



Influence of the ratio of planktonic to benthic diatoms on lacustrine organic matter $\delta^{13}\text{C}$ from Erlongwan maar lake, northeast China

Luo Wang^{a,*}, Anson W. Mackay^b, Melanie J. Leng^{c,d}, Patrick Rioual^a, Virginia N. Panizzo^b, Houyuan Lu^a, Zhaoyan Gu^a, Guoqiang Chu^a, Jingtai Han^a, Christopher P. Kendrick^d

^a Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

^b Environmental Change Research Centre, Department of Geography, UCL, Gower Street, London WC1E 6BT, UK

^c Department of Geology, University of Leicester, Leicester LE1 7RH, UK

^d NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, Nottingham NG12 5GG, UK

ARTICLE INFO

Article history:

Received 17 March 2012

Received in revised form 16 September 2012

Accepted 24 September 2012

Available online 2 October 2012

ABSTRACT

Carbon isotope ratio ($\delta^{13}\text{C}_{\text{org}}$) values of organic matter in lake sediments are commonly used to reconstruct environmental change, but the factors which influence change are varied and complex. Here we report $\delta^{13}\text{C}$ values for sediments from Erlongwan maar lake in northeast China. In this record, changes in $\delta^{13}\text{C}$ cannot be explained by simple changes in aquatic productivity. Instead, values were likely influenced by differences in the ratio between planktonic and benthic algae, as indicated by the remains of diatoms. This is because the variation of $\delta^{13}\text{C}_{\text{org}}$ in algae from different habitats is controlled by the thickness of the diffusive boundary layer, which is dependent on the turbulence of the water. Compared with benthic algae, which grow in relatively still water, pelagic algae are exposed to greater water movement. This is known to dramatically reduce the thickness of the boundary layer and was found to cause even more severe $\delta^{13}\text{C}$ depletion. In Erlongwan maar lake, low values were linked to the dominance of planktonic diatoms during the period commonly known as the Medieval Warm Period. Values gradually increased with the onset of the Little Ice Age, which we interpret as being driven by an increase in the proportion of benthic taxa, due to effect of the colder climate. The increase in planktonic diatoms at the end of the Little Ice Age, linked to higher temperature and a reduction in ice cover, resulted in a further decline in $\delta^{13}\text{C}_{\text{org}}$.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon isotope ratio ($\delta^{13}\text{C}$) values are an important proxy for reconstructing environmental change from lakes, such as changes in temperature, precipitation patterns and evaporation. These changes are all indirectly linked to the carbon cycle (Leng and Marshall, 2004). However, interpretation of $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{org}}$) from bulk organic matter (OM) in lake sediments is complex and dependent on many factors. It is commonly used in palaeolimnological studies to determine OM sources in a lake, e.g. allochthonous vs. autochthonous sources (Meyers, 1994), the source of dissolved carbon used by aquatic plants (Leng et al., 2006), productivity (Leng and Marshall, 2004) and catchment soil respiration (Hammarlund, 1993; Mackay et al., 2012), as well as anthropogenic carbon released into the environment because of fossil fuel combustion (the Suess effect; Keeling, 1979). As far as we are aware, little work has been done to explore the influence of varying

ratio of phytoplankton and benthic algae on $\delta^{13}\text{C}$ in lake sediments, despite the environmental importance that changes in this ratio represent in terms of lake level variability, hydrodynamics of the water column and habitat availability (France, 1995).

Here we discuss the possible reasons for $\delta^{13}\text{C}_{\text{org}}$ variability in the sedimentary record from Erlongwan maar lake (EML) over the past 1000 yr, using, proportion of sedimentary total organic carbon (TOC%), TOC flux, C/N ratio, and the ratio between planktonic and benthic algae as indicated by changes in the composition of diatom assemblages and diatom flux.

Diatoms are characterized by siliceous cell walls, which are generally well preserved as sedimentary fossils (Battarbee et al., 2001). In lakes, diatoms are commonly classified as planktonic, i.e. suspended, unattached in open water, or benthic (i.e. living on the bottom of the lake floor)/periphytic (i.e. attached to substrates such as stones, aquatic vegetation and sand). These habitats have different micro-environmental conditions, such as light availability and exposure to water turbulence, which control nutrient availability. We discuss how turbulence may play an important role in controlling carbon isotope fractionation in different diatom habitats.

* Corresponding author. Tel.: +86 10 82998261.

E-mail address: wangluo@mail.iggcas.ac.cn (L. Wang).

2. Materials and methods

There are eight maar lakes in the Long Gang Volcanic Field (LGVF) region in Jilin Province, NE China. Our study focused on Lake Erlongwan (EML) 42° 18'N, 126° 21'E, a dimictic lake, that occupies an area of ca. 0.3 km² at 724 m above sea level (Fig. 1). It is a closed lake, with a small catchment (0.4 km²) and no natural inflow or outflow (Mingram et al., 2004).

The modern natural vegetation in the LGVF is typical of the temperate mixed coniferous–deciduous forest zone (Editorial board for Flora of China, 1995). In this forest, the conifer *Pinus koraiensis* is dominant. The late Holocene pollen assemblage from EML (Li et al., 2012) also reflects the dominance of a mixed conifer–hardwood and deciduous forest around the EML region. Over the last 1000 yr, *Pinus* was the dominant conifer, while major broad-leaved deciduous trees included *Quercus*, *Betula*, *Juglans*, *Ulmus*, *Carpinus*, *Corylus*, *Tilia* and *Fraxinus*.

In 2001, a 66.5 cm long core was extracted from the central, deepest region of the lake at a water depth of 36 m. The core was laminated from 0 to 50 cm. The sediments are composed of detrital mud with varying amounts of OM. Between 51 and 66.5 cm the sediments are graded, likely representing a rapidly deposited sediment slump (Frank, 2007). We focus therefore only on the laminated record of the top 50 cm.

