

1 **Understanding past climatic and hydrological variability in the Mediterranean from**
2 **Lake Prespa sediment isotope and geochemical record over the last glacial cycle**

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30

31 **Abstract**

32 Here we present stable isotope and geochemical data from Lake Prespa
33 (Macedonia/Albania border) over the last glacial cycle (Marine Isotope Stages 5-1) and
34 discuss past lake hydrology and climate (TIC, oxygen and carbon isotopes), as well as
35 responses to climate of terrestrial and aquatic vegetation (TOC, Rock Eval pyrolysis,
36 carbon isotopes, pollen). The Lake Prespa sediments broadly fall into 5 zones based on
37 their sedimentology, geochemistry, palynology and the existing chronology. The Glacial
38 sediments suggest low supply of carbon to the lake, but high summer productivity;
39 intermittent siderite layers suggest that although the lake was likely to have mixed
40 regularly leading to enhanced oxidation of organic matter, there must have been within
41 sediment reducing conditions and methanogenesis. MIS 5 and 1 sediments suggest
42 much more productivity, higher rates of organic material preservation possibly due to
43 more limited mixing with longer periods of oxygen-depleted bottom waters. We also
44 calculated lakewater $\delta^{18}\text{O}$ from siderite (authigenic/Glacial) and calcite
45 (endogenic/Holocene) and show much lower lakewater $\delta^{18}\text{O}$ values in the Glacial when
46 compared to the Holocene, suggesting the lake was less evaporative in the Glacial,
47 probably as a consequence of cooler summers and longer winter ice cover. In the
48 Holocene the oxygen isotope data suggests general humidity, with just 2 marked arid
49 phases, features observed in other Eastern and Central Mediterranean lakes.

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55 **Keywords:** Late Quaternary, Mediterranean, lake, stable isotopes, Rock Eval pyrolysis,
56 geochemistry

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60 **1. Introduction**

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62 Understanding past climatic (including hydrological) variability is a particular issue in the
63 Mediterranean region because there is an acute link between water resource and socio-
64 economic impacts (e.g. Bolle, 2003; Lionello et al., 2006). Also for future predictions it is
65 necessary to investigate the past response of the region to global climate fluctuations.
66 Today's effective management of groundwater and lake catchment areas, as well as the
67 need to understand and monitor human-induced trends affecting water resources, can be
68 helped by understanding how past variations in climate impact lake water resources
69 (Roberts et al., 2008). Stable isotope data from lacustrine carbonates and organic matter
70 through time can define local climatic and hydrological change (e.g., Leng and Marshall,
71 2004) and when lake records are combined across regions these data can be used to
72 assess the spatial coherency of climate and hydrology (Roberts et al., 2008). There are
73 numerous lacustrine carbonate stable isotope records from the Mediterranean (Leng et
74 al., 1999; Frogley et al., 2001; Roberts et al., 2008), including in the Balkans, Lake
75 Prespa (described here) and the neighbouring Lake Ohrid (Leng et al., 2010). The former
76 records are mainly limited to a few tens of thousands of years, and all have imperfect
77 chronologies. The previous lake isotope records from Prespa and Ohrid are at low
78 resolution and given their mostly relatively long time spans (back to 130 ka) also have
79 significant chronological issues. Here, we discuss new stable isotope and geochemical
80 data from Lake Prespa through the last 4 or 5 Marine Isotope Stages (MIS) and discuss
81 past lake hydrology and climate (TIC, oxygen and carbon isotopes), as well as responses
82 to climate of terrestrial and aquatic vegetation (TOC, Rock Eval pyrolysis, carbon
83 isotopes, pollen).

84

85 **2. General setting**

86

87 Lake Prespa is situated in SE Europe between Albania, Macedonia and Greece (Fig. 1).
88 The lake drains into the larger Lake Ohrid through a karst system within the Mali Thate
89 (2,287 meters above sea level (m.a.s.l.)) and Galicica (2,262 m.a.s.l.) mountains, which
90 form the topographical divide between the two lakes. The lake is thought to have been
91 formed within a tectonic graben during the Alpine Orogeny in the Pliocene (Aliaj et al.,
92 2001). Owing to the lakes position within the rain shadow of the surrounding mountains
93 and the proximity to the Adriatic Sea, the lake catchment is under the influence of a sub-

94 Mediterranean climate with continental influences (Watzin et al., 2002; Panagiotopoulos,
95 in press). Mean July and January temperatures are +21°C and +1°C respectively, with a
96 mean annual temperature of +11°C. Precipitation peaks in winter (when snowfalls are
97 frequent) and drops in summer, varying from 750 mm in the lowlands to over 1,200 mm
98 on the mountains (Hollis and Stevenson, 1997). The diverse topography, the exposure of
99 slopes and valleys, as well as the presence of a large water body create a complex
100 patchwork of microclimates in the catchment that is also reflected in the vegetation. As
101 such we expect that Mediterranean type changes seen across the circum-Mediterranean
102 will also be recorded in Lake Prespa (Roberts et al., 2008).

103
104 Lake Prespa (Megali Prespa) is located at 849 m a.s.l., ca. 150 m above Lake Ohrid, and
105 has a volume of ca. 3.6 km³ (see Table 1). To the south, the lake is connected to a
106 smaller lake, called Mikri Prespa, by a controllable man-made channel with a current
107 hydraulic head of 3 m (Hollis and Stevenson, 1997). The total inflow into Lake Prespa is
108 estimated to be 16.9 m³s⁻¹, with 56% originating from river runoff from numerous small
109 streams, 35% from direct precipitation, and 9% from Mikri Prespa to the south (Matzinger
110 et al., 2006b). Lake Prespa has no natural surface outlet, water loss is through
111 evaporation (52%), irrigation (2%) and outflow through the karst aquifer (46%); the latter
112 leading to springs, some of which flow into Lake Ohrid (Matzinger et al., 2006b). The lake
113 water residence time in Lake Prespa is estimated to be ca. 11 years. Significant lake
114 level lowering in response to climate and exploitation for human use has been recorded
115 in the past (Popovska and Bonacci, 2007; Stefouli et al., 2008). As Lake Prespa is
116 relatively shallow with respect to the large surface area, wind-induced mixing leads to a
117 complete destratification of the water column from autumn to spring (Matzinger et al.,
118 2006b), meaning that the isotope composition of the lake water will be fairly
119 homogeneous and at steady state on a decadal time scale. Summer bottom water anoxia
120 and an average total phosphorus concentration of 31 mg m⁻³ in the water column
121 characterise the modern lake as mesotrophic, although previous work has shown that the
122 lake has been more oligotrophic in the past (Wagner et al., 2010).

123

124 **3. Material and Methods**

125

126 The sediment core described here from Lake Prespa was retrieved using a floating
127 platform, gravity and piston corers (UWITEC Corp. Austria). The coring site is an area of

128 flat lying, largely undisturbed sediment, identified during a hydroacoustic survey (Wagner
129 et al., in press). Core composite records were obtained by correlation of individual 3 m
130 long core sections using a variety of methods including visual inspection of the sediment
131 composition, as well as aligning optical, magnetic and geochemical marker horizons
132 (Wagner et al., in press). The sediment record (core Co1215) forms the best dated and
133 longest sediment record from Lake Prespa to date. Detailed core descriptions,
134 chronology and geochemical measurements back to 17,000 years (except stable
135 isotopes) are discussed in Aufgebauer et al. (in press), while the full record is described
136 in Wagner et al. (in press). The core was sampled continuously at 2 cm intervals
137 (correlated core depth = 1,575 cm), a sample aliquot from each level was freeze-dried
138 and homogenized to <63 μm using an agate ball mill. Total carbon (TC) and total
139 inorganic carbon (TIC) concentrations were determined with a DIMATOC 200 (DIMATEC
140 Co.). Concentrations of total carbon (TC) and total nitrogen (N) were measured with a
141 VARIO MICROCUBE elemental analyzer. Total organic carbon (TOC) was quantified
142 from the difference between total carbon (TC) and total inorganic carbon (TIC), which
143 were measured with a DIMATOC 200 (DIMATEC Co.).

144
145 Here we present: new stable isotope data from the modern waters ($\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$ from
146 NIGL); stable isotope data from organic matter ($\delta^{13}\text{C}$, from IGG) supported by %TOC and
147 %N (from which we calculate TOC/N, Cologne), Rock Eval data (BGS), pollen data
148 (Cologne); and stable isotope data from carbonates ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ from both calcite and
149 siderite, from NIGL). The combined data set within the existing chronology are used to
150 interpret the past environment and climate and some comparisons are made with lakes
151 on a more regional basis.

152

153 3.1. *Stable isotope analysis of modern waters*

154

155 Water isotope data include data from a monitoring period between 1984-2000 published
156 by Anovski et al. (1992) and Anovski (2001) and data from waters reported in Matzinger
157 et al. (2006a), data collected between August 2008 – October 2009 (Leng et al., 2010),
158 and new data from June 2011 (Fig. 2a). The new data (June 2011) were measured at
159 NIGL, the waters were equilibrated with CO_2 using an Isoprep 18 device for oxygen
160 isotope analysis with mass spectrometry using a VG SIRA. For hydrogen isotope

161 analysis, an on-line Cr reduction method was used with a EuroPyrOH-3110 system
162 coupled to a Micromass Isoprime mass spectrometer. Isotopic ratios ($^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$)
163 are expressed in delta units, $\delta^{18}\text{O}$ and δD (‰, parts per mille), and defined in relation to
164 the international standard, VSMOW (Vienna Standard Mean Ocean Water). Analytical
165 precision is typically $<0.2\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.0\text{‰}$ for δD .

166

167 Total dissolved inorganic carbonate (TDIC) was precipitated from the June 2011 water
168 collection (Fig. 2b), ca. 85 ml of water was reacted with c. 15 ml of NaOH-BaCl₂ solution
169 soon after collection. The resultant barium carbonate was filtered in the laboratory under
170 N₂, and rinsed with deionised water. The carbon isotope analysis ($\delta^{13}\text{C}_{\text{TDIC}}$) followed the
171 method described below for the sedimentary calcite.

