

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

3 Luo Wang^{1*}, Anson W. Mackay², Melanie J. Leng^{3&4}, Patrick Rioual¹, Virginia N. Panizzo²,
4 Houyuan Lu¹, Zhaoyan Gu¹, Guoqiang Chu¹, Jingtai Han¹, Christopher P. Kendrick⁴

5

6 1 Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and
7 Geophysics, Chinese Academy of Sciences, Beijing, 100029, China.

8 2 Environmental Change Research Centre, Department of Geography, UCL, Gower Street,
9 London, WC1E 6BT, United Kingdom.

10 3 Department of Geology, University of Leicester, Leicester, LE1 7RH, United Kingdom

11 4 NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth,
12 Nottingham, NG12 5GG, United Kingdom.

13

14

15 * corresponding author's e-mail: wanglu@mail.iggcas.ac.cn, Tel:086-10-82998261

16

17

18

19

20

21

22

23 **ABSTRACT**

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

40

41

42

43

44

45 **1. Introduction**

46 Carbon isotope ratios ($\delta^{13}\text{C}$) are an important proxy to reconstruct environmental change
47 from lakes, such as changes in temperature, precipitation patterns and evaporation. These
48 changes are all indirectly linked to the carbon cycle (Leng and Marshall, 2004). However, the
49 interpretation of $\delta^{13}\text{C}$ from bulk organic material in lake sediments is complex and dependent
50 on many factors. $\delta^{13}\text{C}$ is commonly used in palaeolimnological studies to determine sources
51 of organic material to a lake, e.g. allochthonous versus autochthonous sources (Meyers, 1994),
52 the source of dissolved carbon used by aquatic plants (Leng et al., 2006), productivity (Leng
53 and Marshall, 2004), catchment soil respiration (Hammarlund, 1993; Mackay et al., 2012) as
54 well as anthropogenic carbon released into the environment because of fossil fuel combustion
55 (the Suess effect; Keeling, 1979). As far as we are aware, little work has been done to explore
56 the influence of varying ratios of phytoplankton and benthic algae on $\delta^{13}\text{C}$ in lake sediments,
57 despite the environmental importance that changes in this ratio represents in terms of lake
58 level variability, hydrodynamics of the water column and habitat availability (France, 1995).

59 Here we discuss the possible reasons for $\delta^{13}\text{C}$ variability in the sedimentary record from
60 Erlongwan maar lake (EML) over the past 1000 years, using $\delta^{13}\text{C}$ of organic matter,
61 percentage of sedimentary total organic carbon (%TOC), TOC fluxes, C/N ratios, and the
62 ratio between planktonic and benthic algae as indicated by changes in the composition of
63 diatom assemblages and diatom flux.

64 Diatoms are characterized by their siliceous cell walls, which generally preserve well as
65 sedimentary fossils (Battarbee et al., 2001). In lakes, diatoms are commonly classified as
66 planktonic, i.e. suspended, unattached in open water, or benthic (i.e., living on the bottom of

67 the lake floor) / periphytic (i.e. attached to substrates such as stones, aquatic vegetation and
68 sand). These habitats have very different micro-environmental conditions, such as light
69 availability and exposure to water turbulence, which control nutrient availability. Here we
70 discuss how turbulence may play an important role in controlling carbon isotope fractionation
71 in different diatom habitats.

72 **2. Material and methods**

73 There are 8 maar lakes in the Long Gang Volcanic Field (LGVF) region, located in Jilin
74 Province, NE China. Our study focuses on Lake Erlongwan (EML) 42° 18'N, 126° 21'E), a
75 dimictic lake, that occupies an area of ca. 0.3 km² at 724 m above sea level (Fig. 1). It is a
76 closed lake with a small catchment (0.4 km²) with no natural inflow or outflow (Mingram et
77 al., 2004).

78 The modern natural vegetation in the Long Gang Volcanic Field is typical of the
79 temperate mixed coniferous-deciduous forest zone (Editorial board for Flora of China, 1995).
80 In this forest, the coniferous tree *Pinus koraiensis* is dominant. The late-Holocene pollen
81 assemblage from EML (Li et al., 2012) also reflects the dominance of a mixed
82 coniferous-hardwood and deciduous forest around the Erlongwan lake region. Over the last
83 1000 years, *Pinus* is the dominant conifer, while major broad-leaved deciduous trees present
84 include *Quercus*, *Betula*, *Juglans*, *Ulmus*, *Carpinus*, *Corylus*, *Tilia* and *Fraxinus*.

85 In 2001, a 66.5 cm long sediment core was extracted from the central, deepest region of
86 the lake at a water depth of 36 m. The core is laminated from 0 to 50 cm core depth. The
87 sediments are composed of detrital muds with varying amounts of organic matter. Between 51
88 and 66.5 cm core depth the sediments are graded, likely representing a rapidly deposited

89 sediment slump (Frank, 2007). We focus therefore only on the laminated record of the top 50
90 cm.

91 The age-model was developed by combining results of ^{210}Pb and ^{14}C radiometric dating
92 techniques (Fig. 2). The activities of ^{137}Cs , ^{210}Pb were measured by gamma spectrometry
93 using a low-background well-type germanium detector (EGPC 100P-15R) at the Institute of
94 Geology and Geophysics, Chinese Academy of Science, Beijing. The ^{14}C date (Poz-19967)
95 was analysed on a *Pinus* macrofossil found at the bottom of the sediment core (49.5 cm) using
96 accelerated mass spectrometry (AMS). AMS yielded a date of 1045 ± 30 ^{14}C yrs BP (Fig. 2),
97 which after 2 sigma calibration gave an age range of 900 – 1030 AD (Wang et al., 2012). The
98 ages of the samples below those dated with ^{210}Pb and above the radiocarbon date at 49.5 cm
99 were linearly interpolated. Linear extrapolation was also used to extend the age-model to the
100 base of the core at ca. 980 AD (Fig. 2).