The age model was developed by combining results from ²¹⁰Pb and ¹⁴C radiometric dating (Fig. 2). The activity of ¹³⁷Cs and ²¹⁰Pb were measured using gamma spectrometry with a low background well-type Ge detector (EGPC 100P-15R) at the Institute of Geology and Geophysics, Chinese Academy of Science, Beijing. The ¹⁴C date (Poz-19967) was analysed on a *Pinus* macrofossil found at the bottom of the core (49.5 cm) using accelerator mass spectrometry (AMS). AMS gave a date of 1045 ± 30 ¹⁴C yr BP (Fig. 2), which, after two sigma calibration, gave an age range of 900–1030 AD (Wang et al., 2012b). The ages of the samples below those dated with ²¹⁰Pb and above the radiocarbon date at 49.5 cm were linearly interpolated. Linear extrapolation was also used to extend the age model to the base of the core at ca. 980 AD (Fig. 2).

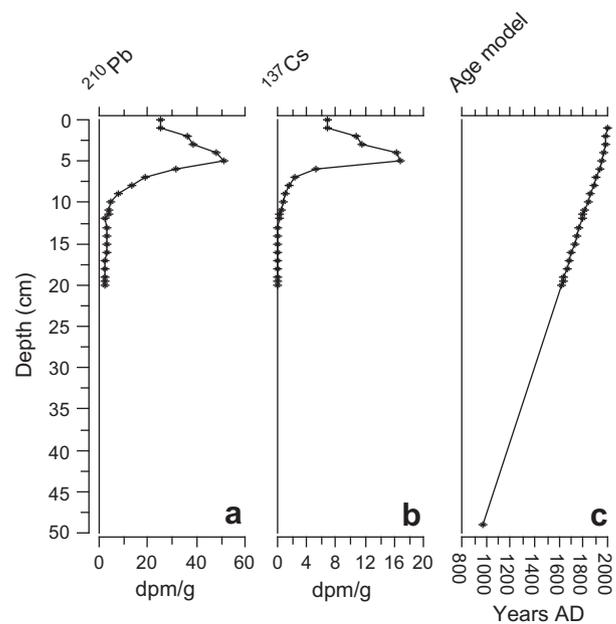


Fig. 2. EML short core ¹³⁷Cs–²¹⁰Pb_{ex} age model diagram. (a and b) activity of ²¹⁰Pb and ¹³⁷Cs, and (c) ²¹⁰Pb, ¹³⁷Cs and AMS ¹⁴C depth–age model.

Diatom samples were prepared according to standard methods (Battarbee et al., 2001; Li et al., 2009). Diatom concentration (valves/g) were calculated by way of addition of divinylbenzene microspheres (Battarbee and Kneen, 1982). Diatom identification followed the guidelines set out by Krammer and Lange-Bertalot (1986). We chose to merge *Discostella pseudostelligera*, *D. woltreckii* and *D. stelligera* into “*Discostella* species” because these three taxa were difficult to distinguish consistently under light microscopy (Haworth and Hurley, 1984; Tanaka, 2007). The diatom data are displayed as relative abundance (%) and total dia-

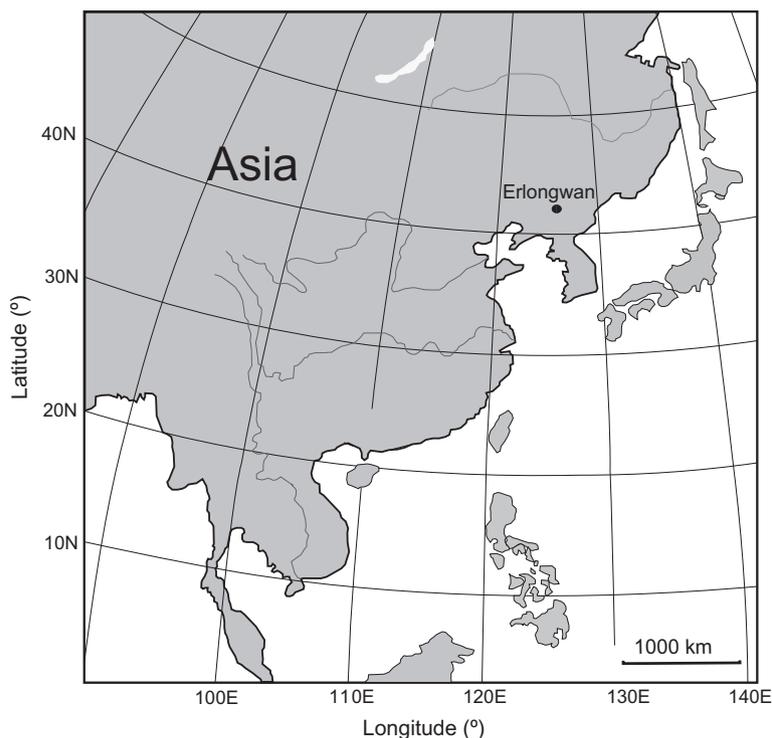


Fig. 1. Location of Erlongwan maar lake in NE China.

tom flux. The ratio values of planktonic to benthic diatoms were calculated using the formula:

$$P/B \text{ ratio} = \frac{\sum_{\text{planktonic taxa}}}{\sum_{\text{planktonic} + \text{benthic taxa}}}$$

Carbonates were removed by leaving the samples overnight in 50 ml of 5% HCl. TOC and total nitrogen (TN) were measured using a Carlo Erba elemental analyser (with internal acetanilide standards for calibration). TOC% was calibrated to TOC flux using the sedimentation rate and dry bulk density. Replicate analyses of well mixed samples showed that precision was ca. $\pm 0.1\%$ (1 SD). C/N values were derived from these data. Stable isotope analysis ($^{13}\text{C}/^{12}\text{C}$) was undertaken via combustion using a Carlo Erba NA1500 (series 1) on line to a VG Triple Trap and Optima dual inlet mass spectrometer. The $\delta^{13}\text{C}$ values were calculated to the Vienna Pee Dee Belemnite (VPDB) scale using a within-run laboratory standard calibrated against NBS19 and NBS22. Analyses of replicates revealed a precision of ca. $\pm 0.1\%$ (1 SD). Measurements were made at the NERC Isotope Geosciences Laboratory, in Keyworth, UK.