172

173 *3.2. Stable isotope and Rock Eval analysis of organic matter*

174

175 The core from Lake Prespa was sampled for carbon isotopes on organic matter at 2 cm
176 intervals from the surface to a correlated depth of 168 cm, and ca. 10 cm from 170 cm to
177 the base at 1,575 cm. The samples were dried at 40°C and powdered. The powders
178 were treated with 10% HCl to remove calcite, washed several times with distilled water to
179 neutral pH, and then dried again at 40°C. CO₂ was evolved by combustion using a Carlo
180 Erba 1108 elemental analyser, interfaced to a Finnigan DeltaPlusXL via the Finnigan
181 MAT ConFlo II interface. Organic carbon isotope values ($\delta^{13}\text{C}_{\text{org}}$) are reported as per
182 mille (‰) deviations of the isotopic ratios ($^{13}\text{C}/^{12}\text{C}$) calculated to the VPDB scale using a
183 within-run laboratory standards (graphite and ANU-sucrose) and international NBS
184 standards. Overall analytical reproducibility for the standards was $<0.1\text{‰}$ for $\delta^{13}\text{C}$. Note
185 that any siderite (see section 3.4) present below 168 cm would not be removed with 10%
186 HCl. In any case, the TIC spikes seen in the TIC data do not correspond to spikes in the
187 $\delta^{13}\text{C}_{\text{org}}$ data, the calculated 1-2% of siderite with an $\delta^{13}\text{C}$ composition of ca. +10‰
188 changes the $\delta^{13}\text{C}_{\text{org}}$ data by $<1\text{‰}$, and within the high frequency (not interpreted)
189 variability of the $\delta^{13}\text{C}_{\text{org}}$ record (Fig. 3).

190

191 Samples for Rock Eval analysis were selected at 5 cm resolution from correlated depths
192 ranging from 10 to 1563 cm. Pyrolysis was performed on approximately 60 mg of
193 powdered sediment (dry/wt) using a Rock-Eval 6 analyser (Vinci Technologies) in

194 standard configuration (pyrolysis and oxidation as a serial process). Samples were
195 heated from 300°C to 650°C at 25°C/min in an inert atmosphere of N₂. The residual
196 carbon was then oxidised at 300°C to 850°C at 20°C/min (hold 5 min). Hydrocarbons
197 released during the two stage pyrolysis were measured using a flame ionization detector.
198 The CO and CO₂ released during thermal cracking of the bound organic matter (OM)
199 were monitored using an IR cell. The performance of the instrument was checked every
200 10 samples against the accepted values of Institut Français du Pétrole (IFP) standard
201 (IFP 160 000, S/N1 5-081840). Classical Rock-Eval parameters were calculated by
202 integration of the amounts of HC (Thermo-vaporized free hydrocarbons) expressed in
203 mg/HC/g rock (S1) and hydrocarbons released from cracking of bound OM expressed in
204 mg/HC/g rock (S2) as well as CO and CO₂. During analysis thirteen acquisition
205 parameters are determined from integration of the amounts of OM, CO and CO₂. Here
206 the data presented are the Hydrogen Index (HI) calculated from S2x100/TOC and the
207 Oxygen Index (OI), S3x100/TOC (Fig. 3 and 4).

208

209 3.3. *Pollen data*

210

211 For pollen analysis 163 subsamples taken at 2-16 cm (average = 10 cm) intervals, and
212 prepared using standard palynological techniques (Faegri et al., 2000). An exotic spike
213 (*Lycopodium* tablets; Stockmarr, 1971) was added to each subsample of a known
214 volume before processing them in order to calculate concentrations. Identification of
215 pollen and other palynomorphs was performed with relevant keys and atlases, as well as
216 the reference collection of the Laboratory of Palynology of the University of Cologne
217 (Panagiotopoulos, in press references therein). The relative percentages of the
218 presented taxa are based upon the sum of terrestrial pollen (excluding obligate aquatics,
219 spores and algae). An average of 500 terrestrial pollen grains were counted per sample
220 (Fig. 4).

221

222 3.4. *Stable isotope and XRD analysis of carbonates*

223

224 The core from Lake Prespa was sampled for oxygen and carbon isotopes on carbonate
225 at 2 cm intervals from the surface to a correlated depth of 168 cm, where after carbonate
226 content becomes negligible, although small (0.5-2%) TIC spikes occur (Fig. 3). The
227 identification of carbonate species was undertaken using X-Ray Diffraction (XRD) using a
228 Bruker D8 Advance powder diffractometer equipped with a LynxEye linear position

229 sensitive detector and using CuK_α radiation over the scan range 4 to $90^\circ 2\theta$. The step
230 size was $0.015^\circ 2\theta$, with 0.8s per step. Phase identification (calcite and siderite) was
231 performed using Bruker DIFFRAC^{plus} EVA search/match software interfaced with the
232 PDF-4+ database from the International Centre for Diffraction Data (ICDD). The Ca,Mg-
233 substituted siderite pattern 04-009-7660 (Heiss, 1988) offers a better match than pure
234 siderite. Calcite is the only carbonate mineral present above 168 cm, thereafter the
235 carbonate is substituted siderite, except for a layer at depth 1458 - 1463 cm which
236 contains shelly fragments (and no siderite).

237
238 1cm^3 subsamples (from 0-168 cm and from the TIC spikes below 168 cm) were
239 disaggregated in 5% sodium hypochlorite solution for 24 hours to oxidise reactive organic
240 material. Samples were then washed three times in distilled water and sieved at $85\ \mu\text{m}$ to
241 remove any potential biogenic carbonate. The $<85\ \mu\text{m}$ fraction was filtered, washed with
242 deionised water and dried at 40°C and ground in agate. Prior to the carbonate isotope
243 analysis, the form of the carbonate was investigated using SEM. Calcite crystals in Lake
244 Prespa are of mixed form, some fragments are platy while others are in the form of fine
245 (partially redissolved) calcite rhombs. The siderite crystals were not found using SEM.
246 For the calcite isotope analysis (0-168 cm and 1,462 cm) the CO_2 was evolved by
247 reaction with anhydrous phosphoric acid within a vacuum overnight at a constant 25°C .
248 For the siderite isotope analysis (TIC spikes between 170 – 1,575 cm, except 1,462 cm)
249 the CO_2 was evolved by reaction with anhydrous phosphoric acid within a vacuum for 72
250 hours at 90°C . For both the calcite and siderite, the CO_2 was cryogenically separated
251 from water vapour under vacuum and collected for analysis using a VG Optima dual inlet
252 mass spectrometer. The mineral-gas fractionation factors for calcite and siderite used
253 were 1.01025 and 1.01006 (derived from Rosenbaum and Sheppard, 1986). Carbon and
254 oxygen isotope values ($\delta^{13}\text{C}_{\text{calcite/siderite}}$, $\delta^{18}\text{O}_{\text{calcite/siderite}}$) are reported as per mille (‰)
255 deviations of the isotopic ratios ($^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$) calculated to the VPDB scale using
256 within-run laboratory standards (calcite = MCS, siderite = CHH8) and international NBS
257 standards. Overall analytical reproducibility for MCS and CHH8 was $<0.1\%$ for $\delta^{13}\text{C}$ and
258 $\delta^{18}\text{O}$.

259

260 **4. Chronology**

261

262 Radiocarbon, tephrochronology and ESR dating have all been used to obtain
263 chronological information for the core Co1215 (Fig. 3). The chronological tie points are
264 presented and discussed in detail in Aufgebauer et al. (in press) and Wagner et al. (in
265 press). The chronology of the lower part of the core is poorly constrained. ESR dating of
266 a shell layer at 1458-1463 cm depth provides a minimum age of 73.9 ± 11.4 ka BP,
267 suggesting deposition at the end of the marine isotope stage (MIS) 5 (cf. Bassinot et al.,
268 1994), which is supported by relatively high, but decreasing organic matter content (Fig.
269 4). Above the shell horizon, tephras at 1079 and 901 cm depth are difficult to correlate
270 with known tephras, but those at 856, 844, 770, 692, and 617 cm depth have been
271 correlated with the Y-6, SMP1a, Y-5, Codola(?), and Y-3 tephras (Wagner et al., in
272 press). The tephrostratigraphy, radiocarbon ages, and the characteristics of the
273 sediments (grey colour, high clastic matter, high K, low TOC, low TIC and spikes in Mn;
274 c.f., Wagner et al., 2010), indicate that this part of the core (>292 cm) was deposited
275 during the last Glacial (Wagner et al., in press). Above a transition between ca. 292 and
276 204 cm, radiocarbon ages, tephras, and the sediments (brownier, lack of coarse grains,
277 gradual increase of TOC and TIC, and the decreasing K) indicate that the topmost part
278 (204 cm) was deposited during the Holocene. Based on these sedimentological and
279 geochemical variations we suggest that core Co1215 covers MIS 5 to 1, from here on we
280 describe these zones within the MIS framework (Fig. 3).

281

282 **5. Results**

283

284 *5.1. Modern waters*

285

286 The oxygen and hydrogen isotope composition of present day waters from a variety of
287 springs around Lakes' Prespa (Mikri and Megali), as well as the lakes themselves are
288 given in Figure 2a (alongside the Global Meteoric Water Line (GMWL) and
289 Mediterranean Meteoric Water Line (MMWL)). In addition there are 3 spot rainfall
290 samples which fall on or close to the MMWL. These data are from samples taken
291 between 1984 and 2009 (described in Leng et al., 2010), and new data (from
292 springs/rivers entering Lake Prespa as well as the lake itself) from June 2011. Also
293 plotted are monthly modelled rainfall isotope compositions (using 41.17°N , 20.75°E ,
294 average altitude of precipitation 1500 m) and mean weighted annual rainfall isotope
295 composition (from G.J. Bowen's on-line calculator at Waterisotopes.org; Bowen et al.,

296 2005) and 3 spot rainfall samples from around Lake Prespa.

297
298 The range in spring/river $\delta^{18}\text{O}$ and δD overlaps with the calculated isotope composition of
299 monthly precipitation, although most of the measured spring water isotope data
300 concentrate in the lower isotope range. The calculated mean weighted annual isotope
301 composition of precipitation is $\delta^{18}\text{O} -8.8\text{‰}$ and $\delta\text{D} -57\text{‰}$ (Bowen et al., 2005) and is
302 above the vast majority of the spring/river data. Therefore the data suggests that the
303 springs/ivers are likely to be recharged by higher altitude and/or cold season
304 snow/rainfall around the calculated winter rainfall isotope composition (November to
305 March). As such the recharge of the springs/ivers by winter precipitation is very
306 important to the lake levels and the isotope composition of the Prespa lakes (c.f. Hollis
307 and Stevenson, 1997).

