Title: The influence of the ratio of planktonic to benthic diatoms on lacustrine organic matter 13C from Erlongwan maar Lake, Northeast China

Article Type: Research Paper

Corresponding Author: Dr. Luo Wang, Ph.D.

Corresponding Author's Institution: Institute of Geology and Geophysics, CAS

First Author: Luo Wang, Ph.D.

Order of Authors: Luo Wang, Ph.D.; Mackay W Anson, Ph.D.; Melanie J Leng, Ph.D; Patrick Rioual, Ph.D; Virginia N Panizzo, Ph.D; Houyuan Lu, Ph.H; Zhaoyan Gu, Ph.D; Guoqiang Chu, Ph.D; Jingtai Han, Ph.D; Christopher P Kendrick, Ph.D

Abstract: Carbon isotope ratios (δ13C) of organic matter within lake sediments are commonly used to reconstruct environmental change, but the factors which influence change in values are varied and complex. Here we report δ13C values determined from organic sediments from Erlongwan maar lake in Northeast China. In this record, changes in δ13C cannot be explained by simple changes in aquatic productivity. Instead, δ13C 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 δ13C$_{org}$ in algae from different habitats is controlled by the thickness of the diffusive boundary layer, which is dependent on how turbulent is the water. By comparison with 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 δ13C depletion. In Erlongwan maar lake low δ13C values are linked to the dominance of planktonic diatoms during the period commonly known as the Medieval Warm Period. δ13C 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 δ13C.

Highlights

$\delta^{13}C_{org}$ of sediments is controlled by the proportion of planktonic to benthic algae.

During warm intervals planktonic algae dominate, resulting in $\delta^{13}C$ depletion.

During cold periods benthic algae dominate, resulting in $\delta^{13}C$ enrichment.

1   **The influence of the ratio of planktonic to benthic diatoms on lacustrine organic matter**

2   **δ^{13}C from Erlongwan maar Lake, Northeast China**

3   Luo Wang[1*], Anson W. Mackay[2], Melanie J. Leng[3&4], Patrick Rioual[1],Virginia N. Panizzo[2],

4   Houyuan Lu[1], Zhaoyan Gu[1], Guoqiang Chu[1], Jingtai Han[1], Christopher P. Kendrick[4]

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: wangluo@mail.iggcas.ac.cn, Tel:086-10-82998261

16

17

18

19

20

21

22

23 **ABSTRACT**

24 Carbon isotope ratios (δ^{13}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 δ^{13}C values determined from organic sediments from Erlongwan

27 maar lake in Northeast China. In this record, changes in δ^{13}C cannot be explained by simple

28 changes in aquatic productivity. Instead, δ^{13}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 $\delta^{13}C_{org}$ 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 δ^{13}C depletion. In Erlongwan maar lake low δ^{13}C values are

35 linked to the dominance of planktonic diatoms during the period commonly known as the

36 Medieval Warm Period. δ^{13}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 δ^{13}C.

40

41

42

43

44

2

1. Introduction

45

46   Carbon isotope ratios ($\delta^{13}C$) 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 $\delta^{13}C$ from bulk organic material in lake sediments is complex and dependent

50   on many factors. $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ variability in the sedimentary record from

60   Erlongwan maar lake (EML) over the past 1000 years, using $\delta^{13}C$ 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

3

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 km^2 at 724 m above sea level (Fig. 1). It is a

76   closed lake with a small catchment (0.4 km^2) 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

4

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

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 ($^{13}C/^{12}C$) 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. $\delta^{13}C$ 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‰ (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 g/m^2/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    $\delta^{13}C$ 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 $\delta^{13}C$ values occur as TOC flux,

136   diatom flux and P/B ratios decline (Fig. 3). For the whole profile, $\delta^{13}C$ and TOC flux are

137   negatively correlated (–0.314[**]; Table 1). Above 12 cm (after ca. 1800 AD), $\delta^{13}C$ 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, $\delta^{13}C$ values are most significantly correlated with the P/B ratio (–0.627[**]; Table 1;

143   Fig.4). $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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    $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$. 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 $\delta^{13}C$ values of ca. 3.7‰. It

212   is unlikely that increasing $\delta^{13}C$ values in EML sediments were caused by declining aquatic

213   productivity.

214   Other factors which may cause increasing $\delta^{13}C$ 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

10

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 $\delta^{13}C$-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 $\delta^{13}C$ for

230   marine and freshwater benthic and planktonic algae and found that the average $\delta^{13}C$ values

231   for benthic algae in lakes was –26‰ ± 3, whereas it was lower at –32‰ ± 3 for planktonic

232   algae, an average difference of about 6‰. Doi et al. (2009) also found significant differences

233   between $\delta^{13}C$ 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 $\delta^{13}C$ 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 subtratum 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 *praetermissa* 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 $\delta^{13}C$

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 δ^{13}C values at this time.

268   The same process could also explain the abrupt decline in δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}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 δ^{13}C values observed in EML during the past 50

280 years. Furthermore, the sharp decline in δ^{13}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 δ^{13}C to lowest values between 1900 and 1950 AD is concurrent with

283 the increase in planktonic diatoms, which as discussed above have lower δ^{13}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

13

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 δ^{13}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 δ^{13}C values of the sediment

304   because of relatively high dissolved carbon concentration in lake water leading to further

305   discrimination against δ^{13}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 $\delta^{13}C$ values than that of P.

310   *praetermissa* and *A. formosa*, but more depleted $\delta^{13}C$ values than benthic algae. Therefore,

311   over the last five decades, the EML sediment record shows that $\delta^{13}C$ 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

15

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 $\delta^{13}C$ 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 $\delta^{13}C$ variation in lake

339　　sediments. In future studies, when trying to explain variations in lacustrine organic $\delta^{13}C$ 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

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   inthe High Artic, In: Stoermer, E.F., Smol, J.P. (Eds.), The Diatoms: Application for the
365   Environmental and Earth Sciences. Carmbridge 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 Internation
376   169, 29-40.
377   Hammarlund, D., 1993. A distinct ^{13}C 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.
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

Figure Captions:

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

440   **Figure 2.**   The EML short core [137]CS -[210]Pb$_{ex}$ 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) δ^{13}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 δ^{13}C, (b)

446   diatom flux and TOC flux, (c) planktonic to benthic (P/B) ratio and δ^{13}C.

