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# Influence of climate change on algal community structure and primary productivity of Lake Malawi (East Africa) from the Last Glacial Maximum to present

Isla S. Castañeda,[a,b,c,1,*] Josef P. Werne,[a,d] and Thomas C. Johnson[a,c]

[a] Large Lakes Observatory, Duluth, Minnesota
[b] Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota
[c] Department of Geological Sciences, University of Minnesota, Duluth, Duluth, Minnesota
[d] Department of Chemistry and Biochemistry, University of Minnesota, Duluth, Duluth, Minnesota

*Abstract*

Biomarkers of aquatic algae and compound-specific carbon isotopes are used to examine past variations in algal community composition and primary productivity in Lake Malawi. We note major changes at the Pleistocene–Holocene boundary. From the Last Glacial Maximum until ~11.8 calendar years before present (kyr B.P.), Lake Malawi was characterized by either low rates of primary productivity or algal productivity that was dominated by a group other than diatoms. At the onset of the Holocene, conditions similar to those of modern Lake Malawi were initiated, with diatoms and nitrogen-fixing cyanobacteria becoming more important contributors to primary productivity. The transition at ~11.8 kyr B.P. is likely related to a shift in the dominant wind direction over Lake Malawi, resulting from a southward shift in the mean latitudinal position of the Intertropical Convergence Zone during the last glacial. Throughout the 23-kyr B.P. record, the effects of wind-induced upwelling are important and may be the main control on the carbon isotopic composition of algal lipids through delivery of $^{13}C$-depleted $CO_2$, derived from organic matter decomposition in deeper waters, to the photic zone. Relationships are also suggested between thermal stratification and primary productivity, with cool conditions at ~12 and 8 kyr B.P. resulting in weaker thermal stratification and increased primary productivity. The opposite situation occurs at 4.9 kyr B.P., when significantly warmer temperatures and decreased algal productivity are observed. Thus, in lentic systems such as Lake Malawi the major influence of climate on algal ecology appears to be through feedbacks in physical circulation mechanisms.

Climate variability in tropical Africa is dominated by hydrological change (Gasse 2000). The East African Rift Lakes experienced major and rapid hydrological fluctuations during the Late Pleistocene and Holocene, with lake-level changes on the order of hundreds of meters noted in Lakes Tanganyika and Malawi (Finney et al. 1996; Johnson 1996; Gasse 2000). These massive shifts between relatively moist and arid conditions resulted in the complete desiccation of shallower lakes, such as Lake Victoria (Johnson 1996), and undoubtedly played a major role in both human and faunal migrations.

At present, little is known regarding the effects of major hydrological fluctuations on the algal ecosystems of these lakes. Did primary productivity increase or decrease with falling lake levels? Were there shifts in the dominant groups present? Primary productivity in the deep East African Rift Lakes is strongly influenced by stratification, which affects wind-induced upwelling and influx of nutrient-rich waters to the photic zone (Hecky and Kling 1987). Previous studies of Lake Malawi have provided evidence for past changes in the dominant wind direction over the lake, which affected diatom productivity (Johnson et al. 2001, 2002; Brown and Johnson 2005). How did such changes in wind regime influence the other main algal groups in the lake? East Africa also underwent significant temperature changes during the Late Pleistocene and Holocene (Powers et al. 2005), but these changes were much less severe than the massive hydrological fluctuations that occurred. However, temperature changes of a few degrees may have affected thermal stratification, which, in turn, would have affected wind-induced upwelling and primary productivity. In Lake Tanganyika, the recent deep-water warming, on the order of 0.2–0.3°C since the early 1900s, is thought to have reduced primary productivity (O'Reilly et al. 2003; Verburg et al. 2003), possibly by as much as 20% (O'Reilly et al. 2003). What was the effect of the mid-Holocene warming when lake surface temperatures were ~3°C warmer than at present (Powers et al. 2005)?

In this study, we investigate these questions by using molecular biomarkers and compound-specific carbon isotopes to examine past algal community composition and primary productivity in Lake Malawi. Diatom and biogenic silica records from Lake Malawi have provided evidence for major shifts in diatom productivity and the dominant species present since the Last Glacial Maximum (LGM) (Gasse et al. 2002; Johnson et al. 2002). However, diatoms are only one of the major algal groups in Lake Malawi, and the response of the other algal groups, which lack hard parts that preserve well, is currently unknown. Understanding how tropical aquatic ecosystems respond to environmental variability is important, as changes in algal productivity and community structure have important implications for higher organisms in the food chain, such as fish.

* Corresponding author: isla.castaneda@nioz.nl

[1] Present address: Royal Netherlands Institute for Sea Research, Department of Marine Organic Biogeochemistry, Den Burg, The Netherlands.

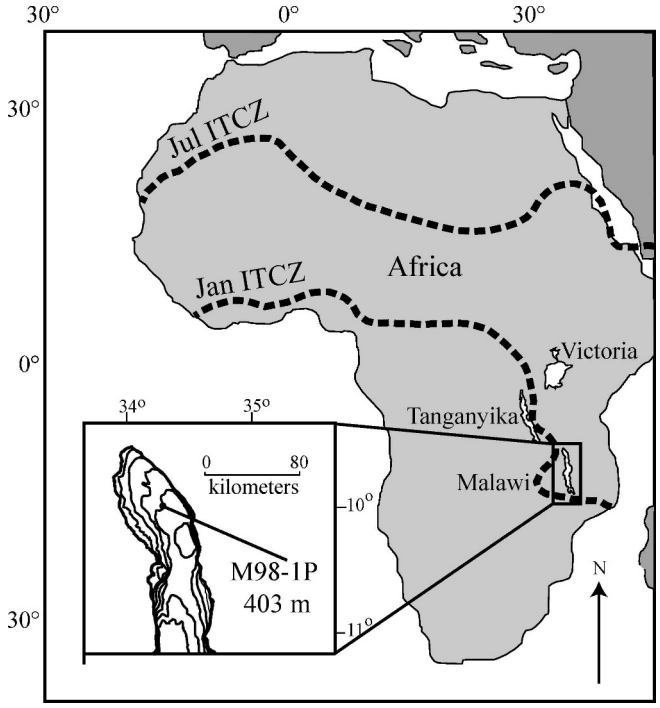


Fig. 1. The location of Lake Malawi in southeast Africa and the location of piston core M98-1P. The July and January positions of the ITCZ are indicated, based on Leroux (2001).

## Methods

*Study location*—Lake Malawi, the southernmost of the East African Rift Lakes, is located between 9°S and 14°S, is 560 km long, and measures up to 75 km wide (Eccles 1974) (Fig. 1). Lake Malawi is at least 5 million years old (Finney et al. 1996), is underlain by over 4 km of sediment (Rosendahl 1987), and has a maximum depth of over 700 m (Johnson and Davis 1989). The lake is permanently anoxic below ~200 m (Eccles 1974) and is characterized by relatively high sedimentation rates of 0.5–1.5 mm $yr^{-1}$ (Finney et al. 1996). The majority of water loss in Lake Malawi occurs through evaporation rather than outflow, making it extremely sensitive to minor changes in aridity (Spigel and Coulter 1996). The level of Lake Malawi is estimated to have dropped about 100 m during the LGM (Scholz et al. 2007).

In addition to having a continuous, high-resolution sedimentary record, Lake Malawi is a good site for paleoenvironmental reconstructions, as the lake exhibits a strong response to changes in global climate. Lake Malawi is situated in a climatically sensitive region that is heavily influenced by the intertropical convergence zone (ITCZ) (Fig. 1). The lake is located at the southern limit of the annual transit of the ITCZ (13–15°S) and therefore experiences one rainy season per year (November to March), while the rift lakes to the north experience two rainy seasons from the biannual overhead passage of the ITCZ (Nicholson 1996; Leroux 2001) (Fig. 1). During the rainy season, the main recharge period for lakes and rivers in southern Africa, the dominant winds are weak and northerly. Between April and May the ITCZ moves northward toward the equator, with strong southerly winds prevailing until September, when winds become more easterly (Eccles 1974). The distinct seasonal patterns of climate are reflected in the sedimentary record of Lake Malawi (Pilskaln and Johnson 1991). During the windy season, phytoplankton blooms occur throughout the lake and provide autochthonous contributions to sedimentation, dominated by diatoms (Patterson and Kachinjika 1995; Bootsma and Hecky 1999). During the rainy season the combination of generally weak winds and increased runoff results in high allochthonous sedimentary contributions. This seasonal pattern results in annual varve couplets, with a light layer representing the windy season and a dark layer representing the rainy season (Pilskaln and Johnson 1991).

The strength of density stratification, which depends on water column gradients of temperature and dissolved solids, is important to algal productivity in tropical lakes, as strong stratification can inhibit wind-induced upwelling and the delivery of nutrients to the photic zone. Stratification is the main controlling factor of phytoplankton composition and succession in Lake Malawi (Hecky and Kling 1987). The lake is permanently stratified, more strongly so during the warm and wet season, when temperature differences between the surface and bottom waters are the greatest. During the dry and windy season, when temperature gradients between the surface and bottom waters are reduced, dissolved solids help to maintain stratification (Wuest et al. 1996). Today, surface-water temperatures of Lake Malawi vary from 23°C to 29°C between austral winter and summer, and bottom waters are 22.5°C (Wuest et al. 1996).

The East African Rift Lakes, dominated by a few widespread algal taxa (Patterson and Kachinjika 1995), provide a suitable location to examine past changes in algal productivity and community structure. Phytoplankton productivity in Lake Malawi is presently dominated by Bacillariophyta (diatoms), followed by contributions from Cyanophyta (cyanobacteria) and Chlorophyta (green algae), with minor contributions from Pyrrophyta (dinoflagellates) (Patterson and Kachinjika 1995). From October to March, the rainy and non-windy season in Malawi, Cyanophyta and Chlorophyta are the dominant phytoplankton (Hecky and Kling 1987). Bacillariophyta dominates the rest of the year, when cool and windy conditions are present (Hecky and Kling 1987).

In this study we use molecular biomarkers and compound-specific carbon isotopes to examine past changes in algal community structure and primary productivity in Lake Malawi. We examine the record of piston core M98-1P, collected from 403-m water depth in the northern basin of Lake Malawi (10°15.99′S, 34°19.19′E) in 1998 by an expedition of the International Decade for East African Lakes (Fig. 1). The lithology and age model (based on $^{14}C$ dating, varve counting, and $^{210}Pb$ dating) of this 7.8-m piston core have been previously described in several studies (Barry et al. 2002; Johnson et al. 2002; Filippi and Talbot 2005), and the age model is available at the National Oceanic and Atmospheric Association (NOAA) web site for the World Data Center for Paleoclimatology (http://

www.ncdc.noaa.gov/paleo/data.html). All ages in this study are reported in thousands of calendar years before present (kyr B.P.).