308
309 The isotopic composition of the present day lake waters fall on a Local Evaporation Line
310 (LEL) away from both the GMWL and the MMWL between -10.9 and $+1.2\text{‰}$ for $\delta^{18}\text{O}$ and
311 -69.4 and -12.9‰ for δD . Both Megali and Mikri Prespa are evaporated and the
312 intersection of the LEL with the MMWL at around $\delta^{18}\text{O} = -8.8\text{‰}$ and $\delta\text{D} = -60.6\text{‰}$, is ca.
313 2‰ in $\delta^{18}\text{O}$ lower than the mean rainfall value, confirming the dominantly spring water
314 recharge (from high altitude and/or cold season snow/rain).

315
316 *5.2. Prespa core Co1215 data*

317
318 Although the chronology is currently limited and does not allow the establishment of a
319 robust age-depth model, the chronological, sedimentological, palynology and
320 geochemical data allows broad palaeoenvironmental information in comparison with
321 Marine Isotope Stages (Fig. 3). In general, the MIS 5 sediments are brown, have
322 relatively high TOC, TOC/N, HI while TIC, OI, are low. Arboreal pollen dominates during
323 MIS 5. The glacial sediments (MIS 4 to 2) are greyish in colour, contain low TOC and
324 TOC/N (except for a slight increase around 45-55 ka), and high $\delta^{13}\text{C}_{\text{organic}}$ (possibly MIS
325 3). Through this period there are spikes in TIC and OI. The TIC spikes were identified as
326 siderite and measured for their isotope composition; both $\delta^{13}\text{C}_{\text{siderite}}$ and $\delta^{18}\text{O}_{\text{siderite}}$ are
327 generally high in comparison to the majority of calcite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. During MIS 4-2
328 several individual peaks of AP values exceed 70%, pollen from aquatic macrophytes and

329 algae are present but in low numbers. The Pleistocene/Holocene transition is likely
330 between 292 and 204 cm based on dating and a change in the proxies, i.e. a return to
331 brown sediments, increasing HI, TOC, TOC/N, TIC, and decreasing OI, $\delta^{13}\text{C}_{\text{organic}}$. The
332 Holocene (MIS 1) sediments in the upper 204 cm have high HI, TOC, TOC/N, TIC and
333 low OI, $\delta^{13}\text{C}_{\text{organic}}$. High TIC is due to calcite precipitation, $\delta^{13}\text{C}$ is consistent around $+1.1$
334 $\pm 0.4\text{‰}$, while $\delta^{18}\text{O}$ is generally low ($-4.6 \pm 0.8\text{‰}$) except for two high phases in the early
335 and late Holocene. Arboreal pollen as well as aquatic macrophytes and algae dominate
336 in the Holocene.

337

338 **6. Discussion**

339

340 *6.1. Modern water oxygen and hydrogen isotope composition*

341

342 Over the lakewater collection period (1984 - 2011) the two Prespa lakes (Megali and
343 Mikri Prespa) had an almost identical range in water isotope composition ($\delta^{18}\text{O}$ ca. -7 to
344 $+1\text{‰}$; δD ca. -47 to -13‰). $\delta^{18}\text{O}$ and δD fall on a Local Evaporation Line (LEL) and as
345 such are evaporated (compared to spring waters), the similarity in the isotope data for the
346 two lakes reflects their hydrological connection (Fig. 2a). The range in isotope data for
347 the lakes suggests that the Prespa lakes are very sensitive to moisture balance (winter
348 precipitation versus summer evaporation) and as such respond dramatically too
349 seasonally (i.e. their isotope composition changes through the season due to winter
350 recharge and summer evaporation). However, large seasonal ranges in lake level (up to
351 1.5 m) have been recorded (Hollis and Stephenson, 1997), so another explanation is that
352 the samples with the intermediary isotope compositions were collected close to rivers or
353 subaqueous springs that flow into the lake (Matzinger 2006a). We know from Lake Ohrid
354 that subaqueous springs result in lakewaters with intermediary isotope compositions
355 (Leng et al., 2010), and that lakes at steady state change very gradually in their isotope
356 composition based on successive, seasonally averaged, either dry or wet conditions at
357 time scales longer than the residence time of the lake water. In addition, Megali Prespa
358 has no surface outlet, although there is subaqueous water outflow through the karst
359 aquifer into Lake Ohrid (Matzinger et al., 2006b). The isotope composition of Lake Ohrid
360 which is very stable with $\delta^{18}\text{O}$ and δD values around -4 and -32‰ since 1989 (Leng et
361 al., 2010). The difference in the isotope composition of Ohrid and Prespa lake water is

362 probably a function of lake size. The volumetrically much larger Lake Ohrid (55.4 km³
363 compared to 3.6km³ of Lake Prespa, Matzinger et al., 2006a) with its longer residence
364 time (70 and 11 years respectively, Matzinger et al., 2006a) makes Lake Ohrid much
365 better buffered and less responsive (on a decadal scale) against high frequency
366 hydrological change compared to Lake Prespa. Overall, in terms of understanding past
367 lake water balance from the oxygen isotope composition of lacustrine carbonates, the
368 modern water isotope data suggest that we should interpret $\delta^{18}\text{O}$ variation in Lake
369 Prespa as mainly representing changes of the amount of winter rainfall water contribution
370 (recharge), winter ice cover (reducing winter evaporation), summer aridity (enhancing
371 evaporation), and changes in lake water residence time at a decadal resolution.

372

373 *6.2. Modern water carbon isotope composition*

374

375 $\delta^{13}\text{C}_{\text{TDIC}}$ of bicarbonate from the Lake Prespa springs, inflowing rivers, and lake waters
376 taken in June 2011 provide a range in $\delta^{13}\text{C}_{\text{TDIC}}$ values between -15.7‰ and -4.7‰ (Fig.
377 2b). Dissolved bicarbonate is derived from dissolution and weathering of catchment
378 rocks, soils and atmospheric CO_2 . The geology around Prespa is largely old basement
379 rocks and Triassic limestones although there are large areas with Quaternary glacial and
380 volcanic deposits (Aufgebauer et al., in press). Geological sources of bicarbonate tend to
381 have high $\delta^{13}\text{C}$ (Andrews et al., 1993; 1997; Hammarlund, 1993) and so are not likely the
382 major source of the isotopically light ion in the springs and rivers. In contrast organic
383 derived C has $\delta^{13}\text{C}$ values generally between -25 and -35‰ (higher up to -16‰ where
384 there is a greater contribution from C4 taxa). Isotopically light CO_2 liberated by decay of
385 terrestrial organic matter in the soil infiltrates springs and rivers by shallow groundwater
386 flow. Under alkaline conditions, and mid range annual temperatures ($+10^\circ\text{C}$), HCO_3^-
387 derived solely from soil CO_2 with $\delta^{13}\text{C}_{\text{organic}}$ of ca. -25‰ should have $\delta^{13}\text{C}_{\text{TDIC}}$ of $\sim -15\text{‰}$.
388 This is remarkably consistent with the measured spring and river water $\delta^{13}\text{C}$ (-15.7‰ ,
389 see also Leng et al., 2001), although once the bicarbonate enters rivers and lakes other
390 processes change $\delta^{13}\text{C}$. Prespa lakewater has high $\delta^{13}\text{C}_{\text{TDIC}}$ (Fig. 2b). High $\delta^{13}\text{C}_{\text{TDIC}}$ is
391 common in lakes which do not have a surface outlet (so called closed lakes) where
392 dissolved bicarbonate has time to exchange with atmospheric CO_2 (Leng and Marshall,
393 2004) or in lakes with a large biomass, so long as there is sedimentation of organic

394 matter (ie removal of ^{12}C , and not recycling of ^{12}C) (Meyers and Teranes, 2001). Both
395 processes (exchange and productivity) are likely in Lake Prespa.

396

397 6.3. Sources of organic matter in the Lake Prespa sedimentary record

398

399 Several measurements through the core profile show similar fluctuations in the organic
400 matter (HI, TOC, N, TOC/N) (Fig. 3) while others (OI and $\delta^{13}\text{C}_{\text{TOC}}$) have an almost
401 inverse relationship being high when the other organic proxies are mostly low. These
402 broad changes in the organic matter broadly fall within zones, which approximate to MIS
403 5 to MIS 1 (Fig. 3) based on our limited chronology. In general, the amount of organic
404 matter in lake sediments is a function of changes in organic production in the lake,
405 catchment vegetation changes and transfer of terrestrial particulate and dissolved
406 organic matter to the lake, loss processes, and dilution effects (by varying inorganic
407 inputs). These processes can sometimes be disentangled by a combination of organic
408 proxy data (Meyers and Teranes, 2001). Sources of organic matter can be estimated
409 from their TOC/N ratio as well as HI versus OI. Organic nitrogen occurs preferentially in
410 proteins and nucleic acids which are relatively abundant in aquatic plants (Talbot and
411 Johannessen, 1992). Here we assume that the term aquatic plants refers both to
412 macrophytes and phytoplankton; in Lake Prespa the aquatic plants mainly comprise
413 green algae (eg. *Pediastrum*, *Botryococcus*) and Dinoflagellates.
414 Phytoplankton have low TOC/N, typically $\sim < 10$ (Meyers and Teranes, 2001) whereas
415 vascular (cellulose rich) plants tend to have high TOC/N, usually greatly in excess of 10,
416 macrophytes generally sit in between. In Co1215, the TOC/N fluctuates but overall the
417 mean TOC/N = 4.9 (SD = 2.0), varying between 1.3 and 10.4. This range in TOC/N would
418 be interpreted as organic material mostly from plankton, although very low values ≤ 6
419 suggest that there are decompositional processes (cf. Meyers and Ishiwatari, 1995), so
420 the ratio is not unequivocal and needs supporting evidence.

421

422 The van Krevelen-type HI-OI diagram distinguishes three main types of organic matter
423 (Types I, II, III) but also can provide information on the amount of oxidation and
424 diagenetic alteration of the organic matter (Talbot and Livingstone, 1989). The data from
425 Lake Prespa shows both Type II and Type III organic matter, which is either a source
426 function or an oxidation artefact (Fig. 4). Type II organic matter corresponds to

427 moderately rich hydrocarbons, and suggests that the sedimentary organic matter is
428 predominantly derived from algae, whereas Type III is poor in hydrocarbon-generating
429 materials and more typical of woody plant material. However, the data fall on a curve of
430 changing OI suggesting that the organic matter has undergone differential amounts of
431 oxidation (which is climate or hydrology related and not time dependent). The down core
432 HI, TOC and N data show that Lake Prespa sediments have changed in their Rock Eval
433 and elemental characteristics through time. Type II sediments with high HI are more
434 typical of the sediments from the Holocene, MIS 3 and MIS 5; whereas Type III with low
435 HI are more common in MIS 2 and 4.

