



## Carbon cycling within an East African lake revealed by the carbon isotope composition of diatom silica: a 25-ka record from Lake Challa, Mt. Kilimanjaro

Philip A. Barker<sup>a,\*</sup>, Elizabeth R. Hurrell<sup>a</sup>, Melanie J. Leng<sup>b,c</sup>, Birgit Plessen<sup>d</sup>, Christian Wolff<sup>d</sup>, Daniel J. Conley<sup>e</sup>, Eddy Keppens<sup>f</sup>, Isla Milne<sup>g</sup>, Brian F. Cumming<sup>g</sup>, Kathleen R. Laird<sup>g</sup>, Chris P. Kendrick<sup>c</sup>, Peter M. Wynn<sup>a</sup>, Dirk Verschuren<sup>h</sup>

<sup>a</sup>Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK

<sup>b</sup>Department of Geology, University of Leicester, Leicester LE1 7RH, UK

<sup>c</sup>NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, Nottingham NG12 5GG, UK

<sup>d</sup>Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, Section 5.2, Climate Dynamics and Landscape Evolution, Telegrafenberg, D-14473 Potsdam, Germany

<sup>e</sup>GeoBiosphere Science Centre, Department of Geology, Lund University, SE-223 62 Lund, Sweden

<sup>f</sup>Department of Geology, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium

<sup>g</sup>Paleoecological Environmental Assessment and Research Laboratory, Queen's University, Kingston, Ontario K7L 3N6, Canada

<sup>h</sup>Limnology Unit, Department of Biology, Ghent University, K. L. Ledeganckstraat 35, B-9000 Gent, Belgium

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### ABSTRACT

The carbon cycle of a lake is a balance between supply from the atmosphere and catchment, and the net demand exerted by primary producers, minus losses back to the atmosphere and to sediment storage. Evaluating the sum of these processes and reconstructing them from sediment records of lake history requires a range of methods and a multi-proxy approach. One promising technique is to explore the carbon-isotope composition ( $\delta^{13}\text{C}_{\text{diatom}}$ ) of organic matter incorporated within the silica frustules of diatom algae. Here we present a 25,000-year record of  $\delta^{13}\text{C}_{\text{diatom}}$  from the sediments of crater Lake Challa on the eastern flank of Mt. Kilimanjaro, and along with other proxy data we make inferences about the three major phases in the history of the lake's carbon cycle. From 25 ka to 15.8 ka years BP,  $\delta^{13}\text{C}_{\text{diatom}}$  is positively correlated with the  $\delta^{13}\text{C}$  of bulk sediment organic matter ( $\delta^{13}\text{C}_{\text{bulk}}$ ), indicating that high diatom productivity, as recorded by high % biogenic silica at this time, was preferentially removing  $^{12}\text{C}$  and enriching the  $\delta^{13}\text{C}$  of lake-water dissolved inorganic carbon. From 15.8 to 5.5 ka the correlation between  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$  breaks down, suggesting carbon supply to the lake satisfied or exceeded the demand from productivity. From 5.5 ka BP the positive correlation resumes, indicating an increase in the internal demand for carbon relative to external supply. Diatom frustule-bound carbon isotopes offer an original tool in examining long-term fluctuations in a lake's carbon budget and how the balance between supply and demand has changed through time.

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### 1. Introduction

The important contribution of lakes to the global carbon cycle is only just beginning to be fully recognised and quantified (Tranvik et al., 2009). The product of carbon inputs to lakes from the atmosphere or catchment, metabolic processes within lake ecosystems, gaseous exports, and temporary or long-term storage in bottom sediments have a significant impact on atmospheric  $\text{CO}_2$  concentrations (Downing et al., 2008; Leavitt et al., 2009). On an

annual scale most lakes are net carbon sources, since the loss of  $\text{CO}_2$  and  $\text{CH}_4$  from respiration exceeds uptake of  $\text{CO}_2$  by photosynthesis, even in highly productive lakes (Hanson et al., 2004). From a Quaternary perspective, periodic expansion and contraction of lakes and wetlands also contributed to the regulation of glacial-interglacial  $\text{CO}_2$  and  $\text{CH}_4$  levels (Street-Perrott, 1994), as well as the non-linear response of regional climate to orbital forcing (Powers et al., 2011). Understanding how carbon cycling in lakes varies as a function of climate and landscape processes, including changes in other biogeochemical cycles, is important if millennial-scale feedback mechanisms between the lake and the surrounding landscape are to be properly evaluated. Long-term fluctuations in a lake's carbon cycle are a function of regional climate, carbon

\* Corresponding author.

E-mail address: [p.barker@lancaster.ac.uk](mailto:p.barker@lancaster.ac.uk) (P.A. Barker).

dynamics within the terrestrial catchment, productivity of the lake ecosystem itself, and hydrological processes including water balance, water-column mixing and water residence time.

Tracing the ecosystem and environmental processes that influence a lake's carbon cycle and reconstructing them from Quaternary lake-sediment records requires a range of methods and a multi-proxy approach. Commonly-employed methods (Meyers and Teranes, 2001) examine changes in the carbon cycle using the nature and flux of organic materials to the lake-sediment repository (Meyers and Lallier-Verges, 1999; Street-Perrott et al., 2007; Barker et al., 2011). These techniques provide a good understanding of long-term carbon storage, but only limited insights into the processing of carbon through the aquatic ecosystem. Stable isotope methods are extremely valuable in identifying the source of carbon contained in the sediments. For example, in tropical regions the relative proportion of organic material from C<sub>3</sub> or C<sub>4</sub> terrestrial plants to a sediment can be estimated from its bulk <sup>13</sup>C/<sup>12</sup>C ratio (hereafter,  $\delta^{13}\text{C}_{\text{bulk}}$ ), as these different photosynthetic pathways involve a markedly different isotopic fractionation in plants (Street-Perrott et al., 1997). In contrast, the stable-isotope signature of freshwater algae is highly variable between species, habitats and even at the cell-scale (Hecky et al., 1973; Hecky and Hesslein, 1995). The majority of freshwater algae have  $\delta^{13}\text{C}$  values similar to those of C<sub>3</sub> higher plants, but some groups also have the ability to use dissolved bicarbonate as carbon source, raising their  $\delta^{13}\text{C}$  value (Moss, 1973). It is therefore difficult to determine whether changes in  $\delta^{13}\text{C}_{\text{bulk}}$  are driven by algae, or by local communities of (terrestrial or aquatic) higher plants. Nevertheless, shifts in the  $\delta^{13}\text{C}_{\text{bulk}}$  of sediment records have been used to infer past changes in aquatic productivity, since photosynthetic aquatic organisms preferentially use the lighter <sup>12</sup>C and this can become depleted if lake productivity is high, causing a shift in  $\delta^{13}\text{C}_{\text{bulk}}$  towards less depleted values (Meyers and Lallier-Verges, 1999; O'Reilly et al., 2003). Using  $\delta^{13}\text{C}_{\text{bulk}}$  to reconstruct aquatic productivity must assume that no change occurred in the amount of particulate carbon derived from (either C<sub>3</sub> or C<sub>4</sub>) terrestrial plants, dissolved organic carbon (DOC) derived from eroding or leaching catchment soils, and dissolved inorganic carbon (DIC) derived from weathering of minerals. Evidently, on time scales longer than a few centuries this assumption is bound to be violated. One solution is to study the organic fraction of lake sediments using the compound-specific carbon-isotope composition of organic biomarkers (Sinninghe Damste et al., 2011). This approach has enabled particular algal and aquatic macrophyte sources to be identified (Ficken et al., 2000, 2002); for example, C<sub>25</sub> highly-branched isoprenoids are thought to be a marker for diatoms (Woltering et al., 2011). Down-core changes in the sum of biomarkers associated with algae and aquatic macrophytes can in turn be used to trace changes in authigenic carbon cycling (Street-Perrott et al., 2004; Woltering et al., 2011).

