The influence of the ratio of planktonic to benthic diatoms on lacustrine organic matter $\delta^{13}C$ from Erlongwan maar Lake, Northeast China

Luo Wang[1*], Anson W. Mackay[2], Melanie J. Leng[3&4], Patrick Rioual[1], Virginia N. Panizzo[2], Houyuan Lu[1], Zhaoyan Gu[1], Guoqiang Chu[1], Jingtai Han[1], Christopher P. Kendrick[4]

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

2 Environmental Change Research Centre, Department of Geography, UCL, Gower Street, London, WC1E 6BT, United Kingdom.

3 Department of Geology, University of Leicester, Leicester, LE1 7RH, United Kingdom

4 NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, Nottingham, NG12 5GG, United Kingdom.

∗ corresponding author's e-mail: wangluo@mail.iggcas.ac.cn, Tel:086-10-82998261

ABSTRACT

Carbon isotope ratios ($\delta^{13}C$) of organic matter within lake sediments are commonly used to reconstruct environmental change, but the factors which influence change are varied and complex. Here we report $\delta^{13}C$ values determined from organic sediments from Erlongwan maar lake in Northeast China. In this record, changes in $\delta^{13}C$ cannot be explained by simple changes in aquatic productivity. Instead, $\delta^{13}C$ are likely influenced by differences in the ratios between planktonic and benthic algae as indicated by the remains of diatoms. This is because the variation of $\delta^{13}C_{org}$ in algae from different habitats is controlled by the thickness of the diffusive boundary layer, which is dependent on how turbulent the water is. Compared to benthic algae that 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 $\delta^{13}C$ depletion. In Erlongwan maar lake low $\delta^{13}C$ values are linked to the dominance of planktonic diatoms during the period commonly known as the Medieval Warm Period. $\delta^{13}C$ 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 the colder climate. The increase in planktonic diatoms at the end of the Little Ice Age, linked to higher temperatures and a reduction in ice-cover, resulted in a further decline in $\delta^{13}C$.

1. Introduction

Carbon isotope ratios ($\delta^{13}C$) are an important proxy to reconstruct 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, the interpretation of $\delta^{13}C$ from bulk organic material in lake sediments is complex and dependent on many factors. $\delta^{13}C$ is commonly used in palaeolimnological studies to determine sources of organic material to a lake, e.g. allochthonous versus autochthonous sources (Meyers, 1994), the source of dissolved carbon used by aquatic plants (Leng et al., 2006), productivity (Leng and Marshall, 2004), 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 ratios of phytoplankton and benthic algae on $\delta^{13}C$ in lake sediments, despite the environmental importance that changes in this ratio represents in terms of lake level variability, hydrodynamics of the water column and habitat availability (France, 1995).

Here we discuss the possible reasons for $\delta^{13}C$ variability in the sedimentary record from Erlongwan maar lake (EML) over the past 1000 years, using $\delta^{13}C$ of organic matter, percentage of sedimentary total organic carbon (%TOC), TOC fluxes, C/N ratios, 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 their siliceous cell walls, which generally preserve well 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 very different micro-environmental conditions, such as light availability and exposure to water turbulence, which control nutrient availability. Here we discuss how turbulence may play an important role in controlling carbon isotope fractionation in different diatom habitats.

2. Material and methods

There are 8 maar lakes in the Long Gang Volcanic Field (LGVF) region, located in Jilin Province, NE China. Our study focuses on Lake Erlongwan (EML) 42° 18'N, 126° 21'E), a dimictic lake, that occupies an area of ca. 0.3 km^2 at 724 m above sea level (Fig. 1). It is a closed lake with a small catchment (0.4 km^2) with no natural inflow or outflow (Mingram et al., 2004).

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

In 2001, a 66.5 cm long sediment core was extracted from the central, deepest region of the lake at a water depth of 36 m. The core is laminated from 0 to 50 cm core depth. The sediments are composed of detrital muds with varying amounts of organic matter. Between 51 and 66.5 cm core depth 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 of ^{210}Pb and ^{14}C radiometric dating techniques (Fig. 2). The activities of ^{137}Cs, ^{210}Pb were measured by gamma spectrometry using a low-background well-type germanium detector (EGPC 100P-15R) at the Institute of Geology and Geophysics, Chinese Academy of Science, Beijing. The ^{14}C date (Poz-19967) was analysed on a *Pinus* macrofossil found at the bottom of the sediment core (49.5 cm) using accelerated mass spectrometry (AMS). AMS yielded a date of 1045 ± 30 ^{14}C yrs BP (Fig. 2), which after 2 sigma calibration gave an age range of 900 – 1030 AD (Wang et al., 2012). The ages of the samples below those dated with ^{210}Pb 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).