3. Results

Organic content of the sediments (inferred from TOC flux) is above average for the core (0.012 g/cm²/y) from 50 to 47 cm (ca. 970–1080 AD) and increased to a peak between 41 and 36 cm (ca. 1070–1280 AD; Fig. 3). Thereafter, TOC flux declined steadily, concurrent with a decrease in diatom flux (Fig. 3). TOC flux values subsequently increased at 10 cm (ca. 1900 AD), as did diatom flux and the proportion of planktonic diatom species (Fig. 3). TOC correlated most significantly with TN flux (0.990**; Table 1), and significantly positively with diatom flux (0.747**) and P/B ratio (0.422*), i.e. increasing abundance of planktonic diatoms (Table 1; Fig. 4). C/N values fluctuated between 10.6 and 15.6. The highest C/N values occurred between 26 and 13 cm (ca. 1500–1780 AD; Fig. 3).

The $\delta^{13}\text{C}$ values fluctuated between -29.3% and -28.0% from 50 cm to 17 cm, but showed a gradual and distinct increase (3.4‰) from 33 cm (-29.0%) to 12 cm (-25.6% ; ca. 1350–1800 AD; Fig. 3). From 33 cm to 12 cm (ca. 1350–1800 AD), increasing $\delta^{13}\text{C}$ values occurred as TOC flux, diatom flux and P/B ratio declined (Fig. 3). For the whole profile, $\delta^{13}\text{C}$ and TOC flux are negatively correlated (-0.314^{**} ; Table 1). Above 12 cm (after ca.

1800 AD), $\delta^{13}\text{C}$ values rapidly declined to the lowest values in the profile (ca. -29.8%), between 10 cm and 9 cm, coincident with a distinct increase in the proportion of planktonic diatom species. More specifically, the shift in diatom composition appeared to be driven by a rapid decline in *Discostella* species and an increase in the planktonic species *Puncticulata praetermissa* and *Asterionella formosa* (Fig. 5). Overall, $\delta^{13}\text{C}$ values correlated most significantly with P/B ratio (-0.627^{**} ; Table 1; Fig. 4); $\delta^{13}\text{C}$ values in the uppermost sediments, spanning the last 50 yr (ca. 6 cm), increased up to the time the core was taken (Fig. 3), coincident with the return to dominance of the *Discostella* species (Fig. 5).

4. Discussion

All the samples have $\delta^{13}\text{C}$ values below -25% (Fig. 3), indicating the dominance of C₃ plants as the principal carbon source to EML. C₃ plants utilize RuBisCO (ribulose-1,5-bisphosphate carboxylase) to fix atmospheric CO₂, which results in $\delta^{13}\text{C}$ values between -22% and -33% (O'Leary, 1981). This photosynthetic pathway is the most common among plants and is used by most trees, shrubs, aquatic vegetation and algae. Pollen evidence from the sediments highlights the idea that extensive pine and deciduous forest cover has persisted throughout the past 1000 yr (Mingram et al., 2004).

The $\delta^{13}\text{C}$ values of bulk sediments cannot be used to distinguish between algae and terrestrial C₃ plants (Meyers and Lallier-Vergès, 1999), so C/N ratio in lake sediments are commonly used to assess the relative importance between allochthonous and autochthonous OM sources (Meyers, 1994); algae generally contain only a small amount of cellulose or lignin (both carbon rich; Leng et al., 2006). Fig. 3 shows that all the samples have C/N ratio < 16, with an average value of 12.8. It is likely that the plant OM in EML is derived from a mixture of sources, especially algae (with relatively low C/N ratio 5–10; Meyers and Lallier-Vergès, 1999) and aquatic vegetation (both submerged and floating) with relatively high C/N ratio (ca. 20 to 30; Fellerhoff et al., 2003) and only a small contribution from terrestrial vegetation (C/N between 20 and 160; Meyers and Lallier-Vergès, 1999).

OM input from terrestrial vegetation is likely to be low because TOC and diatom flux are highly and significantly, correlated (0.747**, Table 1 and Fig. 4), which indicates that algae are a major component of OM in the core. Secondly, the highest C/N values between 28 and 12 cm (1500–1800 AD; Fig. 3) are unlikely caused by

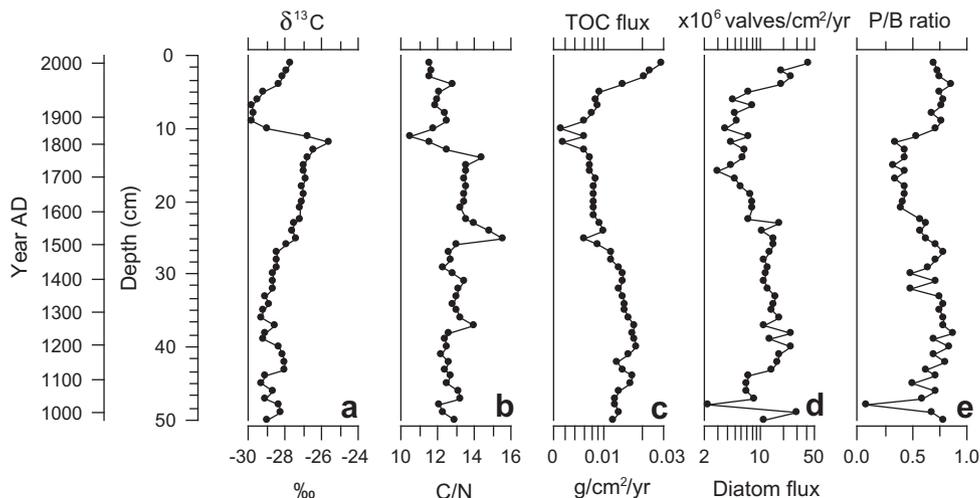


Fig. 3. Stratigraphic profile of organic geochemical variables (a) $\delta^{13}\text{C}$, (b) C/N, (c) TOC flux, and biological indicators, (d) diatom flux, and (e) the ratio of planktonic to benthic diatoms.