436

437 At the end of MIS 5, initial high HI values decrease towards MIS 4, commensurate with a
438 decrease in TOC and low OI and suggest initially high but declining lacustrine
439 productivity. In MIS 4 (and MIS 2) relatively low HI and TOC are more typical of vascular
440 plant organic material (kerogen Type III) although the variable OI values suggests that
441 the organic matter has undergone more extensive oxidation, this is supported by the very
442 low TOC/N perhaps being more likely a function of degradation than source (Talbot and
443 Livingstone, 1989). High rates of oxidation and reduced TOC are more likely in a lake
444 with dimictic or polymictic conditions, although Type III organic matter and high organic
445 oxidation can be found in degraded woody tissues mediated by various types of fungi
446 which cause abiotic diagenetic alterations (Vane and Abbott, 1999; Vane et al., 2003).

447

448 In MIS 3, HI and TOC are intermediary between MIS 1 and 2/4, while OI is generally low
449 apart from some spikes. The most likely explanation of the intermediary values is that of
450 a mixed source (samples from this interval also span the kerogen Type II and III
451 boundary), likely being partially altered terrestrial plant matter but also containing a
452 component of aquatic organic matter which is reflected in the rise in TOC and TOC/N. In
453 MIS 1, HI, and TOC peak, and suggest lake sediments containing significant amounts of
454 aquatic organic material (Jacob et al., 2004; Hetényi et al., 2005; Lojka et al., 2009). High
455 algal productivity is indicated by high TIC, which is fine grained calcium carbonate.
456 Similar <30 µm idiomorphic calcite crystals occur in Lake Ohrid and are typical of
457 photosynthetic phytoplankton endogenic precipitation (Leng et al., 2010; Matter et al.,
458 2010). The high rates of organic material preservation suggest more limited mixing with
459 longer periods of O-depleted bottom waters and might imply less seasonal (i.e. from
460 dimictic to monomictic) overturning. Within MIS 1 there are spikes to lower HI, TOC, TIC

461 (i.e. at 140 cm) which might suggest short perturbations back to cold conditions and
462 better lake mixing. The highest TOC/N ratios of the entire profile occur in MIS 1 (up to 9)
463 but are still suggestive of aquatic productivity and perhaps less
464 decomposition/degradation.

465

466 *6.4. Carbon isotope composition of organic matter from Lake Prespa*

467

468 It is possible that most of the organic matter in Lake Prespa is planktonic in origin as high
469 summer water temperatures and the large surface area of the lake promote algal activity.
470 Moreover, there are only a few inlets to Lake Prespa and those that do occur have
471 relatively low discharge. Therefore the carbon isotope signal should act as a tracer for
472 past changes in the aquatic carbon cycle. Even if the sediments have undergone some
473 selective diagenesis the primary isotope signature of organic matter incorporated during
474 burial is often not significantly altered and most importantly relative isotope variations are
475 often preserved (Hodell and Schelske, 1998; Meyers and Lalier-Verges, 1999).

476 Lacustrine algae utilise dissolved HCO_3^- in hard water lakes so variations in the isotope
477 composition of the dissolved HCO_3^- and changes in $\delta^{13}\text{C}$ related to productivity and
478 nutrient supply are both possible. The modern TDIC data suggest that the main source of
479 carbon ions to the lakes is soil derived CO_2 . The ion will be utilised by the plants growing
480 in the lake. Phytoplankton tend to have $\delta^{13}\text{C}$ that is 20‰ lower than the $\delta^{13}\text{C}$ of the
481 bicarbonate ion (Leng et al., 2005). In Lake Prespa $\delta^{13}\text{C}_{\text{org}}$ is consistent around -25‰
482 and so could be derived from $\delta^{13}\text{C}_{\text{TDIC}}$ with a value similar to the modern lake (of ca. $-$
483 4.7‰) through MIS 5, 4, 3, 2. These stages also have low TOC, except MIS 5. In contrast
484 the Holocene has lower $\delta^{13}\text{C}_{\text{org}}$ (-28‰) and high TOC relative to the other stages. The
485 higher $\delta^{13}\text{C}_{\text{org}}$ in the pre-Holocene sediments suggests high productivity, but in the
486 presence of low TOC suggests productivity under a more limited carbon input, possibly
487 due to more limited recharge of soil- CO_2 leached from the catchment. If soil development
488 is critical that it would follow that the lower $\delta^{13}\text{C}$ in the Holocene could just be a function
489 of greater supply of soil derived CO_2 and an improving climate. Pollen evidence suggests
490 well developed soils during the Holocene inferred from rising amounts of AP pollen types
491 and increasing total pollen concentration values culminating during the Middle and Late
492 Holocene (Fig. 5; Panagiotopoulos et al., in press). Other pollen data from the region
493 suggest a cold climate during MIS 4 and 2 (e.g. Allen et al., 1999, 2000; Wagner et al.,

494 2009; Lézine et al., 2010). During MIS 5 (and to a lesser extent during MIS 3) the total
495 pollen concentration and percentages of AP suggest favourable climate conditions for
496 plant growth (warmer and/or sufficient moisture).

497

498 6.5. Oxygen and carbon isotope composition of carbonate from Lake Prespa: MIS 5-1

499

500 The TIC spike at 1458-1463 cm is calcite, and investigation of the sediments revealed
501 small (<0.5 mm) shelly fragments of *Dreissena* sp. (Wagner et al., in press), no siderite
502 was evident from the XRD analysis. This is the only shelly layer in Co1215 and has been
503 interpreted as a period of low lake level although macrophyte remains were not
504 recovered suggesting the shells may have transported by wave action rather than
505 representing a desiccation horizon (Wagner et al., in press). The $\delta^{13}\text{C}$ from the shell
506 fragments is low (-2.0‰) while the $\delta^{18}\text{O}$ is high ($+0.6\text{‰}$) in comparison to the isotope
507 composition of the endogenic calcites in the Holocene. Low $\delta^{13}\text{C}$ in shell calcite is
508 common as a result of mollusc diet and their microenvironments. Molluscs tend to be
509 most abundant in highly vegetative parts of lakes where there maybe greater recycling of
510 ^{12}C (Leng and Marshall, 2004). High $\delta^{18}\text{O}$ supports the conclusion that lake levels were
511 low driven by a significant arid phase (similar to the $\delta^{18}\text{O}$ highs seen on the Holocene).
512 This arid phase is also recorded in the hydro-acoustic data from Lake Prespa (Wagner et
513 al., in press) and as a decrease in total pollen concentration and a rise in NAP pollen
514 values. Interestingly though there is no endogenic calcite at this level.

515

516 The modern water isotope composition of Lake Prespa shows that the lake is sensitive to
517 the winter recharge (input) versus the summer evaporation ratio (I/E). We assume that
518 the oxygen isotope composition of the lakewater is captured in the carbonates that are
519 precipitated within the lake (Leng and Marshall, 2004). The TIC spikes through MIS 4-2
520 comprise siderite. Siderite is a common early diagenetic mineral in many lake sediments,
521 forming in porewaters close to the sediment-water interface (Giresse et al., 1991), its
522 geochemistry is often used as a indicator of sediment water redox. Siderite precipitation
523 usually occurs under reducing conditions (Berner, 1971) in slightly to strongly reducing
524 methanogenic zones because of relatively low sulphate and high organic carbon
525 concentrations (Coleman, 1985). We do not know why the siderite only occurs
526 sporadically, although the siderite spikes correlate with highs in the OI and low values in

527 the HI, so perhaps the siderite forms under particular environmental conditions, likely
528 involving a more acidic environment where oxides and hydroxyl ferric-oxides are
529 dissolved (Giresse et al., 1991). The formation of siderite over other carbonates suggests
530 low Ca and Mg. The mean $\delta^{13}\text{C}$ values for the Prespa siderites is +11.9‰. Similar high
531 $\delta^{13}\text{C}$ values have been reported elsewhere for other lake carbonates (Mozley and
532 Wersin, 1992) and their formation is described as a function of low sulphate
533 concentrations being consumed at shallower levels in the sediments fairly rapidly leaving
534 a greater quantity of organic matter for decomposition by methanogenic bacteria. The
535 heavy $\delta^{13}\text{C}$ forms as a result of ^{13}C enriched bicarbonate derived from methanogenesis
536 (Berner, 1980). Indeed methane and/or CO_2 gas occur trapped within the Lake Prespa
537 sediments because when the cores were retrieved there was core swelling due to gas
538 expansion and release. There is no evidence to support other causes of high $\delta^{13}\text{C}$, for
539 example ^{13}C -enriched volcanic gas, dissolution of ^{13}C enriched carbonate, and high
540 planktonic productivity (Bahrig, 1988).

541
542 The $\delta^{18}\text{O}$ of the Prespa siderites is, like calcite, a function of lakewater (input vs
543 evaporation; I/E) and temperature. However calcite $\delta^{18}\text{O}$ cannot be directly compared to
544 siderite $\delta^{18}\text{O}$ because of the different equilibration fractionations between the two
545 minerals. The temperature dependent mineral-water fractionation for calcite has been
546 extensively investigated (Epstein et al., 1953; Craig, 1965; O'Neil et al., 1969 etc.) while
547 there are less empirical studies on the siderite-water fractionation (Carothers et al., 1988;
548 Zhang et al., 2001). To compare the two carbonate minerals and their $\delta^{18}\text{O}$ composition
549 we have to use specific mineral fractionation equations and estimate the temperature at
550 the time of the mineral precipitation. For the Holocene aged calcite we use the equation
551 of O'Neil et al. (1969), and assume that the calcite precipitated in the photic zone during
552 the spring and summer months and that the average temperature during these months in
553 the photic zone is ca. 21°C (maximum summer temperature of surface waters can be
554 27°C; Kocev et al., 2010). For those periods containing siderites (in the glacial) we use
555 the equation of Zhang et al. (2001). The estimation of formation temperature for siderite
556 is more difficult, but assuming it is an early diagenetic mineral formed within the sediment
557 during the glacial period then we might assume cold bottom water temperatures of 4°C
558 minimum. The calculated $\delta^{18}\text{O}$ of the lakewater using the different minerals-formation
559 temperatures are given in Figure 3. Just comparing the glacial-Holocene shows much

560 lower modelled lakewater $\delta^{18}\text{O}$ values in the glacial when compared to the Holocene.
561 Even allowing for lower glacial $\delta^{18}\text{O}_{\text{precipitation}}$ it seems likely that the lake was less
562 evaporative in the glacial, probably as a consequence of cooler summers and longer
563 winter ice cover.