101 Diatom samples were prepared according to standard methods (Battarbee et al., 2001; Li
102 et al., 2009). Diatom concentrations (valves/g) were calculated by the addition of
103 divinylbenzene microspheres (Battarbee and Kneen, 1982). Diatom identification followed
104 the guidelines set out by Krammer and Lange-Bertalot (Krammer and Lange-Bertalot,
105 1986-1991). We chose to merge *Discostella pseudostelligera*, *D. woltereckii* and *D. stelligera*
106 into “*Discostella* species” because these three taxa were difficult to distinguish consistently
107 under light microscopy (Haworth and Hurley, 1984; Tanaka, 2007). The diatom data are
108 displayed as percent relative abundances and total diatom flux. The ratios of planktonic to
109 benthic diatoms were calculated using the formula:

110
$$\text{P/B ratio} = \sum_{\text{planktonic taxa}} / \sum_{\text{planktonic} + \text{benthic taxa}}$$

111 For the organic analysis, carbonates were removed by leaving the samples overnight in 50
112 ml of 5% HCl. %TOC and total nitrogen (%TN) were measured using a Carlo Erba elemental
113 analyser (with internal acetanilide standards used for calibration). %TOC was calibrated to
114 TOC flux using the sedimentation rate and dry bulk density. Replicate analyses of well-mixed
115 samples showed that precision was ca. $\pm < 0.1\%$ (1SD). C/N ratios for each sample were
116 derived from these data. Stable isotope analyses ($^{13}\text{C}/^{12}\text{C}$) were undertaken by combustion
117 using a Carlo Erba NA1500 (series 1) on-line to a VG Triple Trap and Optima dual-inlet mass
118 spectrometer. $\delta^{13}\text{C}$ values were calculated to the VPDB scale using a within-run laboratory
119 standard calibrated against NBS19 and NBS22. Analyses of replicates of sample material
120 revealed a precision of ca. $\pm < 0.1\text{‰}$ (1 SD). These analyses were made at the NERC Isotope
121 Geosciences Laboratory, in Keyworth, UK.

122 **3. Results**

123 Organic content of the sediments (as inferred from TOC flux) is above the average for the
124 core ($0.012 \text{ g/m}^2/\text{y}$) from 50 to 47 cm (ca. 970-1080 AD) and increase to a peak between
125 41-36 cm (ca. 1070-1280 AD; Fig.3). Thereafter, TOC flux declines steadily, concurrent with
126 decreases in diatom flux (Fig.3). TOC flux values subsequently increase at the depth of 10 cm
127 (ca.1900 AD), as does diatom fluxes and the proportion of planktonic diatom species (Fig.3).
128 TOC is most significantly correlated with TN flux (0.990^{**} ; Table1), and it is also
129 significantly positively correlated with diatom flux (0.747^{**}) and P/B ratio (0.422^*), i.e.
130 increasing abundances of planktonic diatoms (Table 1; Fig.4). C/N values fluctuate between
131 the core depth 10.6 to 15.6 cm. The highest C/N values occur between 26 and 13 cm (ca.
132 1500-1780 AD; Fig.3).

133 $\delta^{13}\text{C}$ values fluctuate between -29.3‰ and -28.0‰ from 50 to 17 cm, but show a gradual
134 and distinct increase (of 3.4‰) from 33 (-29.0‰) to 12 cm (-25.6‰ ; ca. 1350-1800 AD; Fig.
135 3). From 33 cm to 12 cm (ca. 1350-1800 AD), increasing $\delta^{13}\text{C}$ values occur as TOC flux,
136 diatom flux and P/B ratios decline (Fig. 3). For the whole profile, $\delta^{13}\text{C}$ and TOC flux are
137 negatively correlated (-0.314^{**} ; Table 1). Above 12 cm (after ca. 1800 AD), $\delta^{13}\text{C}$ values
138 rapidly decline to lowest values in the profile (ca. -29.8‰) between 10- 9 cm, coincident with
139 a distinct increase in the proportion of planktonic diatom species. More specifically, the shift
140 in diatom composition appears to be driven by a rapid decline in *Discostella* species and an
141 increase in the planktonic species *Puncticulata praetermissa* and *Asterionella formosa* (Fig.5).
142 Overall, $\delta^{13}\text{C}$ values are most significantly correlated with the P/B ratio (-0.627^{**} ; Table 1;
143 Fig.4). $\delta^{13}\text{C}$ values in the uppermost sediments, spanning the last 50 years (approx. 6 cm),
144 increase up to the time the core was taken (Fig. 3), which is coincident with the return to
145 dominance of the *Discostella* species (Fig. 5).

146 **4. Discussion**

147 All our samples have $\delta^{13}\text{C}$ values that are below -25‰ (Fig. 3), indicating the dominance
148 of C_3 plants as the principal carbon source to EML. C_3 plants utilize the enzyme RuBisCO
149 (ribulose-1,5-bisphosphate carboxylase) to fix atmospheric CO_2 which results in $\delta^{13}\text{C}$ values
150 ranging between -22‰ to -33‰ (O'Leary, 1981). This photosynthetic pathway is the most
151 common among plants and is used by most trees, shrubs, aquatic vegetation and algae. Pollen
152 evidence from EML sediments highlights that extensive pine and deciduous forest cover has
153 persisted throughout the past 1000 years (Mingram et al., 2004).

154 $\delta^{13}\text{C}$ values of bulk sediments cannot be used to distinguish between algae and terrestrial
155 C_3 plants (Meyers and Lallier-Vergès, 1999), so C/N ratios in lake sediments are commonly
156 used to assess the relative importance between allochthonous and autochthonous sources of
157 organic material (Meyers, 1994); algae generally contain only very small amounts of cellulose
158 or lignin (both carbon rich; Leng et al., 2006). Figure 3 shows that all the sediment samples
159 from EML have C/N ratios <16, with an average value of 12.8. It is likely that the plant
160 organic matter in EML is derived from a mixture of sources, especially algae (with relatively
161 low C/N ratios $5 < 10$; Meyers and Lallier-Vergès, 1999) and aquatic vegetation (both
162 submerged and floating) with relatively high C/N ratios (about 20 to 30; Fellerhoff et al.,
163 2003) and only a small contribution from terrestrial vegetation (C/N ratios between 20-160;
164 Meyers and Lallier-Vergès, 1999).