Diatom samples were prepared according to standard methods (Battarbee et al., 2001; Li et al., 2009). Diatom concentrations (valves/g) were calculated by the addition of divinylbenzene microspheres (Battarbee and Kneen, 1982). Diatom identification followed the guidelines set out by Krammer and Lange-Bertalot (Krammer and Lange-Bertalot, 1986-1991). We chose to merge *Discostella pseudostelligera*, *D. woltereckii* 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 percent relative abundances and total diatom flux. The ratios of planktonic to benthic diatoms were calculated using the formula:

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

For the organic analysis, 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 used 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. ± < 0.1% (1SD). C/N ratios for each sample were derived from these data. Stable isotope analyses ($^{13}C/^{12}C$) were undertaken by combustion using a Carlo Erba NA1500 (series 1) on-line to a VG Triple Trap and Optima dual-inlet mass spectrometer. $\delta^{13}C$ values were calculated to the VPDB scale using a within-run laboratory standard calibrated against NBS19 and NBS22. Analyses of replicates of sample material revealed a precision of ca. ± < 0.1‰ (1 SD). These analyses were made at the NERC Isotope Geosciences Laboratory, in Keyworth, UK.

3. Results

Organic content of the sediments (as inferred from TOC flux) is above the average for the core (0.012 $g/m^2/y$) from 50 to 47 cm (ca. 970-1080 AD) and increase to a peak between 41-36 cm (ca. 1070-1280 AD; Fig.3). Thereafter, TOC flux declines steadily, concurrent with decreases in diatom flux (Fig.3). TOC flux values subsequently increase at the depth of 10 cm (ca.1900 AD), as does diatom fluxes and the proportion of planktonic diatom species (Fig.3). TOC is most significantly correlated with TN flux (0.990^{**}; Table1), and it is also significantly positively correlated with diatom flux (0.747^{**}) and P/B ratio (0.422^{*}), i.e. increasing abundances of planktonic diatoms (Table 1; Fig.4). C/N values fluctuate between the core depth 10.6 to 15.6 cm. The highest C/N values occur between 26 and 13 cm (ca. 1500-1780 AD; Fig.3).

$\delta^{13}C$ values fluctuate between –29.3‰ and –28.0‰ from 50 to 17 cm, but show a gradual and distinct increase (of 3.4‰) from 33 (–29.0‰) to 12 cm (–25.6‰; ca. 1350-1800 AD; Fig. 3). From 33 cm to 12 cm (ca. 1350-1800 AD), increasing $\delta^{13}C$ values occur as TOC flux, diatom flux and P/B ratios decline (Fig. 3). For the whole profile, $\delta^{13}C$ and TOC flux are negatively correlated (–0.314**; Table 1). Above 12 cm (after ca. 1800 AD), $\delta^{13}C$ values rapidly decline to lowest values in the profile (ca. –29.8‰) between 10- 9 cm, coincident with a distinct increase in the proportion of planktonic diatom species. More specifically, the shift in diatom composition appears 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, $\delta^{13}C$ values are most significantly correlated with the P/B ratio (–0.627**; Table 1; Fig.4). $\delta^{13}C$ values in the uppermost sediments, spanning the last 50 years (approx. 6 cm), increase up to the time the core was taken (Fig. 3), which is coincident with the return to dominance of the *Discostella* species (Fig. 5).

4. Discussion

All our samples have $\delta^{13}C$ values that are below –25‰ (Fig. 3), indicating the dominance of C_3 plants as the principal carbon source to EML. C_3 plants utilize the enzyme RuBisCO (ribulose-1,5-bisphosphate carboxylase) to fix atmospheric CO_2 which results in $\delta^{13}C$ values ranging between –22‰ to –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 EML sediments highlights that extensive pine and deciduous forest cover has persisted throughout the past 1000 years (Mingram et al., 2004).