564
565 Within the Holocene we assume that the mechanism for calcite precipitation is likely the
566 same as described for Ohrid whereby phytoplankton productivity assimilate CO_2 as long
567 as there is a supply of bicarbonate (Matzinger et al., 2006b) which will be replenished via
568 surface run-off into the lake and concentrated by evaporation. There is likely some
569 seasonal dissolution of calcite in the bottom waters triggered by aerobic decomposition of
570 organic matter, higher CO_2 and lower pH (Vogel et al., 2010b). Indeed, Löffler et al.
571 (1998) have shown that pH in the surface waters (pH = 8.3) is generally higher than at
572 depth (pH = 7.3). Endogenic calcite preservation is coincident with high organic matter
573 and suggests high primary productivity likely as a result of the transition from the former
574 glacial to interglacial together with more ion input due to soil development and
575 weathering. In addition the OI, HI and TOC/N suggest better preservation of organic
576 matter possibly due to less lakewater mixing and due to longer periods of bottom water
577 anoxia.

578
579 Overall, the $\delta^{18}\text{O}_{\text{calcite}}$ data are low (mean = -3.1‰) except for 2 significant $\delta^{18}\text{O}_{\text{calcite}}$ high
580 phases between 10-8 ka and 2-0.5 ka. If we interpret these highs in $\delta^{18}\text{O}_{\text{calcite}}$ as a
581 function of hydrological balance (less winter rainfall, greater summer aridity) as
582 suggested by the modern data, then these changes should be also seen in the other
583 Lake Prespa and Lake Ohrid cores, within the limitations of the dating. However,
584 generally high amounts of AP between 10-8 ka indicate a positive water balance
585 (sufficient annual precipitation) and forest growth in the catchment of lake Prespa. There
586 is only one exception visible in the pollen data: during the 8.2 ka event. During the last 2
587 ka human impact has masked possible climatic interpretation of the vegetational proxies.
588 Although we would expect any change should be significantly damped in the Lake Ohrid
589 due to its greater size and residence time.

590
591 Lake Prespa $\delta^{18}\text{O}_{\text{calcite}}$ shows similarities to $\delta^{18}\text{O}_{\text{calcite}}$ from Lake Ohrid cores (Leng et al.,
592 2010). The basal portions of Co1215 from Prespa and Co1202 from Ohrid show higher

593 values, although the highest values in Prespa between 10 and 8 ka are not evident in
594 Co1202. From ca 6 ka the Ohrid cores show a general trend toward higher $\delta^{18}\text{O}$,
595 although Lake Prespa has low and fairly consistent $\delta^{18}\text{O}$ between 8-2 ka. High $\delta^{18}\text{O}$
596 between 2 to 0.5 ka appear in both cores although the magnitude of variation is
597 significantly different. Prespa $\delta^{18}\text{O}_{\text{calcite}}$ range is -7 to $+6\text{‰}$, while Ohrid is -7 to -3‰ . The
598 enhanced response to lakes level changes in Lake Prespa is not surprising given the
599 difference in water volumes and residence between the lakes.

600
601 Lakes that are sensitive to moisture balance (I/E) often have some hydrological closure
602 and/or longer residence time and precipitate carbonates with high $\delta^{13}\text{C}_{\text{calcite}}$, despite
603 having much more ^{12}C -enriched inflowing waters (Andrews et al., 1993). Evaporating
604 lakes tend to have a covariant relationship between $\delta^{13}\text{C}_{\text{calcite}}$ and $\delta^{18}\text{O}_{\text{calcite}}$ (Talbot, 1990;
605 Leng and Marshall, 2004), this is not the case for Lake Prespa ($r^2 = 0.25$). $\delta^{13}\text{C}_{\text{calcite}}$
606 values in Prespa will reflect $\delta^{13}\text{C}_{\text{T DIC}}$ at the time of calcite formation, and like the
607 composition of aquatic organic material the $\delta^{13}\text{C}_{\text{T DIC}}$ is likely a function of equilibration of
608 the bicarbonate ion with atmospheric CO_2 . High algal productivity is unlikely to explain
609 these values because during MIS 2-4 the algal peaks in our diagram are not
610 synchronous with peaks in TIC (Fig. 3). However, during MIS 1 and 5 algal and TIC
611 peaks are synchronous. Isotopic equilibrium with atmospheric CO_2 will result in lake
612 water $\delta^{13}\text{C}$ having values between $+1$ to $+3\text{‰}$ (Uzdowski and Hoefs, 1990), values similar
613 to the core values within Lake Prespa ($\delta^{13}\text{C}_{\text{calcite}}$ values through the Holocene = $+1.1\text{‰}$ \pm $-$
614 0.4‰) perhaps suggesting the bicarbonate has reached a steady state due to the long
615 water residence time. One explanation for the lack of a co-variation between $\delta^{13}\text{C}_{\text{calcite}}$
616 and $\delta^{18}\text{O}_{\text{calcite}}$ is perhaps low bicarbonate concentration, unlike changes in $\delta^{18}\text{O}$ which will
617 be driven by hydrological balance.

618
619 *6.6. Comparison of $\delta^{18}\text{O}$ between Prespa, Ohrid and other lakes in the region from 15 ka*

620
621 *6.6.1. Late Glacial to Holocene transition*

622
623 The Late Glacial to Holocene transition in Prespa Co1215 initiates at ca.15 ka (Fig. 2)
624 with a gradual increase in organic matter content (interpreted as increased productivity;
625 Aufgebauer et al., in press), increased TOC/N (less decomposition). There is little or poor

626 evidence that a similar change occurs in the existing Lake Ohrid cores. This gradual
627 transition to the Younger Dryas is often marked in Mediterranean lake records by an
628 increase in $\delta^{18}\text{O}_{\text{calcite}}$ (Roberts et al., 2008), this phase and other Pleistocene carbonate
629 isotopic enrichment events seen in Mediterranean lakes may be linked to the North
630 Atlantic Heinrich cold events (Roberts et al., 2008), although chronological imprecision
631 means this suggestion is currently not verifiable. In Lake Prespa the low carbonate
632 content prior to 10 ka cannot confirm this transition from the isotope perspective (the
633 carbonate is too low to analyse for isotopes), although the absence of significant
634 amounts of carbonate perhaps implies a lake with low evaporation. Within this transition,
635 immediately post the harsh climate of the Lateglacial/Oldest Dryas, the pollen show a
636 retreat of steppe herb communities (eg. *Artemisia* and *Chenopodiaceae*) coupled with a
637 gradual rise of pine and oak suggest rising moisture availability within the Prespa
638 catchment. This trend is interrupted by an abrupt millennial vegetational setback (likely
639 the Younger Dryas chronozone) which is characterized by increasing aridity and lower
640 temperatures. Around Prespa this is marked by a major restructuring of the vegetation
641 including a descending treeline and/or a thinning of existing tree stands (Panagiotopoulos
642 et al., in press).

643

644 6.6.2. *Early Holocene*

645

646 In the early Holocene, Lake Prespa shows a small peak in $\delta^{18}\text{O}_{\text{calcite}}$ between 10-8 ka
647 while Lake Ohrid shows a small $\delta^{18}\text{O}_{\text{calcite}}$ peak between 10-9 ka. Other lakes in the
648 Eastern and Central Mediterranean show that the early Holocene carbonates are
649 isotopically depleted at this time (Roberts et al., 2008; their figure 5; Fig. 6). The
650 magnitude of evaporative enrichment in Lake Prespa during the early Holocene is less
651 than the later Holocene (see below). It is difficult to compare directly the $\delta^{18}\text{O}_{\text{calcite}}$ from
652 the early and late Holocene because there are isotope complications, for example, the
653 source composition of precipitation would have likely been different partly because of
654 changes in the Mediterranean Sea at that time. Other lakes around the Eastern
655 Mediterranean show an early Holocene oxygen isotope depletion, which Roberts et al.
656 (2008) ascribe as most likely a function of regional water balance and a difference in the
657 source isotope composition of precipitation due to the formation of sapropel in the
658 Mediterranean Sea. The sapropel formation was thought to be initiated by increased

659 rainfall and runoff from the Nile into the Eastern Mediterranean Sea, which would have
660 contributed significantly to the creation of a freshwater lid and subsequently bottom water
661 anoxia between 9.5 ka and 6.5 ka (Rohling, 1994; Ariztegui et al., 2000). The pollen
662 record shows the gradual formation of closed oak forests and their diversification, with
663 the establishment of thermophilous and drought-sensitive trees after approximately 10 ka
664 which suggests the absence of summer droughts and thus confirms sufficient
665 precipitation for forest growth during this period. Moreover, the parallel appearance and
666 establishment of important maquis constituents exclude the existence of intense late
667 winter and spring droughts. In light of the above, the pollen record suggests a rather even
668 distribution of annual precipitation, which appears to be in agreement with the sapropel
669 formation in the eastern Mediterranean (Panagiotopoulos et al., in press).