447   **Figure 5.**   (a) δ^{13}C, (b) the ratio of planktonic to benthic diatoms, (c) percentages of

448   *Discostella* species complex, (d) combined relative abundances of *P.*
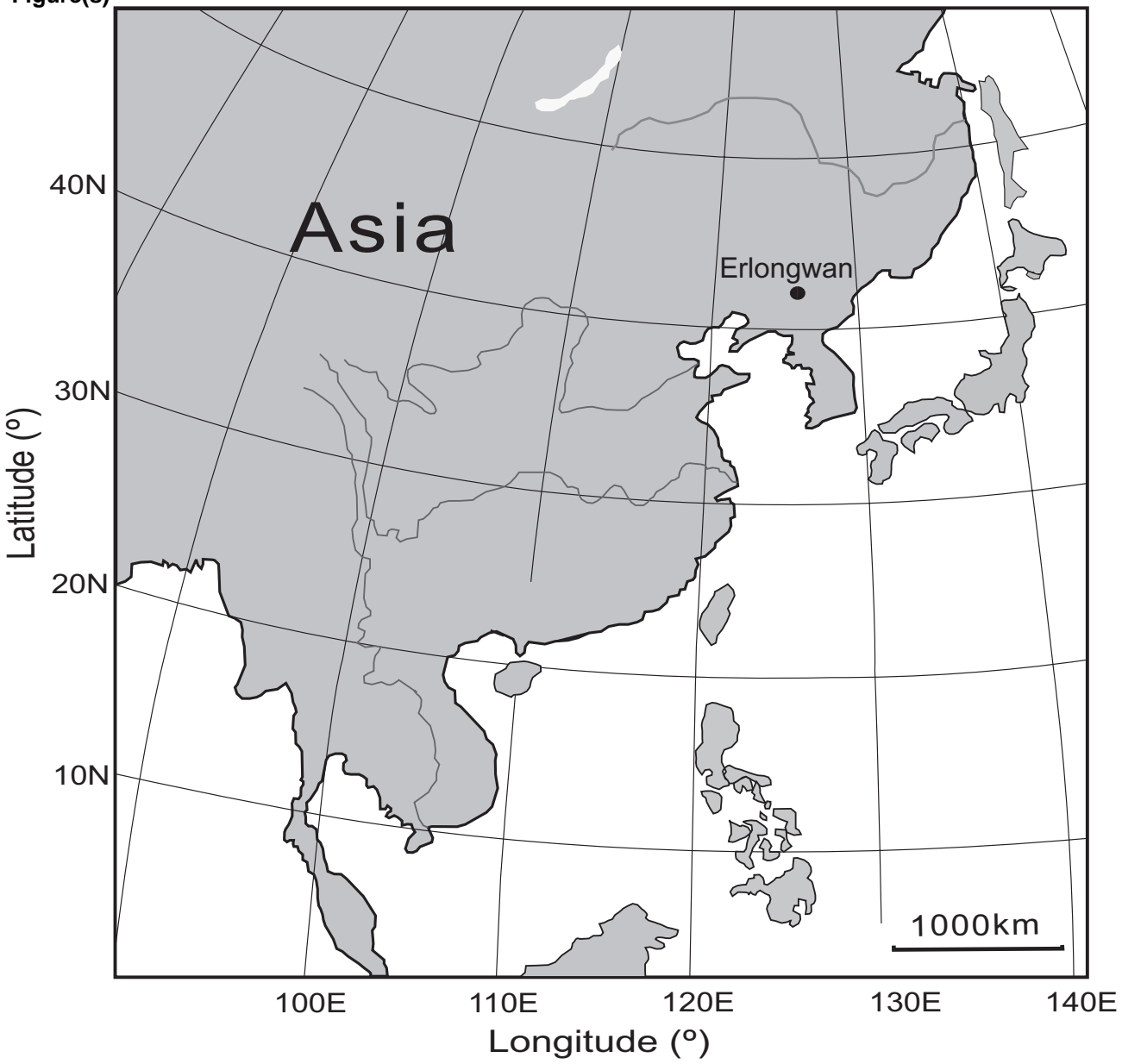
449   *praetermissa* and *A. formosa*