$\delta^{13}C$ values of bulk sediments cannot be used to distinguish between algae and terrestrial C_3 plants (Meyers and Lallier-Vergès, 1999), so C/N ratios in lake sediments are commonly used to assess the relative importance between allochthonous and autochthonous sources of organic material (Meyers, 1994); algae generally contain only very small amounts of cellulose or lignin (both carbon rich; Leng et al., 2006). Figure 3 shows that all the sediment samples from EML have C/N ratios <16, with an average value of 12.8. It is likely that the plant organic matter in EML is derived from a mixture of sources, especially algae (with relatively low C/N ratios 5<10; Meyers and Lallier-Vergès, 1999) and aquatic vegetation (both submerged and floating) with relatively high C/N ratios (about 20 to 30; Fellerhoff et al., 2003) and only a small contribution from terrestrial vegetation (C/N ratios between 20-160; Meyers and Lallier-Vergès, 1999).

Organic input from terrestrial vegetation is likely to be low because TOC and diatom flux are very highly, and significantly, correlated (0.747^{**}; Table 1 and Fig. 4) which indicates that algae are a major component of organic matter in the core. Secondly, the highest C/N ratios observed between 28 to 12 cm (1500 – 1800 AD; Fig. 3) were unlikely caused by 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 based on diatom data from EML (Wang, et al. 2012) and historical documents relating the frequency of snow events in Northeast China (Chu et al., 2008) showed 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 to 0 cm; Fig.2) indicate that there was an increase in run-off input into 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 inputs into 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 ratios, 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 – 12 cm in EML (Wang et al., 2012). This is because spring melting does allow for 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 decline in P/B ratios and higher C/N values (Fig.3) are due to persistent growth of aquatic vegetation with C/N ratio values comprise between 20 and 30 along the littoral zone of the lake, leading to the increase in the relative abundance of organic matter derived from aquatic vegetation.

Primary production in lakes can influence the changes in $\delta^{13}C$ values of organic matter. Primary production through time can be inferred using TOC (Leng and Marshall, 2004). A long decline in TOC flux values occurs between 33 to 12 cm (ca. 1350 to ~1800 AD; Fig.3) indicating that the productivity of algae and aquatic vegetation decreased. TOC can also vary due to changing sedimentation rates in the lake. 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), and therefore we are not able to resolve this issue directly by 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^{-1} over the past 1000 years (You et al., 2008) which is very similar to the sedimentation rate estimated in this study (0.05 cm yr^{-1}). 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, indicating likely close linkages 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 likely therefore that the changes in TOC flux observed 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^- for their source of carbon, and this results in an increase in $\delta^{13}C$. 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 $\delta^{13}C$ values of ca. 3.7‰. It is unlikely that increasing $\delta^{13}C$ values in EML sediments were caused by declining aquatic productivity.

Other factors which may cause increasing $\delta^{13}C$ values include gradual maturation of lakes and changes in catchment vegetation. As lakes mature, ^{12}C-enriched organic matter is transported into bottom sediments (Meyers and Lallier-Vergès, 1999). However the changes observed in EML are quite abrupt, e.g. at 11 cm, and moreover, the increase in values only occurs during a specific timeframe, and so unlikely to be due to lake maturation. On 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 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 this region did not change to such an extent that this could lead to an increase of δ^{13}C-depleted dissolved $CO_{2.}$

Another potential influence on sedimentary ^{13}C values is the difference in proportions of phytoplankton and benthic microalgae (France, 1995), assuming much of the sedimentary organic matter is derived from the algae. France (1995) collated literature data on δ^{13}C for marine and freshwater benthic and planktonic algae and found that the average δ^{13}C values for benthic algae in lakes was –26‰ ± 3, whereas it was lower at –32‰ ± 3 for planktonic algae, an average difference of about 6‰. Doi et al. (2009) also found significant differences between δ^{13}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 to 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 how thick is the boundary layer (Jørgensen and Revsbech, 1985). The diffusive boundary layer constitutes a transfer resistance for fluxes of dissolved organic molecules, inorganic ions and gases such as CO_2