670

671 *6.6.3. Middle Holocene humidity*

672

673 Lake Prespa records the lowest $\delta^{18}\text{O}_{\text{calcite}}$ values for the period (8-2 ka), while Lake Ohrid
674 clearly shows a progressive enrichment in $\delta^{18}\text{O}_{\text{calcite}}$ over this time interval (Fig. 6). This
675 difference could be a function of hydrology and the different lake sizes. Recharge into
676 Lake Prespa was presumably sufficient to counter summer evaporation, whereas in Ohrid
677 with its much larger lake water volume to surface area in comparison to catchment area
678 may mean that Lake Ohrid may be less responsive to winter recharge. The pollen
679 records from the two sites (Wagner et al., 2009; Panagiotopoulos et al., in press) are
680 almost identical during the Holocene implying similar climate regimes in both catchments.
681 Overall, the low and stable $\delta^{18}\text{O}$ values in both Prespa and Ohrid through the middle
682 Holocene is a general feature observed in other eastern and central Mediterranean lakes
683 and speleothems (Bar-Matthews et al., 2000; Zanchetta et al., 2007b; Roberts et al.,
684 2008; Develle et al., 2010), although not always over exactly the same time periods
685 notwithstanding dating issues. Lakes Van and Frassino have a low and stable $\delta^{18}\text{O}$
686 period from 9-4 ka (Baroni et al., 2006), while Eski is low only till about 6 ka (Roberts et
687 al., 2001). The much smaller Golhisar Golu appears to respond very rapidly to moisture
688 balance although values are generally low between 7-5 ka (Eastwood et al., 2007; Fig.
689 6). This mid-Holocene humidity has been interpreted in different ways, for example it has
690 been attributed to increased amounts of precipitation related to an increase in winter
691 precipitation of Atlantic origin (Zanchetta et al., 2007; Zhornyak et al., 2011) or a

692 significant (especially for eastern Mediterranean) freshening of surface marine water of
693 the eastern Mediterranean at that time resulting in lower $\delta^{18}\text{O}$ of precipitation (e.g.,
694 Kolodny et al., 2005; Develle et al., 2010). The Middle Holocene Prespa pollen record
695 suggests similar climatic and environmental conditions to the early Holocene.

696

697 *6.6.4. Late Holocene*

698

699 The higher $\delta^{18}\text{O}_{\text{calcite}}$ in Lake Prespa (and Lake Ohrid) from 2 ka suggests drier
700 conditions, and probably a significant lake level drop in Prespa, as $\delta^{18}\text{O}_{\text{calcite}}$ values are
701 the highest of the entire record. Over this time there is a general trend towards higher
702 $\delta^{18}\text{O}_{\text{calcite}}$ in many other Mediterranean isotopic records both in lakes (e.g. Roberts et al.,
703 2008; Develle et al., 2010) and in speleothems (e.g., Bar-Matthews et al., 2000; Zanchetta
704 et al., 2007b; Verheyden et al., 2008). Lake Van, Eski and Frassino show consistently
705 high values from 4 ka (the latter 2 showing hiatus from between 2-1 ka; Fig. 6). In Golhisar
706 Golu there are high values also from 4 ka but the hydrology likely changes around 3 ka
707 with the effect of the Santorini tephra on the lake catchment (Eastwood et al., 2007; Fig.
708 6). This regional drying has previously been described as related to progressive
709 reduction in moisture advection from the Atlantic linked to a reduction in summer
710 insolation, which also resulted in a decrease in monsoon activity on tropical Africa and
711 progressive aridification of the Sahara (e.g. Gasse, 2000). Isotopically this increase could
712 also be related to progressive increase in isotopic composition in the Mediterranean Sea
713 (Emeis et al., 2000) and the related effect on rainfall amount. Very low lake levels (and
714 highest $\delta^{18}\text{O}_{\text{calcite}}$) at Lake Prespa occur around ca. 1 ka and are thought to correspond
715 with the occurrence of ruins of several buildings at 840-842 m.a.s.l. (Sibinoviç, 1987).
716 These buildings were constructed at the end of the 10th/beginning of the 11th century AD
717 and it is unlikely that they were formed in the water. There is a rapid reversal in the last
718 500 years as $\delta^{18}\text{O}_{\text{calcite}}$ declines to some of the lowest values (-7‰) in the most recent
719 sediments (also seen in Ohrid core Lz1120; Leng et al., 2010; Fig. 6). Why Co1215
720 shows a consistent wet phase (low $\delta^{18}\text{O}$) in the last 500 years is unclear but there is
721 some evidence in Lake Ohrid for very recent (apparent) freshening driven by
722 anthropogenic change including the Roman and recent forest clearance (Wagner et al.,
723 2009).

724

725 Finally, in the modern lakewater, assuming peak precipitation of calcite occurs during the
726 warmer summer months when mean monthly temperatures are high (summer
727 temperatures between 2001 and 2004 averaged between +20 and +22°C, Matzinger et
728 al., 2007), calcite precipitating in Lake Prespa with a lakewater value of -1‰ will have a
729 $\delta^{18}\text{O}_{\text{calcite}}$ of around -2‰ , i.e. an oxygen isotope composition that is higher than most of
730 the Holocene calcite $\delta^{18}\text{O}$ except for the early and late Holocene arid phases. However,
731 the isotopic composition of modern lake water is perhaps as much to do with
732 anthropogenic activities as climate. Indeed the recent receding woodlands and the
733 development of agriculture (cereals and crop trees) occurring alongside the increased
734 accumulation rates of algae suggests that Lake Prespa is undergoing substantial
735 changes that point to intensive anthropogenic activities (Panagiotopoulos et al., in press).
736 In Lake Prespa as with in many other lakes disentangling natural from human impact
737 over the very recent past is challenging.

738

739 **7. Conclusions**

740

741 The current Lake Prespa waters are evaporated compared to the inflowing spring waters.
742 The hydrological balance in Lake Prespa is a function of summer aridity and winter
743 precipitation, on a decadal scale. The spring water bicarbonate ion is likely derived from
744 soil CO_2 which once incorporated into the lakewater likely equilibrates with atmospheric
745 CO_2 .

746

747 The Lake Prespa sediments broadly fall into zones based on their sedimentology,
748 geochemistry, palynology and the existing chronology; these zones roughly equate to
749 Marine Isotope Stages 5 to 1. The Glacial sediments are grey, contain low TOC and
750 TOC/N and high $\delta^{13}\text{C}_{\text{organic}}$ suggesting low supply of carbon to the lake, but high summer
751 productivity. Through this period there are spikes in OI and siderite, which suggest that
752 although the lake was likely to have mixed regularly leading to enhanced oxidation of
753 organic matter, there must have been within sediment reducing conditions and
754 methanogenesis. In contrast the MIS 5 sediments have relatively high TOC, TOC/N, HI
755 while TIC, OI, and $\delta^{13}\text{C}_{\text{org}}$ are low, similar to MIS 1 although the Holocene sediments
756 contain high calcite. MIS 5 and 1 sediment suggest much more productivity, higher rates

757 of organic material preservation possibly due to more limited mixing with longer periods
758 of O-depleted bottom waters.

759

760 The $\delta^{18}\text{O}$ of the glacial siderites is, like calcite, a function of lakewater input:evaporation
761 balance and temperature. However calcite $\delta^{18}\text{O}$ cannot be directly compared to siderite
762 $\delta^{18}\text{O}$ because of the different equilibration fractionations between the two minerals. Here
763 we recalculate lakewater $\delta^{18}\text{O}$ from siderite and calcite, estimating the temperature of
764 formation. The calculated $\delta^{18}\text{O}$ of the lakewater using the different minerals shows much
765 lower modelled lakewater $\delta^{18}\text{O}$ values in the glacial when compared to the Holocene.
766 Even allowing for lower glacial $\delta^{18}\text{O}_{\text{precipitation}}$ it seems likely that the lake was less
767 evaporative in the glacial, probably as a consequence of cooler summers and longer
768 winter ice cover.

769

770 The oxygen isotope composition of calcites and palynology from the Holocene show a
771 generally humid Holocene, a feature observed in other Eastern and Central
772 Mediterranean lakes and speleothems and can be attributed to increased amounts of
773 precipitation related to an increase in winter precipitation of Atlantic origin together with a
774 freshening of the surface of the Mediterranean Sea (lower $\delta^{18}\text{O}$ in rainfall) at that time.
775 Ours and other pollen records and climate reconstructions from this region indicate the
776 importance of seasonality in precipitation regime during the Holocene (Panagiotopoulos
777 et al., in press and references therein). Regional drying in the late Holocene has been
778 ascribed to progressive reduction in moisture advection from the Atlantic linked to a
779 reduction in summer insolation, a decrease in monsoon activity on tropical Africa and
780 progressive aridification of the Sahara leading to regional aridity and an increase in
781 isotopic composition in the Mediterranean Sea (Emeis et al., 2000).

782

783

784

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786

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795 and Baneschi provided the isotope and mineralogy data. Vogel and Zanchetta
796 contributed intellectually to the discussions of the data.

797

798

799

800 **Figures**

801

802 Figure 1. Lake Prespa in SE Europe, situated between Albania, Macedonia and Greece.
803 Coring location of Co1215 is marked.

804

805 Figure 2. The isotopic (a: $\delta^{18}\text{O}$ and δD ; b: $\delta^{13}\text{C}_{\text{TDIC}}$ and $\delta^{18}\text{O}$) composition of present day
806 waters from Lake Prespa and springs. The Global Meteoric Water Line (GMWL) and the
807 Mediterranean Meteoric Water Line (MMWL) (c.f. Anovskiy et al. (1991) and Eftimi and
808 Zoto (1997)) are also given on (a) with the calculated Local Evaporation Line (LEL). All
809 but the June 2011 data are from data compiled in Leng et al. (2010).

810

811 Figure 3. Multi-proxy data from Lake Prespa core Co1215. The data fall into zones which
812 roughly equate to Marine Isotope Stages which are marked. The chronology is based on
813 published dates given on the left hand side of the figure. (The oxygen isotope
814 composition of carbonate was obtained from calcite in MIS 1 and siderite in all other
815 zones).

816

817 Figure 4. Lake Prespa organic matter on a van Krevelen-type discrimination plot (after
818 Meyers and Lallier-Verges, 1999).

819

820 Figure 5. A composite pollen diagram including concentration curves of green algae
821 (*Pediastrum* and *Botryococcus*), dinocysts, aquatics (macrophytes) total pollen (including
822 fern spores) and percentage curve of aboreal (AP) versus non-arboreal pollen (NAP).

823

824 Figure 6. Comparison of oxygen isotope profiles from Lake Prespa core Co1215, to cores
825 from Lake Ohrid and other lakes from around the Mediterranean over the Holocene
826 where carbonate data can be compared (data in Roberts et al. 2008 and references
827 therein).

