude - W	$g/cm^2/yr$	Depth (cm)	Depth (cm)	Years
BH03-3	2003	47° 53' 57"	89° 39' 35"	0.0175	0-10	1.25	9
BH09-2	2009	47° 7' 4"	87° 49' 12"	0.0252	0-20	1.5	9
BH09-3	2009	47° 35' 24"	87° 50' 48"	0.0135	0-4	1.5	17
				0.0193	4-20		
BH09-4	2009	47° 24' 42"	90° 57' 24"	0.0179	0-5	1.5	9
				0.0269	5-20		
LG MC	2010	47° 12' 39"	85° 7' 39"	0.0336	0-18	2.0	4
				0.0269	18-25		
IR MC	2010	47° 58' 23"	88° 27' 58"	0.0161	0-4	1.5	11
				0.0359	4-8		
				0.0135	8-15		
EM MC	2010	47° 33' 43"	86° 35' 24"	0.0091	0-8	1.0	13

TABLE 1-2. Data listed for the eight sediment multicores. MARs have not been constant across Lake Superior over the last 200 years. The far right columns display the varying years encompassed by the bioturbation depth in each core.

remove inorganic carbon from the sediment (acid fumigation). Upon removal, samples were allowed to off-gas residual HCl while being dried on a hotplate set at 60°C; drying time was on the order of 12 hours. In order to ensure dryness samples were additionally placed in an oven set at 60°C overnight. Dried samples were then folded in tin (Sn) foil capsules.

1.1.2.2. Elemental and isotopic analyses

Total organic carbon (TOC) and nitrogen (TON) abundances of bulk sedimentary organic matter were analyzed for weight percent C and N concurrently with isotope ratio determinations. All concentrations are presented for acid fumigated (decarbonated) samples, eliminating variability caused by carbonate concentrations within samples. N_2 and CO_2 peak areas (Isodat v3.0) were converted to weight percent compositions using response factors generated from standards of known composition. Analyses were performed at the Large Lakes Observatory (LLO) Stable Isotope Lab using a Costech Elemental Analyzer coupled with a ThermoFinnigan Delta^{plus}XP stable isotope ratio monitoring mass spectrometer (EA-IRMS). Every tenth sample was run in duplicate. Values are given in standard delta notation as per mil (‰) deviations from the Vienna Pee Dee Belemnite (VPDB) standard.

1.1.3. Lipid analysis for molecular biomarkers

1.1.3.1. Extraction and Separation

Total lipid extract (TLE) was obtained from homogenized dry sediment samples (weighing between 2 and 20 g) that were mixed in a qualitative ratio (4 to 1 by weight) with extracted diatomaceous earth (DE - which acts as an anticaking agent, allowing for maximum lipid extraction) by a DIONEX Automated Solvent Extractor (ASE) 350, using a solvent ratio of 9:1 dichloromethane/methanol (DCM/MeOH), a temperature of 500°C and pressure of 1500 psi.

After sulfur removal by activated (reduced) copper beads, TLEs (not exceeding 5 mg in weight) were separated into individual hydrocarbon classes by activated (150°C for 2 hrs) alumina column chromatography using solvents of increasing polarity (9:1

hexane/DCM, 2:1 DCM/MeOH, and MeOH, for aliphatic/apolar, aromatic, and polar compounds, respectively). The *n*-alkanes were present in the first (apolar) fraction; this fraction was next passed through a Ag^+ impregnated silica pipette column to separate saturated and unsaturated hydrocarbons. The saturated fraction was eluted first with *n*-hexane and was dried under a stream of N_2 gas.

1.1.3.2. Quantification and Identification

The saturated fraction was quantified using an Agilent 6890 Gas Chromatograph (GC) equipped with a 7683 auto-sampler, flame ionization detector (FID) and flame photometric detector (FPD), and fitted with an HP-1 capillary column (320 μm i.d. x 30 m). Aliquots (1 uL) of each saturated fraction were injected (splitless) and separated within the GC using a temperature program of 50°C for 5 min, 10°C min^{-1} to 130°C, and 4°C min^{-1} to 320°C, using He as a carrier gas with a flow rate of 1.5 mL min^{-1}. An internal standard (androstane) was added to each sample prior to injection for quantification of individual *n*-alkanes. Identification of *n*-alkanes was accomplished using an Agilent 6890A Series GC System equipped with an Agilent 5973 single quadrupole mass spectrometer (GC/MS). GC/MS conditions used were the same as GC/FID-FPD conditions.

1.1.3.3. Compound Specific Isotope Analysis

Stable carbon isotope compositions of individual *n*-alkanes were determined with a ThermoFinnigan $Delta^{Plus}XP$ isotope ratio mass spectrometer, using a modified GCC III interface (GC-C-IRMS). Two uL aliquots of each saturated fraction were injected (splitless) onto an HP-1 capillary column (320 μm i.d. x 60 m) and the following temperature program was used during chromatography: 50°C for 1 min, 10°C min^{-1} to 130°C, and 4°C min^{-1} to 320°C. The splitless injector was maintained at 300°C, and the combustion column at 940°C. Reference CO_2 was introduced into the mass spectrometer before and after elution of the *n*-alkanes while column eluent was diverted. Squalane was co-injected with each sample as an internal isotopic standard. Calibration was performed using a mixture of *n*-alkanes (C_{16} to C_{30}, Schimmelman “Mix A”) of known isotopic value. Samples were run in duplicate, with reproducibility better than 0.5‰. In all samples the C_{17} *n*-alkane was not clearly present in enough abundance to obtain an accurate isotopic measurement. Values are expressed in conventional delta notation as per mil (‰) deviations from the Vienna Pee Dee Belemnite (VPDB) standard.

1.2. AGE MODELS

1.2.1. ^{210}Pb Geochronology

^{210}Pb is a widely used, robust method of dating sediments younger than 150 years. The total signal of ^{210}Pb in lacustrine sediments consists of background (supported) ^{210}Pb, which is present due to clastic material washed in from the surrounding landscape and unsupported (excess) ^{210}Pb, which originates from atmospheric deposition (Oldfield and Appleby, 1984). Unsupported ^{210}Pb concentrations are thus the portion of the total signal used for dating; determined by alpha (α), beta (ß), or gamma (γ) - spectrometry in the laboratory.

Multicores were sub sampled at alternating 0.5 cm intervals to 10 cm depth and alternating 1 cm intervals from 10 to 20 cm. Samples at depth were included to determine the background (supported) ^{210}Pb activity. Unsupported ^{210}Pb activity should be negligible at depth, where sediment age expected to exceed 150 years (>6 half-lives). The cores were not analyzed for Cs-137 because the Cs-137 peak in large lakes typically falls at an age younger than the time of maximum atmospheric concentration due to a lag in Cs-137 transport to its final depositional site (Edgington and Robbins, 1990). The ^{210}Pb analyses for the 2003 and 2009 cores were carried out by α-spectrometry in the Department of Soil Science, University of Manitoba, under the direction of Dr. Paul Wilkinson, and at Flett Research Ltd. in Winnipeg, Manitoba under the direction of Dr. Robert J. Flett for the 2010 cores.

The age-depth relationships of the eight cores were estimated from semi-log plots of excess ^{210}Pb activity versus accumulated sediment mass (Figure 1-2) using methods described in Johnson et al. (2012). The slopes of the straight-line segments lower in the core are proportional to sediment mass accumulation rates (MARs), which are applied to arrive at sediment age at each horizon. A bioturbation zone is apparent in the uppermost core and exhibits the steepest slope (Edgington and Robbins, 1990; Robbins and Edgington, 1975). The MAR for this zone is assumed to be constant, and equal to that derived from the slope of the line segment immediately below the bioturbation zone. An excursion occurs in core BH09-4 between 3 and 7 cm and is attributed to the effects of mining beginning in 1955, with court-ordered reductions in effect by 1980; therefore, MARs for this portion are assumed to be equivalent to the slope of the segment immediately above this disturbance, but below the bioturbation zone.

The ^{210}Pb data reveal a bioturbated zone of 1.5 cm on average (Table 1-2) in all cores, which is consistent with Evans et al. (1981). Each zone is equivalent to 9 years in cores BH09-2, BH09-4, and BH03-3; 17, 4, 11, 13, and 18 years of sedimentation for cores BH09-3, LG MC, IR MC, EM MC, and CM MC respectively. MARs in Lake Superior have not been constant over the periods of depositional history recorded in the cores, shown in Figure 1-2 and listed in Table 1-2.

1.2.2. Records of Paleomagnetic Secular Variation (PSV)

Paleomagnetism is an often-used method for the age modeling of lacustrine sediments, especially where measurements of ^{14}C are unsuccessful. Radiocarbon dates are limited in Lake Superior, as macrofossils for dating are rarely present. Additionally, sediments of gravity and piston cores present in the current study are too old for ^{210}Pb dating. Thus wiggle matching via records of PSV are the best method for dating Lake Superior sediments (e.g., Breckenridge et al., 2004). PSV records document regional variations in inclination and declination, which reflect variations in the earth's magnetic field with time. Ferromagnetic grains (e.g., magnetite) align themselves with the local magnetic field during or shortly after deposition, upon consolidation of the sediments the motion of these grains is constrained. Any magnetization acquired by the magnetic grains long after deposition is then removed in the laboratory by alternating field (AF) demagnetization at low fields. In contrast, the natural remanent magnetization (NRM) removed at higher demagnetization fields is assumed to have resulted from burial in the presence of the local magnetic field (Butler, 1994). The PSV records from the post-glacial sediments are 10–100 year averages of the regional field, due to a 1–2 cm

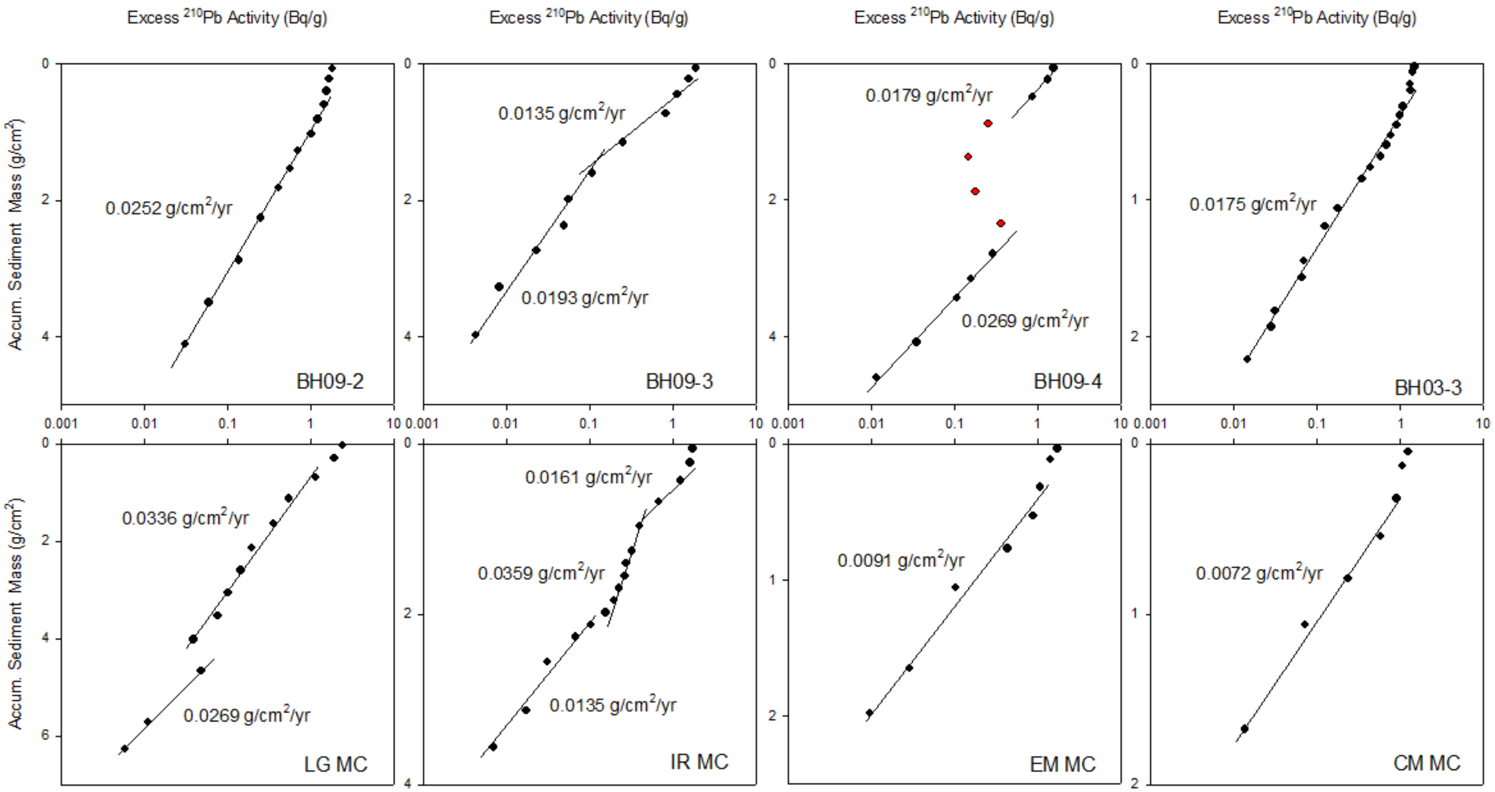


FIGURE 1-2. Excess ^{210}Pb vs. accumulated sediment mass in each core. The sediment mass accumulation rates (MARs) presented correspond to the linear segments that were fitted to the data illustrated in the linear portions of the eight cores from Lake Superior. The excursion seen in BH09-4, indicated in red, is attributed to the effects of mining off of Silver Bay.
*Note varying vertical scales.

bioturbation zone present in the top portions of Lake Superior sediments (Evans et al., 1981). By correlating PSV records from Superior with PSV records from regional, well-dated sites, ages can be assigned to sediment cores (Breckenridge et al., 2004).

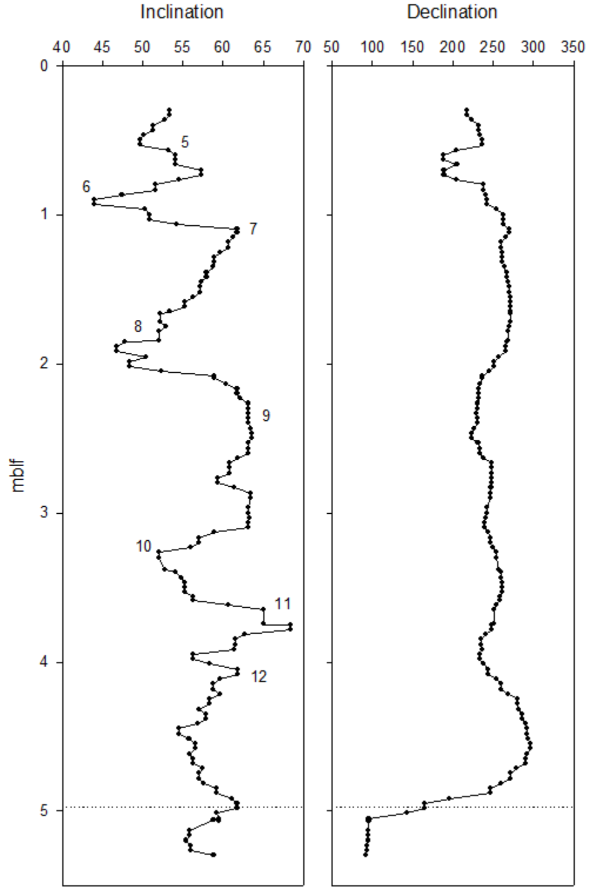
NRM, providing inclination and declination data for correlative purposes, was completed in 2004 at Michigan Technological University – Earth Magnetism Laboratory under the direction of Dr. Suzanne Beske-Diehl for core BH02-10P (Split Rock - SR) and by Dr. Julie Bowles at the Institute for Rock Magnetism at the University of Minnesota for the piston cores Keweenaw - KW in 2009 and Isle Royale - IR in 2012.

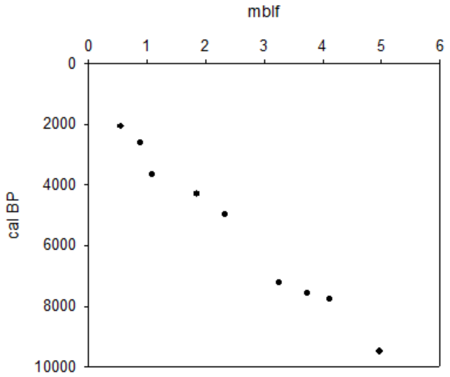
PSV data for the three piston cores were compared to a previously dated core, LU83-8 from Mothersill (1988). Site-specific age-depth profiles for each of the three piston cores were completed using LU83-8 ages and associated features for both inclination and declination (only those features that are clearly apparent in each PSV record were utilized in constructing an age-depth model). Ages of features apparent in each of the cores are presented as calibrated years before 1950.

Correlative features for each of the three cores are shown in Figures 1-3, 1-4, and 1-5. The equation of the regression line (linear in SR and KW and fifth degree polynomial in IR) from the resulting plot of age vs. depth from correlation with the previously dated core LU83-8 was then applied along the length of each of the cores providing the final age-depth assignments (Figures 1-3, 1-4, and 1-5). The R^2 coefficient of determination for the regressions determined from age vs. depth plots are 0.985, 0.990, and 0.995 for SR, KW, and IR piston cores respectively (Figures 1-3, 1-4, and 1-5). R^2 values close to 1 represent an almost perfect approximation between the regression line and the original data points.

Sedimentation rates were then calculated from the slope of the linear regression line fitted to data from both SR and KW cores, which assumes constant sedimentation throughout the last 9000 years (Saarnisto, 1975). Calculated sedimentation rates for SR and KW cores are 0.63 and 0.78 mm/yr respectively. The IR core displays varying sedimentation rates throughout the Holocene (a relatively fast rate after glacial retreat, a leveling off and gradual increase between 9000 and 3000 cal BP, and a slower rate most recently) with an average sedimentation rate of 0.47 mm/yr. The sedimentation rates are

SPLIT ROCK





LEFT: Inclination and declination plotted versus depth. PSV features (after Lund, 1996) used to construct the age model are numbered. The dashed line indicates depth of the glacial varves.

ABOVE: Age vs. Depth plot using LU83-8 ages and associated features for both inclination and declination. The resulting regression (below) was then fitted to the length of the core.

Regression:
$y = 1639.6x + 1361.8$
$R^2 = 0.9850$

RIGHT: Inclination and declination plotted versus age compared to LU83-8, after being fit using the regression. The solid line represents LU83-8 and the dashed line SR.

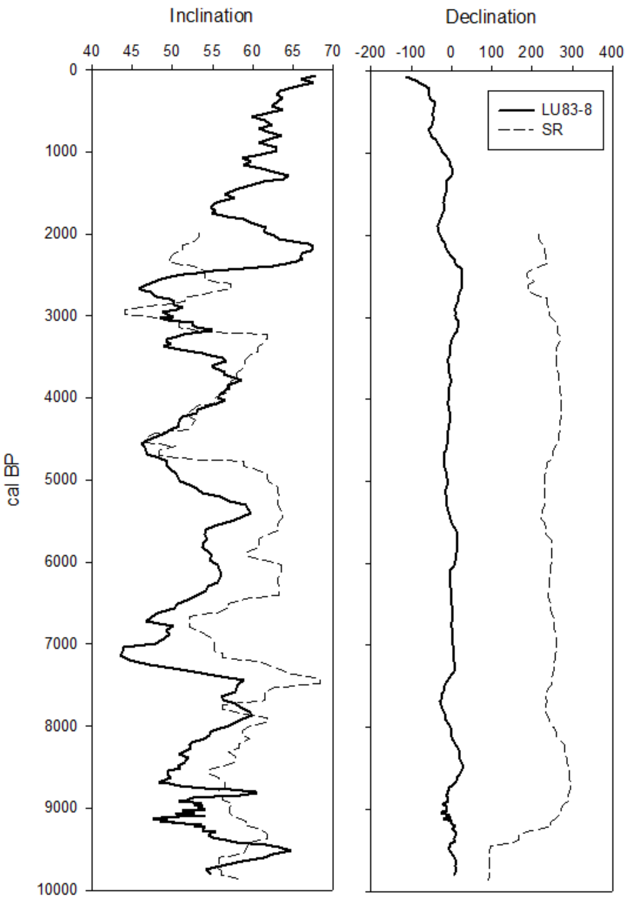
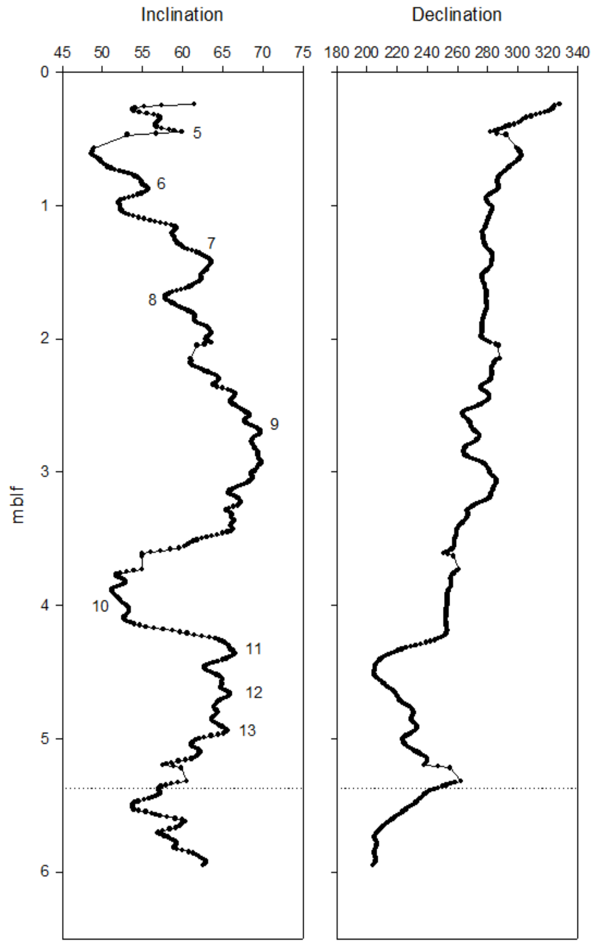
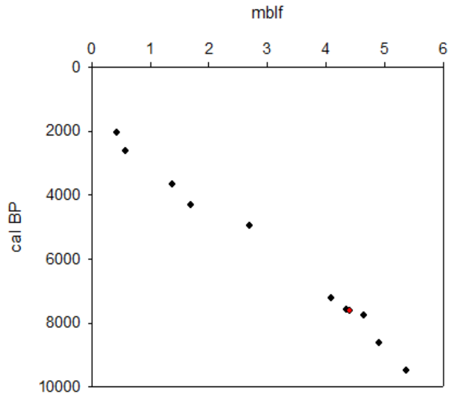
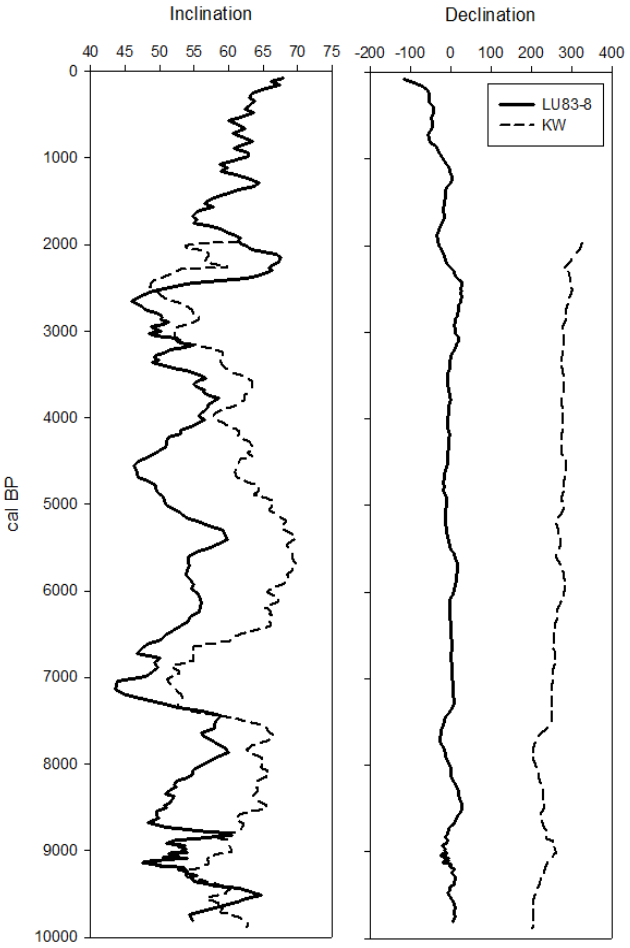


FIGURE 1-3

KEWEENAW







LEFT: Inclination and declination plotted versus depth. PSV features (after Lund, 1996) used to construct the age model are numbered. The dashed line indicates depth of the glacial varves.

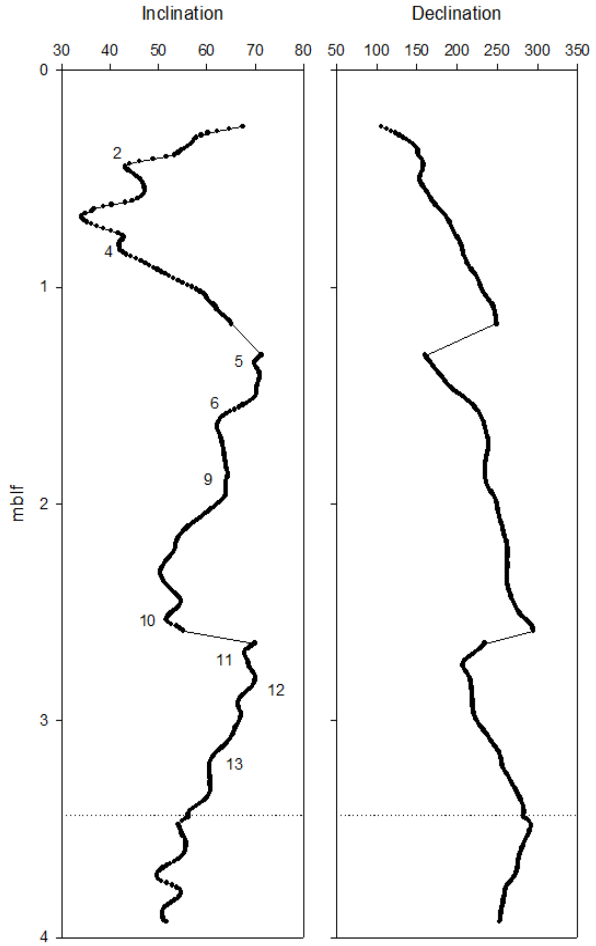
ABOVE: Age vs. Depth plot using LU83-8 ages and associated features for both inclination and declination. The resulting regression (below) was then fitted to the length of the core. The red data point indicates the age and depth of the Mazama ash layer.

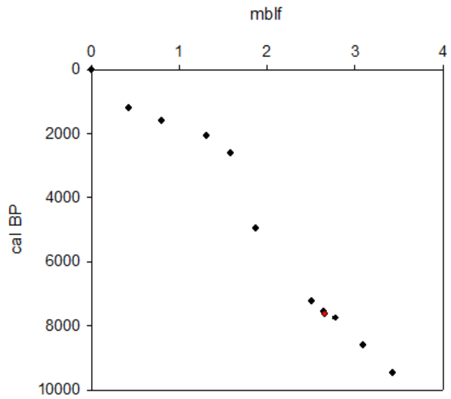
Regression:
$y = 1386.9x + 1636.6$
$R^2 = 0.9901$

RIGHT: Inclination and declination plotted versus age compared to LU83-8, after being fit using the regression. The solid line represents LU83-8 and the dashed line KW.

FIGURE 1-4

ISLE ROYALE





LEFT: Inclination and declination plotted versus depth. PSV features (after Lund, 1996) used to construct the age model are numbered. The dashed line indicates depth of the glacial varves.

ABOVE: Age vs. Depth plot using LU83-8 ages and associated features for both inclination and declination. The resulting regression (below) was then fitted to the length of the core. The red data point indicates the age and depth of the Mazama ash layer.

Regression:

$y = 177.56x^5 - 1850.6x^4 + 6500.7x^3 - 8429.3x^2 + 5227.3x + 30.217$

$R^2 = 0.9946$

RIGHT: Inclination and declination plotted versus age compared to LU83-8, after being fit using the regression. The solid line represents LU83-8 and the dashed line IR.

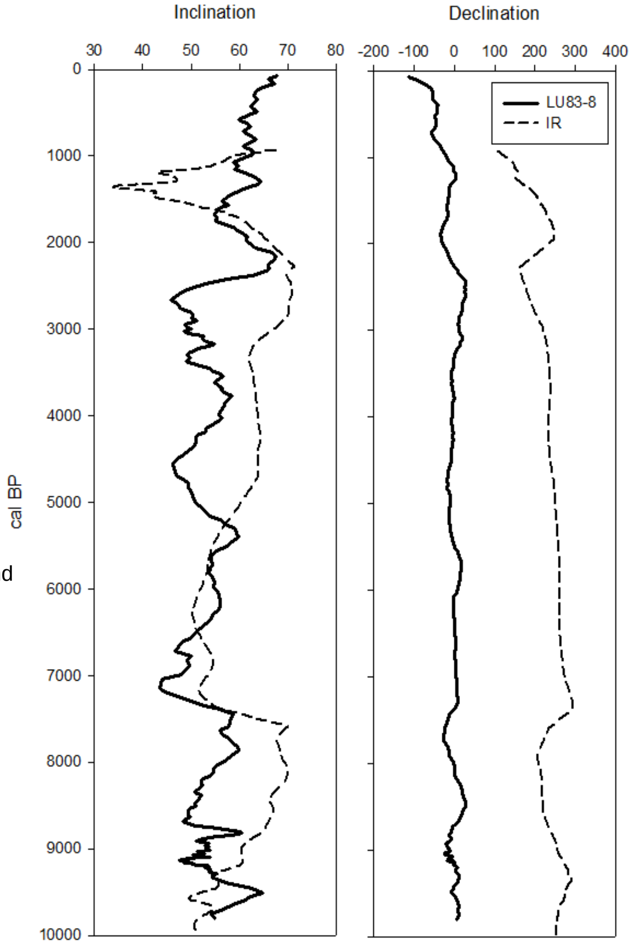


FIGURE 1-5

comparable to those of Kemp et al.'s (1978) average postglacial sedimentation rates from piston cores taken from similar depositional zones in Lake Superior (Table 1-1). Overall, the sedimentation rates calculated are more conservative than Kemp et al.'s (1978), but still follow the same trend, with the highest rates observed in the KW core, followed by SR, and finally IR.

1.2.3. Linear Extrapolation

Age/depth relationships for gravity cores were developed using linear extrapolation from the bottom of corresponding multicores (**SR – BH09-4**, **KW – BH09-2**, **IR – IR MC**) which had previous ^{210}Pb age assignments, as described above. Extrapolation from the ^{210}Pb age model of the multicores to the gravity cores makes the assumption that the gravity cores begin where multicores end. Although not an ideal assumption, this is a valid approach as it provides a conservative age model, in addition to the fact that over penetration of the sediment/water interface is common when recovering both gravity and piston cores whereas multicores are designed to capture the sediment/water interface. Sedimentation rates for the gravity cores are therefore set equal to the multicore sedimentation rate immediately above.

CHAPTER 2

A 10,000 Year Sedimentary Geochemical Record of Paleoproductivity within Lake Superior

2.1. INTRODUCTION: Lake Ontogeny

Postglacial evolution of many lake systems involves a process of ‘natural’ eutrophication, whereby lakes develop from a nutrient-poor, oligotrophic state to one of increased nutrient availability, or eutrophic state. Understanding the process of ‘natural’ eutrophication is often complicated by the many factors that control development (e.g., terrigenous vegetation, soils, hydrology, and changing climate regimes).

Many of the biological responses to changes in nutrient input or availability become preserved in the sedimentary record. This allows us to describe historical changes in lakes, traditionally through the use of total organic carbon content (TOC). A typical pattern of temporal changes in organic carbon for north-temperate lakes is shown in Figure 2-1, (adapted from Whiteside, 1983). This curve shows the initial increase in organic carbon content following glacial retreat (Zone A), a period of ‘trophic equilibrium’ (Hutchinson, 1973; Zone B), and a period reflecting the activities of modern man (Zone C). According to Whiteside (1983) Zone C may have increased or decreased carbon content depending on the primary influence by deposition of either allocthonous or autochthonous organic matter to lake sediments.

There are complications in interpreting changes in the accumulation of TOC as directly related to changes in the availability of nutrients. These can arise from changes in sedimentation rates during lake development, as well as uncertainty of the source of carbon (allocthonous vs. autochthonous). Changes in autochthonous carbon accumulation can also occur independently of changes in nutrient input (i.e. changes may not be a function of increased/decreased nutrient input to the lake). Schindler (1978) has shown that an increase in water residence time, with no accompanying change in nutrient status (i.e. constant supply of nutrients), can increase biomass while primary productivity remains constant. A decrease in water residence time with no additional nutrient input

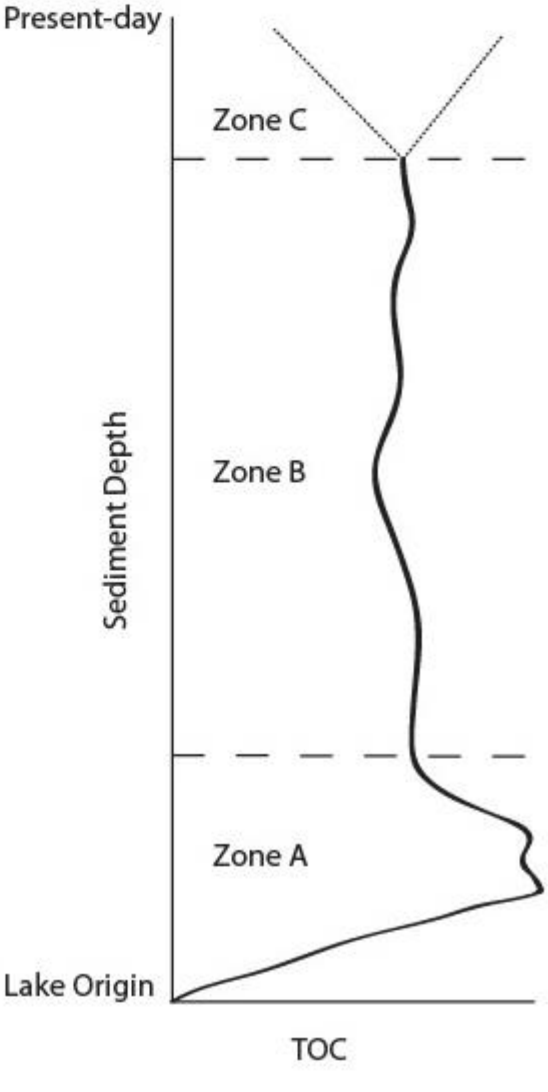


FIGURE 2-1. Temporal changes in organic carbon typical in north-temperate lakes, adapted from Whiteside (1983).

changes would then be reflected as a decrease in sedimented carbon (Hutchinson, 1973). Thus, most paleolimnological studies employ the use of a variety of bulk organic matter proxies (e.g. elemental abundances of both carbon and nitrogen, as well as their stable isotope compositions) in order to address paleoproductivity changes and associated lake ontogeny.

2.2. BACKGROUND: Lake Superior Formation and Early Watershed Maturation

The Lake Superior basin is the result of a series of geologic events beginning over one billion years ago, during the Precambrian, as the North American continental crust separated to form a rift. The rifting continued for 20 million years, allowing molten rock to flow; forming the bedrock of the Lake Superior basin (Habermann et al., 2012). Weathering and glacial scouring shaped Lake Superior into its current form. The Lake Superior basin has been subject to many changes since its formation approximately 13,000 cal BP (Hough, 1958; Prest, 1970; Saarnisto, 1975). Climatic fluctuations, both regional and global, caused changes in temperature and precipitation, in addition to several glacial advances and retreats associated with the Laurentide Ice Sheet (LIS). These glacial dynamics produced differing in-lake conditions until approximately 9000 cal BP when conditions approached those of modern day, as evidenced by glacial varve cessation and the oxygen isotope compositions of ostracode valves (Breckenridge and Johnson, 2009; Hyodo and Longstaffe, 2012).

Maturation of the surrounding watershed/landscape could have impacted in-lake conditions as the co-evolution of root systems and soils would conceivably intensify the weathering of mineral nutrients such as P and Fe, increasing their availability for both terrestrial and lacustrine production. Nitrogen availability would likely increase as well, because soil nitrogen stores increase from N_2 fixation by plants in recently deglaciated landscapes (Cooper, 1923; Reiners et al. 1971; Chapin et al. 1994). As the watershed became forested and regional temperature rose, following the retreat of the LIS, it can be anticipated that greater quantities of nutrients and carbon substrate were delivered to the lake; although terrigenous organic input to the Laurentian Great Lakes is generally considered to have been very small (Halfon, 1984; Meyers and Ishiwatari, 1993; Ostrom et al., 1998).

In order to assess changes, in-lake conditions and vegetative history should be captured in the sedimentary geochemical record. If so, we should expect to see them manifest in the paleoproductivity proxies as changes in TOC and TON concentrations along with their stable isotopes ($\delta^{13}C_{org}$ and $\delta^{15}N_{org}$) of bulk organic matter. Hyodo and Longstaffe (2011) have noted a mild increase in in-lake primary production, using the paleoproductivity proxies mentioned, in postglacial sediments from Lake Superior; however, only one of the four cores presented in their study approaches the most recent past (~300 cal BP).

This study reports trends in paleoproductivity throughout the Holocene within Lake Superior, using bulk elemental and stable isotope compositions of organic carbon and nitrogen of sedimentary organic matter from corresponding piston and gravity sediment cores taken from three locations across the lake. Additionally, the three cores are correlated to previously analyzed multicores from a high-resolution study of the last 200 years, the time of human habitation of the region. This provides a complete record of productivity changes within Lake Superior since its formation, as well as a baseline for the comparison of the more recent trends in productivity (the focus of Chapter 3) as recorded by bulk sedimentary organic geochemical proxies.

2.3. METHODS

See Chapter 1: Methods and Age Models.

2.4. RESULTS

2.4.1. Bulk Organic Geochemical Proxies

Total organic carbon and total organic nitrogen (reported as percent weight of dry sediment) display similar trends throughout the Holocene (Figures 2-2, 2-3, and 2-4). The lowest TOC and TON values occur in the oldest part of the record, before ~9000 cal BP, when the lake was still influenced by glacial meltwater (Breckenridge and Johnson, 2009). In general, values steadily increase after ~9000 cal BP from 1-3% for TOC and 0.1-0.3% TON, with greater increases observed in the last 200 years. The C_{org}:N_{org} record tracks changes in both TOC and TON records, with the highest (lowest) values occurring in unison with the highest (lowest) values of TOC and TON (Figures 2-2, 2-3, and 2-4).