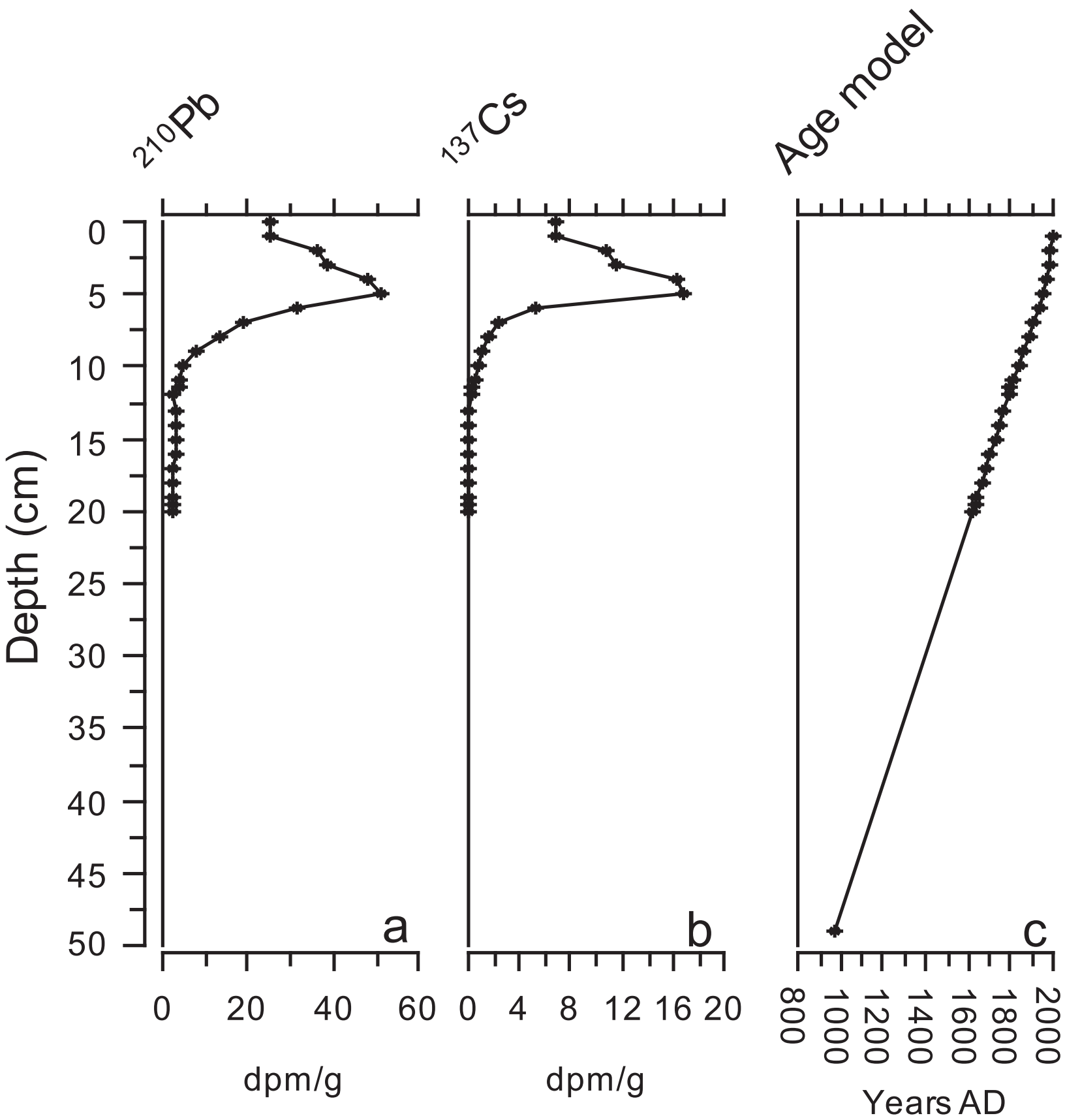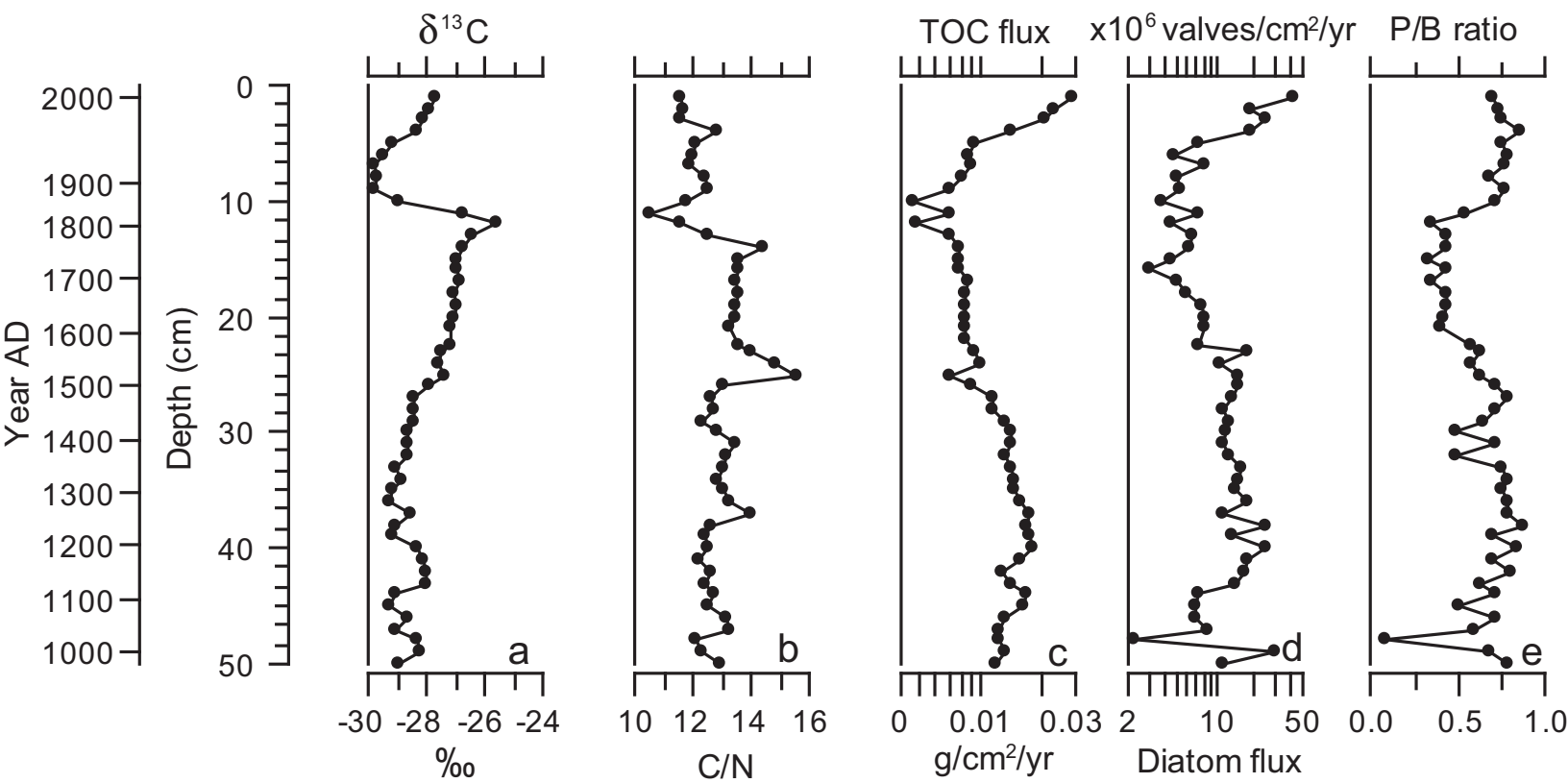Fig.1   Wang L.et al.