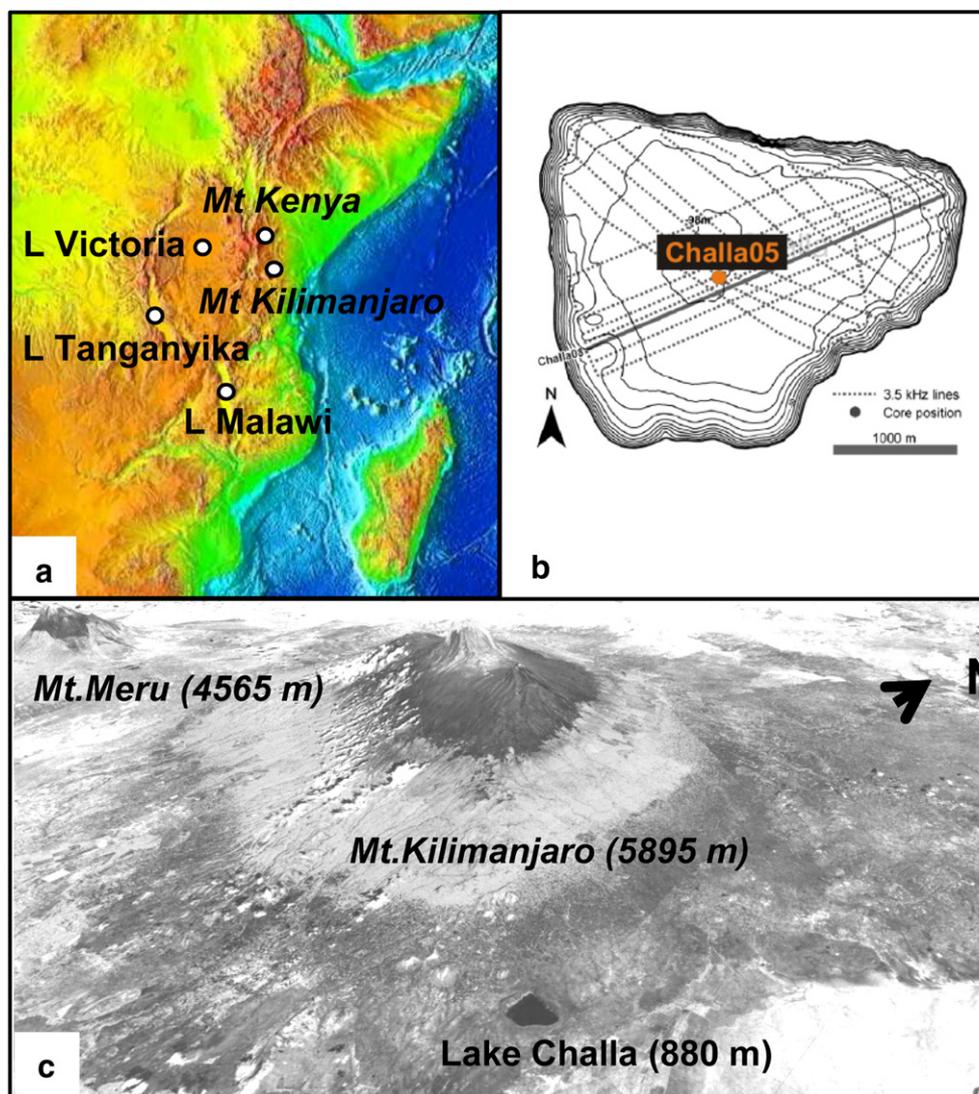
A further promising technique is to explore the stable carbon-isotope composition of organic carbon contained within diatom silica ( $\delta^{13}\text{C}_{\text{diatom}}$ ) (Shemesh et al., 1995; Schneider-Mor et al., 2005; King et al., 2006; Jacot Des Combes et al., 2008; Hurrell, 2009; Hernandez et al., 2011). One advantage of using  $\delta^{13}\text{C}_{\text{diatom}}$  over other organic geochemical methods is that the diatom's silica frustule protects organic material derived from the (easily degraded) proteins in the alga's cell wall from oxidation and mixing with the bulk-sediment carbon pool. Analysis of  $\delta^{13}\text{C}$  from a single group of photosynthetic organisms is clearly preferable to using either bulk organic  $\delta^{13}\text{C}$ , which is dominated by source effects, or the  $\delta^{13}\text{C}$  signature of higher organisms affected by isotopic fractionation at multiple levels of the aquatic food web. The  $\delta^{13}\text{C}_{\text{diatom}}$  method has previously been applied only to marine sediment records in deep waters of the Southern Ocean, where variability in

$\delta^{13}\text{C}_{\text{diatom}}$  values is largely a function of local primary productivity (Shemesh et al., 1995). In comparison, lake sediments may require more complex interpretations and approaches due to a multiplicity of carbon sources. In lakes,  $\delta^{13}\text{C}_{\text{diatom}}$  values are expected to be a balance between the nature and amount of carbon supplied to the lake and the 'demand' placed on the lake's carbon reservoir by the aquatic ecosystem. More explicitly, we expect that  $\delta^{13}\text{C}_{\text{diatom}}$  will primarily reflect the  $\delta^{13}\text{C}$  of the source of the carbon used by the diatoms, and the rate of <sup>12</sup>C depletion by primary biomass production.

Here we combine  $\delta^{13}\text{C}_{\text{diatom}}$  data with a diverse range of other aquatic productivity and carbon cycle proxies extracted from sediments to reconstruct a 25-ka record of carbon-cycle dynamics in Lake Challa, a tropical crater lake on the lower eastern flank of Mt. Kilimanjaro at an altitude of 880 m asl (Fig. 1). This lake is currently the subject of a large multi-proxy palaeoclimate and palaeoecology study (e.g., Verschuren et al., 2009; Barker et al., 2011; Sinninghe Damste et al., 2011, in press; Wolff et al., 2011; van Geel et al., 2011; Nelson et al., in press), which provides ample supporting data to test hypothesised relationships between  $\delta^{13}\text{C}_{\text{diatom}}$  and the lake's carbon cycle. Long-term carbon storage in the lake's profundal sediments is partially recorded by the concentration and (preserved) flux of total organic carbon (TOC). The  $\delta^{13}\text{C}$  signature of this bulk organic carbon is influenced by the influx of terrestrial organic matter, the terrestrial C<sub>3</sub>/C<sub>4</sub> plant ratio from which it derives, and by the amount and relative preservation of organic matter derived from aquatic algae and cyanobacteria (the phytoplankton; Blaauw et al., 2011). A first-order estimate of the relative importance of within-lake processing of carbon by phytoplankton versus influx of carbon from terrestrial plants can be approximated using the carbon/nitrogen (C/N) ratio of the organic sediments, as algae typically have a lower C/N ratio than higher plants (Meyers and Teranes, 2001). The changing nature of terrestrial carbon inputs has been further constrained by analysis of the  $\delta^{13}\text{C}$  of leaf-wax alkanes, which reflect the C<sub>3</sub>/C<sub>4</sub> ratio in terrestrial vegetation within the crater catchment (Sinninghe Damste et al., 2011). There are few direct proxies of lake palaeoproductivity, although diatom productivity is commonly inferred from indicators such as diatom biovolume and assemblage changes (Barker et al., 2001). An approximation of diatom biomass is given by the concentration and flux of biogenic silica (BSi) assuming no temporal changes have occurred in silica dissolution rate before burial, so that the preserved flux has a constant relationship to the size of the annual diatom bloom. In this context, we note that Lake Challa is relatively unique among small tropical lakes in that, despite significant lake-level fluctuations (Moernaut et al., 2010), the lake's lowermost water column remained stratified throughout the past 25,000 years, thus creating the stable conditions at the sediment–water interface which lend themselves to the promotion of constant rates of organic-matter and silica preservation. Together, the available independent proxies of carbon supply and demand in Lake Challa allow the rigorous evaluation of the  $\delta^{13}\text{C}_{\text{diatom}}$  method as a tool to explore past changes in the carbon cycle of lakes. With it, we show the interconnectivity between lake carbon processing and climate-induced landscape changes at glacial-interglacial time scales.

## 2. Study site

Lake Challa (3°19'S, 37°42'E) is a relatively large (4.5 km<sup>2</sup>) and deep (94 m) tropical crater lake (Fig. 1). Rainfall in this region is highly seasonal due to the twice-annual passage of the ITCZ, and occurs during the long rains of March–May and short rains of October–December. The wet seasons are warmer and less windy than the main dry season of June to September. The local



**Fig. 1.** (a) Location of Lake Challa in equatorial East Africa, with other key sites marks. (b) Lake bathymetry diagram indicating location of cores. (c) Aerial view of the lake on the flank of Kilimanjaro.

precipitation/evaporation (P/E) balance is highly negative, estimated to be  $\sim 600$  mm/yr rainfall and  $\sim 1700$  mm/yr lake-surface evaporation (Payne, 1970). The water balance of Lake Challa is maintained by inputs from a shallow groundwater aquifer draining the flanks of Mt. Kilimanjaro. Natural vegetation in the lowlands surrounding the Challa crater mostly consists of deciduous wooded savanna grassland and bushland, but irrigated agriculture in this region has rapidly expanded in recent decades. Relatively dense tree cover on its northern and western outer slopes form a dry savanna forest, and inside the crater the lakeshore is fringed by evergreen forest (Sinninghe Damste et al., 2011).

The lower water column of Lake Challa is warm ( $+22.3$  °C) and permanently stratified or meromictic, as testified by finely laminated profundal sediments throughout its 25,000-year record (Wolff et al., 2011). A pronounced thermocline develops around 15–20 m depth during the long stratified season from November to May, when lake-surface temperature can exceed  $+27$  °C. Deep mixing to 45–60 m depth occurs during the main dry season, when the temperature difference between the epilimnion and lower water column is reduced to less than 1 °C (Wolff et al., 2011). The lake is alkaline with a surface pH of 8.5–9.3 decreasing to around 7.0 in the hypolimnion, and dilute with electrical conductivity of

$300\text{--}350$   $\mu\text{S cm}^{-1}$  increasing to  $450$   $\mu\text{S cm}^{-1}$  in the permanently stratified lower water column below 65 m depth (Fig. 2a). DIC was measured in August 2007 (i.e., during the dry season) at  $38$   $\text{mg l}^{-1}$  in surface water, increasing to  $>50$   $\text{mg l}^{-1}$  below 65 m (Kristen, 2009). The  $\delta^{13}\text{C}_{\text{DIC}}$  composition of this DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ; Fig. 2) shows a maximum of  $-3\text{‰}$  at the surface, a minimum of  $-7\text{‰}$  at 35 m and higher values again in the hypolimnion. It is likely that high  $\delta^{13}\text{C}_{\text{DIC}}$  values in the mixed epilimnion are due to photosynthetic depletion of  $^{12}\text{C}$ . Respiration of  $\text{CO}_2$  from bacteria mineralising sinking organic matter and slow release of deep stored carbon in the hypolimnion and surface sediment could explain the low  $\delta^{13}\text{C}_{\text{DIC}}$  values in the metalimnion. Higher  $\delta^{13}\text{C}_{\text{DIC}}$  values in the deepest waters reflect the high concentrations of accumulated carbon providing a long-term store in this meromictic lake.

### 3. Material and methods

In 2003 and 2005, 22 m-long lake-sediment cores were retrieved from a central location (Fig. 1b) in Lake Challa (Verschuren et al., 2009). Cross-correlation of the overlapping core sections produced a continuous, 20.82 m-long composite sequence. Its chronology was established through high-resolution  $^{14}\text{C}$  dating