Bulk sediment organic carbon isotopic values ($\delta^{13}C_{org}$) range from -32‰ to -24‰. The most ^{13}C-enriched values are observed in the last 200 years, where $\delta^{13}C_{org}$ values display a 2‰ increase (Figures 2-2, 2-3, and 2-4). A period of ^{13}C-depletion in the KW core is noted between ~9000 and 7000 cal BP, after which values increase until present (Figure 2-3). Interestingly, TOC, TON, and C_{org}:N_{org} ratios remain stable or increase slightly during the same time interval as the ^{13}C-depletion of bulk organic matter in the KW core. Within each of the three cores, the bulk stable isotopic values of nitrogen ($\delta^{15}N_{org}$) trend in the same manner as $\delta^{13}C_{org}$, until the last 200 years where a period of ^{15}N-depletion is noted.

The most salient feature in all three cores is the rapid increase of all bulk proxy data (decreases are noted in $\delta^{15}N_{org}$) during the last 200 years. The increase (decrease in $\delta^{15}N_{org}$) occurs faster than any other time interval in the history of Lake Superior reported here (Figures 2-2, 2-3, and 2-4).

2.5. DISCUSSION

2.5.1. Lake Ontogeny

The postglacial evolution of Lake Superior, as inferred from bulk geochemical proxy data, displays trends unlike those typical of north-temperate lakes following deglaciation (Whiteside, 1983). Initial TOC and TON abundances are low, less than 1% for TOC and near 0% for TON. As in-lake conditions approach those of modern-day following the termination of meltwater supply and initial collapse of the LIS between ~9000 and 8000 cal BP (Breckenridge and Johnson, 2009), TOC and TON values begin to increase concurrently. This correlation between TOC and TON (Figures 2-2, 2-3, and 2-4) is indicative of increasing primary productivity within Lake Superior. Atomic

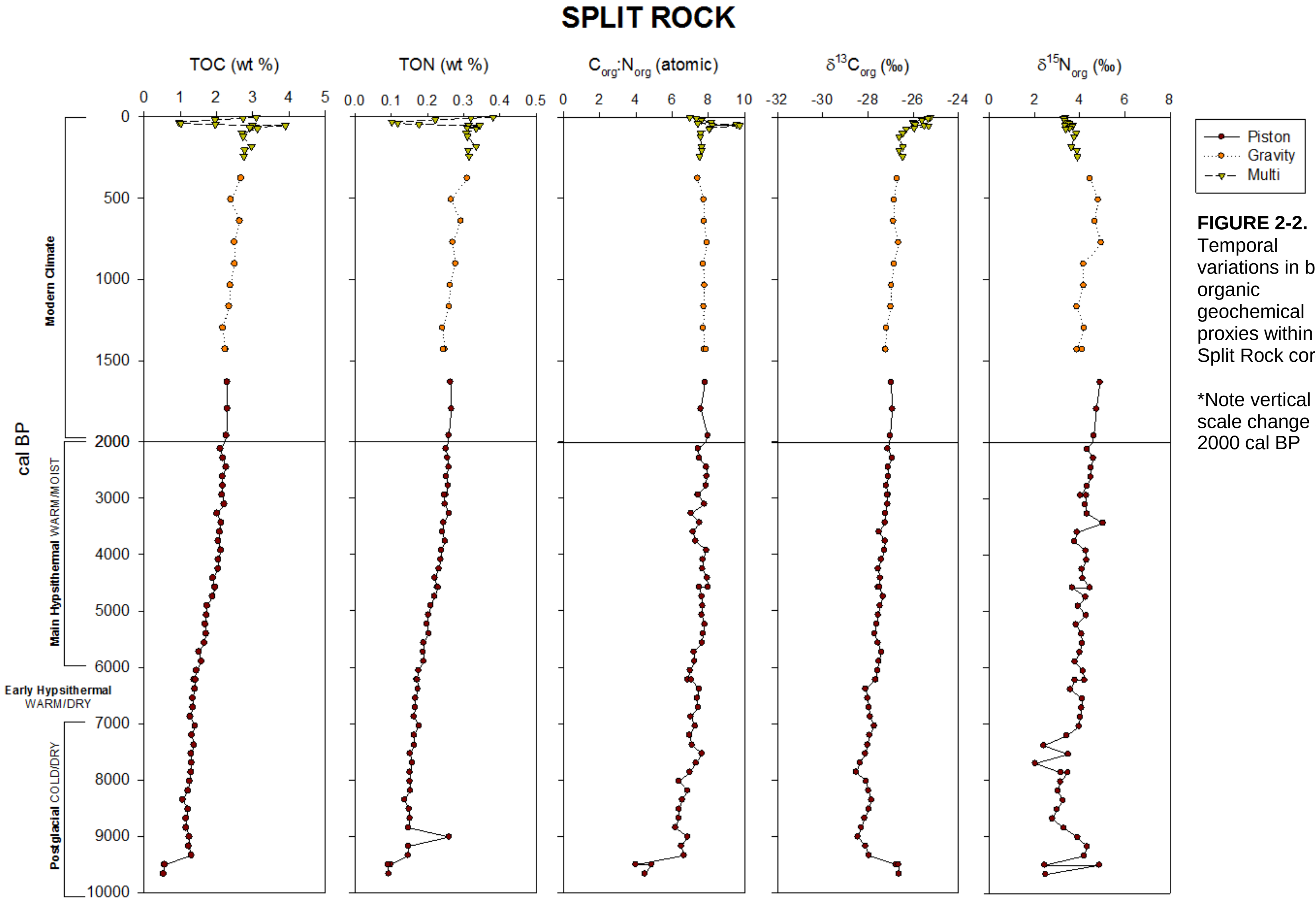


FIGURE 2-2. Temporal variations in bulk organic geochemical proxies within the Split Rock cores.

*Note vertical scale change at 2000 cal BP

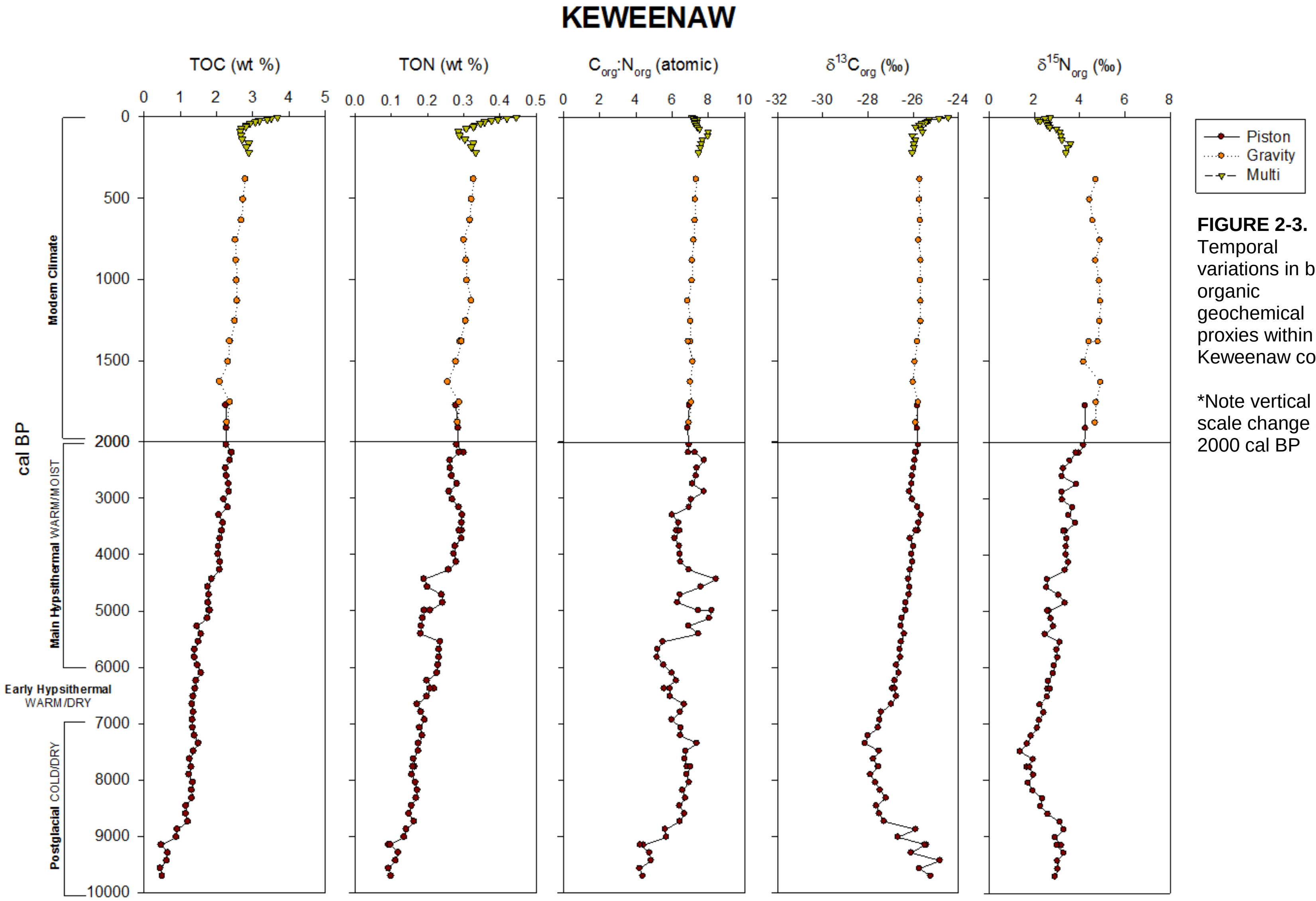


FIGURE 2-3. Temporal variations in bulk organic geochemical proxies within the Keweenaw cores.

*Note vertical scale change at 2000 cal BP

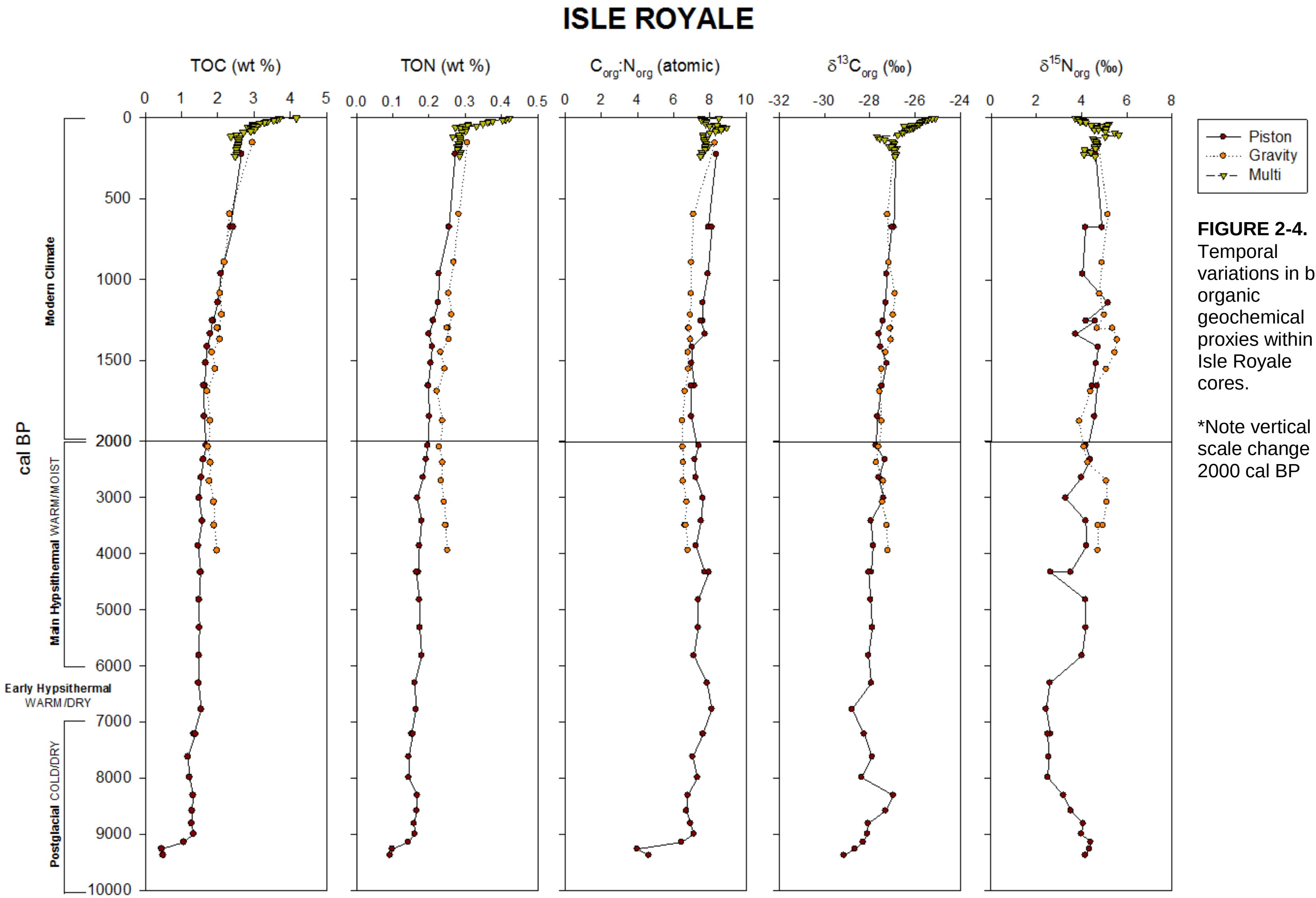


FIGURE 2-4. Temporal variations in bulk organic geochemical proxies within the Isle Royale cores.

*Note vertical scale change at 2000 cal BP

C_{org}:N_{org} ratios fall to around 7, which is also suggestive of sediments dominated by algal sourced organic matter (Meyers, 2003). Gradual, long-term increases in TOC and C_{org}:N_{org} suggest the possibility of slightly increased terrestrial input to the lake basin; however, a cross-plot of C_{org}:N_{org} vs. $\delta^{13}C_{org}$ (Figure 2-5) demonstrates that in-lake primary production is the dominant factor influencing the sedimentary organic record (Meyers, 2003). Throughout the entire post-glacial period (~9000 cal BP – present) values from all three cores plot in the range typical of lacustrine algae, rather than those of terrigenous C_3 or C_4 plants (Figure 2-5). Interestingly, Lake Superior seems to have never reached a state of stable organic carbon content (Zone B; Figure 2-1), but rather trends toward a consistent slow increase in primary production and sedimentary organic carbon content.

The stable isotope composition of organic matter ($\delta^{13}C_{org}$) is often used to infer changes in primary production within lake settings (Meyers, 2003) because the $\delta^{13}C$ of organic carbon produced photosynthetically is controlled by primary productivity in the water column. Essentially, due to kinetic isotope effects, ^{12}C is preferentially incorporated into algal biomass. As productivity (i.e. growth rate) increases, the ratio of $^{12}C/^{13}C$ in the water column decreases, thus greater amounts of ^{13}C are subsequently incorporated during periods of higher algal productivity. A long trend of gradually increasing $\delta^{13}C_{org}$ (Figures 2-2, 2-3, and 2-4) is observed through the Holocene, which is consistent with the notion of increasing primary production within Lake Superior inferred from other bulk proxy data. There are a number of other factors that can contribute to isotopic shifts in the $\delta^{13}C$ of algal biomass, however, without changing primary production within the water column. Changes in the source of inorganic carbon, isotope effects associated with carbon assimilation and metabolism, temperature effects, changes in nutrient concentrations, or shifts in the phytoplankton community structure could all influence the isotopic signature of bulk organic matter without actually increasing or decreasing primary productivity. Such scenarios; however, do not preclude the claim of increasing primary productivity, especially since the increases in $\delta^{13}C_{org}$ occur in concert with increases in other bulk proxy data.

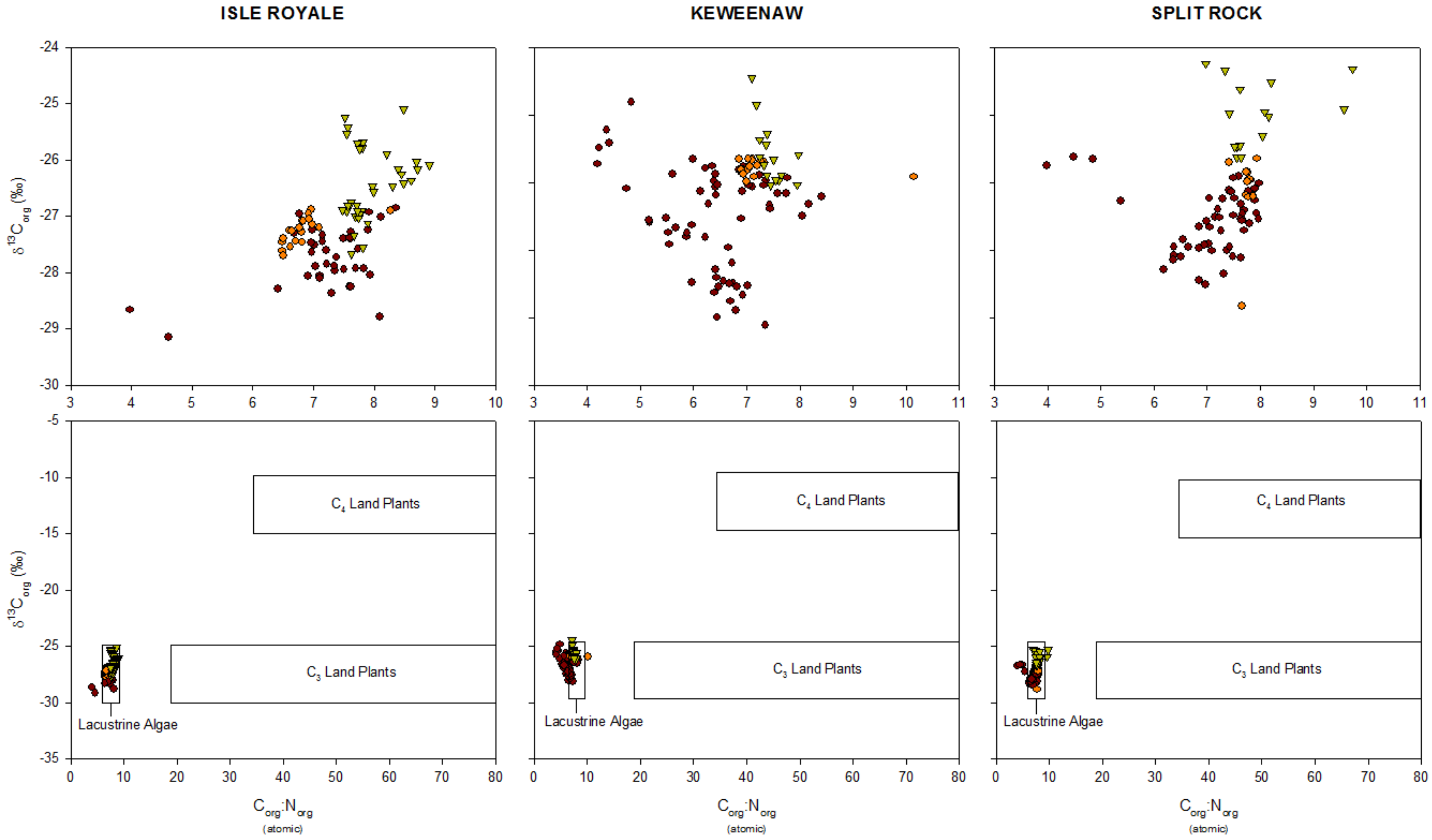


FIGURE 2-5. Cross-plots of C_{org}:N_{org} vs. $\delta^{13}C_{org}$ demonstrate that in-lake primary production is the dominant factor influencing the sedimentary organic carbon record through the Holocene in all three core locations from Lake Superior.

The stable isotope composition of organic nitrogen ($\delta^{15}N_{org}$) follows the trends in $\delta^{13}C_{org}$. The correspondence between these two proxies provides further indication of increasing primary production in Lake Superior. In general, increases in primary production will increase the utilization of dissolved inorganic nitrogen, thereby reducing algal discrimination against ^{15}N (Meyers, 2003), much like the kinetic isotope effects associated with the incorporation of ^{13}C. Because of the dynamics of the nitrogen cycle within lakes, other factors may influence the nitrogen isotope composition of primary producers, which are not necessarily related to increases or decreases in primary productivity. For example, during the process of denitrification $^{14}NO_3^-$ is selectively utilized by bacteria, leaving ^{15}N-enriched nitrate behind (Collister and Hayes, 1991). This enriched nitrate is subsequently incorporated during algal photosynthesis, leading to higher $\delta^{15}N$ values. Denitrification requires anoxic conditions, which do not occur in the water column of Lake Superior, and given the low TOC contents in sediments denitrification is not expected to be a significant process here either. Thus, the observation of concurrent increases in all bulk proxy data provides strong indication that productivity has increased throughout the Holocene within Lake Superior.

The period of ^{13}C and ^{15}N-depletion between ~9000 and 7000 cal BP in the KW core (Figure 2-3) could be due to a decrease in productivity; however, TOC and TON do not show this same decrease, suggesting that this period of ^{13}C-depletion is most likely the result of other factors. The transport of isotopically light sources of carbon and nitrogen from the developing watershed after the collapse of the LIS is a more plausible scenario. These isotopically light source materials would subsequently be utilized by primary producers thereby accounting for the decreases in $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$. This hypothesis is further supported by increases in C_{org}:N_{org} during the same time period. It is worth noting that this period, ~9000 and 7000 cal BP, is characterized by a cold and dry climate with an abrupt shift to warm and dry conditions (onset of the hypsithermal) at 7000 cal BP, which would additionally favor increases in lacustrine productivity.

The most recent changes in $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ during the last century in all the cores are unprecedented and can be attributed to recent climatic changes, as well as other anthropogenic influences (see Chapter 3 for a more thorough discussion). These changes

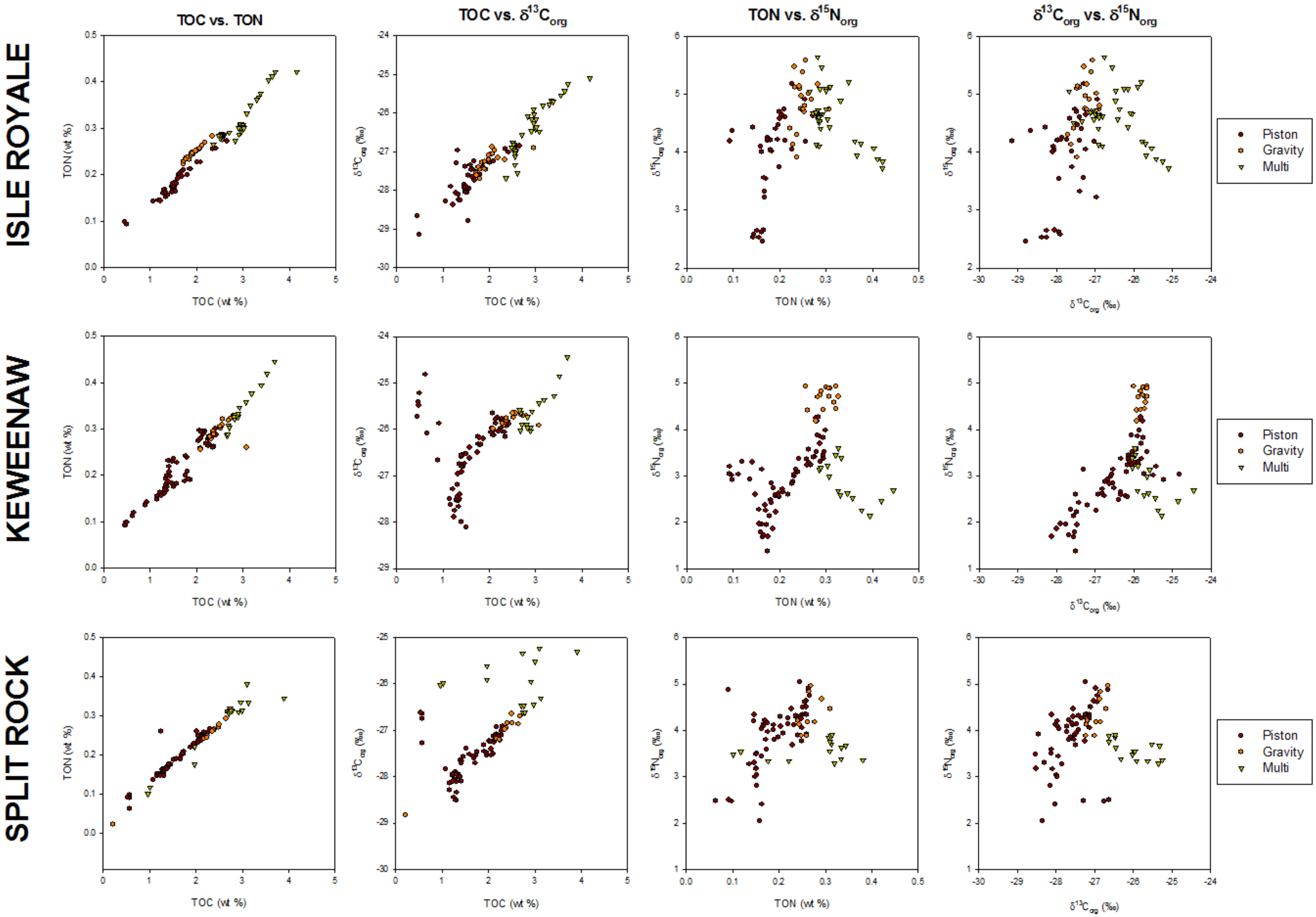


FIGURE 2-6. Cross-plots of bulk organic geochemical proxy data demonstrate that in-lake primary production is the dominant factor influencing the sedimentary organic record through the Holocene in all three core locations from Lake Superior.

correspond to Zone C (Figure 2-1) from Whiteside et al. (1983), a period reflecting the activities of modern man and of 'cultural' eutrophication. The bulk sedimentary organic geochemical data presented here show a slow steady increase in primary productivity within Lake Superior over the better part of the Holocene. The general agreement among all bulk proxy data in all three cores (Figure 2-6) supports the interpretation of increasing primary productivity and the process of 'natural' eutrophication during conventional lake ontogeny.

2.5.2. Comparison of Recent and Past Climatic Influences on the Paleoproductivity Record

The Laurentian Great Lakes have experienced shifting regional climate patterns throughout the Holocene (Edwards et al., 1996; Lewis et al., 2008b). Four distinct climate regimes are present during this time period, beginning with a postglacial cold and dry period from ~12,000 to 7000 cal BP. During this early Holocene period (~8300 cal BP) the Great Lakes experienced closed basin conditions (Lewis et al., 2008a; McCarthy and McAndrews, 2012). Between 7000 and 6000 cal BP, conditions shifted to those of warm and dry, known as the early hypsithermal period. The next four thousand years – the main hypsithermal (6000-2000 cal BP) are characterized by warm and moist conditions. Regional climate conditions after 2000 cal BP begin to approach those of modern times. These changing conditions, from cold and dry to warm and wet, are conducive to gradual increases in primary production within lacustrine systems and correlate well with increasing primary productivity presented in this study.

Evidence of past abrupt climate changes are not evident in the data presented here (an exception being in the KW core around ~7000 cal BP, discussed earlier). For example, an ~200 yr period of cooling following the collapse of the LIS (the so-called 8.2 ka event; Clarke et al., 2004) which would possibly reduce algal productivity is not apparent in the bulk proxy data. Likewise, evidence of the Medieval Climate Anomaly - MCA (950-1250 AD; Mann et al., 2009) as well as the Little Ice Age - LIA (1400 to 1900 AD; Mann et al., 2009) is not apparent. One possibility as to why these abrupt climate changes are not apparent in the record presented here is the buffering capacity of

Lake Superior’s large volume (Hyodo and Longstaffe, 2011). It is widely recognized that large lakes like Superior tend to record long-term climate trends or climatic extremes, rather than short-term variability (Fritz, 1996).

Increases in productivity most recently (within the last 200 years) are coincident with the development of the Lake Superior basin after European settlement (see: Chapter 3). They also occur during a time of rapid climate and environmental change. Warming temperatures have been noted in the last two centuries, with a 2°C increase in lake surface temperature in the last two decades (Austin and Colman, 2007; 2008). Decreased ice cover allowing for a longer stratified period in Lake Superior is also apparent over the last 200 years (Austin and Colman, 2007;2008; Desai et al., 2009). Additionally, anthropogenic changes in the watershed have increased nutrient flux to the lake. These changes have impacted in-lake conditions, as observed increases in $\delta^{13}C_{org}$, TOC, and TON. Even though past climate perturbations are not apparent in the paleoproductivity record presented here, it is likely that the rate at which the most recent environmental and climatic changes have occurred has overcome the buffering capacity of Lake Superior’s large volume, allowing for changes to become manifest as increases in productivity. The warmest 50-year period of Northern Hemisphere mean annual temperature before 1900 A.D. was 1146 to 1195 A.D. (the height of the MCA), which was similar to the mean annual temperature between 1901 and 1970 A.D. (Mann et al., 2003; Bradley et al., 2003). It is clear that what is occurring in the most recent history of Lake Superior hasn’t been experienced previously.

2.6. CONCLUSION

Postglacial sediments of three piston cores taken from across the Lake Superior basin provide a historic baseline of primary productivity which is characterized by a slow and steady increase in TOC and TON percentages, as well as $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ compositions throughout the past 10,000 years. These trends indicate a long-term “eutrophication” of the lake that is consistent with the conventional definition of lake ontogeny (i.e. lake evolution from a state of oligotrophy to eutrophy) but not with the typical carbon profile of north-temperate lakes according to Whiteside (1983).

Furthermore, known high-resolution climate events such as the 8.2 ka event, the LIA and the MCA are not reflected in Lake Superior sediment geochemistry. Both of these observations are likely due, at least in part, to the buffering capacity of large lakes such as Lake Superior. In contrast, the most recent changes in the system, spanning the last 200 years are well represented in the geochemical record. These changes, likely reflecting anthropogenic environmental and climatic influences, are exceptional in the last 10,000 years.

CHAPTER 3

Anthropogenic Influences on the Sedimentary Organic Geochemical Record within Lake Superior over the Last 200 Years

3.1. INTRODUCTION: “Anthropogenic” Eutrophication

The natural, slow aging process of a lake consists of evolving from being less productive to more productive in a process of eutrophication (Whiteside, 1983). According to the National Academy of Sciences, 1969, “The term ‘eutrophic’ means well nourished; thus, ‘eutrophication’ refers to natural or artificial addition of nutrients to bodies of water and to the effects of the added nutrients.” Anthropogenic or cultural eutrophication is the process of speeding up the inherent natural eutrophication of a lake system because of human activity (Art, 1993).

Human activity in and around lake systems involves a myriad of processes involving changes to both watershed and lake system. The watersheds of lakes are often very populous due to the critical resources they provide - i.e. water for drinking, hygiene, industry, power generation, and recreation (Williamson et al., 2008); this is especially true when discussing large lakes. Because lake systems are homes to a large populace the likelihood for cultural eutrophication increases through the development of their surrounding watersheds. The building of cities and clearing of land for agriculture increases nutrient loading, mainly phosphate and nitrate, to lake systems. For example, in Lake Erie, a number of documented changes took place during the 1960s and 1970s when the population within the watershed increased from 3.8 million to 11.2 million between 1910 and 1960 (Sweeney, 1993). Localized effects are not the only ways in which lake systems are impacted by increasing human populations, atmospheric deposition is also a major contributor of excess nutrients (mainly from the burning of fossil fuels), but is much harder to control.

Global climate changes can impact lakes by increasing productivity as has been documented in Lake Baikal (Hampton et al. 2008; Moore et al. 2009) or decreasing productivity as in Lake Tanganyika (O’Reilly et al. 2003, Tierney et al. 2010). Where cultural eutrophication is concerned, the effects of humans on lake ecosystems and trophic status can have great effects.

The most notable sign that eutrophication is occurring is an increase in biological production within lake systems. Organic geochemical proxies preserved in lake sediment records provide a history of such changes in biological production, which enables us to gauge the historical impacts of regional development, as well as the subsequent regulations within lake systems. This is especially useful in lake systems where historical data is lacking.

3.2. BACKGROUND: Lake Superior Today

Lake Superior is the first in a chain of large lakes that comprise the Laurentian Great Lakes along the border between the United States and Canada. Its importance is widely acknowledged, as it provides invaluable resources to the surrounding economy through shipping, manufacturing and industry, tourism, and recreation. Although the population within the drainage basin remains low with little consequential development relative to the other Laurentian Great Lakes, the lake has not been immune to anthropogenic influences.

The Lake Superior watershed witnessed its first settlements in the early 1800s, with the beginning of the fur trade. Consequent population increases occurred with the further developments of logging, mining, shipping, and processing of raw materials, until the Duluth-Superior Harbor region reached its historic maximum of 100,000 people in 1922. Changes in Lake Superior’s physical, biological and chemical processes have been documented. Observations of rising nitrate concentrations since the 1900s (Sterner, et al. 2007; Weiler, 1978), as well as increasing water temperatures over the past two decades (Austin and Colman, 2007, 2008) and changes in primary productivity (Urban et al. 2005; Urban 2007; Vollenweider et al., 1974) indicate that anthropogenic activities have and continue to exert influences on Lake Superior.

Documenting the duration and extent of anthropogenic environmental change within Lake Superior is often difficult because of the paucity of historical data, particularly from lake-wide sampling. One way to track the response of Lake Superior to anthropogenic environmental change is to use a suite of sedimentary organic geochemical proxies. Traditional approaches include elemental analysis of bulk sediments as well as bulk carbon and nitrogen stable isotope compositions. This approach has proven effective in the other Laurentian Great Lakes (Schelske and Hodell, 1995; Hodell and Schelske 1998; Meyers 2002). In particular, the carbon isotope composition ($\delta^{13}C$) of sedimented organic matter has been used as an indicator of changes in primary productivity. This approach is based on the premise that the $\delta^{13}C$ of organic carbon produced photosynthetically is controlled by primary productivity in the water column (Farquhar et al. 1982; Laws et al. 1995).

This study delivers results from the analysis of eight sediment multicores sampled at high resolution (four unique to this study and four from Strzok (2011)) allowing for a basin-wide study of productivity trends in Lake Superior from 1800-present; the time of human habitation of the region. Here, we report trends in productivity, through the use of bulk organic and stable isotope compositions of carbon and nitrogen, as contained within the most recent sedimentary geochemical record of Lake Superior.

3.3. METHODS

See Chapter 1: Methods and Age Models.

3.4. RESULTS

3.4.1. Total Organic Carbon (TOC) and Total Organic Nitrogen (TON)

Total organic carbon and total organic nitrogen MARs are similar in all cores from Lake Superior, ranging between 25-200 mg C/cm^2/yr and 2-20 mg N/cm^2/yr for the entire time period from 1700 to present (Figures 3-1 and 3-2). Exceptions to this are seen in core BH09-4 where TOC and TON values decrease from 75 – 25 mg C/cm^2/yr and 7-3 mg N/cm^2/yr between 1950 and 1975. Additionally, an excursion to higher TOC and TON MARs occurs between 1935 and 1960 in core IR with values jumping approximately 50 and 7 mg/cm^2/yr for TOC and TON MARs, respectively. Cores BH09-2 and LG display an overall greater MAR of TOC and TON than the other cores, with LG exhibiting the highest TOC and TON MARS of any of the cores (75-175 mg C/cm^2/yr and 8-18 mg N/cm^2/yr).

3.4.2. Ratio of Carbon and Nitrogen (C_{org}:N_{org} atomic)

Ratios of carbon and nitrogen in all cores remain relatively stable, between 7 and 8, until 1900, after which values diverge (Figure 3-3). C_{org}:N_{org} values within cores BH03-3, BH09-3, BH09-4, IR, and LG display in increasing trend until 1960, decreasing thereafter. Values within cores BH09-2, CM, and EM show an overall decrease between 1900 and 2010.

3.4.3. Stable Isotopes of Carbon and Nitrogen ($\delta^{13}C_{org}$ and $\delta^{15}N_{org}$)

The general pattern observed in the bulk sediment carbon isotope values ($\delta^{13}C_{org}$) for all cores is a period of ^{13}C-enrichment (~2‰) beginning near 1900 and continuing until present day (Figures 3-4 and 3-5). Cores BH09-4 and EM show a decrease in $\delta^{13}C_{org}$ values of ~1‰ between 1950 and 1975; after which $\delta^{13}C_{org}$ values increase to the present.

Before 1900, $\delta^{15}N_{org}$ values remain relatively stable for each of the cores, varying from 3-7‰. Unlike $\delta^{13}C_{org}$ values, $\delta^{15}N_{org}$ values display a decreasing trend in the eight cores after 1900. Cores LG, IR, and EM show an overall decrease of ~2‰, while an ~1‰ decrease is observed in cores BH09-2, BH09-3, BH09-4, and CM. $\delta^{15}N_{org}$ values in core BH03-3 remain stable for the entire time period fluctuating between 3.5 and 4‰.

3.5. DISCUSSION

3.5.1. Anthropogenic Influences – as recorded by bulk proxy data

3.5.1.1. Cultural Eutrophication and Climatic Influences

The mass accumulation rates of TOC and TON in all cores exhibit a general increase throughout the last 200 years. TOC_{MAR} and TON_{MAR} appear to be highly correlated with similar temporal patterns, suggesting dominant controls from in lake primary production (Figures 3-1, 3-2, 3-6). Cores from shallow, near-shore sites (i.e.