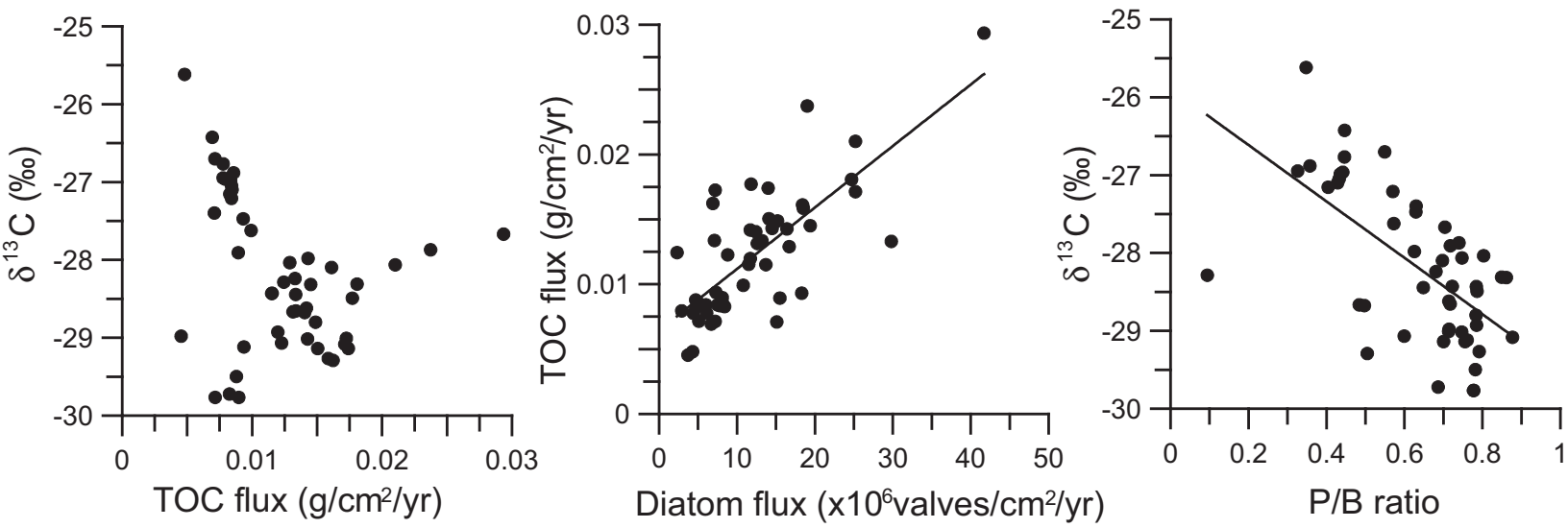**Figure2.**   **Wang L.**
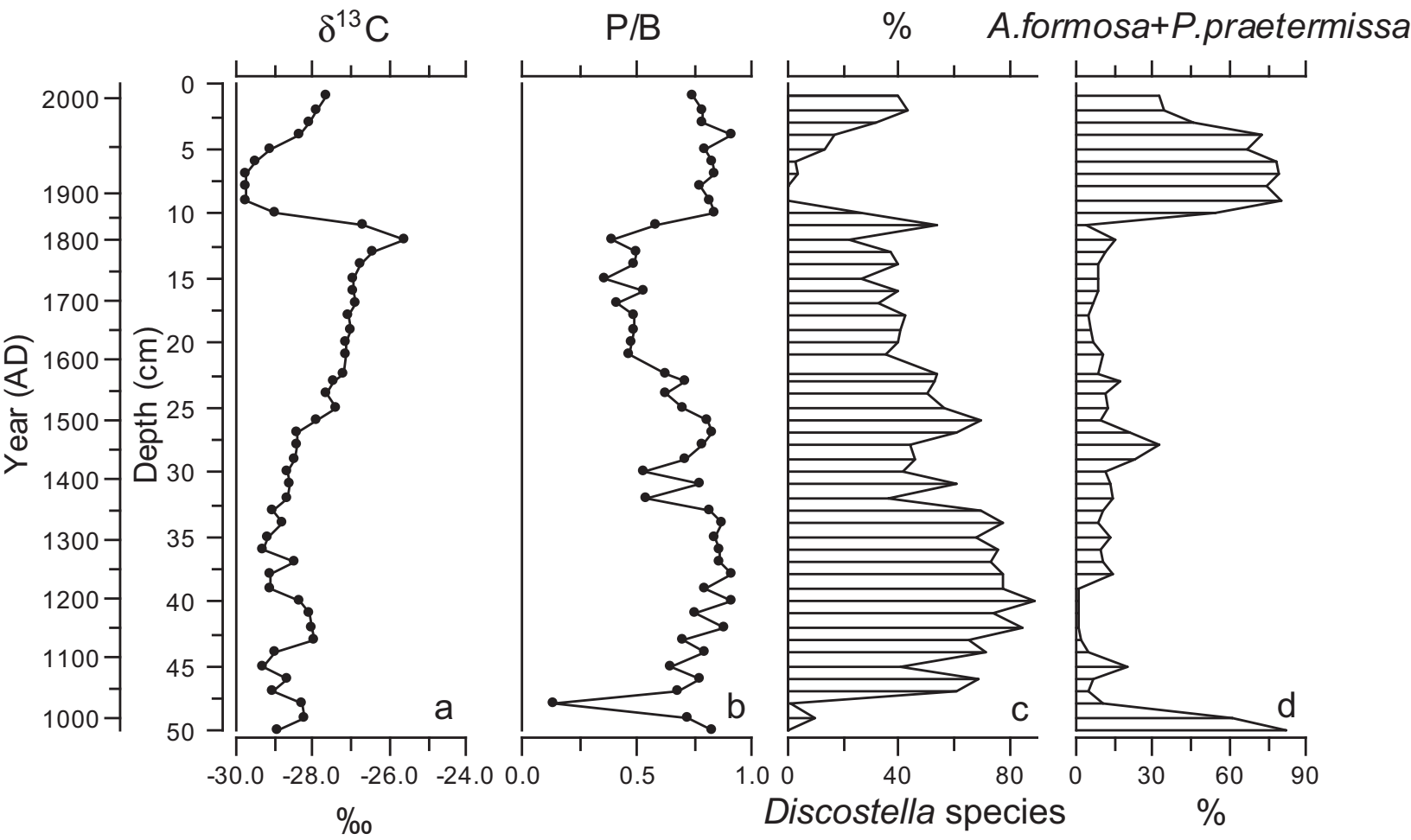
Figure3. Wang L. et al.

Figure 4.   Wang L. et al.

Figure5. Wang L. et al.

Table 1: Pearson Product Moment Correlation Coefficients

	$\delta^{13}C$	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).						

Dear Prof. Maxwell and Dr. van Dongen,

Thank you sincerely for all your help.

Please find in the attached files the revised version of our manuscript (OG-1717) originally entitled " The relationship between δ13C and the ratio of planktonic to benthic diatoms: an assessment from the sedimentary record of Erlongwan maar lake, northeastern China ".

We are most grateful to you and the reviewers for your valuable comments and suggestions that have been fully considered in this revised version.

Please note we changed the title of this manuscript to "The influence of the ratio of planktonic to benthic diatoms on lacustrine organic matter $d^{13}C$ from Erlongwan maar Lake, Northeast China"

Best wishes,

Luo Wang (corresponding author)

Ms. Ref. No.: OG-1717
Title: The relationship between <delta>13C and the ratio of planktonic to benthic diatoms: an assessment from the sedimentary record of Erlongwan maar lake, northeastern China
Organic Geochemistry

Reviewers' comments:

Reviewer #1: General Comments:

This manuscript presents a novel concept of using stable istotopes (<delta>13C) as a means of tracking changes in planktonic to benthic algae (diatoms) ratios. The authors suggest that changes in this ratio together with changes in the organic geochemical signal can be used to track changes in climate.

Although I am not an expert in the field of organic geochemistry, this review will focus on the diatom aspects of the manuscript. More detailed comments are included in the attached annotated pdf.

1) The premise of this approach is that greater water turbulence causes a depletion of <delta>13C relative (this is an important word here) to aquatic habitats that have less water movement.

In this context it is very important that the authors clarify that they are not actually tracking well mixed versus very thermally stable water column properties as a result of cooler and warmer climates (respectively). Rather, the benthic habitats of the lake offer a less turbulent environment for algae than the pelagic habitats where planktonic algae live. This follows the earlier work of France (1995). The authors are aware of this but the way that sections of this paper are written, the reader can easily mis-interpret this.

During periods of warming, overall water turbulence and mixing strength decreases as thermal stability increases..in Erlongwan this leads to a strongly stratified water column that favours small planktonic diatoms such as Discostella stelligera varieties that are able to take advantage of this density gradient. During cooler periods with longer ice cover, benthic diatoms tend to dominate as mixing is stronger and thermal stratification diminishes (thermal stability decreases). The authors are very familiar with these relationships.

As written, it almost sounds as thought the warmer conditions resulted in more turbulent water column conditions thereby favouring planktonic diatoms...as the authors realize, this is not the case. I think you need to carefully word this to clarify that this is a relative comparison between the quieter benthic environment and the greater water movement experienced in the pelagic zones of lakes. Therefore this <delta>13C depletion is not because the water is warmer and stratifies per se BUT because of this, planktonic diatoms prevail under these warmer water column conditions AND the prevalence of planktonic diatoms can drive the lower <delta>13C values during these warmer periods.

We have clarified our statement about turbulence and made a better distinction between benthic, small planktonic and large planktonic diatoms according to the reviewers' suggestions. Please see the lines: 31-34, 247-258, 299-307, 308-312.

2) I think it would help the reader immensely if the authors were to explain the meaning of the values for C/N etc. What do the values of ~10.5 - ~15.5 indicate in terms of the sources of terrestrial versus aquatic. Perhaps a few sentences in your methods will go a long way here. For example, on P. 7 lines ~130-142 what values are typical for algae? For aquatic vegetation? The values cited for both are either too low or too high to fit into the range measured in this core. What does this indicate? Also what indicates that there is little input from terrestrial vegetation? Perhaps a short sentence explaining why low D13C is indicative of autochthonous sources etc.will go a long way for the reader. This also needs clarification as not many readers will be familiar with the values cited for these trends/determinations.

Done. In this new version we gave more explanations and details regarding the expected ranges in d13C values for the various sources of organic matter. Please see lines: 166-178.

3) TOC and diatom concentration data: It should be noted by the authors that changes in TOC may not always be indicative of changes in productivity as these values can be greatly influenced by changes in the rates of sediment accumulation (as is the case as well for diatom concentration data) - this can even vary substantially across a given lake.
It should also be noted that when using TOC as an indicator of productivity you need to acknowledge that changes in these values can also be unrelated to productivity and can be a result of increased clastic inputs from the surrounding catchment. More confidence can be given to the ratio data (<delta>13C, C/N and P/B).

Done. We have changed the TOC% and diatom concentration to TOC and diatom flux, and gave more evidence to argue that changes observed in the TOC curve are real and not an "artifact" of changing rate of sediment accumulation. Please see lines: 192-208.

4) Before delving into the <delta>13C trends being an indication of changes in P/B, I think that you need to first strengthen your argument against productivity changes and <delta>13C vs TOC. Are there any difficulties or limitations to using these data to directly infer algal productivity? I mentioned some of these above. The ratios are not as influenced by sedimentation changes etc.
Done. We strengthen our argument against productivity change. Please see lines: 192-208.

5) Shifts among the planktonic taxa: Is there a reference you could use that show A. Formosa and P. praetermissa bloom during fall and spring overturn? If not, I would word this more cautiously. As well, have Wang et al. 2012 determined that these plankters bloom during spring and autumn in this lake? If so, be clear about this ...through sediment trap studies etc....Other studies from other parts of the world may not have observe the same timing of blooms for these particular taxa. etc.

Done. We cite three references to back –up our claim that *A. formosa* and *P. praetermissa* bloom during the fall and spring overturn. Please see lines: 253-255, 286-294.

6) Looking at differences between periods dominated by Discostella taxa and A. Formosa and P. praetermissa, what differences are there in the climate/thermal stability of the lake between periods of dominance by these plankters? If there is simply a difference in the season in which they bloom, then why do P. praetermissa and A. formosa dominate from 1840 to ~1960 and Discostella taxa dominate for all other periods? I can see that in the early part of the record, benthic taxa increase at the expense of Discostella taxa ~20cm to 12 cm - but what does this suggest climatically? What is different about the climate of the last 40 years and why does it now favour Discostella once more?

Done. The main difference between the period dominated by *Discostella* taxa on a one hand and the period dominated by *A.formosa* and *P. praetermissa* on the other hand is in the relative length of the seasons, especially how long was the summer season of thermal stratification compared with the spring and autumn seasons with mixing of the water column. We added more information about this in the text. Please see lines: 295-302.

I can see that in the early part of the record, benthic taxa increase at the expense of Discostella taxa ~20cm to 12 cm - but what does this suggest climatically?

The benthic taxa increased at the expense of *Discostella* taxa from 20 cm to 12 cm. We associated this diatom shift with a decrease in temperature causing in particular an increased in the seasonal duration of ice-cover. Please see lines: 259-267.

What is different about the climate of the last 40 years and why does it now favour Discostella once more?

During the last 40 years global warming has been reported in the recent sediments of numerous lakes throughout the Northern Hemisphere. The diatom sedimentary record from EML also shows a similar trend. Please see lines: 308-322.

If the premise for using stable isotopes is to determine changes in climate via changes in benthic to planktonic ratios, then do you think that the high dominance of D. stelligera taxa in the earlier parts of the core (~80-40%) will not have an effect on the <delta>13C - ie. what kind of contribution do the benthic algae make here if the plankters dominate so strongly.is it enough to drive the <delta>13C values to be higher? Or is the relatively low % benthic taxa enough to show a trend? How would this differ with respect to <delta>13C in lakes with more benthic taxa or lakes with even less benthic taxa?

When organic matter mostly comes from algae, the $d^{13}C$ values represent the values of algae. For the moment we can only assume that the influence of the benthic/planktonic diatoms on the $d^{13}C$ values is proportional to their contributions to the assemblages. When the contribution of benthic diatoms is very low, we argue that changes among planktonic species with markedly different seasonal preference will influence the $d^{13}C$ values (e.g. difference between small *Discostella* mainly growing in summer and the larger spring-blooming diatoms: *A.formosa* and *P. praetermisa*). In the particular case of a sediment record dominated by benthic taxa, we don't know how much changes in species composition

(i.e. assemblage shift between different species of benthic diatoms) would affect the d^{13}C values.

7) How applicable is this technique to other lakes from other parts of the world? Are there any cautionary notes that you should pass on in this paper? I understand that it is a very new approach but perhaps you can outline some cautions. For example, in a very eutrophic lake (or a lake that has been subjected to acidification or cultural eutrophication), then a ratio of planktonic to benthic may be too broad a brushstroke to use if some discretion is not applied. For example, in eutrophic systems you will likely have many planktonic diatoms indicative of eutrophication that is included in the assemblage (e.g. Stephanodiscus). If there is a change from Stephanodiscus to Cyclotella/Discostella (which is commonly the case after remediaton efforts over the last decades), then combining these plankters can be problematic and will undoubtedly blur the climate signal - particularly in the case of using <delta>13C and increases in planktonic taxa to indicate warming etc. Perhaps a paragraph near the end of the paper (before conclusions) outlining some cautionary notes etc. will be of interest.
Done. As suggested, we added some cautionary notes at the end of the discussion. Please see lines: 326-336.

In addition Reviewer#2 gave a lot of detailed comments as notes on the PDF file. Here below are our responses to these comments, except for those we have answered above and those concerned with wording and grammar.

Line 45: it would be more informative to be a bit more explicit here...reconstructing what type of environmental change?
Done. Please see lines: 47-48

Line 60: Considering the readership for this journal, it would be best to explain these terms a bit better as they are biological. For example after the word "planktonic" you could put in brackets....planktonic (free-floating in open water) etc. - the same with benthic.
Done. Please see lines: 66-70.

Line119: It would be good to point out that at this time *Discostella* species return to dominance...Figure 5.
Done. Please see lines 145-146.

Line151-152: This last sentence is not altogether clear. Do you mean that declining TOC and increasing D13C appear to suggest differing trends in productivity? One suggests an increase and one a decrease...
Done. We re-wrote this sentence and clarified it as follows: Enhanced productivity in lakes results in dissolved CO_2 becoming limited, algae can adapt by switching to the utilization of HCO_3^- for their source of carbon, and this results in an increase in δ^{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 δ^{13}C values of ca. 3.7‰. It is unlikely that increasing

δ^{13}C values in EML sediments were caused by declining aquatic productivity. Please see lines: 209-214.

Line196 "at this time" is a bit confusing as you mention that between ~1840 to 2000 there is a decline in D13C but in this sentence you are only referring to the initial stages right after ~1840 where your records show a sharp decline...it then has an equally sharp increase to the top.
We re-wrote this sentence and clarified it. For the sharp decline, Please see lines: 278-280. For the late increase to the top, please see lines: 308-317.

Line 193: You may want to indicate a typical magnitude of decline that the Suess effect could make here.
We revised this sentence. In the present studies, the magnitude of the changes observed cannot be explained solely by the Suess effect. Please see lines: 278-283.

Line 207: Yes - but how is this turbulence compare to that of the habitat of benthic algae...is it still higher and therefore lower D13C than periods in the core where benthic diatoms dominate?
We added more information to clarify the effect that the strength of turbulence has on the thickness of the boundary layer and how this effect varies according to the habitat of the various groups of diatoms. *Discostella* species rank between the large planktonic species and benthic diatoms. Please see lines: 247-258, 300-304.

Reviewer #2: Review of Wang et al - <delta>13C and planktonic verses benthic diatoms in Erlongwan Lake

This paper reports the relationships between bulk carbon, d13C, C/N ratios and diatom assemblages for a short (60 cm) core extracted from a maar lake in China. The authors argue that the relative proportions of diatom species, which are driven by changing climatic conditions, can be used to explain the approximately 3 ? variation in down core bulk d13C during the last 1000 years. This is hypothesised to be a function of changing species dominance, which influences the bulk sediment 13C due to differences in the assimilation of 12C/13C across the diffusive layer surrounding the diatom cells.

This paper presents an interesting idea, but it is a rather short (too short) and in my view suffers due to: 1) a relatively limited description of the site/study context and presentation of the data, 2) a lack of clarity in the interpretations made in the discussion section. It also contains numerous typographic errors and confusingly written sentences, which coupled with its brevity, give the impression that this is more of a draft than a finished product. I suggest that major revisions are required before publication.
Major points

Page 3 - The paper suffers from a lack of context, which makes it hard for readers to follow the key ideas and more importantly assess the validity of the points being made. The materials and methods section provides only the briefest description of the site and study area. Having looked at the lead author's recent paper in Quaternary Research it is clear more background information could be provided on the study site, the nature of the lake, the core extraction and the sedimentology of the core. Although work has already been published on the site this manuscript still needs to "stand alone" - in fact, the authors hardly mention the QR paper until near the end of the manuscript.   So, for example I found myself asking several question as I was reading the manuscript - where was the core from in the lake? What water depth? Is this the same core as that reported in Mingram et al. 2004, which looks to be of a similar length? What is the sediment in the core like? I notice Mingram et al report laminated, diatomaceous sediments in one lake - are these found in the Erlongwan sediments as well?

Done. We have provided more information about this lake. Including the vegetation cover (Lines: 79-85). Where the core was taken, the depth of the lake and the description of the sediment core (Lines: 86-90). This core is not the same core as that reported in Mingram et al. (2004) which was taken from Sihailongwan maar lake (located 18 km to the east of Lake Erlongwan).

Is this related to the paper's major assumption, that the bulk OM and the associated d13C are dominated by algal-derived organic matter? This issue is critical to the interpretation offered by the authors, but I never feel much evidence to support it is provided.
Done.
Done. In this new version we gave more explanations and details regarding the expected ranges in d13C values for the various sources of organic matter. Please see lines: 166-178.

Page 4 - related to the last point. Although the lead author has published a detailed explanation of the diatom records from this site in their QR paper, I think it would be helpful for the readers of OG if clearer explanation (still a summary) of the habitats and analysis of the diatoms considered in this paper is provided, as these are critical to the interpretation of the bulk isotope record. For example, in this manuscript it is stated that the key taxa are displayed as relative abundance. The Wang et al QR paper provides flux data and accumulation rate data. This confirms that the changes in the diatom ratios presented here are not an artefact of a few taxa being presented as % (which was a query I had when initially reading the manuscript), but are indeed real changes - with some marked differences in flux between the different taxa.

Done. We are presenting diatom and TOC fluxes and provide more information to support our argument regarding the changes in ratios of planktonic and benthic algae. Please see lines: 259-265.

Page 5 - the results are very brief. It would also be useful to see the scatter plots of some of the relationships between the measured parameters along with their correlation coefficients. One of the key relationships P/B versus TOC has a relatively low correlation coefficient.

Done. We now provide three scatter plots of the relationships between TOC, delta 13C and P/B. Please see fig.4.

Lines 103-104 - what is the purpose and significance of this graph with the lowess line? It is not clear to me what point is being made here - simply that a split has been made. The line plotted does not split the data in the most obvious manner, at least when considered visually. How does such a split related to our understanding of these parameters in lake sedimentary environments? Make some reference to the literature here?

We have deleted this graph in this new version of the manuscript.

Page 5 - This discussion begins with a description of C3 photosynthesis. It would have been worth providing some of the background information on local vegetation earlier in the introduction and site description. More significantly, the paper's central hypothesis is that the c. 3 ? variability in bulk d13C is driven largely by the changing proportions of different algae in the water column. The assumption is therefore that allochthonous/vegetal inputs have little impact on the TOC and its isotopic signature. I think therefore that the authors should make a stronger case that they are confident that the TOC 13C signature is dominated by algal-derived OM. Given that the end member values for benthic and planktonic algal 13C reported at the top of page 8 (from France's paper) are not *hugely* different, the impact of allochthonous inputs could be significant. In the Wang et al. QR paper there is reference to changing run-off inputs into the lake (e.g. top of page 7 of the QR paper). How much vegetation is found around the lake? Is the delivery of terrestrial OM or riparian OM likely to have a significant impact on the sediments accumulating at the core location? Are the C/N values of 12-14 (for a lot of the core) sufficiently low to assume *no* vascular/terrestrial plant OM contribution (see for example Meyers 1997 OG 27)? The C/N ratio doesn't really change that much between 50 and 12 cm - these are subtle changes relative to the changes in the upper 11 cm. Incidentally within this section of the paper (page 7) lines 135 - 141 are rather poorly written (several typos as well). This section needs writing with much greater clarity.

In the "material and methods" section of this new version we provide detailed information about the modern vegetation and how vegetation cover changed over the last 1000 year. Please see lines: 78-84.

We also give more evidence to support our point that most of the TOC was derived from autochthonous input. 1) We are now presenting fluxes instead of %TOC and diatom concentration. 2) The coefficient of correlation between the TOC flux and diatom flux curves is 0.747. 3) From 20 to 0 cm core depth, the section of the core for which we have detailed information on the sediment density and sediment accumulation rate, the trend in TOC flux is similar to that of diatom flux. 4) Although the abnormal changes in 210Pb and the high sediment accumulation rate at the top of the core (5 to 0 cm) 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, indicating that the proportion of allochthonous inputs into the lake has remained small. Please see line: 166-178.

We agree that the C/N values of 12-14 (for a lot of the core) is not sufficiently low to assume *no* input of vascular/terrestrial plants. However, aquatic vegetation with C/N ratio values comprise between 20 and 30, would have also contributed to the values of 12-14 for the sediment C/N ratio. We therefore assume that the contribution from vascular/terrestrial

plants was very little and that most came from autochthonous sources (algae and aquatic plants). In this new version of the manuscript, we have discussed this point in details. Please see lines: 179-190.

Page 7 lines 147-149 -needs simplification/clarification - the increase in d13C may be a result of a reduced dissolved carbon supply and less discrimination against 13C by the algae. Could this reduced supply of carbon not be interpreted as a *cause* of the decline in TOC accumulation and productivity? Can that be related to known environmental perturbations? How does this relate to analyses of the diatom record and lake conditions provided in the Wang et al QR paper? Can this be used to bridge to the next paragraph at the bottom of page 7 - which concerns to the role of algae/diatoms/plankton type in influencing d13C of the sediment?

Done. We have re-written this paragraph. The main idea is that the productivity of algae, gradual maturation of lakes and changes in catchment vegetation are not the driving factor controlling the observed changes in d13C in the EML sediment record (Lines: 209-227). In the following paragraph, we also discussed the correlation between diatom taxa and d13C. Please see lines: 228-322.

Page 8 - here you should also quote the standard deviations that were reported by France (1995) - which were ± 3 ? and suggest that the differences might be a bit more subtle than this section/analysis implies.

The average $\delta^{13}C$ values given by France (1995) were -26‰ ±3‰ for benthic algae in lakes and -32‰ ±3‰ for planktonic diatoms. Therefore, the average difference between benthic and planktonic algae is about 6‰.

Page 9 line 193 - please clarify: You state "if dissolved carbon supplies in the lake are limited, then a *decline* (my emphasis) in 13C values may be indicative of a decline in algal productivity because algae are not able to discriminate..." If you are referring to the influence on bulk sediment TOC, which is assumed to be dominated by algal derived biomass, then is this statement not the wrong way around? If the algae discriminate against 13C *less*, then should the resulting d13C of the algal biomass not *increase*? Please clarify. Related to this: Figure 5 column D shows that the *A formosa* and *P praetermissa* taxa increase substantially at about 1900 and these are interpreted as evidence of more mixing and turnover in the Wang et al 2012 paper. Could the increased mixing and atmospheric exchange account for at least some of the decline in d13C of the sediment at this time (i.e. higher dissolved carbon concentrations)?

We have re-written this paragraph. Please see lines 276-283, 284-294.

Could the increased mixing and atmospheric exchange account for at least some of the decline in d13C of the sediment at this time (i.e. higher dissolved carbon concentrations)?

Yes, it is possible that during periods with strong mixing of the water column, atmospheric exchange could contribute to the decline in d13C of the sediment because of the relatively high dissolved carbon concentration. We added this possibility in our interpretation. Please

see lines: 304-307.

Page 10 - line 215 - "we did not consider other factors such as duration of ice cover and water depth". Although you don't have modern constraints on these factors, these are all factors considered in the Wang et al QR paper. So, I think there is more scope to integrate the isotopic data here with the diatom data already published. In some ways I think this relates to the points I made earlier concerning the study context and the information provided on the site setting and environmental history / processes.

We deleted this statement in conclusion and re-phrased this part of the discussion that caused some confusion. We also provided more details about the effect of the duration of the ice-cover season on 1) the lake productivity and 2) the ratio between planktonic/benthic diatoms and therefore on the d13C. Please see lines: 259-269.

Specific queries/corrections/clarifications
Line 54   - correct and rewrite this sentence
Done. Please see lines: 61-65.
Line 73 - is this the 2 sigma age range produced by the 14C calibration? Usually it is worth noting the calibration curve/method used. Or refer to the Wang et al 2012 QR paper.
Done. Please see lines: 97-98.
Line 77 diatom concentrations *were* calculated
Done. Please see line: 103.
Line 85 change "their" to "samples"
This sentence now reads: "For the organic analysis, carbonates were removed by leaving the samples overnight in 50 ml of 5% HCl.", Please see lines:112-113.

Lines 91-93 - None of the text here is a proper sentence - lines 92-93 need correction
This long sentence has been split into two shorter sentences. Please see lines:117-120.

Line 110 - space needed before TOC
Done.

Line 112 - space needed before "9 cm" (and between "9" and "cm")
Done.

Line 116 - what is "P/L"? I don't see it anywhere else. Do you mean "P/B" - is this a typo?
Done. "P/B". We have corrected this typo.

Line 121 "tadominance"?
Corrected.

Line 123 "ranging"
We have revised it. Please see line: 151.

Line 129 - I think you need to add "assuming dissolved CO2 is in equilibrium with the atmosphere" to this statement? Again - see useful description in Meyers 1997.
We have re-written this sentence. Please see lines: 151-158.

Line 133 - "both"? Also "C/N ratios"
Done. Please see lines: 159-160.

Line 135 - close bracket missing
We revised this sentence. Please see line: 160.

Line 136-139 - check the grammar and wording of this section
We revised this sentence. Please see lines: 160-165.

Line 168 "iis" and "s" needed after "rate"
We have revised it. Please see line: 243.

Line 173 - too many closed brackets
We have revised it.

Line 186 - "haa" should be "has"
We have re-written this sentence. Please see lines: 272-276.

Line 190 - Full stop after Verburg reference. "This is apparent..."
Changed as suggested, see lines: 277.