and oxygen across the solid-water interface and it is especially limiting for plants and algae at high uptake rates (Jørgensen and Revsbech, 1985). A thick boundary layer, because it leads to an entrapment of otherwise expelled ^{13}C, results in more positive δ^{13}C 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 subtratum are generally less exposed to turbulent waters, and so likely to 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 waters with weak turbulence (Wang et al., 2008; 2012a; 2012b), whereas large planktonic diatoms, such as *P. praetermissa* and *A. formosa* (Rioual et al., 2009; Wang et al., 2012), need more turbulence to enable their suspension in the photic zone. These three functional groups have different δ^{13}C values on the basis of different diffusive boundary layers. Their rank in order of increasing boundary layer thickness is as follows: 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, diatoms data (Wang et al., 2012) 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 fluxes, and the decline in planktonic diatom biovolume accumulation rates (Wang et al., 2012). At this time there is also a marked decline in the P/B ratio, 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 compared to planktonic algae which may also contribute to the sustained increase in $\delta^{13}C$ values at this time.

The same process could also explain the abrupt decline in $\delta^{13}C$ 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 $\delta^{13}C$ values at EML at this time is also coincident with the onset of the industrial revolution and release of greater ^{12}C into 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 years, which in turn has resulted in their decline in other reservoirs, including oceans and lakes. This process is referred to as the Suess effect (Keeling, 1979), and is apparent in $\delta^{13}C$ records from several lake sediment records (e.g. Verburg, 2007; Castaneda et al., 2011; Jiang et al., 2011). Between ca. 1840-2000 AD, the decline in atmospheric $\delta^{13}C$ values was ca. 1.6‰ (Verburg, 2007). Therefore, the magnitude of change in EML during this period cannot be attributed to the sole Suess effect. Moreover, the Suess effect cannot explain increasing $\delta^{13}C$ values observed in EML during the past 50 years. Furthermore, the sharp decline in $\delta^{13}C$ values cannot be explained by a decline in algal productivity, because TOC and diatom fluxes increase after ca. 1800 AD (Fig.3).

The late decline in $\delta^{13}C$ to lowest values between 1900 and 1950 AD is concurrent with the increase in planktonic diatoms, which as discussed above have lower $\delta^{13}C$ 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, located 18 km east from Lake Erlongwan, analyses of sediment trap samples show that *P. praetermissa* blooms seasonally in spring and in autumn, when windy conditions cause turnover and the water column is well mixed (Rioual et al., 2009). Detailed experimental studies in 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 abundances of these two large planktonic diatoms indicate 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 differs in the relative length of the seasons (Wang et al., 2012). 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 were favoring blooms of large planktonic diatoms (*P. praetermissa* and *A. formosa*; Wang et al., 2012). In such turbulent conditions cells of these planktonic diatoms are expected to have thinner diffusive boundary layers and more depleted $\delta^{13}C$ values than that of *Discostella* species. We also acknowledge that during periods with strongly turbulent conditions, atmospheric exchange could also contribute to the decline in $\delta^{13}C$ values of the sediment because of relatively high dissolved carbon concentration in lake water leading to further discrimination against $\delta^{13}C$ by the algae.

By contrast with the 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 δ^{13}C values than that of *P. praetermissa* and *A. formosa*, but more depleted δ^{13}C values than benthic algae. Therefore, over the last five decades, the EML sediment record shows that δ^{13}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 temperatures leading to strong thermal stratification of the water column (Wang et al., 2012). The increase of *Discostella* (and other small centric diatoms of the genus *Cyclotella*) with global warming has been reported in 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).

Here, we have shown that changes in the carbon isotopes signal of a lake sedimentary record could be interpreted by climate changes (warm and cold), and their control upon the duration of ice-cover and the associated variations in the ratio of planktonic and benthic algae.

In our opinion, this new approach has great potential for interpreting carbon isotopes as proxy records for climate changes and should be considered in future studies. However, this interpretation is useful only if due attention is paid to the following points: i) the lake sedimentary organic matter should be derived almost exclusively from algae and aquatic vegetation, ii) as water level changes also cause variations in the ratio between planktonic and benthic diatom, they 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 $\delta^{13}C$ 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 $\delta^{13}C$ variation in lake sediments. In future studies, when trying to explain variations in lacustrine organic $\delta^{13}C$ 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 number: 2010CB950201) and NSFC (grant number: 40572105, 40971121). Additional support was provided by the UCL Simon Li Fund and Ensis Trust Fund. We are grateful to two anonymous reviewers for their helpful and constructive comments on the manuscript and the associate editor Bart van Dongen who helped to improve the manuscript.

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.

Editorial Board for flora of China, 1995. Flora of China. Science Press, Beijing.

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, doi: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 inthe High Artic, In: Stoermer, E.F., Smol, J.P. (Eds.), The Diatoms: Application for the Environmental and Earth Sciences. Carmbridge University Press, Cambridge, pp. 227-244.

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 37Ka. Geophysics Journal Internation 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.

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: 13Carbon-14carbon interrelations. Environment International 2, 229-300.

Krammer, K., Lange-Bertalot, H., 1986-1991. 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, doi:10.1016/j.quaint.2012.1008.2104.

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, doi:10.1016/j.quaint.2012.09.008.

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, 11th International Paleolimnology Symposium, Guadalajara, Mexico, p. 120.

Smol, J.P., 1983. Paleophycology of a high arctic lake near Cape Herschel, Ellesmere island. Canadian Journal of Botany 61, 2195-2204.

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., 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., 2012. 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.

Figure Captions:

Figure 1. The location of Erlongwan maar lake in Northeast China.

Figure 2. The EML short core ^{137}CS -^{210}Pb$_{ex}$ age model diagram. (a-b). activities of ^{210}Pb and ^{137}Cs. (c). ^{210}Pb, ^{137}Cs and AMS^{14}C depth-age model.

Figure 3. Stratigraphical profile of organic geochemical variables (a) δ^{13}C, (b) C/N, (c) TOC flux, and biological indicators, (d) diatom flux, (e) the ratio of planktonic to benthic diatoms.

Figure 4. Scatter plots showing strong correlations between (a) TOC flux and δ^{13}C, (b) diatom flux and TOC flux, (c) planktonic to benthic (P/B) ratio and δ^{13}C.

Figure 5. (a) δ^{13}C, (b) the ratio of planktonic to benthic diatoms, (c) percentages of *Discostella* species complex, (d) combined relative abundances of *P. praetermissa* and *A. formosa*

Figure(s)

Fig.1 Wang L.et al.