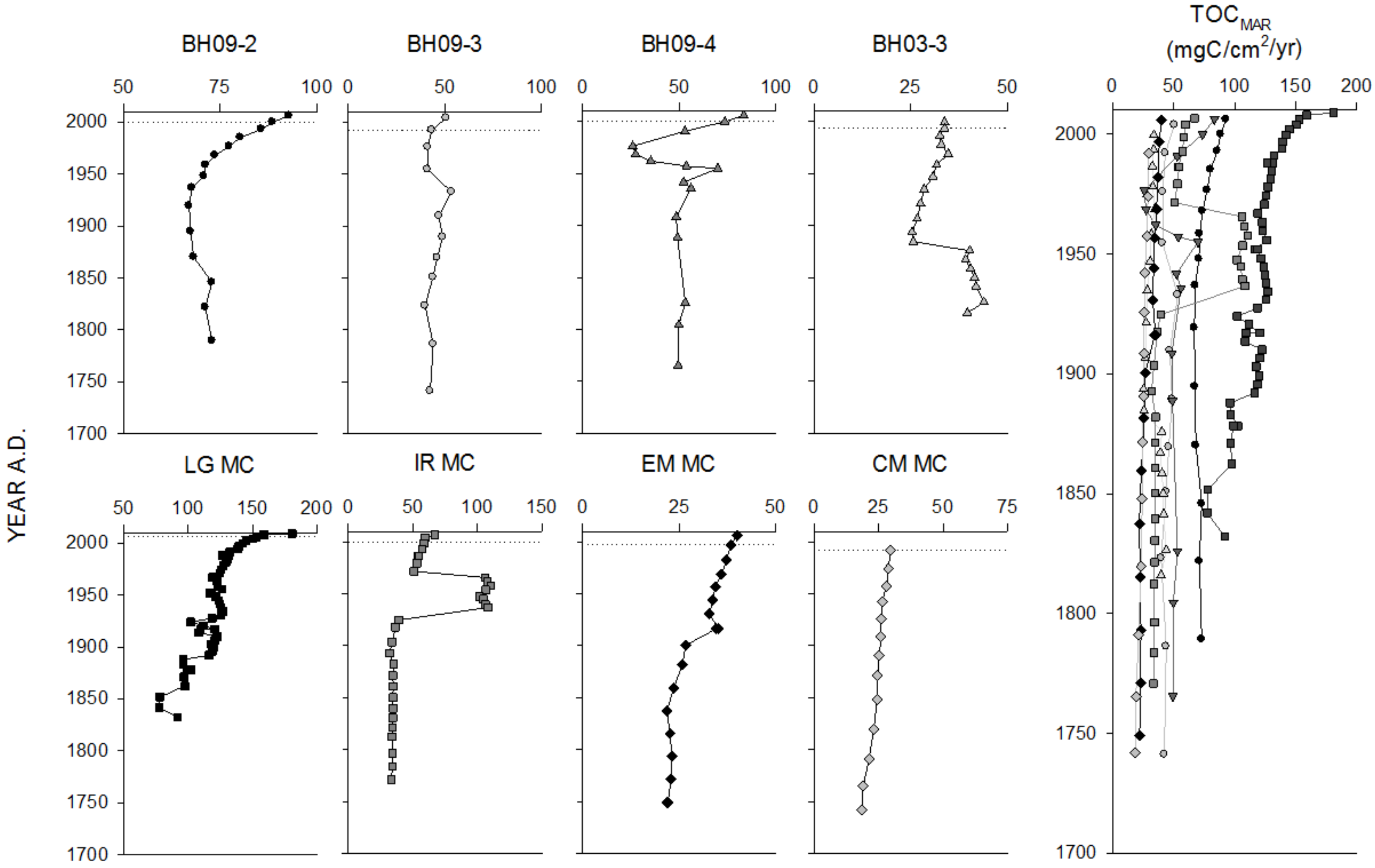


FIGURE 3-1. Temporal variations in TOC MARs among eight sediment multicores from across the Lake Superior basin. The dotted lines represent the depth of the bioturbation zone in each core.

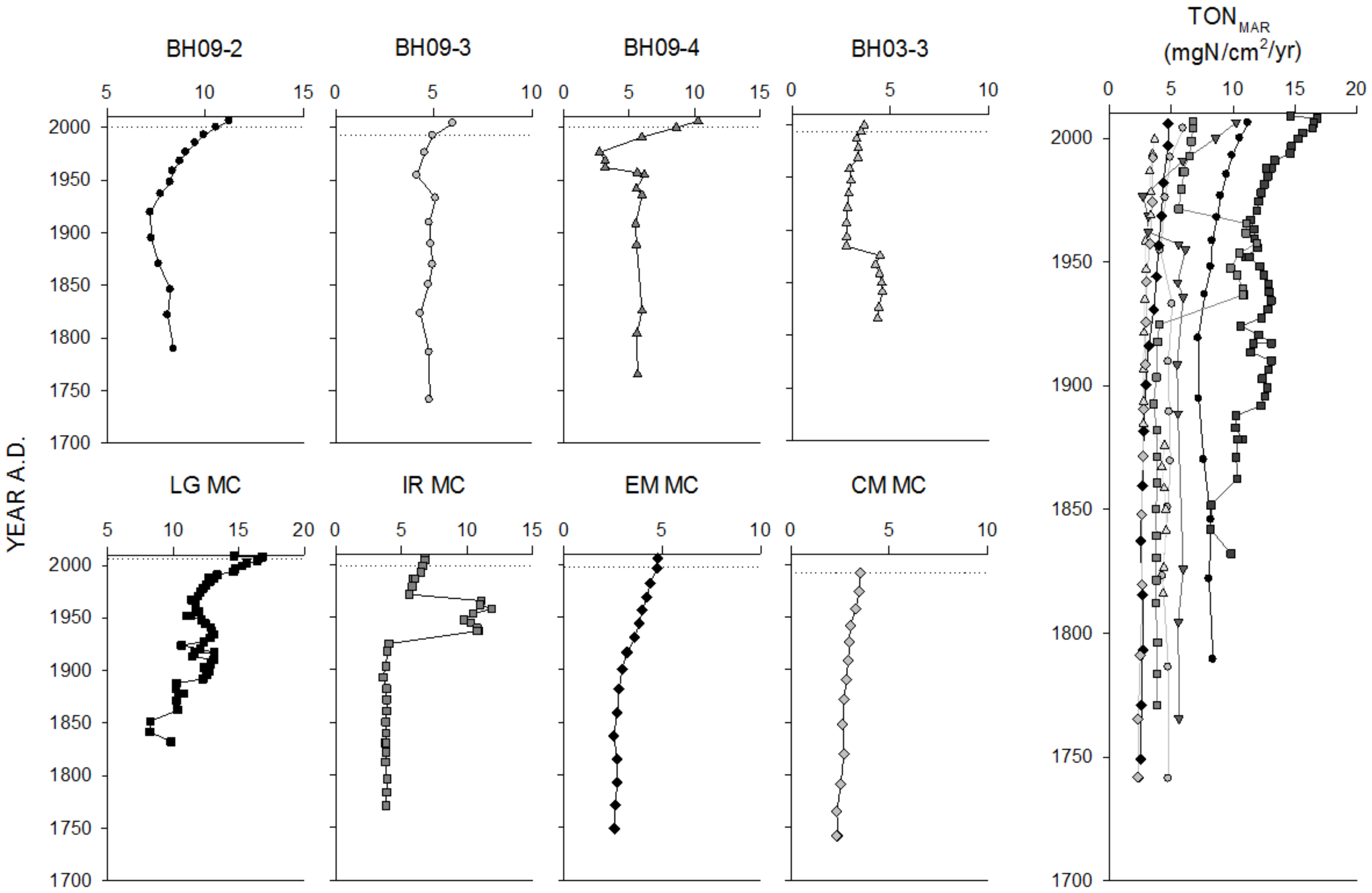


FIGURE 3-2. Temporal variations in TON MARs among eight sediment multicores from across the Lake Superior basin. The dotted lines represent the depth of the bioturbation zone in each core.

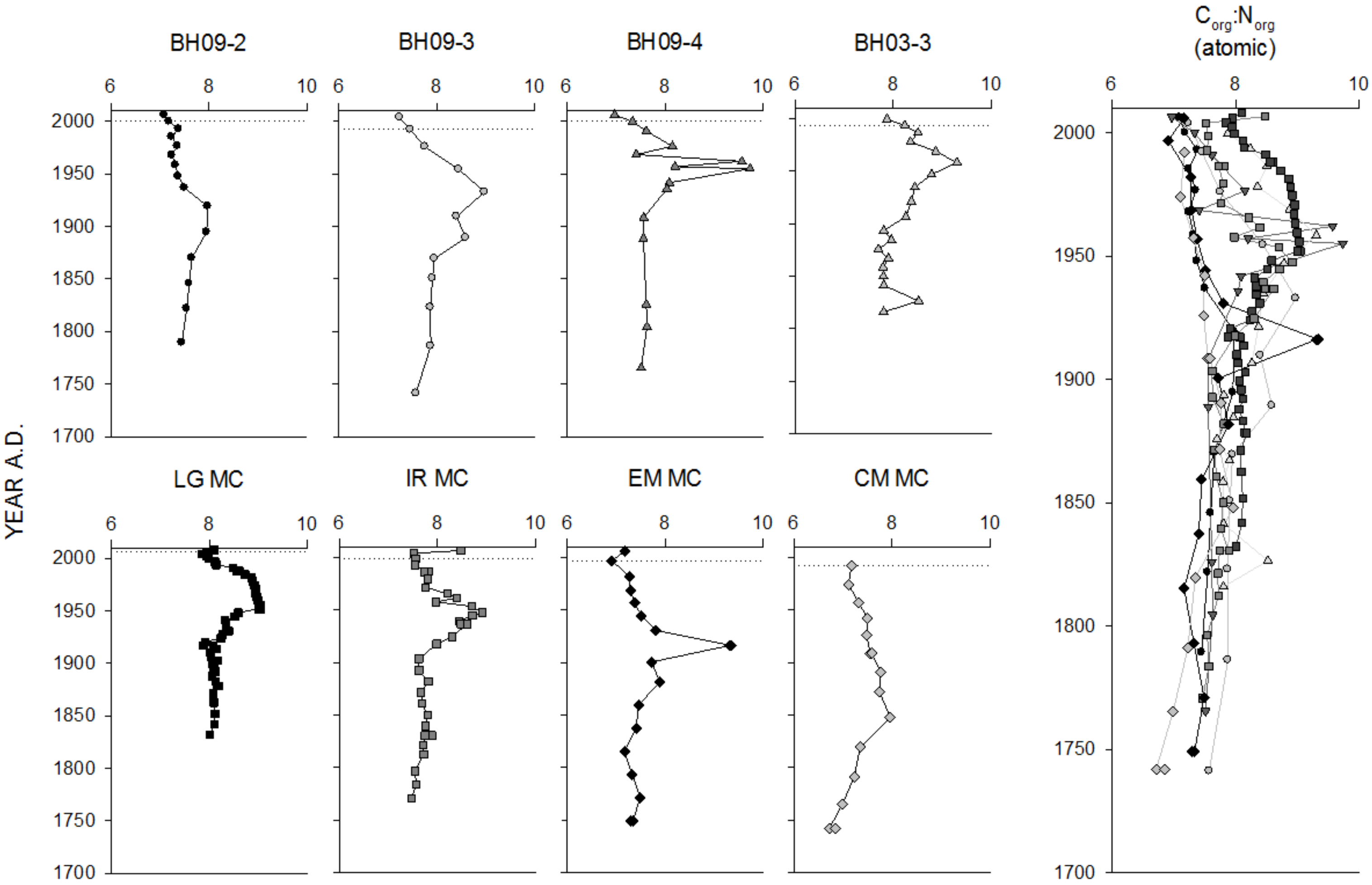


FIGURE 3-3. Temporal variations in atomic C_{org}:N_{org} ratios among eight sediment multicores from across the Lake Superior basin. The dotted lines represent the depth of the bioturbation zone in each core.

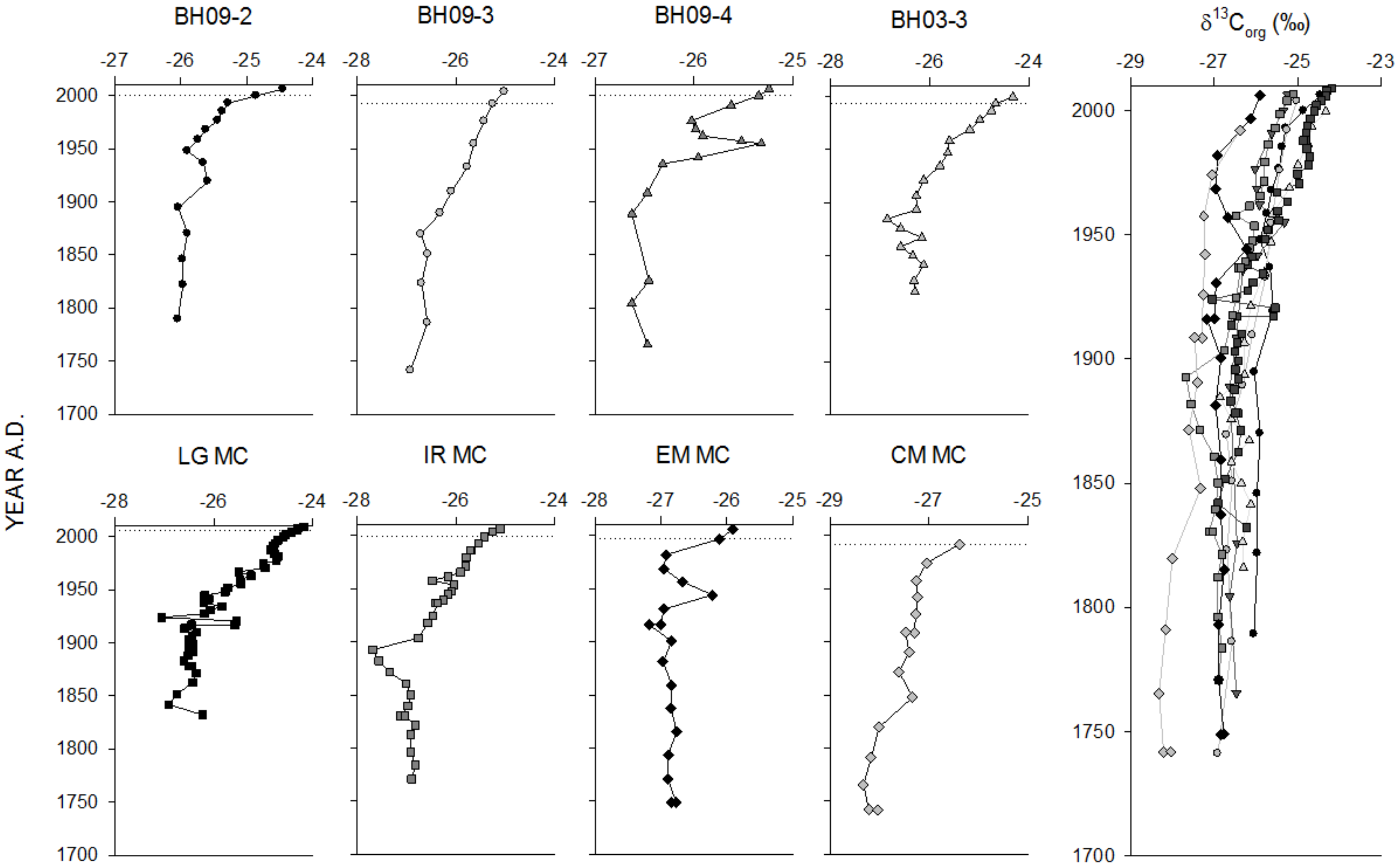


FIGURE 3-4. Temporal variations in $\delta^{13}C_{org}$ compositions among eight sediment multicores from across the Lake Superior basin. The dotted lines represent the depth of the bioturbation zone in each core.

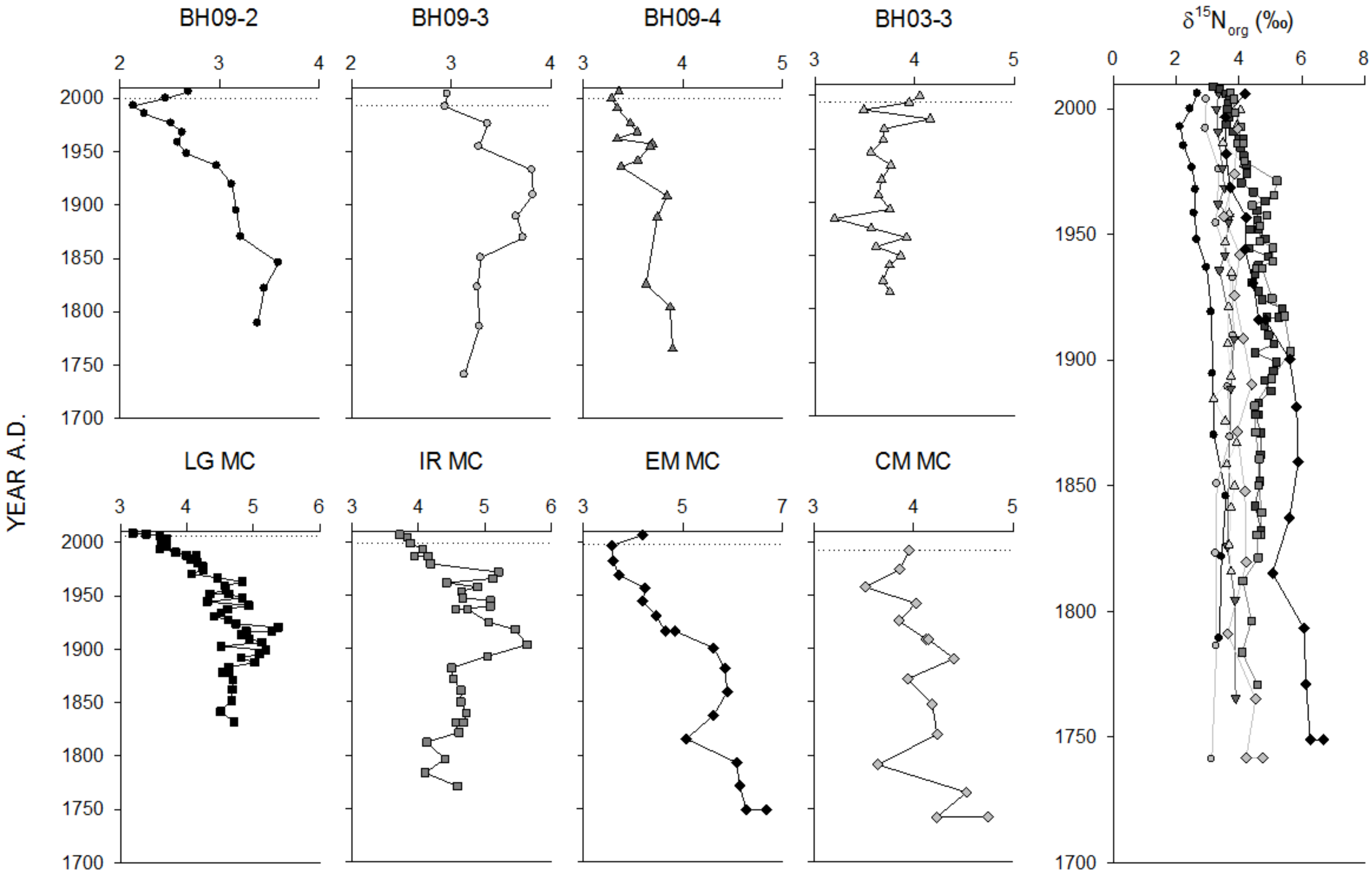
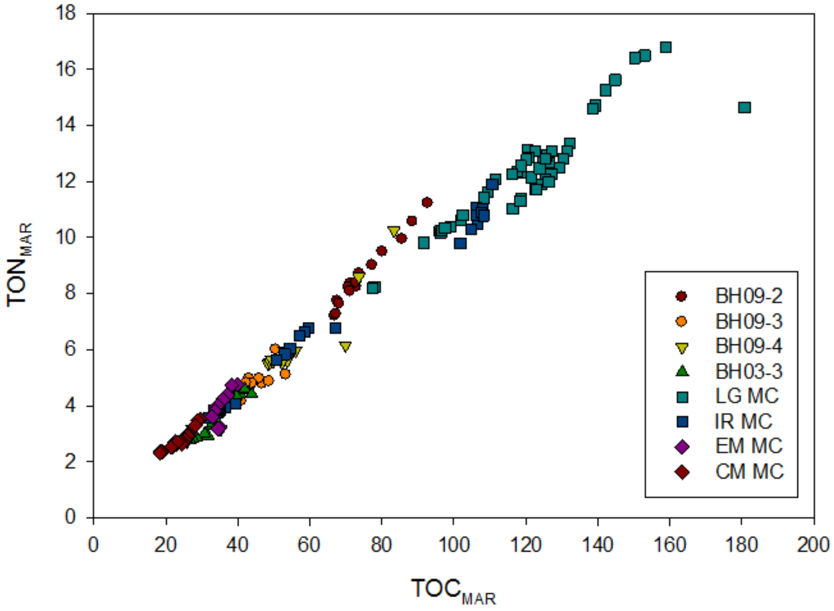


FIGURE 3-5. Temporal variations in $\delta^{15}N_{org}$ among eight sediment multicores from across the Lake Superior basin. The dotted lines represent the depth of the bioturbation zone in each core.

BH09-2 and LG) have the highest accumulation rates, whereas those from deeper, off-shore sites are much lower. MARs in core LG are most comparable to cores from the far western arm of Lake Superior, which are attributed to anthropogenic influences (O'Beirne et al., submitted).

The atomic C_{org}:N_{org} ratios, on average, fall around 8 which indicates sediments dominated by algal sourced organic matter. Increases in atomic C_{org}:N_{org} ratios after 1900 likely reflect the increased transport of terrigenous material to the lake due to anthropogenic disturbances within the watershed, most notably in cores from western Lake Superior; however, ratios remain well within the lacustrine algae range of 4-10 (Meyers, 1994; Figure 3-3). Furthermore, a cross-plot of C_{org}:N_{org} vs. $\delta^{13}C_{org}$ emphasizes the inference of in-lake primary production as the dominant factor influencing the sedimentary organic record; with values from all eight cores plotting in the range typical of lacustrine algae, rather than those of terrigneous C_3 or C_4 plants (Figure 3-6).

During periods of high algal growth rates, typically associated with high productivity, isotopic fractionation can decrease due to a rise in the rate of fixation relative to the supply of CO_2 across the membrane of a cell (Farquhar et al. 1982; Laws et al. 1995); thus ^{13}C-enrichment is often associated with high rates of productivity. Pre-settlement $\delta^{13}C$ values in all cores remain relatively stable until 1900. Increasing $\delta^{13}C_{org}$ values are consistent with increasing in-lake primary production from 1900 to 1970 (Figure 3-4) and coincide with increased anthropogenic disturbance (increasing nutrient flux) within the Lake Superior watershed (Schelske et al., 2006; Chraibi, 2012; O'Beirne et al., submitted). Beginning in the late 1970s strict regulation on nutrient inputs to Lake Superior, as well as the other Laurentian Great Lakes, began with the signing of the 1978 joint bi-national Great Lakes Water Quality Agreement between the US and Canada. Thus, one may expect $\delta^{13}C_{org}$ values to decrease or remain stable, instead of increasing as they do. We observe greater increases in lacustrine productivity, as inferred from $\delta^{13}C_{org}$ values, since 1960 (1975 in cores EM and CM). The causes for this observed productivity increase are enigmatic (Figure 3-4), though some possible explanations can be explored.



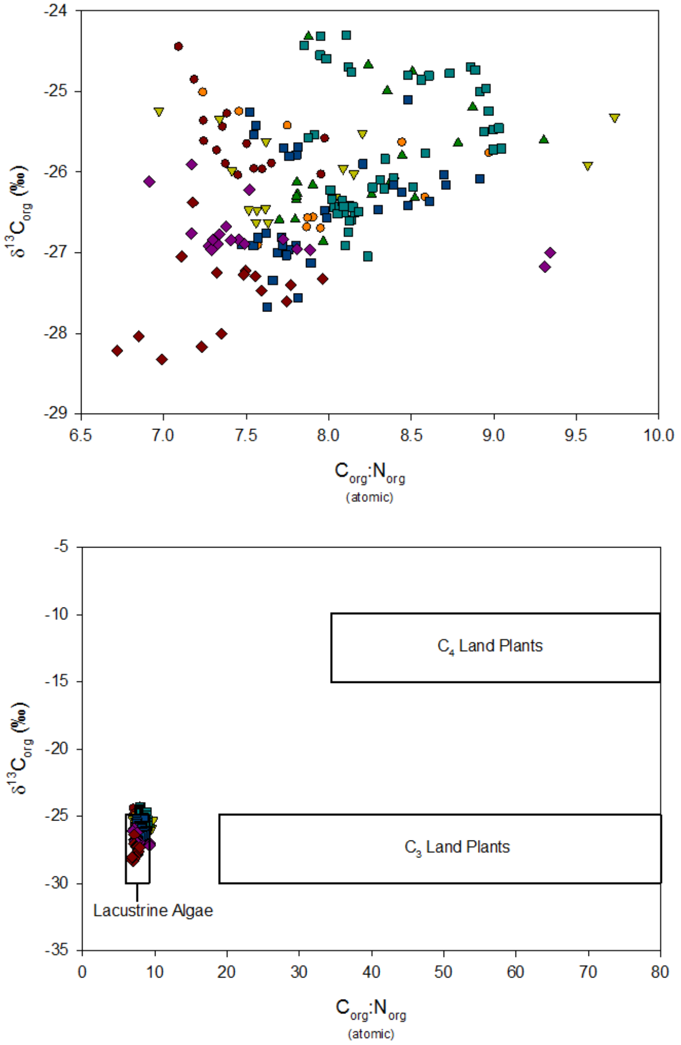


FIGURE 3-6.

TOP: Cross-plot of TOC MARs vs. TON MARS from all cores illustrating their correlation, which is indicative that OM is coming from the same source. Units are in mg/cm^2/yr.

RIGHT: Cross-plot of C_{org}:N_{org} vs. $\delta^{13}C_{org}$ from all multicores demonstrates that in-lake primary production is the dominant factor influencing the sedimentary organic carbon record for the last 200 years.

One possibility entails the preferential mineralization of isotopically light carbon compounds; however, this seems unlikely, as isotopic discrimination associated with mineralization appears to have a minor influence on the $\delta^{13}C_{org}$ within low organic content (<2-3%) sediments, such as Lake Superior (Meyers, 1994; Talbot and Livingstone, 1989). Furthermore, Hodell and Schelske (1998) found that in Lake Ontario postburial diagenesis reduced the mass of organic carbon buried within sediment cores taken six years apart, but did not change the $\delta^{13}C_{org}$ values, a condition also observed in cores from western Lake Superior (O'Beirne et al., submitted). The variable number of years encompassed by the bioturbation zones in each of the cores also suggests that the observed isotopic increases are independent of diagenetic processes.

Other explanations include changes in environmental and/or physiological factors that may alter the isotopic composition of photosynthetic organisms, thus altering the isotopic signature of bulk organic matter without actually increasing or decreasing primary productivity. Processes that may contribute to isotopic variation in phytoplankton might include changes in the source of inorganic carbon, isotope effects associated with carbon assimilation and metabolism, temperature effects, or a shift in the phytoplankton community structure to one with a greater abundance of ^{13}C-rich organisms (e.g. diatoms; Fry and Wainright, 1991).

Temperature effects could contribute to shifts in the isotopic composition of primary producers. Over the last 200 years Lake Superior has warmed considerably, with shifts to longer ice free and stratified periods (Austin and Colman, 2007; 2008; Desai et al, 2009). Increasing temperatures could shift the equilibrium of dissolved inorganic carbon (DIC), reducing $[CO_{2(aq)}]$ leading to an overall ^{13}C-enrichment in primary photosynthate (Mehrbach et al. 1973; Mook et al. 1974). Lake Superior is presently supersaturated with respect to atmospheric CO_2 (Atilla et al., 2011; Urban, 2009). Because little, if any, carbonate is preserved in the sediments, it probably has been supersaturated since in-lake conditions approached modern-day at ~ 9000 cal BP (Breckenridge and Johnson, 2009). Thus, even with increases in temperature DIC equilibrium has probably not undergone a significant shift that could cause the overall ^{13}C-enrichment of $\delta^{13}C_{org}$.

Increasing temperatures can also stimulate primary productivity, especially in otherwise cold oligotrophic systems, thereby decreasing isotopic fractionation in primary producers. A recent three-dimensional model of Lake Superior, including dynamic and thermodynamic ice cover as well as biogeochemistry, shows an increasing trend in total annual primary production (for the simulation period of 1985-2008) that correlates with decreasing winter ice cover and increasing annual average surface water temperatures (White et al., 2012). Results of the simulation are in agreement with the biomass increase documented by Munawar and Munawar (2001) as well as data presented here. Accordingly, any temperature effects which may cause enrichment of $CO_{2(aq)}$ are conceivably obscured by increases in primary production generating the primary ^{13}C-enrichment of bulk organic matter which subsequently becomes buried within the sediments of Lake Superior.

A shift in the dominant phytoplankton community, from Cryptophyceae (red algae) to Diatomeae (diatoms), was documented in Lake Superior between 1973 and 2001 (Munawar and Munawar, 2001); however, this same study also documented a ten-fold increase in mean phytoplankton biomass over the same time period. This increase in biomass indicates increasing primary production, which, as stated earlier, would cause enrichment of $\delta^{13}C_{org}$ values. Therefore, it is not likely that the change in community composition to ^{13}C-rich diatoms is the sole factor producing the ^{13}C-enrichment of bulk sedimentary organic matter between 1900 and present.

In addition to the shifts in phytoplankton community noted by Munawar and Munawar (2001), a more recent study by Chraibi (2012) analyzing diatom species and abundance in the IR and LG multicores found a shift in diatom assemblage from *Alacoseira* to *Cyclotella* species beginning in 1995 with further increases in 2010. While this species change is generally favored in oligotrophic, nitrogen-rich waters (Stoermer and Kreis, 1980), in many northern lakes (Rühland et al., 2008) increases in *Cyclotella* are best correlated with increases in the length of the ice-free period and air temperature, rather than increases in nitrogen concentrations.

Data presented here show a clear increasing trend in primary production within the eight cores from across the Lake Superior basin over the last 200 years. The observed correspondence between bulk organic proxy data and historic watershed development presented in the current study provides evidence of the influence of anthropogenically induced changes on the trophic state of Lake Superior, with lake-wide increases in primary production being a likely result of climatic influences (i.e. increasing water temperatures and duration of the ice-free period).

3.5.1.2. Effects of Atmospheric Deposition on $\delta^{15}N_{org}$

Between 1900 and ~1980 the cores exhibit progressive ^{15}N-depletion (BH03-3 being the only exception), which is counter to expectation if $\delta^{15}N_{org}$ is controlled by algal productivity. One would expect $\delta^{15}N_{org}$ values to be ^{15}N-enriched similar to the ^{13}C-enrichment of the $\delta^{13}C_{org}$ values, during this time period due to increased primary productivity. Because N fixation is thought to be of little importance in Lake Superior due to a high concentration of nitrate in the lake (Mague and Burris, 1973), decreasing $\delta^{15}N_{org}$ values must then indicate other (likely anthropogenic) sources of isotopically light N to the lake – the most likely being fossil fuel combustion and synthetic fertilizers. The contribution of fertilizers to the depletion of $\delta^{15}N_{org}$ is unlikely in Lake Superior, given the small watershed with little agricultural development. Large increases in NO_x emissions were seen in the U.S. (EPA, 2000) and Canada (Chen et. al., 2000) between 1940 and 1980, after which emissions have remained constant. Increasing $\delta^{15}N_{org}$ values after 1980 in some of the cores may be a response to constant NO_x emissions, whereby $\delta^{15}N_{org}$ values begin to reflect the influence of primary production rather than anthropogenic NO_x inputs.

3.5.2. Climate induced variations in Primary Productivity: A comparison with other Great Lakes of the World

Lake Superior is generally considered an oligotrophic end member when discussing global Great Lakes and while this is true, it is worthwhile to compare the changes in productivity with those that have been observed in other Great Lakes of the world that correlate with climate change. Lake Superior is the third largest lake in the world by volume. Lake Baikal in Russia and Lake Tanganyika in Africa are the only two lakes to surpass Lake Superior in this aspect. This is of significance because, in general, the most voluminous lakes are considered to be less susceptible to climate changes than their smaller counterparts. That said, all three lakes have responded to changes in their respective climate regimes.

Lake Baikal is an oligotrophic, temperate lake, similar to Lake Superior. It has experienced increasing water temperatures (~2°C) during the last 60-100 years (Shimaraev et al., 2002; Hampton et al., 2008). This increase in temperature has resulted in longer ice-free periods, lengthening by 18 days over the same time period as the temperature increase (Shimaraev et al., 2002). This, in turn, provides a longer stratified season, thereby enhancing primary production within the water column (Hampton et al., 2008; Moore et al., 2009). Lake Superior has experienced very similar changes. Over the last century, open water summer temperatures in Lake Superior have increased by 3.5°C (Austin and Colman, 2007). During the same time period average ice cover has decreased 12-23% (Austin and Colman, 2008; Desai et al., 2009), resulting in a stratified season that has increased by 25 days and begins earlier in the spring (Austin and Colman, 2008). The increases in productivity observed in Lake Superior within the present study are consistent with increasing temperatures stimulating primary productivity through a positive feedback related to the length of the ice-free period.

In contrast, Lake Tanganyika, an oligotrophic, permanently stratified tropical lake, has experienced *reduced* primary production with increasing temperature. Increased lake surface temperatures are restricting productivity by enhancing the density gradient between the epilimnion and hypolimnion, thereby limiting water column mixing and reducing the flux of hypolimnetic nutrients to the epilimnion (O’Reilly et al., 2003; Tierney et al., 2010). In Lake Superior, the increasing temperature difference between surface and subsurface layers during summer stratification does not lead to decreasing primary productivity, because the water column mixes completely twice a year. Furthermore, much of the productivity occurs in the hypolimnion because the thermocline is so shallow, with abundant sunlight reaching deeper waters. Thus, in temperate lakes such as Superior and Baikal, increasing temperatures seem to enhance primary productivity, as evidenced by Munawar and Munawar (2001) and the present study.

Despite its large volume, Lake Superior is experiencing systematic changes in its critical processes (e.g., ice cover, water temperature, stratification, mixing, and productivity) driven by rapid anthropogenically induced climate change, much like those witnessed in Lake Baikal.

3.6 CONCLUSION

The sedimentary organic geochemical record spanning the Lake Superior basin provides insight to changes occurring within the lake since the time of European settlement; namely, lake-wide increases in aquatic primary productivity as evidenced by the ^{13}C-enrichment of bulk organic matter beginning in 1900 and continuing until present. The most recent increases in aquatic productivity (which continue after regulatory action limited discharges to the lake), are consistent with increasing temperatures stimulating primary productivity through a positive feedback related to the length of the ice-free period within Lake Superior. Additional anthropogenic influences are seen in the $\delta^{15}N_{org}$ record, marked by a period of ^{15}N-depletion coinciding with increased NO_x emissions in the United States and Canada. These observations ultimately show that Lake Superior is sensitive to environmental change - both regionally and globally.

CHAPTER 4

N-alkane biomarkers – applications and implications as related to carbon cycling within Lake Superior.

4.1. INTRODUCTION

Past productivity trends in lake systems are often inferred from the stable carbon isotope composition of bulk sedimentary organic matter ($\delta^{13}C_{org}$). The biggest caveat to this approach is that bulk sediments contain a mixture of organic matter from both aquatic/autochthonous and terrigenous/allochthonous sources. In order to elucidate the source of organic matter responsible for any changes in the $\delta^{13}C_{org}$, a variety of molecular biomarkers can be employed. Molecular biomarkers, in this case, are defined as compounds that characterize certain biotic sources and selectively retain their source information, even after stages of decomposition and diagenesis (Meyers, 2003). Of the suite of molecular biomarkers available, *n*-alkanes – linear aliphatic hydrocarbons – are lipid biomarkers of particular interest in paleolimnological reconstructions as they are the most refractory of the lipid classes, and are simplest to obtain and identify. The $\delta^{13}C$ values and distributions of *n*-alkanes can provide insight into environmental conditions in which they were formed as well as pathways of carbon flow.

Aquatic and terrigenous organisms each produce a distinctive set of *n*-alkanes, thus their characteristic molecules may serve as proxies for the source and delivery of organic matter within lacustrine sediments. Lacustrine paleoproductivity trends are reflected in the abundances of the odd-numbered short chain *n*-alkanes (n-C_{17}+n-C_{19}+n-C_{21}) produced by photosynthetic algae and bacteria (Cranwell et al., 1987; Giger et al., 1980). Vascular land plants produce large proportions of the odd-numbered long chain *n*-alkanes (n-C_{27}+n-C_{29}+n-C_{31}), which are produced in their epicuticular waxy coatings (Cranwell, 1981; Eglinton and Hamilton, 1963; 1967; Rieley et al., 1991). The relative abundances of both short and long chained *n*-alkanes found in lake sediments therefore reflect the proportion of organic matter produced within and around a lake system.

The stable carbon isotope composition of *n*-alkanes ($\delta^{13}C_{n\text{-alkane}}$), when compared to the bulk $\delta^{13}C_{org}$ record, can provide an indication of the individual contributions of terrigenous and aquatic sourced organic carbon to the bulk $\delta^{13}C_{org}$ record (Meyers, 2003). Interpretation of compound specific isotopes requires some finesse, as isotope compositions of individual sedimentary hydrocarbons are determined by isotope effects associated with specific reactions of biosynthesis and diagenesis that are unique to the molecule (Hayes, 1993).

Although previous studies have demonstrated the utility of *n*-alkane biomarkers as indicators of organic matter sources to lake sediments, the *n*-alkane record in Lake Superior provides equivocal results. Discussed herein are the implications of this apparent discrepancy on the application of *n*-alkane biomarkers in paleolimnological studies.

4.2. METHODS

See Chapter 1: Methods and Age Models.

4.3. RESULTS

4.3.1. Multicores

Fluxes of both aquatic and terrigenous *n*-alkane biomarkers exhibit marked differences among cores (Figure 4-1 and 4-2). For the most part, aquatic biomarker fluxes in cores BH09-3, BH09-4, BH03-3, and LG display an overall decrease from ~1860 to present; during the same time period terrigenous biomarker fluxes display an overall increase. Aquatic and terrigneous biomarker fluxes in cores IR, EM, and CM remain relatively stable over the entire time period from 1750 to 2010. In core BH09-2 the aquatic biomarker flux remains stable, while the terrigenous biomarker flux increases from ~1830 to 2009. The ratio of terrigenous to aquatic hydrocarbons, represented in equation (1) and plotted in Figure (4-1 and 4-2), shows increased variation down core among the eight cores; most recently, all cores approach a value of 0.8.

$$TAR_{HC} = C_{27}+C_{29}+C_{31}/[(C_{27}+C_{29}+C_{31})+(C_{17}+C_{19}+C_{21})] \text{ (eqn. 1)}$$

Variations in the weighted isotopic averages of both aquatic (i.e. $\delta^{13}C_{19}$, $\delta^{13}C_{21}$ expressed as $\delta^{13}C_{aquatic}$) and terrigenous (i.e. $\delta^{13}C_{27}$, $\delta^{13}C_{29}$, $\delta^{13}C_{31}$, expressed as $\delta^{13}C_{terrigenous}$) *n*-alkane biomarkers are used to examine changes in primary productivity as observed in the bulk $\delta^{13}C_{org}$ record. Generally, aquatic *n*-alkane biomarker $\delta^{13}C$ values fluctuate between -37‰ and -33‰, while terrigenous *n*-alkane biomarker $\delta^{13}C$ values fluctuate between -34‰ and -30‰ (Figure 4-1 and 4-3). Individual cores display differing trends. Cores BH09-2, BH09-3, BH03-3, and LG exhibit an overall increase of ~2.5‰ in $\delta^{13}C_{aquatic}$ values and decrease of ~1.5‰ in $\delta^{13}C_{terrigenous}$ values for the entire time period. In core IR, $\delta^{13}C$ values for both aquatic and terrigenous *n*-alkane biomarkers remain stable throughout at -36.5‰ and -33.5‰, respectively. $\delta^{13}C_{aquatic}$ and $\delta^{13}C_{terrigenous}$ values in core CM display an increase and decrease, respectively, of ~2‰ between 1760 and 1910, after which $\delta^{13}C_{aquatic}$ values remain stable while $\delta^{13}C_{terrigenous}$ increase by ~1‰. Before 1960, in core BH09-4, aquatic *n*-alkane biomarker $\delta^{13}C$ values increase ~4‰ and terrigenous *n*-alkane biomarker $\delta^{13}C$ values decrease ~2‰; after 1960 aquatic biomarker $\delta^{13}C$ values decrease ~3‰ and terrigenous *n*-alkane biomarker $\delta^{13}C$ values increase ~2‰.