165 Organic input from terrestrial vegetation is likely to be low because TOC and diatom flux
166 are very highly, and significantly, correlated (0.747^{**} ; Table 1 and Fig. 4) which indicates that
167 algae are a major component of organic matter in the core. Secondly, the highest C/N ratios
168 observed between 28 to 12 cm (1500 – 1800 AD; Fig. 3) were unlikely caused by increased
169 in-wash of terrestrial vegetation to the lake, because pollen concentration data suggest a
170 period of relatively drier summers and a less dense vegetation cover (Mingram et al., 2004; Li
171 et al., 2012) during that interval. Previous studies based on diatom data from EML (Wang, et
172 al. 2012) and historical documents relating the frequency of snow events in Northeast China
173 (Chu et al., 2008) showed that a cold climate prevailed for this interval. Third, although the
174 abnormal changes in ^{210}Pb and the high sediment accumulation rate at the top of the core (5 to
175 0 cm; Fig.2) indicate that there was an increase in run-off input into the lake during the most

176 recent part of the core, the values for the C/N ratio are still low (Fig.3), indicating that the
177 proportion of allochthonous inputs into the lake has remained small.

178 Relatively high C/N values during the cold period (1500 –1800 AD) do coincide with an
179 increase in benthic taxa and a concomitant decline in P/B ratios, which were controlled by the
180 duration of ice cover. Longer ice cover leads to a restriction in the development of planktonic
181 communities during cold periods. Unlike planktonic taxa, benthic taxa such as the fragilarioid
182 species increase between 28 – 12 cm in EML (Wang et al., 2012). This is because spring
183 melting does allow for suitable benthic and periphytic habitats to develop in narrow ice-free
184 moats throughout the littoral zone (Smol, 1983). These species are common in high latitude
185 and alpine lakes which are characterized by long seasonal ice cover (e.g. Douglas and Smol,
186 1999; Enache et al., 2011; Mackay et al., 2012). In EML we suggest that decline in P/B ratios
187 and higher C/N values (Fig.3) are due to persistent growth of aquatic vegetation with C/N
188 ratio values comprise between 20 and 30 along the littoral zone of the lake, leading to the
189 increase in the relative abundance of organic matter derived from aquatic vegetation.

190 Primary production in lakes can influence the changes in $\delta^{13}\text{C}$ values of organic matter.
191 Primary production through time can be inferred using TOC (Leng and Marshall, 2004). A
192 long decline in TOC flux values occurs between 33 to 12 cm (ca. 1350 to ~1800 AD; Fig.3)
193 indicating that the productivity of algae and aquatic vegetation decreased. TOC can also vary
194 due to changing sedimentation rates in the lake. Here we can only provide a constant sediment
195 accumulation rate from 50 to 20 cm because of only one ^{14}C date anchoring the base of the
196 core (Fig.2), and therefore we are not able to resolve this issue directly by the data. However,
197 a previous Holocene core taken from EML was reported to be varved, with a relatively

198 constant sedimentation accumulation rate of ca. 0.06 cm yr^{-1} over the past 1000 years (You et
199 al., 2008) which is very similar to the sedimentation rate estimated in this study (0.05 cm yr^{-1}).
200 In addition, it is possible to exclude the impact of sediment rate on %TOC for the
201 radiometrically dated top of the core between 20 and 0 cm. The data also show that the
202 changes in TOC flux are very similar to changes in diatom flux, indicating likely close
203 linkages between the two (Fig 3). Between 50 and 12 cm, TOC flux is also almost concurrent
204 with the change in diatom flux and their correlation over the whole 1000-yr record is high
205 (0.747). It is likely therefore that the changes in TOC flux observed are real and not caused by
206 changing sedimentation rate and therefore that they can be used as indicator of aquatic
207 productivity.

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

214 Other factors which may cause increasing $\delta^{13}\text{C}$ values include gradual maturation of lakes
215 and changes in catchment vegetation. As lakes mature, ^{12}C -enriched organic matter is
216 transported into bottom sediments (Meyers and Lallier-Vergès, 1999). However the changes
217 observed in EML are quite abrupt, e.g. at 11 cm, and moreover, the increase in values only
218 occurs during a specific timeframe, and so unlikely to be due to lake maturation. On the
219 catchment, the development of stable, mature soils can result in increased soil respiration and

220 the supply of ^{13}C -depleted dissolved CO_2 to lakes, leading to lower ^{13}C values (Hammarlund,
221 1993). Conversely, increasing ^{13}C values may be interpreted due to forest retreat and
222 subsequent reduction in catchment soil respiration. At EML, there is evidence for a decline in
223 tree pollen concentration during the period of increasing ^{13}C values (Li et al., 2012), but
224 almost no change in the composition of pollen assemblage took place. This suggests that the
225 vegetation cover in this region did not change to such an extent that this could lead to an
226 increase of $\delta^{13}\text{C}$ -depleted dissolved CO_2 .

227 Another potential influence on sedimentary ^{13}C values is the difference in proportions of
228 phytoplankton and benthic microalgae (France, 1995), assuming much of the sedimentary
229 organic matter is derived from the algae. France (1995) collated literature data on $\delta^{13}\text{C}$ for
230 marine and freshwater benthic and planktonic algae and found that the average $\delta^{13}\text{C}$ values
231 for benthic algae in lakes was $-26\text{‰} \pm 3$, whereas it was lower at $-32\text{‰} \pm 3$ for planktonic
232 algae, an average difference of about 6‰. Doi et al. (2009) also found significant differences
233 between $\delta^{13}\text{C}$ values of plankton (lower) and benthic (higher) microalgae sampled
234 simultaneously across a range of lakes. These differences may be explained by the diffusive
235 boundary layer effect (Jørgensen and Revsbech, 1985). The boundary layer is caused by the
236 viscous properties of water and is composed of a film of water that sticks to the surface of the
237 solid (e.g. sediment, plants, biofilm or detritus) and does not participate to the general
238 circulation of the surrounding water. Its thickness can vary from 0.2 to >1 mm and water
239 turbulence above the solid-water interface has a major influence on how thick is the boundary
240 layer (Jørgensen and Revsbech, 1985). The diffusive boundary layer constitutes a transfer
241 resistance for fluxes of dissolved organic molecules, inorganic ions and gases such as CO_2

242 and oxygen across the solid-water interface and it is especially limiting for plants and algae at
243 high uptake rates (Jørgensen and Revsbech, 1985). A thick boundary layer, because it leads to
244 an entrapment of otherwise expelled ^{13}C , results in more positive $\delta^{13}\text{C}$ for the plants or algae
245 (Jørgensen and Revsbech, 1985; Doi et al., 2009).

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

257 In cold conditions with extensive ice-cover, the productivity of benthic communities in a
258 lake is proportionally less affected than that of the planktonic communities, because the littoral
259 zone may still melt and open up during summer months (Douglas and Smol, 1999). From ca.
260 1350 to 1800 AD, diatoms data (Wang et al., 2012) suggests the prevalence of a cooler
261 climate, possibly concurrent with the Little Ice Age. A cooler climate seems the most likely
262 cause for the observed decline in TOC and diatom fluxes, and the decline in planktonic
263 diatom biovolume accumulation rates (Wang et al., 2012). At this time there is also a marked

264 decline in the P/B ratio, indicative of increased proportion of benthic diatoms in the
265 sedimentary record. As discussed by France (1995) and Doi et al. (2009) benthic algae are ^{13}C -
266 enriched compared to planktonic algae which may also contribute to the sustained increase in
267 $\delta^{13}\text{C}$ values at this time.

268 The same process could also explain the abrupt decline in $\delta^{13}\text{C}$ values by ca. 4.2‰ after
269 ca. 1800 AD that occurred simultaneously with an increase in the proportion of planktonic
270 diatoms (Fig.5). The decline in $\delta^{13}\text{C}$ values at EML at this time is also coincident with the
271 onset of the industrial revolution and release of greater ^{12}C into the atmosphere due to fossil
272 fuel combustion and deforestation. This has resulted in the relative decline of ^{13}C (and ^{14}C) in
273 atmospheric CO_2 over the past ca. 200 years, which in turn has resulted in their decline in
274 other reservoirs, including oceans and lakes. This process is referred to as the Suess effect
275 (Keeling, 1979), and is apparent in $\delta^{13}\text{C}$ records from several lake sediment records (e.g.
276 Verburg, 2007; Castaneda et al., 2011; Jiang et al., 2011). Between ca. 1840-2000 AD, the
277 decline in atmospheric $\delta^{13}\text{C}$ values was ca. 1.6‰ (Verburg, 2007). Therefore, the magnitude
278 of change in EML during this period cannot be attributed to the sole Suess effect. Moreover,
279 the Suess effect cannot explain increasing $\delta^{13}\text{C}$ values observed in EML during the past 50
280 years. Furthermore, the sharp decline in $\delta^{13}\text{C}$ values cannot be explained by a decline in algal
281 productivity, because TOC and diatom fluxes increase after ca. 1800 AD (Fig.3).

282 The late decline in $\delta^{13}\text{C}$ to lowest values between 1900 and 1950 AD is concurrent with
283 the increase in planktonic diatoms, which as discussed above have lower $\delta^{13}\text{C}$ values,
284 specifically *P. praetermissa* and *A. formosa* (Fig.5), both of which have been shown to thrive
285 during periods of spring and autumn turnover, when turbulence in the lake is particularly high

286 (Morabito et al., 2002; Ptacnik et al., 2003; Rioual et al., 2009). For example, in the
287 neighbouring Lake Sihailongwan, located 18 km east from Lake Erlongwan, analyses of
288 sediment trap samples show that *P. praetermissa* blooms seasonally in spring and in autumn,
289 when windy conditions cause turnover and the water column is well mixed (Rioual et al.,
290 2009). Detailed experimental studies in oligotrophic lakes showed that *A. formosa* is also
291 abundant under conditions with high water turbulence (Morabito et al., 2002; Ptacnik et al.,
292 2003).

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

306 By contrast with the large planktonic species, cells of *Discostella* species, a group of
307 planktonic species which blooms in summer months when the water column is thermally

308 stratified and water turbulence is weak (Sorvari et al., 2002; Smol et al., 2005; Rühland et al.,
309 2008; Wang et al., 2008; 2012a) would have less depleted $\delta^{13}\text{C}$ values than that of *P.*
310 *praetermissa* and *A. formosa*, but more depleted $\delta^{13}\text{C}$ values than benthic algae. Therefore,
311 over the last five decades, the EML sediment record shows that $\delta^{13}\text{C}$ values increased slowly
312 with increasing proportions of *Discostella* species (Fig.5). The increase in the relative
313 abundance of small planktonic *Discostella* species and the concurrent decrease in large
314 diatoms *Asterionella* and *Puncticulata* are consistent with increased temperatures leading to
315 strong thermal stratification of the water column (Wang et al., 2012). The increase of
316 *Discostella* (and other small centric diatoms of the genus *Cyclotella*) with global warming has
317 been reported in the recent sediments of numerous lakes throughout the Northern Hemisphere
318 (Sorvari et al., 2002; Rühland et al., 2003; 2008; 2010; Smol et al., 2005; Wang et al., 2012b)
319 including nearby Xiaolongwan Lake (Panizzo et al., 2012).

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

323 In our opinion, this new approach has great potential for interpreting carbon isotopes as
324 proxy records for climate changes and should be considered in future studies. However, this
325 interpretation is useful only if due attention is paid to the following points: i) the lake
326 sedimentary organic matter should be derived almost exclusively from algae and aquatic
327 vegetation, ii) as water level changes also cause variations in the ratio between planktonic and
328 benthic diatom, they may also affect the carbon isotopes signal; iii) eutrophication, as it often

329 leads to large increase in the abundance of planktonic algae, may also alter the carbon isotope
330 record and should also be taken into account when interpreting the record.

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

334 **5. Conclusions**

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

342

343 **Acknowledgements**

344 This research was supported by National Basic Research Program of China (973 Program)
345 (grant number: 2010CB950201) and NSFC (grant number: 40572105, 40971121). Additional
346 support was provided by the UCL Simon Li Fund and Ensis Trust Fund. We are grateful to
347 two anonymous reviewers for their helpful and constructive comments on the manuscript and
348 the associate editor Bart van Dongen who helped to improve the manuscript.

349 **References**

350 Battarbee, R.W., Jones, V.J., Flower, B.P., Cameron, N.G., Bennion, H., Carvalho, L.,
351 Juggins, S., 2001. Diatoms, In: Smol, J.P., Birks, H.J.B., Last, W.M. (Eds.), Tracking

352 Environmental Change Using Lake Sediments. Kluwer Academic Publishers, Dordrecht,
353 pp. 155-201.

354 Battarbee, R.W., Kneen, M.J., 1982. The use of electronically counted microspheres in
355 absolute diatom analysis. *Limnology and Oceanography* 27, 184-188.

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

357 Chu, G.Q., Sun, Q., Wang, X.H., Sun, J.Y., 2008. Snow anomaly events from historical
358 documents in eastern China during the past two millennia and implication for
359 low-frequency variability of AO/NAO and PDO. *Geophysical Research Letters* 35,
360 doi:14810.11029/12008GL034475.

361 Doi, H., Kikuchi, E., Shikano, S., Takagi, S., 2009. Differences in nitrogen and carbon stable
362 isotopes between planktonic and benthic microalgae. *Limnology* 11, 185-192.

363 Douglas, M.S.V., Smol, J.P., 1999. Freshwater diatoms as indicators of environmental change
364 in the High Arctic, In: Stoermer, E.F., Smol, J.P. (Eds.), *The Diatoms: Application for the*
365 *Environmental and Earth Sciences*. Cambridge University Press, Cambridge, pp.
366 227-244.

367 Enache, M.D., Paterson, A.M., Cumming, B.F., 2011. Changes in diatom assemblages since
368 pre-industrial times in 40 reference lakes from the Experimental Lakes Area
369 (northwestern Ontario, Canada). *Journal of Paleolimnology* 46, 1-15.

370 Fellerhoff, C., Voss, M., Wantzen, K.M., 2003. Stable carbon and nitrogen isotope signatures
371 of decomposing tropical macrophytes. *Aquatic Ecology* 37, 361-375.

372 France, R.L., 1995. Carbon-13 enrichment in benthic compared to planktonic algae: foodweb
373 implications. *Marine Ecology Progress Series* 124, 307-312.

374 Frank, U., 2007. Palaeomagnetic investigations on lake sediments from NE China: a new
375 record of geomagnetic secular variation for the last 37Ka. *Geophysics Journal International*
376 169, 29-40.

377 Hammarlund, D., 1993. A distinct ¹³C decline in organic lake sediments at the
378 Pleistocene-Holocene transition in southern Sweden. *Boreas* 22, 236-243.

379 Jørgensen, B.B., Revsbech, N.P., 1985. Diffusive boundary layers and the oxygen uptake of
380 sediments and detritus. *Limnology and Oceanography* 30, 111-122.

381 Keeling, C.D., 1979. The Suess effect: 13Carbon-14carbon interrelations. *Environment*
382 *International* 2, 229-300.

383 Krammer, K., Lange-Bertalot, H., 1986-1991. *Bacillariophyceae. Süßwasserflora von*
384 *Mitteleuropa, Band 2*. Spektrum Akademischer Verlag Heidelberg, Berlin.

385 Leng, M.J., Lamb, A.L., Heaton, T.H.E., Marshall, J.D., Wolfe, B.B., Jones, M.D., Holmes,
386 J.A., Arrowsmith, C., 2006. *Isotopes in Lake Sediments*, In: Leng, M.J. (Ed.), *Isotopes in*
387 *Palaeoenvironmental Research*. Springer, Netherlands, pp. 147-184.

388 Leng, M.J., Marshall, J.D., 2004. Palaeoclimate interpretation of stable isotope data from lake
389 sediment archives. *Quaternary Science Reviews* 23, 811-831.

390 Li, J., Mackay, A.W., Zhang, Y., Li, J.J., 2012. A 1000-year record of vegetation change and
391 wildfire from maar lake Erlongwan in northeast China. *Quaternary International*,
392 doi:10.1016/j.quaint.2012.1008.2104.

393 Li, J.J., Li, J., Wang, L., 2009. The best duration of settling for diatom suspension.
394 *Quaternary Sciences* 29, 183-184 (in Chinese with English abstract).

395 Mackay, A.W., Bezrukova, E.V., Leng, M.J., Meaney, M., Nunes, A., Piotrowska, N., Self,
396 A., Shchetnikov, A., Shilland, E., Tarasov, P., Wang, L., White, D., 2012. Aquatic
397 ecosystem responses to Holocene climate change and biome development in boreal,
398 central Asia. *Quaternary Science Reviews* 41, 119-131.

399 Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of
400 sedimentary organic matter. *Chemical Geology* 144, 289-302.

401 Meyers, P.A., Lallier-Vergès, E., 1999. Lacustrine sedimentary organic matter records of Late
402 Quaternary paleoclimates. *Journal of Paleolimnology* 21, 345-372.

403 Mingram, J., Allen, J.R.M., Bruchmann, C., Liu, J., Luo, X., Negendank, J.F.W., Nowaczyk,
404 N., Schettler, G., 2004. Maar and crater lakes of the Long Gang Volcanic Field (NE China)
405 - overview, laminated sediments, and vegetation history of the last 900 years. *Quaternary*
406 *International* 123-25, 135-147.

407 Morabito, G., Ruggiu, D., Panzani, P., 2002. Recent dynamics (1995-1999) of the
408 phytoplankton assemblages in Lago Maggiore as a basic tool for defining association
409 patterns in the Italian deep lakes. *Journal of Limnology* 61, 129-145.

410 O'Leary, M.H., 1981. Carbon isotope fractionation in plants. *Phytochemistry* 20, 553-567.

411 Panizzo, V.N., Mackay, A.W., Rose, N.L., Rioual, P., Leng, M.J., 2012. Recent
412 palaeolimnological change recorded in Lake Xiaolongwan, northeast China: Climatic
413 versus anthropogenic forcing. *Quaternary International*, [doi:10.1016/j.quaint.2012.09.008](https://doi.org/10.1016/j.quaint.2012.09.008).

414 Ptacnik, R., Diehl, S., Berger, S., 2003. Performance of sinking and nonsinking phytoplankton
415 taxa in a gradient of mixing depths. *Limnology and Oceanography* 48, 1903-1912.

416 Rioual, P., Chu, G.Q., Li, D., Mingram, J., Han, J., Liu, J., 2009. Climate-induced shifts in
417 planktonic diatoms in lake Sihailongwan (North-East China): a study of the sediment trap
418 and palaeolimnological records, 11th International Paleolimnology Symposium,
419 Guadalajara, Mexico, p. 120.

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

422 Verburg, P., 2007. The need to correct for the Suess effect in the application of delta C-13 in
423 sediment of autotrophic Lake Tanganyika, as a productivity proxy in the Anthropocene.
424 *Journal of Paleolimnology* 37, 591-602.

425 Wang, L., Rioual, P., Panizzo, V.N., Leng, M.J., Lu, H.Y., Gu, Z.Y., Chu, G.Q., Yang, D.G.,
426 Han, J.T., Liu, J.Q., Mackay, A.W., 2012. A 1000-yr record of environmental change in
427 NE China indicated by diatom assemblages from maar lake Erlongwan. *Quaternary*
428 *Research* 78, 24-34.

429 You, H.T., Liu, J.Q., Liu, Q., Chu, G.Q., Rioual, P., Han, J.T., 2008. Study of the varve
430 record from Erlongwan maar lake, NE China, over the last 13 ka BP. *Chinese Science*
431 *Bulletin* 53, 262-266.

432

433

434

435

436

437

438 **Figure Captions:**

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

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

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

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

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

Figure(s)

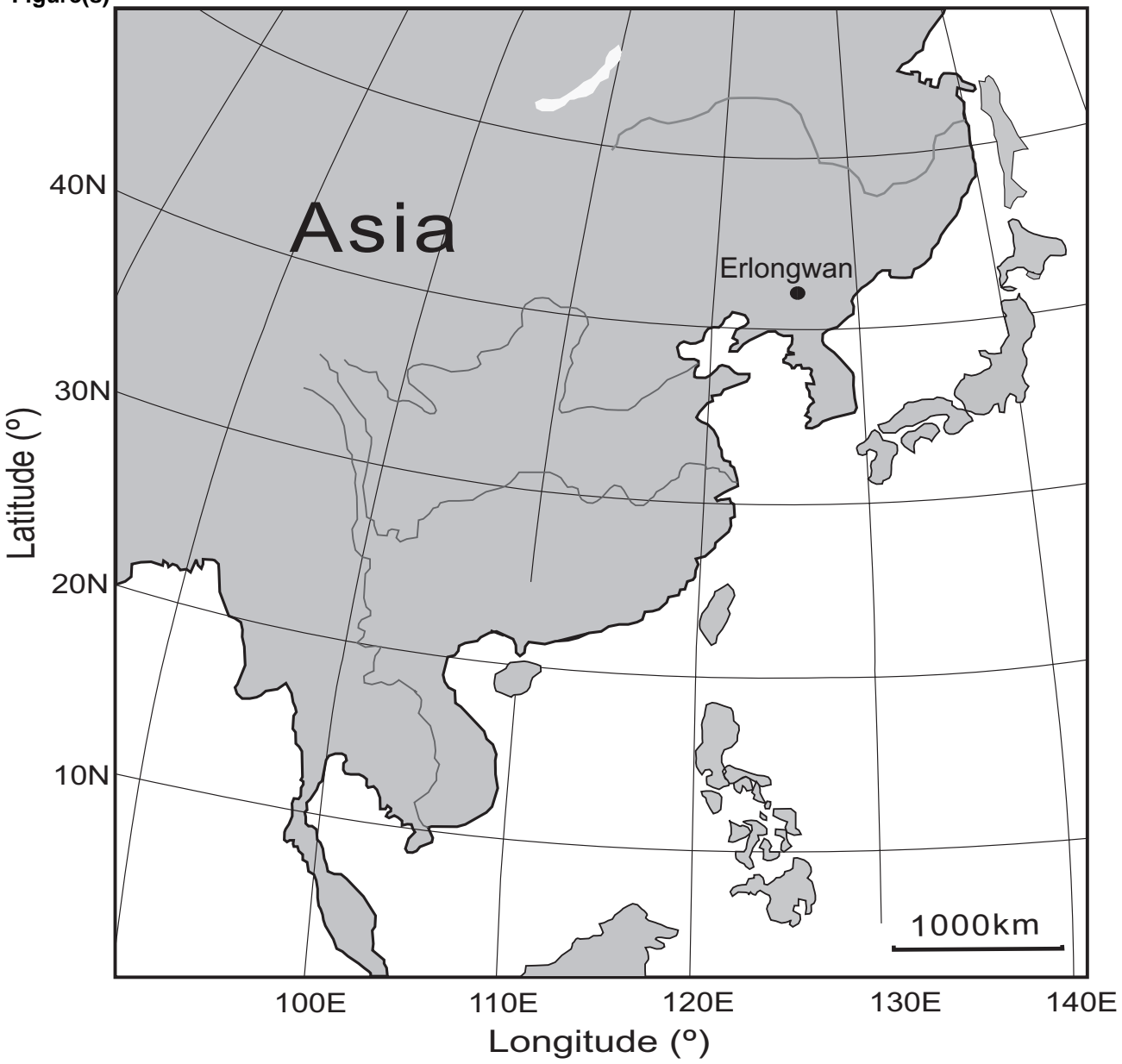


Fig.1 Wang L.et al.

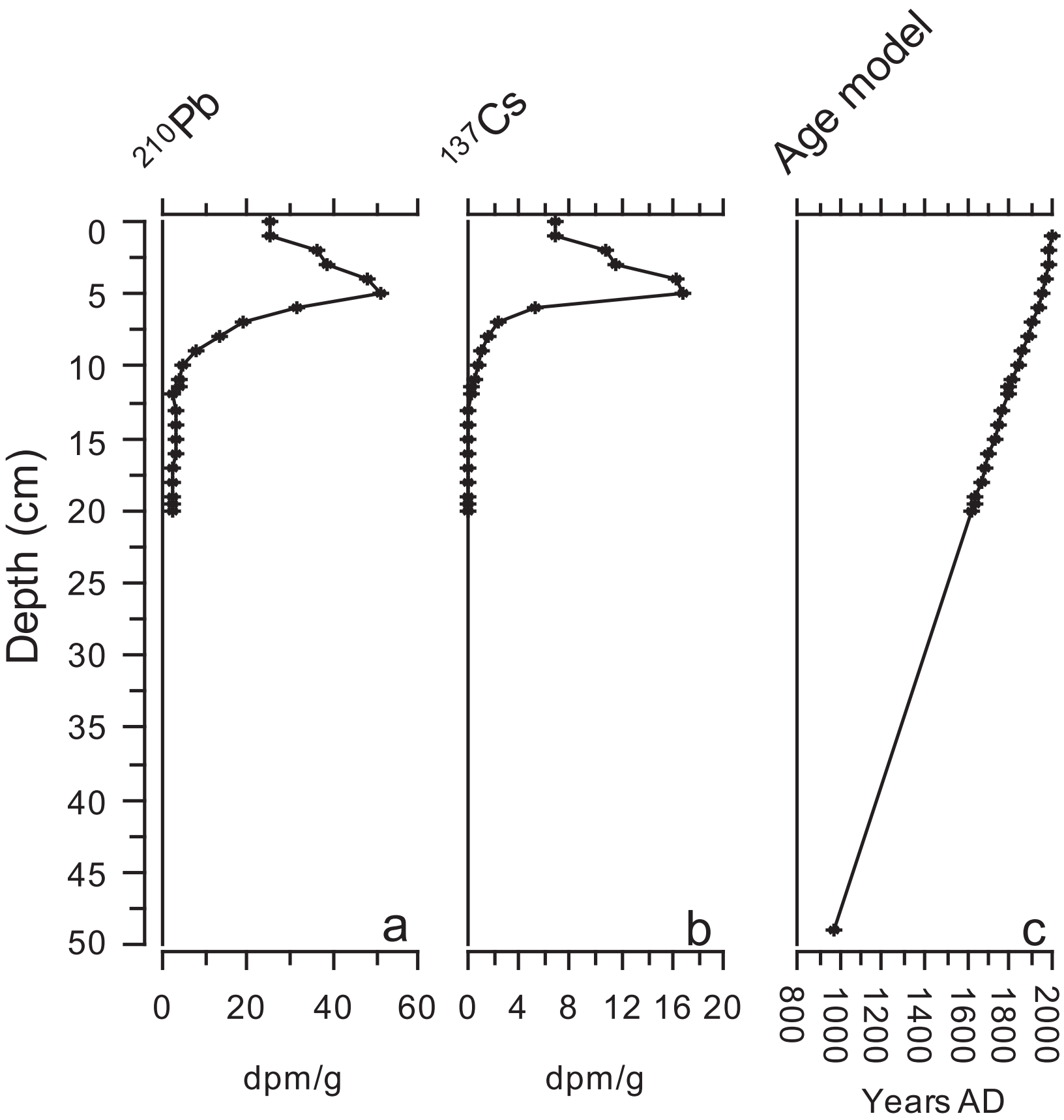


Figure2.

Wang L.

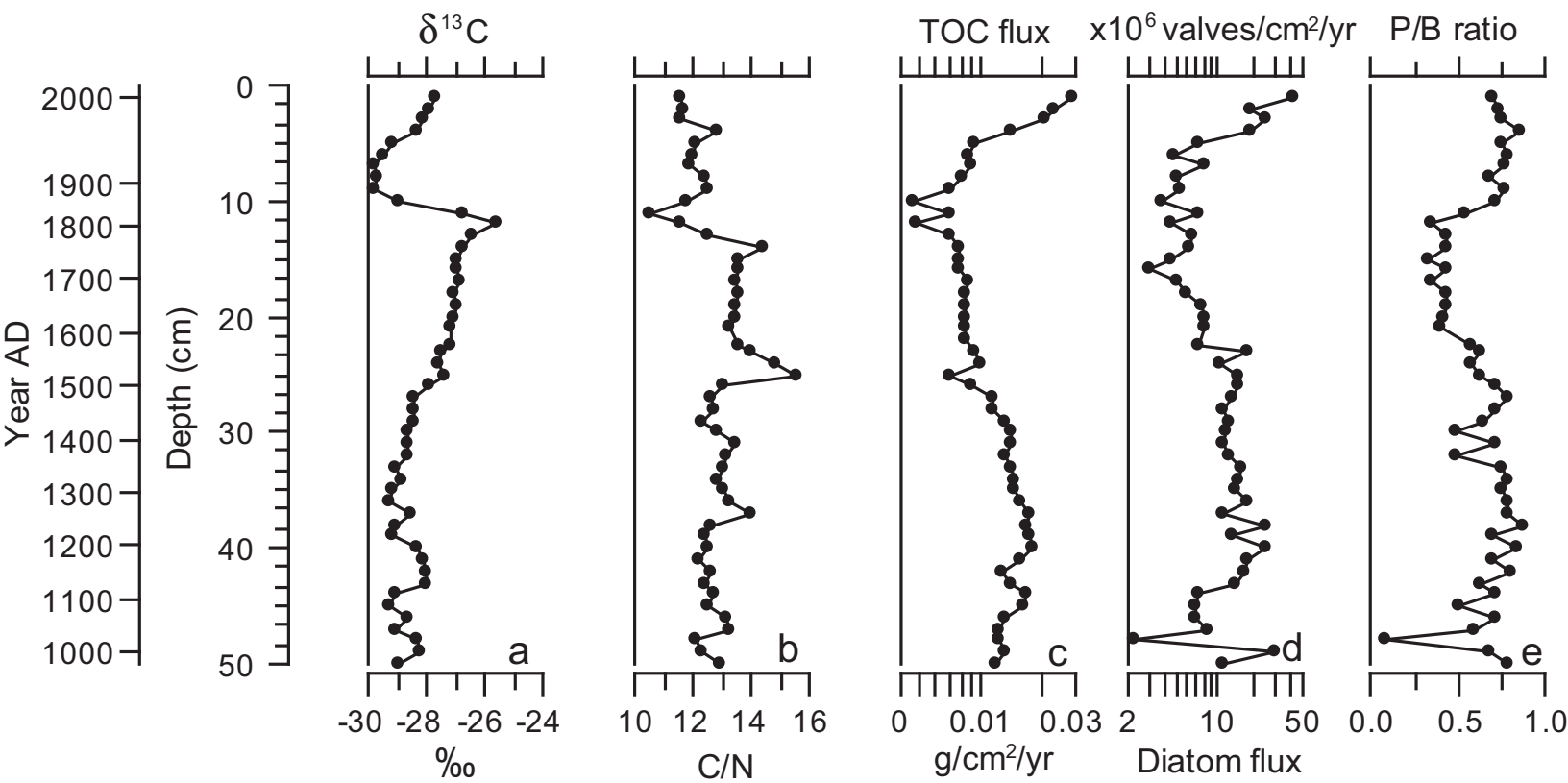


Figure3. Wang L. et al.