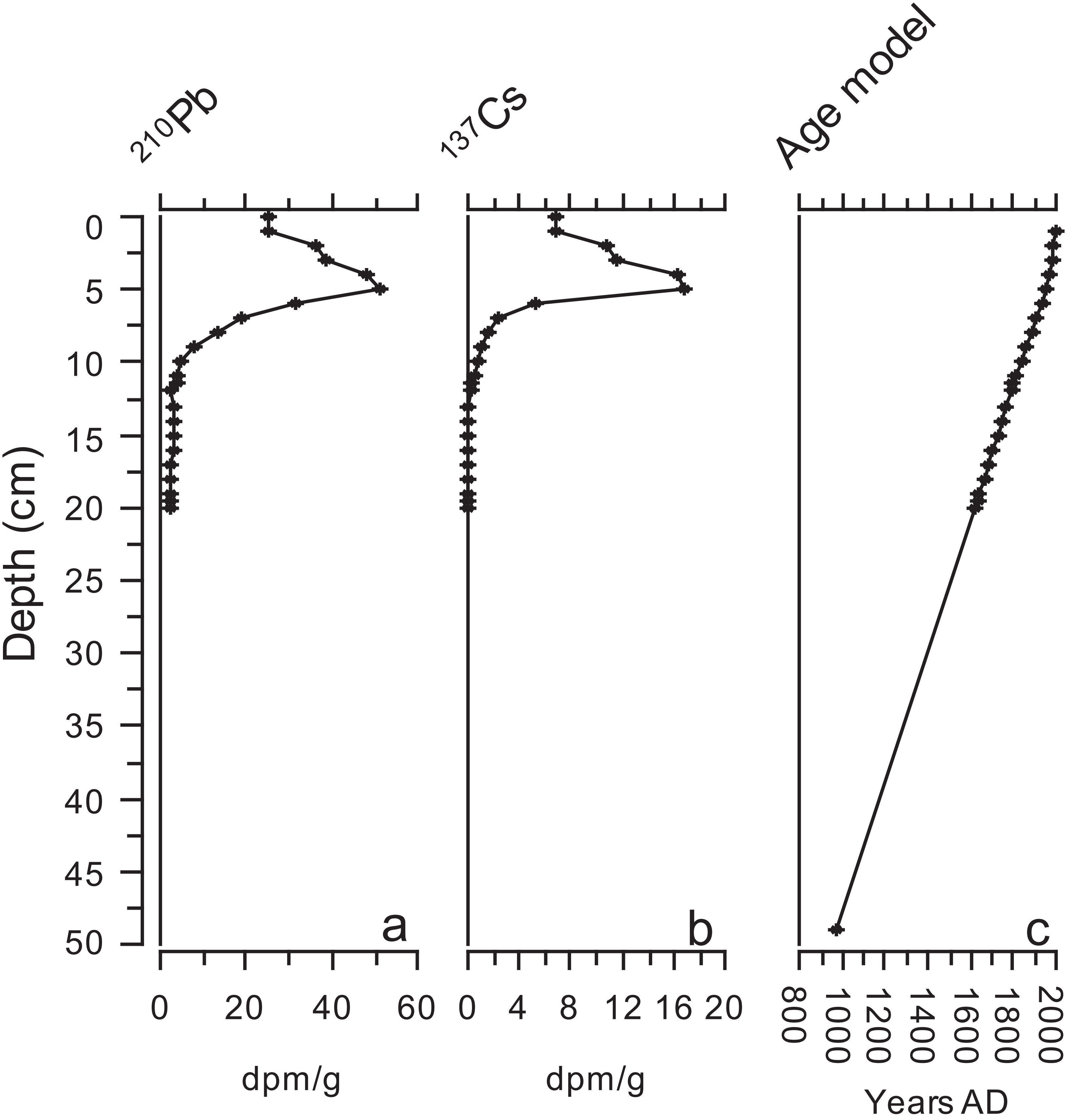

Figure2. Wang L.