828

829 Table 1. Characteristics of Lake Prespa (data from Matzinger et al., 2006a; Wilke et al.,
830 2010).

831

832

833 **References**

- 834
- 835 Aliaj, S. H., Baldassarre, G., Shkupi, D., 2001. Quaternary subsidence zones in Albania:
836 some case studies. *Bulletin of Engineering Geology and the Environment*, 59, 313-318.
837
- 838 Allen, J.R.M., Brandt, U., Brauer, A., Hubberten, H-W., Huntley, B., Keller, J., Kraml, M.,
839 Mackensen, A., Mingram, J., Negendank, J.F.W., Nowaczyk, N.R., Oberhänsli, H.,
840 Watts, W.A., Wulf, S., Zolitschka, B., 1999. Rapid environmental changes in southern
841 Europe during the last glacial period. *Nature* 400, 740-743.
842
- 843 Allen, J.R.M., Huntley, B., 2000. Weichselian palynological records from southern
844 Europe: correlation and chronology. *Quaternary International*, 73, 111-125.
845
- 846 Andrews, J.E., Riding, R., Dennis, P.F., 1993. Stable isotope compositions of recent
847 freshwater cyanobacterial carbonates from the British Isles: local and regional
848 environmental controls. *Sedimentology*, 40, 303-314.
849
- 850 Andrews, J.E., Riding, R., Dennis, P.F., 1997. The stable isotope record of environmental
851 and climatic signals in modern terrestrial microbial carbonates from Europe.
852 *Palaeogeography, Palaeoclimatology, Palaeoecology*, 129, 171-189.
853
- 854 Anovski, T., Andonovski, B., Minceva, B., 1992. Study of the hydrological relationship
855 between Lake Ohrid and Prespa. In *Proceedings of Symposium on Isotope Techniques*
856 *in Water Resources Development*. IAEA, Vienna, Austria.
857
- 858 Anovski, T. (ed.), 2001. Progress in the Study of Prespa Lake using Nuclear and Related
859 Techniques, Project Report. IAEA Regional Project RER/8/008, ISBN 9989-650-21-7,
860 Skopje, Macedonia.
861
- 862 Ariztegui, D., Asioli, A., Lowe, J.J., Trincardi, F., Vigliotti, L., Tamburini, F.,
863 Chondrogianni, C., Accorsi, C.A., Mazzanti, M.B., Mercuri, A.M., van der Kaars, S.,
864 McKenzie, J.A., Oldfield, F., 2000. Palaeoclimate and the formation of sapropel
865 S1: inferences from Late Quaternary lacustrine and marine sequences in the
866 central Mediterranean region. *Palaeogeography, Palaeoclimatology, Palaeoecology*
867 158, 215-240.
868
- 869 Aufgebauer, A., Panagiatopoulos, K., Wagner, B., Schäbitz, F., Viehberg, F.A., Vogel, H.,
870 Zanchetta, G., Sulpizio, R., Leng, M.J., Damaschke, M., in press. Climate and
871 environmental change in the Balkans over the last 17 ka recorded in sediments from
872 Lake Prespa (Albania/F.Y.R. of Macedonia/Greece). *Quaternary International*.
873
- 874 Bahrig, B. 1988. Palaeo-environment information from deep water siderite (Lake of
875 Laach, West Germany). *Geological Society, London, Special Publications*, 40, 153-158.
876
- 877 Baroni, C., Zanchetta, G., Fallick, A.E., Longinelli, A., 2006. Mollusca stable isotope
878 record of a core from Lake Frassino, northern Italy: hydrological and climatic
879 changes during the last 14 ka. *The Holocene* 16, 827-837.

- 880 Bar-Matthews, M., Ayalon, A., Kaufman, A. 2000. Timing and hydrological conditions of
881 Sapropel events in the Eastern Mediterranean, as evident from speleothems, Soreq
882 Cave, Israel. *Chemical Geology*, 169, 145–156.
- 883 Bassinot, F.C., Labeyrie, L.D., Vincent, E., Quidelleur, X., Shackleton, N.J., Lancelot, Y.,
884 1994. The astronomical theory of climate and the age of the Brunhes-Matuyama
885 magnetic reversal. *Earth and Planetary Science Letters*, 126, 91–108.
- 886
- 887 Berner, R.A. 1971. *Principals of sedimentology*. New York, McGraw-Hill, pp. 240.
- 888
- 889 Berner, R.A. 1980. *Early diagenesis: A theoretical approach*. Princeton, New Jersey,
890 Princeton University Press, pp. 241.
- 891
- 892 Bolle, H.J., 2003. *Mediterranean Climate. Variability and Trends*. Springer, Berlin.
- 893
- 894 Danzeglocke, U., Jöris, O., Weninger, B. CalPal-2007^{online}, online available at:
895 <http://www.calpal-online.de>, accessed 2009-11-21.
- 896 Bowen, G. J., Wassenaar, L. I., Hobson, K. A., 2005. Global application of stable
897 hydrogen and oxygen isotopes to wildlife forensics. *Oecologia*, 143, 337-348.
- 898 Carothers, W.W., Adami, L.H., Rosenbauer, R.J. 1988. Experimental oxygen isotope
899 fractionation between siderite-water and phosphoric acid liberated CO₂-siderite.
900 *Geochimica Cosmochimica Acta*, 52, 2445–2450.
- 901 Coleman, M.L., 1985. Geochemistry of diagenetic non-silicate minerals: Kinetic
902 considerations. In: Eglington, G. et al. (Eds.), *Geochemistry of buried sediments*.
903 London, Royal Society, pp. 39-54.
- 904
- 905 Craig, H., 1965. The measurement of oxygen isotope palaeotemperatures. In: Tongiorgi,
906 E. (Ed.), *Stable Isotopes in Oceanographic Studies and Palaeotemperatures*. Pisa,
907 Consiglio Nazionale delle Ricerche Laboratorio di Geologia Nucleare, pp 161-182.
- 908
- 909 Develle, A. L., Herreros, J., Vidal, L., Sursock, A., Gasse, F., 2010. Controlling factors on
910 paleo-lake oxygen isotope record (Yammouneh, Lebanon) since the Last Glacial
911 Maximum. *Quaternary Science Reviews*, 29, 865-886.
- 912
- 913 Eastwood, W.J., Leng, M.J., Roberts, N., Davis, B., 2007. Holocene climate change in
914 the eastern Mediterranean region: a comparison of stable isotope and pollen data from a
915 lake record in southwest Turkey. *Journal of Quaternary Science*, 22, 327-341.
- 916
- 917 Emeis, K.C., Struck, U., Schulz, H.M., Rosenberg, R., Bernasconi, S., Erlenkeuser, H.,
918 Sakamoto, T., Martinez-Ruiz, F., 2000. Temperature and salinity variations of
919 Mediterranean Sea surface waters over the last 16,000 years from records of
920 planktonic stable oxygen isotopes and alkenone unsaturation ratios. *Palaeogeography,*
921 *Palaeoclimatology, Palaeoecology* 158, 259–280.
- 922
- 923 Epstein, S., Buchsbaum, R., Lowenstam, H.A., Urey, H.C., 1953. Revised carbonate-
924 water isotopic temperature scale. *Geological Society of America Bulletin*, 64, 1315–1325.

925
926 Fægri, K., Iversen, J., Kaland, P.E., Krzywinski, K., 2000. Textbook of pollen analysis. 4th
927 edition, Blackburn Press, Caldwell. Pp. 340.
928
929 Frogley, M.R., Griffiths, H.I., Heaton, T.H.E., 2001. Historical biogeography and Late
930 Quaternary environmental change of Lake Pamvotis, Ioannina (north-western Greece):
931 evidence from ostracods. *Journal of Biogeography*, 28, 745-756.
932
933 Gasse, F., 2000. Hydrological changes in the African tropics since the Last Glacial
934 Maximum. *Quaternary Science Reviews*, 19, 189 – 211.
935
936 Giresse, P., Maley, J., Kelts, K., 1991. Sedimentation and palaeoenvironment in crater
937 lake Barombi Mbo, Cameroon, during the last 25,000 years. *Sedimentary Geology*, 71,
938 151-175.
939
940 Hammarlund, D., 1993. A distinct $\delta^{13}\text{C}$ decline in organic lake sediments at the
941 Pleistocene-Holocene transition in southern Sweden. *Boreas*, 22, 236–243.
942
943 Heiss, G. 1988. Crystal structure refinement of a synthetic Fe-Mg-Ca-carbonate phase.
944 *Zeitschrift für Kristallographie*, 185, 604.
945
946 Hetényi, M., Nyilas, T., Tóth, T., 2005. Stepwise Rock-Eval pyrolysis as a tool for typing
947 heterogeneous organic matter in soils. *Journal of Analytical and Applied Pyrolysis*, 74,
948 45–54.
949
950 Hodell, D.A., Schelske, C.L., 1998. Production, sedimentation and isotopic composition
951 of organic matter in Lake Ontario. *Limnology and Oceanography*, 43, 200–14.
952
953 Hollis, G. E., Stevenson, A.C., 1997. The physical basis of the lake Mikri Prespa
954 systems: geology, climate, hydrology and water quality. *Hydrobiologia*, 351, 1–19.
955
956 Jacob, J., Disnar, J-R., Boussafir, M., Sifeddine, A., Turcq, B., Spadano Albuquerque,
957 A.L., 2004. Major environmental changes recorded by lacustrine sedimentary organic
958 matter since the last glacial maximum near the equator (Lagoa do Caçó, NE Brazil).
959 *Palaeogeography, Palaeoclimatology, Palaeoecology*, 205, 183-197.
960
961 Kocev, D., Naumoski, A., Mitreski, K., Krstić, S., Džeroski, S., 2010. Learning habitat
962 models for the diatom community in Lake Prespa. *Ecological Modelling*, 221, 330-337.
963
964 Kolodny, Y., Stein, M., Machlus, M., 2005. Sea–rain–lake relation in the Last Glacial East
965 Mediterranean revealed by $d^{18}\text{O}$ – $d^{13}\text{C}$ Lake Lisan aragonites. *Geochimica et*
966 *Cosmochimica Acta*, 69, 4045–4060.
967
968 Leng, M.J., Lamb A.L., Heaton T.H.E., Marshall J.D., Wolfe B.B., Jones M.D, Holmes
969 J.A., Arrowsmith C.. 2005. Isotopes in lake sediments. In: Leng M. J. (ed.). *Isotopes in*
970 *Palaeoenvironmental Research*. Springer, Dordrecht, The Netherlands. 148-176 pp.
971
972 Leng, M.J., Marshall, J.D., 2004. Palaeoclimate interpretation of stable isotope data
973 from lake sediment archives. *Quaternary Science Reviews*, 23, 811–831.
974