*Biomarkers of aquatic algae*—A variety of different compound classes provide biomarkers for aquatic algae. The straight-chain *n*-alkanes, *n*-alkanoic acids, and *n*-alkanols, with 17–21 carbon atoms, are dominantly produced by aquatic algae and are a general biomarker for aquatic algae (Giger et al. 1980; Cranwell et al. 1987). However, as terrestrial plants and bacteria also produce small amounts of these compounds, several other groups of compounds are often used as biomarkers for aquatic algae. Sterols, compounds that occur in all eukaryotes, are membrane rigidifiers, and the specificity of these compounds for different phytoplankton groups is well known (Volkman 1986; Volkman et al. 1998). Sterols commonly provide biomarkers for diatoms and dinoflagellates, which are two of the four main algal groups present in Lake Malawi. The dominant sterol(s) in diatoms varies depending on the species present, but brassicasterol (24-methylcholesta-5,22-dien-3$\beta$-ol), fucosterol (24-methylcholesta-5,24(28)-dien-3$\beta$-ol), and $\beta$-sitosterol (24-ethylcholesta-5-en-3$\beta$-ol) are common lipids of diatoms (Barrett et al. 1995; Volkman et al. 1998). The compound dinosterol (4$\alpha$,23,24-trimethyl-5$\alpha$-cholest-22-en-3$\beta$-ol) is found in many dinoflagellate species (Boon et al. 1979; Withers 1983; Pirretti et al. 1997) and is commonly used as a biomarker for these organisms (Robison et al. 1984; Brassell et al. 1987; Volkman et al. 1998). The other two main algal groups in Lake Malawi, green algae and cyanobacteria, also have specific biomarkers. Biomarkers of green algae include botryococcane and botryococcene, which are produced by the green algae *Botryococcus braunii* (Maxwell et al. 1968; Volkman et al. 1998). Other biomarkers for green algae include the $C_{25}$ and $C_{27}$ *n*-alkenes and lycopadiene (Volkman et al. 1998). Many cyanobacteria have been shown to contain 7- and 8-methylheptadecanes (me-*n*-$C_{17}$; Gelpi et al. 1970) or 2-methylhopanoids (Summons et al. 1999). Two new cyanobacterial markers recently have also been suggested from the glycolipids, docosanyl 3-*O*-methyl-$\alpha$-rhamnopyranoside and docosanyl 3-*O*-methylxylopyranoside (Sinninghe Damsté et al. 2001).

*Bulk organic geochemistry*—Total inorganic carbon (TIC) and total carbon (TC) measurements were determined on a UIC $CO_2$ Coulometer. In these samples, TC is total organic carbon (TOC), because TIC was not present in any of the samples analyzed from core M98-1P. Carbon to nitrogen ratios (C : N) were determined on a Costech ECS 4010 elemental analyzer. Sediment samples did not receive acid pretreatment prior to analysis on the elemental analyzer. Therefore, the C : N ratios reported here reflect the ratio of TOC to total nitrogen ($C_{org} : N_{tot}$). TOC, C : N, and bulk carbon isotope data ($\delta^{13}C_{TOC}$) included here are presented in Castañeda et al. (2009), and the methods for $\delta^{13}C_{TOC}$ analysis are detailed in this publication.

*Compound extraction and separation*—Sixty sediment samples were selected for molecular analysis at a sampling resolution of approximately one sample per 500 yr. During time periods in which previous studies of Lake Malawi had documented significant changes, such as during the Younger Dryas cold period (Johnson et al. 2002), samples were taken at higher resolution. Freeze-dried sediment samples were Soxhlet-extracted with 2 : 1 methylene chloride : methanol for 24 h to obtain a total lipid extract (TLE). The TLE was further separated into neutral lipid, fatty acid, and phospholipid fatty acid fractions using Aminopropylsilyl bond elute columns, and the neutral fraction was further separated via silica gel column chromatography using the methods detailed in Castañeda et al. (2009). After column chromatography, the apolar fraction containing the *n*-alkanes was passed through an $Ag^+$ impregnated silica pipette column to separate the saturated and unsaturated hydrocarbons. Polar fractions were derivatized to their trimethylsilyl-ethers in 100 mL bistrimethylsilyltrifluoroacetamide and 100 mL acetonitrile at 60–70°C for 2 h immediately prior to gas chromatograph (GC) analysis.

*Compound identification and quantification*—Molecular identification of compounds (*n*-alkanes) was performed on a Hewlett-Packard 6890 GC coupled to a Hewlett Packard (HP) 5973 mass spectrometer (MS). An HP-1 capillary column (25 m $\times$ 32 mm $\times$ 0.5 $\mu$m) was used with helium (He) flow rates set at 2 mL $min^{-1}$. The GC-MS oven temperature program initiated at 50°C and increased at a rate of 10°C $min^{-1}$ to 130°C and then next increased at a rate of 4°C to 320°C. The final temperature of 320°C was held for 10 min. Mass scans were made over the interval from 50 to 650 m/z (mass to charge ratio). Compounds were identified by interpretation of characteristic mass spectra fragmentation patterns, gas chromatographic relative retention times, and by comparison with literature.

Quantification of compounds was performed on a Hewlett-Packard HP 6890 GC with a FID detector using 5$\alpha$-androstane as an internal standard. Compound concentrations were determined by relating chromatogram peak area to the concentration of the internal standard. Column type and the temperature program used for GC analysis are the same as described above for GC-MS. He flow rates were set at 2.6 mL $min^{-1}$.

*Compound-specific carbon isotopes*—Twenty-eight samples were selected for compound-specific carbon isotopic analysis and were analyzed in the Department of Geological Sciences at Brown University. The carbon isotopic composition of *n*-alkanes was determined through GC–isotope ratio–MS (GC-IRMS). An HP 6890 GC (DB-1 column: 60 m, 0.32-mm diameter, 0.1-$\mu$m film thickness) was connected to a Finnigan MAT Delta+ XL mass spectrometer via a combustion interface. The GC temperature program initiated at 40°C and increased at a rate of 20°C $min^{-1}$ to 220°C and next at a rate of 6°C $min^{-1}$ to 315°C. The final temperature of 315°C was held for 10 min. Compounds (*n*-alkanes) separated by the GC column were oxidized at 940°C and converted to $CO_2$. Six pulses of reference $CO_2$ gas with a known $\delta^{13}C$ value were injected into the IRMS for determination of the $\delta^{13}C$ values of compounds in the sample. A standard mixture consisting of

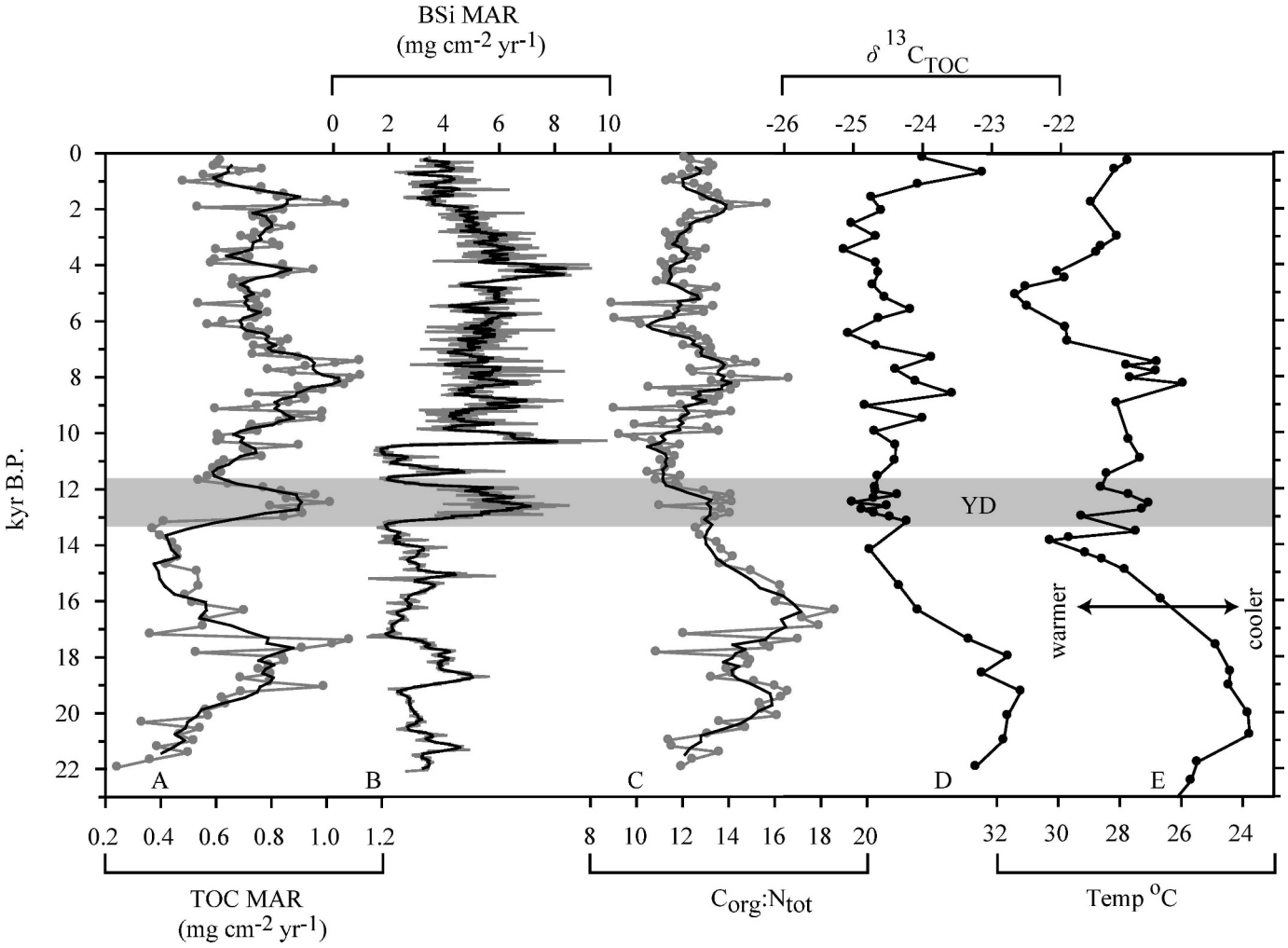


Fig. 2. Bulk geochemical data from core M98-1P. The interval of the Younger Dryas cold period (YD) is highlighted. (A) Mass accumulation rates of total organic carbon (TOC MARs), plotted against age in thousands of calendar years before present (kyr B.P.), are shown by the gray dots, while the black line represents the smoothed TOC MAR record (five-point running average). (B) MARs of biogenic silica (BSi) are plotted in gray, while the black line represents the smoothed BSi MAR data (data from Johnson et al. 2002). (C) The ratio of total organic carbon to total nitrogen ($C_{org}:N_{tot}$) is shown by the gray dots, while the black line represents the smoothed $C_{org}:N_{tot}$ data. (D) The carbon isotopic composition of bulk sediment samples ($\delta^{13}C_{TOC}$). The TOC, $C_{org}:N_{tot}$, and $\delta^{13}C_{TOC}$ data from M98-1P are from Castañeda et al. (2009). (E) Lake Malawi temperature reconstruction based on the $TEX_{86}$ paleotemperature proxy (data from Powers et al. 2005). Note that the *x*-axis scale is reversed to facilitate comparisons with the bulk geochemical records.

four fatty acids with known $\delta^{13}C$ values was measured multiple times daily to ensure accuracy. The standard deviation of all compounds in this standard mixture was less than ±0.28‰. Each *n*-alkane sample was run in duplicate, and the reproducibility of the $C_{17}$, $C_{19}$, and $C_{21}$ *n*-alkanes is better than ±1.5‰, ±0.9‰, and ±2.0‰, respectively. All $\delta^{13}C$ values are reported relative to the Vienna Pee Dee Belemnite standard using standard delta (per mil) notation.

## Results

*Bulk geochemical data*—The overall trends observed in the bulk geochemical data are that low TOC mass accumulation rates (MARs) are noted at ~22–20 kyr B.P. and from 16–13.5 kyr B.P., while generally high TOC MAR values are noted in the intervals from 19–17.5 kyr B.P., 13–11.9 kyr B.P., 10–7 kyr B.P., and from 2–1.5 kyr B.P. (Fig. 2). The $C_{org}:N_{tot}$ record generally tracks changes in the TOC MAR record (Fig. 2), with the highest $C_{org}:N_{tot}$ values occurring when TOC MAR values are the highest, and vice versa. An exception to this observation occurs following the LGM, when the TOC MAR peaks at 17.5 kyr B.P., while the $C_{org}:N_{tot}$ ratio peaks later, at 16.3 kyr B.P. A particularly striking feature of both the TOC MAR and $C_{org}:N_{tot}$ records is the Younger Dryas cold period (11.7–13 kyr B.P.), which is marked by an abrupt increase in both TOC MAR and $C_{org}:N_{tot}$ (Fig. 2).

Bulk sediment carbon isotopic values ($\delta^{13}C_{TOC}$) range from −22.5‰ to −25‰, with the most enriched values noted from 20–18 kyr B.P. (Fig. 2). Following the LGM, $\delta^{13}C_{TOC}$ values become increasingly depleted until ~13 kyr B.P. Unlike the TOC MAR and $C_{org}:N_{tot}$ records, $\delta^{13}C_{TOC}$ values do not exhibit a significant excursion during the

Younger Dryas, but a trend toward slightly more depleted values is noted. Following the Younger Dryas, $\delta^{13}C_{TOC}$ values generally fluctuate between −25‰ and −23.5‰ for the remainder of the Holocene.

*Molecular data*—A number of compounds were present and abundant in the polar fractions of M98-1P that can be attributed to algal sources. These compounds include the short-chain *n*-alkanols, 24-methylcholesta-5,22-dien-3$\beta$-ol, 24-ethylcholesta-5-en-3$\beta$-ol, docosanyl 3-*O*-methylxylopyranoside, the long-chain *n*-alkenes, loliolide, isololiolide, and the long-chain *n*-alkyl diols (Figs. 3, 4). MARs of each of these individual compounds exhibit considerable variability during the past 23 kyr B.P., and the paleoenvironmental significance of these records is discussed in detail in the following sections of this manuscript.

The $C_{17}$–$C_{21}$ *n*-alkanes are a general algal biomarker, and variations in the carbon isotopic composition of these compounds can be used to examine changes in primary productivity. The $C_{17}$, $C_{19}$, and $C_{21}$ *n*-alkanes exhibit similar trends in both abundance (Fig. 4) and isotopic composition (Fig. 5) and thus reflect a common algal source. Here we use the weighted mean of the $C_{17}$–$C_{21}$ *n*-alkanes (Fig. 5) to examine changes in the primary productivity of Lake Malawi and hereafter refer to this record as the $\delta^{13}C_{algal}$ record. The Lake Malawi $\delta^{13}C_{algal}$ record exhibits an overall change of ~8‰, with the most depleted value of −34.2‰ noted at 12 kyr B.P. and the most enriched value of −26.7‰ noted at 3 kyr B.P. The $\delta^{13}C_{algal}$ record can be divided into three main intervals: the Late Pleistocene (23–13 kyr B.P.), the Younger Dryas (12.9–11.6 kyr B.P.), and the Holocene (11 kyr B.P. to the present). Mean $\delta^{13}C_{algal}$ values of −30.1‰ characterize the Late Pleistocene, while the Younger Dryas is marked by a shift to more depleted $\delta^{13}C_{algal}$ values, which average −32.3‰ from 12.9 to 11.6 kyr B.P. During the Holocene, a shift occurs to more enriched $\delta^{13}C_{algal}$ values, with an average value of −27.8‰.

## Discussion

*Algal biomarkers*—Biomarkers of Bacillariophyceae (diatoms): Two of the common sterol biomarkers for diatoms, brassicasterol (24-methylcholesta-5,22-dien-3$\beta$-ol) and $\beta$-sitosterol (24-ethylcholesta-5-en-3$\beta$-ol) (Volkman et al. 1998), are found in low abundance in Lake Malawi sediments. Only a very small number of Lake Malawi samples contained brassicasterol, and $\beta$-sitosterol was present in only about half of the samples analyzed. Thus, given that diatoms dominate algal productivity in Lake Malawi (Hecky and Kling 1987; Patterson and Kachinjika 1995) and that abundant diatoms are present throughout the entire core (Gasse et al. 2002), these sterols do not provide reliable biomarkers for diatoms in Lake Malawi. Additionally, these sterols can also be synthesized by land and emergent water plants (Nishimura and Koyama 1977), and given the proximity of the shore to the coring site, terrestrial sources of sterols are likely in Lake Malawi. However, Lake Malawi sediments contain the compounds loliolide and isololiolide, which provide a reliable diatom biomarker.

Loliolide and isololiolide are the anoxic degradation products of the pigment fucoxanthin, the major carotenoid present in diatoms (Klock et al. 1984; Repeta 1989), and are relatively abundant in Lake Malawi sediments (Fig. 3). Although dinoflagellates and haptophyte algae can also contain fucoxanthin (Klock et al. 1984; Jeffrey and Vesk 1997), loliolide (or isololiolide) provides a reliable marker for diatoms since dinoflagellates are only a minor contributor to algal productivity in Lake Malawi and because haptophyte algae are not present in the lake (Patterson and Kachinjika 1995).

The loliolide record generally tracks changes noted in the biogenic silica record (Johnson et al. 2002), which is another proxy for diatom productivity (Fig. 3). Biogenic silica and loliolide MARs indicate low abundances from 23–12.9 kyr B.P. A rapid increase in accumulation rates marks the start of the Younger Dryas interval, with peak values being reached at ~12.5 kyr B.P. Following the Younger Dryas, a return to lower values occurs until ~10 kyr B.P., when a rapid increase in accumulation rates is again noted. Throughout the Holocene accumulation rates of biogenic silica and loliolide fluctuate but are generally higher than Late Pleistocene accumulation rates.

Biomarkers of Chlorophyceae (green algae): The green algae *Botryococcus braunii* has received much research attention, and, thus, several compounds have been identified as biomarkers of this group. Common biomarkers of *B. braunii* include botryococcenes and lycopadiene or lycopane derivatives (Metzger and Largeau 2005; Adam et al. 2006). *B. braunii* is found in freshwaters and brackish waters from alpine, temperate, and tropical regions and is classified into three different chemical races: A, B, and L. Algae of race A produce *n*-alkadienes and alkatrienes, those of race B produce botryococcenes, while lycopadiene and lycopane derivatives are produced by race L (Metzger and Largeau 2005). Core M98-1P did not contain any biomarkers of *B. braunii*, although the species is included in lists of algae present in the lake (Patterson and Kachinjika 1995). However, it should be noted that *B. braunii* is not the most common species of green algae present in Lake Malawi, and, instead, *Closterium*, *Staurastrum*, and *Mougeotia* are the most abundant types (Hecky et al. 1999), with minor contributions from a number of other groups, including *Pediastrum* (Cocquyt et al. 1993). Furthermore, the presence of *B. braunii* in Lake Malawi and in the other tropical lakes of East Africa is currently under debate, and it is more likely that the species present is *Botryococcus terribilis* Komarek and Marvan, a species that is primarily found in tropical lakes (Hedy Kling pers. comm.). For these reasons, it is not surprising that biomarkers of *B. braunii* were not detected in Lake Malawi sediments. Lake Malawi samples also did not contain any lycopadiene or lycopane derivatives.

The $C_{25}$ and $C_{27}$ *n*-alkenes are recognized as biomarkers of Chlorophyceae (Volkman et al. 1998) and are present in Lake Malawi sediments (Fig. 4). However, these compounds can also be produced by diatoms (Volkman et al. 1998), and in Lake Malawi a mixed source from green algae and diatoms is likely, given that diatoms are the dominant

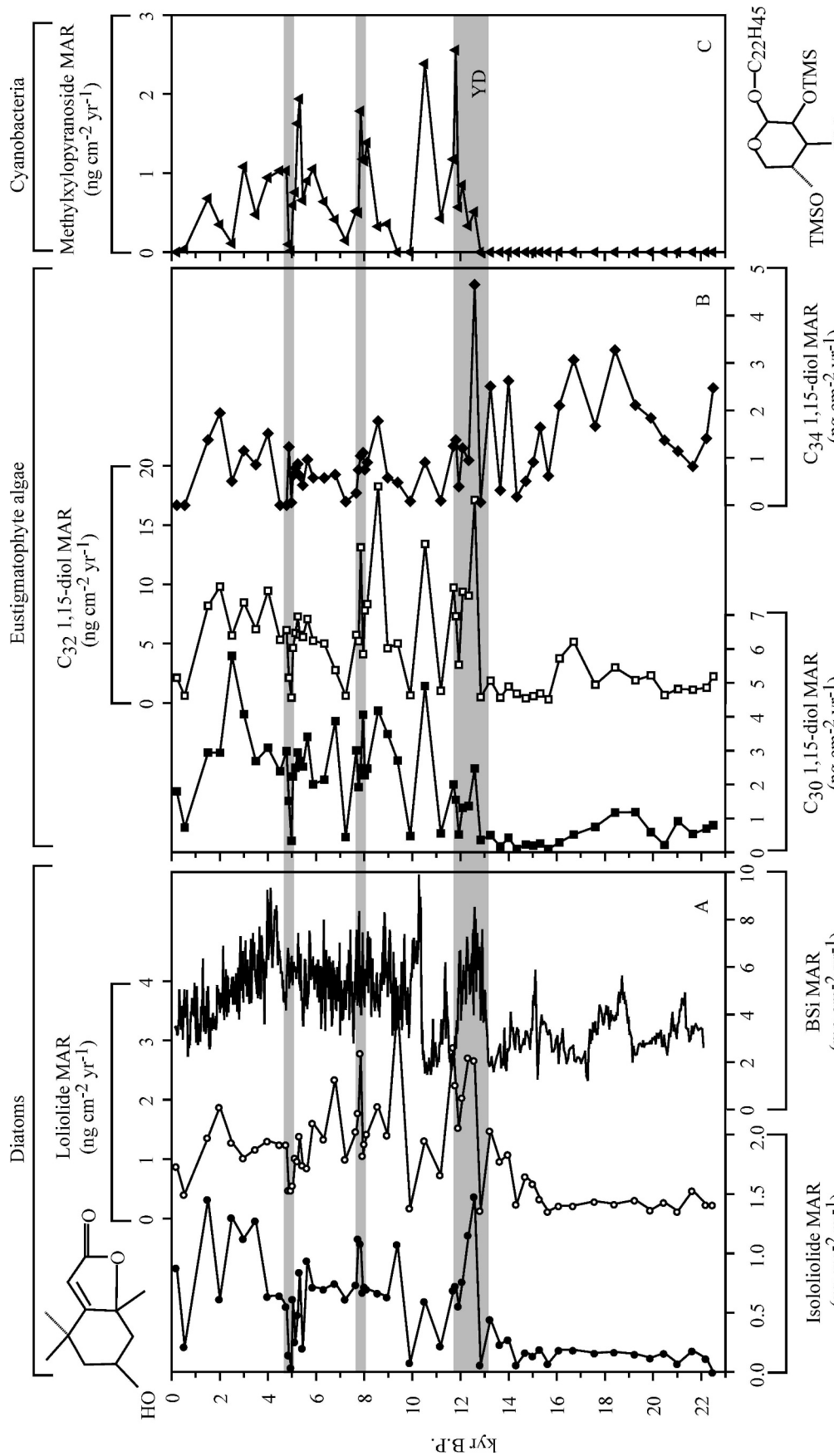


Fig. 3. Mass accumulation rates of algal biomarkers. The interval of the Younger Dryas (YD) cold period is highlighted. In addition, two events at ~8 and 4.9 kyr B.P. are highlighted, and these events are characterized by relatively high and low abundances of biomarkers, respectively. These events may be related to changes in thermal stratification. (A) Mass accumulation rates of isololiolide and loliolide, biomarkers of diatoms. The derivatized structure of loliolide is indicated near the left side of the graph. The mass accumulation rate of biogenic silica (BSi) is shown for comparison (BSi data from Johnson et al. 2002). (B) Mass accumulation rates of the $C_{30}$, $C_{32}$, and $C_{34}$ *n*-alkyl diols, biomarkers of eustigmatophyte algae. (C) Mass accumulation rates of the glycolipid docosanyl 3-*O*-methylxylopyranoside, a suggested biomarker for cyanobacteria (Sinninghe Damsté et al. 2001). The derivatized structure of this compound is indicated below the graph.

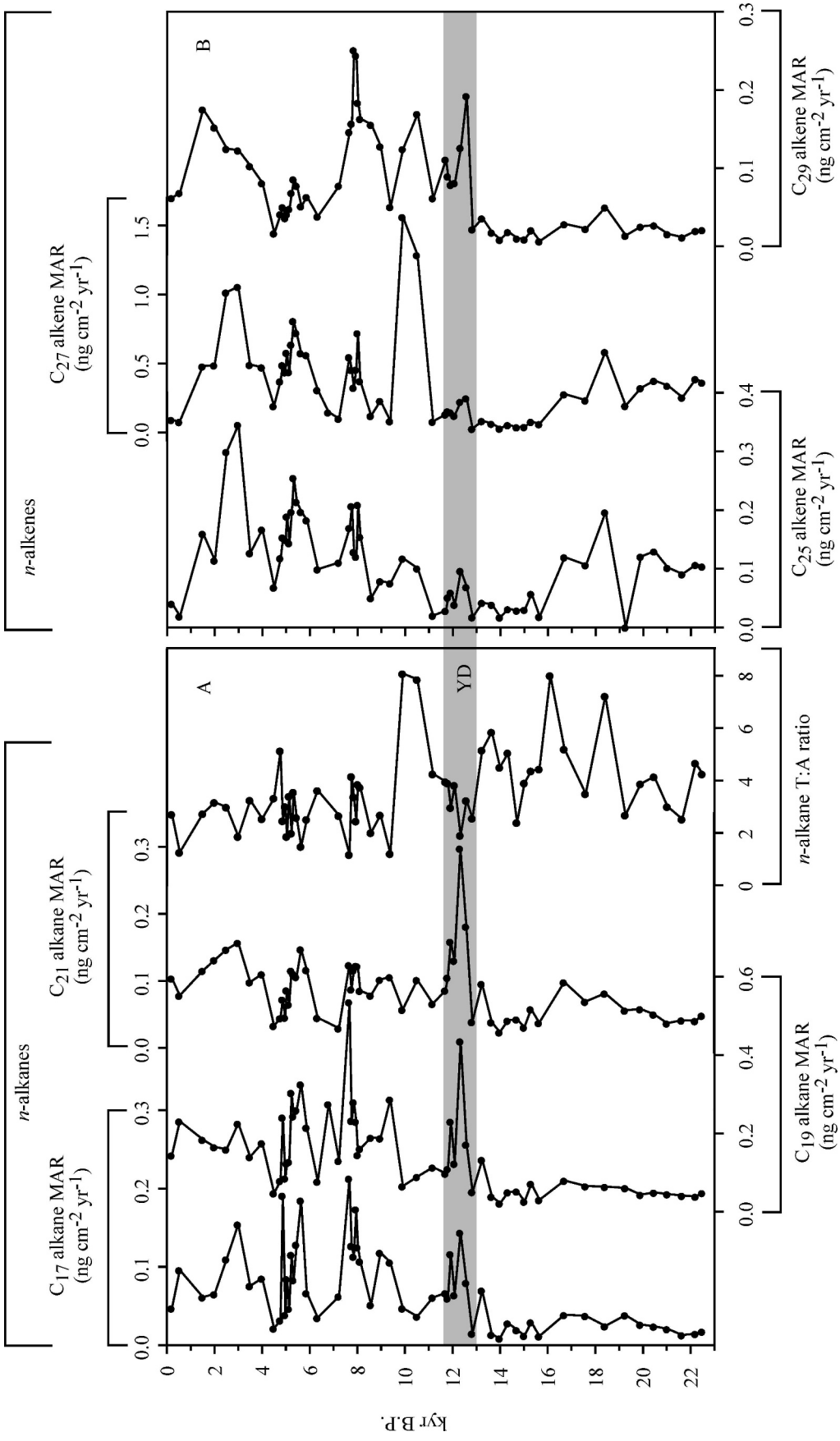


Fig. 4. Mass accumulation rates of general algal biomarkers. In all graphs, the interval of the Younger Dryas (YD) is highlighted. (A) Mass accumulation rates of the $C_{17}$, $C_{19}$, and $C_{21}$ *n*-alkanes and the terrestrial to aquatic (T : A) *n*-alkane ratio. The T : A ratio is a proxy for terrestrial vs. aquatic input (Bourbonniere and Meyers 1996), with higher values indicating greater terrestrial input. (B) Mass accumulation rates of the $C_{25}$, $C_{27}$, and $C_{29}$ *n*-alkenes.

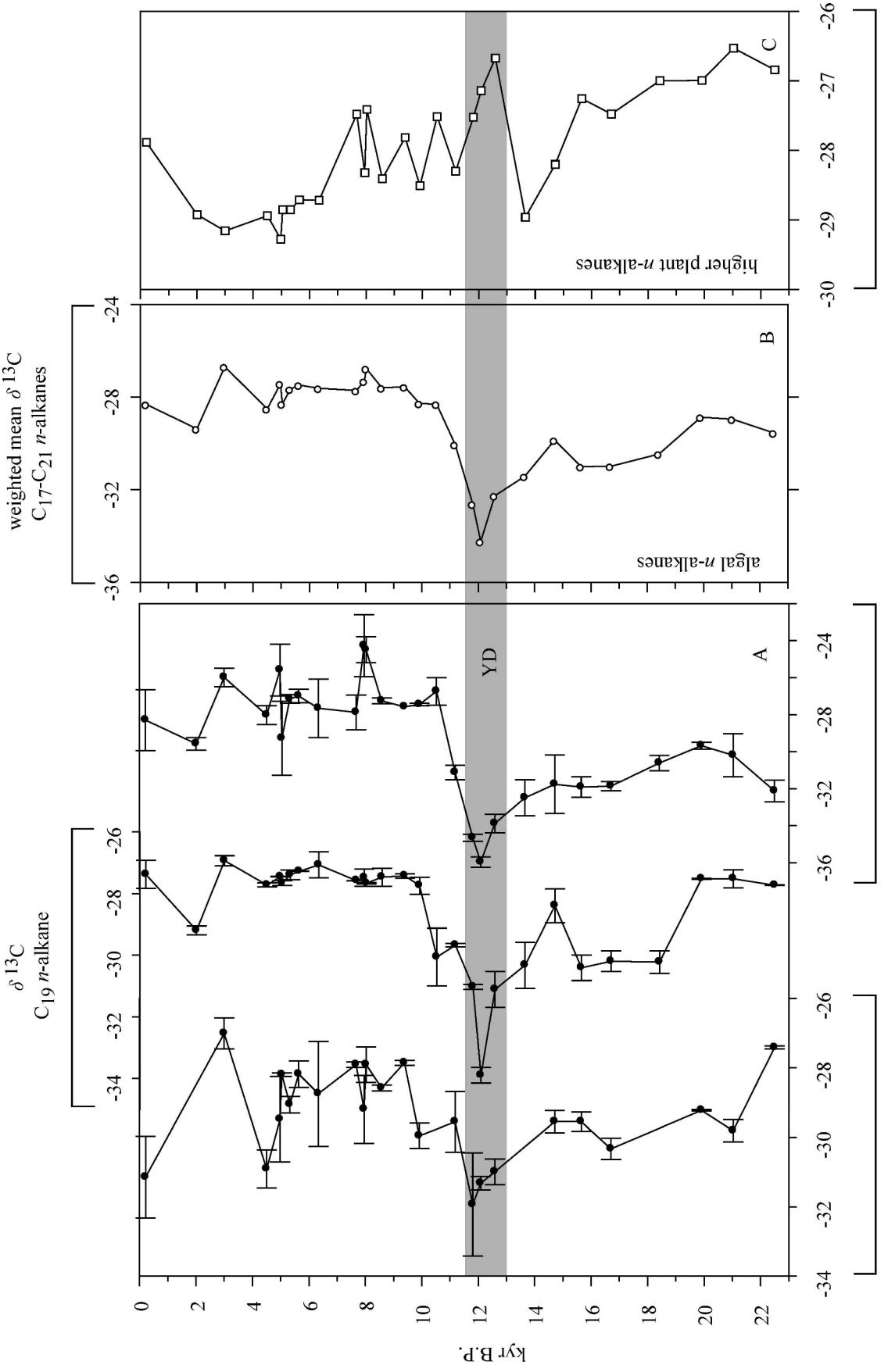


Fig. 5. Compound-specific carbon isotopes. The error bars represent the reproducibility of duplicate sample runs. In all graphs, the interval of the Younger Dryas (YD) is highlighted. (A) Carbon isotopic composition of the $C_{17}$, $C_{19}$, and $C_{21}$ *n*-alkanes. (B) The weighted mean carbon isotopic composition of the $C_{17}$, $C_{19}$, and $C_{21}$ *n*-alkanes. (C) The weighted mean carbon isotopic composition of the $C_{29}$, $C_{31}$, and $C_{33}$ *n*-alkanes, biomarkers of terrestrial plants (data from Castañeda et al. 2007).

algae in the lake. We note that abundances of the $C_{25}$ and $C_{27}$ *n*-alkenes track each other, whereas abundances of the $C_{29}$ *n*-alkene more closely track abundances of loliolide (Figs. 3, 4). This indicates that diatoms are the dominant source of the $C_{29}$ *n*-alkene in Lake Malawi, whereas the $C_{25}$ and $C_{27}$ *n*-alkenes may be dominantly derived from green algae.

MARs of the $C_{25}$ and $C_{27}$ *n*-alkenes indicate a general trend of decreasing abundance from the LGM until 16 kyr B.P. (Fig. 4). From 16 to 11 kyr B.P., the $C_{25}$ and $C_{27}$ *n*-alkenes exhibit the lowest abundances of the record, with a very slight increase in accumulation rates noted during the Younger Dryas. Throughout the Holocene, the $C_{25}$ and $C_{27}$ *n*-alkene accumulation rates are generally higher than in the Late Pleistocene, with peaks occurring at approximately 10, 8, 5.3, and 3 kyr B.P., followed by a general decline in abundances occurring over the past 3 kyr B.P. Like the $C_{25}$ and $C_{27}$ *n*-alkenes, the $C_{29}$ *n*-alkenes display low abundances from the LGM until 13 kyr B.P. and increased abundances during the Holocene. Peaks in the accumulation rate of the $C_{29}$ *n*-alkene are centered at 12.5 (the Younger Dryas), 10.5, 7.8, 5.3, and 1.5 kyr B.P.

Biomarkers of Cyanophyceae (cyanobacteria): Common cyanobacterial biomarkers such as the 7- and 8-methylheptadecanes (Gelpi et al. 1970) and the 2-methylhopanoids (Summons et al. 1999) are not present in Lake Malawi sediments. However, the glycolipid docosanyl 3-*O*-methylxylopyranoside is present (Fig. 3), which is believed to derive from a cyanobacterial source (Sinninghe Damsté et al. 2001). Docosanyl 3-*O*-methylxylopyranoside, hereafter referred to as methylxylopyranoside, was first recognized in sediments from Ace Lake (Antarctica), a saline lake that is permanently anoxic at depth (Sinninghe Damsté et al. 2001). To our knowledge, Lake Malawi is presently the only location besides Ace Lake from which methylxylopyranoside has been identified. Additionally, Lake Malawi presently represents the oldest samples from which methylxylopyranoside has been reported (up to 12.5 kyr B.P.). The presence of methylxylopyranoside in Lake Malawi indicates that the compound can be produced by freshwater organisms and thus is not derived solely from marine organisms, as has previously been suggested (Sinninghe Damsté et al. 2001).

In the Lake Malawi record, methylxylopyranoside is absent prior to ~12.5 kyr B.P. (Fig. 3). The compound first appears at this time, coinciding with the Younger Dryas interval, and is present in varying abundances throughout most of the Holocene. At ~11.8, 8, and 5.3 kyr B.P. methylxylopyranoside is present in maximum abundance (ignoring the peak at 10.5 kyr B.P. that is defined by only one data point).

Biomarkers of eustigmatophyte algae: Lake Malawi samples contain abundant long-chain 1,15-*n*-alkyl diols (Fig. 3). These compounds are recognized as biomarkers of the algal class Eustigmatophyceae (yellow–green algae) (Volkman et al. 1992; Versteegh et al. 1997). Relatively little is known about Eustigmatophyceae, which is a small class that presently contains only eight genera (Ott and Oldham-Ott 2003). Eustigmatophytes have one or two flagella, contain the pigments violaxanthin and vaucheriaxanthin, and lack chlorophyll *c* and fucoxanthin (the common pigment in diatoms and dinoflagellates) (Ott and Oldham-Ott 2003). Although Lake Malawi sediments contain abundant long-chain *n*-alkyl diols, it is interesting to note that eustigmatophyte algae have never been identified in algal or sediment samples from the lake (Hedy Kling pers. comm.). There are several possible explanations for the occurrence of these compounds in Lake Malawi sediments. First, it is possible that eustigmatophyte algae are present in Lake Malawi but have been overlooked in previous algal surveys. Most species of eustigmatophytes are very small (2–4 $\mu$m) and can be easily confused with coccoid forms of Chlorophyceae or Xanthophyceae (Gelin et al. 1999; Ott and Oldham-Ott 2003). In Lake Malawi the most abundant species of chlorophytes are small chlorococcales (Hecky et al. 1999), so it is possible that members of Eustigmatophyceae have been confused with members of Chlorophyceae. Second, the class eustigmatophyceae includes members that inhabit terrestrial soils (Ott and Oldham-Ott 2003); thus, it is possible that soil eustigmatophytes are the source of the long-chain *n*-alkyl diols in Lake Malawi sediments. However, as abundances of the long-chain *n*-alkyl diols closely track abundances of other aquatic biomarkers, such as the diatom biomarker loliolide, a solely terrestrial source of the long-chain *n*-alkyl diols to Lake Malawi sediments is unlikely. It is also possible that the long-chain *n*-alkyl diols are coming from another source besides eustigmatophyte algae. It has been noted that the $C_{32}$ *n*-alkyl diol is dominant in eustigmatophytes of the genus *Nannochloropsis* (Volkman et al. 1992), yet in marine sediments the dominant chain lengths are $C_{28}$ or $C_{30}$, indicating an additional source of these compounds. As eustigmatophyte algae are not abundant in seawater, it has been suggested that eustigmatophytes are probably not the dominant source of long-chain *n*-alkyl diols in marine environments (Gelin et al. 1999). However, in Lake Malawi samples, the $C_{32}$ *n*-alkyl diol is more abundant than either the $C_{28}$ or $C_{30}$ *n*-alkyl diols, which may point to the presence of eustigmatophytes in the lake. Furthermore, a study of the phytoplankton of nearby Lake Tanganyika, based on polymerase chain reaction–amplified 18S ribosomal DNA, provides evidence for the presence of eustigmatophytes possessing a sequence similar to marine and freshwater members of *Nannochloropsis* (De Wever 2006). At present, we are unable to resolve the issue of production of long-chain *n*-alkyl diols by another group or by eustigmatophytes in Lake Malawi having been mistaken for coccolid members of the chlorophytes. The close agreement between the *n*-alkyl diols and other algal biomarkers strongly indicates an aquatic source for these compounds, and, thus, the record of long-chain *n*-alkyl diols provides important paleoenvironmental information, although the exact biological source is presently unknown. The $C_{30}$ and $C_{32}$ 1,15-diols display similar trends, with abundances being low from 23 to ~13 kyr B.P. (Fig. 3). An initial increase in abundance is noted during the Younger Dryas, and values remain high, but variable, throughout the Holocene. In contrast, the $C_{34}$ 1,15-diol exhibits

elevated abundances in the Late Pleistocene and lower abundances in the Holocene, although in the Holocene, trends in accumulation rates are similar to the $C_{30}$ and $C_{32}$ 1,15-diols. This indicates that the $C_{34}$ 1,15-diol is produced by a different source than the $C_{30}$ and $C_{32}$ 1,15-diols.

*Algal history of Lake Malawi*—The long-term algal history of Lake Malawi has been previously examined by Johnson et al. (2002), Gasse et al. (2002), and Filippi and Talbot (2005). The Johnson et al. (2002) and Gasse et al. (2002) studies concentrated on the record of diatom productivity in Lake Malawi based on biogenic silica and diatom assemblage data, respectively. A more recent study by Filippi and Talbot (2005) combined bulk geochemical analyses, including %TOC, %biogenic silica, C : N ratios, bulk carbon and nitrogen isotopes, and Rock-Eval hydrogen index (HI) data, to examine changes in the type of organic matter preserved in Lake Malawi during the past 25 kyr B.P. HI is a measure of the amount of hydrocarbon-type compounds (mg hydrocarbons per gram of sediment) that is produced from the cracking of kerogen as a sample is heated to 600°C (Espitalié et al. 1977; Filippi and Talbot 2005). Changes in the HI, which reflect the hydrogen content of bulk organic matter, can be used to distinguish terrestrial and aquatic sources of organic matter, because aquatic material is rich in hydrogen compared to terrestrial material (Talbot and Livingstone 1989). HI is used to examine the kerogen (non–solvent extractable) fraction of organic matter, while in this study the bitumen (solvent-extractable) fraction of the organic matter is examined. Some of the results of our molecular study conflict with the HI index results of Filippi and Talbot (2005), and these differences will be presented following the discussion of results obtained in this study. We note that Filippi and Talbot (2005) examined three piston cores from the northern basin of Lake Malawi, including core M98-1P, the core examined in this study. The other two cores, M98-2P and M98-3P, were collected from slightly shallower water depths of 363 and 392 m, respectively. We also note that in this study we examine the TOC and biogenic silica records in terms of MARs to account for the effects of sediment dilution, whereas Filippi and Talbot (2005) examined these records in terms of weight percent. This causes the timing of peaks noted in the biogenic silica and TOC records to differ somewhat between the two studies.

The LGM (23–18 kyr B.P.): Nearly all algal biomarkers exhibit low abundances in the interval from the LGM until ~14 kyr B.P. (Figs. 3, 4). Aridity in southeastern Africa during the LGM has been well documented (Gasse 2000; Johnson et al. 2002; Castañeda et al. 2007), and although the magnitude of the lake-level change during the LGM has not been precisely quantified, it is now thought to have been on the order of 100 m (Scholz et al. 2007). A lake-level change of 100 m would bring the coring site of M98-1P, located at 403 m in depth, closer to the oxic zone and, with the colder temperature of the Late Pleistocene, perhaps into the oxic zone. Therefore, one possibility is that the generally low abundances of algal biomarkers observed prior to ~14 kyr B.P. result from the oxic degradation of the organic matter. However, several independent lines of evidence indicate that the coring site remained anoxic throughout the past 23 kyr B.P.

First, no inorganic carbon was detected in any of the samples examined from core M98-1P. In modern Lake Malawi, carbonates are not preserved in the sediments because the water column is undersaturated with respect to calcite below the upper few meters (Ricketts and Johnson 1996). If the coring site was located within the oxic zone during the LGM, then carbonate minerals may have been preserved. Second, a study of lignin phenols, compounds produced by higher plants, indicates that no major periods of oxic degradation have occurred in core M98-1P (Castañeda et al. 2009). The extent of oxygenic diagenetic alteration of lignin phenols can be examined from the ratios of vanillic acid to vanillin $(Ac : Al)_v$ and syringic acid to syringealdehyde $(Ac : Al)_s$ (Hedges et al. 1982; Ertel and Hedges 1985). In core M98-1P these ratios are relatively constant throughout the past 23 kyr B.P., with values falling within a range that indicates the lignin is well-preserved (Castañeda et al. 2009). Third, TOC MAR values are high, and some of the highest values of the entire record are reached at 18 kyr B.P. If oxic conditions were present, it might be expected that TOC MAR would be lower as a result of increased degradation of organic matter. Finally, the compounds loliolide and isololiolide are present throughout core M98-1P. When fucoxanthin, the major pigment in diatoms, undergoes anoxic degradation, loliolide or isololiolide is produced on a mole-to-mole basis (Repeta 1989). As loliolide and isololiolide are anoxic degradation products, the formation of these compounds from fucoxanthin during oxic conditions is very unlikely (Repeta 1989; Menzel et al. 2003). Thus, these independent lines of evidence do not provide support for the oxygenation of bottom waters at the coring site. However, we cannot rule out the possibility that the lake floor may have been periodically oxic, with the oxic–anoxic boundary at the sediment–water interface.

If the coring site indeed remained anoxic during the past 23 kyr B.P., then lower accumulation rates of algal biomarkers during the LGM (Figs. 3, 4) indicate reduced algal productivity in Lake Malawi. This idea is supported by both bulk and molecular geochemical records. Throughout this interval, $C_{org} : N_{tot}$ values indicate mixed terrestrial and aquatic inputs to sedimentary organic matter, but these values increase from 23 to 18 kyr B.P., indicating greater relative inputs of terrestrial organic matter (Fig. 2). Likewise, the terrestrial to aquatic ratio of *n*-alkanes (T : A ratio), which is another proxy for terrestrial vs. aquatic input (Bourbonniere and Meyers 1996), generally tracks changes noted in the $C_{org} : N_{tot}$ record and displays higher values during the Late Pleistocene than during the Holocene (Fig. 4). These two records indicate either increased delivery of terrestrial organic matter or decreased algal inputs to Lake Malawi at this time. During the LGM and throughout the Late Pleistocene, $\delta^{13}C_{algal}$ values are relatively depleted compared to Holocene values (Fig. 5), indicating lower rates of primary productivity in Lake Malawi. Furthermore, measurements of total phosphorus (TP) and inorganic phosphorus (IP) in nearby piston core

M98-2P indicate that MARs of TP and IP were significantly lower from ~23–13 kyr B.P. than during the Holocene (Johnson et al. 2002). Phosphorus is a limiting nutrient for algal growth, and, thus, low MARs of phosphorus prior to ~13 ka likely reflect low rates of algal productivity. Lower algal productivity in Lake Malawi is the simplest scenario to explain the observed trends in bulk geochemical and lipid biomarker records during the Late Pleistocene.

The Late Pleistocene (18–13 kyr B.P.): Following the LGM, most algal biomarkers either continue to exhibit consistently low accumulation rates (loliolide and *n*-alkanes) or display a general decrease in abundances (*n*-alkenes and *n*-alkyl diols) between 18 and 13 kyr B.P. (Figs. 3, 4). This period is also characterized by a decreasing trend in $\delta^{13}C_{TOC}$, which can be attributed to increasing abundances of $C_3$ vegetation in the Lake Malawi basin from 18 to13.6 kyr B.P. (Castañeda et al. 2009). Lignin phenol $\Lambda_8$ values (a measure of the total lignin phenol input) also display a generally increasing trend from the LGM to ~13 kyr B.P., indicating increasing terrestrial input throughout this interval (Castañeda et al. 2009). Thus, a likely explanation for the decrease in $\delta^{13}C_{TOC}$ is an increase in $C_3$ vegetation in the catchment, which was accompanied by elevated inputs of terrestrial organic matter to Lake Malawi. The switch from $C_4$ to $C_3$ vegetation is not surprising given that a rapid and major lake-level rise occurred from 15.7 to 15 kyr B.P. (Gasse et al. 2002), reflecting increased moisture availability in the southeastern African tropics at this time. Similarly, Filippi and Talbot (2005) suggest that drowning of lakeshore vegetation and soils can account for the trend in $\delta^{13}C_{TOC}$, as oxidation of terrestrial organic matter would lower the $^{13}C$ of dissolved inorganic carbon (DIC) and also increase $[CO_2]_{aq}$, which would lower algal $\delta^{13}C$. Given the strong evidence for both a major lake-level rise (Gasse et al. 2002) and an increase in $C_3$ vegetation throughout this interval (Castañeda et al. 2007), both processes likely contributed to the overall decreasing trends in the $\delta^{13}C_{TOC}$ and $\delta^{13}C_{algal}$ records.

From 18 to 13 kyr B.P., algal biomarkers generally display low but rising abundances (Figs. 3, 4). There is firm evidence for a major rise in lake level at 15.7 kyr B.P. (Gasse et al. 2002), and if the coring site had been oxygenated or periodically oxygenated at the LGM, rising lake levels would have led to the establishment of anoxic conditions, thereby enhancing preservation of sedimentary organic matter. However, the low abundances of algal biomarkers may be explained by increasing temperatures throughout this interval, which may have led to progressively stronger thermal stratification, possibly limiting upwelling and primary productivity. From 20 to 13 kyr B.P., temperatures in Lake Malawi steadily increased from ~24°C to 30°C (Powers et al. 2005). The general decline in TOC MAR values from 18 to ~13 kyr B.P. is consistent with increasing stratification due to increasing temperature. Algal biomarkers are low throughout this interval, with the *n*-alkyl diols, *n*-alkanes, and *n*-alkenes exhibiting the lowest abundances of the entire record from ~16 to 13 kyr B.P. (Figs. 3, 4).

The Younger Dryas (12.9–11.6 kyr B.P.): The onset of the Younger Dryas interval, at 12.9 kyr B.P., marks the start of a major increase in productivity in Lake Malawi. The Younger Dryas clearly stands out in mass accumulation records of biogenic silica and TOC (Fig. 2) and is also marked by high abundances of most algal biomarkers (Figs. 3, 4). During the Younger Dryas, increased northerly winds were present over Lake Malawi (Johnson et al. 2002; Talbot et al. 2007) and a 2°C drop in temperature occurred (Powers et al. 2005) (Fig. 2). At this time, diatom assemblages indicate increased diversity (Gasse et al. 2002), an abrupt shift to more arid conditions is noted by an increase in $C_4$ vegetation (Castañeda et al. 2007), and both $\delta^{13}C_{algal}$ and $\delta^{13}C_{TOC}$ values indicate a shift to more negative values. While cool and arid conditions are noted during the Younger Dryas, conditions were not as cool or as arid as they were during the LGM (Powers et al. 2005; Castañeda et al. 2007).

The high rates of primary productivity are not surprising given the fact that cooling (Powers et al. 2005) may have led to a less strongly stratified water column, in addition to the enhanced northerly winds that were present (Johnson et al. 2002). Both effects would facilitate upwelling in the northern basin of Lake Malawi and would lead to increased primary productivity, as is reflected in the biogenic silica, TOC, and biomarker records. The shift to more negative $\delta^{13}C_{algal}$ and $\delta^{13}C_{TOC}$ values is likely caused by increased amounts of isotopically depleted $CO_2$ being upwelled to the surface waters and made available for primary productivity. It should be noted that the Younger Dryas is the only interval of the past 23 kyr B.P. during which terrestrial plant leaf wax $\delta^{13}C$ does not track the $\delta^{13}C_{TOC}$ signal. At this time, an abrupt shift to increased amounts of $C_4$ vegetation occurred (Castañeda et al. 2007); however, it appears that the increase in primary productivity was of great enough magnitude to counteract any effects of an increase in surface water DIC values from increased inputs of $C_4$ vegetation.

Another notable feature of the Younger Dryas is that methylxylopyranoside (the cyanobacterial biomarker) makes its first appearance at this time and then remains present throughout the Holocene (Fig. 3). It is not clear why cyanobacteria first appear at this time, since in the modern lake cyanobacteria are dominant when the lake is stable and strongly stratified.

The Holocene: Following the Younger Dryas, an early-Holocene dry spell occurred in the Malawi basin (Castañeda et al. 2007) that may account for the observed low BSi MAR and TOC MAR and the low accumulation rates of the diatom biomarker loliolide (Figs. 2, 3). All of these records display low values from the end of the Younger Dryas (~11.9 kyr B.P.) until ~10 kyr B.P. The magnitude of this early-Holocene aridity is not precisely known, and the timing varies somewhat between the various records. However, numerous independent proxies all provide firm evidence for a significant fall in lake level in the early Holocene. For example, a lowstand is noted in seismic records (Johnson and Ng'ang'a 1990; Owen et al. 1990) and is dated to ~10.7 kyr B.P. (Owen et al. 1990). A study

(Brown et al. 2000) of redox metals from a sediment core collected from the central basin of Lake Malawi indicates that the water column was oxygenated at a site that is now at a depth of ~300 m. Diatom assemblage records indicate poor preservation and indicate that the lowstand was centered at 10.6 kyr B.P. (Gasse et al. 2002), while HI data indicate a shift from well-preserved to strongly oxidized organic matter occurring from 12 to 11.3 kyr B.P. (Filippi and Talbot 2005). Increased inputs of terrestrial organic matter are observed in smear slides (Filippi and Talbot 2005), and molecular analyses indicate increased abundances of terrestrial plant leaf waxes (long-chain *n*-alkanes) centered at ~10 kyr B.P. (Castañeda et al. 2009). Additionally, the terrestrial to aquatic ratio of *n*-alkanes indicates an abrupt increase in terrestrial inputs in the early Holocene (Fig. 4). Elevated, but fluctuating, inputs of $C_4$ vegetation are also noted from ~11.5 to 8 kyr B.P., attesting to the generally arid conditions throughout this interval (Castañeda et al. 2007). Cyanobacterial and eustigmatophyte biomarkers display major changes in abundance throughout this interval, indicating variable conditions.

From 10 kyr B.P. to the present, algal biomarkers display fluctuating abundances but are generally higher than during the Late Pleistocene (Figs. 3, 4). Several of the algal biomarkers, including methylxylopyranoside, loliolide, and the *n*-alkanes and the *n*-alkenes, exhibit peaks in abundance centered at 8 kyr B.P., whereas a period of low abundances of loliolide, *n*-alkyl diols, and methylxylopyranoside occurs at 4.9 kyr B.P. It appears that these high and low peaks in accumulation rates of algal biomarkers may be at least partly related to changes in thermal stratification. Holocene temperatures of Lake Malawi were highly variable, with temperatures of ~28°C noted from 11 to 9 kyr B.P.; a cooling of ~2°C occurs at ~8 kyr B.P. (perhaps coinciding with the 8.2 kyr B.P. cold event noted in the Northern Hemisphere [Thomas et al. 2007]), followed by a gradual warming until the warmest temperatures of the past 25 kyr B.P. (~32°C) are reached at 4.9 kyr B.P. (Powers et al. 2005). After this time a gradual cooling occurs, with temperatures reaching 27.7°C at 0.2 kyr B.P. (Powers et al. 2005). Thus, increased abundances in algal biomarkers at ~8 kyr B.P. may be attributed to the cooler surface-water temperatures, which could have reduced thermal stratification and facilitated wind-induced upwelling. The opposite situation may have occurred at 4.9 kyr B.P., when warmer surface-water temperatures could have increased thermal stratification, making it more difficult for upwelling to occur. Although temperatures began rising steadily at ~8 kyr B.P. (Powers et al. 2005), the response of algal biomarkers did not gradually decrease, and, instead, a sudden drop in algal biomarker abundances is noted at 4.9 kyr B.P. This might indicate that either a threshold was reached such that temperatures were warm enough to inhibit upwelling, or perhaps an interval of weaker winds combined with the more strongly stratified water column to impede upwelling and limit nutrient supply, thereby causing the abrupt decrease in primary productivity.

Increasing abundances of $C_3$ vegetation are noted from ~8 to 4.9 kyr B.P., attesting to the establishment of wetter conditions in southeast Africa, with the highest proportion of $C_3$ vegetation of the past 23 kyr B.P. noted at 4.9 kyr B.P. (Castañeda et al. 2007). An elevated influx of lignin phenol $\Lambda_8$ values also provides evidence for increased terrestrial input from runoff at ~5 kyr B.P. (Castañeda et al. 2009). With the exception of the abrupt event at 4.9 kyr B.P., accumulation rates of algal biomarkers and biogenic silica are higher than during the Late Pleistocene (Figs. 3, 4), indicating a generally more productive lake. In addition, $\delta^{13}C_{algal}$ values are higher during the Holocene than in the Late Pleistocene (Fig. 5), providing further support for increased productivity in Lake Malawi during this interval.

The later part of the Holocene, from 4.9 kyr B.P. to the present, is characterized by a decline in $C_3$ vegetation and an increase in $C_4$ vegetation, indicating increasing aridity in southeastern Africa (Castañeda et al. 2007). The vegetation shift is consistent with diatom assemblage records, which also indicate lower lake levels throughout this interval (Gasse et al. 2002). Accumulation rates of algal biomarkers fluctuate throughout this interval but fall within the range of abundances noted during the earlier part of the Holocene. As accumulation rates of algal biomarkers are generally similar throughout the entire Holocene, it appears that precipitation in the northern basin of Lake Malawi is not the main control on primary productivity.

Molecular biomarker vs. HI records: In contrast to the results of this study, which indicate generally low algal productivity from the LGM until the start of the Younger Dryas, the HI record provides a different picture of conditions in Lake Malawi. Filippi and Talbot (2005) find that higher HI values characterize the LGM, indicating that algal material comprised a greater portion of the organic matter. They suggest that Lake Malawi was a significantly smaller but productive lake at this time, with bottom waters that may have been periodically oxygenated. Elevated $\delta^{13}C_{TOC}$ values characterize this interval (Fig. 2), which Filippi and Talbot (2005) attribute to elevated primary productivity in the lake. However, a recent study of Lake Malawi indicates that changes in $C_3$ vs. $C_4$ vegetation are mainly responsible for driving changes in $\delta^{13}C_{TOC}$ values and that the elevated $\delta^{13}C_{TOC}$ values noted during the LGM can be attributed to increased inputs of $C_4$ vegetation (Castañeda et al. 2009). However, terrestrial control of the $\delta^{13}C_{TOC}$ signal does not rule out the possibility of increased algal productivity at the LGM. Although the molecular biomarker and HI data results appear to be distinctly different, it is feasible that the two records are both accurately reflecting conditions in Lake Malawi during the Late Pleistocene. One possibility is that a change in depositional or preservational conditions occurred and affected the abundances of lipid biomarkers. First, even if the coring site was not oxygenated during the LGM, the oxic–anoxic boundary certainly would have been located in closer proximity to the coring site. Thus, it is likely that some portion of the organic matter would have been transported from the oxygenated shallow areas of the lake, which may explain the generally low abundances of algal biomarkers. Second, loliolide and isololiolide are anoxic degradation products, but it may be possible that these compounds were not formed in the water column but

rather in the sediments after burial. Third, lower $\delta^{13}C_{algal}$ values noted during the LGM do not rule out the possibility of increased algal productivity in the lake. In anoxic systems, anaerobic respiration of organic matter produces $^{13}C$-depleted methane and respired $CO_2$ (Woltemate et al. 1984; Whiticar et al. 1986), which can be incorporated into surface waters during upwelling events and can produce algal biomass that is $^{13}C$-depleted during a time of enhanced productivity (Hollander and Smith 2001). If at least part of the lake was anoxic at depth, upwelling of $^{13}C$-depleted $CO_2$ could lead to $^{13}C$-depleted algal biomass.

A second possibility that may account for the differences between the lipid biomarker and HI records is that perhaps the types of algae that existed in Lake Malawi were rich in kerogen-type compounds but not in bitumen and thus would be apparent from HI data but not from analysis of solvent-extractable lipids. For example, algaenans are compounds derived from algal material that are insoluble in organic solvents and that are resistant to treatment with strong acids and bases. Members of Chlorophyceae, including *Chlorella*, *Oocystus*, *Pediastrum*, and *Closterium*, all of which are present in Lake Malawi (Cocquyt et al. 1993; Patterson and Kachinjika 1995), are known to contain algaenans (Blokker et al. 1998, 2006; Gelin et al. 1999). Eustigmatophytes of *Nannochloropsis* and the dinoflagellate *Gymnodinium catenatum* also contain algaenans, whereas diatoms lack these compounds (Gelin et al. 1999). Therefore, it is possible that a type of algae that produced algaenans was abundant in Lake Malawi at the LGM, which contributed to the HI signal but not to the lipid biomarker signal. Such compounds would also contribute to the TOC signal and may explain the high TOC MAR values in this interval. Although not a highly specific biomarker, the $C_{25}$ and $C_{27}$ *n*-alkenes, which are biomarkers of green algae, exhibit slightly elevated abundances at this time compared to other algal biomarkers (Fig. 4). A relative percent plot of diatom (loliolide), eustigmatophyte ($C_{32}$, 1,15 diol), green algae ($C_{27}$ *n*-alkene), and cyanobacteria (docosanyl 3-*O*-methylxylopyranoside) biomarkers also indicates that algal groups capable of producing algaenans comprised a greater portion of the algal taxa in Lake Malawi at the LGM and indicates increased abundances of green and eustigmatophyte algae (Fig. 6). Furthermore, the Younger Dryas does not appear as a major event in the HI record, although a fall in HI is observed, centered at 13 kyr B.P. (Filippi and Talbot 2005). Large increases in the MARs of biogenic silica and loliolide provide firm evidence for a major increase in diatom productivity at this time (Figs. 2, 3), which is not surprising, as diatoms dominate modern Lake Malawi when cool and windy conditions are present. The fact that the Younger Dryas does not appear as a major event in the HI record offers further support for the idea that HI data mainly reflect input from an algal group other than diatoms, which respond to a different set of environmental conditions. Given the multiple independent lines of evidence that indicate that the coring site remained anoxic during the LGM, a shift to an algal group rich in algaenan-type compounds is presently the preferred explanation to account for the differences noted in Lake Malawi

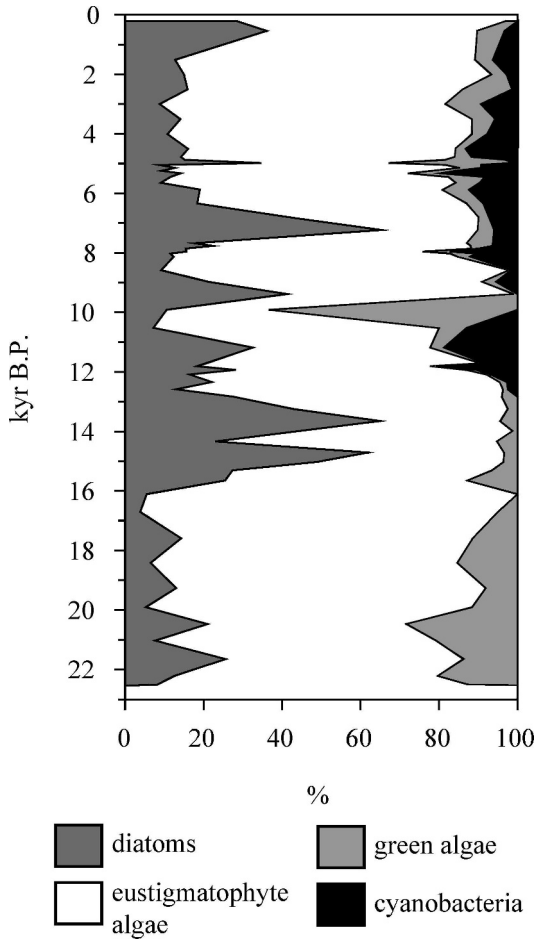


Fig. 6. Relative abundance plot of the main algal biomarkers in Lake Malawi samples. One compound was chosen as a representative of each group, and abundances were normalized to 100%. Loliolide is the compound used to represent diatom productivity (indicated by the dark gray shading on the left of the graph). The $C_{32}$ *n*-alkyl diol is used to represent inputs from eustigmatophyte algae (indicated in white), the $C_{27}$ *n*-alkene is used to represent inputs from green algae (indicated by the light gray shading), and docosanyl 3-*O*-methylxylopyranoside is used to represent inputs from cyanobacteria (indicated in black).

bitumen and kerogen records. However, the algaenan content of Lake Malawi organic matter must be examined in order to confirm this hypothesis.

In contrast to the Late Pleistocene, the molecular biomarker and HI records exhibit more coherence in the Holocene. In the interval of 10–4.5 kyr B.P., HI data indicate that organic matter was relatively poor in algal material and that hydrogen-poor organic matter, indicating elevated inputs of terrestrial organic matter from high rates of runoff, was abundant (Filippi and Talbot 2005). Like the HI data, the molecular data support elevated inputs of terrestrial organic matter to Lake Malawi from the early Holocene until ~4.9 kyr B.P. However, molecular records also indicate higher levels of algal productivity, compared to the Late Pleistocene. As there is strong evidence for high terrestrial inputs in this interval, it might be possible that dilution effects are responsible for the apparent low

abundances of algal material noted in the HI record. Similarly, in the later part of the Holocene, from 4.9 to 1.9 kyr B.P., the HI record indicates increased algal productivity, while molecular records indicate similar levels of productivity compared with the early Holocene. Again, dilution effects from increased inputs of terrestrial organic matter during the early–middle Holocene wet phase may be responsible for the apparent increase in algal material noted in the HI record during the late Holocene.

Late Pleistocene vs. Holocene conditions: Overall, when geochemical records from the Holocene and Late Pleistocene are compared, several differences are readily apparent. First, algal biomarkers and biogenic silica records indicate generally low abundances in the Late Pleistocene and high abundances in the Holocene. Second, $\delta^{13}C_{algal}$ algal values are more enriched in the Holocene compared to the Late Pleistocene. Third, HI values are lower in the Holocene than in the Late Pleistocene. Although the HI data may conflict with the lipid records, all three lines of evidence point to a major change in primary productivity occurring at the Pleistocene–Holocene boundary. There is evidence for a major change in the wind regime over Lake Malawi that occurred at ~11.8–11 kyr B.P. as the result of a shift in the mean latitudinal position of the ITCZ, with northerly winds being more prevalent before this time and less so after this time (Johnson et al. 2002; Filippi and Talbot 2005; Talbot et al. 2007). A switch in the mean latitudinal position of the ITCZ is also noted over Lake Masoko, a small crater lake located in the highlands at the northern end of Lake Malawi, at 11.7 kyr B.P. (Garcin et al. 2007). This switch in the dominant wind regime over the lake appears to have had a major influence on algal productivity in Lake Malawi.

The overall trends in the $\delta^{13}C_{algal}$ record (relatively depleted values from 23 to 13 kyr B.P., more depleted values during the Younger Dryas, and relatively enriched values in the Holocene) can be explained by a switch in the dominant wind regime. Prior to the Holocene, longer annual exposure to northerly winds likely would have increased upwelling in the northern basin of the lake, thereby supplying isotopically depleted $CO_2$ to the surface waters and resulting in isotopically depleted algal biomass. During the Younger Dryas, when winds intensified, an increased amount of isotopically depleted $CO_2$ was supplied to the surface waters, producing algae that were further depleted in $^{13}C$. In the Holocene, when winds switched to a more southerly dominated regime, upwelling and the supply of isotopically depleted bottom waters to the photic zone was reduced in the northern basin of Lake Malawi, resulting in increased competition for the available DIC and, thus, enriched $\delta^{13}C_{algal}$ values. Despite the more frequent or stronger northerly winds over the lake prior to ~11.8 kyr B.P., the relatively cool, arid conditions retarded nutrient input to the lake, resulting in generally lower abundances of algal biomarkers and biogenic silica throughout this interval. Although many questions remain regarding primary productivity prior to ~11.8 kyr B.P., it is clear that after this time, primary productivity in Lake Malawi operated in a mode similar to the way it does today. In the Holocene, the coolest (~8 kyr B.P.) and warmest (4.9 kyr B.P.) periods of the record (Fig. 2) are associated with relatively high and low abundances of algal biomarkers (Fig. 3), respectively, indicating that changes in thermal stratification can either facilitate or impede wind-induced upwelling and thus influence primary productivity on short-term time scales.

One of the major features of the algal biomarker records is the presence of the methylxylopyranoside in the Holocene (Fig. 3). Low $\delta^{15}N_{TOC}$ values characterize the interval from 10 to 4.5 kyr B.P., and it has been suggested that nitrogen-fixing cyanobacteria were more abundant at this time and, thus, that Lake Malawi was prone to prolonged periods of stable stratification (Filippi and Talbot 2005). The biomarker evidence presented here provides further support for the presence of nitrogen-fixing cyanobacteria in the Holocene. In modern Lake Malawi, diatoms dominate the algal taxa during the dry and windy season, whereas cyanobacteria dominate in November–December, at the onset of the calm and rainy season that follows the period of deep mixing and maximum diatom productivity (Hecky and Kling 1987; Hecky et al. 1999). Throughout the Holocene, wind-induced upwelling was important in Lake Malawi; however, the presence of methylxylopyranoside also indicates that the lake experienced calm seasons, when cyanobacteria were abundant. As the cyanobacterial glycolipid is absent prior to ~12.5 kyr B.P., we speculate that before this time Lake Malawi may not have experienced as distinct calm seasons as it has during the Holocene. The sedimentary record offers support to this idea, as sediments deposited prior to ~13 kyr B.P. lack varve couplets that are present throughout much of the Lake Malawi record (Barry et al. 2002; Filippi and Talbot 2005) and that reflect the distinct seasonal conditions of high diatom productivity in the windy season and high clastic input in the calm and wet season (Pilskaln and Johnson 1991). Although lower lake levels may account for the lack of varves at around the time of the LGM, high lake levels had been reached by 15 kyr B.P. (Gasse et al. 2002), and with the establishment of anoxic conditions (or more widespread anoxic conditions) in the lake, it is expected that varves would be preserved. The lack of varved sediments throughout this interval might be explained by reduced seasonality in East Africa during the Late Pleistocene.

This molecular and isotopic study has provided important information regarding the influence of climate change on primary productivity and algal community structure of Lake Malawi. The main conclusions are the following: (1) Results of this study provide additional support for a major change in wind regime that occurred at around ~11.8 kyr B.P. as a result of a change in the mean latitudinal position of the ITCZ (Johnson et al. 2002; Filippi and Talbot 2005; Talbot et al. 2007). Prior to this time it appears that stronger or more frequent northerly winds promoted more frequent upwelling in the northern basin of the lake, bringing isotopically depleted $CO_2$ to the surface waters and thereby producing algal biomass with relatively depleted $\delta^{13}C$ values. The degree of upwelling of hypolimnetic waters may be the main control on $\delta^{13}C_{algal}$ throughout the entire record, as has previously been

suggested (Filippi and Talbot 2005). A shift in the dominant algal taxa of Lake Malawi appears to have accompanied the shift in wind regime over the lake. Diatoms were present in low abundance during the Late Pleistocene, and at this time it is possible that green algae, rich in algaenan-type compounds, were the dominant algal group in the lake. At the start of the Holocene, diatoms and cyanobacteria become more abundant, indicating conditions similar to those observed in modern Lake Malawi. (2) Wind-induced upwelling appears to be a main control on algal productivity in the northern basin of Lake Malawi. However, the effects of thermal stratification are also apparent in lipid biomarker records. During the cool periods of the Younger Dryas and the early Holocene (cooling centered at ~8 kyr B.P.), thermal stratification was likely weakened, which may have facilitated wind-driven upwelling and nutrient supply to the surface waters, resulting in increased primary productivity. Productivity was especially high during the Younger Dryas, when both cooler temperatures and stronger northerly winds were present in Lake Malawi. Conversely, the opposite situation occurred at 4.9 kyr B.P., when maximum temperatures in Lake Malawi were reached. At this time, strong stratification, perhaps combined with weakened winds, likely either prevented or significantly reduced upwelling in the northern basin of Lake Malawi and caused an abrupt decline in algal productivity. This observation is significant, as it has been suggested that global warming will lead to decreased algal productivity in tropical lakes, as has already been observed in recent records from Lake Tanganyika (O'Reilly et al. 2003; Verburg et al. 2003). While significant changes in precipitation occurred during the Holocene, they do not appear to be a main control on algal productivity in Lake Malawi. (3) The occurrence of abundant long-chain 1,15–*n*-alkyl diols in Lake Malawi sediments indicates that eustigmatophyte algae are present in the lake. It is possible that this group has been mistaken for coccoid members of green algae in past algal surveys of Lake Malawi. (4) The occurrence of the glycolipid docosanyl 3-*O*-methylxylopyranoside in M98-1P indicates that nitrogen-fixing cyanobacteria were present in Lake Malawi throughout the Holocene but were absent in the Late Pleistocene prior to 12.5 kyr B.P. It is suggested that during much of the Late Pleistocene, Lake Malawi may have experienced less distinct calm seasons than during the Holocene.

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