Table 1
Pearson product moment correlation coefficients.

	$\delta^{13}\text{C}$	C/N	P/B_ratio	Diatom_flux	TN_flux	TOC_flux
$\delta^{13}\text{C}$	1					
C/N	0.201	1				
P/B_ratio	-0.627 ^{a**}	-0.179	1			
Diatom_flux	-0.105	-0.154	0.508 ^{a**}	1		
TN_flux	-0.298 ^{b*}	-0.369 ^{a**}	0.410 ^{a**}	0.748 ^{a**}	1	
TOC_flux	-0.314 ^{b*}	-0.256	0.422 ^{a**}	0.747 ^{a**}	0.990 ^{a**}	1

^a **Correlation significant at 0.01 level (2-tailed).

^b *Correlation significant at 0.05 level (2-tailed).

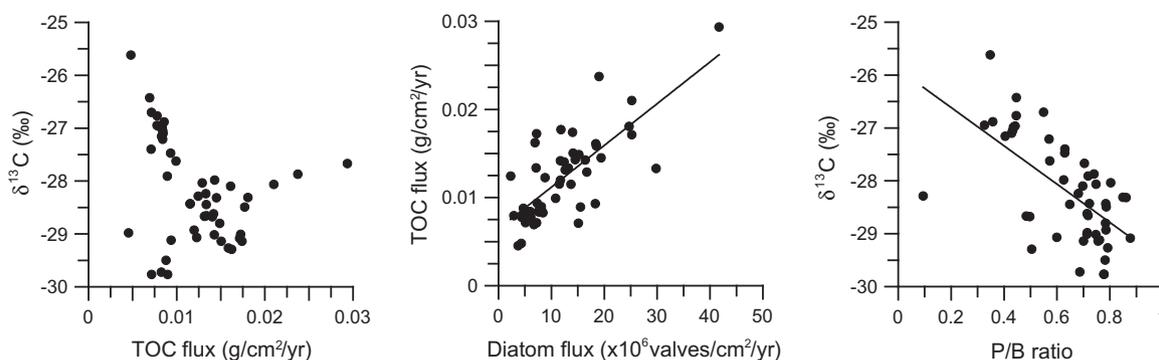


Fig. 4. Scatter plots showing strong correlation between (a) TOC flux and $\delta^{13}\text{C}$, (b) diatom flux and TOC flux, and (c) planktonic to benthic (P/B) ratio and $\delta^{13}\text{C}$.

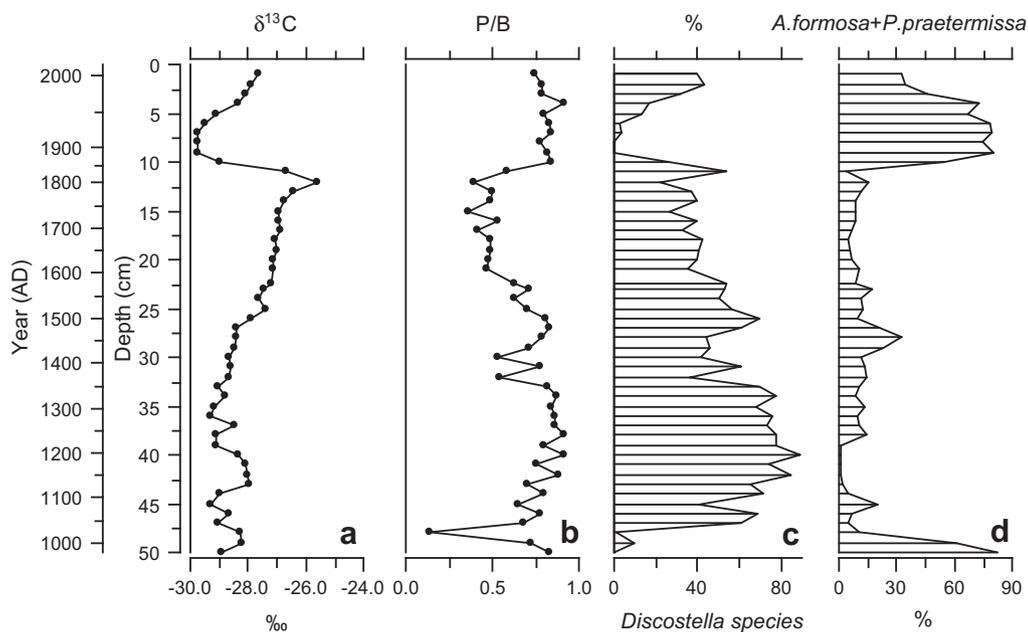


Fig. 5. (a) $\delta^{13}\text{C}$, (b) ratio of planktonic to benthic diatoms, (c) proportion (%) of *Discostella* species complex, and (d) combined relative abundance of *P. praetermissa* and *A. formosa*.

increased in-wash of terrestrial vegetation to the lake, because pollen concentration data suggest a period of relatively drier summers and a less dense vegetation cover (Mingram et al., 2004; Li et al., 2012) during that interval. Previous studies of EML diatom data (Wang et al., 2012b) and historical documents relating the frequency of snow events in NE China (Chu et al., 2008) shows that a cold climate prevailed for this interval. Third, although the abnormal changes in ^{210}Pb and the high sediment accumulation rate at the top of the core (5–0 cm; Fig. 2) indicate that there was an increase in run-off input to the lake during the most recent part of

the core, the values for the C/N ratio are still low (Fig. 3), indicating that the proportion of allochthonous input to the lake has remained small.

Relatively high C/N values during the cold period (1500–1800 AD) do coincide with an increase in benthic taxa and a concomitant decline in P/B ratio, which were controlled by the duration of ice cover. Longer ice cover leads to a restriction in the development of planktonic communities during cold periods. Unlike planktonic taxa, benthic taxa, such as the fragilarioid species, increase between 28 and 12 cm in EML (Wang et al.,

2012b). This is because spring melting does allow suitable benthic and periphytic habitats to develop in narrow ice-free moats throughout the littoral zone (Smol, 1983). These species are common in high latitude and alpine lakes, which are characterized by long seasonal ice cover (e.g. Douglas and Smol, 1999; Enache et al., 2011; Mackay et al., 2012). In EML we suggest that the decline in P/B ratio and higher C/N values (Fig. 3) are due to persistent growth of aquatic vegetation with C/N values between 20 and 30 along the littoral zone of the lake, leading to the increase in the relative abundance of OM derived from aquatic vegetation.

Primary production in lakes can influence the changes in OM $\delta^{13}\text{C}$ values. Primary production through time can be inferred using TOC (Leng and Marshall, 2004). A long decline in TOC flux occurs between 33 and 12 cm (ca. 1350 to ca. 1800 AD; Fig. 3), indicating that the productivity of algae and aquatic vegetation decreased. TOC can also vary due to changing sedimentation rate. Here we can only provide a constant sediment accumulation rate from 50 to 20 cm because of only one ^{14}C date anchoring the base of the core (Fig. 2), so we are not able to resolve this issue directly from the data. However, a previous Holocene core taken from EML was reported to be varved, with a relatively constant sedimentation accumulation rate of ca. 0.06 cm/yr over the past 1000 yr (You et al., 2008), which is very similar to the sedimentation rate estimated in this study (0.05 cm/yr). In addition, it is possible to exclude the impact of sediment rate on TOC% for the radiometrically dated top of the core between 20 and 0 cm. The data also show that the changes in TOC flux are very similar to changes in diatom flux, likely indicating a link between the two (Fig. 3). Between 50 and 12 cm, TOC flux is also almost concurrent with the change in diatom flux and their correlation over the whole 1000 yr record is high (0.747). It is therefore likely that the changes in TOC flux are real and not caused by changing sedimentation rate, and therefore that they can be used as indicator of aquatic productivity.

Enhanced productivity in lakes results in dissolved CO_2 becoming limited; algae can adapt by switching to the utilisation of HCO_3^- as carbon source, resulting in an increase in $\delta^{13}\text{C}$. However, it is noticeable in our record that the sustained decline in TOC flux and diatom flux is concurrent with an equally sustained increase in $\delta^{13}\text{C}$ values of ca. 3.7‰. It is unlikely that increasing $\delta^{13}\text{C}$ values in EML sediments were caused by declining aquatic productivity.

Other factors which may cause increasing $\delta^{13}\text{C}$ values include gradual maturation of lakes and changes in catchment vegetation. As lakes mature, ^{12}C -enriched OM is transported to bottom sediments (Meyers and Lallier-Vergès, 1999). However, the changes in EML are quite abrupt, e.g. at 11 cm and, moreover, the increase in values only occurs during a specific timeframe, and so is unlikely to be due to lake maturation. In the catchment, the development of stable mature soils can result in increased soil respiration and the supply of ^{13}C -depleted dissolved CO_2 to lakes, leading to lower ^{13}C values (Hammarlund, 1993). Conversely, increasing ^{13}C values may be interpreted to be due to forest retreat and subsequent reduction in catchment soil respiration. At EML, there is evidence for a decline in tree pollen concentration during the period of increasing ^{13}C values (Li et al., 2012), but almost no change in the composition of pollen assemblage took place. This suggests that the vegetation cover in the region did not change to such an extent that it could lead to an increase in $\delta^{13}\text{C}$ -depleted dissolved CO_2 .

Another potential influence on sedimentary ^{13}C values is the difference in the proportion of phytoplankton and benthic microalgae (France, 1995), assuming much of the sedimentary OM is derived from the algae. France (1995) collated literature data on $\delta^{13}\text{C}$ for marine and freshwater benthic and planktonic algae and found that the average value for benthic algae in lakes was $-26\text{‰} \pm 3$, whereas it was lower at $-32\text{‰} \pm 3$ for planktonic algae, an average difference of ca. 6‰. Doi et al. (2009) also found

significant differences between $\delta^{13}\text{C}$ values of plankton (lower) and benthic (higher) microalgae sampled simultaneously across a range of lakes. These differences may be explained by the diffusive boundary layer effect (Jørgensen and Revsbech, 1985). The boundary layer is caused by the viscous properties of water and is composed of a film of water that sticks to the surface of the solid (e.g. sediment, plants, biofilm or detritus) and does not participate in the general circulation of the surrounding water. Its thickness can vary from 0.2 to >1 mm and water turbulence above the solid–water interface has a major influence on the thickness of the boundary layer (Jørgensen and Revsbech, 1985). The diffusive boundary layer constitutes a transfer resistance for fluxes of dissolved organic compounds, inorganic ions and gases such as CO_2 and O_2 across the solid–water interface, and is especially limiting for plants and algae at high uptake rate (Jørgensen and Revsbech, 1985). A thick boundary layer, because it leads to an entrapment of otherwise expelled ^{13}C , results in more positive $\delta^{13}\text{C}$ values for the plants or algae (Jørgensen and Revsbech, 1985; Doi et al., 2009).

In the EML sediments, diatoms fall into three important functional groups, related to their preferred habitat. Benthic and periphytic diatoms, growing on the lake bottom or attached to a sub-stratum are generally less exposed to turbulent water, and so likely have a thick boundary layer. By contrast, planktonic diatoms, as they grow floating and unattached in the open water, have a thinner boundary layer. Among planktonic diatoms, small species such as *D. stelligera* and *D. pseudostelligera*, grow well in strongly stratified water with weak turbulence (Wang et al., 2008, 2012a, b), whereas large planktonic diatoms, such as *P. praetermissa* and *A. formosa* (Rioual et al., 2009; Wang et al., 2012b), need more turbulence to enable their suspension in the photic zone. These three functional groups have different $\delta^{13}\text{C}$ values on the basis of different diffusive boundary layers. Their rank in order of increasing boundary layer thickness is large planktonic < small planktonic < benthic.

In cold conditions with extensive ice cover, the productivity of benthic communities in a lake is proportionally less affected than that of the planktonic communities, because the littoral zone may still melt and open up during summer months (Douglas and Smol, 1999). From ca. 1350 to 1800 AD, diatom data (Wang et al., 2012b) suggests the prevalence of a cooler climate, possibly concurrent with the Little Ice Age. A cooler climate seems the most likely cause for the observed decline in TOC and diatom flux, and the decline in planktonic diatom biovolume accumulation rate (Wang et al., 2012b). At this time there is also a marked decline in P/B, indicative of increased proportion of benthic diatoms in the sedimentary record. As discussed by France (1995) and Doi et al. (2009), benthic algae are ^{13}C -enriched vs. planktonic algae, which may also contribute to the sustained increase in $\delta^{13}\text{C}$ values at this time.

The same process could also explain the abrupt decline in $\delta^{13}\text{C}$ values by ca. 4.2‰ after ca. 1800 AD that occurred simultaneously with an increase in the proportion of planktonic diatoms (Fig. 5). The decline in $\delta^{13}\text{C}$ values at EML then is also coincident with the onset of the industrial revolution and release of greater ^{12}C to the atmosphere due to fossil fuel combustion and deforestation. This has resulted in the relative decline of ^{13}C (and ^{14}C) in atmospheric CO_2 over the past ca. 200 yr, which in turn has resulted in their decline in other reservoirs, including oceans and lakes. The process is referred to as the Suess effect (Keeling, 1979), and is apparent in $\delta^{13}\text{C}$ records from several lake sediment records (e.g. Verburg, 2007; Castaneda et al., 2011; Jiang et al., 2011). Between ca. 1840 and 2000 AD, the decline in atmospheric $\delta^{13}\text{C}$ values was ca. 1.6‰ (Verburg, 2007). Therefore, the magnitude of change in EML during this period cannot be attributed solely to the Suess effect. Moreover, the Suess effect cannot explain increas-

ing $\delta^{13}\text{C}$ values observed in EML during the past 50 yr. Furthermore, the sharp decline in $\delta^{13}\text{C}$ values cannot be explained by a decline in algal productivity, because TOC and diatom flux increase after ca. 1800 AD (Fig. 3).

The late decline in $\delta^{13}\text{C}$ to the lowest values between 1900 and 1950 AD is concurrent with the increase in planktonic diatoms which, as discussed above, have lower $\delta^{13}\text{C}$ values, specifically *P. praetermissa* and *A. formosa* (Fig. 5), both of which have been shown to thrive during periods of spring and autumn turnover, when turbulence in the lake is particularly high (Morabito et al., 2002; Ptacnik et al., 2003; Rioual et al., 2009). For example, in the neighbouring Lake Sihailongwan, 18 km east of Lake Erlongwan, analysis of sediment trap samples shows that *P. praetermissa* blooms seasonally in spring and autumn, when windy conditions cause turnover and the water column is well mixed (Rioual et al., 2009). Detailed experimental studies of oligotrophic lakes showed that *A. formosa* is also abundant under conditions with high water turbulence (Morabito et al., 2002; Ptacnik et al., 2003).

The increased abundance of these two large planktonic diatoms indicates that the climatic conditions changed from cold during the Little Ice Age to warm in the 20th Century. This latest warm period is, however, not identical to the Medieval Warm period as the two differ in the relative length of the seasons (Wang et al., 2012b). During the MWP the duration of summer was longer, while the spring and autumn were shorter than in the 20th Century. During the 20th Century, long spring and autumn seasons, with strong turbulence due to strong wind, favoured blooms of large planktonic diatoms (*P. praetermissa* and *A. formosa*; Wang et al., 2012b). In such turbulent conditions, cells of these planktonic diatoms would be expected to have thinner diffusive boundary layers and more depleted $\delta^{13}\text{C}$ values than those of *Discostella* species. We also acknowledge that, during periods with strongly turbulent conditions, atmospheric exchange could also contribute to the decline in $\delta^{13}\text{C}$ values of the sediment because of relatively high dissolved carbon concentration in lake water leading to further discrimination against $\delta^{13}\text{C}$ by the algae.

By contrast with large planktonic species, cells of *Discostella* species, a group of planktonic species which blooms in summer months when the water column is thermally stratified and water turbulence is weak (Sorvari et al., 2002; Smol et al., 2005; Rühland et al., 2008; Wang et al., 2008, 2012a) would have less depleted $\delta^{13}\text{C}$ values than those of *P. praetermissa* and *A. formosa*, but more depleted $\delta^{13}\text{C}$ values than benthic algae. Therefore, over the last five decades, the EML sediment record shows that $\delta^{13}\text{C}$ values increased slowly with increasing proportions of *Discostella* species (Fig. 5). The increase in the relative abundance of small planktonic *Discostella* species and the concurrent decrease in large diatoms (*Asterionella* and *Puncticulata*) are consistent with increased temperature, leading to strong thermal stratification of the water column (Wang et al., 2012b). The increase in *Discostella* (and other small centric diatoms of the genus *Cyclotella*) with global warming has been reported for the recent sediments of numerous lakes throughout the northern Hemisphere (Sorvari et al., 2002; Rühland et al., 2003, 2008, 2010; Smol et al., 2005; Wang et al., 2012b), including nearby Xiaolongwan Lake (Panizzo et al., 2012).

We have shown that changes in the carbon isotopes signal of a lake sedimentary record can be interpreted by way of climatic changes (warm and cold) and their control of the duration of ice cover and associated variation in the ratio of planktonic and benthic algae.

In our opinion, this new approach has potential for interpreting carbon isotopes as proxy records for climate change and should be considered in future studies. However, the interpretation is useful only if due attention is paid to the following points: (i) the lake sedimentary OM should be derived almost exclusively from algae

and aquatic vegetation, (ii) as water level change also cause variation in the ratio between planktonic and benthic diatom, it may also affect the carbon isotopes signal, (iii) eutrophication, as it often leads to large increase in the abundance of planktonic algae, may also alter the carbon isotope record and should also be taken into account when interpreting the record.

Besides the usefulness of this new approach for interpreting carbon isotope records, it is interesting to note that diatom oxygen isotope values are also likely to be influenced by the effect of turbulence on the boundary layer thickness.

5. Conclusions

Interpretation of $\delta^{13}\text{C}$ values in lakes sediments is complex and necessitates a multiproxy approach to unpick changes in lake productivity, the dominant producers and changes in the lake catchment. To our knowledge this study is the first to suggest that the difference in the ratio of planktonic and benthic diatoms helps interpret some of the $\delta^{13}\text{C}$ variation in lake sediments. In future studies, when trying to explain variations in lacustrine organic $\delta^{13}\text{C}$, more attention should be given to the difference in isotope signatures between phytoplankton and benthic microalgae, especially when major shifts between these two groups are evident.

Acknowledgements

This research was supported by National Basic Research Program of China (973 Program) (Grant 2010CB950201) and NSFC (Grant 40572105, 40971121). Additional support was provided by the UCL Simon Li Fund and Ensis Trust Fund. We are grateful to two anonymous reviewers for helpful and constructive comments which helped improve the manuscript.

Associate Editor – Bart van Dongen

References

- Battarbee, R.W., Jones, V.J., Flower, B.P., Cameron, N.G., Bennion, H., Carvalho, L., Juggins, S., 2001. Diatoms. In: Smol, J.P., Birks, H.J.B., Last, W.M. (Eds.), *Tracking Environmental Change Using Lake Sediments*. Kluwer Academic Publishers, Dordrecht, pp. 155–201.
- Battarbee, R.W., Kneen, M.J., 1982. The use of electronically counted microspheres in absolute diatom analysis. *Limnology and Oceanography* 27, 184–188.
- Castaneda, I.S., Werne, J.P., Johnson, T.C., Powers, L.A., 2011. Organic geochemical records from Lake Malawi (East Africa) of the last 700 years, part II: Biomarker evidence for recent changes in primary productivity. *Palaeogeography Palaeoclimatology Palaeoecology* 303, 140–154.
- Chu, G.Q., Sun, Q., Wang, X.H., Sun, J.Y., 2008. Snow anomaly events from historical documents in eastern China during the past two millennia and implication for low-frequency variability of AO/NAO and PDO. *Geophysical Research Letters* 35, 14810.11029/12008GL034475.
- Doi, H., Kikuchi, E., Shikano, S., Takagi, S., 2009. Differences in nitrogen and carbon stable isotopes between planktonic and benthic microalgae. *Limnology* 11, 185–192.
- Douglas, M.S.V., Smol, J.P., 1999. Freshwater diatoms as indicators of environmental change in the high Arctic. In: Stoermer, E.F., Smol, J.P. (Eds.), *The Diatoms: Application for the Environmental and Earth Sciences*. Cambridge University Press, Cambridge, pp. 227–244.
- Editorial Board for Flora of China, 1995. *Flora of China*. Science Press, Beijing.
- Enache, M.D., Paterson, A.M., Cumming, B.F., 2011. Changes in diatom assemblages since pre-industrial times in 40 reference lakes from the experimental lakes area (northwestern Ontario, Canada). *Journal of Paleolimnology* 46, 1–15.
- Fellerhoff, C., Voss, M., Wantzen, K.M., 2003. Stable carbon and nitrogen isotope signatures of decomposing tropical macrophytes. *Aquatic Ecology* 37, 361–375.
- France, R.L., 1995. Carbon-13 enrichment in benthic compared to planktonic algae: foodweb implications. *Marine Ecology Progress Series* 124, 307–312.
- Frank, U., 2007. Palaeomagnetic investigations on lake sediments from NE China: a new record of geomagnetic secular variation for the last 37 ka. *Geophysics Journal International* 169, 29–40.
- Hammarlund, D., 1993. A distinct ^{13}C decline in organic lake sediments at the pleistocene–holocene transition in southern Sweden. *Boreas* 22, 236–243.
- Haworth, E.Y., Hurley, M.A., 1984. Comparison of the stelligeroid taxa of the centric diatom genus *Cyclotella*. In: Ricard, M. (Ed.), *Proceedings of the 8th*

- International Diatom Symposium, – Paris. Koeltz Scientific Books, Koenigstein, pp. 43–58.
- Jiang, S., Liu, X.D., Sun, J., Yuan, L.X., Sun, L.G., Wang, Y.H., 2011. A multi-proxy sediment record of late Holocene and recent climate change from a lake near Ny-Alesund, Svalbard. *Boreas* 40, 468–480.
- Jørgensen, B.B., Revsbech, N.P., 1985. Diffusive boundary layers and the oxygen uptake of sediments and detritus. *Limnology and Oceanography* 30, 111–122.
- Keeling, C.D., 1979. The Suess effect: ^{13}C – ^{14}C interrelations. *Environment International* 2, 229–300.
- Krammer, K., Lange-Bertalot, H., 1986. Bacillariophyceae. *Süßwasserflora von Mitteleuropa*, Band 2. Spektrum Akademischer Verlag Heidelberg, Berlin.
- Leng, M.J., Lamb, A.L., Heaton, T.H.E., Marshall, J.D., Wolfe, B.B., Jones, M.D., Holmes, J.A., Arrowsmith, C., 2006. Isotopes in lake sediments. In: Leng, M.J. (Ed.), *Isotopes in Palaeoenvironmental Research*. Springer, Netherlands, pp. 147–184.
- Leng, M.J., Marshall, J.D., 2004. Palaeoclimate interpretation of stable isotope data from lake sediment archives. *Quaternary Science Reviews* 23, 811–831.
- Li, J., Mackay, A.W., Zhang, Y., Li, J.J., 2012. A 1000-year record of vegetation change and wildfire from maar lake Erlongwan in northeast China. *Quaternary International*. <http://dx.doi.org/10.1016/j.quaint.2012.08.2104>.
- Li, J.J., Li, J., Wang, L., 2009. The best duration of settling for diatom suspension. *Quaternary Sciences* 29, 183–184 (in Chinese with English abstract).
- Mackay, A.W., Bezrukova, E.V., Leng, M.J., Meaney, M., Nunes, A., Piotrowska, N., Self, A., Shchetnikov, A., Shilland, E., Tarasov, P., Wang, L., White, D., 2012. Aquatic ecosystem responses to Holocene climate change and biome development in boreal, central Asia. *Quaternary Science Reviews* 41, 119–131.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology* 144, 289–302.
- Meyers, P.A., Lallier-Vergès, E., 1999. Lacustrine sedimentary organic matter records of late quaternary paleoclimates. *Journal of Paleolimnology* 21, 345–372.
- Mingram, J., Allen, J.R.M., Bruchmann, C., Liu, J., Luo, X., Negendank, J.F.W., Nowaczyk, N., Schettler, G., 2004. Maar and crater lakes of the Long Gang volcanic field (NE China) – overview, laminated sediments, and vegetation history of the last 900 years. *Quaternary International* 123–25, 135–147.
- Morabito, G., Ruggiu, D., Panzani, P., 2002. Recent dynamics (1995–1999) of the phytoplankton assemblages in Lago Maggiore as a basic tool for defining association patterns in the Italian deep lakes. *Journal of Limnology* 61, 129–145.
- O’Leary, M.H., 1981. Carbon isotope fractionation in plants. *Phytochemistry* 20, 553–567.
- Panizzo, V.N., Mackay, A.W., Rose, N.L., Rioual, P., Leng, M.J., 2012. Recent palaeolimnological change recorded in lake Xiaolongwan, northeast China: climatic versus anthropogenic forcing. *Quaternary International*. <http://dx.doi.org/10.1016/j.quaint.2012.07.033>.
- Ptacnik, R., Diehl, S., Berger, S., 2003. Performance of sinking and nonsinking phytoplankton taxa in a gradient of mixing depths. *Limnology and Oceanography* 48, 1903–1912.
- Rioual, P., Chu, G.Q., Li, D., Mingram, J., Han, J., Liu, J., 2009. Climate-induced shifts in planktonic diatoms in lake Sihailongwan (north-east China): a study of the sediment trap and palaeolimnological records. Abstract. 11th International Paleolimnology Symposium, Guadalajara, Mexico, p. 120.
- Rühland, K., Paterson, A.M., Smol, J.P., 2008. Hemispheric-scale patterns of climate-related shifts in planktonic diatoms from North American and European lakes. *Global Change Biology* 14, 1–15.
- Rühland, K., Priesnitz, A., Smol, J.P., 2003. Paleolimnological evidence from diatoms for recent environmental changes in 50 lakes across Canadian arctic treeline. *Arctic, Antarctic, and Alpine Research* 35, 110–123.
- Rühland, K.M., Paterson, A.M., Hargan, K., Jenkins, A., Clark, B.J., Smol, P., 2010. Reorganization of algal communities in the Lake of the Woods (Ontario, Canada) in response to turn-of-the-century damming and recent warming. *Limnology and Oceanography* 55, 2433–2451.
- Smol, J.P., 1983. Paleophycology of a high arctic lake near Cape Herschel, Ellesmere island. *Canadian Journal of Botany* 61, 2195–2204.
- Smol, J.P., Wolfe, A.P., Birks, H.J.B., Douglas, M.S., Jones, V.J., Korhola, A., Pienitz, R., Rühland, K., Sorvari, S., Antoniades, D., Brooks, S.J., Fallu, M.A., Mike, H., Keatley, B.E., Laing, T.E., Michelutti, N., Nazarova, L., Nyman, M., Paterson, A.M., Perren, B., Quinlan, R., Rautio, M., Talbot, E.S., Siitonen, S., Solovieva, N., Wechström, J., 2005. Climate-driven regime shifts in the biological communities of arctic lakes. *Proceedings of the National Academy of Sciences* 102, 4392–4402.
- Sorvari, S., Korhola, A., Thompson, R., 2002. Lake diatom response to recent Arctic warming in Finnish Lapland. *Global Change Biology* 8, 153–163.
- Tanaka, H., 2007. Taxonomic studies of the genera *Cyclotella* (Kützing) Brébisson, *Discostella* Houk et Klee and *Puncticulata* Håkansson in the family Stephanodiscaceae Glezer et Makarova (Bacillariophyta) in Japan. *Journal of Cramer*, Berlin.
- Verburg, P., 2007. The need to correct for the Suess effect in the application of delta C-13 in sediment of autotrophic lake Tanganyika, as a productivity proxy in the anthropocene. *Journal of Paleolimnology* 37, 591–602.
- Wang, L., Lu, H.Y., Liu, J.Q., Gu, Z.Y., Mingram, J., Chu, G.Q., Li, J.J., Rioual, P., Negendank, J.F.W., Han, J.T., Liu, T.S., 2008. Diatom-based inference of variations in the strength of Asian winter monsoon winds between 17,500 and 6000 calendar years BP. *Journal of Geophysical Research–Atmospheres* 113, D21101. <http://dx.doi.org/21110.21029/22008JD010145>.
- Wang, L., Li, J., Lu, H., Gu, Z., Rioual, P., Hao, Q., Mackay, A.W., Jiang, W., Cai, B., Xu, B., Han, J., Chu, G., 2012a. The East Asian winter monsoon over the last 15,000 yr its links to high-latitudes and tropical climate systems and complex correlation to the summer monsoon. *Quaternary Science Reviews* 32, 131–142.
- Wang, L., Rioual, P., Panizzo, V.N., Leng, M.J., Lu, H.Y., Gu, Z.Y., Chu, G.Q., Yang, D.G., Han, J.T., Liu, J.Q., Mackay, A.W., 2012b. A 1000-yr record of environmental change in NE China indicated by diatom assemblages from maar lake Erlongwan. *Quaternary Research* 78, 24–34.
- You, H.T., Liu, J.Q., Liu, Q., Chu, G.Q., Rioual, P., Han, J.T., 2008. Study of the varve record from Erlongwan maar lake, NE China, over the last 13 ka BP. *Chinese Science Bulletin* 53, 262–266.