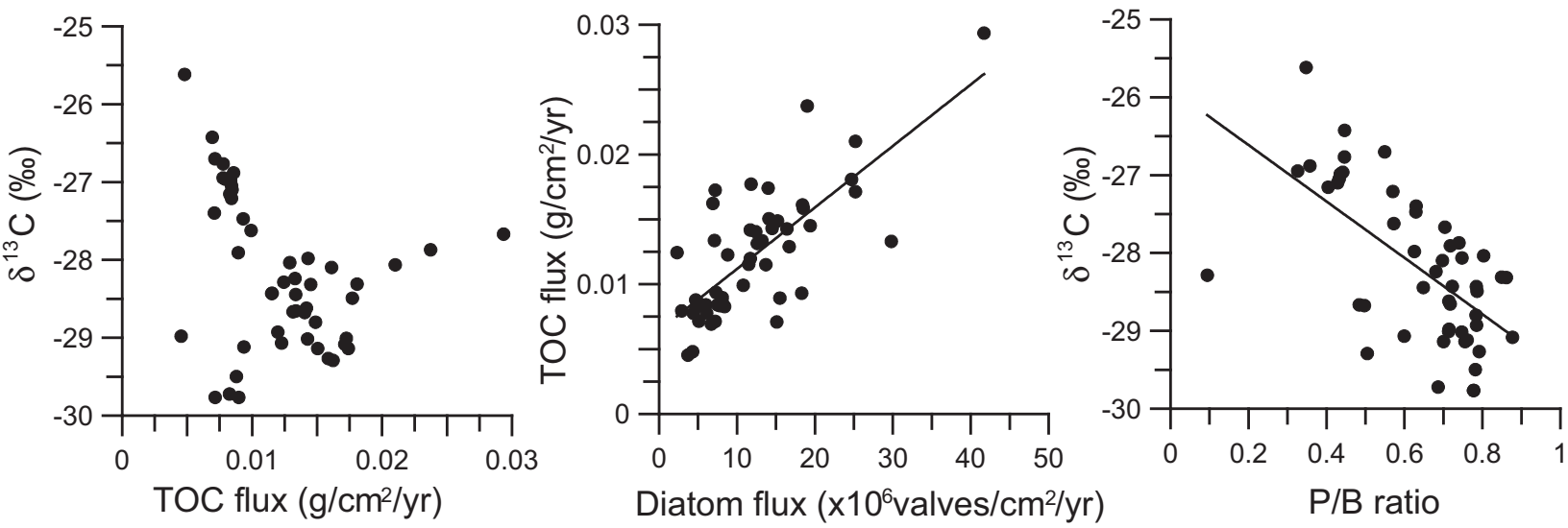


Figure 4. Wang L. et al.

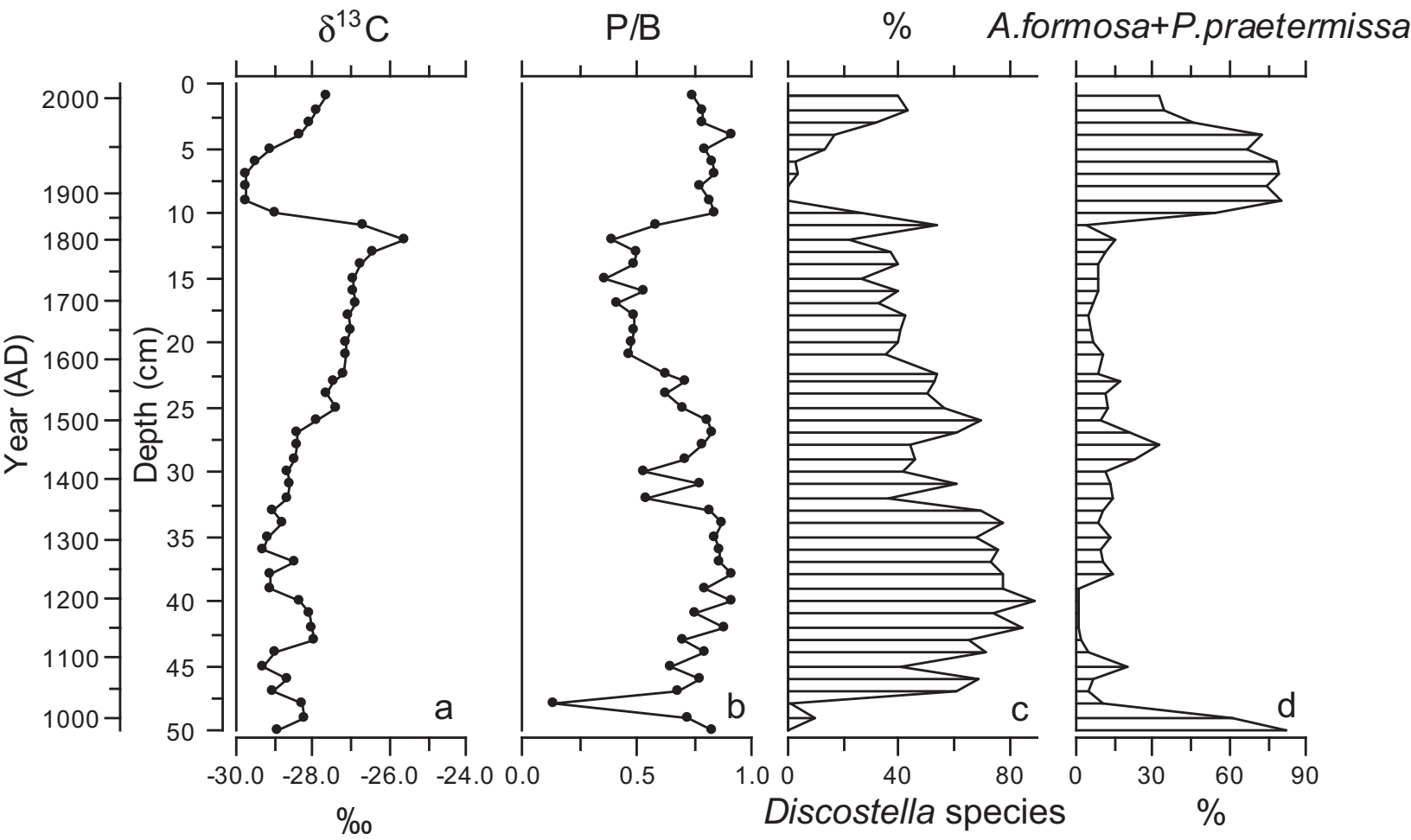


Figure5. Wang L. et al.

Table 1: Pearson Product Moment Correlation Coefficients

	$\delta^{13}\text{C}$	C/N	P/B_ratio	diatom_flu	TN_flux	TOC_flux
$\delta^{13}\text{C}$	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).						