975 Leng, M.J., Roberts, N., Reed, J.M., Sloane, H.J., 1999. Late Quaternary climatic and
976 limnological variations based on carbon and oxygen isotope data from authigenic and
977 ostracod carbonate in the Konya Basin, Turkey. *Journal of Paleolimnology*, 22, 187-204.
978

979 Leng, M. J., Baneschi, I., Zanchetta, G., Jex, C. N., Wagner, B., Vogel, H.: 2010. Late
980 Quaternary palaeoenvironmental reconstruction from Lakes Ohrid and Prespa
981 Macedonia/Albania border) using stable isotopes. *Biogeosciences*, 7, 3109–3122.
982

983 Lézine, A.-M., von Grafenstein, U., Andersen, N., Belmecheri, S., Bordon, A., Caron, B.,
984 Cazet, J. P., Erlenkeuser, H., Fouache, E., Grenier, C., Huntsman-Mapila, P., Hureau-
985 Mazaudier, D., Manelli, D., Mazaud, A., Robert, C., Sulpizio, R., Tiercelin, J. J.,
986 Zanchetta, G., and Zeqollari, Z., 2010. Lake Ohrid, Albania, provides an exceptional
987 multi-proxy record of environmental changes during the last glacial–interglacial cycle.
988 *Palaeogeography, Palaeoclimatology, Palaeoecology*, 287, 116–127.
989

990 Lojka, R., Drábková, J., Zajíc, J., Sýkorová, I., Franců, J., Bláhová, A., Grygar, T., 2009.
991 Climate variability in the Stephanian B based on environmental record of the Mšec Lake
992 deposits (Kladno-Rakovník Basin, Czech Republic). *Palaeogeography,
993 Palaeoclimatology, Palaeoecology*, 280, 78-93.
994

995 Lionello, P., Malanotte-Rizzoli, P., Boscolo, R., 2006. *Mediterranean Climate Variability*.
996 Elsevier, The Netherlands.
997

998 Löffle, H., Schiller, E., Kusel, E., Kraill, H., 1998. Lake Prespa, a European natural
999 monument, endangered by irrigation and eutrophication? *Hydrobiologia*, 384, 69-74.
1000

1001 Matter, M., Anselmetti, F.S., Jordanoska, B., Wagner, B., Wessels, M., Wüest, A., 2010.
1002 Carbonate sedimentation and effects of eutrophication observed at the Kalista
1003 subaquatic springs in Lake Ohrid (Mazedonia). *Biogeosciences*, 7, 3755-3767.
1004

1005 Matzinger, A., Jordanoski, M., Veljanoska-Sarafiloska, E., Sturm, M., Müller, B., Wüest,
1006 A., 2006a. Is Lake Prespa jeopardizing the ecosystem of ancient Lake Ohrid?
1007 *Hydrobiology*, 553, 89–109.
1008

1009 Matzinger, A., Spirkovski, Z., Patceva, S., Wüest, A., 2006b. Sensitivity of ancient Lake
1010 Ohrid to local anthropogenic impacts and global warming. *Journal of Great Lakes
1011 Research*, 32, 158–179.
1012

1013 Meyers, P.A., Ishiwatari, R., 1995. Organic matter accumulation records in lake
1014 sediments. In: Lerman A., Imboden D. M., Gat J. R. (eds.). *Physics and chemistry of
1015 lakes*. Springer-Verlag Berlin, Heidelberg, New York, 279–328.
1016

1017 Meyers, P.A., Lallier-Vergès, E., 1999. Lacustrine sedimentary organic matter records of
1018 late Quaternary paleoclimates. *Journal of Paleolimnology*, 21, 345–372.
1019

1020 Meyers, P.A., Teranes, J.L., 2001. Sediment organic matter. In *Developments in
1021 Paleoenvironmental Research, Volume 2. Tracking environmental change using lake
1022 sediments*, Last WM, Smol JP (eds). Kluwer Academic Publishers: Dordrecht; pp. 239-
1023 269.
1024

- 1025 Mozley, P.S., Wersin, P., 1992. Isotopic composition of siderite as an indicator of
1026 depositional environment. *Geology*, 20, 817-820.
- 1027 O'Neil, J.R., Clayton, R.N., Mayeda, T.K., 1969. Oxygen isotope fractionation in divalent
1028 metal carbonates. *Journal of Chemical Physics*, 51, 5547–5558.
- 1029 Panagiotopoulos, K., Aufgebauer, A., Schäbitz, F., Wagner, B. Vegetation and climate
1030 history of Lake Prespa region since the Lateglacial. *Quaternary International* – in press.
1031
- 1032 Popovska, C., Bonacci, O., 2007. Basic data on the hydrology of Lakes Ohrid and
1033 Prespa. *Hydrological Processes*, 21, 658-664.
1034
- 1035 Roberts, N., Jones, M.D., Benkaddour, A., Eastwood, W.J., Filippi, M.L., Frogley, M.R.,
1036 Lamb, H.F., Leng, M.J., Reed, J.M., Stein, M., Stevens, L., Valero-Garcés B., Zanchetta,
1037 G., 2008. Stable isotope records of Late Quaternary climate and hydrology from
1038 Mediterranean lakes: the ISOMED synthesis. *Quaternary Science Reviews*, 27, 2426-
1039 2441.
1040
- 1041 Roberts, N., Reed, J., Leng, M.J., Kuzucuoğlu, C., Fontugne, M., Bertaux, J., Woldring,
1042 H., Bottema, S., Black, S., Hunt, E., Karabiyıkoğlu, M., 2001. The tempo of Holocene
1043 climatic change in the eastern Mediterranean region: new high-resolution crater-lake
1044 sediment data from central Turkey. *The Holocene*, 11, 721–736.
1045
- 1046 Rohling, E.J., 1994. Review and new aspects concerning the formation of eastern
1047 Mediterranean sapropels. *Marine Geology*, 122, 1–28.
1048
- 1049 Rosenbaum, J., Sheppard, S.M.F., 1986. An isotopic study of siderites, dolomites and
1050 ankerites at high temperatures. *Geochimica et Cosmochimica Acta*, 50, 1147–1150.
1051
- 1052 Sibinoviç, M., 1987. *Ezera Prespansko i Ohridsko*. The SRC & Agency of Water
1053 Resources of R. of Macedonia, Skopje (in Macedonian).
1054
- 1055 Stefouli, M., Kouraev, A., Charou, E., 2008. Proceedings of the 2nd MERIS / (A) ATSR
1056 User Workshop, Frascati, Italy, 22-26 September 2008.
1057
- 1058 Stockmarr, J., 1971. Tablets with spores used in absolute pollen analysis. *Pollen et*
1059 *Spores*, 13, 615-621.
1060
- 1061 Talbot, M.R., 1990. A review of the palaeohydrological interpretation of carbon and
1062 oxygen isotopic ratios in primary lacustrine carbonates. *Chemical Geology*, 80, 261-79.
1063
- 1064 Talbot, M.R., Johannessen, T., 1992. A high resolution palaeoclimatic record for the last
1065 27500 years in tropical West Africa from the carbon and nitrogen isotopic composition of
1066 lacustrine organic matter. *Earth and Planetary Science Letters*, 110, 23-37.
1067
- 1068 Talbot, M.R., Livingstone, D.A., 1989. Hydrogen index and carbon isotopes of lacustrine
1069 organic matter as lake level indicators. *Palaeogeography, Palaeoclimatology,*
1070 *Palaeoecology*, 70, 121-137.
1071

1072 Usdowski, E., Hoefs, J., 1990. Kinetic C-13 C-12 and O-18 O-16 effects upon dissolution
1073 and outgassing of CO₂ in the system CO₂-H₂O. *Chemical Geology*, 80, 109-118.
1074

1075 Vane, C.H., Abbott, G.D., 1999. Proxies for land plant biomass: closed system pyrolysis
1076 of some methoxyphenols. *Organic Geochemistry*, 30, 1535-1541.
1077

1078 Vane, C.H., Drage, T.C., Snape, C.E., 2003. Biodegradation of Oak (*Quercus alba*) wood
1079 during growth of the shiitake mushroom (*lentinula edodes*): A molecular approach.
1080 *Journal of Agricultural and Food Chemistry*, 51, 947-956.
1081

1082 Verheyden, S., Nader, F.H., Cheng, H.J., Edwards, L.R., Swennen, R., In press.
1083 Paleoclimate reconstruction in the Levant region from the geochemistry of a Holocene
1084 stalagmite from the Jeita cave, Lebanon, *Quaternary Research*.
1085

1086 Vogel, H., Wagner, B., Zanchetta, G., Sulpizio, R., Rosén, P., 2010. A paleoclimate
1087 record with tephrochronological age control for the last glacial-interglacial cycle from
1088 Lake Ohrid, Albania and Macedonia. *Journal of Paleolimnology*, 44, 295–310.
1089

1090 Wagner, B., Lotter, A.F., Nowaczyk, N., Reed, J.M., Schwalb, A., Sulpizio, R., Valsecchi,
1091 V., Wessels, M., Zanchetta, G., 2009. A 40,000-year record of environmental change
1092 from ancient Lake Ohrid (Albania and Macedonia). *Journal of Paleolimnology*, 41, 407–
1093 430.
1094

1095 Wagner, B., Vogel, H., Zanchetta, G., Sulpizio, R., 2010. Environmental changes on the
1096 Balkans recorded in the sediments from lakes Prespa and Ohrid. *Biogeosciences*, 7,
1097 3187–3198.
1098

1099 Wagner, B., Aufgebauer, A., Vogel, H., Zanchetta, G., Sulpizio, R., Damaschke, M., in
1100 press. Late Pleistocene and Holocene contourite drift in Lake Prespa (Albania/F.Y.R. of
1101 Macedonia/Greece), *Quaternary International*.
1102

1103 Watzin, M.C., Puka, V., Naumoski, T.B., (eds). 2002. Lake Ohrid and its Watershed,
1104 State of the Environment Report. Lake Ohrid Conservation Project. Tirana, Albania and
1105 Ohrid, Macedonia, pp. 134.
1106

1107 Wilke, T., Schultheiß, R., Albrecht, C., Bornmann, N., Trajanovski, S., Kevrekidis, T.
1108 2010. Native *Dreissena* freshwater mussels in the Balkans: in and out of ancient lakes.
1109 *Biogeosciences*, 7, 3051-3065.
1110

1111 Zanchetta, G., Drysdale, R.N., Hellstrom, J.C., Fallick, A.E., