Palaeogeography, Palaeoclimatology, Palaeoecology 303 (2011) 140–154

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Organic geochemical records from Lake Malawi (East Africa) of the last 700 years, part II: Biomarker evidence for recent changes in primary productivity

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ARTICLE INFO

Article history:
Received 17 March 2008
Received in revised form 5 November 2009
Accepted 2 January 2010
Available online 11 January 2010

Keywords:
Biomarker
Phytoplankton
Primary productivity
Lake Malawi
C_{25} *n*-alkanol

ABSTRACT

Relatively few well-dated and high-resolution paleoclimate records of the past few centuries presently exist from tropical East Africa. Here, we examine the bulk and molecular geochemical records of two varved sediment cores from Lake Malawi, which together provide a continuous record of environmental variability in East Africa of the last 730 years. We observe a number of changes in the aquatic ecosystem of Lake Malawi, which are likely attributed to both natural climatic forcing and anthropogenic activities. Biomarkers of dinoflagellates (dinosterol) and bacterivorous ciliates (tetrahymanol) display increased accumulation rates from ~1900 AD to the present, while a simultaneous decrease in accumulation rates of diatom biomarkers (isoloiliolide/loliolide) is observed. Increased accumulation rates of retene, a compound derived from conifers, are also noted since ~1930 AD and likely reflect increased soil erosion due to deforestation of the Lake Malawi watershed. Spectral analysis of the high-resolution TOC record indicates a periodicity of 204 years, similar to the 206 year cycle noted in ^{14}C and ^{10}Be records, suggesting a link between East African climate and solar forcing.

1. Introduction

Warming during the twentieth century has been observed in many of the lakes in the East African Rift Valley including Lakes Tanganyika (Verburg et al., 2003; O'Reilly et al., 2003), Victoria (Hecky et al., 1994), Albert (Lehman et al., 1998), and Malawi (Powers et al., 2011-this issue; Patterson and Kachinjika, 1995; Vollmer et al., 2005). At Lake Tanganyika, surface water temperature has increased by 0.9 °C since 1913 while deep-water temperature has increased by 0.31 °C (Verburg et al., 2003; O'Reilly et al., 2003). This strong warming of the surface waters relative to deep waters, possibly in combination with reduced wind speeds over Lake Tanganyika (O'Reilly et al., 2003), is thought to have increased density stratification resulting in decreased nutrient exchange between the deep and surface waters, and thus, decreased primary productivity (Verburg et al., 2003; O'Reilly et al., 2003). In Lake Malawi, a similar increase in surface water temperatures is noted during the twentieth century (Powers et al., 2011-this issue). However, in contrast to Lake Tanganyika, a strong deep-water warming of 0.7 °C is observed in Lake Malawi from ~1940 to 2000 AD (Vollmer et al., 2005). It is suggested that this deep-water warming of Lake Malawi, which is attributed to warmer winters reducing the amount of cold water intrusions to the deep waters of the lake, may have decreased the density stratification of the lake (Vollmer et al., 2005).

In addition to temperature changes that have occurred during the twentieth century, the East African Rift lakes have concurrently experienced the effects of anthropogenic activities such as land use change due to rapidly growing human populations in their watersheds. At Lake Malawi, deforestation is one of the most noticeable changes. Calder et al. (1995) report that forest cover in Malawi declined by 13% between 1967 and 1990, equivalent to a rate of 1.8% per year, which is also the deforestation rate reported in a study of the Mwanza district of southern Malawi (Hudak and Wessman, 2000). The demand for wood is high, and exceeds supply in southern and central Malawi because a great majority of the population relies on wood as a fuel source for cooking (Hudak and Wessman, 2000). The northern end of Lake Malawi is less densely populated than the southern end and contains a higher proportion of forested land, which is increasingly being converted to agriculture (Hecky et al., 2003). In areas where watersheds have been significantly disturbed by agricultural activities, it is estimated that nutrient loading to the lake has increased by as much as 50%, in comparison to regions with forested watersheds (Hecky et al., 2003). Elevated nutrient supply has produced blooms of the cyanobacteria *Anabaena* in some areas of Lake Malawi (Hecky et al., 1999), and a number of other recent shifts in algal taxa have also

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doi:10.1016/j.palaeo.2010.01.006

been noted. These include filamentous chlorophytes of the *Mougeotia*/*Oedogonium* complex, which have appeared in Lake Malawi since the 1960s, and at the south end of the lake diatoms indicative of higher nutrient availability and poorer light conditions have become dominant (Hecky et al., 1999).

Quantitative algal sampling in Lake Malawi is limited to the period since 1987, while qualitative studies extend back to the turn of the century (Hecky et al., 1999). Here, we utilize molecular and isotopic techniques in an attempt to extend the existing records of changes in the algal community structure of Lake Malawi further back in time and examine primary productivity during the past 730 years. The East African Rift Lakes are an important source of food and water to the large human populations occupying the East African Rift Valley, and therefore, it is of interest to gain a better understanding of the environmental factors influencing primary productivity in these large lakes.

2. Background

2.1. Study location

Lake Malawi (9°S to 14°S) is situated between the countries of Malawi, Mozambique, and Tanzania, and is 560 km long and up to 75 km wide (Eccles, 1974) (Fig. 1). Lake Malawi has a maximum depth of about 700 m (Johnson and Davis, 1989), is permanently anoxic below 200–250 m (Patterson and Kachinjika, 1995), and is characterized by high sedimentation rates of 0.5–1.5 mm/yr (Finney et al., 1996). Lake Malawi is an excellent site for paleoenvironmental reconstructions as the lake contains both continuous and high-resolution sedimentary record. In addition, Lake Malawi experiences its majority of water loss by evaporation rather than outflow making it extremely sensitive to minor changes in aridity (Spigel and Coulter, 1996). Moreover, Lake Malawi is situated in a climatically sensitive geographical location 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 experiences one rainy season per year from November to March (Nicholson, 1996; Leroux, 2001). During the rainy season, the dominant winds are weak and northerly. Between April and May the ITCZ moves northward towards 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). The combination of generally weak winds and increased runoff during the rainy season results in high allochthonous sedimentary contributions. This 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 East African Rift lakes are dominated by a few but widespread taxa (Patterson and Kachinjika, 1995) and thus provide an excellent location to examine past changes in algal productivity and community structure. Primary productivity in Lake Malawi is presently dominated by diatoms (Bacillariophyta), followed by contributions from cyanobacteria (Cyanophyta) and green algae (Chlorophyta), with minor contributions from dinoflagellates (Pyrrophyta) (Patterson and Kachinjika, 1995). From October to March, the rainy season in Malawi, cyanobacteria and green algae are the dominant phytoplankton (Hecky and Kling, 1987). Diatoms dominate the rest of the year, when cool and windy conditions are present (Hecky and Kling, 1987). Phytoplankton composition and succession in Lake Malawi are mainly dependent on the strength of density stratification (Hecky and Kling, 1987), which is affected by water column gradients of temperature and dissolved solids (Wuest et al., 1996).

Density stratification is important to algal productivity in tropical lakes because strong stratification can inhibit wind induced upwelling and the delivery of nutrients to the photic zone. Lake Malawi is permanently stratified below 200–250 m. Stratification in the photic zone is most intense during the warm and wet season (November to April) when temperature differences between the surface and mid-depth waters are the greatest. Dissolved solids help to maintain stratification in the deep waters during the dry and windy season, when temperature gradients between the surface and bottom waters are reduced (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).

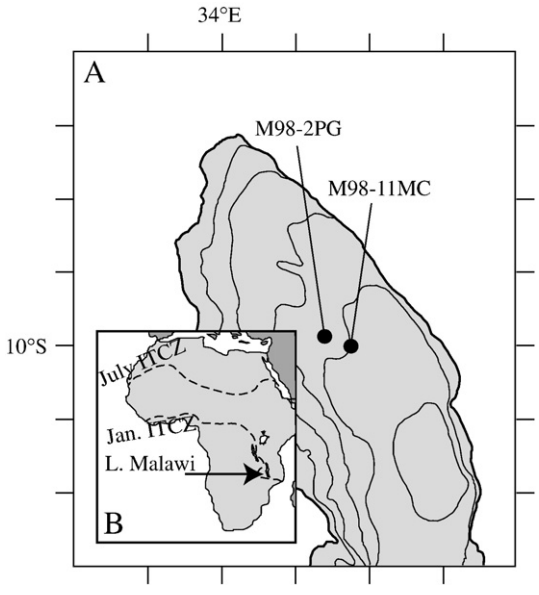

Fig. 1. Study location. A) The location of coring sites M98-11MC and M98-2PG in the northern basin of Lake Malawi. B) The location of Lake Malawi in East Africa. The July and January positions of the Intertropical Convergence Zone (ITCZ) are illustrated based on Leroux (2001).

2.2. Biomarkers of phytoplankton

The *n*-alkanes are straight-chained hydrocarbons that exhibit strong odd carbon-number predominance in living organisms and are a major component of the epicuticular waxes of terrestrial plant leaves (Eglinton and Hamilton, 1967). Although *n*-alkanes are produced by many organisms, carbon-number distributions and isotopic compositions vary depending on the source organism. Terrestrial plants are dominated by the long-chain (C_{25}–C_{33}) *n*-alkanes while aquatic algae are dominated by the short-chain *n*-alkanes (C_{17}–C_{21}) (Giger et al., 1980; Cranwell et al., 1987). In addition to the short-chain *n*-alkanes, a variety of other compound classes provide more specific 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, but brassicasterol (24-methylcholesta-5,22-dien-3β-ol), fucosterol (24-methylcholesta-5,24(28)-dien-3β-ol), and β-sitosterol (24-ethylcholesta-5-en-3β-ol) are common lipids of diatoms (Barrett et al., 1995; Volkman et al., 1998). The compound dinosterol (4α,23,24-trimethyl-5α-cholest-22-en-3β-ol) is found in many dinoflagellate species (Withers, 1983; Pirretti et al., 1997) and is commonly used as a biomarker for these organisms (Boon et al., 1979; Robinson et al., 1984; 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 the botryococcenes, which are produced by the green algae *Botryococcus braunii* (Maxwell et al., 1968; Volkman et al., 1998), as well as the C_{25} and C_{27} *n*-alkenes and lycopadiene (Volkman et al., 1998; Adam et al., 2006). 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). Additionally, new cyanobacterial biomarkers recently have been suggested from two glycolipids, docosanyl 3-*O*-methyl-α-rhamnopyranoside and docosanyl 3-*O*-methylxylopyranoside (Sinninghe Damsté et al., 2001).

3. Methods

3.1. Chronology

Multicore M98-11MC (10°0.2′S, 34°17.3′E) and gravity trigger core M98-2PG (9°58.6′S, 34°13.8′E) were collected from 403 and 363 m water depths, respectively, in 1998 by an expedition of the International Decade for East African Lakes (IDEAL) (Fig. 1). The chronology of both cores has been previously published, and is based on varve counting and ^{210}Pb dating (Johnson et al., 2001). Both cores consist entirely of varved sediments and possess several distinctive marker beds, including tephras and homogenites, which can be correlated between the two cores. Core M98-11MC contains a record spanning from 1998 to 1646 AD while core M98-2PG contains a record spanning from 1908 to 1270 AD. When plotted on their individual timescales, bulk geochemical records from cores M98-11MC and M98-2PG agree closely with each other (Fig. 2), attesting to the strength of the chronologies. As a high degree of correlation exists between the geochemical records of these two cores, we treat them as one continuous record spanning the past ~730 years. It is estimated that the uncertainty in absolute ages is ± 7% of the stated age (Johnson and McCave, 2008).

3.2. TOC and bulk $\delta^{13}C$

Total inorganic carbon (TIC) and total carbon (TC) measurements were determined on a UIC CO_2 Coulometer. TIC was not present in any of the samples analyzed from either core M98-11MC or M98-2PG and therefore TC is total organic carbon (TOC). For bulk carbon isotopes ($\delta^{13}C_{TOC}$), freeze dried sediment samples were treated with excess 0.1 N hydrochloric acid for 3 h. After acidification, sediment samples were filtered through organic-free Whatman GF/F glass fiber filters (0.7 μm nominal pore size) and rinsed 4× with excess distilled and deionized water (Millipore filtration system). Sediment samples were then dried in an oven at 35 °C and stored in a desiccator until they could be packed into tin capsules for isotopic analysis. Bulk organic carbon isotope ($\delta^{13}C_{TOC}$) samples from core M98-11MC were analyzed at the College of Marine Science at the University of South Florida on a Thermo-Finnigan Delta-Plus XL mass spectrometer coupled to a Carlo-Erba NA2500 Elemental Analyzer. For core M98-2PG, $\delta^{13}C_{TOC}$ samples were measured at the Stable Isotope Laboratory at the University of Saskatchewan using a Thermo-Finnigan Flash 1112 EA coupled to a Thermo-Finnigan Delta-Plus XL mass spectrometer. To ensure consistency, four duplicate samples from M98-11MC were also run at the University of Saskatchewan. The $\delta^{13}C_{TOC}$ values of these replicate samples agree closely with the values obtained from the University of South Florida, and standard deviations are better than ± 0.1‰.

3.3. Molecular biomarkers

A total of 27 biomarker samples were analyzed; seventeen from core M98-11MCB, representing the record from 1646 AD to 1986, and ten from core M98-2PG, representing the record from 1270–1669 AD. Freeze dried sediment samples were Soxhlet extracted with 2:1 methylene chloride:methanol for 24 h to obtain a total lipid extract (TLE). Compounds in the total lipid extract were further separated

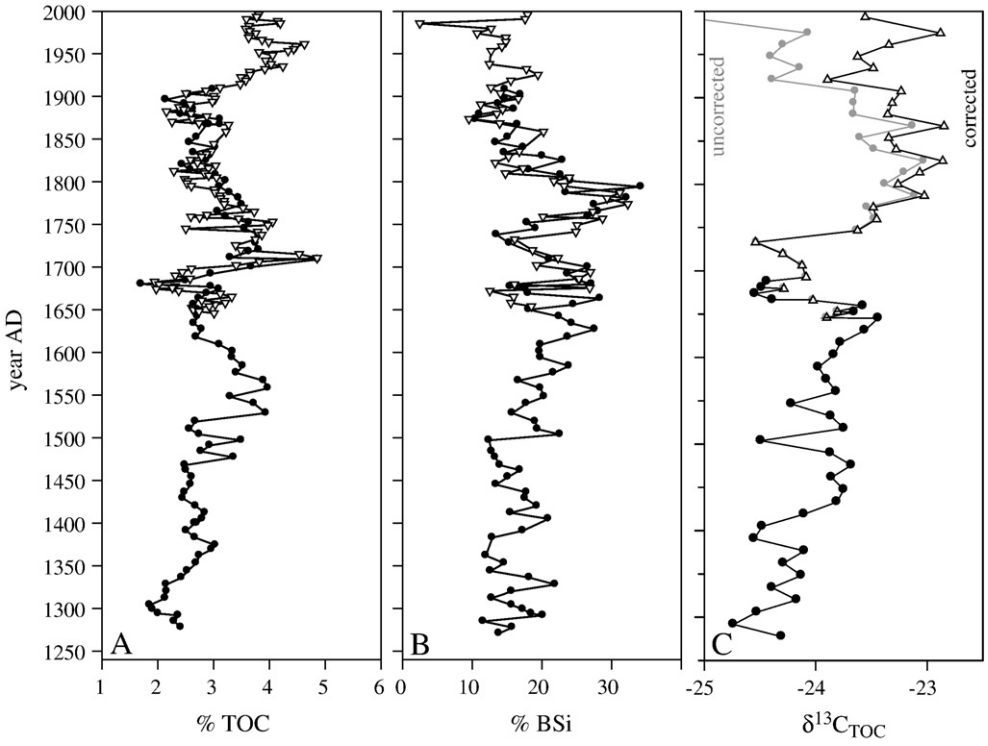

Fig. 2. Bulk geochemical data from cores M98-11MC and M98-2PG. In all graphs, data points from M98-11MC are represented by the open triangles while data points from M98-2PG are represented by the solid circles. A) Percent total organic carbon (TOC). B) Percent biogenic silica (BSi). Data from Johnson et al. (2001). C) Bulk carbon isotope ($\delta^{13}C_{TOC}$) data. Samples younger than 1700 AD were corrected for the Suess effect using the equation provided by Verburg (2007). The uncorrected $\delta^{13}C_{TOC}$ values, indicated by the grey data points, are shown for comparison.

into several compound classes using the methods described in detail by Castañeda et al. (2009a), which include passing the sample through an Aminopropylsilyl bond elute column and silica gel column chromatography. Polar fractions were derivitized with 100 μL of bistrimethylsilyltrifluoroacetamide (BSTFA) and 100 μL of acetonitrile for 2 h at 60–70 °C to convert compounds into trimethylsilyl-ethers. A blank sample was extracted with every batch of samples and was processed in the same manner as the sediment samples to ensure that no contamination was introduced to the samples during any of the steps.

3.4. Biomarker identification and quantification

Molecular identification of compounds was performed on a Hewlett-Packard 6890 gas chromatograph (GC) coupled to an HP 5973 mass spectrometer (MS). An HP-1 capillary column (25 m × 0.32 mm × 0.5 μm) was used with 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 next at a rate of 4 °C min^{-1} 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. Compounds were identified by interpretation of characteristic mass spectral fragmentation patterns, gas chromatographic relative retention times, and by comparison with literature.

Quantification of compounds was performed on a Hewlett-Packard HP 6890 gas chromatograph (GC) with a FID detector using 5α-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 except for that He flow rates were set at 2.6 mL min^{-1}.

Mass accumulation rates (MAR) of individual compounds were calculated from the following formula:

$$MAR_{compound} = LSR*DBD*C$$

where $MAR_{compound}$ is the MAR in ng cm^{-2} yr^{-1}, LSR = linear sedimentation rate (cm yr^{-1}), DBD = dry bulk density (g cm^{-3}), and C = the mass of compound (ng g^{-1}) in dry sediment.

3.5. Compound-specific carbon isotopes

Twelve 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 gas-chromatography isotope–ratio mass spectrometry (GC–IRMS). An HP 6890 GC (DB-1 column: 60 m, 0.32 mm internal diameter, 0.1 μm 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. For calibration, six pulses of reference CO_2 gas with a known $\delta^{13}C$ value were injected to the IRMS. A standard mixture consisting of 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 better than ±0.28‰. Each *n*-alkane sample was run in duplicate and the reproducibility is better than 0.4‰ for the long-chain (C_{29}–C_{33}) *n*-alkanes (Castañeda, 2007). The reproducibility is poorer for the short-chain *n*-alkanes (C_{17}–C_{21}) due to low concentrations of these compounds in Lake Malawi sediments and is better than 0.6‰ and 1‰ for the C_{19} and C_{21} *n*-alkanes, respectively. In most samples the C_{17} *n*-alkane was not present in enough abundance to obtain an isotopic measurement. All $\delta^{13}C$ values are reported relative to the Vienna Pee Dee Belemnite (vPDB) standard using standard delta (per mil) notation.

3.6. Correction for the Suess effect

To account for the change in the $\delta^{13}C$ of atmospheric CO_2 from anthropogenic fossil fuel burning (the Suess effect), it is necessary to correct bulk carbon and *n*-alkane $\delta^{13}C$ values in the recent part of the Lake Malawi record. We corrected the Lake Malawi $\delta^{13}C$ records using both the equations of Schelske and Hodell (1995) and Verburg (2007) and found that both methods produced nearly identical results. Here, we choose to apply the Verburg (2007) equation as it covers a slightly longer time period (2000 back to 1700 AD) than does the Schelske and Hodell (1995) method, which can be applied back to 1840 AD.

4. Results and discussion

4.1. TOC and solar forcing

Total organic carbon (TOC) is a proxy for the amount of organic matter contained in sediments. Although TOC is often used as a proxy for primary productivity in lacustrine sediments, it is important to note that lakes contain TOC from multiple sources (aquatic, bacterial and terrestrial) and TOC concentrations reflect both the initial production of biomass as well as subsequent degradation (Meyers, 2003). TOC values range from 1.95 to 4.86% in core M98-11MC and from 1.70 to 4.87% in core M98-2PG (Fig. 2). The lowest TOC values are noted at 1675 AD in both cores while the highest values occur at ~1700 AD.

In cores M98-11MC and M98-2PG, samples for TOC were taken at 0.5 cm resolution and therefore the TOC record is the highest-resolution dataset of the present study. For this reason, we performed spectral analysis on the TOC record to examine the possible influence of solar forcing on the Lake Malawi record since several recent studies of East African lakes have suggested links between climate variability and solar forcing (Verschuren et al., 2000; Stager et al., 2005; Cohen et al., 2006; Garcin et al., 2007). Indeed, spectral analysis of the TOC record revealed a strong signal with a period of 204 years (Fig. 3A), similar to the 206 year cycle noted in ^{14}C and ^{10}Be records, which is thought to reflect solar forcing or a combination of solar forcing and oceanic response (Raisbeck et al., 1990; Stuiver and Braziunas, 1993; Bard and Frank, 2006). Furthermore, when the Lake Malawi TOC record is plotted as deviation from a linear fit, the record exhibits some coherence with atmospheric ^{14}C production and displays generally positive values during the Spörer and Maunder minima (Fig. 3B). Thus, it appears that a link may also exist between solar forcing and environmental variability at Lake Malawi.

During periods of low sunspot activity, including the Dalton (~1790–1820 AD), Maunder (1645–1715 AD), Spörer (~1420–1570 AD), and Wolf (~1280–1340 AD) minima, changes in lake level (precipitation) have been noted throughout East Africa, although the response is inconsistent (Fig. 3). At Lake Naivasha, solar minima correspond with precipitation maxima (Verschuren et al., 2000). At Lake Tanganyika links between solar minima and laminae thickness are noted, reflecting changes in primary productivity (Cohen et al., 2006). However, at Lakes Tanganyika (Cohen et al., 2006) and Masoko (Garcin et al., 2007) the trend is opposite to that observed at Lake Naivasha with drier conditions noted during solar minima. Ties between lake level and solar forcing have also been noted at Lake Victoria (Fig. 3) but the response varies. Lake Victoria rose during the Wolf, Spörer and Maunder sunspot minima but the relationship changed sign ~200 years ago and drought is noted during the Dalton minimum (Stager et al., 2005). In contrast, at Lake Edward no correlations between geochemical records and solar forcing are observed (Russell and Johnson, 2005). At Lake Malawi, it is not apparent if changes in lake level occurred during periods of low

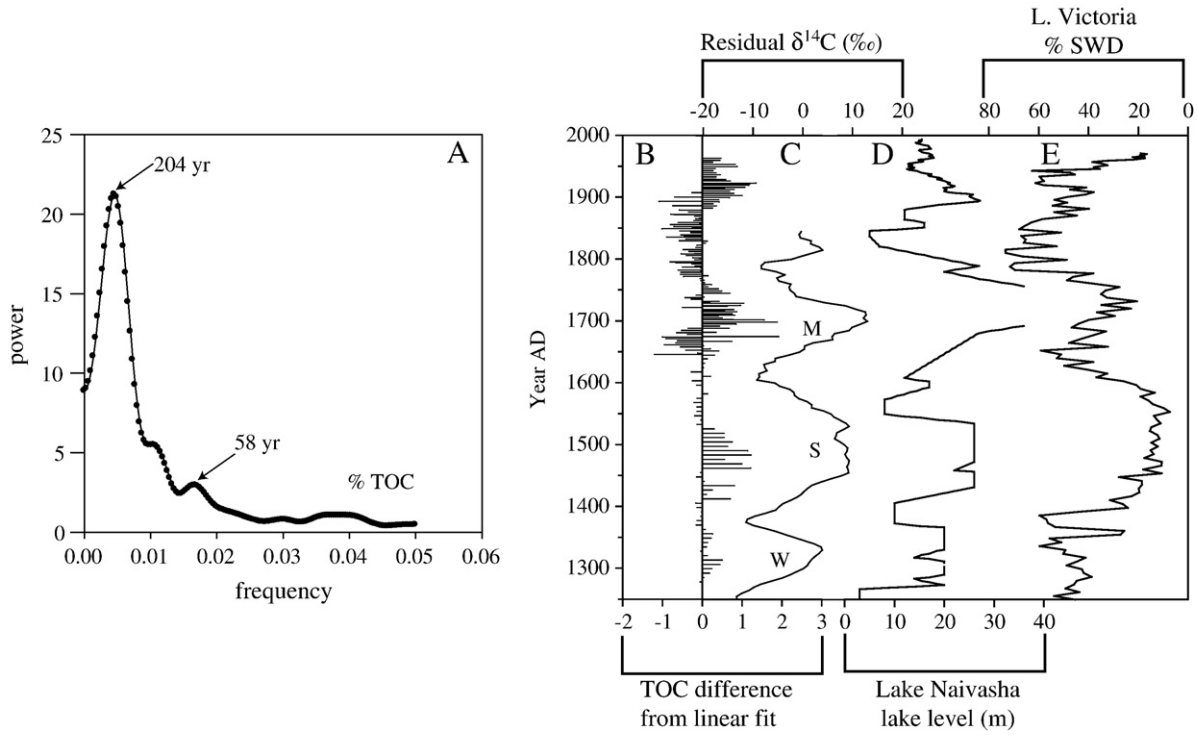

Fig. 3. A) Power spectrum of the percent TOC record of cores M98-11MC and M98-2PG. The program Analyseries (Paillard et al., 1996) was used to calculate the power spectrum by interpolating the signal at constant time and depth increments and linear detrending. Estimates were made at the 90% confidence interval using a Bartlett window, 1/3 lag, and no prewhitening constant was applied. Significant peaks are noted at 204 and 58 years. B) The Lake Malawi TOC record plotted as the deviation from a linear fit compared to the atmospheric ^{14}C residual series (Stuiver et al., 1998), which is shown in C. The Wolf (W), Spörer (S) and Maunder (M) minima are indicated. D) Lake level data from Lake Naivasha in Kenya (Verschuren et al., 2000). E) Percent shallow water diatom (SWD) data for Lake Victoria (Stager et al., 2005).

sunspot activity because no clear relationship is observed between our TOC data and historic lake level data, which extends back to 1930 AD (Vollmer et al., 2005). Many outstanding questions exist regarding the physical mechanisms through which solar forcing influences tropical climate; however, the number of records suggesting ties between solar forcing and climate variability in East Africa is substantial (Verschuren et al., 2000; Cohen et al., 2006; Stager et al., 2005; Garcin et al., 2007). In East Africa, the highly variable response, or lack of response, to solar forcing suggests that other climate parameters, including variability in the positions of the ITCZ and Congo Air Boundary (Nicholson, 1996), may locally enhance, diminish, or override the response to solar forcing.

4.2. Bulk and n-alkane $\delta^{13}C$

The carbon isotopic composition of bulk organic matter ($\delta^{13}C_{TOC}$) is widely used as a proxy for aquatic productivity in lakes, with enriched $\delta^{13}C_{TOC}$ values generally indicating increased productivity and vice versa (e.g. Hollander and McKenzie, 1991). However, in anoxic systems, such as Lake Malawi, 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 produce algal biomass that is ^{13}C-depleted during a time of enhanced productivity (Hollander and Smith, 2001). Furthermore, $\delta^{13}C_{TOC}$ can also be influenced by terrestrial inputs. Plants utilizing the C_4 photosynthetic pathway are ^{13}C enriched in comparison to plants utilizing the C_3 photosynthetic pathway (O'Leary, 1981) and therefore, in lakes that receive significant terrestrial inputs the $\delta^{13}C_{TOC}$ record may mainly reflect vegetation changes in the watershed. Previous studies of Lake Malawi have provided evidence for both the upwelling of isotopically light CO_2 into surface waters (Castañeda et al., 2009b) as well as for a mainly terrestrial control of the bulk ^{13}C signal (Castañeda et al., 2009a). Thus, the $\delta^{13}C_{TOC}$ record of cores M98-11MC and M98-2PG likely does not solely reflect changes in primary productivity.

The bulk carbon isotope ($\delta^{13}C_{TOC}$) record of cores M98-11MC and M98-2PG, corrected for the Suess effect, displays an overall change of 1.8‰ and ranges from a low value of −24.7‰ in 1292 AD to a high value of −22.9‰ in 1867 AD (Fig. 2). From ~1275 AD until ~1650 AD, the $\delta^{13}C_{TOC}$ record indicates an overall trend to heavier values. Between ~1650 and 1730 AD an excursion to lighter $\delta^{13}C_{TOC}$ values is noted, while the heaviest values of the record occur between 1750 AD and the present (Fig. 2).

To shed light on the origin of variability noted in the $\delta^{13}C_{TOC}$ record, the carbon isotopic composition of the short-chain (C_{19} and C_{21}) *n*-alkanes was determined. The Suess-corrected carbon isotopic values of the C_{19} *n*-alkane (the most abundant of the short-chain *n*-alkanes) exhibit a relatively small range and vary from −26.6 to −28‰ (Fig. 4). The weighted mean $\delta^{13}C$ of the C_{19} and C_{21} *n*-alkanes (C_{17} *n*-alkanes were not abundant enough to measure in most samples), hereafter referred to as $\delta^{13}C_{algal}$, displays relatively constant values of around −27.5‰ from ~1350 until ~1800 AD, with a spike to more ^{13}C-enriched values of −26.3‰ noted at ~1690 AD (Fig. 4). The lowest $\delta^{13}C_{algal}$ value of −28.1‰ is noted at 1861 AD, followed by a general trend toward more ^{13}C-enriched values from 1861 AD to 1941 AD. In piston core M98-1P, average Holocene $\delta^{13}C_{algal}$ values are −27.8‰, and range from −26.7‰ to −29.4‰, similar to the trends observed during the past 730 years (Castañeda et al., 2009b). We note that our $\delta^{13}C_{algal}$ record ends at ~1970 AD and thus may be insufficient for capturing the most recent changes in the primary productivity of Lake Malawi. Given the similarities noted between accumulation rates of short and long-chain *n*-alkanes (Fig. 5), the short-chain *n*-alkanes also may not reflect a purely algal signal. Furthermore, we note that there are relatively large errors associated with the $\delta^{13}C_{algal}$ measurements due to low concentrations of the short-chain *n*-alkanes. For this reason, we do not further discuss the $\delta^{13}C_{algal}$ record in the following sections of this manuscript. It would

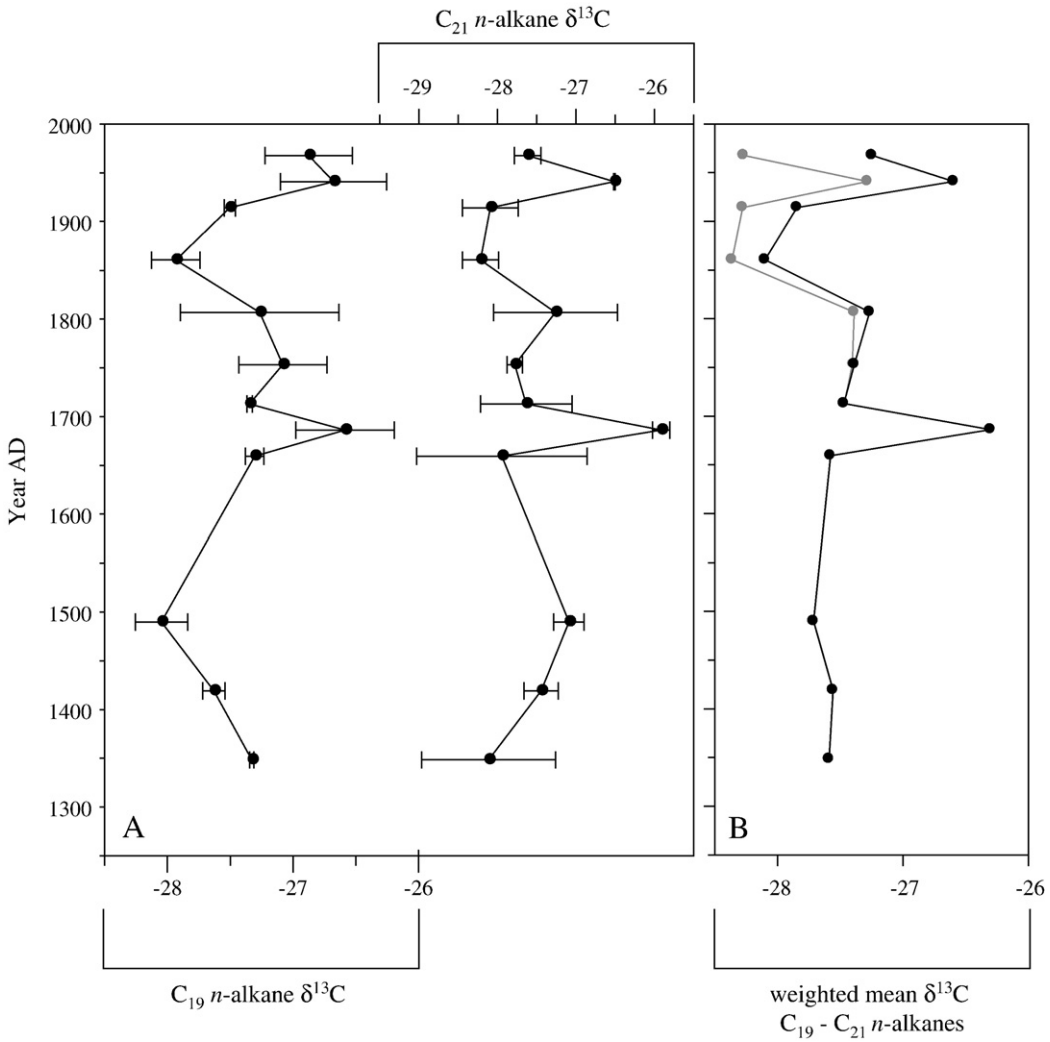

Fig. 4. Algal *n*-alkane carbon isotope records corrected for the Suess effect. A) The carbon isotopic composition of the C_{19} and C_{21} *n*-alkanes. Error bars representing the reproducibility are shown. B) The weighted mean of the C_{19}–C_{21} *n*-alkanes. The uncorrected values are shown in grey for comparison.

be useful to obtain isotopic measurements on a more specific algal lipid and given the high abundances of the long-chain *n*-alkyl diols in Lake Malawi sediments (see Section 4.3.1), these compounds may be suitable candidates for compound-specific isotope analysis.

4.3. Biomarkers present in Lake Malawi sediments

Cores M98-11MC and M98-2PG contained several compounds that provide biomarkers for aquatic algae and terrestrial higher plants. The significance of these compounds is discussed in the following paragraphs.

4.3.1. Aquatic biomarkers

Diatoms are the dominant algal group in Lake Malawi and are present in highest abundance during the cool and windy season (Hecky and Kling, 1987). The compound loliolide/isololiolide, which is produced by the anoxic degradation of the pigment fucoxanthin (Klock et al., 1984; Repeta, 1989), is relatively abundant in Lake Malawi sediments. Fucoxanthin is the major carotenoid present in diatoms and can also be produced by dinoflagellates and haptophyte algae (Klock et al., 1984; Jeffrey and Vesk, 1997). However, in Lake Malawi dinoflagellates are only a minor contributor to algal productivity and haptophyte algae are not present (Patterson and Kachinjika, 1995). Thus, loliolide/isololiolide provides a reliable marker for diatoms. When compared to the record of biogenic silica (Johnson et al., 2001), another proxy for diatom productivity, it is clear that accumulation rates of loliolide exhibit the same overall trends as the biogenic silica record (Fig. 6), demonstrating that loliolide is a robust indicator of diatom productivity in Lake Malawi. Accumulation rates of loliolide plus isololiolide range from 1.5 to 8.6 ng $cm^2 yr^{-1}$.

In modern Lake Malawi, cyanobacteria dominate the algal taxa 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). Common cyanobacterial biomarkers such as the 7- and 8-methylheptadecanes (me-*n*-C_{17}, 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, which is attributed to cyanobacterial source (Sinninghe Damsté et al., 2001). Docosanyl 3-*O*-methylxylopyranoside, hereafter referred to as methylxylopyranoside, is present in low abundances in Lake Malawi sediments prior to 1750 AD but is absent in younger sediments (Fig. 6). Accumulation rates of methylxylopyranoside range from 0.2 to 0.9 ng $cm^2 yr^{-1}$.

The compound dinosterol is present in many Lake Malawi samples and provides a biomarker for dinoflagellates (Withers, 1983; Pirretti et al., 1997; Boon et al., 1979; Robinson et al., 1984; Volkman, 1998). In contrast to many sterols that are produced by both aquatic algae and terrestrial plants, dinosterol is not synthesized by higher plants and is thus recognized as a robust biomarker for dinoflagellates

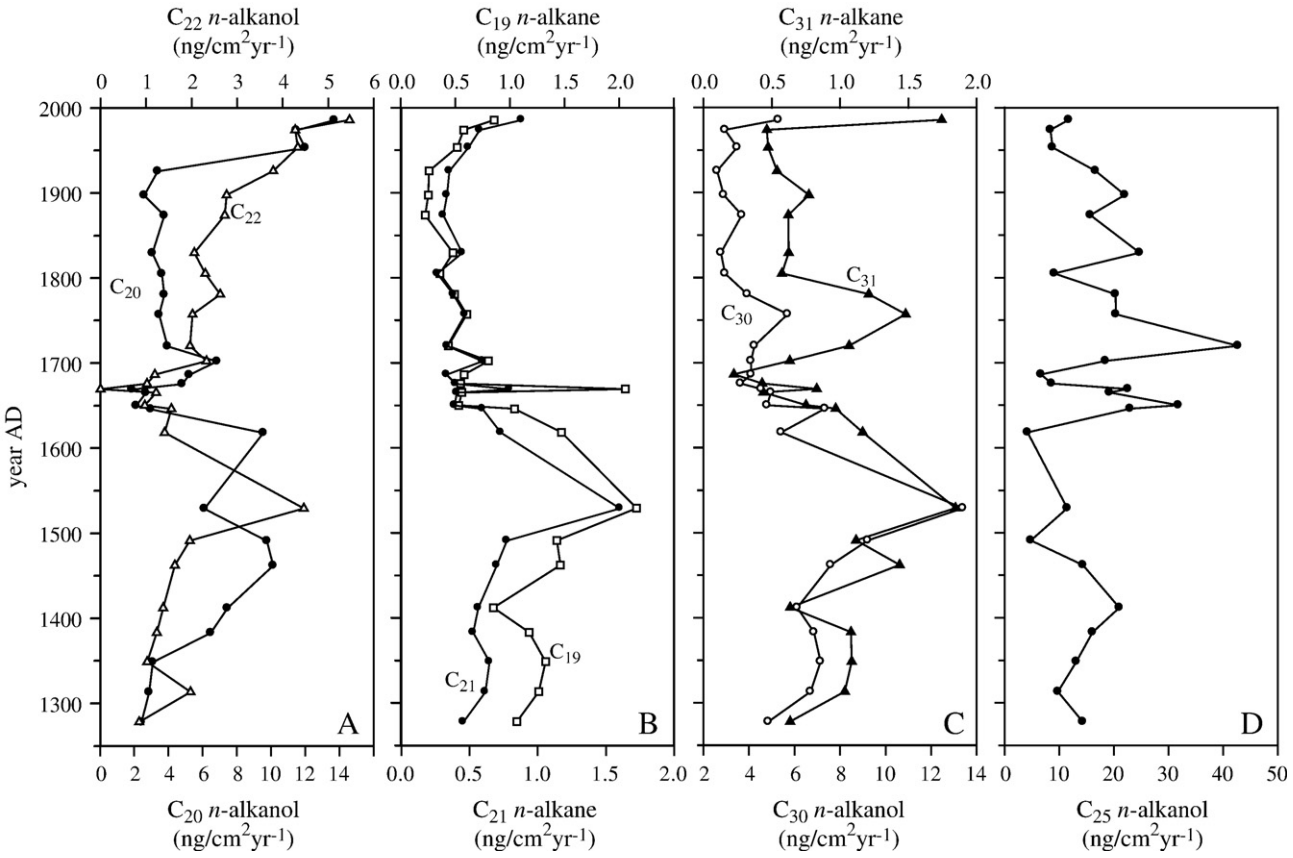

Fig. 5. Mass accumulation rates of the *n*-alkanes and *n*-alkanols in cores M98-11MC and M98-2PG. A) Mass accumulation rates of the C_{20} (open triangles) and C_{22} *n*-alkanols (filled circles). The short-chain *n*-alkanols provide a general biomarker for algal productivity. B) Mass accumulation rates of the C_{19} (open squares) and C_{21} (filled circles) *n*-alkanes. The short-chain *n*-alkanes also provide a general algal biomarker. C) Mass accumulation rates of the C_{30} *n*-alkanol (open circles) and the C_{31} *n*-alkane (closed triangles). The long-chain *n*-alkanes and *n*-alkanols are biomarkers for terrestrial higher plants. D) Mass accumulation rates of the C_{25} *n*-alkanol. The presence of an odd carbon-numbered *n*-alkanol is highly unusual and the source of this compound in presently unknown.

(Volkman et al., 1999). Accumulation rates of dinosterol range from 1.0 to 8.8 ng cm^2 yr^{-1} (Fig. 6).

Biomarkers of green algae were not identified in Lake Malawi sediments of the past 700 years, although the lake contains a number of green algae with *Closterium*, *Staurastrum* and *Mougeotia* being the most abundant species (Hecky et al., 1999). Common biomarkers of green algae include botryococcenes and lycopadiene/lycopane derivatives (Metzger and Largeau, 2005; Adam et al., 2006), which are biomarkers of the green algae *Botryococcus braunii*. Lake Malawi sediments did not contain any biomarkers of *B. braunii* but this particular species of Botryococcus may not be present in the lake (Castañeda et al., 2009b). Other biomarkers of green algae include the C_{25} and C_{27} *n*-alkenes (Volkman et al., 1998) but these compounds are not a highly specific biomarker because they can be produced by other sources. Interestingly, the C_{25} and C_{27} *n*-alkenes are present in low abundance in a 23 cal ka record of Lake Malawi (Castañeda et al., 2009b) but are absent from the recent sedimentary record.

In contrast to green algae, which are present in Lake Malawi but presently lack sedimentary biomarkers, Lake Malawi sediments were found to contain biomarkers of eustigmatophyte algae, an algal group about which little is known (Ott and Oldham-Ott, 2003), and which have not been identified in the lake. The long-chain 1,15 *n*-alkyl diols are recognized as biomarkers of the algal class Eustigmatophycae (yellow-green algae) (Volkman et al., 1992; Versteegh et al., 1997), and are abundant in Lake Malawi sediments (Fig. 6) with accumulation rates of the C_{30} 1,15 *n*-alkyl diol ranging from 1.8 to 5.2 ng cm^2 yr^{-1} and of the C_{32} 1,15 *n*-alkyl diol ranging from 1.5 to 11.3 ng cm^2 yr^{-1}. To date, eustigmatophyte algae have never been identified in algal or sediment samples from Lake Malawi (Hedy Kling, pers. comm.) but may have been overlooked or misidentified in previous algal surveys (Castañeda et al., 2009b). Futhermore, a study of the phytoplankton of nearby Lake Tanganyika, based on PCR-amplified 18S rDNA, provides evidence for the presence of eustigmatophytes possessing a sequence similar to marine and freshwater members of *Nannochloropsis* (De Wever, 2006). Alternatively, the class Eustigmatophyceae includes members that inhabit terrestrial soils (Ott and Oldham-Ott, 2003) and therefore, it is possible that soil eustigmatophytes are the source of the long-chain *n*-alkyl diols. However, in older Lake Malawi sediments accumulation rates of the long-chain *n*-alkyl diols closely track accumulation rates of other algal biomarkers (Castañeda et al., 2009b), including the diatom biomarker loliolide, making a solely terrestrial source of the long-chain *n*-alkyl diols to Lake Malawi sediments unlikely. It has been suggested that long-chain *n*-alkyl diols may be produced by other algal groups in addition to eustigmatophyte algae (Versteegh et al., 1997; Gelin et al., 1999). Thus, the exact source of the long-chain *n*-alkyl diols to Lake Malawi sediments is currently unknown.

The compound tetrahymanol (gammaceran-3β-ol) is one of the most abundant compounds in Lake Malawi sediments (Fig. 6), with accumulation rates ranging from 2.4 to 78 ng cm^2 yr^{-1}, and is produced by bacterivorous ciliates, such as the freshwater ciliate *Tetrahymena* (Mallory et al., 1963; Harvey and McManus, 1991). Tetrahymanol can also be produced by the anaerobic purple bacterium *Rhodopseudomonas palustris* (Kleemann et al., 1990), anaerobic rumen fungus (Kemp et al., 1984), and in small amounts by a fern (Zander et al., 1969). Sources from rumen fungus and ferns are unlikely in Lake Malawi sediments. Although production by anaerobic purple bacteria cannot be ruled out, in aquatic sediments

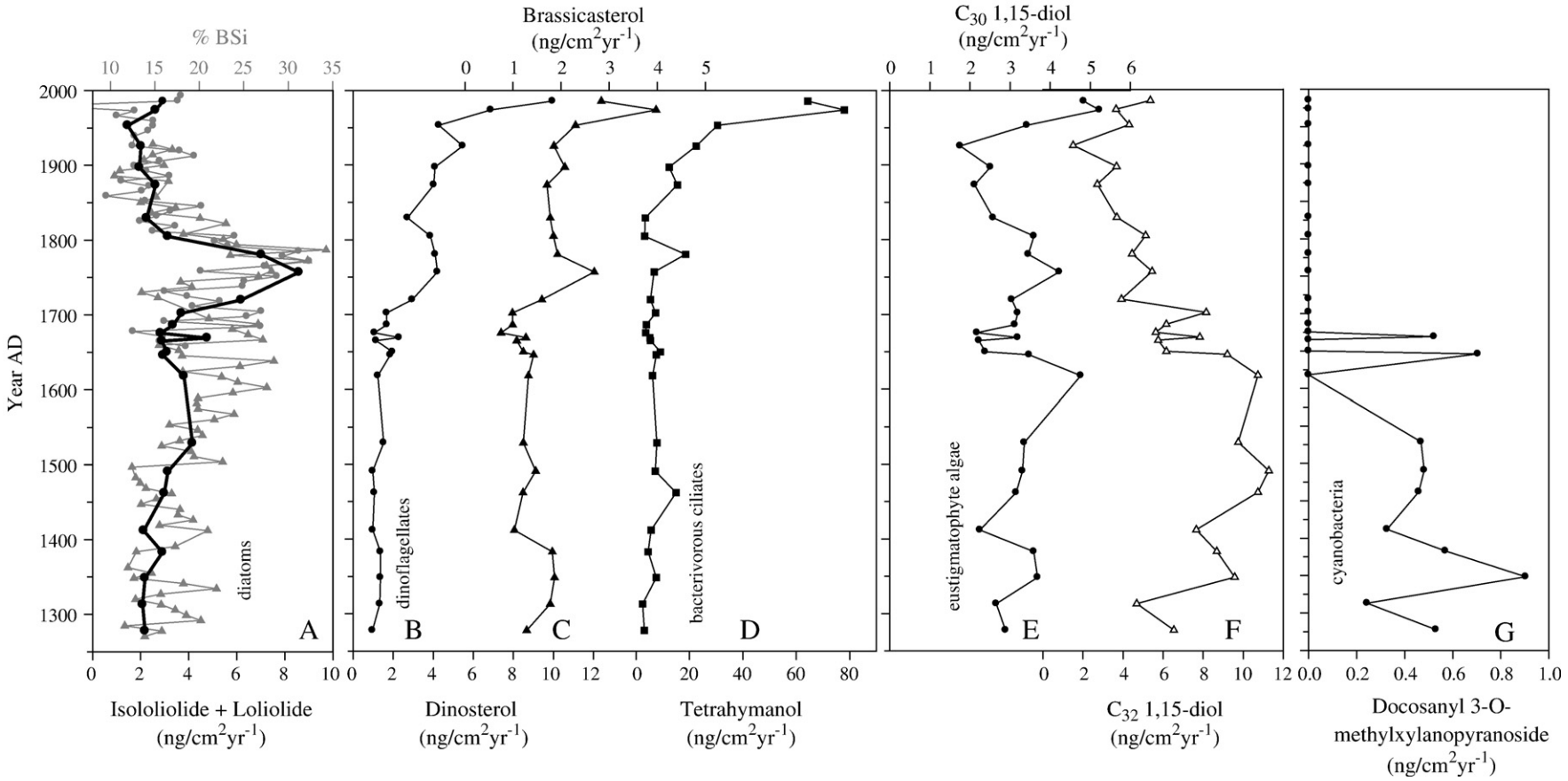

Fig. 6. Mass accumulation rates of aquatic biomarkers in Lake Malawi. A) Mass accumulation rates of the diatom biomarkers isololiolide and loliolide added together (filled black circles) and percent biogenic silica (grey triangles). Biogenic silica data is from Johnson et al. (2001). Mass accumulation rates of dinosterol (filled circles), brassicasterol (filled triangles) and tetrahymanol (filled squares) are shown in panels B, C, and D, respectively. Dinosterol provides a biomarker for dinoflagellates and tetrahymanol provides a biomarker for bacterivorous ciliates. Brassicasterol is produced by both diatoms and terrestrial higher plants and may reflect a mixed source in Lake Malawi because mass accumulation rates of brassicasterol do not track the record of isololiolide and loliolide. Figures E and F show the mass accumulation rates of the C_{30} and C_{32} 1,15 alkyl diols, which are biomarkers for eustigmatophyte algae. Panel G shows the mass accumulation rate of docosanyl 3-*O*-methylxylopyranoside, which has been suggested as a biomarker for cyanobacteria.

tetrahymanol typically derives from ciliates (Harvey and McManus, 1991), and several genera of bacterivorous ciliates are present in Lake Malawi (Yasindi and Taylor, 2003). Previous studies have attributed the occurrence of tetrahymanol in sediments to the presence of a stratified water column (Hanisch et al., 2003) since bacterivorous ciliates are typically found at the oxic–anoxic boundary where large bacterial populations are present (Sinninghe Damsté et al., 1995; Thiel et al., 1997). The published information on ciliates in Lake Malawi is presently limited to one study (Yasindi and Taylor, 2003) and thus controls on their abundance are not fully understood. However, in other systems, studies have indicated that ciliate biomass is controlled by food availability (Beaver and Crisman, 1989 and references therein).

Lake Malawi sediments contained short-, mid- and long-chain *n*-alkanes and *n*-alkanols. The short-chain *n*-alkanes (C_{17}–C_{21}) and *n*-alkanols (C_{18}–C_{22}) provide general algal biomarkers although terrestrial higher plants and bacteria can also produce these compounds in small amounts. In Lake Malawi, the short-chain *n*-alkanols exhibit higher accumulation rates than the short-chain *n*-alkanes (Fig. 5).

4.3.2. Terrestrial higher plant biomarkers

The long-chain *n*-alkanes (C_{27}–C_{31}) and *n*-alkanols (C_{28}–C_{32}) are present in Lake Malawi and provide a biomarker for terrestrial higher plants. Like the short-chain *n*-alkanes and alkanols, accumulation rates of the long-chain *n*-alkanols are higher than the long-chain *n*-alkanes (Fig. 5). It should be noted that downcore profiles of the short-chain and long-chain *n*-alkanes/alkanols are somewhat similar and thus it may be possible that terrestrial plants are a significant contributor of short-chain *n*-alkanes/alkanols to Lake Malawi sediments. Alternatively, decadal- to centennial-scale increases in precipitation and associated influx of terrestrial vegetation and nutrients to the lake may also enhance primary production of algae and their burial in the underlying sediments.

The compound retene is present in cores M98-11MC and 2PG (Fig. 7) and is of interest since this compound is absent in the 23,000 year sedimentary record from Lake Malawi (Castañeda, 2007). Retene is a biomarker for higher plants and is formed by diageneis of the diterpenoid abietic acid, which is found in conifer tree resin (Laflamme and Hites, 1978). Retene is commonly found in soils and can also be formed by combustion of coniferous wood (Ramdahl, 1983). Lake Malawi sediments also contained the compound de-A-lupane, which is a tetracyclic terpane thought to derive from angiosperms (Oung and Philip, 1994). Accumulation rates of retene range from 0.2 to 0.6 ng $cm^2 yr^{-1}$ while accumulation rates of de-A-lupane range from 0 to 0.4 ng $cm^2 yr^{-1}$.

The sterol brassicasterol (24-methylcholesta-5,22-dien-3β-ol) is commonly used as a biomarker for diatoms and is present in Lake Malawi sediments with accumulation rates ranging from 0.8 to 4.0 $cm^2 yr^{-1}$ (Fig. 6). However, brassicasterol can also be synthesized by land and emergent water plants (Nishimura and Koyama, 1977). In Lake Malawi, accumulation rates of brassicasterol do not track accumulation rates of either loliolide/isololiolide or biogenic silica particularly closely (Fig. 6), and given the proximity of the shore to the coring site, terrestrial sources of sterols are likely. Similarly, the compound β-sitosterol derives from both higher plant and algal sources (Nishimura and Koyama, 1977; Volkman et al., 1998) but in

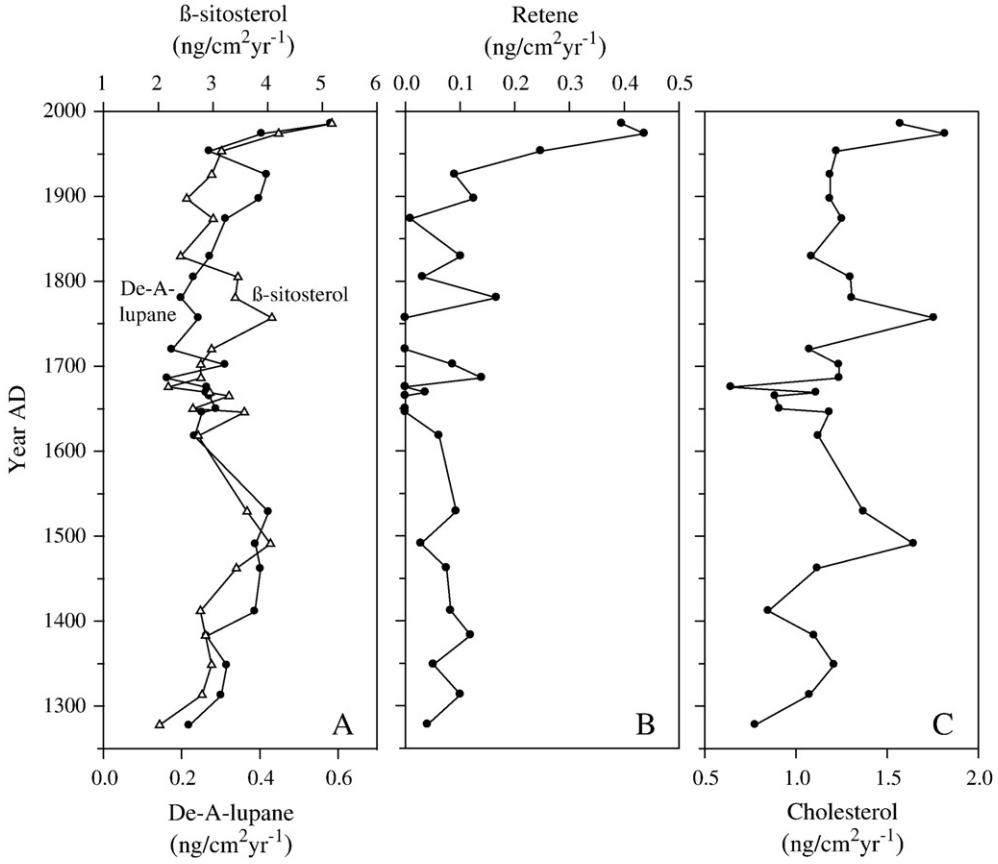

Fig. 7. Biomarkers of terrestrial vegetation. A) Mass accumulation rates of de-A-lupane (filled circles) and β-sitosterol (open triangles). De-A-lupane is thought to derive from angiosperms while β-sitosterol is produced by both land and emergent water plants and diatoms. In Lake Malawi, β-sitosterol appears to reflect a source from terrestrial higher plants. B) Mass accumulation rates of retene, a compound derived from conifers. C) Mass accumulation rates of cholesterol, which is produced by multiple sources including aquatic algae, terrestrial higher plants and zooplankton.

Lake Malawi it appears that β-sitosterol derives from a mainly higher plant source because accumulation rates of this compound more closely track accumulation rates of retene and de-A-lupane but do not track accumulation rates of other algal biomarkers (Figs. 6, 7). The compound cholesterol (Fig. 7), is produced both by aquatic algae and terrestrial higher plants, as well as zooplankton, and likely reflects mixed sources in Lake Malawi.

4.3.3. An unusual compound in Lake Malawi sediments

It is interesting to note that in cores M98-11MC and 2PG, one of the most abundant compounds is the C_{25} *n*-alkanol, which exhibits accumulation rates ranging from 4.2 to 42.7 $ng\,cm^2\,yr^{-1}$ (Fig. 5; tetrahymanol is the only compound that exhibits higher accumulation rates). The presence of this compound in Lake Malawi sediments is highly unusual as *n*-alkanols typically exhibit strong even over odd carbon-number predominance in living organisms. In these samples, the C_{25} *n*-alkanol is the only odd carbon-numbered *n*-alkanol present in measurable quantities, and is not a contaminant because the compound is not present in any of the blank samples. The C_{25} *n*-alkanol is also present in high abundances in Lake Malawi piston core M98-1P (Castañeda, 2007). The source of the C_{25} *n*-alkanol is unknown; however, the presence of this compound in Lake Malawi sediments is noteworthy and requires more investigation.

4.3.4. Assessing diagenetic effects on biomarker records

It is important to consider possible diagenetic effects on lipid biomarker distributions before making paleoenvironmental interpretations. The degradation of lipid biomarkers is strongly influenced by oxygen, with lipids being more rapidly degraded under oxic conditions than under anoxic conditions (Sun et al., 1997; Harvey and Macko, 1997; Teece et al., 1998; Sun and Wakeham, 1998). Lake Malawi is permanently anoxic below 200–250 m water depth (Patterson and Kachinjika, 1995) and the coring sites, located at 363 and 403 m water depths, are believed to have remained anoxic during the past 730 years. Thus, changes in bottom water oxygenation can be eliminated as a factor influencing the degradation of sedimentary organic matter. It has been shown that in the Cariaco basin, which like Lake Malawi contains oxygenated surface waters overlying anoxic bottom waters, organic matter is mainly altered in the water column but does not change significantly upon reaching the sediments (Wakeham and Ertel, 1988). The effects of enhanced preservation with increased sediment accumulation rates (Henrichs and Reeburgh, 1987; Canfield, 1989) also can be eliminated as a factor affecting lipid preservation because cores M98-11MC and M98-2PG have fairly constant sedimentation rates.

Differential degradation of lipids during diagenesis is another factor that must be considered when examining the sedimentary record. For example, in anoxic sediments polyunsaturated fatty acids are more labile than monounsaturated alkenes, which are more labile than alkanols, which are more labile than sterols (Grossi et al., 2001). Additionally, selective preservation is known to occur within the same class of lipids. For example, in anoxic sediments selective preservation between individual sterols has been noted, with cholesterol being more reactive than the C_{29} sterols (Taylor et al., 1981; Grossi et al., 2001). One method of separating the effects of differential degradation and early diagenesis from the paleoenvironmental signal is to apply a correction factor to the measured lipid concentrations (Zimmerman and Canuel, 2002). Although downcore abundance profiles of some compounds in Lake Malawi sediments (i.e. cholesterol, brassicasterol, dinosterol and tetrahymanol) appear to resemble early diagenesis curves (Figs. 6 and 7), we chose not to apply such a correction factor to the measured lipid abundances for several reasons. First, nearly all compounds are present in higher concentrations in older sediments. Piston core M98-1P was collected from a site immediately adjacent to core M98-11MC and has a sedimentary record spanning from 0.2 to 23 cal ka. In this core, compounds including tetrahymanol, β-sitosterol, cholesterol, dinosterol, the long-chain *n*-alkyl diols, the long-chain *n*-alkanols, isololiolide and docosanyl 3-*O*-methyl-methylxylopyranoside, are all present in higher concentrations than in cores M98-11MC or M98-2PG (Castañeda, 2007; Castañeda et al., 2009b). Second, while some biomarker abundance profiles resemble early diagenesis curves, it should be noted that the uppermost data point of several of these compounds (i.e. cholesterol (Fig. 7C), brassicasterol (Fig. 6C), tetrahymanol (Fig. 6D)) actually exhibit slightly lower abundances than the sample directly below it. This pattern is atypical of an early diagenesis curve, which displays a steady exponential decrease from surface to deep sediments. Third, it has been observed that in anoxic sediments cholesterol is more reactive than the C_{29} sterols (Taylor et al., 1981; Grossi et al., 2001); however, the downcore profiles of cholesterol and other sterols are dissimilar (Figs. 4 and 5), and the profile of cholesterol correlates well with downcore profiles of the long-chain *n*-alkanes (Figs. 4 and 5), which is one of the most stable lipid classes (Meyers, 1997). Thus, abundances of cholesterol, which is one of the most reactive compounds examined in this study, do not appear to be reflecting changes due to early diagenesis so it is reasonable to assume the same is true for more refractory classes of lipids. For these reasons, we assume that the Lake Malawi record mainly reflects changes in primary productivity. It is important to note that biomarker abundances cannot be directly correlated to biomass due to complications arising from degradation and heterotrophy, yet changes in accumulation rates of lipids can be used to examine past trends in ecosystem structure and productivity.

4.4. Paleoenvironmental history of the past 700 years in Lake Malawi

The trends in the biomarker data are complex and interpretation of the records, in terms of the paleoenvironmental history of Lake Malawi over the past 700 years, is not always straightforward. For this reason we have based our sub-division of the major periods in the Lake Malawi record on the TOC record but note that overall trends noted in individual biomarker records do not always coincide with these intervals.

4.4.1. Pre-1550 AD

In the interval from 1270–1550 AD, % TOC values exhibit an overall increasing trend towards higher values. Some of the lowest % TOC values of the entire record are noted at ~1300 AD, when values fall below 2% TOC (Fig. 2). A number of other biomarkers also exhibit an overall increasing trend towards higher abundances throughout this interval including the short-chain *n*-alkanols and *n*-alkanes, the long-chain *n*-alkanes, the C_{32} 1,15-diol, de-A-lupane, ß-sitosterol, and cholesterol (Figs. 5 and 6). Abundances of isololiolide/loliolide and % BSi are relatively low (Figs. 2 and 6) as are abundances of dinosterol, brassicasterol and tetrahymanol (Fig. 6). TEX_{86}-based temperatures are relatively stable at around 26 °C from 1270 AD until ~1430 AD (Fig. 8; Powers et al., 2011-this issue). A cooling of ~1 °C is noted at ~1470 AD and subsequently warming is noted until ~1550 AD when a temperature of ~27 °C is reached (Powers et al., 2011-this issue). $\delta^{13}C_{TOC}$ values indicate an overall trend from more ^{13}C-depleted values at 1270 AD to more ^{13}C-enriched values at 1550 AD (Fig. 2).

Overall, the bulk geochemical and biomarker data suggest relatively low algal productivity at 1270 AD and gradually increasing productivity until 1550 AD, which is reflected by the overall increasing trend of several biomarkers and an increase in total algal lipids (Fig. 8). However, although an increase in total algal lipids is noted, accumulation rates of diatoms (loliolide/isololiolide), dinoflagellates (dinosterol) and bacterivorous ciliates (tetrahymanol) remain relatively low this interval (Fig. 6). Accumulation rates of the C_{32} 1–15 diol increase throughout this interval suggesting an increase in eustigmatophyte algae (Fig. 6). Terrestrial inputs to Lake Malawi also increased throughout this interval as reflected by

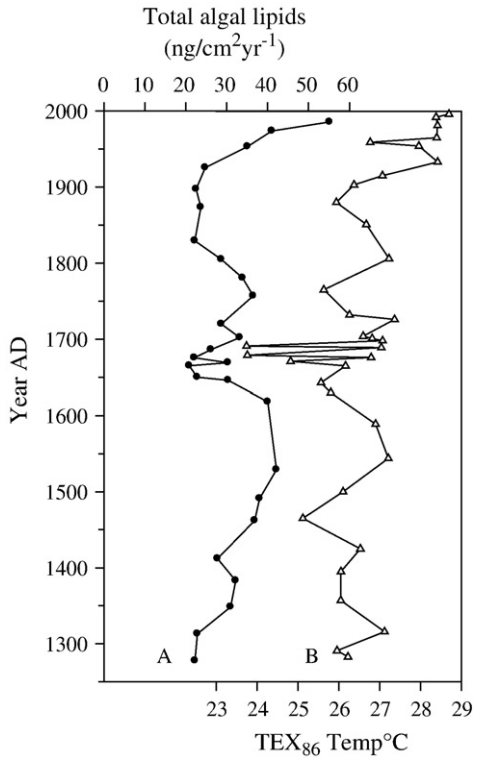

Fig. 8. Comparison of total algal biomarkers and mean annual lake surface temperature. A) Mass accumulation rates of total algal lipids in cores M98-11MC and 2PG (filled circles; includes the C_{17}–C_{21} *n*-alkanes, C_{20}–C_{22} *n*-alkanols, C_{30}–C_{34} 1,15-diols, docosanyl 3-*O*-methylxylopyranoside, and dinosterol). B) Mean annual lake surface temperature reconstructed from the TEX_{86} paleothermometer for cores M98-11MC and 2PG (data from Powers et al., 2011-this issue).

increasing accumulation rates of the long-chain *n*-alkanes and *n*-alkanols, which display the highest values of the entire record at 1525 AD (Fig. 5).

4.4.2. 1550–1650 AD

The interval from 1550 to 1650 AD is characterized by a decreasing trend in % TOC, which is accompanied by increasing values of % BSi. Only a few biomarker samples span this interval and thus not all records are discussed in detail. Accumulation rates of dinosterol and tetrahymanol remain low (Fig. 6), suggesting that dinoflagellates and bacterivorous ciliates were not important contributors to aquatic productivity in this interval. Both the C_{30} and C_{32} 1,15 diols exhibit increasing accumulation rates until ~1600 AD (Fig. 6), suggesting that at this time eustigmatophyte algae were relatively more important contributors to aquatic productivity than before. Accumulation rates of the long-chain *n*-alkanes and *n*-alkanols decrease throughout this interval (Fig. 5) suggesting decreased terrestrial inputs to Lake Malawi. TEX_{86} temperatures indicate a 2 °C cooling, from 27 °C at 1550 AD to 25 °C at ~1650 AD (Fig. 8; Powers et al., 2011-this issue), while $\delta^{13}C_{TOC}$ values continue to become increasingly ^{13}C-enriched throughout this interval (Fig. 2).

4.4.3. 1650–1900 AD

The interval from 1650 to 1900 AD exhibits the most variability of the past 700 years in many of the bulk and molecular records. At ~1670 AD a rapid decrease in % TOC is noted with low values of 1.7% reached at 1680 AD (Fig. 2). Subsequently, a rapid increase in % TOC concentrations is noted until ~1710 AD, when values of 4.9% TOC are reached. Following this rapid increase in TOC, an overall decreasing trend is noted until ~1900 AD when values of ~2% TOC are reached. The rapid changes noted in the TOC record from 1670–1710 AD coincide in timing with the Maunder Minimum in solar activity; however, similar changes in the TOC record are not observed during other periods of solar minima and thus it is unclear whether these events are related.

Like the % TOC record, the $\delta^{13}C_{TOC}$ record also indicates increased variability in this interval (Fig. 2). At ~1650 AD a reversal in the overall trend towards increasingly enriched values occurs and $\delta^{13}C_{TOC}$ values become 1‰ more ^{13}C-depleted by 1670 AD. More depleted $\delta^{13}C_{TOC}$ values are noted until 1730 AD but by 1750 AD $\delta^{13}C_{TOC}$ values are again 1‰ more ^{13}C-enriched. From 1750 until 1900 AD, generally more enriched $\delta^{13}C_{TOC}$ values are noted with some of the highest values of the entire record observed.

Due to the large changes observed in the % TOC and $\delta^{13}C_{TOC}$ records, the interval from 1670 to 1710 AD was sampled at higher resolution for TEX_{86} and biomarker analyses. Throughout this interval TEX_{86} temperatures are highly variable and fluctuate by 3 °C (Fig. 8; Powers et al., 2011-this issue). However, most of the biomarker records do not indicate increased variability or any notable excursions in this interval (Figs. 5–7). Although the C_{19} and C_{21} *n*-alkanes exhibit a peak at 1670 AD, superimposed on an overall decreasing trend from 1525 until ~1900 AD, it is defined by only one data point (Fig. 5). Accumulation rates of tetrahymanol continue to remain low throughout this interval while accumulation rates of dinosterol and brassicasterol are also low but increase slightly after 1700 AD (Fig. 6). The % BSi record exhibits high variability between 1650 and 1750 AD, with values ranging from 13 to 27% BSi (Fig. 2), but peak and low values noted in the % BSi record do not coincide with the high and low % TOC values. Thus, the cause of increased variability noted in the % TOC and $\delta^{13}C_{TOC}$ records at this time remains unclear.

Besides the event noted in the % TOC and $\delta^{13}C_{TOC}$ records from 1650–1750 AD, several other features characterize in the interval from 1650 to 1900 AD. The records of loliolide/isololiolide and biogenic silica indicate a general trend of increasing abundances from 1270 AD until ~1750 AD, when maximum abundances are noted, followed by a return to lower abundances between 1750 AD and the present (Fig. 6). Brown and Johnson (2005) interpreted the biogenic silica record, in combination with trace element data, as reflecting increased northerly winds over Lake Malawi during the Little Ice Age (LIA). The loliolide/isololiolide record obtained in this study is consistent with this idea.

Another interesting feature of the biomarker records is that the cyanobacterial biomarker methylxylopyranoside is present in Lake Malawi sediments prior to 1750 AD but is absent after this time (Fig. 6). It should be noted that the highest concentration of methylxylopyranoside observed during the past 730 years is $<0.1\ ng\,cm^{-2}yr^{-1}$. When compared to older Lake Malawi sediments, these concentrations are low as methylxylopyranoside obtains maximum concentrations of $\sim 2.5\ ng\,cm^{-2}yr^{-1}$ in the longer piston core (Castañeda, 2007). In Ace Lake, Antarctica, the site from which methylxylopyranoside was first reported, a trend of increasing concentration with increasing depth is also noted in the uppermost 25 cm of the sediments (Sinninghe Damsté et al., 2001). Cyanobacteria are one of the main primary producers in modern day Lake Malawi (Patterson and Kachinjika, 1995), and thus, the absence of this compound in the youngest sediments is intriguing. Presently, methylxylopyranoside has only been reported from Ace Lake and Lake Malawi and because both lakes display a similar pattern of increasing glycolipid abundance with depth in surface sediments, it may be possible that this compound forms or derives from another compound, and completion of this process may require a certain amount of time. Alternatively, it is possible that a different group of cyanobacteria is now present in Lake Malawi that does not produce methylxylopyranoside. Another possibility is that perhaps cyanobacteria were more abundant in the past and a certain amount of biomass may be required for a signal to be preserved in the sedimentary record. It is also possible that methylxylopyranoside is produced by a group other than, or in addition to, cyanobacteria.

4.4.4. Post-1900 AD

Both the aquatic and terrestrial biomarker records indicate a number of changes in the interval between 1900 AD and the present. The short-chain *n*-alkanols and *n*-alkanes exhibit increasing accumulation rates after ~1900 AD (Fig. 5) as does the record of total algal lipids (Fig. 8). Retene, dinosterol, brassicasterol and tetrahymanol display dramatic increases in accumulation rates (Figs. 6 and 7) while accumulation rates of loliolide and % BSi values are relatively low (Figs. 2 and 6). Accumulation rates of the long-chain *n*-alkyl diols increase after ~1930 AD (Fig. 6). TOC increases from 1900 to 1950 AD with somewhat lower values noted after this time (Fig. 2). The $\delta^{13}C_{TOC}$ record exhibits a trend towards more ^{13}C-enriched values from 1920 to 1975 AD.

The record of dinosterol indicates little variability from 1270 until ~1700 AD; however, after this time an overall trend of increasing accumulation rates is noted and even more so after ~1900 AD (Fig. 6). Dinoflagellates are presently a minor contributor to algal productivity in Lake Malawi (Patterson and Kachinjika, 1995) but algal surveys of Lake Malawi offer support to the increased presence of dinoflagellates with recent blooms of *Peridinium* observed (Hecky et al., 1999), which are of concern since this group can produce phycotoxins. Most dinoflagellates are warm-temperature organisms and exhibit maximum growth rates during summer (Carty, 2003). In addition, stratification is another important factor influencing dinoflagellate abundance and studies have suggested that dinoflagellate blooms are favored by a stable water column with minimal mixing (Pollingher, 1987). Since dinoflagellates possess a flagellum and are motile, they are capable of remaining in the surface waters of a stratified water column (Carty, 2003). In contrast to diatoms, which rely on turbulent mixing to remain in the photic zone, turbulent mixing can destroy or damage dinoflagellate cells (Pollingher, 1987).

The compound tetrahymanol displays a similar trend to dinosterol in core M98-11MC and 2PG, indicating an overall trend of increasing accumulation rates since ~1900 AD (Fig. 6). A plot of total algal biomarkers suggests an increase in the algal biomass of Lake Malawi since ~1900 AD (Fig. 8), and therefore increased accumulation rates of bacterivorous ciliates may be a reflection of increased food availability. Alternatively, both the trends of increasing accumulation rates of tetrahymanol and dinosterol could result from increased stratification. Vollmer et al. (2005) suggest that the strength of thermal stratification of Lake Malawi may have decreased since the ~1940s. However, even though the strength of density stratification may have varied, Lake Malawi is believed to have remained permanently stratified throughout most of the past 730 years. For this reason, it seems likely that factors other than stratification are more important controls on the accumulation rates of dinoflagellates and ciliates. One possibility is that the increase in dinosterol may be a reflection of generally less turbulent conditions in the northern basin of Lake Malawi during the past few centuries. While historical wind measurements in Malawi are scarce, trace element data from Lake Malawi has provided insight into past changes in the dominant wind regime over Lake Malawi since volcanic beds located at the northern end of the lake are enriched in Nb/Ti, which is transported to the lake during times of more frequent or stronger northerly winds (Johnson et al., 2002; Brown and Johnson, 2005). The Nb/Ti record displays its lowest values from ~1800 AD to the present, suggesting relatively weak northerly winds over Lake Malawi (Brown and Johnson, 2005), coincident with the increase in dinosterol. Decreased accumulation rates of loliolide/isololide and biogenic silica throughout this interval are also consistent with reduced windiness. Another possibility is that poorer light conditions from increased sediment input (Hecky et al., 1999) may be at least partly responsible for the increased accumulation rates of dinoflagellates, which are motile and can remain in the photic zone. Finally, studies have also shown that some dinoflagellate species prefer urea, which is present in fertilizers, as a nitrogen source (Gilbert and Terlizzi, 1999; Kudela and Cochlan, 2000; Horner Rosser and Thompson, 2001; Dyhrman and Anderson, 2003; Gilbert et al., 2006). It may be possible that elevated urea supply to Lake Malawi has occurred as forested land has been increasingly converted to agriculture.

In Lake Malawi sediments, retene is present for much of the past 730 years, and displays increased accumulation rates since ~1930 AD (or possibly later, given the resolution of our data) (Fig. 7). At Lake Victoria, higher concentrations of retene are noted in sediments since 1960 AD, and are thought to derive from increased soil erosion due to deforestation and human activities (Lipiatou et al., 1996). Rapid deforestation is also occurring in the Lake Malawi basin (Calder et al., 1995) and thus enhanced soil erosion due to deforestation may account for the greater accumulation rates of retene noted in surface sediments. Alternatively, wood is a main fuel source for cooking in Malawi (Hudak and Wessman, 2000) and as human populations have grown, elevated accumulation rates of retene in surface sediments may also be attributed to increased biomass burning. Mass accumulation rates of two other compounds, de-A-lupane, and β-sitosterol, also derived from higher plants, display similar downcore profiles to retene (Fig. 7). Like retene, the generally higher accumulation rates of de-A-lupane and β-sitosterol noted since ~1930 AD also may be the result of deforestation.

4.5. Summary

The most notable changes in the biomarker records are the increase in dinoflagellate and bacterivorous ciliate biomarkers over the past few centuries, accompanied by a decrease in diatom lipids (Fig. 9). In addition, the record of total algal lipids also displays significantly higher accumulation rates throughout the past century (Fig. 8). A number of natural and anthropogenic factors are likely responsible for these ecosystem changes including temperature variability, increased nutrient loading, changes in wind strength and direction, and increased deforestation. Although none of the individual algal lipids appear to vary directly with changes in temperature, the plot of total algal lipids roughly tracks TEX_{86}-inferred lake surface temperature (Powers et al., 2011-this issue) with higher accumulation rates of algal lipids noted at times of increased temperature and vice versa (Fig. 8). Rapid deforestation

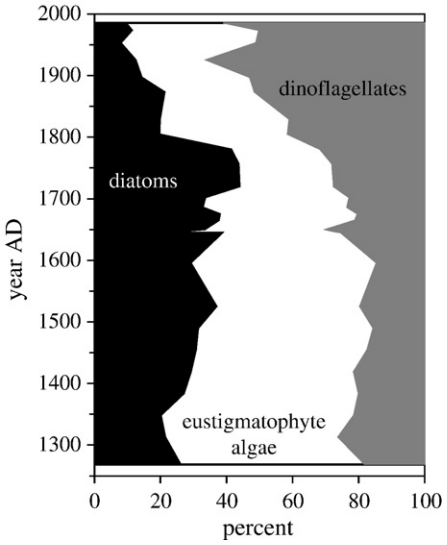

Fig. 9. Relative percentage plot of the main aquatic biomarkers present in Lake Malawi sediments. One compound representative of each group was chosen and abundances were normalized to 100%. Loliolide is the compound used to represent diatom productivity (indicated by the black shading), the C_{30} 1, 15-diol is used to represent contributions from eustigmatophyte algae (indicated in white), and dinosterol was used to represent contributions from dinoflagellates (indicated by the grey shading). An increase in dinoflagellates accompanied by a decrease in diatoms is noted since ~1900 AD.

of the watershed (Calder et al., 1995; Hudak and Wessman, 2000) and increased nutrient loading (Hecky et al., 2003) has been observed in Lake Malawi during the past few decades, and appears to be an important factor influencing primary productivity. In addition, it appears that a change in the dominant wind direction over Lake Malawi occurred at the end of the LIA (Brown and Johnson, 2005), with the northern end of Lake Malawi experiencing stronger or more frequent northerly winds prior to this time. Diatom productivity in the northern basin of Lake Malawi is sensitive to changes in wind strength and direction, which affect upwelling, and decreased diatom productivity is noted in Lake Malawi since ~1780 AD.

This study has demonstrated that biomarkers of aquatic algae can be successfully used to examine past changes in algal productivity. However, in order to interpret the molecular records from Lake Malawi more accurately it is essential to gain a better understanding of the algal groups present in the modern day lake and the lipids they produce. A study combining quantification of the main primary producers in the water column, lipid analysis of organic matter filtered from the water column, and lipid analysis of surface sediment samples would be useful for resolving these issues and for gaining a better understanding of what ultimately is preserved in the Lake Malawi sedimentary record.

5. Conclusions

1) Lake Malawi sediments were found to contain several classes of lipids that provide biomarkers for some of the main primary producers in the lake:
   - The compound loliolide/isololiolide provides a biomarker for diatom productivity in Lake Malawi and accumulation rates of this compound closely track abundances of biogenic silica. Together, these records indicate increased diatom productivity during the Little Ice Age and decreased diatom productivity from ~1800 AD to the present.
   - The glycolipid docosanyl 3-*O*-methylxylopyranoside is present in Lake Malawi sediments prior to ~1750 AD and may provide a biomarker for nitrogen-fixing cyanobacteria.
   - Lake Malawi sediments contain abundant long-chain 1,15 *n*-alkyl diols. The presence of these compounds in Lake Malawi sediments suggests that eustigmatophyte algae may be present in the lake.
   - No lipids of green algae were discovered in Lake Malawi sediments even though green algae are presently one of the dominant primary producers in the lake.
2) A number of changes are observed the Lake Malawi algal biomarker record since ~1900 AD. Biomarkers of dinoflagellates and bacterivorous ciliates display increased accumulation rates during the past few centuries, while diatom biomarkers display decreased accumulation rates. It is likely that a number of factors are responsible for these changes including increased temperature, watershed deforestation, nutrient loading, and possibly, changes in wind strength and direction.
3) During the past century, an increase in the abundance of the compound retene is noted and can likely be attributed to increased soil erosion due to deforestation, or from an increase in wood burning in the Lake Malawi basin.
4) One of the most unusual and abundant compounds in Lake Malawi sediments is the C_{25} *n*-alkanol. The source of this compound is presently unknown.
5) Spectral analysis of the TOC record reveals a 204 year periodicity, suggesting links between climate and solar variability in southeastern Africa. However, the cause of this relationship is presently unclear.

Acknowledgements

We wish to thank Yongsong Huang (Brown University) for providing *n*-alkane $\delta^{13}C$ analyses, and David Hollander (University of South Florida) and William P. Patterson (University of Saskatchewan) for providing bulk ^{13}C analyses. We also wish to thank Sarah Grosshuesch (Large Lakes Observatory) and Marcelo Alexandre (Brown University) for analytical assistance. Stefan Schouten (Royal Netherlands Institute for Sea Research) and Simon Brassell (Indiana University) are thanked for assistance with compound identification. We thank Phil Meyers and an anonymous reviewer for comments that improved this manuscript. This material is based in part upon work supported by the National Science Foundation under Grant No. ATM-9709291 to T. Johnson. Additional support was provided by an award from the Research Corporation to J. Werne and fellowship support from the University of Minnesota and the Ford Foundation to I. Castañeda.

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