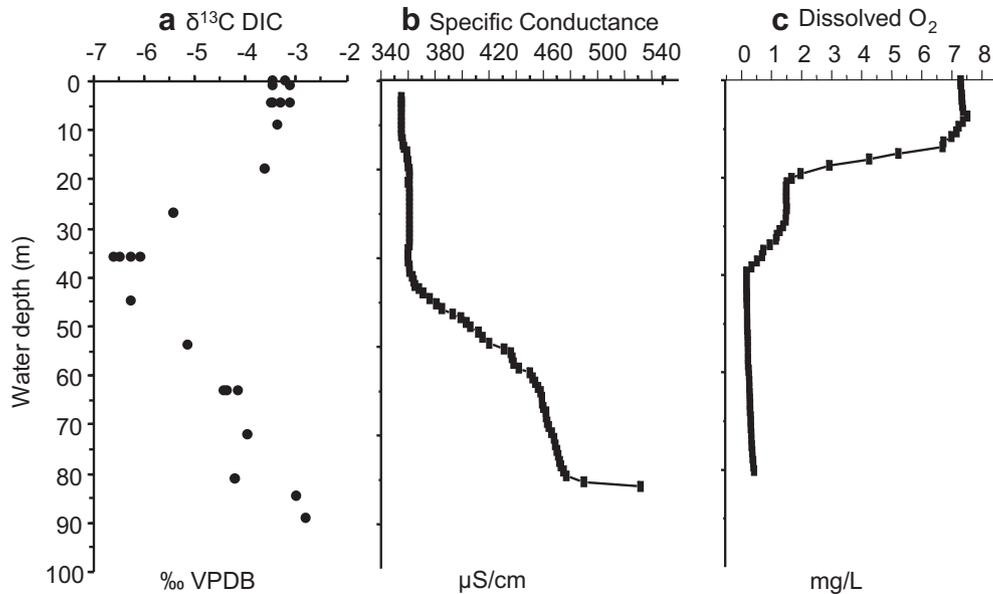


Fig. 2. (a)  $\delta^{13}\text{C}$  values of dissolved inorganic carbon (DIC) from the water column, (b) specific conductivity and (c) dissolved oxygen profiles collected in March 2004.

of bulk organic matter, corrected for an evolving old-carbon age-offset ('reservoir effect') by comparing overlapping  $^{210}\text{Pb}$  and  $^{14}\text{C}$  dates, paired  $^{14}\text{C}$  dates on bulk organic matter and terrestrial plant macrofossils, and wiggle-matching well-dated core sections with  $^{14}\text{C}$  anomalies in the INTAL04 curve (Blaauw et al., 2011).

For this study, a total of 249 samples at mostly constant intervals of 8 cm (~100 years, on average) were selected for determination of  $\delta^{13}\text{C}_{\text{diatom}}$ . The method of sample preparation followed experimental work by Hurrell et al. (2011). In brief, samples were treated with HCl,  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  to remove carbonates and external organic matter. Samples were then sieved at 63  $\mu\text{m}$ , 38  $\mu\text{m}$  and 20  $\mu\text{m}$  to remove mineral matter and sponge spicules, resulting in >90% pure diatom frustules as verified by SEM and light microscopy (Hurrell, 2009). The percentage organic carbon left after this preparation ( $\% \text{TOC}_{\text{diatom}}$ ) and its  $\delta^{13}\text{C}$  value were analysed using an online system comprised of a Costech ECS4010 elemental analyser, a VG TripleTrap, and a VG Optima mass spectrometer. Each analytical run contained replicates of the laboratory primary standard (BROC) and a secondary low percentage C standard (SOILB).  $\delta^{13}\text{C}_{\text{diatom}}$  values were calibrated to the VPDB (Vienna Pee Dee Belemnite) standard using reference samples NBS-19 and NBS-22. Typical errors for standard materials were 0.1‰ ( $\delta^{13}\text{C}_{\text{diatom}}$ ) and 0.1% ( $\% \text{TOC}_{\text{diatom}}$ ). TOC analysis of the cleaned diatom samples showed that 22 samples contained 1–4% carbon, opening the possibility of residual organic matter external to the diatom frustule and therefore these samples were rejected even though there was no systematic difference between the  $\delta^{13}\text{C}_{\text{diatom}}$  values of these samples and the remainder. Interpretation of the down-core variation in  $\delta^{13}\text{C}_{\text{diatom}}$  is based on the 227 samples with  $\% \text{TOC}_{\text{diatom}} < 1.0$ . A discussion of methodological issues in the analysis of  $\delta^{13}\text{C}_{\text{diatom}}$  in lakes is given in Hurrell et al. (2011).

The TOC, total nitrogen (TN) and  $\delta^{13}\text{C}_{\text{bulk}}$  were analysed at the GeoForschungsZentrum Potsdam after acid treatment (20% HCl) in silver capsules using a Carlo Erba elemental analyser on a DELTA-plusXL mass spectrometer. The elemental values were calibrated using Urea as a standard, and  $\delta^{13}\text{C}_{\text{bulk}}$  values were calibrated to VPDB using reference samples USGS24 and IAEA-CH-7. Typical errors on the reproducibility for replicate samples are 0.2% for TOC and TN and 0.2‰ for  $\delta^{13}\text{C}_{\text{bulk}}$ .

BSi was measured by digesting sediment samples in 1%  $\text{Na}_2\text{CO}_3$  for 3 h at 85 °C in a heated shaking bath. Sub-samples were taken

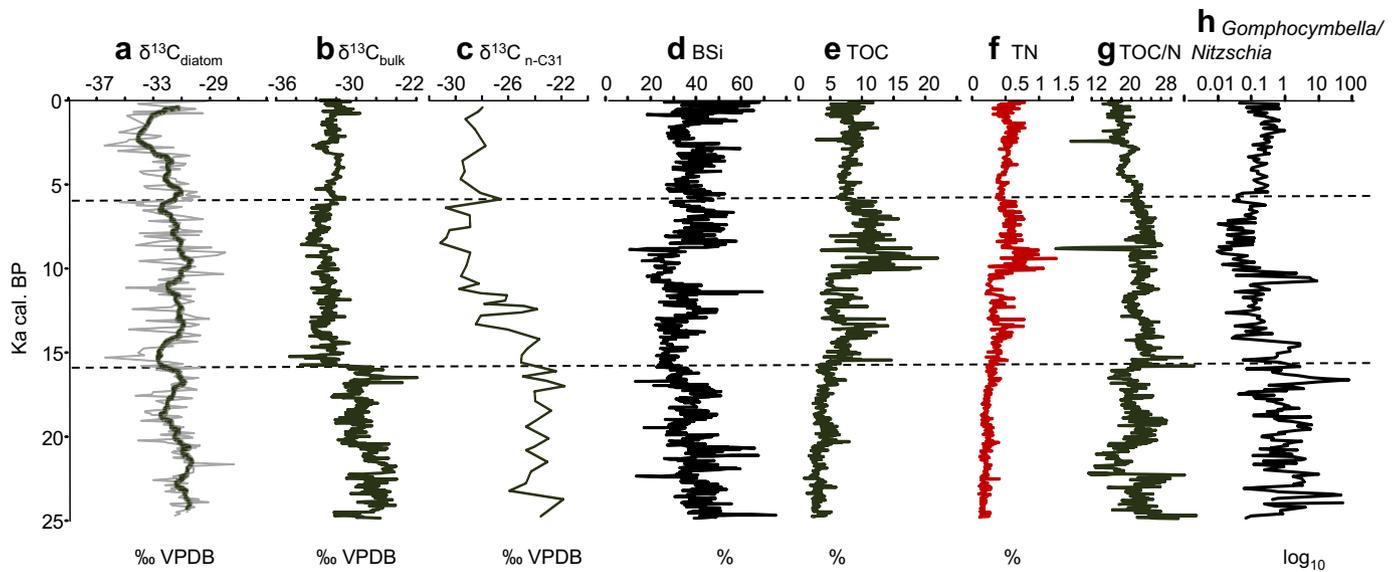
and neutralised with HCl, then measured for the dissolved silica extracted (Conley and Schelske, 2001). Increases in dissolved silica concentrations did not occur through time (D. Conley, unpubl. data) and, therefore, corrections for mineral dissolution were not made (Conley, 1998).

Diatoms were enumerated for palaeoecological interpretation using standard methods. Percentage composition of fossil diatom assemblages based on counts of >400 valves were presented by Milne (2007), whereas here we report only on the two major taxa that comprise over 90% of the assemblages; *Gomphocymbella* and *Nitzschia* spp. The *Gomphocymbella* spp. are stalked species typically occurring in attached epiphytic life-forms although their great abundance in the offshore profundal sediments of Lake Challa indicates that here they may be occupying a facultative planktonic niche. The needle-like *Nitzschia* spp. can also occupy multiple habitats but are abundant in the offshore sediments and are thus likely to be predominantly planktonic (Milne, 2007). Additional counts of 200 valves were made following the cleaning process for isotope analysis, to control for species effects on  $\delta^{13}\text{C}_{\text{diatom}}$  (Hurrell, 2009). *Gomphocymbella* spp. cells have 24 $\times$  the volume of a *Nitzschia* spp. cell, and will therefore be preferentially represented in the isotope values (Barker et al., 2011; Hurrell et al., 2011). Hurrell et al. (2011) showed that the  $\delta^{13}\text{C}_{\text{diatom}}$  of *Gomphocymbella* was 1‰ higher than *Nitzschia* spp. from within the same sample, possibly reflecting differences in habitat although the errors on this experiment were high because of small sample size.

Moving-average correlations between  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$  were performed using the Pearson product moment correlation function in Microsoft Excel. For this purpose the higher-resolution  $\delta^{13}\text{C}_{\text{bulk}}$  data were re-sampled at intervals corresponding to the 227  $\delta^{13}\text{C}_{\text{diatom}}$  samples. Each window was constrained to be equivalent to 3 ka and contained a minimum of 24 samples. A 3-ka window was selected to focus on multi-millennial correlations, reduce the impact of possible outliers and to ensure a large enough sample size to enable statistical significance estimates to be made.

#### 4. Results

The full range of  $\delta^{13}\text{C}_{\text{diatom}}$  values in Lake Challa's 25,000-year record is 9.1‰, lying between  $-27.3$ ‰ and  $-36.4$ ‰ with a mean of  $-31.6$ ‰ and SD of 1.6‰ (Fig. 3a). Values are typically more



**Fig. 3.** Results of (a)  $\delta^{13}\text{C}_{\text{diatom}}$  showing raw data and a 10 sample running mean. (b)  $\delta^{13}\text{C}$  of bulk sediment total organic carbon (TOC). (c) The biomarker  $\delta^{13}\text{C}_{\text{n-C31}}$  used to indicate C4 grass species. (d) Percentages of biogenic silica (% BSi), (e) total organic carbon (TOC) and (f) total nitrogen (TN) and (g) the TOC/TN ratio. (h) The ratio of *Gomphocymbella* spp. to *Nitzschia* spp. expressed on a  $\log_{10}$  scale to emphasise the minor component.

negative than  $\delta^{13}\text{C}_{\text{bulk}}$  (Fig. 3b) by up to 6‰, although the difference varies with depth down-core. Both  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$  are strongly depleted probably reflecting the high DIC levels found in the lake and indicating an excess of  $\text{CO}_2$  available to algae for photosynthesis during much of the record. The most likely source of light carbon is respired  $\text{CO}_2$  and possibly  $\text{CH}_4$  rising up from the anoxic bottom waters. However, the broad similarity in absolute  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$  values indicates a strong contribution of diatom organic matter to the sediments. This is consistent with very high biogenic silica concentrations, derived from diatom remains, in many parts of the core (Fig. 3d).  $\delta^{13}\text{C}_{\text{diatom}}$  also shows considerable variation between adjacent depth intervals, equivalent to up to 0.7‰ per decade (Fig. 3a). While these high-frequency changes, substantially greater than analytical error ( $\pm 0.3\text{‰}$ ), on this time scale are possible, it is prudent to be cautious of compound errors resulting from low carbon percentages, cleaning procedures and sample homogenisation (Hurrell et al., 2011). Therefore, we focus on the millennial-scale temporal variation revealed by a 10-sample running mean through the  $\delta^{13}\text{C}_{\text{diatom}}$  data. The largest systematic shifts in  $\delta^{13}\text{C}_{\text{diatom}}$ ,  $\delta^{13}\text{C}_{\text{bulk}}$ ,  $\delta^{13}\text{C}_{\text{diatom}} - \delta^{13}\text{C}_{\text{bulk}}$ , TOC, TN and BSi values occurs between three time zones or periods dated to 25–15.8 ka, 15.8–5.5 ka and 5.5–0 ka BP, and around which we develop our discussion. In defining these zones we also acknowledge temporal changes in other climate-related variables such as  $\delta^{18}\text{O}_{\text{diatom}}$  (Barker et al., 2011), which support this tripartite division of the record and will be discussed below.

#### 4.1. Period 25.0–15.8 ka BP

The mean value of  $\delta^{13}\text{C}_{\text{diatom}}$  is  $-31.3\text{‰}$  in this time zone but values are substantially higher (less depleted) in several parts of it, with a maximum of  $-27.3\text{‰}$  at 21.6 ka BP (Fig. 3a). Sustained high values  $> -30\text{‰}$  are also recorded throughout the time periods 22–20.5 ka and 17.1–15.8 ka. These diatom data correspond to high mean  $\delta^{13}\text{C}_{\text{bulk}}$  values of  $-27.1\text{‰}$  for this section of the sequence. TOC and TN are typically low ( $< 5\%$  and  $< 0.5\%$  respectively) (Fig. 3e and f) whereas BSi is high, averaging 39.1% by weight (range 30–60%) of the sediment. Given these low TOC and TN values the TOC/TN ratio should be viewed cautiously, although it does have

pronounced minima at 22–20.5 ka and 17.1–16 ka coeval with high sustained values of  $\delta^{13}\text{C}_{\text{diatom}}$ . The fossil diatom assemblages are dominated by *Gomphocymbella* spp and this genus comprises the major part of the diatom biovolume (Fig. 3h). Sediment fluxes (Fig. 4) are also greater in this section of the core with peaks in BSi, TOC and TN corresponding to the high  $\delta^{13}\text{C}_{\text{diatom}}$  values at 20.5 ka and 16.8 ka.

#### 4.2. Period 15.8–5.5 ka BP

A brief period of low (more depleted)  $\delta^{13}\text{C}_{\text{diatom}}$  values occurs between 15.8 and 14.6 ka BP. Values then rise and fluctuate around a mean of  $-31\text{‰}$  throughout this central section of the record. In contrast,  $\delta^{13}\text{C}_{\text{bulk}}$  falls sharply by 4‰ at 15.8 ka and then remains around  $-30\text{‰}$  throughout both this central part and the upper section of the core. TOC and TN, which had started a gradual increase near 17 ka, reach peak values at 13.3 ka, fall back to near-minimal values from 12.8 to 10.0 ka, and then rise sharply to maximum values between 9.8 and 8.6 ka. Maximum fluxes of both TOC and TN are found at 10 ka BP (Fig. 4e and f). BSi fluxes are relatively low in this section. The TOC/TN ratio is slightly higher than in the preceding period (mean ratio 24), apart from a trough of lower values 12–13 ka. *Nitzschia* spp. are relatively more important in this section except for a short period around 10.5 ka corresponding to the episode of lowest TOC and TN values noted above. In terms of diatom biovolume, the larger-celled *Gomphocymbella* remain important from 15.8 to 10.0 ka then *Nitzschia* spp. become dominant until 5.5 ka BP.

#### 4.3. Period 5.5 ka BP to present

From 5.5 ka onwards,  $\delta^{13}\text{C}_{\text{diatom}}$  starts a prominent declining trend towards the lowest (most depleted) values of the entire sequence, reaching a minimum centred upon 2 ka. In contrast,  $\delta^{13}\text{C}_{\text{bulk}}$  increases to slightly higher values relative to the central section of the sequence. Throughout this upper zone, TOC and TN are both low (7–10% and 0.4–0.7% respectively) while BSi is mostly high (40%) (Fig. 3). The TOC/TN ratio is lower than in other sections of the core, with declining values throughout this uppermost zone.

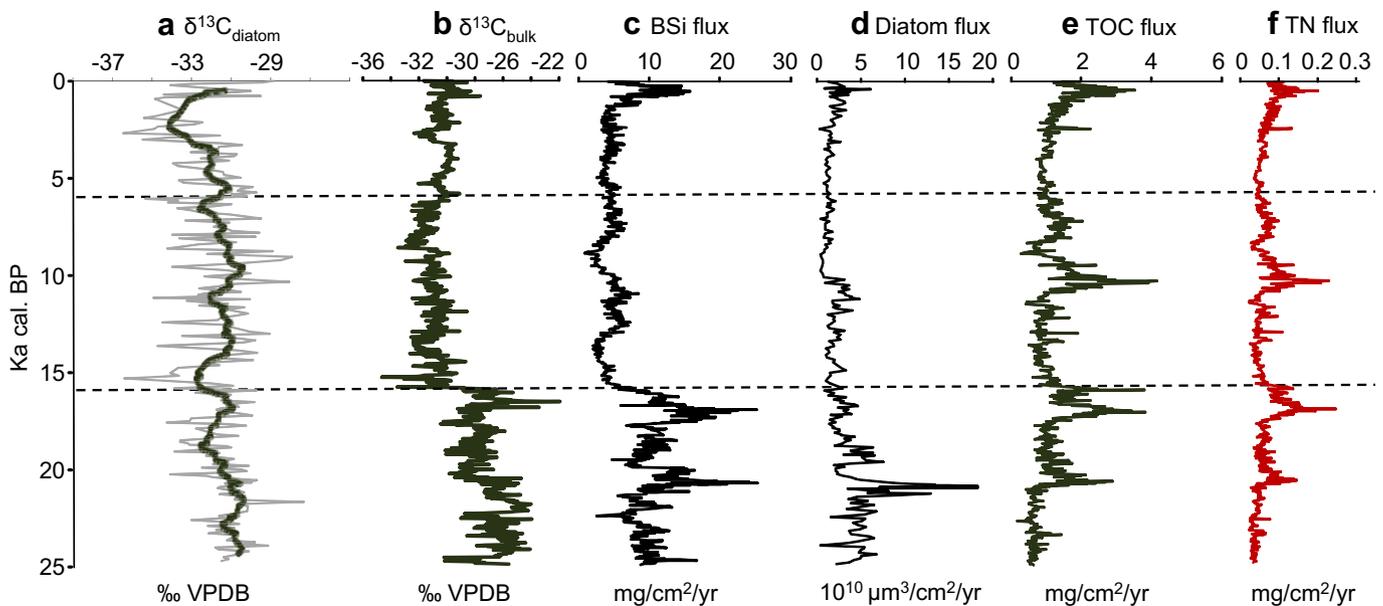


Fig. 4. (a)  $\delta^{13}\text{C}_{\text{diatom}}$  and (b)  $\delta^{13}\text{C}_{\text{bulk}}$  compared with fluxes of (c) biogenic silica (BSi), (d) diatom biovolume (e) total organic carbon (TOC) and (f) total nitrogen (TN).

The last 1 ka shows an increase in both  $\delta^{13}\text{C}_{\text{diatom}}$  and % BSi as well as in the fluxes of TOC, TN and BSi. Diatom assemblages are mixed throughout this zone (Milne, 2007) but the relative importance of *Gomphocymbella* spp. again increases gradually towards the top of the sequence.

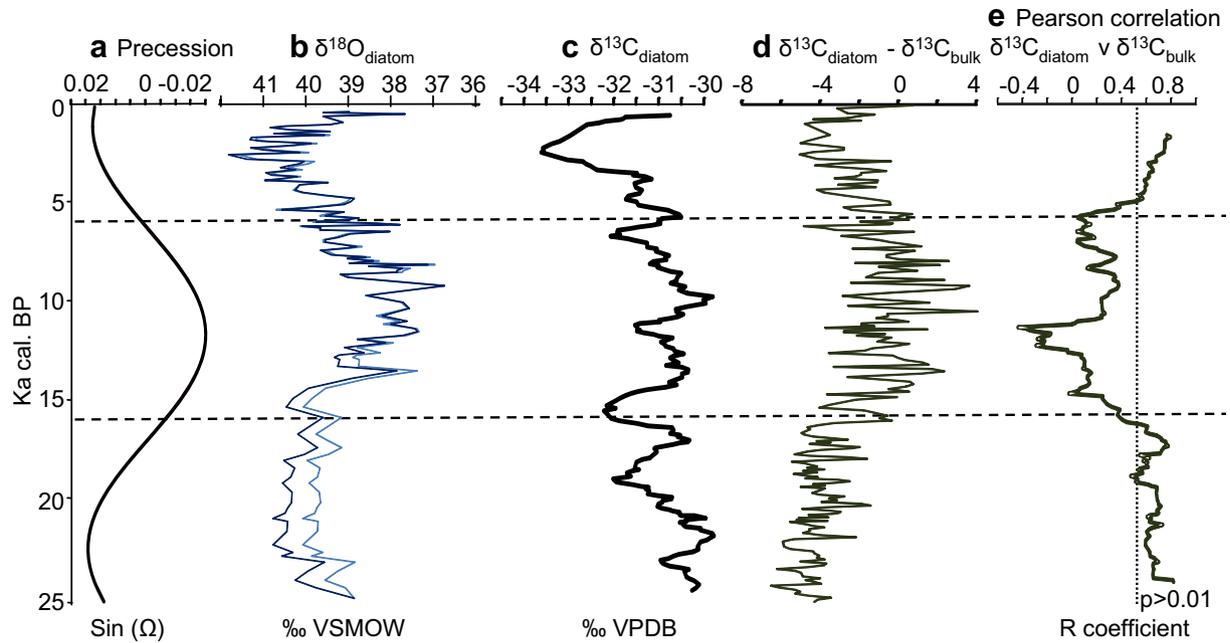
## 5. Discussion

Carbon dynamics in aquatic ecosystems over long time scales (millennia) are strongly modulated by climate, which ultimately controls terrestrial productivity, soil formation and nutrient and carbon fluxes from the catchment, as well as hydrology and physical effects on aquatic ecology and nutrient cycling. Independent measurement of all these variables is not possible, although we are able to compare our  $\delta^{13}\text{C}_{\text{diatom}}$  data to hydrological changes inferred from the oxygen-isotope composition of a subset of the same fossil diatom samples (Barker et al., 2011). In this (nearly) closed-basin lake, changes in  $\delta^{18}\text{O}_{\text{diatom}}$  (Fig. 5b) are driven largely by the climatic balance between precipitation and evaporation (P/E ratio), with results biased towards the period of maximum diatom growth during the dry season of peak evaporation. Therefore, in Lake Challa,  $\delta^{18}\text{O}_{\text{diatom}}$  is a proxy for the length and intensity of the dry season balanced against the amount of annual rainfall. During the last 15.8 ka, a broadly negative relationship occurs between  $\delta^{18}\text{O}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{diatom}}$  with relatively dry (wet) periods corresponding to low (high)  $\delta^{13}\text{C}_{\text{diatom}}$ . Moreover, a long-term decline occurs in  $\delta^{13}\text{C}_{\text{diatom}}$  during the Holocene from peak values near 10 ka to the pronounced minimum at 2 ka (when enriched  $\delta^{18}\text{O}_{\text{diatom}}$  values suggests extreme seasonal drought) followed by a full recovery during the last millennium. Despite these apparent similarities, the relationship between the aquatic ecosystem and climate is indirect and instead is intimately coupled with biogeochemical controls exerted by the terrestrial ecosystem and lake dynamics. None of the relationships between  $\delta^{13}\text{C}_{\text{diatom}}$  and various supporting proxies are simple linear correlations extending throughout the whole 25,000-year record, yet some concordance is noted for key periods. We investigated these transient correlations further, using Pearson correlations ( $R$ ) derived from 3000-year moving windows (Fig. 5e). Tri-millennium scale correlations between  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$  also suggest three major phases in

the history of the lake's carbon cycle that map onto the discussed time zones.

Dry conditions were experienced in much of East Africa during the Last Glacial Maximum (LGM) (Barker and Gasse, 2003) and also at Lake Challa the P/E balance (as indicated by  $\delta^{18}\text{O}_{\text{diatom}}$ ) was low during much of this period, especially from 23 ka to 15 ka (Barker et al., 2011). This relative aridity can be expected to have reduced the terrestrial above-ground biomass, impoverished soils and restricted transport of biogenic carbon to the lake. Seismic data suggest that the lake experienced a lowstand (Moernaut et al., 2010), probably enhancing mixing and internal recycling of deep-water nutrients and carbon. Modest but significant climatic cooling in equatorial East Africa during the glacial period (Sinninghe Damste et al., in press), as also proposed for the wider region (Powers et al., 2011; Tierney et al., 2008) would have further promoted deep mixing. Strong mixing at Lake Challa is indicated by the dominance of *Gomphocymbella* over *Nitzschia* spp., especially if the former taxon occupied a tychoplanktonic niche and the latter taxa more typically planktonic.

The carbon cycle of the lake responded to this (at least seasonally) arid climate and associated hydrological situation. From 25 ka to 15.8 ka BP,  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$  were positively correlated ( $R$  values 0.5 to 0.8,  $p > 0.01$ ), indicating that high diatom carbon biomass was depleting the lake's DIC, a scenario supported by high BSi values, high diatom biovolume and the relative dominance of the large-celled *Gomphocymbella* at this time. A low flux of both TOC and TN may suggest a restricted terrestrial carbon input or, alternatively, their more advanced oxidation. Remaining vegetation within the Challa crater consisted almost exclusively of drought-adapted  $\text{C}_4$  grasses (Fig. 3c; Sinninghe Damste et al., 2011) consequently the high  $\delta^{13}\text{C}_{\text{bulk}}$  values partly reflect the high values associated with these taxa. It is likely that the high  $\delta^{13}\text{C}_{\text{diatom}}$  values, which we interpret as primarily a result of high diatom productivity, are accentuated during the glacial period by the relatively enriched nature of  $\text{C}_4$ -derived carbon entering the lake in particulate or dissolved form and being made available in the DIC pool. Maxima in  $\delta^{13}\text{C}_{\text{diatom}}$  and other productivity indicators at 21.4 ka and 16.7 ka are coincident with the LGM and Heinrich event 1 (H1) thought to be particularly dry intervals in this region (Barker and Gasse, 2003; Thomas et al., 2012).



**Fig. 5.** Orbital precession plotted on a reversed scale (Berger and Loutre, 1991). Oxygen-isotope ratio ( $\delta^{18}\text{O}$ ) in diatom silica (grey), with a correction for reduced temperature during the glacial period (black) (Barker et al., 2011), plotted against a reversed axis. The 10-sample running mean of  $\delta^{13}\text{C}_{\text{diatom}}$ . The difference between  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$ . Pearson correlation coefficients ( $R$ ) between  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$ , based on 3000-yr moving windows of the respective data series.

For much of the period from 15.8 ka to 5.5 ka BP there is no, or limited, correlation between  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$ , while relatively low  $\delta^{18}\text{O}_{\text{diatom}}$  values over this period suggest a strongly positive water balance. The 4‰ negative shift in  $\delta^{13}\text{C}_{\text{bulk}}$  that occurs at 15.8 ka, is thought to reflect the establishment of a forest fringe with mixed C3/C4 vegetation inside the crater (Sinninghe Damste et al., 2011). This vegetation change brings the  $\delta^{13}\text{C}_{\text{bulk}}$  and  $\delta^{13}\text{C}_{\text{diatom}}$  values closer together (Fig. 5d:  $\delta^{13}\text{C}_{\text{diatom}}$  minus  $\delta^{13}\text{C}_{\text{bulk}}$  approaches zero). However, lack of correlation between variations in  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$  suggests that carbon supply to the lake was sufficient to satisfy demand from the aquatic primary producers, without measurably depleting DIC. Pervasive meromixis enabling the accumulation of high DIC concentrations in the hypolimnion would help sustain dissolved carbon stocks throughout the lake providing it was released during seasonal deep mixing events. A higher TOC/TN ratio implies a lower proportion of algal material in the sediment's total organic carbon. Carbon cycling in Lake Challa during the dry Younger Dryas period (Verschuren et al., 2009) largely resembled that of the LGM and H1, with high  $\delta^{13}\text{C}_{\text{diatom}}$  at the beginning and end of the period, although notable fluctuations within the YD also occurred. The peak in  $\delta^{13}\text{C}_{\text{diatom}}$  at 9.8 ka, coincides with lowest  $\delta^{18}\text{O}_{\text{diatom}}$  values representing the most positive water balance, and suggests aquatic productivity was high, even though the relative algal contribution to the lake's carbon cycle was reduced. We infer that under these wet conditions, standing terrestrial biomass and the soil carbon pool must have been enhanced, with rapid delivery of carbon (as POC and DOC) to the lake. During this interval both the particulate carbon and nitrogen fluxes to the sediments increase, consistent with an enhanced delivery of autochthonous materials. The increase in TN probably also indicates more available nitrogen to the aquatic ecosystem, thereby changing nutrient resource ratios and may subsequently have contributed to a shift from *Gomphocymbella* to *Nitzschia* dominance (Fig. 4h). Stronger stratification would also favour needle-like *Nitzschia* spp. which could be easily lost from the plankton if mixing had been strong. We also note that from the base of the middle period (15.8 ka BP)

until 8 ka BP,  $\delta^{13}\text{C}_{\text{diatom}}$  and %BSi are inversely correlated. One explanation is that strong stratification weakened the internal supply of dissolved silica to the epilimnion. A Si:N ratio shift in favour of non-siliceous algae emphasises the need to consider the contribution of all primary producers and their individualistic response to multiple biogeochemical cycles and limnological conditions.

From 5.5 ka BP to the present, positive correlation between  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$  develops again with  $R$  values of +0.4 to +0.8 indicating increased demand by aquatic productivity in relation to the available lake carbon pool. TOC/TN declined throughout this period, supporting our interpretation of a greater relative contribution of algal organic matter to sedimentary organic carbon. Strongly depleted  $\delta^{13}\text{C}_{\text{diatom}}$  values indicate that aquatic productivity fell sharply around 2 ka, before recovering during the last millennium. Similarly, increasing  $\delta^{18}\text{O}_{\text{diatom}}$  values indicate a decline in P/E to a minimum at 2 ka. The dramatic decline in  $\delta^{13}\text{C}_{\text{diatom}}$  during this episode of strong seasonal drought is intriguing. Release of DIC from the hypolimnion during strong mixing may have helped satisfy demand by the diatoms for carbon and depress  $\delta^{13}\text{C}_{\text{diatom}}$  values, provided that their productivity was modest and not exerting a large demand on the lake carbon pool. Relatively low BSi concentration and flux during this interval does indicate limited diatom productivity (Figs. 3 and 4), probably as a result of biogenic silica and other nutrients being held in soils and not released to the lake.

The multi-proxy data available for Lake Challa illustrate the complex interaction of the lake carbon cycle with climate, terrestrial vegetation, nutrient sources and aquatic productivity at different temporal scales. When viewed across the entire 25 ka record, the absolute difference between the  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$  values (Fig. 5d) has a strikingly similar pattern to the  $\delta^{18}\text{O}_{\text{diatom}}$  record, with greatest divergence during intervals of high seasonal aridity. This is likely to be an indirect relationship and requires solid understanding of linkages between the terrestrial and aquatic ecosystems. Under dry (and probably windy) conditions the lake would be better mixed, enhancing

nutrient recycling and algal processing of DIC, whereas under wetter climates the carbon delivered to the lake exceeds demand. At shorter, century-to-millennium time scales, especially when terrestrial carbon fluxes are limited, aquatic productivity imposes a measurable influence on the lake's carbon cycle as is displayed by positive correlations between  $\delta^{13}\text{C}_{\text{diatom}}$  and  $\delta^{13}\text{C}_{\text{bulk}}$ . Conversely, if terrestrial carbon and nutrient supply is high, then high aquatic productivity can be sustained by external delivery and internal regeneration from the lower water column during seasonal mixing, with little evidence for modification by the lake ecosystem. This finding would not be evident from more traditional sedimentary proxies such as  $\delta^{13}\text{C}_{\text{bulk}}$ , where changes in terrestrial supply overwhelm any aquatic productivity signal.

Lakes respond individually to changes in the carbon cycle, and this is most apparent at shorter temporal scales where catchment processes dominate. Unless major landscape changes are activated, it is unlikely that concordance will be found between regional lake catchments. Through a longer lens, the carbon-cycle changes reconstructed here echo Kilham's 'endless summer' hypothesis (Kilham and Kilham, 1990). In the East African tropics, lakes remained highly productive despite their great depth during the early Holocene humid period, as a result of nutrient replenishment from decaying terrestrial vegetation, and partial seasonal turnover. Deep lakes today such as Kivu, Tanganyika and Malawi all have large carbon stores in their lower waters (Pasche et al., 2009). These lakes may have been hotspots for carbon emission to the atmosphere during the early Holocene, if enhanced productivity at that time did not keep pace with biogenic carbon supply from terrestrial catchments and release from depth. It is likely that Lake Challa, and other much larger water bodies made an enhanced contribution to atmospheric carbon, despite also capturing particulate carbon into sedimentary storage at a greater rate. During the drier glacial and Late Holocene the land-to-lake carbon transfer probably slowed and more carbon was recycled from within the lake.

## 6. Conclusions

Understanding the carbon cycle of lakes requires an appreciation of the balance of 'demand' exerted by lake productivity regulated by nutrient availability, and changes in the amount and nature of carbon supplied from the catchment. Periods of disequilibria between the carbon cycled through terrestrial ecosystems and that consumed by algae could lead to a net surplus in the lake and enhanced release to the atmosphere. Diatom carbon isotopes offer a complementary approach to other indicators of palaeoproductivity in examining long-term fluctuations in a lake's carbon budget. They show that even in sediments dominated by authigenic material as at Lake Challa, carbon isotope records on bulk organic matter are primarily a reflection of catchment vegetation and are a relatively blunt tool for reconstructing lake productivity. Unlike some marine records, these lake data do not display any direct response to changes in atmospheric  $\text{CO}_2$  concentrations or even long-term glacial-interglacial climate variation, but do show responses to local landscape and related biogeochemical changes at millennial scales. Such investigations can demonstrate how the balance between carbon supply and demand has changed through time and provide insights into Late Quaternary carbon emission from lakes.

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