4.3.2. Piston and Gravity Cores

The Holocene record shows a systematic ^{13}C-depletion of aquatic *n*-alkanes to the present, while the $\delta^{13}C$ of terrigenous *n*-alkane biomarkers remains relatively stable throughout the Holocene with a period of ^{13}C-depletion noted in the last 200 years (Figures 4-4, 4-5, and 4-6). During this same time period, the abundance of both aquatic and terrigenous *n*-alkane biomarkers at all three sites remains relatively stable overall, until the last 200 years when terrigenous *n*-alkane biomarker abundance begins to increase. The two most striking features recorded are 1) temporal changes in the $\delta^{13}C$ of *n*-alkanes do not correspond to changes in the relative abundance of *n*-alkane biomarkers and 2) down-core variations in the $\delta^{13}C$ composition of neither algal-derived short-chain

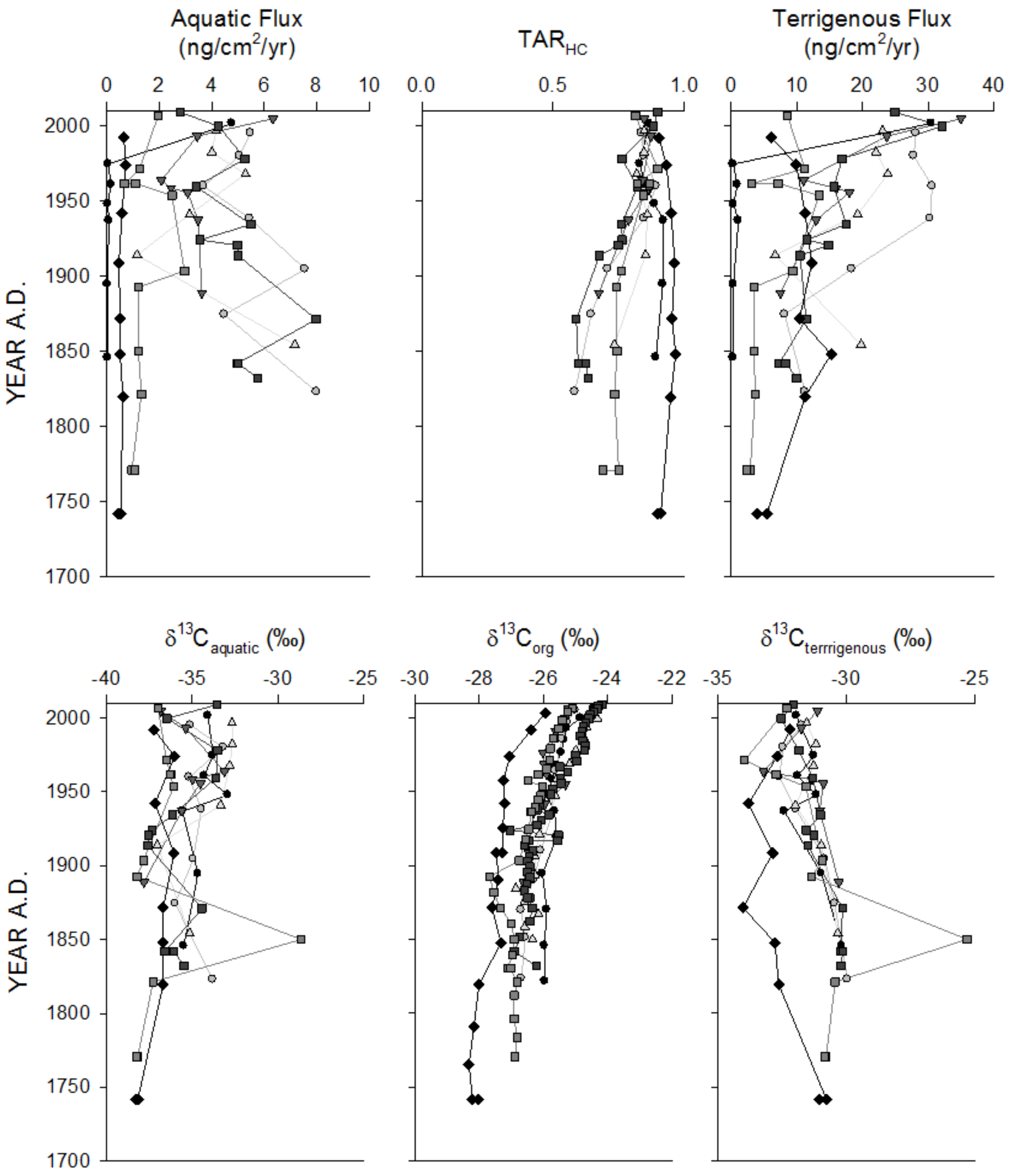


FIGURE 4-1

TOP: Temporal variations in the flux of both aquatic and terrigenous *n*-alkane biomarkers among seven multicores from across the Lake Superior basin. The middle plot represents the ratio of terrigenous to aquatic biomarkers.

BOTTOM: Comparison of temporal variations in molecular $\delta^{13}C_{aquatic}$, $\delta^{13}C_{terrigenous}$, and bulk $\delta^{13}C_{org}$ values among seven multicores from across the Lake Superior basin.

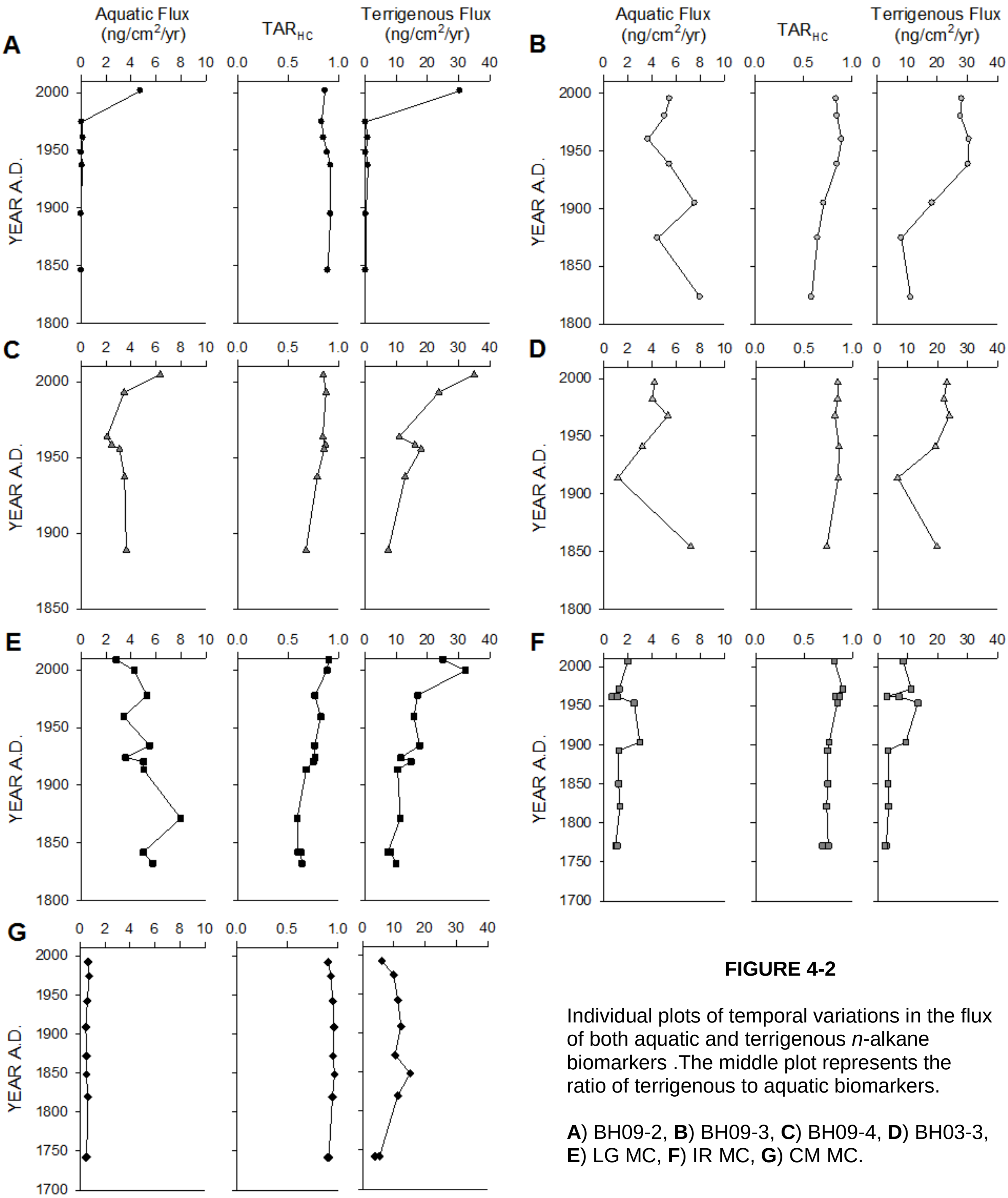


FIGURE 4-2

Individual plots of temporal variations in the flux of both aquatic and terrigenous *n*-alkane biomarkers .The middle plot represents the ratio of terrigenous to aquatic biomarkers.

A) BH09-2, **B**) BH09-3, **C**) BH09-4, **D**) BH03-3, **E**) LG MC, **F**) IR MC, **G**) CM MC.

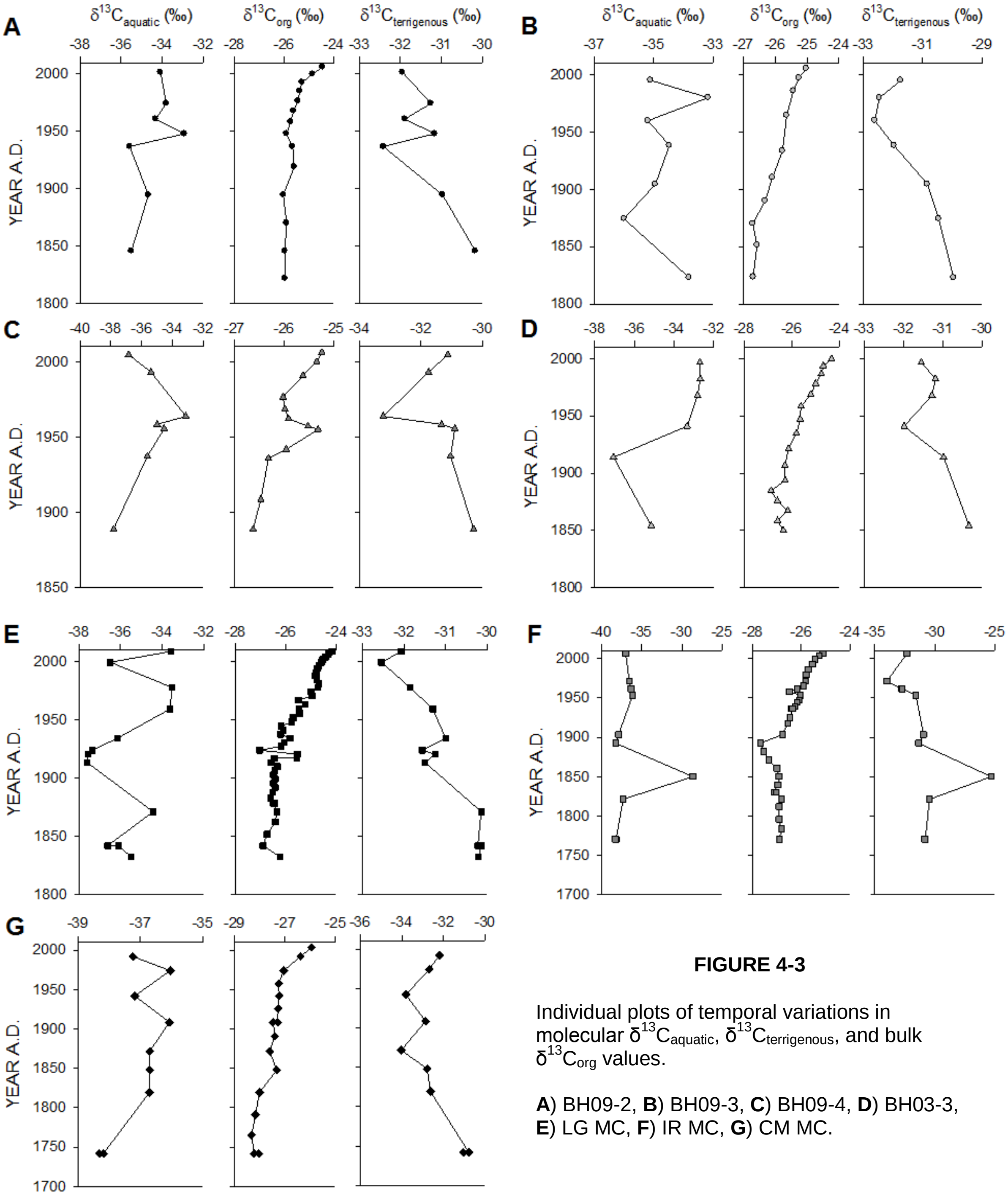
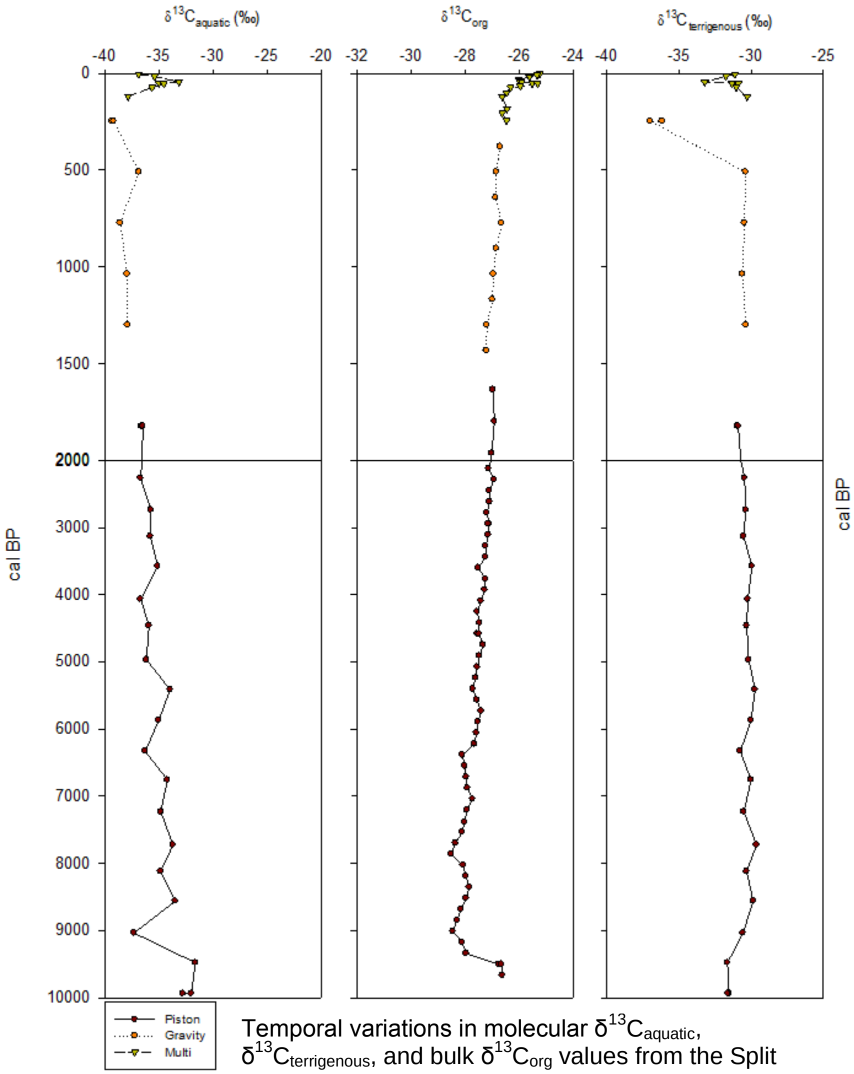


FIGURE 4-3

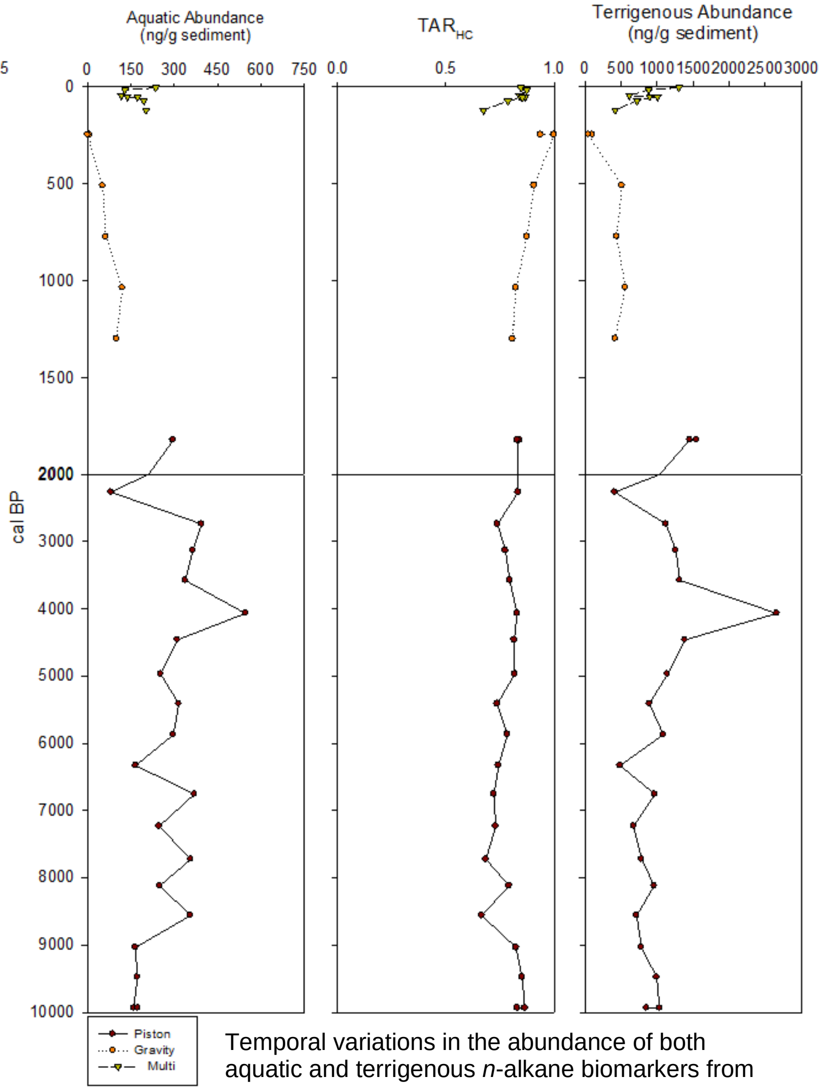
Individual plots of temporal variations in molecular $\delta^{13}C_{aquatic}$, $\delta^{13}C_{terrigenous}$, and bulk $\delta^{13}C_{org}$ values.

A) BH09-2, **B**) BH09-3, **C**) BH09-4, **D**) BH03-3, **E**) LG MC, **F**) IR MC, **G**) CM MC.

SPLIT ROCK



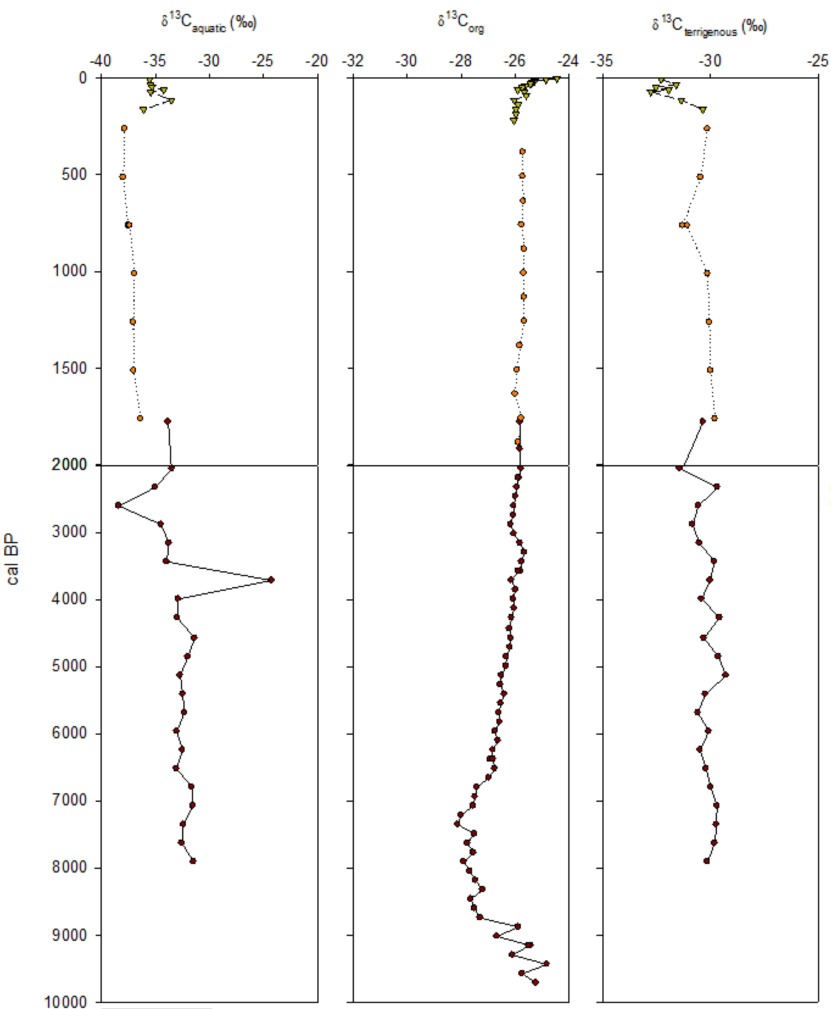
Temporal variations in molecular $\delta^{13}C_{aquatic}$, $\delta^{13}C_{terrigenous}$, and bulk $\delta^{13}C_{org}$ values from the Split Rock sediment cores.



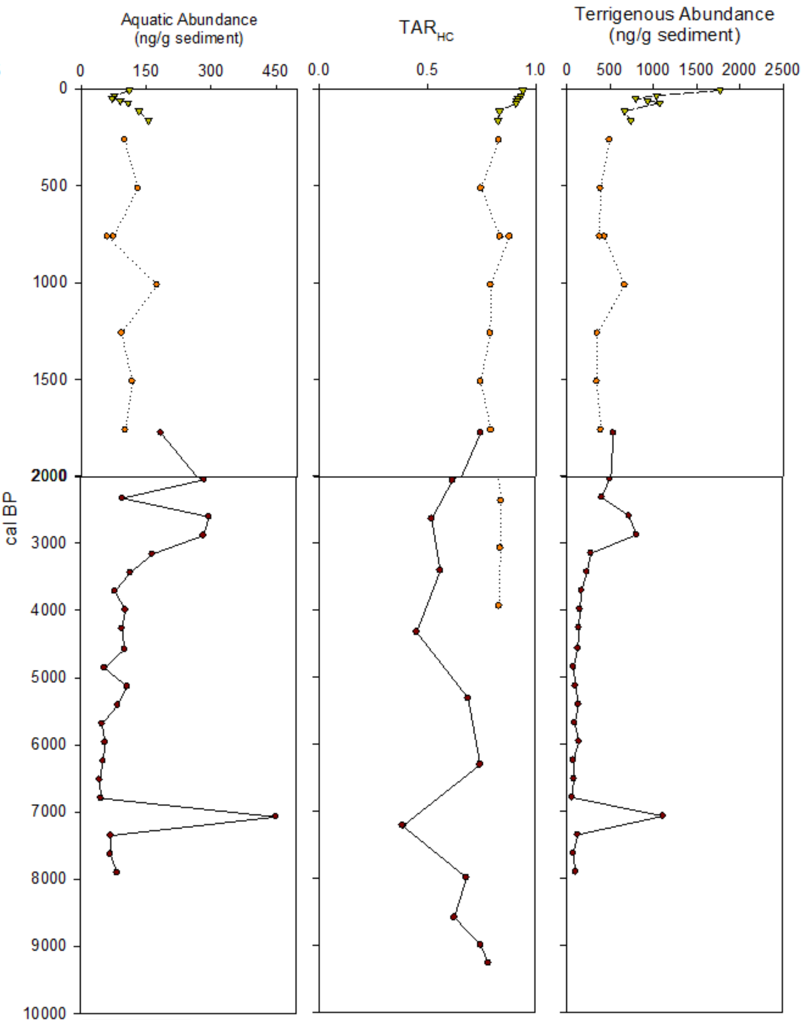
Temporal variations in the abundance of both aquatic and terrigenous *n*-alkane biomarkers from the Split Rock sediment cores

FIGURE 4-4

KEWEENAW



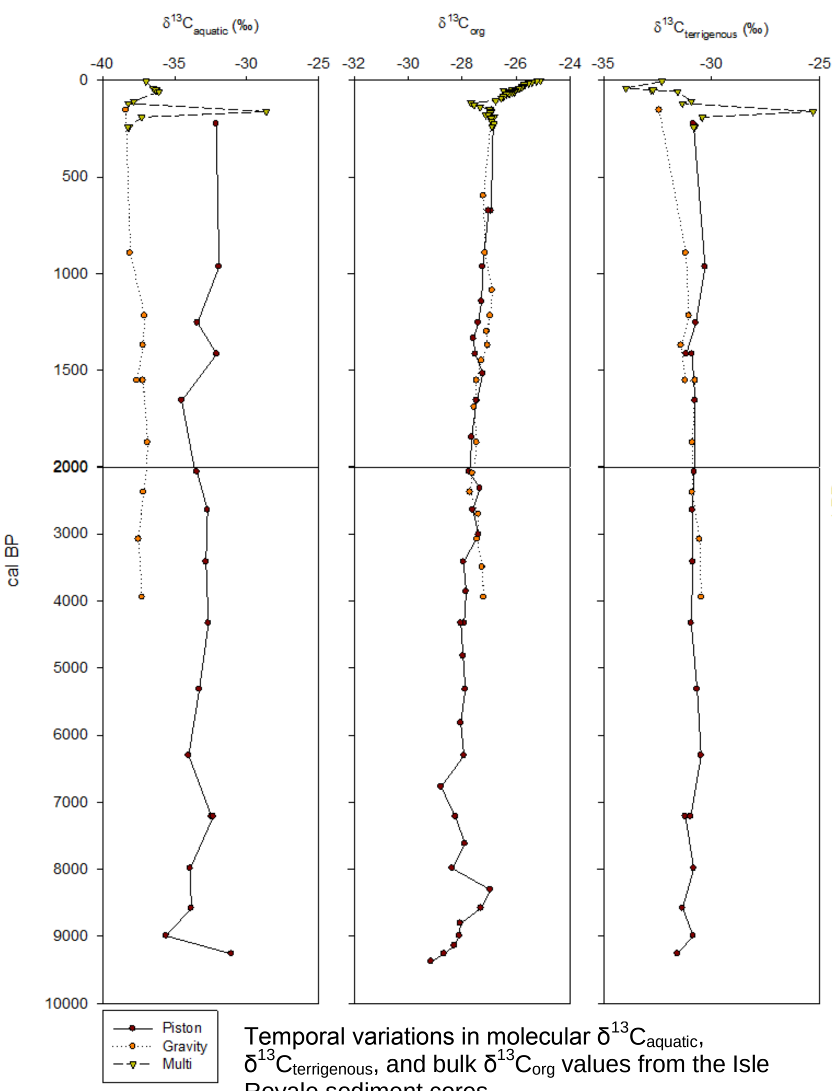
Temporal variations in molecular δ13Caquatic, δ13Cterrigenous, and bulk δ13Corg values from the Keweenaw sediment cores.



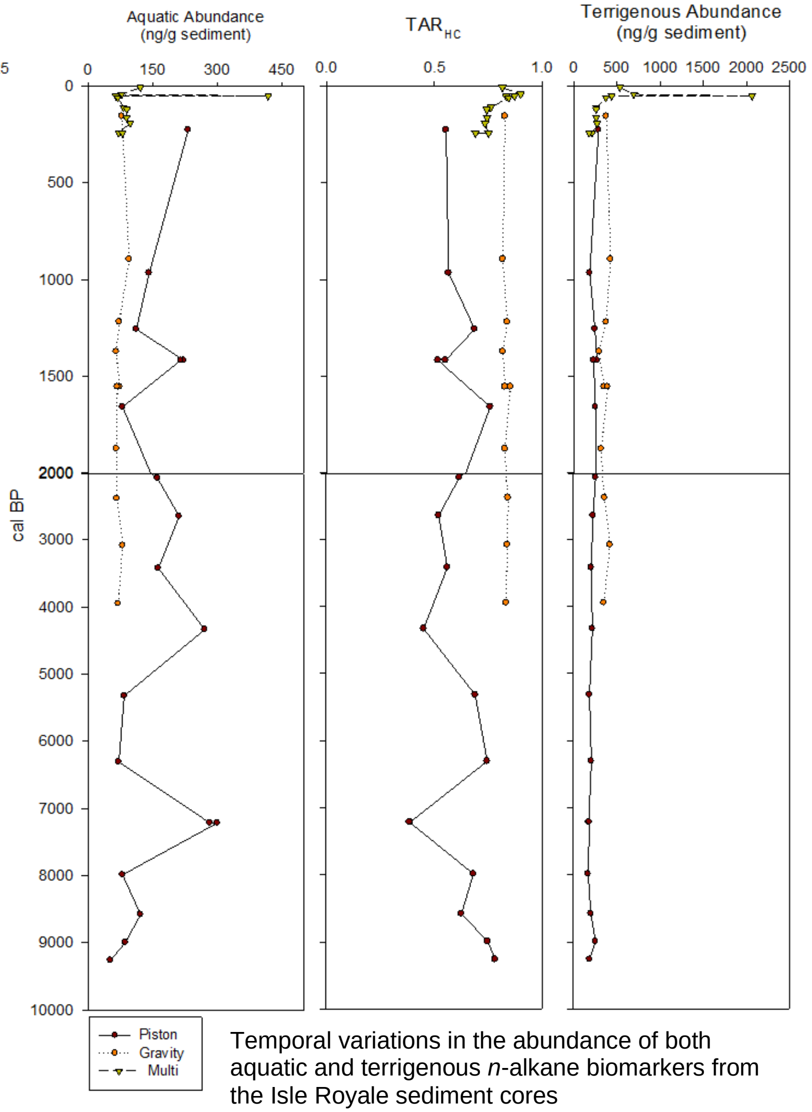
Temporal variations in the abundance of both aquatic and terrigenous *n*-alkane biomarkers from the Keweenaw sediment cores

FIGURE 4-5

ISLE ROYALE



Temporal variations in molecular $\delta^{13}C_{aquatic}$, $\delta^{13}C_{terrigenous}$, and bulk $\delta^{13}C_{org}$ values from the Isle Royale sediment cores.



Temporal variations in the abundance of both aquatic and terrigenous *n*-alkane biomarkers from the Isle Royale sediment cores

FIGURE 4-6

n-alkanes nor terrigenous long-chain *n*-alkanes exhibit the same trend as that observed for bulk sedimentary organic matter ($\delta^{13}C_{org}$; Figures 4-4, 4-5, and 4-6).

4.4. DISCUSSION

4.4.1. Controls on $\delta^{13}C_{aquatic}$ and Their Implications

Previous studies have shown the utility of *n*-alkane biomarkers as proxies for the source and delivery of organic matter within lacustrine sediments; whether the majority of organic matter delivered to sediments is dominated by aquatic or terrigenous sources. However, in the case of Lake Superior, the *n*-alkane record presents equivocal results. Despite evidence that TOC within Lake Superior is predominantly autochthonous (see: Chapters 2 and 3), the down-core trends in the $\delta^{13}C$ of aquatic *n*-alkanes and bulk sedimentary organic matter differ (Figures 4-4, 4-5, and 4-6). Interestingly, the Holocene record shows a systematic ^{13}C-depletion of aquatic *n*-alkanes to the present, while the $\delta^{13}C$ of bulk sedimentary organic matter shows systematic ^{13}C-enrichment. Thus, the isotope compositions of individual short-chain *n*-alkanes do not record the changes in ^{13}C incorporation seen in the bulk record; this discrepancy has also been documented in recent sediments of Lake Erie (Ostom et al., 1998). Therefore, other factors affecting the carbon isotope composition of short-chain *n*-alkanes must be taken into account.

The recognized controls on the carbon isotope compositions of bulk biomass and *n*-alkanes in both algae and bacteria are diverse and, although incompletely understood, include the availability and source of carbon substrate (Farquhar et al., 1982; Laws et al., 1995; Goericke et al., 1994), the biological mechanism of carbon metabolism and assimilation (Rau et al., 1996; Schouten et al., 1998; Hayes, 2001), and pathways of lipid biosynthesis (Monson and Hayes, 1982; van der Meer et al., 1998). In Lake Superior it is not clear what the dominant control on *n*-alkane $\delta^{13}C$ values are. However, if the major control was from carbon source/substrate, we would see that the $\delta^{13}C_{aquatic}$ trends in the same manner as $\delta^{13}C_{org}$, which it doesn't. Additionally, the biological mechanism of carbon metabolism and assimilation is not likely the determining factor as it is assumed that the lacustrine organisms present utilize the C_3 (Calvin-Benson) cycle in the assimilation of dissolved inorganic carbon (DIC). Thus, it is most likely that the pathway of lipid biosynthesis exerts the major control on *n*-alkane $\delta^{13}C$ values.

Lipids, including *n*-alkanes, within organisms are biosynthesized using the acetogenic pathway from acetyl coenzyme-A (acetyl Co-A). The major carbon isotope fractionation during lipid biosynthesis is associated with the oxidation of pyruvate to acetyl-CoA (DeNiro and Epstein, 1977) and is expressed as $(1-f)\varepsilon_{pdh}$, where f is the fraction of pyruvate transformed into acetyl-CoA during decarboxylation (Monson and Hayes, 1982). Additional fractionation occurs with the partitioning of carbon at branch points within the carbon metabolic pathway utilized (Hayes, 1993). Accordingly, isotopic depletion of lipids relative to bulk biomass becomes more marked as the fraction of lipids synthesized becomes reduced (Hayes, 2001). Hayes (1993) shows that the fractionation between lipids (e.g., fatty acids and acetogenic/straight-chain hydrocarbons) relative to biomass within most organisms is ca. 4‰. The fractionation seen between bulk sedimentary organic matter and *n*-alkane $\delta^{13}C$ values in Lake Superior ranges between 4 and >10‰; this additional depletion suggests that the fraction of pyruvate flowing to acetyl-CoA during lipid biosynthesis is small, which is consistent with the relatively low abundance of *n*-alkanes produced overall in algae and bacteria (Gelpi et al., 1970; Tornabene, 1980; Ladygina et al., 2006). Moreover, the light isotopic values of $\delta^{13}C_{aquatic}$ indicate little lipid biomass production overall within Lake Superior.

In algae, the concentration of lipid biomass is mostly determined by the availability of nitrogen (Fogg, 1953; Piorreck and Pohl, 1984). Essentially, in nitrogen-replete conditions most carbon, through photosynthetic processes, is directed towards the formation of protoplasm (protein and carbohydrates) of algal cells; whereas, in nitrogen deficient conditions carbon flow shifts to lipid production (Uriarte et al., 1993; Bell and Pond, 1996). Ergo, N starvation induces increased lipid production, resulting in the progressive ^{13}C-enrichment of lipids. Under such conditions $\delta^{13}C_{aquatic}$ would approach $\delta^{13}C_{org}$ (Hayes, 2001). In oligotrophic Lake Superior, it's quite possible that lake-wide primary productivity may not reach a point where the availability of nitrogen becomes low enough to prompt significant lipid production in algal cells. In areas of the lake with the highest productivity rates, it is conceivable that localized depletion of nitrogen within the water column may induce lipid production and subsequently the carbon isotopic value of lipids would approach that of $\delta^{13}C_{org}$. This scenario may explain the observed correlation between $\delta^{13}C_{org}$ and $\delta^{13}C_{aquatic}$ in the western arm of Lake Superior, where TOC MARs and $\delta^{13}C_{org}$ values are highest and TON MARs and $\delta^{15}N_{org}$ are lowest (O'Beirne et al., submitted).

The cause of the overall systematic depletion of $\delta^{13}C_{aquatic}$ values through the Holocene is unclear (although the progressive increase in N availability within Lake Superior could have led to a progressive decrease in lipid synthesis, overall). This enigma illustrates the need for further studies on the isotope effects associated with *n*-alkane biosynthesis in both autotrophs and heterotrophs in lacustrine systems. Since *n*-alkanes are common in both bacteria and algae, they are not diagnostic as a class. Furthermore, the tight coupling between heterotrophic bacteria and autotrophic phytoplankton within oligotrophic systems, i.e. Lake Superior (Cotner and Biddanda, 2002), provides additional limitations on the interpretation of sedimentary *n*-alkanes as related to carbon cycling and source. Future isotopic studies utilizing lipid biomarkers more specific to bacteria (i.e. hopanols) and algae (i.e. sterols) have the ability to provide a better understanding of carbon cycling and *n*-alkane production in Lake Superior.

N-alkane biomarkers are not immune to paleolimnetic changes and diagenetic alterations. Studies have shown that short chain aquatic *n*-alkanes are preferentially degraded in the water column, relative to long chain *n*-alkanes (see: Meyers, 1993 and references therein). Thus, it is possible that the short chain *n*-alkanes in samples presented here are not dominated by *n*-alkanes derived from algae but are, instead, dominated by degradation products of other sedimentary components. For example, isotopically light acids, alcohols, or esters can become defunctionalized during diagenesis, producing relatively refractory, isotopically light *n*-alkanes as their end products.

4.4.2. Controls on $\delta^{13}C_{terrigenous}$ and Their Implications

Terrigenous long chain *n*-alkanes transported to a lake are representative of the most refractory fractions of plant-wax lipids and in general do not undergo further degradation within lacustrine sedimentary environments. Through the Holocene the abundance of terrigenous biomarkers is relatively invariant, until the last 200 years when their abundance is greatly increased (Figures 4-4, 4-5, and 4-6). This is indicative of increased watershed disturbance (i.e. development and logging) after European settlement (discussed further below).

The $\delta^{13}C$ of terrigenous *n*-alkane biomarkers do not vary considerably throughout the Holocene; a period of ^{13}C-depletion is noted in the last 200 years (Figures 4-3, 4-4, and 4-5). The landscape surrounding Lake Superior over the last ca. 10,000 years has been dominated by C_3 vegetation, so it is unlikely that fluctuations in $\delta^{13}C_{terrigenous}$ values represent vegetative shifts between C_3/C_4 plant communities within the watershed. According to pollen records (Bernabo and Webb, 1977; Huber, 1996; Wright 1968), prior to 10,000 cal BP the watershed transitioned from shrub parkland to open conifer forest; dominated by herbaceous species, birch and spruce. From 10,000 to 9000 cal BP a shift to mixed forest is seen with the dominant species transitioning from spruce to pine. Forest assemblages within the watershed are currently dominated by coniferous/mixed forests (~74%), with hardwood forests constituting less than 8% (Frelich, 1995). Diefendorf et al. (2011) have shown that *n*-alkanes (*n*-C_{25} – *n*-C_{31}) are preferentially produced by angiosperms, while gymnosperms produce few, if any, *n*-alkanes. Thus, in the case of Lake Superior, it is safe to assume that the long-chain *n*-alkanes within lake sediments are almost entirely derived from angiosperms within the watershed. The ^{13}C-depletion in $\delta^{13}C_{terrigenous}$ values in the last 200 years must then reflect changes in lipid synthesis influenced by ontogenetic variability, climate conditions, and/or plant physiology on the incorporation of ^{13}C within the leaves of angiosperms.

To date, *n*-alkane production within plants corresponding to ontogenetic variation is complicated and not well described (Lockheart et al., 1997; Jetter and Schaffer, 2001). Climate variations (i.e. changes in precipitation and humidity) have been shown to cause ^{13}C-enrichment of bulk leaf $\delta^{13}C$ values (Panek and Waring, 1997; Diefendorf et al., 2010); however, this same ^{13}C-enrichment is not seen in *n*-alkanes (Diefendorf et al., 2010) and is suggested to be due to carbon partitioning and fractionation occurring during lipid biosynthesis (much like what occurs in aquatic organisms using the same acetogenic pathway for lipid biosynthesis, see above). Additionally, Diefendorf et al. (2010) found no correlation between *n*-alkane abundances and biosynthetic fractionation of *n*-alkanes in leaf biomass; a trend also observed between *n*-alkane biomarker abundance and stable isotope composition in Lake Superior sediments. This further emphasizes the inference that variation in $\delta^{13}C$ values of long-chain *n*-alkanes is most likely due to changes in the sources and/or fates of pyruvate in acetyl-CoA during the biosynthesis of *n*-alkanes.

Since $\delta^{13}C_{terrigenous}$ values in Lake Superior remain relatively constant through the Holocene, the sources and/or fates of pyruvate in acetyl-CoA during the biosynthesis of *n*-alkanes most likely remained unchanged as well, until the last ~200 years. The most recent ^{13}C-depletion of long-chain *n*-alkanes suggests changes in the biosynthesis of *n*-alkanes by angiosperms, although further investigation needs to be undertaken in order to confirm this interpretation.

4.5. CONCLUSION

Stable carbon isotope compositions of *n*-alkane biomarkers within sediments from across the Lake Superior basin for both aquatic and terrigenous *n*-alkane biomarkers provide ambiguous results in terms of addressing carbon flow and environmental conditions within Lake Superior over the last ca. 9000 years. It appears that the dominant influences on *n*-alkane $\delta^{13}C$ compositions in the Lake Superior system are associated with carbon isotope complexities involved in the biosynthesis of *n*-alkanes, which are often overlooked in paleolimnological reconstructions. Clearly, more work is required to confirm this hypothesis and to work out the details of the carbon isotope systematics of Lake Superior primary productivity.

CONCLUSION

Postglacial sediments of three piston and corresponding gravity cores taken from across the Lake Superior basin provide a historic baseline of primary productivity which is characterized by a slow and steady increase in TOC and TON abundances, as well as $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ compositions throughout the past 10,000 years. Analysis of eight sediment multicores sampled at high resolution encompassing the last 200 years reveal that 20th century increases in primary production are unique in the context of the Holocene. The latest increases in productivity are synchronous with recent climate change, suggesting that warming is prompting directional shifts towards more productive ecological and biogeochemical states in an otherwise pristine ecosystem. The most likely mechanisms linking climate warming to increasing primary production in Lake Superior involve increasing temperatures stimulating primary productivity through a positive feedback related to the length of the ice-free period.

Despite evidence that TOC within Lake Superior is predominantly autochthonous, the down-core trends in the $\delta^{13}C$ of aquatic *n*-alkanes and bulk sedimentary organic matter differ. The $\delta^{13}C$ of bulk sedimentary organic matter shows systematic ^{13}C-enrichment over the last ~9000 years, whereas the $\delta^{13}C$ values of aquatic derived *n*-alkanes exhibit a systematic ^{13}C-depletion to present-day. Down-core variation in $\delta^{13}C$ values of *n*-alkanes likely reflect multiple isotope effects associated with carbon partitioning and fractionation associated with the biosynthesis of *n*-alkanes, which are often overlooked in paleolimnological reconstructions. More work is required to confirm this hypothesis and to work out the details of the carbon isotope systematics of Lake Superior primary productivity.

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Appendices

APPENDIX A: General Core Information

SPLIT ROCK PISTON		KEWEENAW PISTON		ISLE ROYALE PISTON	
Core Section	**Length (cm)**	**Core Section**	**Length (cm)**	**Core Section**	**Length (cm)**
1	109	**1**	47	**1**	123
2	100	**2**	153	**2**	133
3	150	**3**	152	**3**	153
4	150	**4**	153	**4**	146
5	150	**5**	152		
6	100	**6**	154		
7	114	**7**	48		

APPENDIX B: ^{210}Pb and PSV data

BH09-2						
Center of Interval	Cum. Dry Mass	Unsup. Activity	MAR	AGE	Error of Age	Date A.D.
(cm)	(g/cm2)	(Bq/g)	(g/cm2/yr)	(yr)	(±s.d.)	
0.25	0.0720	1.8390	0.0252	2.857	1.30	2006.14
1.25	0.2286	1.6590	0.0252	9.072	1.27	1999.93
2.25	0.4051	1.5590	0.0252	16.077	1.29	1992.92
3.25	0.5994	1.4490	0.0252	23.787	1.30	1985.21
4.25	0.8155	1.2190	0.0252	32.362	1.32	1976.64
5.25	1.0371	1.0090	0.0252	41.156	1.34	1967.84
6.25	1.2744	0.7020	0.0252	50.573	1.40	1958.43
7	1.5395	0.5710	0.0252	61.090	1.44	1947.91
8	1.8189	0.4100	0.0252	72.178	1.54	1936.82
9.5	2.2633	0.2490	0.0252	89.812	1.82	1919.19
11.5	2.8822	0.1370	0.0252	114.372	2.26	1894.63
13.5	3.5004	0.0600	0.0252	138.905	3.73	1870.09
15.5	4.1135	0.0310	0.0252	163.235	5.48	1845.77
17.5	4.7186	0.0069	0.0252	187.247	17.96	1821.75

BH09-3						
Center of Interval	Cum. Dry Mass	Unsup. Activity	MAR	AGE	Error of Age	Date A.D.
(cm)	(g/cm2)	(Bq/g)	(g/cm2/yr)	(yr)	(±s.d.)	
0.25	0.0693	1.9089	0.0135	5.133	1.29	2003.87
1.25	0.2275	1.5689	0.0135	16.855	1.29	1992.14
2.25	0.4466	1.1489	0.0135	33.082	1.30	1975.92
3.25	0.7351	0.8309	0.0135	54.455	1.34	1954.55
4.25	1.1536	0.2509	0.0193	76.137	1.46	1932.86
5.25	1.6019	0.1079	0.0193	99.365	1.99	1909.63
6.25	1.9940	0.0565	0.0193	119.680	3.13	1889.32
7.25	2.3786	0.0492	0.0193	139.608	3.15	1869.39
8.25	2.7384	0.0231	0.0193	158.252	4.85	1850.75
9.5	3.2737	0.0083	0.0193	185.987	8.93	1823.01
11.5	3.9850	0.0043	0.0193	222.840	15.05	1786.16

BH09-4						
Center of Interval	Cum. Dry Mass	Unsup. Activity	MAR	AGE	Error of Age	Date A.D.
(cm)	(g/cm2)	(Bq/g)	(g/cm2/yr)	(yr)	(±s.d.)	
0.25	0.0735	1.5487	0.0269	2.731	1.33	2006.27
1.25	0.2428	1.3287	0.0269	9.025	1.33	1999.97
2.25	0.4898	0.8707	0.0269	18.207	1.32	1990.79
3.25	0.8900	0.2537	0.0269	33.086	1.63	1975.91
4.25	1.3808	0.1487	0.0269	51.331	1.89	1957.67
5.25	1.8767	0.1797	0.0269	69.765	1.89	1939.23
6.25	2.3462	0.3607	0.0269	87.221	1.50	1921.78
7.25	2.7941	0.2877	0.0179	146.941	1.58	1955.00
8.25	3.1655	0.1567	0.0179	160.210	1.92	1941.73
9.25	3.4363	0.1077	0.0179	166.162	2.28	1935.78
11.5	4.0908	0.0350	0.0179	193.456	3.82	1908.48
13.5	4.6017	0.0114	0.0179	213.225	9.62	1888.72
15.5	5.1048	0.0035	0.0179	276.028	24.39	1825.91
17.5	5.6227	0.0059	0.0179	297.483	16.56	1804.46

BH03-3

Center of Interval	Cum. Dry Mass	Unsup. Activity	MAR	AGE	Error of Age	Date A.D.
(cm)	(g/cm2)	(Bq/g)	(g/cm2/yr)	(yr)	(±s.d.)	
0.15	0.0482	0.4256	0.0857	0.562	1.18	2002.44
1.05	0.2462	0.4453	0.0857	2.873	1.16	2000.13
1.35	0.3251	0.4397	0.0857	3.793	1.17	1999.21
1.95	0.4904	0.3997	0.0857	5.722	1.21	1997.28
2.25	0.5780	0.3797	0.0857	6.744	1.23	1996.26
2.85	0.7608	0.3651	0.0857	8.877	1.29	1994.12
3.15	0.8570	0.3497	0.0857	10.000	1.32	1993.00
3.75	1.0546	0.3137	0.0857	12.306	1.38	1990.69
4.7	1.4031	0.3002	0.0857	16.372	1.51	1986.63
5.1	1.5490	0.2734	0.0857	18.075	1.58	1984.93
5.9	1.8446	0.2530	0.0857	21.524	1.73	1981.48
6.3	1.9971	0.2120	0.0857	23.303	1.81	1979.70
7.1	2.3163	0.1564	0.0857	27.028	1.95	1975.97
7.5	2.4793	0.1454	0.0857	28.930	2.03	1974.07
8.3	2.8162	0.1139	0.0857	32.861	2.19	1970.139
9.5	3.3395	0.0969	0.0857	38.967	2.46	1964.033
10.7	3.8858	0.0915	0.0857	45.342	2.82	1957.658
11.9	4.4155	0.0696	0.0857	51.523	3.18	1951.477
12.3	4.589	0.0689	0.0857	53.547	3.31	1949.453
14.5	5.7624	0.0629	0.0942	66.004	4.63	1936.996
16.5	6.7202	0.0486	0.0942	76.171	6.31	1926.829
20.5	8.6837	0.0198	0.0942	97.015	5.95	1905.985
24.5	10.5608	0.0142	0.0942	116.942	9.81	1886.058
29.5	12.8872	0.0066	0.0942	141.639	17.44	1861.361

LG MC

Center of Interval	Cum. Dry Mass	Unsup. Activity	MAR	AGE	Error of Age	Date A.D.
(cm)	(g/cm2)	(Bq/g)	(g/cm2/yr)	(yr)	(±s.d.)	
0.5	0.0347	2.4451	0.0336	1.033	3.43	2009.00
2.5	0.2985	1.9194	0.0336	8.884	4.02	1998.70
4.5	0.6852	1.1535	0.0336	20.393	4.34	1983.80
6.5	1.1307	0.5442	0.0336	33.652	3.57	1969.80
8.5	1.6332	0.3583	0.0336	48.607	3.82	1955.80
10.5	2.1387	0.1965	0.0336	63.652	3.47	1942.90
12.5	2.5997	0.1461	0.0336	77.372	4.00	1931.80
14.5	3.0623	0.1025	0.0336	91.140	4.81	1920.30
16.5	3.5359	0.0771	0.0336	105.235	6.35	1907.90
18.5	4.0256	0.0391	0.0336	119.810	7.91	1896.80
21	4.6660	0.0482	0.0269	143.616	14.34	1876.20
25	5.7187	0.0112	0.0269	182.750	14.78	1830.00
27	6.2664	0.0060	0.0269	203.111	28.59	1806.50

IR MC

Center of Interval	Cum. Dry Mass	Unsup. Activity	MAR	AGE	Error of Age	Date A.D.
(cm)	(g/cm2)	(Bq/g)	(g/cm2/yr)	(yr)	(±s.d.)	
0.5	0.0551	1.7535	0.0161	3.422	1.56	2006.58
1.5	0.2258	1.6446	0.0161	14.025	1.82	1995.98
2.5	0.4310	1.2507	0.0161	26.770	2.17	1983.23
3.5	0.6837	0.6859	0.0161	42.466	1.87	1967.53
4.5	0.9679	0.4015	0.0359	50.382	1.30	1959.62
5.5	1.2588	0.3286	0.0359	58.485	1.32	1951.51
6	1.4040	0.2760	0.0359	62.530	1.41	1947.47
6.5	1.5505	0.2658	0.0359	66.611	1.55	1943.39
7	1.6951	0.2291	0.0359	70.639	1.78	1939.36
7.5	1.8411	0.1992	0.0359	74.705	2.18	1935.29
8	1.9851	0.1577	0.0135	85.372	2.83	1924.63
8.5	2.1270	0.1047	0.0135	95.883	3.68	1914.12
9	2.2718	0.0689	0.0135	106.609	4.72	1903.39
10	2.5614	0.0312	0.0135	128.061	5.87	1881.939
12	3.1343	0.0174	0.0135	170.498	8.82	1839.502
13.5	3.5637	0.0071	0.0135	202.305	13.7	1807.695

EM MC						
Center of Interval	Cum. Dry Mass	Unsup. Activity	MAR	AGE	Error of Age	Date A.D.
(cm)	(g/cm2)	(Bq/g)	(g/cm2/yr)	(yr)	(±s.d.)	
0.5	0.0361	1.7268	0.0090	4.008	0.46	2005.99
1.0	0.1187	1.4327	0.0090	13.194	0.38	1996.81
2.0	0.3189	1.0772	0.0090	35.438	0.43	1974.56
3.0	0.5321	0.8877	0.0090	59.124	0.55	1950.88
4.0	0.7737	0.4353	0.0090	85.962	0.74	1924.04
5.0	1.0569	0.1023	0.0090	117.428	2.27	1892.57
7.0	1.6532	0.0290	0.0090	183.694	6.57	1826.31
8.0	1.9782	0.0097	0.0090	219.800	9.70	1790.20
9.0	2.3828	0.0000				

CM MC						
Center of Interval	Cum. Dry Mass	Unsup. Activity	MAR	AGE	Error of Age	Date A.D.
(cm)	(g/cm2)	(Bq/g)	(g/cm2/yr)	(yr)	(±s.d.)	
0.5	0.0475	1.2407	0.0072	6.600	0.43	2003.40
1.0	0.1291	1.0722	0.0072	17.928	0.45	1992.07
2.0	0.3234	0.9096	0.0072	44.917	0.54	1965.08
3.0	0.5439	0.5837	0.0072	75.538	0.64	1934.46
4.0	0.7923	0.2346	0.0072	110.042	1.15	1899.96
5.0	1.0648	0.0726	0.0072	147.882	3.19	1862.12
7.0	1.6782	0.0136	0.0072	233.079	7.03	1776.92
9.0	2.3518	0.0000				

SPLIT ROCK	Inclination		
FEATURE	DEPTH	AGE	Error of Age
(Lund, 1996)	(mblf)	cal BP	(±s.d.)
5	0.56	2065	95
6	0.89	2610	150
7	1.09	3655	185
8	1.85	4300	350
9	2.33	4975	225
10	3.26	7225	195
11	3.74	7580	80
12	4.12	7760	80
Glacial Varves	4.97	9485	65
Regression	y = 1639.6x + 1361.8		
r^2	0.9850		

SPLIT ROCK			
DEPTH	DEC	INC	AGE
mblf	3 pt Avg.	3 pt Avg.	cal BP
0.06	191.10	18.87	1564
0.10	176.90	24.45	1616
0.13	176.90	24.45	1669
0.16	186.70	34.80	1721
0.20	196.20	39.60	1774
0.23	196.20	39.60	1826
0.26	207.00	43.43	1879
0.30	217.45	53.30	1931
0.33	217.45	53.30	1984
0.36	223.47	52.73	2036
0.40	232.05	51.35	2089
0.43	232.05	51.35	2142
0.46	233.77	50.17	2194
0.50	236.35	49.70	2247
0.53	236.35	49.70	2299
0.56	204.17	53.23	2352
0.60	188.50	54.05	2404
0.63	188.50	54.05	2457
0.66	205.13	54.10	2509
0.70	189.10	57.25	2562
0.73	189.10	57.25	2615
0.76	205.03	54.50	2667
0.80	237.65	51.60	2719
0.83	237.65	51.60	2772
0.86	240.90	47.43	2825
0.90	242.15	44.05	2877
0.93	242.15	44.05	2930
0.96	253.83	50.27	2982
1.00	262.30	50.90	3035
1.03	262.30	50.90	3087
1.06	262.23	54.20	3140
1.10	269.65	61.75	3192
1.12	269.65	61.75	3224
1.15	265.93	61.30	3276
1.18	260.30	60.60	3329
1.22	260.30	60.60	3382
1.25	261.67	59.57	3434
1.28	261.45	58.95	3487
1.32	261.45	58.95	3539
1.35	263.83	58.77	3592
1.38	266.50	57.95	3644
1.42	266.50	57.95	3697
1.45	268.33	57.23	3749
1.48	270.30	57.10	3802
1.52	270.30	57.10	3854
1.55	271.07	56.27	3907
1.58	272.30	55.20	3960
1.62	272.30	55.20	4012
1.65	271.67	53.37	4065
1.66	271.50	52.15	4086
1.72	271.50	52.15	4170
1.75	270.00	52.90	4222
1.78	268.70	52.05	4275
1.85	268.70	52.05	4375
1.85	266.97	47.73	4380

1.88	265.25	46.75	4432
1.92	265.25	46.75	4485
1.95	256.57	50.40	4537
1.98	251.35	48.40	4590
2.02	251.35	48.40	4643
2.05	245.67	52.30	4695
2.08	236.75	58.90	4748
2.10	236.75	58.90	4771
2.13	234.30	60.40	4824
2.17	231.85	61.75	4876
2.20	231.85	61.75	4929
2.23	232.17	62.13	4981
2.27	231.10	63.15	5034
2.30	231.10	63.15	5087
2.33	229.83	63.20	5139
2.37	230.05	63.10	5192
2.40	230.05	63.10	5244
2.43	226.43	63.40	5297
2.47	223.25	63.65	5349
2.50	223.25	63.65	5402
2.53	231.40	63.20	5454
2.57	233.45	63.15	5507
2.60	233.45	63.15	5560
2.63	238.27	61.87	5612
2.67	247.80	60.80	5665
2.70	247.80	60.80	5717
2.73	247.80	60.80	5770
2.77	247.90	59.30	5822
2.80	247.90	59.30	5875
2.83	247.55	61.40	5927
2.87	247.20	63.50	5980
2.90	247.20	63.50	6032
2.97	242.10	63.10	6138
3.00	242.10	63.10	6190
3.03	241.63	63.30	6243
3.07	238.85	63.20	6295
3.10	238.85	63.20	6348
3.13	243.27	58.90	6400
3.17	246.40	57.00	6453
3.20	246.40	57.00	6505
3.23	249.60	55.97	6558
3.27	254.05	52.10	6610
3.30	254.05	52.10	6663
3.38	257.37	52.80	6794
3.40	260.00	54.05	6821
3.43	259.53	54.80	6873

3.47	261.30	55.25	6926
3.50	261.30	55.25	6978
3.53	261.30	55.25	7031
3.57	258.60	56.30	7083
3.58	258.60	56.30	7110
3.62	254.70	60.65	7162
3.65	250.80	65.00	7215
3.75	250.80	65.00	7370
3.75	247.85	68.35	7372
3.78	247.85	68.35	7425
3.82	240.43	62.67	7477
3.85	235.25	61.50	7530
3.88	235.25	61.50	7583
3.92	236.97	61.43	7635
3.95	233.00	56.30	7688
3.98	233.00	56.30	7740
4.02	237.90	58.33	7793
4.05	244.05	61.85	7845
4.08	244.05	61.85	7898
4.12	253.83	59.60	7950
4.15	260.55	58.75	8003
4.18	260.55	58.75	8055
4.22	269.30	59.67	8108
4.25	280.10	58.30	8160
4.28	280.10	58.30	8213
4.32	282.23	56.97	8266
4.35	286.65	57.90	8318
4.38	286.65	57.90	8371
4.42	290.53	56.87	8423
4.45	292.40	54.55	8476
4.48	292.40	54.55	8528
4.52	293.17	55.77	8581
4.55	296.50	56.50	8633
4.58	296.50	56.50	8686
4.62	292.80	55.80	8738
4.65	290.05	56.30	8791
4.68	290.05	56.30	8844
4.72	278.97	57.43	8896
4.75	271.10	57.05	8949
4.78	271.10	57.05	9001
4.82	259.87	57.60	9054
4.85	247.10	59.20	9106
4.88	247.10	59.20	9159
4.92	195.97	61.07	9211
4.95	165.55	61.75	9264
4.98	165.55	61.75	9316

KEWEENAW	Inclination		
FEATURE	DEPTH	AGE	Error of Age
(Lund, 1996)	(mblf)	cal BP	(±s.d.)
5	0.44	2065	95
6	0.58	2610	150
7	1.38	3655	185
8	1.69	4300	350
9	2.69	4975	225
10	4.09	7225	195
11	4.35	7580	80
Mazama Ash	4.4	7627	150
12	4.64	7760	80
13	4.91	8625	425
Glacial Varves	5.37	9485	65
Regression	y = 1386.9x + 1636.6		
r^2	0.9901		

KEWEENAW			
DEPTH	DEC	INC	AGE
mblf	3 pt Avg.	3 pt Avg.	cal BP
0	116.41	20.54	1637
0.01	115.13	21.66	1650
0.02	114.52	22.66	1664
0.03	114.40	23.14	1678
0.04	115.15	23.65	1692
0.05	116.68	24.57	1706
0.06	119.08	26.10	1720
0.07	122.43	28.41	1734
0.08	126.82	31.07	1748
0.09	132.40	33.74	1761
0.1	139.02	35.74	1775
0.11	145.66	37.08	1789
0.12	150.47	37.67	1803
0.13	151.96	37.61	1817
0.14	150.28	36.96	1831
0.15	146.82	36.53	1845
0.16	142.76	37.40	1859
0.17	138.21	40.42	1872
0.18	131.86	46.03	1886
0.19	120.79	54.41	1900
0.2	99.65	64.49	1914
0.21	58.72	71.75	1928
0.22	134.72	72.53	1942
0.23	219.97	67.54	1956
0.24	327.76	61.41	1969
0.25	324.62	57.34	1983
0.26	324.14	55.18	1997
0.27	323.63	54.08	2011
0.28	322.49	53.72	2025
0.29	320.45	53.92	2039
0.3	317.88	54.59	2053
0.31	315.09	55.54	2067
0.32	312.09	56.43	2080
0.33	308.87	56.99	2094
0.34	305.86	57.18	2108
0.35	303.72	57.17	2122
0.36	302.75	57.05	2136
0.37	302.06	56.89	2150
0.38	300.47	56.76	2164
0.39	297.70	56.63	2177
0.4	294.59	56.55	2191
0.41	292.01	56.76	2205
0.42	289.88	57.42	2219
0.43	287.48	58.28	2233
0.44	284.58	58.94	2247
0.45	282.05	59.89	2261
0.46	286.43	56.67	2275
0.47	292.40	53.12	2288
0.57	299.02	48.98	2427
0.58	300.23	48.83	2441
0.59	300.99	48.87	2455

0.6	301.68	48.74	2469
0.61	302.13	48.63	2483
0.62	302.56	48.69	2496
0.63	302.55	48.96	2510
0.64	302.03	49.27	2524
0.65	301.07	49.54	2538
0.66	300.02	49.73	2552
0.67	299.01	49.88	2566
0.68	298.00	50.04	2580
0.69	296.86	50.24	2594
0.7	295.63	50.45	2607
0.71	294.45	50.70	2621
0.72	293.44	51.08	2635
0.73	292.55	51.57	2649
0.74	291.66	52.16	2663
0.75	290.69	52.72	2677
0.76	289.68	53.25	2691
0.77	288.74	53.70	2705
0.78	287.93	54.06	2718
0.79	287.26	54.36	2732
0.8	286.78	54.64	2746
0.81	286.54	54.81	2760
0.82	286.53	54.87	2774
0.83	286.70	54.86	2788
0.84	286.96	54.96	2802
0.85	287.27	55.19	2815
0.86	287.49	55.49	2829
0.87	287.43	55.70	2843
0.88	286.92	55.74	2857
0.89	285.92	55.61	2871
0.9	284.47	55.30	2885
0.91	282.75	54.88	2899
0.92	280.99	54.38	2913
0.93	279.66	53.87	2926
0.94	279.03	53.29	2940
0.95	279.03	52.74	2954
0.96	279.31	52.30	2968
0.97	279.70	52.07	2982
0.98	280.37	52.04	2996
0.99	281.38	52.14	3010
1	282.48	52.23	3024
1.01	283.27	52.23	3037
1.02	283.48	52.22	3051
1.03	283.17	52.30	3065
1.04	282.71	52.46	3079
1.05	282.37	52.66	3093
1.06	282.15	52.92	3107
1.07	281.84	53.32	3121
1.08	281.37	53.86	3134
1.09	280.84	54.52	3148
1.1	280.43	55.23	3162
1.11	280.16	55.93	3176
1.12	279.95	56.59	3190
1.13	279.72	57.24	3204
1.14	279.50	57.93	3218
1.15	279.19	58.60	3232
1.16	278.75	59.07	3245
1.17	278.14	59.23	3259
1.18	277.48	59.14	3273
1.19	276.92	58.91	3287
1.2	276.64	58.71	3301
1.21	276.70	58.64	3315
1.22	276.95	58.74	3329
1.23	277.15	58.89	3342
1.24	277.22	58.96	3356
1.25	277.28	59.00	3370
1.26	277.42	59.06	3384
1.27	277.69	59.17	3398
1.28	278.02	59.32	3412
1.29	278.32	59.54	3426
1.3	278.63	59.78	3440
1.31	278.98	59.99	3453
1.32	279.59	60.22	3467
1.33	280.49	60.61	3481
1.34	281.54	61.13	3495
1.35	282.42	61.69	3509
1.36	282.93	62.13	3523
1.37	283.14	62.45	3537
1.38	283.20	62.72	3551
1.39	283.24	63.01	3564
1.4	283.20	63.26	3578
1.41	283.09	63.44	3592
1.42	282.87	63.53	3606
1.43	282.79	63.52	3620
1.44	282.74	63.44	3634
1.45	282.61	63.32	3648
1.46	282.14	63.20	3661
1.47	281.40	63.10	3675
1.48	280.46	62.97	3689
1.49	279.30	62.80	3703
1.5	278.04	62.60	3717
1.51	277.01	62.41	3731

1.52	276.50	62.29	3745
1.53	276.43	62.28	3759
1.54	276.57	62.33	3772
1.55	276.68	62.35	3786
1.56	276.79	62.25	3800
1.57	277.02	62.03	3814
1.58	277.43	61.73	3828
1.59	277.91	61.44	3842
1.6	278.21	61.17	3856
1.61	278.35	60.83	3870
1.62	278.50	60.36	3883
1.63	278.85	59.81	3897
1.64	279.23	59.24	3911
1.65	279.48	58.74	3925
1.66	279.52	58.34	3939
1.67	279.39	58.06	3953
1.68	279.25	57.86	3967
1.69	279.14	57.75	3980
1.7	279.13	57.77	3994
1.71	279.21	57.96	4008
1.72	279.34	58.28	4022
1.73	279.50	58.65	4036
1.74	279.71	58.99	4050
1.75	279.87	59.31	4064
1.76	279.89	59.59	4078
1.77	279.69	59.90	4091
1.78	279.34	60.28	4105
1.79	278.90	60.69	4119
1.8	278.46	61.05	4133
1.81	278.11	61.31	4147
1.82	277.86	61.48	4161
1.83	277.64	61.55	4175
1.84	277.44	61.51	4188
1.85	277.25	61.44	4202
1.86	277.04	61.45	4216
1.87	276.83	61.60	4230
1.88	276.65	61.88	4244
1.89	276.57	62.26	4258
1.9	276.53	62.65	4272
1.91	276.50	62.97	4286
1.92	276.50	63.19	4299
1.93	276.51	63.36	4313
1.94	276.59	63.50	4327
1.95	276.54	63.57	4341
1.96	276.32	63.55	4355
1.97	276.00	63.41	4369
1.98	275.92	63.17	4383
1.99	276.47	62.91	4397
2	277.60	62.78	4410
2.01	279.05	62.92	4424
2.02	280.45	63.25	4438
2.03	281.84	63.51	4452
2.04	285.42	62.71	4466
2.05	287.24	61.76	4480
2.15	287.98	60.97	4618
2.16	285.77	61.01	4632
2.17	284.89	61.09	4646
2.18	284.44	60.98	4660
2.19	284.08	61.05	4674
2.2	283.53	61.26	4688
2.21	283.01	61.61	4702
2.22	282.70	61.96	4716
2.23	282.64	62.29	4729
2.24	282.79	62.70	4743
2.25	283.00	63.15	4757
2.26	283.08	63.61	4771
2.27	282.95	63.99	4785
2.28	282.71	64.25	4799
2.29	282.53	64.40	4813
2.3	282.31	64.46	4826
2.31	281.67	64.44	4840
2.32	280.49	64.29	4854
2.33	278.97	64.01	4868
2.34	277.51	63.78	4882
2.35	276.42	63.82	4896
2.36	275.84	64.25	4910
2.37	275.92	64.93	4924
2.38	276.65	65.58	4937
2.39	277.96	66.06	4951
2.4	279.41	66.35	4965
2.41	280.46	66.49	4979
2.42	280.95	66.52	4993
2.43	281.12	66.47	5007
2.44	281.18	66.32	5021
2.45	280.97	66.12	5035
2.46	280.24	65.94	5048
2.47	279.03	65.89	5062
2.48	277.55	65.99	5076
2.49	275.96	66.23	5090
2.5	274.15	66.56	5104
2.51	272.00	66.90	5118
2.52	269.56	67.14	5132

2.53	267.14	67.34	5145
2.54	265.19	67.58	5159
2.55	264.00	67.88	5173
2.56	263.55	68.14	5187
2.57	263.68	68.29	5201
2.58	264.26	68.26	5215
2.59	265.16	68.05	5229
2.6	266.19	67.79	5243
2.61	267.14	67.65	5256
2.62	267.91	67.70	5270
2.63	268.42	67.88	5284
2.64	268.76	68.17	5298
2.65	268.98	68.52	5312
2.66	269.19	68.90	5326
2.67	269.51	69.21	5340
2.68	270.21	69.45	5353
2.69	271.41	69.62	5367
2.7	272.88	69.72	5381
2.71	274.12	69.68	5395
2.72	274.79	69.46	5409
2.73	274.86	69.18	5423
2.74	274.48	68.92	5437
2.75	273.79	68.72	5451
2.76	272.87	68.58	5464
2.77	271.74	68.53	5478
2.78	270.36	68.57	5492
2.79	268.70	68.65	5506
2.8	266.99	68.74	5520
2.81	265.57	68.84	5534
2.82	264.76	68.96	5548
2.83	264.47	69.10	5562
2.84	264.38	69.24	5575
2.85	264.31	69.33	5589
2.86	264.42	69.36	5603
2.87	265.06	69.36	5617
2.88	266.38	69.38	5631
2.89	268.24	69.43	5645
2.9	270.36	69.50	5659
2.91	272.53	69.61	5672
2.92	274.77	69.74	5686
2.93	276.80	69.75	5700
2.94	278.29	69.60	5714
2.95	279.14	69.40	5728
2.96	279.71	69.30	5742
2.97	280.31	69.26	5756
2.98	280.84	69.16	5770
2.99	281.28	68.93	5783
3	281.59	68.64	5797
3.01	281.99	68.47	5811
3.02	282.68	68.52	5825
3.03	283.63	68.68	5839
3.04	284.64	68.76	5853
3.05	285.34	68.67	5867
3.06	285.79	68.50	5881
3.07	285.97	68.29	5894
3.08	285.82	68.03	5908
3.09	285.37	67.67	5922
3.1	284.87	67.26	5936
3.11	284.54	66.89	5950
3.12	284.26	66.55	5964
3.13	283.80	66.19	5978
3.14	283.14	65.85	5991
3.15	282.57	65.64	6005
3.16	282.34	65.69	6019
3.17	282.34	65.96	6033
3.18	282.24	66.36	6047
3.19	281.69	66.70	6061
3.2	280.54	66.96	6075
3.21	278.79	67.09	6089
3.22	276.73	67.21	6102
3.23	274.70	67.24	6116
3.24	272.93	67.14	6130
3.25	271.32	66.82	6144
3.26	269.64	66.33	6158
3.27	268.06	65.77	6172
3.28	266.87	65.41	6186
3.29	266.48	65.42	6200
3.3	266.76	65.74	6213
3.31	267.16	66.04	6227
3.32	267.20	66.10	6241
3.33	266.81	66.01	6255
3.34	266.36	66.02	6269
3.35	265.99	66.19	6283
3.36	265.51	66.36	6297
3.37	264.66	66.35	6310
3.38	263.51	66.19	6324
3.39	262.38	66.02	6338
3.4	261.44	65.97	6352
3.41	260.74	66.07	6366
3.42	260.21	66.21	6380
3.43	259.91	66.23	6394
3.44	259.71	66.00	6408

3.45	259.62	65.57	6421
3.46	259.51	64.94	6435
3.47	259.39	64.26	6449
3.48	259.16	63.57	6463
3.49	258.86	62.97	6477
3.5	258.50	62.38	6491
3.51	258.13	61.79	6505
3.52	257.91	61.29	6518
3.53	257.91	60.93	6532
3.54	258.08	60.69	6546
3.55	258.23	60.51	6560
3.56	258.14	60.19	6574
3.57	257.51	59.54	6588
3.58	256.22	58.49	6602
3.59	254.45	57.24	6616
3.6	252.59	56.05	6629
3.61	250.66	54.96	6643
3.62	253.91	55.03	6657
3.63	257.27	54.97	6671
3.73	260.93	54.97	6810
3.74	259.82	53.94	6824
3.75	258.79	53.05	6837
3.76	257.81	52.27	6851
3.77	256.87	51.76	6865
3.78	256.15	51.73	6879
3.79	255.75	52.04	6893
3.8	255.63	52.43	6907
3.81	255.69	52.72	6921
3.82	255.83	52.89	6935
3.83	255.98	52.86	6948
3.84	256.08	52.64	6962
3.85	256.07	52.25	6976
3.86	255.80	51.84	6990
3.87	255.32	51.47	7004
3.88	254.72	51.23	7018
3.89	254.21	51.17	7032
3.9	253.81	51.26	7046
3.91	253.54	51.39	7059
3.92	253.39	51.53	7073
3.93	253.35	51.68	7087
3.94	253.40	51.87	7101
3.95	253.49	52.07	7115
3.96	253.54	52.24	7129
3.97	253.53	52.38	7143
3.98	253.48	52.54	7156
3.99	253.43	52.74	7170

4	253.36	52.96	7184
4.01	253.22	53.16	7198
4.02	253.01	53.29	7212
4.03	252.78	53.34	7226
4.04	252.63	53.35	7240
4.05	252.62	53.31	7254
4.06	252.71	53.22	7267
4.07	252.71	53.07	7281
4.08	252.62	52.88	7295
4.09	252.44	52.70	7309
4.1	252.35	52.61	7323
4.11	252.36	52.74	7337
4.12	252.48	53.07	7351
4.13	252.64	53.52	7364
4.14	252.74	54.03	7378
4.15	252.79	54.63	7392
4.16	252.84	55.42	7406
4.17	253.00	56.44	7420
4.18	253.21	57.59	7434
4.19	253.36	58.69	7448
4.2	253.26	59.66	7462
4.21	252.83	60.54	7475
4.22	252.04	61.43	7489
4.23	250.86	62.39	7503
4.24	249.31	63.31	7517
4.25	247.34	64.07	7531
4.26	245.00	64.58	7545
4.27	242.22	64.94	7559
4.28	239.20	65.25	7573
4.29	235.90	65.53	7586
4.3	232.56	65.69	7600
4.31	229.11	65.75	7614
4.32	225.94	65.81	7628
4.33	223.09	65.97	7642
4.34	220.68	66.23	7656
4.35	218.47	66.47	7670
4.36	216.43	66.56	7683
4.37	214.54	66.43	7697
4.38	212.87	66.20	7711
4.39	211.32	65.85	7725
4.4	209.89	65.44	7739
4.41	208.59	64.92	7753
4.42	207.56	64.36	7767
4.43	206.78	63.80	7781
4.44	206.22	63.35	7794
4.45	205.80	62.97	7808

4.46	205.54	62.71	7822
4.47	205.40	62.63	7836
4.48	205.24	62.79	7850
4.49	205.03	63.08	7864
4.5	204.77	63.42	7878
4.51	204.74	63.77	7892
4.52	205.03	64.19	7905
4.53	205.66	64.58	7919
4.54	206.51	64.84	7933
4.55	207.48	64.95	7947
4.56	208.49	64.92	7961
4.57	209.55	64.86	7975
4.58	210.67	64.86	7989
4.59	211.78	64.88	8002
4.6	212.82	64.84	8016
4.61	213.81	64.75	8030
4.62	214.90	64.76	8044
4.63	216.14	64.95	8058
4.64	217.43	65.28	8072
4.65	218.52	65.63	8086
4.66	219.26	65.88	8100
4.67	219.81	65.93	8113
4.68	220.26	65.78	8127
4.69	220.75	65.48	8141
4.7	221.20	65.09	8155
4.71	221.74	64.71	8169
4.72	222.56	64.42	8183
4.73	223.72	64.24	8197
4.74	225.22	64.11	8211
4.75	226.76	64.00	8224
4.76	228.14	63.90	8238
4.77	229.24	63.90	8252
4.78	230.08	64.02	8266
4.79	230.69	64.21	8280
4.8	231.03	64.32	8294
4.81	231.04	64.30	8308
4.82	230.77	64.16	8321
4.83	230.25	63.97	8335
4.84	229.77	63.75	8349
4.85	229.51	63.60	8363
4.86	229.68	63.59	8377
4.87	230.18	63.73	8391
4.88	231.00	63.97	8405
4.89	231.92	64.25	8419
4.9	232.75	64.55	8432
4.91	233.21	64.90	8446
4.92	233.19	65.22	8460
4.93	232.74	65.47	8474
4.94	231.94	65.57	8488
4.95	230.83	65.46	8502
4.96	229.40	65.06	8516
4.97	227.65	64.38	8529
4.98	225.87	63.52	8543
4.99	224.50	62.70	8557
5	223.78	62.05	8571
5.01	223.67	61.63	8585

ISLE ROYALE	Inclination		
FEATURE	DEPTH	AGE	Error of Age
(Lund, 1996)	(mblf)	cal BP	(±s.d.)
2	0.43	1205	135
4	0.8	1610	100
5	1.315	2065	95
6	1.585	2610	150
9	1.875	4975	225
10	2.505	7225	195
11	2.645	7580	80
Mazama Ash	2.66	7627	150
12	2.785	7760	80
13	3.095	8625	425
Glacial Varves	3.435	9485	65
Regression	$y = 177.56x^5 - 1850.6x^4 + 6500.7x^3 - 8429.3x^2 + 5227.3x + 30.217$		
r^2	0.9946		

ISLE ROYALE			
DEPTH	DEC	INC	AGE
mblf	3 pt Avg.	3 pt Avg.	cal BP
0.19	271.11	78.70	761
0.25	96.16	70.94	905
0.26	105.43	67.47	926
0.27	112.50	64.60	945
0.28	118.39	62.11	965
0.29	123.61	60.27	983
0.3	128.54	58.84	1001
0.31	133.06	57.92	1018
0.32	137.30	57.37	1034
0.33	141.21	57.14	1050
0.34	145.01	56.75	1065
0.35	148.40	56.12	1079
0.36	150.67	55.30	1093
0.37	151.43	54.60	1106
0.38	151.33	54.09	1119
0.39	151.83	53.28	1131
0.4	153.64	51.62	1143
0.41	156.07	48.92	1154
0.42	157.79	46.10	1165
0.43	158.34	44.02	1176
0.44	158.14	43.11	1186
0.45	157.71	43.12	1195
0.46	157.13	43.65	1205
0.47	156.19	44.29	1214
0.48	155.01	44.88	1222
0.49	153.94	45.51	1231
0.5	153.53	46.14	1239
0.51	153.94	46.57	1247
0.52	155.16	46.81	1255
0.53	156.95	46.94	1262
0.54	158.89	47.09	1269
0.55	160.78	47.19	1277
0.56	162.53	47.20	1283
0.57	164.21	47.01	1290
0.58	165.89	46.50	1297
0.59	167.51	45.68	1304
0.6	169.13	44.57	1310
0.61	170.86	43.18	1317
0.62	173.10	40.30	1323
0.63	175.53	38.50	1329
0.64	178.17	36.67	1336
0.65	180.80	36.19	1342
0.66	183.46	34.84	1348
0.67	185.82	34.10	1355
0.68	187.72	34.02	1361

0.69	189.28	34.44	1368
0.7	190.68	35.15	1374
0.71	191.96	36.05	1381
0.72	193.18	37.20	1388
0.73	194.38	38.61	1394
0.74	195.56	40.20	1401
0.75	197.07	41.63	1408
0.76	198.76	42.56	1415
0.77	200.57	42.80	1423
0.78	202.11	42.51	1430
0.79	203.45	42.12	1438
0.8	204.65	41.88	1446
0.81	205.70	41.84	1454
0.82	206.58	41.91	1462
0.83	207.19	42.13	1471
0.84	207.69	42.58	1479
0.85	208.27	43.27	1488
0.86	209.17	44.21	1497
0.87	210.32	45.29	1507
0.88	211.57	46.36	1517
0.89	212.87	47.31	1527
0.9	214.38	48.13	1537
0.91	216.18	48.95	1547
0.92	218.24	49.77	1558
0.93	220.28	50.57	1569
0.94	222.28	51.39	1581
0.95	224.07	52.24	1592
0.96	225.71	53.16	1604
0.97	227.02	54.07	1617
0.98	228.09	55.04	1629
0.99	229.02	56.01	1642
1	229.93	56.96	1656
1.01	230.93	57.84	1670
1.02	232.23	58.67	1684
1.03	233.86	59.33	1698
1.04	235.79	59.77	1713
1.05	237.82	60.03	1728
1.06	239.94	60.34	1744
1.07	242.07	60.83	1760
1.08	243.96	61.38	1776
1.09	245.40	61.80	1793
1.1	246.29	62.07	1810
1.11	246.90	62.39	1827
1.12	247.44	62.87	1845
1.13	247.89	63.44	1863
1.14	248.30	64.01	1882
1.15	248.72	64.56	1901
1.16	248.98	64.84	1921
1.17	249.33	65.11	1940
1.315	160.43	71.37	2275
1.325	162.49	70.71	2301
1.335	164.39	70.26	2327
1.345	166.33	69.92	2355
1.355	168.30	69.91	2382
1.365	170.36	70.10	2410
1.375	172.51	70.42	2438
1.385	174.78	70.71	2467
1.395	177.05	70.90	2496
1.405	179.25	70.99	2525
1.415	181.36	70.97	2555
1.425	183.44	70.87	2586
1.435	185.60	70.71	2616
1.445	187.90	70.54	2647
1.455	190.36	70.42	2679
1.465	193.02	70.37	2710
1.475	196.02	70.37	2743
1.485	199.44	70.37	2775
1.495	203.24	70.29	2808
1.505	207.04	70.08	2841
1.515	210.82	69.65	2875
1.525	214.23	69.02	2909
1.535	217.36	68.27	2944
1.545	220.05	67.46	2978
1.555	222.40	66.66	3013
1.565	224.61	65.79	3049
1.575	226.61	64.91	3085
1.585	228.52	64.06	3121
1.595	230.15	63.38	3157
1.605	231.50	62.90	3194
1.615	232.60	62.57	3231
1.625	233.51	62.34	3268
1.635	234.27	62.21	3306
1.645	234.95	62.17	3344
1.655	235.58	62.23	3383
1.665	236.24	62.39	3421
1.675	236.94	62.60	3460
1.685	237.72	62.81	3499
1.695	238.40	62.96	3539
1.705	238.90	63.06	3579
1.715	239.23	63.14	3619
1.725	239.42	63.24	3659
1.735	239.47	63.36	3699

1.745	239.22	63.47	3740
1.755	238.68	63.53	3781
1.765	237.98	63.60	3822
1.775	237.34	63.66	3864
1.785	236.85	63.73	3906
1.795	236.38	63.79	3948
1.805	235.90	63.86	3990
1.815	235.49	63.91	4032
1.825	235.24	63.95	4075
1.835	235.21	64.06	4118
1.845	235.31	64.25	4161
1.855	235.38	64.41	4204
1.865	235.34	64.43	4247
1.875	235.33	64.31	4291
1.885	235.60	64.14	4334
1.895	236.19	63.98	4378
1.905	236.99	63.90	4422
1.915	237.94	63.90	4466
1.925	239.09	63.94	4510
1.935	240.60	63.99	4555
1.945	242.42	64.01	4599
1.955	244.36	63.97	4644
1.965	246.05	63.85	4688
1.975	247.46	63.51	4733
1.985	248.54	63.05	4778
1.995	249.40	62.49	4823
2.005	249.98	61.96	4868
2.015	250.44	61.41	4913
2.025	250.87	60.85	4958
2.035	251.36	60.30	5004
2.045	251.88	59.78	5049
2.055	252.50	59.24	5094
2.065	253.22	58.63	5140
2.075	254.06	57.97	5185
2.085	254.95	57.32	5230
2.095	255.76	56.74	5276
2.105	256.50	56.17	5321
2.115	257.09	55.68	5367
2.125	257.74	55.21	5412
2.135	258.38	54.83	5457
2.145	259.20	54.44	5503
2.155	260.02	54.13	5548
2.165	260.89	53.88	5593
2.175	261.60	53.70	5638
2.185	262.17	53.60	5684
2.195	262.58	53.55	5729

2.205	262.83	53.49	5774
2.215	262.95	53.32	5819
2.225	262.99	53.03	5864
2.235	262.96	52.67	5908
2.245	262.84	52.28	5953
2.255	262.74	51.89	5998
2.265	262.71	51.55	6042
2.275	262.81	51.27	6087
2.285	262.87	51.00	6131
2.295	262.81	50.71	6175
2.305	262.66	50.44	6219
2.315	262.52	50.30	6263
2.325	262.51	50.35	6307
2.335	262.53	50.55	6350
2.345	262.55	50.80	6393
2.355	262.54	51.04	6437
2.365	262.63	51.29	6480
2.375	262.97	51.66	6522
2.385	263.56	52.14	6565
2.395	264.34	52.63	6607
2.405	265.15	53.10	6650
2.415	266.04	53.55	6692
2.425	267.05	53.99	6734
2.435	268.19	54.39	6775
2.445	269.33	54.65	6816
2.455	270.49	54.69	6858
2.465	271.64	54.49	6898
2.475	272.92	54.12	6939
2.485	274.35	53.64	6979
2.495	276.07	53.08	7020
2.505	278.00	52.54	7059
2.515	280.31	52.05	7099
2.525	283.02	51.72	7138
2.535	286.11	51.61	7177
2.545	289.12	51.89	7216
2.555	291.65	52.60	7255
2.565	293.47	53.76	7293
2.575	294.23	54.40	7331
2.585	294.74	55.18	7368
2.645	234.52	70.01	7587
2.655	232.39	69.33	7622
2.665	229.71	68.68	7657
2.675	226.65	68.11	7692
2.685	223.22	67.78	7726
2.695	219.37	67.77	7760
2.705	215.51	68.00	7794

2.715	212.05	68.28	7827
2.725	209.39	68.49	7860
2.735	207.84	68.60	7892
2.745	207.37	68.68	7925
2.755	207.89	68.85	7956
2.765	209.23	69.15	7988
2.775	211.19	69.52	8019
2.785	213.30	69.87	8050
2.795	215.06	70.05	8080
2.805	216.22	70.07	8110
2.815	216.90	69.99	8139
2.825	217.37	69.87	8168
2.835	217.73	69.67	8197
2.845	218.04	69.35	8226
2.855	218.22	68.88	8254
2.865	218.43	68.34	8281
2.875	218.67	67.79	8308
2.885	218.96	67.32	8335
2.895	219.32	66.94	8362
2.905	219.58	66.65	8388
2.915	219.73	66.46	8413
2.925	219.69	66.42	8439
2.935	219.66	66.54	8464
2.945	219.80	66.77	8488
2.955	220.19	66.98	8512
2.965	220.83	67.09	8536
2.975	221.64	67.09	8559
2.985	222.60	67.01	8582
2.995	223.79	66.85	8605
3.005	225.30	66.65	8627
3.015	227.09	66.41	8649
3.025	229.10	66.13	8670
3.035	231.15	65.91	8691
3.045	233.27	65.73	8712
3.055	235.36	65.60	8732
3.065	237.34	65.44	8752
3.075	239.21	65.19	8771
3.085	240.91	64.87	8791
3.095	242.70	64.48	8809
3.105	244.64	64.09	8828
3.115	246.75	63.65	8846
3.125	248.77	63.16	8864
3.135	250.57	62.61	8881
3.145	252.05	62.11	8898
3.155	253.32	61.68	8915
3.165	254.30	61.34	8931
3.175	255.02	61.05	8947
3.185	255.45	60.80	8963
3.195	255.82	60.62	8979
3.205	256.34	60.54	8994
3.215	257.19	60.51	9009
3.225	258.43	60.51	9023
3.235	259.97	60.56	9037
3.245	261.64	60.62	9051
3.255	263.39	60.68	9065
3.265	265.11	60.70	9078
3.275	266.80	60.71	9091
3.285	268.27	60.69	9104
3.295	269.61	60.69	9117
3.305	270.95	60.74	9129
3.315	272.41	60.78	9141
3.325	273.94	60.76	9153
3.335	275.41	60.61	9165
3.345	276.84	60.37	9177
3.355	278.17	60.07	9188
3.365	279.42	59.69	9199
3.375	280.48	59.20	9210
3.385	281.50	58.59	9221
3.395	282.46	57.91	9231
3.405	283.20	57.18	9242
3.415	283.49	56.55	9252
3.425	283.34	56.20	9262
3.435	283.06	56.14	9273

APPENDIX C: Bulk Organic Geochemical Data

SAMPLE ID	Depth	Year	TOC	TON	$\delta^{15}N_{org}$	C_{org}:N_{org}	C_{org}:N_{org}	$\delta^{13}C_{org}$ (uncorrected)	$\delta^{13}C$ Atmosphere	SUESS correction	$\delta^{13}C_{org}$ (corrected)	Sediment Accumulation
	cm	**A.D.**	**(%)**	**(%)**	**(‰)**	**(wt. ratio)**	**(atomic)**	**(‰)**	**(‰)**		**(‰)**	**$g/cm^2/yr$**
BH09-2MC	0.25	2006	3.68	0.44	2.69	8.28	7.09	-26.45	-8.26	2.00	-24.45	0.0252
BH09-2MC	1.25	2000	3.51	0.42	2.46	8.39	7.19	-26.62	-8.02	1.76	-24.86	0.0252
BH09-2MC	2.25	1993	3.40	0.39	2.14	8.62	7.39	-26.80	-7.79	1.52	-25.28	0.0252
BH09-2MC	3.25	1985	3.18	0.38	2.25	8.45	7.24	-26.66	-7.56	1.30	-25.37	0.0252
BH09-2MC	4.25	1977	3.07	0.36	2.52	8.59	7.36	-26.53	-7.35	1.09	-25.44	0.0252
BH09-2MC	5.25	1968	2.92	0.35	2.63	8.45	7.25	-26.53	-7.17	0.91	-25.62	0.0252
BH09-2MC	6.25	1958	2.83	0.33	2.58	8.55	7.32	-26.49	-7.02	0.76	-25.74	0.0252
BH09-2MC	7	1948	2.81	0.33	2.68	8.61	7.38	-26.53	-6.89	0.62	-25.90	0.0252
BH09-2MC	8	1937	2.69	0.31	2.98	8.76	7.51	-26.17	-6.78	0.52	-25.66	0.0252
BH09-2MC	9.5	1919	2.66	0.29	3.13	9.31	7.98	-25.99	-6.67	0.40	-25.59	0.0252
BH09-2MC	11.5	1895	2.67	0.29	3.17	9.28	7.96	-26.35	-6.58	0.31	-26.03	0.0252
BH09-2MC	13.5	1870	2.71	0.30	3.21	8.93	7.66	-26.16	-6.52	0.26	-25.90	0.0252
BH09-2MC	15.5	1846	2.89	0.33	3.59	8.87	7.60	-26.19	-6.48	0.21	-25.97	0.0252
BH09-2MC	17.5	1822	2.82	0.32	3.45	8.81	7.55	-26.13	-6.43	0.16	-25.96	0.0252
BH09-2MC	19.5	1789	2.89	0.33	3.38	8.70	7.45	-26.13	-6.35	0.09	-26.04	0.0252

SAMPLE ID	Depth	Year	TOC	TON	$\delta^{15}N_{org}$	$C_{org}:N_{org}$	$C_{org}:N_{org}$	$\delta^{13}C_{org}$ (uncorrected)	$\delta^{13}C$ Atmosphere	SUESS correction	$\delta^{13}C_{org}$ (corrected)	Sediment Accumulation
	cm	A.D.	(%)	(%)	(‰)	(wt. ratio)	(atomic)	(‰)	(‰)		(‰)	$g/cm^2/yr$
BH09-3MC	0.25	2004	3.75	0.44	2.96	8.45	7.24	-26.99	-8.17	1.91	-25.08	0.0135
BH09-3MC	1.25	1992	3.20	0.37	2.94	8.70	7.46	-26.92	-7.76	1.50	-25.42	0.0135
BH09-3MC	2.25	1976	3.05	0.34	3.37	9.05	7.75	-26.74	-7.33	1.07	-25.67	0.0135
BH09-3MC	3.25	1955	3.03	0.31	3.28	9.85	8.45	-26.49	-6.97	0.70	-25.78	0.0135
BH09-3MC	4.25	1933	2.77	0.26	3.81	10.47	8.97	-26.26	-6.75	0.49	-25.77	0.0193
BH09-3MC	5.25	1910	2.43	0.25	3.82	9.80	8.40	-26.45	-6.62	0.36	-26.09	0.0193
BH09-3MC	6.25	1889	2.52	0.25	3.66	10.02	8.59	-26.62	-6.56	0.30	-26.32	0.0193
BH09-3MC	7.25	1869	2.38	0.26	3.73	9.28	7.95	-26.96	-6.52	0.26	-26.71	0.0193
BH09-3MC	8.25	1851	2.27	0.25	3.30	9.23	7.91	-26.79	-6.49	0.22	-26.57	0.0193
BH09-3MC	9.5	1823	2.06	0.22	3.27	9.18	7.87	-26.86	-6.43	0.17	-26.69	0.0193
BH09-3MC	11.5	1786	2.28	0.25	3.29	9.19	7.88	-26.66	-6.34	0.08	-26.58	0.0193
BH09-3MC	13.5	1741	2.20	0.25	3.14	8.84	7.57	-26.91	-6.26	0.00	-26.91	0.0193
BH09-3MC	15.5	1698	2.17	0.25	3.11	8.72	7.48	-26.78	-6.27	0.00	-26.77	0.0193
BH09-3MC	17.5	1655	2.24	0.26	3.65	8.72	7.47	-26.68	-6.38	0.12	-26.56	0.0193
BH09-3MC	19.5	1610	2.23	0.25	3.19	8.91	7.64	-26.85	-6.49	0.23	-26.62	0.0193

SAMPLE ID	Depth	Year	TOC	TON	$\delta^{15}N_{org}$	C_{org}:N_{org}	C_{org}:N_{org}	$\delta^{13}C_{org}$ (uncorrected)	$\delta^{13}C$ Atmosphere	SUESS correction	$\delta^{13}C_{org}$ (corrected)	Sediment Accumulation
	cm	A.D.	(%)	(%)	(‰)	(wt. ratio)	(atomic)	(‰)	(‰)		(‰)	g/cm^2/yr
BH09-4MC	0.25	2006	3.10	0.38	3.36	8.13	6.97	-27.25	-8.27	2.00	-25.24	0.0269
BH09-4MC	1.25	2000	2.74	0.32	3.28	8.56	7.34	-27.11	-8.02	1.76	-25.34	0.0269
BH09-4MC	2.25	1991	1.97	0.22	3.34	8.90	7.62	-27.08	-7.72	1.46	-25.62	0.0269
BH09-4MC	3.25	1977	0.96	0.10	3.47	9.51	8.15	-27.11	-7.35	1.08	-26.02	0.0269
BH09-4MC	4.25	1969	1.02	0.12	3.54	8.65	7.41	-26.91	-7.19	0.92	-25.98	0.0269
BH09-4MC	5.25	1962	1.97	0.18	3.34	11.16	9.57	-26.72	-7.08	0.81	-25.91	0.0179
BH09-4MC	6.25	1957	3.00	0.31	3.70	9.57	8.20	-26.26	-7.00	0.74	-25.52	0.0179
BH09-4MC	7.25	1955	3.91	0.34	3.67	11.35	9.73	-26.03	-6.97	0.71	-25.32	0.0179
BH09-4MC	8.25	1942	2.92	0.31	3.55	9.44	8.09	-26.52	-6.82	0.56	-25.96	0.0179
BH09-4MC	9.25	1936	3.13	0.33	3.38	9.38	8.04	-26.82	-6.77	0.51	-26.31	0.0179
BH09-4MC	11.5	1908	2.70	0.31	3.84	8.83	7.57	-26.83	-6.62	0.36	-26.47	0.0179
BH09-4MC	13.5	1889	2.74	0.31	3.75	8.82	7.56	-26.92	-6.56	0.30	-26.63	0.0179
BH09-4MC	15.5	1826	2.97	0.33	3.63	8.89	7.62	-26.63	-6.44	0.17	-26.45	0.0179
BH09-4MC	17.5	1804	2.78	0.31	3.87	8.90	7.63	-26.75	-6.39	0.12	-26.63	0.0179
BH09-4MC	19.5	1765	2.76	0.31	3.90	8.77	7.52	-26.50	-6.30	0.03	-26.47	0.0179

SAMPLE ID	Depth	Year	TOC	TON	$\delta^{15}N_{org}$	$C_{org}:N_{org}$	$C_{org}:N_{org}$	$\delta^{13}C_{org}$ (uncorrected)	$\delta^{13}C$ Atmosphere	SUESS correction	$\delta^{13}C_{org}$ (corrected)	Sediment Accumulation
	cm	A.D.	(%)	(%)	(‰)	(wt. ratio)	(atomic)	(‰)	(‰)		(‰)	$g/cm^2/yr$
BH03-3MC	0.25	2000	3.01	0.33	4.05	9.19	7.88	-26.07	-8.01	1.75	-24.32	0.0112
BH03-3MC	0.75	1994	3.01	0.31	3.95	9.61	8.24	-26.21	-7.81	1.54	-24.67	0.0112
BH03-3MC	1.25	1987	2.90	0.29	3.49	9.92	8.51	-26.09	-7.60	1.33	-24.75	0.0112
BH03-3MC	1.75	1978	2.94	0.30	4.16	9.75	8.35	-26.11	-7.38	1.12	-24.99	0.0112
BH03-3MC	2.25	1969	3.10	0.30	3.70	10.35	8.87	-26.12	-7.19	0.93	-25.20	0.0112
BH03-3MC	2.75	1958	2.83	0.26	3.69	10.85	9.30	-26.36	-7.02	0.76	-25.61	0.0112
BH03-3MC	3.25	1947	2.74	0.27	3.56	10.25	8.78	-26.25	-6.88	0.61	-25.64	0.0112
BH03-3MC	3.75	1935	2.54	0.26	3.76	9.85	8.44	-26.30	-6.76	0.50	-25.80	0.0112
BH03-3MC	4.25	1921	2.46	0.25	3.67	9.77	8.37	-26.54	-6.68	0.41	-26.12	0.0112
BH03-3MC	4.75	1907	2.38	0.25	3.64	9.63	8.26	-26.63	-6.61	0.35	-26.28	0.0112
BH03-3MC	5.25	1894	2.26	0.25	3.75	9.11	7.81	-26.58	-6.57	0.31	-26.27	0.0112
BH03-3MC	5.75	1885	2.29	0.25	3.20	9.29	7.97	-27.15	-6.55	0.29	-26.86	0.0112
BH03-3MC	6.25	1876	2.30	0.26	3.57	8.98	7.70	-26.86	-6.53	0.27	-26.59	0.0175
BH03-3MC	6.75	1867	2.24	0.24	3.92	9.22	7.90	-26.41	-6.52	0.25	-26.16	0.0175
BH03-3MC	7.25	1859	2.31	0.25	3.61	9.09	7.80	-26.83	-6.50	0.24	-26.59	0.0175
BH03-3MC	7.75	1850	2.37	0.26	3.86	9.10	7.80	-26.57	-6.49	0.22	-26.35	0.0175
BH03-3MC	8.25	1841	2.39	0.26	3.75	9.11	7.81	-26.33	-6.47	0.21	-26.12	0.0175
BH03-3MC	8.75	1826	2.51	0.25	3.68	9.98	8.52	-26.50	-6.44	0.18	-26.32	0.0175
BH03-3MC	9.25	1816	2.26	0.25	3.75	9.11	7.80	-26.45	-6.42	0.15	-26.30	0.0175

SAMPLE ID	Depth	Year	TOC	TON	$\delta^{15}N_{org}$	C_{org}:N_{org}	C_{org}:N_{org}	$\delta^{13}C_{org}$ (uncorrected)	$\delta^{13}C$ Atmosphere	SUESS correction	$\delta^{13}C_{org}$ (corrected)	Sediment Accumulation
	cm	A.D.	(%)	(%)	(‰)	(wt. ratio)	(atomic)	(‰)	(‰)		(‰)	g/cm^2/yr
LG 0 - 0.5	0.25	2009	5.38	0.44	3.19	12.34	10.58	-26.30	-8.38	2.12	-24.18	0.0336
LG 0.5 - 1	0.75	2008	4.73	0.50	3.39	9.46	8.11	-26.38	-8.34	2.08	-24.30	0.0336
LG 1 - 1.5	1.25	2006	4.55	0.49	3.59	9.28	7.95	-26.31	-8.26	1.99	-24.31	0.0336
LG 1.5 - 2	1.75	2004	4.47	0.49	3.70	9.16	7.85	-26.35	-8.18	1.92	-24.43	0.0336
LG 2 - 2.5	2.25	2002	4.31	0.46	3.65	9.27	7.95	-26.39	-8.10	1.84	-24.55	0.0336
LG 2.5 - 3	2.75	2000	4.23	0.45	3.62	9.32	7.98	-26.35	-8.01	1.75	-24.60	0.0336
LG 3 - 3.5	3.25	1997	4.15	0.44	3.69	9.47	8.12	-26.35	-7.91	1.65	-24.70	0.0336
LG 3.5 - 4	3.75	1994	4.13	0.43	3.60	9.49	8.14	-26.32	-7.82	1.55	-24.76	0.0336
LG 4 - 4.5	4.25	1991	3.93	0.40	3.83	9.89	8.48	-26.26	-7.73	1.46	-24.80	0.0336
LG 4.5 - 5A	4.75	1988	3.91	0.39	3.99	10.04	8.61	-26.18	-7.64	1.37	-24.81	0.0336
LG 4.5 - 5B	4.75	1988	3.76	0.38	4.15	9.99	8.56	-26.23	-7.64	1.37	-24.86	0.0336
LG 5 - 5.5	5.25	1985	3.88	0.38	4.05	10.19	8.73	-26.06	-7.55	1.28	-24.78	0.0336
LG 5.5 - 6	5.75	1981	3.85	0.37	4.16	10.33	8.86	-25.90	-7.46	1.20	-24.70	0.0336
LG 6 - 6.5	6.25	1978	3.78	0.36	4.24	10.37	8.89	-25.85	-7.38	1.12	-24.73	0.0336
LG 6.5 - 7	6.75	1974	3.74	0.36	4.25	10.40	8.92	-26.04	-7.30	1.04	-25.00	0.0336
LG 7 - 7.5	7.25	1971	3.70	0.35	4.07	10.45	8.95	-25.93	-7.23	0.96	-24.96	0.0336
LG 7.5 - 8	7.75	1967	3.54	0.34	4.46	10.43	8.94	-26.39	-7.16	0.89	-25.50	0.0336
LG 8 - 8.5	8.25	1963	3.65	0.35	4.84	10.46	8.97	-26.07	-7.09	0.83	-25.24	0.0336
LG 8.5 - 9	8.75	1960	3.66	0.35	4.57	10.49	8.99	-26.25	-7.04	0.77	-25.47	0.0336
LG 9 - 9.5	9.25	1956	3.76	0.36	4.58	10.54	9.03	-26.17	-6.98	0.72	-25.45	0.0336
LG 9.5 - 10A	9.75	1952	3.47	0.33	4.35	10.55	9.04	-26.38	-6.93	0.67	-25.71	0.0336
LG 9.5 - 10B	9.75	1952	3.53	0.34	4.63	10.50	9.00	-26.39	-6.93	0.67	-25.72	0.0336
LG 10 - 10.5	10.25	1948	3.62	0.36	4.83	10.01	8.58	-26.40	-6.89	0.63	-25.77	0.0336

LG 10.5 - 11	10.75	1945	3.68	0.37	4.31	9.93	8.51	-26.77	-6.85	0.59	-26.18	0.0336
LG 11 - 11.5	11.25	1941	3.71	0.38	4.93	9.70	8.31	-26.66	-6.82	0.55	-26.10	0.0336
LG 11.5 - 12	11.75	1938	3.74	0.38	4.62	9.73	8.34	-26.73	-6.79	0.52	-26.20	0.0336
LG 12 - 12.5	12.25	1934	3.79	0.39	4.51	9.73	8.34	-26.33	-6.76	0.50	-25.84	0.0336
LG 12.5 - 13	12.75	1931	3.73	0.38	4.41	9.79	8.39	-26.54	-6.74	0.47	-26.07	0.0336
LG 13 - 13.5	13.25	1927	3.53	0.37	4.62	9.64	8.27	-26.64	-6.71	0.45	-26.19	0.0336
LG 13.5 - 14	13.75	1924	3.03	0.32	4.74	9.61	8.24	-27.47	-6.69	0.43	-27.05	0.0336
LG 14 - 14.5	14.25	1921	3.32	0.36	5.38	9.23	7.91	-25.94	-6.67	0.41	-25.53	0.0336
LG 14.5 - 15A	14.75	1917	3.58	0.39	5.28	9.19	7.88	-25.97	-6.66	0.39	-25.58	0.0336
LG 14.5 - 15B	14.75	1917	3.26	0.35	4.89	9.42	8.08	-26.84	-6.66	0.39	-26.45	0.0336
LG 15 - 15.5	15.25	1914	3.23	0.34	4.81	9.49	8.13	-26.97	-6.64	0.38	-26.59	0.0336
LG 15.5 - 16	15.75	1910	3.65	0.39	4.94	9.36	8.02	-26.70	-6.62	0.36	-26.34	0.0336
LG 16 - 16.5	16.25	1907	3.59	0.38	5.13	9.37	8.03	-26.79	-6.61	0.35	-26.44	0.0336
LG 16.5 - 17	16.75	1903	3.50	0.37	4.51	9.52	8.16	-26.83	-6.60	0.34	-26.50	0.0336
LG 17 - 17.5	17.25	1899	3.58	0.38	5.19	9.41	8.06	-26.75	-6.59	0.32	-26.43	0.0336
LG 17.5 - 18	17.75	1896	3.53	0.37	5.09	9.44	8.09	-26.81	-6.58	0.31	-26.50	0.0336
LG 18 - 18.5	18.25	1892	3.46	0.36	4.82	9.48	8.12	-26.73	-6.57	0.30	-26.42	0.0336
LG 18.5 - 19	18.75	1888	3.57	0.38	5.02	9.40	8.05	-26.81	-6.56	0.29	-26.52	0.0269
LG 19 - 19.5	19.25	1883	3.58	0.38	4.63	9.48	8.12	-26.89	-6.55	0.28	-26.60	0.0269
LG 19.5 - 20A	19.75	1878	3.81	0.40	4.64	9.50	8.15	-26.71	-6.54	0.27	-26.43	0.0269
LG 19.5 - 20B	19.75	1878	3.68	0.39	4.53	9.54	8.18	-26.77	-6.54	0.27	-26.49	0.0269
LG 20 - 21	20.5	1871	3.59	0.38	4.69	9.43	8.08	-26.62	-6.52	0.26	-26.36	0.0269
LG 21 - 22	21.4	1862	3.63	0.38	4.69	9.44	8.09	-26.67	-6.51	0.25	-26.43	0.0269
LG 22 - 23	22.5	1852	2.90	0.31	4.67	9.47	8.12	-26.97	-6.49	0.23	-26.74	0.0269
LG 23 - 24	23.5	1842	2.88	0.30	4.51	9.45	8.10	-27.12	-6.47	0.21	-26.91	0.0269
LG 24 - 25	24.5	1832	3.41	0.37	4.71	9.35	8.01	-26.41	-6.45	0.19	-26.22	0.0269

SAMPLE ID	Depth	Year	TOC	TON	$\delta^{15}N_{org}$	C_{org}:N_{org}	C_{org}:N_{org}	$\delta^{13}C_{org}$ (uncorrected)	$\delta^{13}C$ Atmosphere	SUESS correction	$\delta^{13}C_{org}$ (corrected)	Sediment Accumulation
	cm	A.D.	(%)	(%)	(‰)	(wt. ratio)	(atomic)	(‰)	(‰)		(‰)	g/cm^2/yr
IR 0 - 0.5	0.25	2007	4.17	0.42	3.72	9.89	8.48	-27.12	-8.28	2.02	-25.10	0.0161
IR 0.5 - 1	0.75	2004	3.70	0.42	3.83	8.77	7.52	-27.16	-8.17	1.91	-25.25	0.0161
IR 1 - 1.5	1.25	1999	3.63	0.41	3.88	8.82	7.56	-27.13	-7.98	1.71	-25.42	0.0161
IR 1.5 - 2	1.75	1993	3.55	0.40	4.06	8.80	7.54	-27.06	-7.78	1.52	-25.54	0.0161
IR 2 - 2.5A	2.25	1986	3.34	0.37	3.94	9.12	7.81	-27.01	-7.59	1.33	-25.69	0.0161
IR 2 - 2.5B	2.25	1986	3.38	0.38	4.14	9.02	7.73	-27.03	-7.59	1.33	-25.70	0.0161
IR 2.5 - 3	2.75	1979	3.30	0.36	4.18	9.10	7.80	-26.94	-7.41	1.15	-25.79	0.0161
IR 3 - 3.5	3.25	1971	3.16	0.35	5.21	9.05	7.76	-26.79	-7.24	0.98	-25.81	0.0161
IR 3.5 - 4	3.75	1966	2.96	0.31	5.12	9.58	8.21	-26.77	-7.13	0.87	-25.90	0.0359
IR 4 - 4.5	4.25	1962	3.01	0.31	4.42	9.79	8.39	-26.96	-7.07	0.80	-26.16	0.0359
IR 4.5 - 5	4.75	1958	3.08	0.33	4.89	9.31	7.98	-27.22	-7.01	0.74	-26.48	0.0359
IR 5 - 5.5	5.25	1954	2.97	0.29	4.65	10.15	8.70	-26.73	-6.95	0.69	-26.04	0.0359
IR 5.5 - 6	5.75	1947	2.83	0.27	4.67	10.40	8.91	-26.70	-6.88	0.62	-26.08	0.0359
IR 6 - 6.5	6.25	1945	2.92	0.29	5.08	10.16	8.71	-26.75	-6.85	0.59	-26.16	0.0359
IR 6.5 - 7	6.75	1939	2.96	0.30	5.08	9.85	8.44	-26.79	-6.80	0.54	-26.25	0.0359
IR 7 - 7.5A	7.25	1937	3.00	0.30	4.56	9.89	8.48	-26.93	-6.78	0.51	-26.42	0.0359
IR 7 - 7.5B	7.25	1937	3.02	0.30	4.74	10.05	8.61	-26.88	-6.78	0.51	-26.37	0.0359
IR 7.5 - 8	7.75	1925	2.91	0.30	5.05	9.68	8.30	-26.90	-6.69	0.43	-26.47	0.0135
IR 8 - 8.5	8.25	1918	2.71	0.29	5.46	9.32	7.99	-26.96	-6.66	0.39	-26.56	0.0135
IR 8.5 - 9	8.75	1903	2.51	0.28	5.63	8.89	7.62	-27.10	-6.60	0.34	-26.76	0.0135
IR 9 - 9.5	9.25	1893	2.36	0.27	5.04	8.90	7.63	-27.98	-6.57	0.31	-27.68	0.0135
IR 9.5 - 10	9.75	1882	2.60	0.29	4.50	9.12	7.81	-27.84	-6.55	0.28	-27.56	0.0135
IR 10 - 10.5	10.25	1871	2.56	0.29	4.53	8.94	7.66	-27.60	-6.53	0.26	-27.34	0.0135

IR 10.5 - 11	10.75	1861	2.58	0.29	4.64	8.97	7.69	-27.24	-6.51	0.24	-27.00	0.0135
IR 11 - 11.5	11.25	1850	2.56	0.28	4.64	9.10	7.80	-27.14	-6.49	0.22	-26.91	0.0135
IR 11.5 - 12	11.75	1840	2.56	0.28	4.72	9.05	7.76	-27.17	-6.47	0.20	-26.96	0.0135
IR 12 - 12.5A	12.25	1830	2.56	0.28	4.68	9.21	7.89	-27.31	-6.45	0.18	-27.13	0.0135
IR 12 - 12.5B	12.25	1830	2.55	0.28	4.56	9.03	7.74	-27.22	-6.45	0.18	-27.03	0.0135
IR 12.5 - 13	12.75	1821	2.54	0.28	4.61	9.00	7.71	-26.98	-6.43	0.16	-26.81	0.0135
IR 13 - 13.5	13.25	1812	2.51	0.28	4.13	9.01	7.72	-27.05	-6.41	0.14	-26.91	0.0135
IR 13.5 - 14	13.75	1796	2.54	0.29	4.40	8.80	7.54	-27.02	-6.37	0.10	-26.91	0.0135
IR 14 - 14.5	14.25	1784	2.52	0.29	4.10	8.83	7.57	-26.89	-6.34	0.07	-26.82	0.0135
IR 14.5 - 15	14.75	1771	2.48	0.28	4.59	8.72	7.47	-26.94	-6.31	0.04	-26.90	0.0135

SAMPLE ID	**Depth**	**Year**	**TOC**	**TON**	**$\delta^{15}N_{org}$**	**$C_{org}:N_{org}$**	**$C_{org}:N_{org}$**	**$\delta^{13}C_{org}$ (uncorrected)**	**$\delta^{13}C$ Atmosphere**	**SUESS correction**	**$\delta^{13}C_{org}$ (corrected)**	**Sediment Accumulation**
	cm	**A.D.**	**(%)**	**(%)**	**(‰)**	**(wt. ratio)**	**(atomic)**	**(‰)**	**(‰)**		**(‰)**	**$g/cm^2/yr$**
EM 5A-1	0.25	2006	4.43	0.53	4.19	8.37	7.17	-27.90	-8.26	1.99	-25.91	0.0090
EM 5A-2	0.75	1997	4.26	0.53	3.57	8.07	6.91	-27.77	-7.91	1.65	-26.12	0.0090
EM 5A-3	1.25	1982	4.13	0.49	3.59	8.48	7.27	-28.13	-7.48	1.21	-26.92	0.0090
EM 5A-4	1.75	1969	3.99	0.47	3.72	8.51	7.29	-27.89	-7.19	0.92	-26.96	0.0090
EM 5A-5	2.25	1957	3.82	0.44	4.24	8.61	7.38	-27.41	-7.00	0.73	-26.68	0.0090
EM 5A-6	2.75	1944	3.73	0.43	4.19	8.77	7.52	-26.80	-6.85	0.58	-26.22	0.0090
EM 5A-7	3.25	1931	3.65	0.40	4.45	9.11	7.81	-27.43	-6.73	0.47	-26.96	0.0090
EM 5A-8A	3.75	1916	3.89	0.36	4.64	10.90	9.34	-27.39	-6.65	0.39	-27.00	0.0090
EM 5A-8B	3.75	1916	3.84	0.35	4.84	10.86	9.31	-27.56	-6.65	0.39	-27.18	0.0090
EM 5A-9	4.25	1900	2.96	0.33	5.61	9.01	7.72	-27.16	-6.59	0.33	-26.84	0.0090
EM 5A-10	4.75	1882	2.86	0.31	5.83	9.20	7.89	-27.25	-6.55	0.28	-26.96	0.0090
EM 5A-11	5.25	1859	2.62	0.30	5.89	8.70	7.45	-27.08	-6.50	0.24	-26.84	0.0090
EM 5A-12	5.75	1837	2.43	0.28	5.61	8.64	7.41	-27.04	-6.46	0.20	-26.84	0.0090
EM 5A-13	6.25	1815	2.51	0.30	5.07	8.36	7.17	-26.91	-6.41	0.15	-26.76	0.0090
EM 5A-14	6.75	1793	2.57	0.30	6.07	8.55	7.33	-26.99	-6.36	0.10	-26.89	0.0090
EM 5A-15	7.25	1771	2.54	0.29	6.14	8.74	7.49	-26.94	-6.31	0.05	-26.89	0.0090
EM 5A-16A	7.75	1749	2.45	0.29	6.26	8.56	7.34	-26.78	-6.27	0.01	-26.77	0.0090
EM 5A-16B	7.75	1749	2.43	0.28	6.68	8.51	7.30	-26.84	-6.27	0.01	-26.84	0.0090

SAMPLE ID	Depth	Year	TOC	TON	$\delta^{15}N_{org}$	$C_{org}:N_{org}$	$C_{org}:N_{org}$	$\delta^{13}C_{org}$ (uncorrected)	$\delta^{13}C$ Atmosphere	SUESS correction	$\delta^{13}C_{org}$ (corrected)	Sediment Accumulation
	cm	A.D.	(%)	(%)	(‰)	(wt. ratio)	(atomic)	(‰)	(‰)		(‰)	g/cm^2/yr
CM 3A-1	0.25	2003	7.47	0.41	4.25	18.19	15.59	-27.83	-8.15	1.89	-25.94	0.0072
CM 3A-2	0.75	1992	4.10	0.49	3.96	3.89	7.18	-27.88	-7.76	1.49	-26.38	0.0072
CM 3A-3	1.25	1974	4.01	0.48	3.86	3.79	7.11	-28.08	-7.30	1.03	-27.05	0.0072
CM 3A-4	1.75	1957	3.90	0.46	3.52	3.45	7.32	-27.99	-7.01	0.74	-27.25	0.0072
CM 3A-5	2.25	1942	3.66	0.42	4.02	3.94	7.50	-27.79	-6.83	0.56	-27.22	0.0072
CM 3A-6	2.75	1926	3.60	0.41	3.85	3.77	7.48	-27.71	-6.70	0.44	-27.27	0.0072
CM 3A-7A	3.25	1909	3.57	0.41	4.13	4.04	7.55	-27.65	-6.62	0.36	-27.29	0.0072
CM 3A-7B	3.25	1909	3.59	0.41	4.15	4.06	7.59	-27.82	-6.62	0.36	-27.47	0.0072
CM 3A-8	3.75	1890	3.52	0.39	4.41	4.31	7.77	-27.70	-6.56	0.30	-27.40	0.0072
CM 3A-9	4.25	1872	3.41	0.38	3.94	3.85	7.74	-27.87	-6.53	0.26	-27.61	0.0072
CM 3A-10	4.75	1848	3.39	0.36	4.19	4.09	7.96	-27.55	-6.48	0.22	-27.33	0.0072
CM 3A-11	5.25	1820	3.21	0.37	4.24	4.11	7.35	-28.17	-6.42	0.16	-28.01	0.0072
CM 3A-12	5.75	1791	2.96	0.35	3.64	3.51	7.23	-28.26	-6.36	0.09	-28.17	0.0072
CM 3A-13	6.25	1765	2.65	0.32	4.53	4.39	6.99	-28.36	-6.30	0.03	-28.32	0.0072
CM 3A-14A	6.75	1742	2.58	0.33	4.23	4.09	6.72	-28.21	-6.26	0.00	-28.21	0.0072
CM 3A-14B	6.75	1742	2.56	0.32	4.75	4.59	6.85	-28.03	-6.26	0.00	-28.03	0.0072

SAMPLE ID	**Section**	**Range**	**Depth**	**Depth**	**Age**	**TOC**	**TON**	**$\delta^{15}N_{org}$**	**$C_{org}:N_{org}$**	**$C_{org}:N_{org}$**	**$\delta^{13}C_{org}$**
Isle Royale	**GRAVITY**	**cm**	**cm**	**mblf**	**Year BP**	**(%)**	**(%)**	**(‰)**	**(wt. ratio)**	**(atomic)**	**(‰)**
IRG 1	1	2-3	2.5	0.03	156	2.96	0.31	4.73	9.65	8.27	-26.90
IRG 2	1	13-14	13.5	0.14	598	2.34	0.28	5.16	8.28	7.10	-27.21
IRG 3	1	24-25	24.5	0.25	894	2.19	0.27	4.90	8.14	6.98	-27.15
IRG 4	1	35-36	35.5	0.36	1086	2.07	0.25	4.79	8.13	6.97	-26.88
IRG 5	1	47-48	47.5	0.48	1218	2.12	0.26	5.00	8.07	6.92	-26.96
IRG 6 A	1	58-59	58.5	0.59	1300	2.01	0.25	4.69	7.95	6.81	-27.08
IRG 6 B	1	58-59	58.5	0.59	1300	1.99	0.25	5.37	7.97	6.83	-27.10
IRG 7	1	69-70	69.5	0.70	1371	2.07	0.26	5.58	8.09	6.93	-27.06
IRG 8	1	80-81	80.5	0.81	1450	1.84	0.23	5.47	7.93	6.80	-27.29
IRG 9	1	91-92	91.5	0.92	1553	1.93	0.24	5.09	7.95	6.81	-27.46
IRG 10	2	7-8	102.5	1.03	1691	1.72	0.22	4.40	7.72	6.62	-27.55
IRG 11	2	18-19	113.5	1.14	1873	1.79	0.24	3.91	7.56	6.48	-27.46
IRG 12	2	28-30	124.5	1.25	2102	1.73	0.23	4.13	7.57	6.49	-27.62
IRG 13	2	40-41	135.5	1.36	2382	1.80	0.24	4.30	7.59	6.51	-27.71
IRG 14	2	51-52	146.5	1.47	2710	1.77	0.23	5.11	7.59	6.51	-27.40
IRG 15	2	62-63	157.5	1.58	3085	1.90	0.24	5.13	7.83	6.71	-27.44
IRG 16 A	2	73-74	168.5	1.69	3499	1.90	0.25	4.96	7.70	6.60	-27.26
IRG 16 B	2	73-74	168.5	1.69	3499	1.91	0.25	4.74	7.76	6.65	-27.26
IRG 17	2	84-85	179.5	1.80	3948	1.99	0.25	4.74	7.90	6.77	-27.21

SAMPLE ID	Section	Range	Depth	Depth	Age	TOC	TON	$\delta^{15}N_{org}$	$C_{org}:N_{org}$	$C_{org}:N_{org}$	$\delta^{13}C_{org}$
Keweenaw	**GRAVITY**	**cm**	**cm**	**mblf**	**Year BP**	**(%)**	**(%)**	**(‰)**	**(wt. ratio)**	**(atomic)**	**(‰)**
KWG 1	1	4-5	4.5	0.05	259	3.08	0.26	4.41	11.85	10.15	-25.92
KWG 2	1	15-16	15.5	0.16	384	2.80	0.33	4.71	8.56	7.34	-25.71
KWG 3	1	26-27	26.5	0.27	509	2.74	0.32	4.44	8.50	7.28	-25.72
KWG 4	1	37-38	37.8	0.38	637	2.69	0.32	4.58	8.48	7.27	-25.69
KWG 5	1	48-49	48.5	0.49	758	2.52	0.30	4.90	8.40	7.20	-25.76
KWG 6	1	59-60	59.5	0.60	883	2.54	0.31	4.70	8.30	7.11	-25.66
KWG 7	1	70-71	70.5	0.71	1007	2.56	0.31	4.88	8.29	7.10	-25.68
KWG 8	1	81-82	81.5	0.82	1132	2.57	0.32	4.92	8.00	6.86	-25.66
KWG 9	1	92-93	92.5	0.93	1257	2.51	0.31	4.89	8.21	7.03	-25.66
KWG 10 A	1	103-104	103.5	1.04	1381	2.38	0.29	4.82	8.19	7.02	-25.82
KWG 10 B	1	103-104	103.5	1.04	1381	2.37	0.29	4.42	8.04	6.89	-25.82
KWG 11	1	114-115	114.5	1.15	1506	2.32	0.28	4.18	8.34	7.15	-25.92
KWG 12	2	4-5	125.5	1.26	1631	2.09	0.26	4.93	8.17	7.01	-26.00
KWG 13	2	14-15	136.5	1.37	1755	2.37	0.29	4.73	8.25	7.07	-25.77
KWG 14	2	25-26	147.5	1.48	1880	2.29	0.28	4.69	8.09	6.94	-25.88

SAMPLE ID	Section	Range	Depth	Depth	Age	TOC	TON	$\delta^{15}N_{org}$	$C_{org}:N_{org}$	$C_{org}:N_{org}$	$\delta^{13}C_{org}$
Split Rock	**GRAVITY**	**cm**	**cm**	**mblf**	**BP**	**(%)**	**(%)**	**(‰)**	**(wt. ratio)**	**(atomic)**	**(‰)**
SRG 1	1	2-3	2.5	0.03	247	-	-	-	-	-	-
SRG 2	1	13-14	13.5	0.14	378	2.68	0.31	4.46	8.64	7.41	-26.70
SRG 3	1	24-25	24.5	0.25	510	2.40	0.27	4.83	9.05	7.76	-26.84
SRG 4	1	35-36	35.5	0.36	641	2.65	0.29	4.67	9.06	7.76	-26.87
SRG 5	1	46-47	46.5	0.47	773	2.50	0.27	4.96	9.25	7.93	-26.65
SRG 6	1	57-58	57.5	0.58	904	2.51	0.28	4.18	9.02	7.73	-26.85
SRG 7	1	68-69	68.5	0.69	1036	2.39	0.26	4.17	9.09	7.79	-26.95
SRG 8	1	79-80	79.5	0.80	1167	2.35	0.26	3.88	9.05	7.76	-26.99
SRG 9	1	90-91	90.5	0.91	1299	2.18	0.24	4.21	9.02	7.73	-27.19
SRG 10 A	1	101-102	101.5	1.02	1430	2.25	0.25	3.89	9.07	7.77	-27.22
SRG 10 B	1	101-102	101.5	1.02	1430	2.24	0.24	4.12	9.18	7.87	-27.21

SAMPLE ID	Core Section	Range	Depth	Age	TOC	TON	$\delta^{15}N_{org}$	C_{org}:N_{org}	C_{org}:N_{org}	$\delta^{13}C_{org}$
Isle Royale	**PISTON**	**(cm)**	**mblf**	**cal BP**	**(%)**	**(%)**	**(‰)**	**(wt. ratio)**	**(atomic)**	**(‰)**
IR 1-1	1	3-5	0.04	226	2.66	0.27	4.62	9.75	8.36	-26.85
IR 1-2-A	1	15-17	0.16	676	2.36	0.26	4.90	9.23	7.91	-26.93
IR 1-2-B	1	15-17	0.16	676	2.42	0.26	4.17	9.47	8.11	-27.02
IR 1-3	1	27-29	0.28	965	2.09	0.23	4.05	9.21	7.89	-27.24
IR 1-4	1	39-41	0.40	1143	2.01	0.23	5.18	8.88	7.61	-27.28
IR 1-5-A	1	51-53	0.52	1255	1.88	0.21	4.20	8.88	7.61	-27.41
IR 1-5-B	1	51-53	0.52	1255	1.86	0.21	4.60	8.74	7.49	-27.40
IR 1-6	1	63-65	0.64	1336	1.80	0.20	3.74	9.02	7.73	-27.59
IR 1-7	1	75-77	0.76	1415	1.71	0.21	4.74	8.19	7.02	-27.52
IR 1-8	1	87-89	0.88	1517	1.67	0.20	4.64	8.15	6.99	-27.24
IR 1-9A	1	99-101	1.00	1656	1.65	0.20	4.46	8.34	7.15	-27.45
IR 1-9B	1	99-101	1.00	1656	1.62	0.20	4.69	8.13	6.97	-27.47
IR 1-10	1	111-113	1.12	1845	1.63	0.20	4.57	8.14	6.97	-27.65
IR 2-1	2	1-3	1.23	2079	1.69	0.20	4.21	8.60	7.37	-27.74
IR 2-2	2	13-15	1.34	2327	1.60	0.19	4.40	8.34	7.15	-27.34
IR 2-3	2	25-27	1.45	2647	1.55	0.18	4.01	8.42	7.21	-27.61
IR 2-4	2	37-39	1.56	3013	1.49	0.17	3.31	8.87	7.60	-27.39
IR 2-5	2	49-51	1.67	3421	1.58	0.18	4.20	8.75	7.50	-27.95
IR 2-6	2	61-63	1.78	3864	1.46	0.17	4.24	8.42	7.22	-27.86
IR 2-7A	2	73-75	1.89	4334	1.54	0.17	3.54	8.98	7.70	-27.93
IR 2-7B	2	73-75	1.89	4334	1.53	0.17	2.65	9.25	7.93	-28.05
IR 2-8	2	85-87	2.00	4823	1.49	0.17	4.20	8.57	7.35	-27.97
IR 2-9	2	97-99	2.11	5321	1.50	0.17	4.21	8.57	7.34	-27.89
IR 2-10	2	109-111	2.22	5819	1.49	0.18	4.04	8.28	7.10	-28.06

IR 2-11	2	121-123	2.33	6307	1.47	0.16	2.62	9.14	7.83	-27.93
IR 3-1	3	1-3	2.44	6775	1.55	0.16	2.45	9.44	8.09	-28.79
IR 3-2A	3	13-15	2.55	7216	1.35	0.15	2.64	8.85	7.59	-28.25
IR 3-2B	3	13-15	2.55	7216	1.39	0.16	2.52	8.89	7.62	-28.25
IR 3-3	3	25-27	2.66	7622	1.18	0.14	2.57	8.21	7.03	-27.90
IR 3-4	3	37-39	2.77	7988	1.22	0.14	2.52	8.52	7.30	-28.37
IR 3-5	3	49-51	2.88	8308	1.32	0.17	3.22	7.90	6.77	-26.96
IR 3-6	3	61-63	2.99	8582	1.30	0.17	3.55	7.80	6.68	-27.30
IR 3-7	3	73-75	3.10	8809	1.28	0.16	4.09	8.07	6.91	-28.07
IR 3-8	3	85-87	3.21	8994	1.34	0.16	4.00	8.29	7.10	-28.10
IR 3-9	3	97-99	3.32	9141	1.07	0.14	4.42	7.49	6.42	-28.29
IR 3-10	3	109-111	3.43	9262	0.46	0.10	4.37	4.64	3.97	-28.67
IR 3-11	3	121-123	3.54	9375	0.50	0.09	4.19	5.39	4.62	-29.15
IR 3-12	3	133-135	3.65	9489	0.48	0.09	4.38	5.31	4.55	-29.55
IR 3-13	3	145-147	3.76	9632	0.47	0.09	4.04	5.43	4.65	-29.86
IR 4-1A	4	5-7	3.87	9831	0.47	0.08	4.29	5.64	4.83	-30.20
IR 4-1B	4	5-7	3.87	9831	0.49	0.09	4.34	5.62	4.82	-30.14
IR 4-2	4	17-19	3.98	10118	0.46	0.08	4.39	5.40	4.63	-31.16
IR 4-3	4	29-31	4.09	10534	0.45	0.08	4.29	5.61	4.81	-31.27
IR 4-4A	4	41-43	4.20	11090	0.45	0.08	4.01	5.64	4.83	-31.73
IR 4-4B	4	41-43	4.20	11090	0.46	0.09	3.87	5.35	4.59	-31.45
IR 4-5	4	53-55	4.31	11888	0.48	0.09	4.62	5.44	4.66	-31.67

SAMPLE ID	Core Section	Range	Depth	Age	TOC	TON	$\delta^{15}N_{org}$	$C_{org}:N_{org}$	$C_{org}:N_{org}$	$\delta^{13}C_{org}$
Keweenaw	**PISTON**	**cm**	**mblf**	**cal BP**	**(%)**	**(%)**	**(‰)**	**(wt. ratio)**	**(atomic)**	**(‰)**
1	1	10-11	0.10	1775	2.26	0.28	4.24	8.63	6.96	-25.81
2	1	20-21	0.20	1914	2.27	0.28	4.26	8.60	6.86	-25.82
3	1	30-31	0.30	2053	2.27	0.28	4.18	8.59	6.93	-25.77
4A	1	40-41	0.40	2191	2.41	0.30	3.97	8.50	6.89	-25.85
4B	1	40-41	0.40	2191	2.43	0.29	3.85	8.57	7.25	-25.89
5	2	3-4	0.50	2330	2.38	0.26	3.57	9.45	7.77	-25.93
6	2	13-14	0.60	2469	2.25	0.26	3.28	9.25	7.36	-25.98
7	2	23-24	0.70	2607	2.28	0.27	3.23	9.22	7.32	-26.04
8	2	33-34	0.80	2746	2.34	0.28	3.87	8.88	7.11	-26.06
9	2	43-44	0.90	2885	2.35	0.26	3.23	9.67	7.75	-26.17
10	2	53-54	1.00	3024	2.20	0.27	3.23	8.94	7.04	-26.04
11	2	63-64	1.10	3162	2.32	0.29	3.69	8.34	6.93	-25.81
12	2	73-74	1.20	3301	2.07	0.30	3.51	7.42	5.99	-25.66
13	2	83-84	1.30	3440	2.18	0.29	3.82	7.58	6.35	-25.76
14A	2	93-94	1.40	3578	2.14	0.30	3.36	7.54	6.23	-25.79
14B	2	93-94	1.40	3578	2.15	0.29	3.30	7.17	6.41	-25.88
15	2	103-104	1.50	3717	2.10	0.29	3.44	7.30	6.14	-26.14
16	2	113-114	1.60	3856	2.06	0.28	3.41	7.63	6.38	-25.98
17	2	123-124	1.70	3994	2.05	0.27	3.40	7.80	6.42	-26.07
18	2	133-134	1.80	4133	2.10	0.28	3.52	7.35	6.46	-26.03
19	2	143-144	1.90	4272	2.08	0.26	3.36	8.38	6.92	-26.13
20	3	1-2	2.02	4438	1.87	0.19	2.57	10.17	8.42	-26.21
21	3	11-12	2.12	4577	1.76	0.20	2.54	9.38	7.58	-26.16
22	3	21-22	2.22	4716	1.79	0.24	3.08	7.73	6.43	-26.19

23	3	31-32	2.32	4854	1.77	0.24	3.36	7.77	6.29	-26.32
24A	3	41-42	2.42	4993	1.80	0.21	2.65	8.99	7.44	-26.34
24B	3	41-42	2.42	4993	1.82	0.19	2.58	9.61	8.17	-26.33
25	3	51-52	2.52	5132	1.75	0.19	2.73	9.78	8.05	-26.50
26	3	61-62	2.62	5270	1.47	0.18	2.84	8.38	6.90	-26.54
27	3	71-72	2.72	5409	1.58	0.18	2.47	9.11	7.45	-26.40
28	3	81-82	2.82	5548	1.50	0.24	3.13	6.67	5.48	-26.53
29	3	91-92	2.92	5686	1.40	0.23	2.99	6.29	5.18	-26.59
30	3	101-102	3.02	5825	1.39	0.23	3.03	6.16	5.16	-26.57
31	3	111-112	3.12	5964	1.48	0.23	2.87	6.62	5.52	-26.74
32	3	121-122	3.22	6102	1.58	0.23	2.83	6.99	5.97	-26.63
33	3	131-132	3.32	6241	1.44	0.20	2.61	7.59	6.22	-26.81
34A	3	141-142	3.42	6380	1.41	0.22	2.60	6.73	5.55	-26.92
34B	3	141-142	3.42	6380	1.42	0.21	2.72	7.00	5.87	-26.81
35	3	151-152	3.52	6518	1.36	0.20	2.57	7.02	5.88	-26.75
36	4	8-9	3.62	6657	1.33	0.17	2.24	8.11	6.66	-26.97
37	4	18-19	3.72	6796	1.37	0.18	2.41	7.94	6.44	-27.41
38	4	28-29	3.82	6935	1.34	0.19	2.22	7.35	5.97	-27.48
39	4	38-39	3.92	7073	1.34	0.18	2.13	7.85	6.47	-27.55
40	4	48-49	4.02	7212	1.40	0.19	1.86	7.75	6.44	-28.00
41	4	58-59	4.12	7351	1.50	0.18	1.69	8.52	7.35	-28.12
42	4	68-69	4.22	7489	1.37	0.17	1.37	8.24	6.74	-27.50
43	4	78-79	4.32	7628	1.26	0.16	1.95	8.19	6.70	-27.76
44A	4	88-89	4.42	7767	1.30	0.16	1.67	8.18	6.82	-27.55
44B	4	88-89	4.42	7767	1.31	0.16	1.79	8.21	7.02	-27.53
45	4	98-99	4.52	7905	1.24	0.16	1.96	7.96	6.80	-27.90

46	4	108-109	4.62	8044	1.35	0.17	1.72	8.27	6.93	-27.67
47	4	118-119	4.72	8183	1.32	0.17	1.94	7.98	6.57	-27.46
48	4	128-129	4.82	8321	1.32	0.17	2.37	8.02	6.73	-27.20
49	4	138-139	4.92	8460	1.16	0.16	2.27	7.73	6.39	-27.63
50	4	148-149	5.02	8599	1.15	0.15	2.60	7.86	6.68	-27.50
51	5	5-6	5.12	8738	1.22	0.16	3.14	7.75	6.42	-27.29
52	5	15-16	5.22	8876	0.93	0.14	3.30	6.45	5.61	-25.88
53	5	25-26	5.32	9015	0.90	0.14	2.92	6.81	5.67	-26.67
54A	5	35-36	5.42	9154	0.48	0.09	3.20	5.06	4.42	-25.41
54B	5	35-36	5.42	9154	0.48	0.10	3.00	5.21	4.22	-25.49
55	5	45-46	5.52	9292	0.66	0.12	3.30	5.45	4.74	-26.10
56	5	55-56	5.62	9431	0.63	0.11	3.02	5.72	4.83	-24.82
57	5	65-66	5.72	9570	0.45	0.09	3.04	5.05	4.19	-25.73
58	5	75-76	5.82	9708	0.50	0.10	2.92	4.68	4.37	-25.23
59	5	85-86	5.92	9847	0.48	0.09	3.07	5.57	4.45	-26.06
60	5	95-96	6.02	9986	0.49	0.09	3.17	5.27	4.42	-26.25
61	5	105-106	6.12	10124	0.56	0.10	3.26	5.20	4.97	-26.26
62	5	115-116	6.22	10263	0.55	0.09	3.16	5.42	5.18	-26.22
63	5	125-126	6.32	10402	0.59	0.09	3.20	5.31	5.58	-26.33
64A	5	135-136	6.42	10540	0.59	0.09	3.39	4.90	5.73	-26.46
64B	5	135-136	6.42	10540	0.58	0.09	3.53	4.93	5.51	-26.33
65	5	145-146	6.52	10679	0.66	0.07	3.62	4.66	7.94	-26.13
66	6	4-5	6.65	10859	0.60	0.09	3.55	5.07	5.75	-26.22
67	6	14-15	6.75	10998	0.55	0.08	3.42	4.83	5.75	-26.33
68	6	24-25	6.85	11137	0.58	0.09	3.34	5.15	5.70	-26.23
69	6	34-35	6.95	11276	0.64	0.09	3.76	5.23	6.21	-26.28

70	6	44-45	7.05	11414	0.50	0.08	3.43	4.91	5.03	-26.23
71	6	54-55	7.15	11553	0.69	0.07	3.48	4.94	7.95	-26.31
72	6	64-65	7.25	11692	0.43	0.08	3.60	4.72	4.49	-26.22
73	6	74-75	7.35	11830	0.41	0.08	3.42	4.85	4.54	-26.38
74A	6	84-85	7.45	11969	0.49	0.08	3.28	5.15	5.41	-26.42
74B	6	84-85	7.45	11969	0.47	0.08	3.64	5.32	5.38	-26.48
75	6	94-95	7.55	12108	0.54	0.07	3.67	4.86	6.41	-26.75
76	6	104-105	7.65	12246	0.48	0.07	4.03	4.69	5.80	-26.80
77	6	114-115	7.75	12385	0.49	0.06	3.93	4.36	6.56	-26.80
78	6	124-125	7.85	12524	0.44	0.07	3.31	4.46	5.48	-27.43
79	6	134-135	7.95	12662	0.92	0.06	3.28	4.33	13.19	-27.62

SAMPLE ID	**Core Section**	**Range**	**Depth**	**Age**	**TOC**	**TON**	**$\delta^{15}N_{org}$**	**C_{org}:N_{org}**	**C_{org}:N_{org}**	**$\delta^{13}C_{org}$**
Split Rock	**PISTON**	**cm**	**mblf**	**cal BP**	**(%)**	**(%)**	**(‰)**	**(wt. ratio)**	**(atomic)**	**(‰)**
1	1	6-7	0.07	1468						
2	1	16-17	0.17	1632	2.30	0.26	4.90	9.12	7.82	-26.97
3	1	26-27	0.27	1796	2.31	0.27	4.75	8.85	7.59	-26.91
4	1	36-37	0.37	1960	2.28	0.26	4.63	9.31	7.98	-27.02
5	1	46-47	0.47	2124	2.11	0.25	4.34	8.67	7.43	-27.13
6	1	56-57	0.57	2288	2.18	0.26	4.61	8.74	7.49	-26.94
7	1	66-67	0.67	2452	2.27	0.26	4.51	9.20	7.88	-27.11
8	1	77-78	0.77	2616	2.17	0.25	4.50	9.22	7.90	-27.09
9	1	86-87	0.87	2780	2.18	0.26	4.34	9.18	7.86	-27.19
10	1	96-97	0.97	2944	2.16	0.25	4.05	8.65	7.42	-27.11
10-2	1	96-97	0.97	2944	2.16	0.25	4.30	8.69	7.45	-27.14
11	1	106-107	1.07	3108	2.22	0.25	4.25	9.07	7.77	-27.14
12	2	4-5	1.17	3272	2.02	0.26	4.34	8.22	7.04	-27.24
13	2	14-15	1.27	3436	2.13	0.25	5.04	8.76	7.51	-27.24
14	2	24-25	1.37	3600	2.10	0.24	3.90	8.34	7.15	-27.51
15	2	34-35	1.47	3764	2.05	0.25	3.76	8.50	7.29	-27.25
16	2	44-45	1.57	3928	2.13	0.24	4.28	9.21	7.89	-27.27
17	2	54-55	1.67	4092	2.06	0.24	4.31	8.97	7.69	-27.41
18	2	64-65	1.77	4256	2.05	0.23	4.11	8.95	7.67	-27.55
19	2	74-75	1.87	4420	1.91	0.22	4.14	9.25	7.93	-27.46
20	2	84-85	1.97	4584	1.96	0.23	4.46	9.29	7.97	-27.55
20-2	2	84-85	1.97	4584	1.97	0.23	3.68	8.75	7.50	-27.49
21	2	94-95	2.07	4748	1.89	0.22	4.27	8.91	7.64	-27.33
22	3	4-5	2.17	4912	1.75	0.21	3.94	8.95	7.67	-27.47

23	3	14-15	2.27	5075	1.73	0.20	4.29	8.90	7.63	-27.55
24	3	24-25	2.37	5239	1.69	0.20	3.85	9.10	7.80	-27.61
25	3	34-35	2.47	5403	1.72	0.20	4.08	8.98	7.70	-27.71
26	3	44-45	2.57	5567	1.67	0.19	4.11	8.93	7.65	-27.57
27	3	54-55	2.67	5731	1.52	0.19	4.01	8.40	7.20	-27.40
28	3	64-65	2.77	5895	1.59	0.19	3.80	8.43	7.23	-27.52
29	3	74-75	2.87	6059	1.45	0.18	4.16	8.15	6.99	-27.58
30	3	84-85	2.97	6223	1.39	0.17	4.22	7.99	6.85	-27.66
30-2	3	84-85	2.97	6223	1.43	0.17	3.80	8.22	7.05	-27.67
31	3	94-95	3.07	6387	1.41	0.17	3.59	8.73	7.48	-28.10
32	3	104-105	3.17	6551	1.34	0.17	4.12	8.61	7.38	-28.01
33	3	114-115	3.27	6715	1.35	0.17	4.08	8.66	7.43	-27.96
34	3	124-125	3.37	6879	1.28	0.16	4.03	8.20	7.03	-27.91
35	3	134-135	3.47	7043	1.41	0.18	3.97	8.47	7.26	-27.72
36	3	144-145	3.57	7207	1.32	0.16	3.44	8.11	6.95	-27.93
37	4	5-6	3.67	7383	1.39	0.16	2.41	8.28	7.09	-28.01
38	4	15-16	3.77	7535	1.30	0.15	3.50	8.91	7.64	-28.11
39	4	25-26	3.87	7699	1.32	0.16	2.04	8.53	7.31	-28.35
40	4	35-36	3.97	7863	1.30	0.15	3.17	8.14	6.97	-28.51
40-2	4	35-36	3.97	7863	1.30	0.15	3.48	1.12	0.96	-28.52
41	4	45-46	4.07	8027	1.26	0.15	3.16	7.44	6.38	-28.08
42	4	55-56	4.17	8191	1.22	0.15	3.04	7.99	6.85	-27.98
43	4	65-66	4.27	8355	1.08	0.14	3.27	7.64	6.55	-27.84
44	4	75-76	4.37	8519	1.22	0.15	3.00	7.43	6.37	-27.96
45	4	85-86	4.47	8683	1.17	0.15	2.80	7.42	6.36	-28.15
46	4	95-96	4.57	8847	1.17	0.15	3.30	7.21	6.18	-28.29

47	4	105-106	4.67	9011	1.25	0.26	3.91	8.00	6.85	-28.45
48	4	115-116	4.77	9174	1.24	0.15	4.34	7.59	6.50	-28.11
49	4	125-126	4.87	9338	1.31	0.15	4.20	7.75	6.64	-27.96
50	4	135-136	4.97	9502	0.57	0.10	2.46	4.65	3.98	-26.76
50-2	4	135-136	4.97	9502	0.57	0.09	4.87	5.66	4.85	-26.65
51	4	145-156	5.07	9666	0.54	0.09	2.50	5.24	4.49	-26.63
52	5	5-6	5.17	9830	0.69	0.09	4.18	6.68	5.72	-26.14
53	5	15-16	5.27	9994	0.88	0.10	3.73	8.81	7.55	-22.20
54	5	25-26	5.37	10158	0.69	0.10	4.76	7.11	6.10	-27.20
55	5	35-36	5.47	10322	0.66	0.10	3.14	5.77	4.95	-27.30
56	5	45-46	5.57	10486	0.58	0.09	3.46	6.43	5.51	-27.44

APPENDIX D: Molecular (*n*-alkane) Abundance and C-isotope Data

CORE	Depth	YEAR	CARBON NUMBER (ng/cm^2/yr)						Aquatic Flux	Terrigenous Flux	TAR
	(cm)	AD	17	19	21	27	29	31	ng/cm^2/yr	ng/cm^2/yr	(Terr/Terr+Aq)
BH09 - 2MC	0.5	2005	1.15	0.00	2.68	23.37	7.28	5.33	3.83	35.97	0.90
BH09 - 2MC	2.5	1991	4.62	0.00	2.88	35.21	10.84	7.24	7.50	53.29	0.88
BH09 - 2MC	4.5	1974	0.49	0.00	1.92	12.71	7.84	5.59	2.41	26.15	0.92
BH09 - 2MC	6.5	1955	1.80	0.00	1.79	10.82	5.51	3.74	3.59	20.07	0.85
BH09 - 2MC	8.5	1931	0.82	0.00	2.72	13.15	8.40	5.54	3.54	27.09	0.88
BH09 - 2MC	8.5	1931	0.84	0.00	1.66	7.50	5.10	3.67	2.50	16.27	0.87
BH09 - 2MC	10.5	1907	0.46	0.00	2.64	5.61	3.32	1.72	3.10	10.66	0.77
BH09 - 2MC	12.5	1882	0.83	0.00	4.08	10.92	7.16	4.91	4.91	22.99	0.82
BH09 - 2MC	14.5	1858	0.36	0.00	3.39	7.43	5.36	3.96	3.75	16.74	0.82
BH09 - 2MC	16.5	1834	0.00	0.00	4.44	8.98	7.03	4.54	4.44	20.56	0.82

CORE	Depth	YEAR	CARBON NUMBER (ng/cm^2/yr)						Aquatic Flux	Terrigenous Flux	TAR
	(cm)	AD	17	19	21	27	29	31	ng/cm^2/yr	ng/cm^2/yr	(Terr/Terr+Aq)
BH09 - 3MC	1.0	1999	1.33	2.63	2.86	15.14	7.22	5.81	6.82	28.17	0.81
BH09 - 3MC	2.0	1989	1.31	2.23	2.84	16.02	6.76	5.03	6.38	27.80	0.81
BH09 - 3MC	3.0	1970	0.65	1.58	2.11	18.00	6.85	5.78	4.33	30.63	0.88
BH09 - 3MC	4.0	1941	1.81	2.59	2.87	15.10	8.21	6.99	7.27	30.31	0.81
BH09 - 3MC	5.5	1905	3.26	5.06	2.50	6.70	7.12	4.56	10.82	18.38	0.63
BH09 - 3MC	7.0	1875	1.90	3.10	1.38	3.15	2.70	2.29	6.38	8.15	0.56
BH09 - 3MC	9.5	1824	2.54	4.85	3.15	4.10	3.50	3.62	10.54	11.23	0.52

CORE	Depth	YEAR	CARBON NUMBER (ng/cm^2/yr)						Aquatic Flux	Terrigenous Flux	TAR
	(cm)	AD	17	19	21	27	29	31	ng/cm^2/yr	ng/cm^2/yr	(Terr/Terr+Aq)
BH09 - 4MC	0.5	2005	0.55	1.37	4.96	18.14	9.23	7.63	6.89	35.00	0.84
BH09 - 4MC	2.0	1993	0.19	0.74	2.72	12.49	6.01	5.22	3.64	23.71	0.87
BH09 - 4MC	5.0	1964	0.22	0.79	1.30	7.12	2.21	1.70	2.30	11.03	0.83
BH09 - 4MC	6.0	1958	0.18	0.62	1.83	8.06	4.46	3.48	2.63	16.00	0.86
BH09 - 4MC	7.0	1956	0.24	0.78	2.30	8.62	5.34	4.05	3.32	18.01	0.84
BH09 - 4MC	9.0	1937	0.17	1.12	2.37	6.38	3.72	2.80	3.66	12.90	0.78
BH09 - 4MC	13.5	1889	0.07	0.73	2.90	3.65	2.32	1.53	3.70	7.50	0.67

CORE	Depth	YEAR	CARBON NUMBER (ng/cm^2/yr)						Aquatic Flux	Terrigenous Flux	TAR
	(cm)	AD	17	19	21	27	29	31	ng/cm^2/yr	ng/cm^2/yr	(Terr/Terr+Aq)
BH03 - 3MC	0.5	1997	1.77	2.26	1.91	11.49	7.15	4.41	5.94	23.05	0.80
BH03 - 3MC	1.5	1982	1.78	2.23	1.78	10.10	7.46	4.51	5.79	22.07	0.79
BH03 - 3MC	2.3	1968	2.96	2.74	2.55	10.83	7.68	5.35	8.25	23.86	0.74
BH03 - 3MC	3.5	1941	1.09	1.61	1.55	10.03	5.16	4.08	4.25	19.26	0.82
BH03 - 3MC	4.5	1914	0.10	0.23	0.93	2.49	2.69	1.50	1.26	6.68	0.84
BH03 - 3MC	7.5	1854	2.56	4.11	3.06	6.37	8.68	4.75	9.73	19.79	0.67

CORE	Depth	YEAR	CARBON NUMBER (ng/cm^2/yr)						Aquatic Flux	Terrigenous Flux	TAR
	(cm)	AD	17	19	21	27	29	31	ng/cm^2/yr	ng/cm^2/yr	(Terr/Terr+Aq)
LG MC	0.25	2009	0.00	0.73	2.08	15.19	5.36	4.38	2.81	24.93	0.90
LG MC	2.75	2000	0.00	0.80	3.47	20.22	6.66	5.31	4.27	32.18	0.88
LG MC	6.25	1978	0.49	1.63	3.64	10.28	3.93	2.71	5.76	16.91	0.75
LG MC	8.75	1960	0.00	1.10	2.31	8.17	4.37	3.13	3.41	15.67	0.82
LG MC	12.25	1934	3.64	1.53	3.96	9.00	5.07	3.46	9.14	17.53	0.66
LG MC	13.75	1924	1.24	0.90	2.66	5.80	3.28	2.44	4.80	11.52	0.71
LG MC	14.25	1921	1.66	1.40	3.59	7.55	4.33	2.96	6.66	14.84	0.69
LG MC	15.25	1914	2.83	1.52	3.49	5.54	3.04	1.93	7.84	10.51	0.57
LG MC	20.50	1871	6.19	3.06	4.93	4.92	3.85	2.65	14.17	11.42	0.45
LG MC	23.50	1842	3.74	2.72	1.71	1.31	0.73	0.35	8.18	2.40	0.23
LG MC	23.50	1842	1.52	1.45	2.43	3.00	2.14	1.44	5.40	6.57	0.55
LG MC	24.50	1832	3.64	2.27	3.48	4.62	3.18	2.17	9.39	9.97	0.51

CORE	Depth	YEAR	CARBON NUMBER (ng/cm^2/yr)						Aquatic Flux	Terrigenous Flux	TAR
	(cm)	AD	17	19	21	27	29	31	ng/cm^2/yr	ng/cm^2/yr	(Terr/Terr+Aq)
IR MC	0.25	2007	0.95	0.56	1.40	5.01	2.00	1.59	2.91	8.60	0.75
IR MC	3.25	1971	0.46	0.31	0.96	8.19	1.77	1.25	1.73	11.20	0.87
IR MC	4.25	1962	1.59	1.94	4.79	20.03	7.69	5.50	8.31	33.23	0.80
IR MC	4.25	1962	0.08	0.24	0.81	4.15	1.69	1.24	1.13	7.07	0.86
IR MC	5.25	1954	0.97	0.86	1.63	6.71	3.78	2.92	3.46	13.41	0.79
IR MC	8.75	1903	0.44	0.78	2.19	4.53	2.79	2.08	3.41	9.39	0.73
IR MC	9.25	1893	0.02	0.22	1.00	1.82	1.01	0.69	1.24	3.52	0.74
IR MC	11.25	1850	0.00	0.27	0.94	1.86	1.02	0.65	1.21	3.52	0.74
IR MC	12.75	1821	0.09	0.32	1.01	1.66	1.20	0.79	1.41	3.66	0.72
IR MC	14.75	1771	0.00	0.17	0.79	1.26	0.95	0.68	0.96	2.89	0.75
IR MC	14.75	1771	0.00	0.23	0.86	1.10	0.81	0.50	1.08	2.40	0.69

CORE	Depth	YEAR	CARBON NUMBER (ng/cm^2/yr)						Aquatic Flux	Terrigenous Flux	TAR
	(cm)	AD	17	19	21	27	29	31	ng/cm^2/yr	ng/cm^2/yr	(Terr/Terr+Aq)
EM MC	0.25	2006	0.28	0.26	0.79	3.66	1.29	1.10	1.33	6.05	0.82
EM MC	1.25	1982	1.05	0.34	1.01	8.89	3.00	2.58	2.40	14.47	0.86
EM MC	2.25	1957	0.92	0.33	0.85	8.34	2.36	1.92	2.10	12.62	0.86
EM MC	2.75	1944	1.21	0.43	0.87	9.63	2.25	1.79	2.50	13.66	0.85
EM MC	3.75	1916	0.72	0.26	0.69	6.18	2.67	2.06	1.67	10.92	0.87
EM MC	4.75	1882	1.01	0.30	0.76	3.97	2.27	2.22	2.06	8.46	0.80
EM MC	6.25	1815	0.47	0.20	0.48	1.68	1.08	0.96	1.16	3.73	0.76
EM MC	6.25	1815	0.40	0.21	0.43	1.20	0.79	0.67	1.04	2.66	0.72
EM MC	7.75	1749	0.48	0.22	0.42	1.35	0.86	0.77	1.12	2.98	0.73

CORE	Depth	YEAR	CARBON NUMBER (ng/cm^2/yr)						Aquatic Flux	Terrigenous Flux	TAR
	(cm)	AD	17	19	21	27	29	31	ng/cm^2/yr	ng/cm^2/yr	(Terr/Terr+Aq)
CM MC	0.75	1992	0.00	0.00	0.66	3.72	1.33	1.11	0.66	6.15	0.90
CM MC	1.25	1974	0.00	0.00	0.73	6.00	2.16	1.75	0.73	9.92	0.93
CM MC	2.25	1942	0.00	0.00	0.59	7.60	2.04	1.60	0.59	11.24	0.95
CM MC	3.25	1909	0.00	0.00	0.47	7.55	2.67	2.05	0.47	12.27	0.96
CM MC	4.25	1872	0.00	0.00	0.52	7.59	1.65	1.18	0.52	10.43	0.95
CM MC	4.75	1848	0.00	0.00	0.52	9.02	3.51	2.68	0.52	15.21	0.97
CM MC	5.25	1820	0.00	0.15	0.48	6.53	2.66	2.08	0.62	11.26	0.95
CM MC	6.75	1742	0.00	0.00	0.54	2.43	1.71	1.30	0.54	5.45	0.91
CM MC	6.75	1742	0.00	0.00	0.46	1.82	1.28	0.92	0.46	4.03	0.90

SAMPLE ID	DEPTH	AGE	CARBON NUMBER (ng/g sediment)						Aquatic Abundance	Terrigenous Abundance	TAR
GRAVITY	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**ng/g sed**	**ng/g sed**	**(Terr/Terr+Aq)**
SRG 2-3A	0.025	251	-	-	6.85	81.70	14.68	8.00	6.85	104.38	0.94
SRG 2-3B	0.025	251	-	-	0.00	49.35	0.00	0.00	0.00	49.35	1.00
SRG 24-25	0.245	512	-	-	51.96	220.03	167.67	124.29	51.96	512.00	0.91
SRG 46-47	0.465	777	-	-	62.94	193.82	146.52	101.03	62.94	441.37	0.88
SRG 68-69	0.685	1040	-	-	120.02	248.15	179.85	131.91	120.02	559.90	0.82
SRG 90-91	0.905	1303	-	-	99.64	182.19	140.52	98.11	99.64	420.83	0.81

SAMPLE ID	DEPTH	AGE	CARBON NUMBER (ng/g sediment)						Aquatic Abundance	Terrigenous Abundance	TAR
GRAVITY	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**ng/g sed**	**ng/g sed**	**(Terr/Terr+Aq)**
KWG 4-5	0.045	263	-	-	100.55	202.07	174.00	118.13	100.55	494.21	0.83
KWG 26-27	0.265	513	-	15.87	114.89	178.12	127.41	83.41	130.76	388.94	0.75
KWG 48-49A	0.485	762	-	-	74.42	207.22	109.75	62.74	74.42	379.72	0.84
KWG 48-49B	0.485	762	-	-	59.98	231.13	128.54	77.77	59.98	437.44	0.88
KWG 70-71	0.705	101	-	26.80	148.36	303.36	211.22	156.03	175.17	670.61	0.79
KWG 92-93	0.925	1261	-	10.29	83.09	172.47	109.71	70.82	93.39	352.99	0.79
KWG 114-115	1.145	1510	-	19.12	98.86	167.86	109.70	70.22	117.99	347.78	0.75
KWG 2: 14-15	1.365	1760	-	9.66	92.35	174.43	130.58	89.62	102.00	394.63	0.79

SAMPLE ID	DEPTH	AGE	CARBON NUMBER (ng/g sediment)						Aquatic Abundance	Terrigenous Abundance	TAR
Isle Royale Gravity	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**ng/g sed**	**ng/g sed**	**(Terr/Terr+Aq)**
IRG 2-3	0.025	258	-	-	79.02	206.85	102.57	67.78	79.02	377.19	0.83
IRG 24-25	0.245	608	-	-	95.81	210.70	135.13	81.94	95.81	427.76	0.82
IRG 47-48	0.475	974	-	-	73.09	186.37	117.45	73.32	73.09	377.14	0.84
IRG 69-70	0.695	1325	-	-	66.02	151.38	90.23	53.68	66.02	295.29	0.82
IRG 91-92A	0.915	1675	-	-	73.74	183.82	114.36	53.30	73.74	351.47	0.83
IRG 91-92B	0.915	1675	-	-	68.62	191.62	124.91	78.91	68.62	395.44	0.85
IRG 2: 18-19	1.135	2025	-	-	66.93	147.72	101.21	71.39	66.93	320.31	0.83
IRG 2: 40-41	1.355	2376	-	-	67.65	175.37	111.05	78.77	67.65	365.19	0.84
IRG 2: 62-63	1.575	2726	-	-	81.10	187.68	140.00	100.05	81.10	427.73	0.84
IRG 2: 84-85	1.795	3076	-	-	70.49	159.33	115.51	81.38	70.49	356.23	0.83

SAMPLE ID	DEPTH	AGE	CARBON NUMBER (ng/g sediment)						Aquatic Abundance	Terrigenous Abundance	TAR
Split Rock Piston	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**ng/g sed**	**ng/g sed**	**(Terr/Terr+Aq)**
BH02-10P-1_27-29A	0.28	1821	12.02	61.87	232.35	657.34	483.49	409.10	306.24	1549.93	0.84
BH02-10P-1_27-29B	0.28	1821	11.62	61.54	234.77	623.98	452.18	375.80	307.93	1451.96	0.83
BH02-10P-1_54-56	0.55	2264	0.00	13.89	66.92	160.78	132.61	113.71	80.81	407.09	0.83
BH02-10P-1_83-85	0.84	2739	111.06	131.47	263.36	481.66	358.32	276.48	505.90	1116.46	0.69
BH02-10P-1_107-109	1.08	3133	23.76	115.06	248.76	519.90	401.40	333.40	387.58	1254.70	0.76
BH02-10P-2_22-24	1.35	3575	62.78	121.56	216.11	504.69	435.42	367.90	400.45	1308.01	0.77
BH02-10P-2_52-54	1.65	4067	31.48	95.67	450.66	1070.01	891.85	692.20	577.80	2654.06	0.82
BH02-10P-2_76-78	1.89	4461	17.94	71.60	239.03	538.04	451.24	389.43	328.57	1378.71	0.81
BH02-10P-3_7-9	2.20	4969	13.27	56.77	195.99	431.21	378.59	329.00	266.03	1138.80	0.81
BH02-10P-3_34-36	2.47	5412	275.08	170.23	145.43	338.32	303.28	245.58	590.73	887.18	0.60
BH02-10P-3_62-64	2.75	5871	43.19	116.74	180.27	413.70	355.27	311.74	340.19	1080.72	0.76
BH02-10P-3_90-92	3.03	6330	29.09	50.51	115.49	202.38	155.72	124.14	195.09	482.24	0.71
BH02-10P-3_116-118	3.29	6756	275.99	180.36	189.77	348.22	318.43	294.35	646.13	961.00	0.60
BH02-10P-3_145-147	3.58	7232	31.36	97.08	149.87	243.57	222.40	203.05	278.30	669.02	0.71
BH02-10P-4_26-28	3.88	7724	573.41	176.69	180.81	280.17	261.85	235.90	930.90	777.91	0.46
BH02-10P-4_51-53	4.12	8117	86.11	86.35	163.72	349.91	315.53	288.89	336.18	954.33	0.74
BH02-10P-4_77-79	4.39	8560	629.09	201.44	154.90	250.17	239.36	219.80	985.44	709.33	0.42
BH02-10P-4_106-108	4.68	9036	9.60	40.01	125.48	284.86	261.41	230.30	175.09	776.57	0.82
BH02-10P-4_133-135A	4.95	9478	64.95	76.38	95.58	387.45	318.38	282.34	236.91	988.17	0.81
BH02-10P-4_133-135B	5.23	9937	32.21	67.94	91.60	387.30	331.96	308.52	191.75	1027.78	0.84
BH02-10P-5_11-13	5.23	9937	14.75	52.91	121.27	331.01	274.51	244.96	188.93	850.48	0.82
BH02-10P-5_37-39	5.49	10364	36.93	54.48	72.06	182.81	147.78	125.21	163.47	455.80	0.74

SAMPLE ID	DEPTH	AGE	CARBON NUMBER (ng/g sediment)						Aquatic Abundance	Terrigenous Abundance	TAR
Keweenaw Piston	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**ng/g sed**	**ng/g sed**	**(Terr/Terr+Aq)**
KW 17	0.10	1775	16.86	65.01	118.67	224.81	174.45	140.55	200.54	539.82	0.73
KW 19	0.30	2053	39.30	125.38	161.24	213.44	156.59	133.01	325.92	503.03	0.61
KW 21	0.50	2330	0.00	11.86	84.99	158.59	139.26	113.60	96.85	411.45	0.81
KW 23	0.70	2607	85.04	122.93	175.11	324.92	229.62	172.22	383.08	726.77	0.65
KW 25	0.90	2885	22.69	107.80	176.52	374.32	235.11	202.51	307.01	811.94	0.73
KW 27	1.10	3162	7.23	65.98	100.29	113.88	98.38	74.01	173.50	286.27	0.62
KW 29	1.30	3440	10.54	39.42	76.18	88.85	79.92	72.42	126.14	241.19	0.66
KW 31	1.50	3717	3.64	22.90	56.75	68.68	60.23	48.32	83.29	177.23	0.68
KW 33	1.70	3994	7.65	45.66	58.53	62.08	54.06	42.37	111.83	158.51	0.59
KW 35	1.90	4272	14.00	40.45	55.82	56.76	50.50	37.93	110.27	145.19	0.57
KW 37	2.12	4577	6.50	42.98	59.49	52.99	46.35	35.50	108.97	134.84	0.55
KW 39	2.32	4854	4.14	23.24	32.22	32.67	27.55	25.01	59.60	85.23	0.59
KW 41	2.52	5132	0.00	46.24	61.78	38.13	36.59	30.01	108.02	104.72	0.49
KW 43	2.72	5409	8.25	35.75	50.93	52.97	51.35	39.33	94.92	143.65	0.60
KW 45	2.92	5686	0.00	15.24	35.08	37.56	35.13	27.18	50.32	99.87	0.66
KW 47	3.12	5964	5.70	21.04	35.93	55.95	50.09	40.43	62.67	146.47	0.70
KW 49	3.32	6241	0.00	20.15	32.70	30.22	30.32	21.97	52.85	82.52	0.61
KW 51	3.52	6518	0.00	14.49	30.18	31.38	31.49	25.47	44.68	88.35	0.66
KW 53	3.72	6796	0.00	13.66	34.12	25.90	23.66	18.55	47.78	68.12	0.59
KW 55	3.92	7073	0.00	207.14	245.14	344.90	373.88	401.01	452.29	1119.79	0.71
KW 57	4.12	7351	0.00	27.33	43.04	52.49	43.12	37.93	70.36	133.54	0.65
KW 59	4.32	7628	4.53	33.34	35.90	29.36	26.86	23.78	73.77	80.00	0.52
KW 61	4.52	7905	0.80	25.75	58.95	39.35	38.57	30.72	85.50	108.64	0.56

SAMPLE ID	DEPTH	AGE	CARBON NUMBER (ng/g sediment)						Aquatic Abundance	Terrigenous Abundance	TAR
Isle Royal Piston	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**ng/g sed**	**ng/g sed**	**(Terr/Terr+Aq)**
IR 1-1	0.04	226	5.74	81.92	150.79	129.69	85.23	74.09	238.45	289.01	0.55
IR 1-3	0.28	965	4.19	46.79	95.63	81.72	57.61	46.49	146.61	185.82	0.56
IR 1-5	0.52	1255	2.94	25.14	87.55	109.24	74.22	62.89	115.62	246.35	0.68
IR 1-7A	0.76	1415	11.58	88.25	133.54	110.64	85.29	76.47	233.36	272.40	0.54
IR 1-7B	0.76	1415	12.23	82.93	132.38	94.52	73.00	62.49	227.54	230.01	0.50
IR 1-9	1.00	1656	0.72	11.23	69.28	105.89	78.38	68.76	81.23	253.03	0.76
IR 2-1	1.23	2079	5.16	42.38	118.72	114.74	79.36	67.11	166.26	261.21	0.61
IR 2-3	1.45	2647	11.80	62.40	149.19	96.00	73.60	62.19	223.39	231.79	0.51
IR 2-5	1.67	3421	10.54	45.68	117.67	91.23	63.28	55.56	173.89	210.07	0.55
IR 2-7	1.89	4334	67.75	122.86	148.18	100.57	66.73	57.39	338.79	224.69	0.40
IR 2-9	2.11	5321	1.17	15.92	68.74	79.16	60.35	50.42	85.83	189.93	0.69
IR 2-11	2.33	6307	0.00	11.53	60.47	83.13	67.87	61.58	72.00	212.58	0.75
IR 3-2A	2.55	7216	37.73	126.25	156.43	75.10	57.22	48.84	320.41	181.16	0.36
IR 3-2B	2.55	7216	12.70	116.40	183.49	77.93	58.54	53.36	312.58	189.83	0.38
IR 3-4	2.77	7988	0.88	16.37	64.12	68.93	54.81	50.16	81.36	173.90	0.68
IR 3-6	2.99	8582	2.43	32.25	90.24	85.26	66.29	54.81	124.92	206.36	0.62
IR 3-8	3.21	8994	0.63	14.22	72.85	106.28	83.37	70.89	87.70	260.53	0.75
IR 3-10	3.43	9262	0.38	7.06	45.69	80.48	59.62	51.48	53.14	191.58	0.78
IR 4-3A	4.09	10534	0.50	3.98	35.48	74.77	55.29	52.46	39.95	182.53	0.82
IR 4-3B	4.09	10534	0.00	7.72	49.08	91.86	71.37	68.14	56.81	231.38	0.80
IR 4-9	4.75	13217	5.85	76.66	114.14	41.12	29.53	27.38	196.65	98.03	0.33

Core	Depth	Year	SUESS CORRECTION	CARBON NUMBER (‰)						$\delta^{13}C_{aquatic}$ (‰)	$\delta^{13}C_{terrigenous}$ (‰)
	(cm)	A.D.		17	19	21	27	29	31	Flux weighted	Flux weighted
BH09-2	1.0	2001	1.82	-	-35.01	-35.52	-33.58	-30.09	-29.42	-34.07	-31.95
BH09-2	4.5	1974	1.04	-	-34.57	-35.45	-34.08	-29.72	-28.57	-33.80	-31.26
BH09-2	6.0	1961	0.79	-	-34.93	-35.32	-34.70	-30.42	-29.40	-34.32	-31.89
BH09-2	7.0	1948	0.62	-	-33.83	-34.23	-34.46	-29.80	-28.63	-32.91	-31.16
BH09-2	8.0	1937	0.52	-	-36.24	-35.44	-34.93	-31.07	-30.22	-35.58	-32.41
BH09-2	11.5	1895	0.31	-	-35.37	-33.51	-33.01	-30.16	-29.16	-34.67	-30.97
BH09-2	15.5	1846	0.21	-	-36.39	-36.10	-31.84	-29.61	-28.58	-35.49	-30.17

Core	Depth	Year	SUESS CORRECTION	CARBON NUMBER (‰)						$\delta^{13}C_{aquatic}$ (‰)	$\delta^{13}C_{terrigenous}$ (‰)
	(cm)	A.D.		17	19	21	27	29	31	Flux weighted	Flux weighted
BH09-3	1.0	1999	1.74	-	-33.46	-36.62	-33.55	-29.72	-29.50	-35.11	-31.74
BH09-3	2.0	1989	1.39	-	-30.70	-35.11	-34.24	-30.30	-29.68	-33.17	-32.46
BH09-3	3.0	1970	0.95	-	-34.06	-36.05	-34.32	-30.06	-30.29	-35.19	-32.61
BH09-3	4.0	1941	0.56	-	-32.80	-35.98	-33.86	-30.23	-29.90	-34.47	-31.96
BH09-3	5.5	1905	0.34	-	-34.09	-36.67	-32.38	-30.14	-29.65	-34.94	-30.84
BH09-3	7.0	1875	0.27	-	-35.56	-36.97	-32.15	-29.81	-28.89	-36.00	-30.45
BH09-3	9.5	1824	0.17	-	-32.53	-35.79	-30.69	-29.89	-29.18	-33.81	-29.95

Core	Depth	Year	SUESS CORRECTION	CARBON NUMBER (‰)						$\delta^{13}C_{aquatic}$ (‰)	$\delta^{13}C_{terrigenous}$ (‰)
	(cm)	A.D.		17	19	21	27	29	31	Flux weighted	Flux weighted
BH09-4	0.5	2005	1.94	-	-34.56	-37.47	-32.49	-29.91	-29.35	-36.84	-31.12
BH09-4	2.0	1993	1.53	-	-33.19	-35.98	-33.36	-30.15	-29.73	-35.38	-31.75
BH09-4	5.0	1964	0.84	-	-30.77	-34.55	-34.87	-30.63	-29.68	-33.12	-33.22
BH09-4	6.0	1958	0.76	-	-34.58	-35.13	-32.80	-30.03	-29.59	-34.99	-31.33
BH09-4	7.0	1956	0.72	-	-34.01	-34.71	-32.16	-29.90	-29.52	-34.53	-30.90
BH09-4	9.0	1937	0.52	-	-35.22	-35.81	-32.42	-29.87	-29.43	-35.62	-31.04
BH09-4	13.5	1889	0.30	-	-37.53	-37.90	-31.04	-29.89	-29.11	-37.83	-30.29

Core	Depth	Year	SUESS CORRECTION	CARBON NUMBER (‰)						$\delta^{13}C_{aquatic}$ (‰)	$\delta^{13}C_{terrigenous}$ (‰)
	(cm)	A.D.		17	19	21	27	29	31	Flux weighted	Flux weighted
BH03 - 3	0.5	1997	1.64	-	-31.37	-34.26	-33.38	-29.85	-29.53	-32.69	-31.55
BH03 - 3	1.5	1982	1.22	-	-31.28	-34.42	-32.99	-29.78	-29.49	-32.67	-31.19
BH03 - 3	2.5	1968	0.91	-	-31.13	-34.63	-32.98	-30.03	-29.61	-32.81	-31.28
BH03 - 3	3.5	1941	0.55	-	-31.63	-35.11	-33.61	-30.36	-30.04	-33.34	-31.98
BH03 - 3	4.5	1914	0.38	-	-36.10	-37.29	-32.35	-30.24	-30.02	-37.05	-30.98
BH03 - 3	7.5	1854	0.23	-	-33.68	-37.13	-31.28	-30.19	-29.35	-35.15	-30.34

Core	Depth	Year	SUESS CORRECTION	CARBON NUMBER (‰)						$\delta^{13}C_{aquatic}$ (‰)	$\delta^{13}C_{terrigenous}$ (‰)
	(cm)	A.D.		17	19	21	27	29	31	Flux weighted	Flux weighted
LG MC	0.25	2009	2.12	-	-30.92	-34.50	-33.48	-30.19	-29.43	-33.58	-32.06
LG MC	2.75	2000	1.75	-	-34.25	-37.00	-34.21	-29.88	-29.52	-36.48	-32.54
LG MC	6.25	1978	1.12	-	-32.70	-33.88	-33.51	-29.49	-28.99	-33.51	-31.85
LG MC	8.75	1960	0.77	-	-33.65	-33.60	-33.05	-29.59	-29.15	-33.62	-31.31
LG MC	12.25	1934	0.50	-	-34.87	-36.64	-32.64	-29.49	-28.95	-36.15	-31.00
LG MC	13.75	1924	0.43	-	-36.45	-37.65	-33.25	-30.17	-29.42	-37.35	-31.56
LG MC	14.25	1921	0.41	-	-36.98	-37.76	-32.92	-29.89	-28.99	-37.54	-31.25
LG MC	15.25	1914	0.38	-	-36.81	-37.95	-33.20	-29.93	-29.06	-37.61	-31.50
LG MC	20.5	1871	0.26	-	-29.20	-37.68	-31.34	-29.81	-28.41	-34.43	-30.15
LG MC	23.5	1842	0.21	-	-32.76	-38.54	-31.63	-29.40	-28.62	-36.61	-30.23
LG MC	23.5	1842	0.21	-	-32.45	-38.03	-31.53	-29.38	-28.43	-36.08	-30.14
LG MC	24.5	1832	0.19	-	-32.75	-37.26	-31.58	-29.48	-28.39	-35.48	-30.21

Core	**Depth**	**Year**	**SUESS CORRECTION**	**CARBON NUMBER (‰)**						**$\delta^{13}C_{aquatic}$ (‰)**	**$\delta^{13}C_{terrigenous}$ (‰)**
	(cm)	**A.D.**		**17**	**19**	**21**	**27**	**29**	**31**	**Flux weighted**	**Flux weighted**
IR MC	0.25	2007	2.02	-	-35.34	-37.65	-33.88	-30.56	-29.57	-36.99	-32.31
IR MC	3.25	1971	0.98	-	-36.69	-36.45	-35.32	-30.45	-30.05	-36.51	-33.96
IR MC	4.25	1962	0.80	-	-36.15	-36.30	-34.27	-30.74	-30.23	-36.25	-32.75
IR MC	4.25	1962	0.80	-	-36.13	-36.36	-34.44	-30.29	-30.27	-36.31	-32.73
IR MC	5.25	1954	0.69	-	-36.35	-35.96	-33.14	-30.05	-29.94	-36.09	-31.57
IR MC	8.75	1903	0.34	-	-38.02	-37.80	-32.40	-29.50	-29.69	-37.86	-30.94
IR MC	9.25	1893	0.31	-	-38.29	-38.22	-32.50	-30.41	-29.72	-38.23	-31.35
IR MC	11.25	1850	0.22	-	-28.69	-28.63	-25.95	-24.68	-24.46	-28.64	-25.31
IR MC	12.75	1821	0.16	-	-37.25	-37.31	-31.10	-30.16	-29.48	-37.29	-30.44
IR MC	14.75	1771	0.04	-	-37.84	-38.25	-31.47	-30.64	-29.72	-38.18	-30.78
IR MC	14.75	1771	0.04	-	-37.51	-38.46	-31.60	-30.46	-29.74	-38.26	-30.83

Core	Depth	Year	SUESS CORRECTION	CARBON NUMBER (‰)						$\delta^{13}C_{aquatic}$ (‰)	$\delta^{13}C_{terrigenous}$ (‰)
	(cm)	A.D.		17	19	21	27	29	31	Flux weighted	Flux weighted
CM MC	0.75	1992	1.49	-	-35.04	-37.23	-33.86	-29.83	-29.42	-37.23	-32.19
CM MC	1.25	1974	1.03	-	-35.89	-36.04	-34.39	-30.56	-29.50	-36.04	-32.69
CM MC	2.25	1942	0.56	-	-33.94	-37.17	-35.51	-30.45	-29.99	-37.17	-33.80
CM MC	3.25	1909	0.36	-	-34.68	-36.07	-34.73	-29.93	-29.79	-36.07	-32.86
CM MC	4.25	1872	0.26	-	-33.50	-36.70	-35.47	-30.37	-29.85	-36.70	-34.02
CM MC	4.75	1848	0.22	-	-32.88	-36.70	-34.62	-30.31	-29.79	-36.70	-32.77
CM MC	5.25	1820	0.16	-	-34.52	-37.36	-34.54	-30.18	-29.77	-36.70	-32.63
CM MC	6.75	1742	0.00	-	-36.39	-38.18	-32.00	-30.01	-29.51	-38.18	-30.78
CM MC	6.75	1742	0.00	-	-36.55	-38.31	-32.11	-30.34	-29.92	-38.31	-31.04

SAMPLE ID	Depth	AGE	CARBON NUMBER (‰)						$\delta^{13}C_{aquatic}$ (‰)	$\delta^{13}C_{terrigenous}$ (‰)
Split Rock Gravity	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**Weighted Avg.**	**Weighted Avg.**
SRG 2-3 A	0.03	247	-	-19.63	-39.34	-37.40	-32.15	-31.03	-39.34	-36.17
SRG 2-3 B	0.03	247	-	-19.41	-39.16	-36.99	-31.79	-31.04	-39.16	-36.99
SRG 24-25	0.25	510	-	-35.88	-36.82	-31.35	-30.18	-28.97	-36.82	-30.39
SRG 46-47	0.47	773	-	-37.52	-38.57	-31.37	-30.12	-29.23	-38.57	-30.47
SRG 68-69	0.69	1036	-	-37.06	-37.91	-31.46	-30.25	-29.46	-37.91	-30.60
SRG 90-91	0.91	1299	-	-36.55	-37.88	-30.99	-30.22	-29.43	-37.88	-30.37

SAMPLE ID	Depth	AGE	CARBON NUMBER (‰)						$\delta^{13}C_{aquatic}$ (‰)	$\delta^{13}C_{terrigenous}$ (‰)
Keweenaw Gravity	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**Weighted Avg.**	**Weighted Avg.**
KWG 4-5	0.05	263	-	-38.08	-37.84	-31.24	-29.82	-28.72	-37.84	-30.14
KWG 26-27	0.27	513	-	-36.87	-38.12	-31.42	-30.00	-29.12	-37.97	-30.46
KWG 48-49 A	0.49	762	-	-36.66	-37.52	-32.63	-30.00	-29.06	-37.52	-31.28
KWG 48-49B	0.49	762	-	-36.47	-37.38	-32.45	-29.92	-28.87	-37.38	-31.07
kWG 70-71	0.71	1011	-	-35.79	-37.12	-31.39	-29.47	-28.57	-36.91	-30.13
KWG 92-92	0.93	1261	-	-35.50	-37.23	-31.21	-29.30	-28.43	-37.04	-30.06
KWG 114-115	1.15	1510	-	-35.79	-37.23	-31.15	-29.26	-28.39	-37.00	-29.99
KWG 2:14-15	1.37	1759	-	-34.98	-36.52	-30.71	-29.41	-28.56	-36.37	-29.79

SAMPLE ID	Depth	AGE	CARBON NUMBER (‰)						$\delta^{13}C_{aquatic}$ (‰)	$\delta^{13}C_{terrigenous}$ (‰)
Isle Royale Gravity	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**Weighted Avg.**	**Weighted Avg.**
IRG 2-3	0.03	156	-	-38.66	-38.40	-33.95	-30.70	-30.34	-38.40	-32.42
IRG 24-25	0.25	894	-	-36.71	-38.08	-31.93	-30.71	-30.07	-38.08	-31.19
IRG 47-48	0.48	1218	-	-36.67	-37.09	-31.95	-30.41	-29.76	-37.09	-31.05
IRG 69-70	0.70	1371	-	-36.98	-37.19	-32.30	-30.57	-30.30	-37.19	-31.41
IRG 91-92 A	0.92	1553	-	-37.28	-37.62	-31.97	-30.59	-29.96	-37.62	-31.22
IRG 91-92 B	0.92	1553	-	-38.26	-37.19	-31.42	-29.45	-31.20	-37.19	-30.75
IRG 2:18-19	1.14	1873	-	-35.96	-36.87	-31.83	-30.32	-29.73	-36.87	-30.88
IRG 2:40-41	1.36	2382	-	-35.58	-37.16	-31.76	-30.27	-29.83	-37.16	-30.89
IRG 2:62-63	1.58	3085	-	-35.62	-37.50	-31.44	-29.97	-29.71	-37.50	-30.55
IRG 2:84-85	1.80	3948	-	-36.22	-37.27	-31.32	-30.00	-29.51	-37.27	-30.48

SAMPLE ID	Depth	AGE	CARBON NUMBER (‰)						$\delta^{13}C_{aquatic}$ (‰)	$\delta^{13}C_{terrigenous}$ (‰)
Split Rock Piston	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**Weighted Avg.**	**Weighted Avg.**
BH02-10P-1_27-29A	0.28	1821	-	-33.67	-37.37	-32.05	-30.66	-29.56	-36.59	-30.96
BH02-10P-1_27-29B	0.28	1821	-	-33.48	-37.24	-31.98	-30.61	-29.44	-36.46	-30.90
BH02-10P-1_54-56	0.55	2264	-	-34.11	-37.20	-31.10	-30.48	-29.54	-36.67	-30.46
BH02-10P-1_83-85	0.84	2739	-	-33.78	-36.68	-31.25	-29.88	-29.45	-35.71	-30.37
BH02-10P-1_107-109	1.08	3133	-	-33.22	-36.94	-31.59	-30.00	-29.51	-35.77	-30.53
BH02-10P-2_22-24	1.35	3575	-	-32.84	-36.35	-30.56	-29.75	-29.34	-35.09	-29.95
BH02-10P-2_52-54	1.65	4067	-	-35.51	-36.91	-31.11	-29.76	-29.49	-36.66	-30.23
BH02-10P-2_76-78	1.89	4461	-	-35.24	-36.09	-31.14	-29.96	-29.58	-35.89	-30.32
BH02-10P-3_7-9	2.20	4969	-	-35.54	-36.30	-30.81	-30.00	-29.53	-36.13	-30.17
BH02-10P-3_34-36	2.47	5412	-	-32.27	-35.91	-30.00	-29.72	-29.38	-33.95	-29.73
BH02-10P-3_62-64	2.75	5871	-	-34.02	-35.63	-30.30	-29.78	-29.88	-35.00	-30.01
BH02-10P-3_90-92	3.03	6330	-	-34.89	-36.84	-31.16	-30.50	-30.45	-36.25	-30.77
BH02-10P-3_116-118	3.29	6756	-	-32.87	-35.46	-30.30	-29.89	-29.81	-34.20	-30.02
BH02-10P-3_145-147	3.58	7232	-	-33.76	-35.48	-30.72	-30.44	-30.35	-34.80	-30.52
BH02-10P-4_26-28	3.88	7724	-	-33.09	-34.26	-29.70	-29.56	-29.64	-33.68	-29.63
BH02-10P-4_51-53	4.12	8117	-	-33.19	-35.67	-30.35	-30.31	-30.30	-34.81	-30.32
BH02-10P-4_77-79	4.39	8560	-	-33.25	-33.76	-29.70	-29.94	-29.96	-33.47	-29.86
BH02-10P-4_106-108	4.68	9036	-	-36.51	-37.52	-30.68	-30.44	-30.59	-37.28	-30.57
BH02-10P-4_133-135A	4.95	9478	-	-31.02	-32.06	-31.51	-31.57	-31.93	-31.60	-31.65
BH02-10P-4_133-135B	5.23	9937	-	-31.36	-32.46	-31.41	-31.39	-31.85	-31.99	-31.53
BH02-10P-5_11-13	5.23	9937	-	-32.67	-32.80	-31.54	-31.48	-31.85	-32.76	-31.61
BH02-10P-5_37-39	5.49	10364	-	-32.19	-32.17	-31.32	-31.30	-31.57	-32.18	-31.38

SAMPLE ID	**Depth**	**AGE**	**CARBON NUMBER (‰)**						**$\delta^{13}C_{aquatic}$ (‰)**	**$\delta^{13}C_{terrigenous}$ (‰)**
Keweenaw Piston	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**Weighted Avg.**	**Weighted Avg.**
KW 17	0.10	1775	-	-33.01	-34.24	-31.61	-29.08	-29.91	-33.81	-30.35
KW 19	0.30	2053	-	-32.47	-34.22	-32.98	-31.49	-28.89	-33.46	-31.43
KW 21	0.50	2330	-	-33.97	-35.15	-29.62	-30.09	-29.26	-35.00	-29.68
KW 23	0.70	2607	-	-34.71	-40.98	-30.61	-31.68	-28.98	-38.39	-30.56
KW 25	0.90	2885	-	-32.63	-35.59	-31.76	-29.92	-30.16	-34.47	-30.83
KW 27	1.10	3162	-	-32.60	-34.47	-31.65	-30.45	-28.86	-33.73	-30.52
KW 29	1.30	3440	-	-34.11	-33.88	-30.66	-29.62	-28.98	-33.96	-29.81
KW 31	1.50	3717	-	-	-34.01	-30.71	-30.11	-28.92	-24.23	-30.02
KW 33	1.70	3994	-	-32.29	-33.33	-30.92	-30.49	-29.57	-32.88	-30.41
KW 35	1.90	4272	-	-32.38	-33.39	-29.92	-29.57	-29.08	-32.96	-29.58
KW 37	2.12	4577	-	-30.12	-32.26	-30.83	-30.79	-28.88	-31.37	-30.30
KW 39	2.32	4854	-	-30.45	-33.09	-30.86	-28.80	-28.94	-31.98	-29.63
KW 41	2.52	5132	-	-32.97	-32.50	-30.95	-28.57	-28.02	-32.70	-29.28
KW 43	2.72	5409	-	-32.30	-32.57	-30.24	-30.60	-29.76	-32.46	-30.24
KW 45	2.92	5686	-	-30.12	-33.27	-31.20	-30.60	-29.71	-32.32	-30.58
KW 47	3.12	5964	-	-32.84	-33.12	-30.20	-30.28	-29.65	-33.02	-30.08
KW 49	3.32	6241	-	-32.88	-32.25	-30.53	-30.73	-30.06	-32.49	-30.48
KW 51	3.52	6518	-	-33.37	-32.88	-29.86	-30.79	-29.91	-33.04	-30.21
KW 53	3.72	6796	-	-31.04	-31.83	-29.88	-30.40	-29.64	-31.60	-30.00
KW 55	3.92	7073	-	-31.07	-31.89	-29.81	-30.38	-28.96	-31.51	-29.70
KW 57	4.12	7351	-	-30.37	-33.67	-30.42	-29.62	-28.88	-32.39	-29.72
KW 59	4.32	7628	-	-32.38	-32.71	-30.00	-30.17	-29.15	-32.55	-29.80
KW 61	4.52	7905	-	-31.31	-31.52	-30.28	-30.47	-29.57	-31.46	-30.15

SAMPLE ID	**Depth**	**AGE**	**CARBON NUMBER (‰)**						**$\delta^{13}C_{aquatic}$ (‰)**	**$\delta^{13}C_{terrigenous}$ (‰)**
Isle Royale Piston	**mblf**	**cal BP**	**17**	**19**	**21**	**27**	**29**	**31**	**Weighted Avg.**	**Weighted Avg.**
IR 1-1	0.04	226	-	-31.16	-32.64	-31.79	-30.04	-30.11	-32.12	-30.84
IR 1-3	0.28	965	-	-31.08	-32.33	-30.84	-29.95	-29.80	-31.92	-30.30
IR 1-5	0.52	1255	-	-31.41	-34.00	-31.33	-30.39	-30.10	-33.42	-30.73
IR 1-7A	0.76	1415	-	-31.12	-32.70	-31.51	-31.09	-30.80	-32.07	-31.18
IR 1-7B	0.76	1415	-	-31.16	-32.63	-31.19	-30.58	-30.87	-32.07	-30.91
IR 1-9	1.00	1656	-	-31.98	-34.92	-30.22	-30.48	-31.92	-34.51	-30.76
IR 2-1	1.23	2079	-	-33.31	-33.50	-31.27	-30.62	-30.23	-33.45	-30.80
IR 2-3	1.45	2647	-	-32.86	-32.66	-31.29	-30.56	-30.67	-32.72	-30.89
IR 2-5	1.67	3421	-	-32.00	-33.15	-31.48	-30.52	-30.26	-32.83	-30.86
IR 2-7	1.89	4334	-	-32.71	-32.61	-31.65	-30.54	-30.19	-32.65	-30.95
IR 2-9	2.11	5321	-	-32.58	-33.45	-30.78	-30.60	-30.58	-33.29	-30.67
IR 2-11	2.33	6307	-	-33.98	-34.04	-30.52	-30.76	-30.14	-34.03	-30.49
IR 3-2A	2.55	7216	-	-32.22	-32.62	-31.13	-30.99	-30.68	-32.44	-30.97
IR 3-2B	2.55	7216	-	-32.34	-32.30	-31.59	-31.03	-30.87	-32.32	-31.22
IR 3-4	2.77	7988	-	-33.13	-34.13	-30.95	-30.76	-30.72	-33.92	-30.83
IR 3-6	2.99	8582	-	-32.70	-34.25	-31.64	-31.19	-31.08	-33.84	-31.35
IR 3-8	3.21	8994	-	-33.77	-35.96	-31.21	-30.77	-30.41	-35.60	-30.85
IR 3-10	3.43	9262	-	-29.68	-31.27	-31.37	-32.02	-31.41	-31.05	-31.58
IR 4-3A	4.09	10534	-	-30.83	-32.34	-31.71	-31.96	-32.10	-32.19	-31.90
IR 4-3B	4.09	10534	-	-30.51	-32.01	-31.78	-31.84	-31.81	-31.80	-31.81
IR 4-9	4.75	13217	-	-31.32	-30.47	-31.60	-31.65	-31.78	-30.81	-31.67