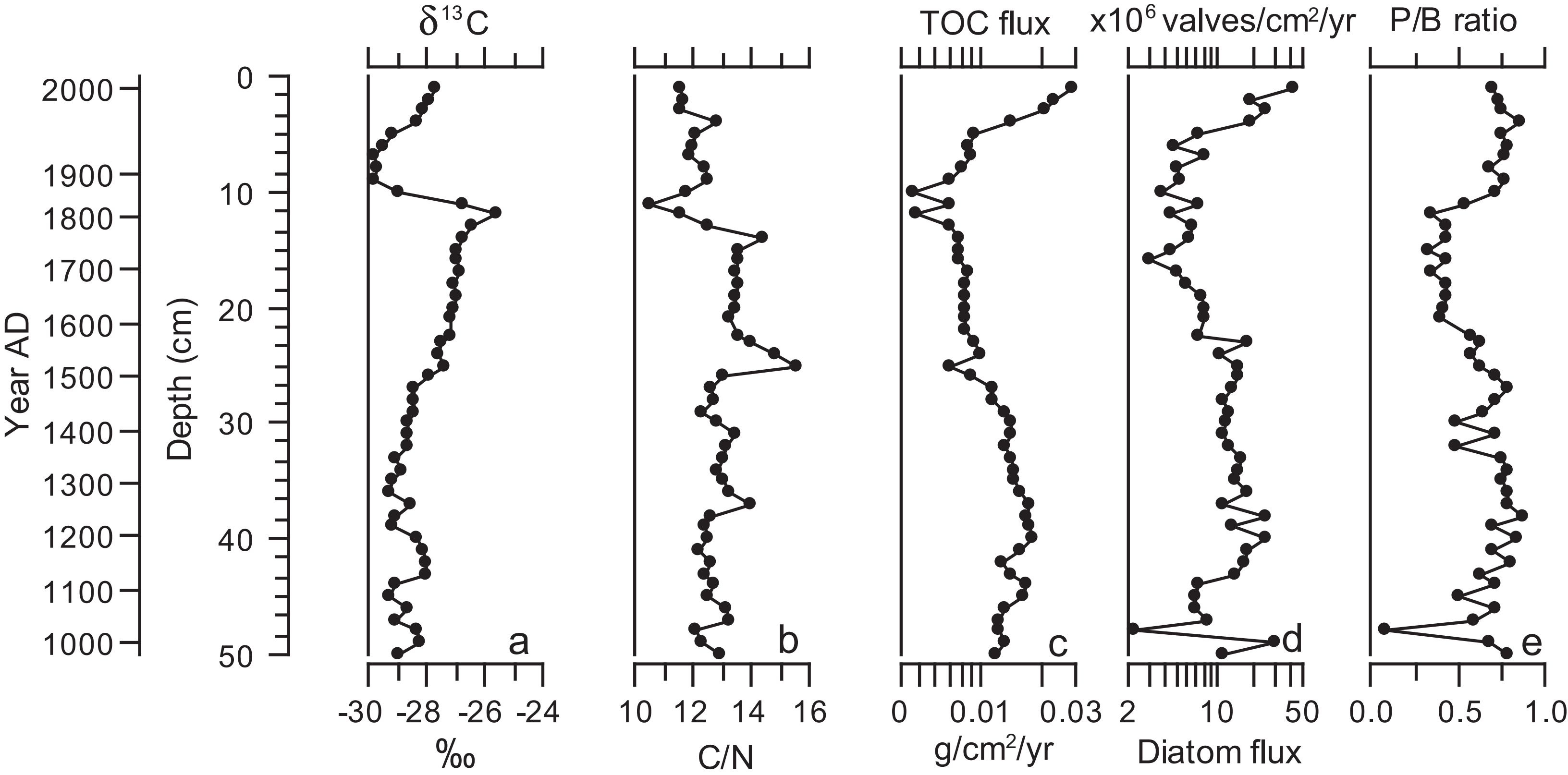

Figure3. Wang L. et al.

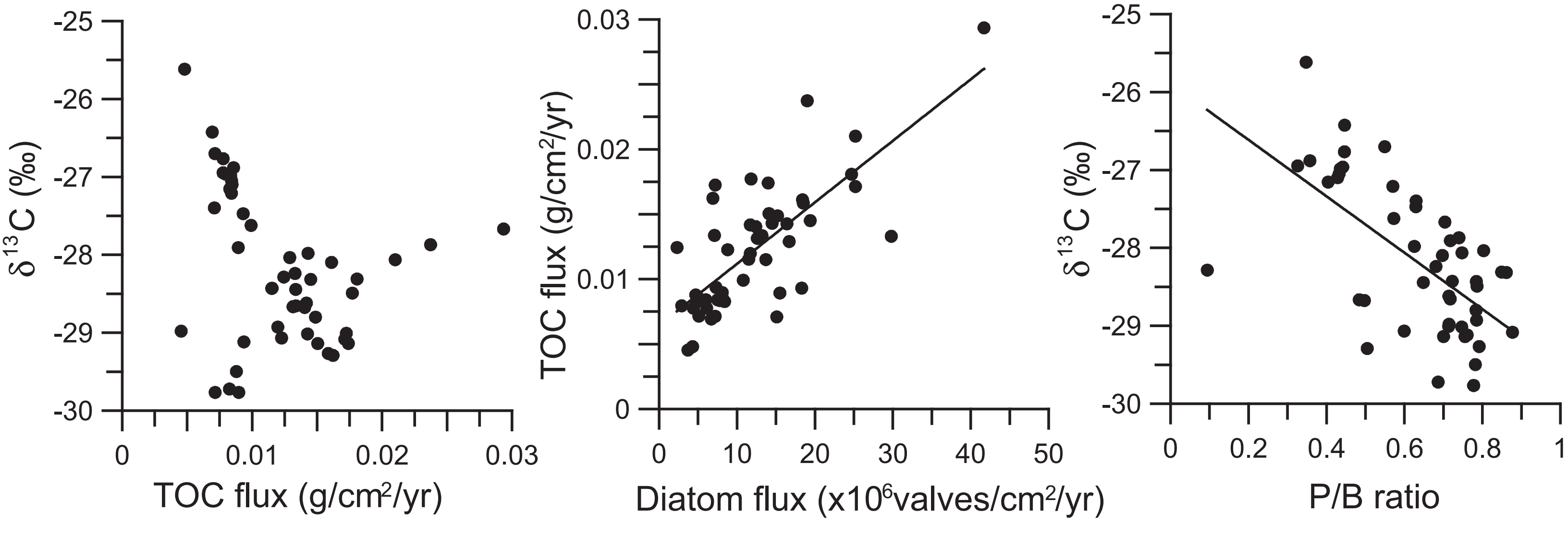

Figure 4. Wang L. et al.

Figure(s)

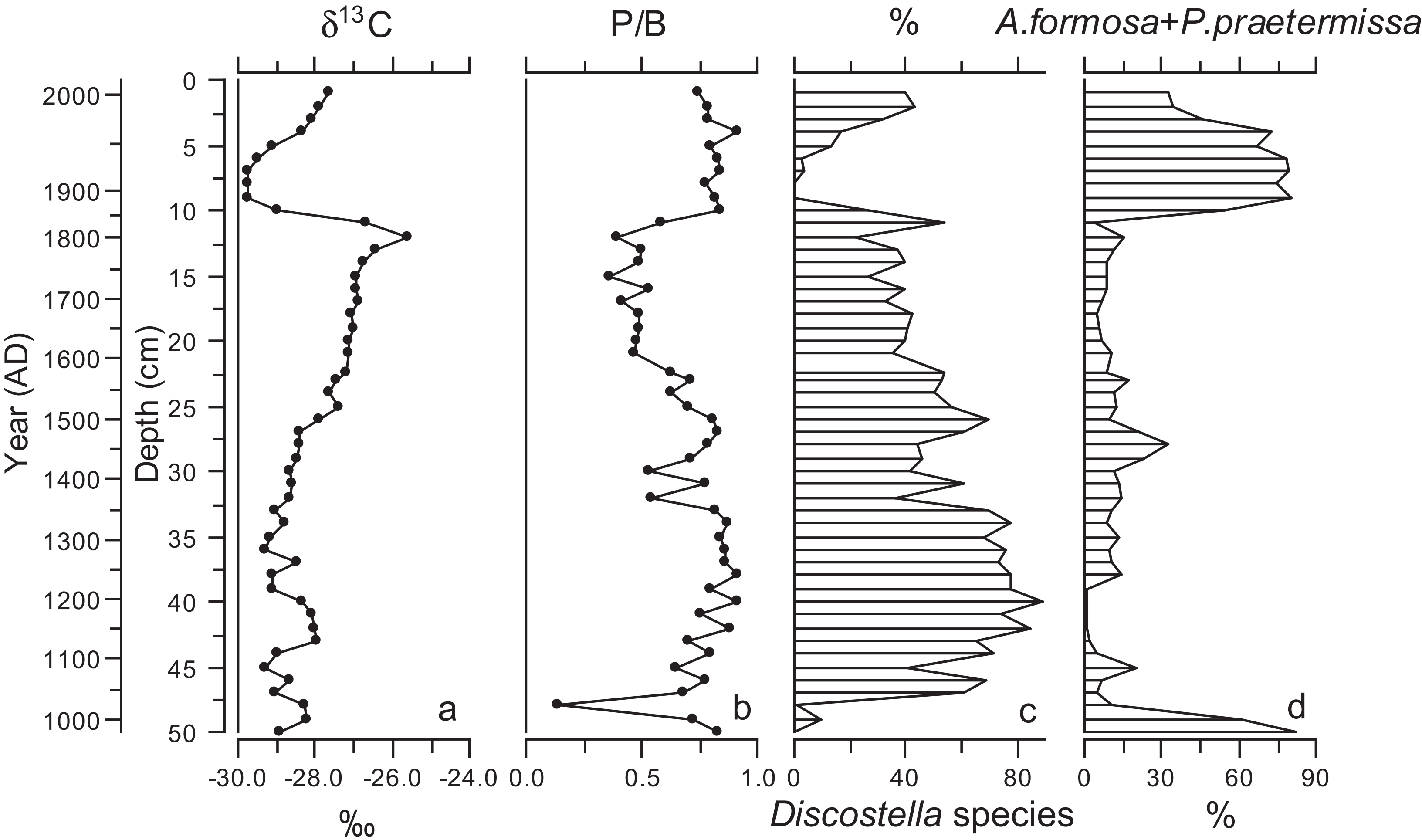

Figure5. Wang L. et al.

Table 1: Pearson Product Moment Correlation Coefficients

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

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).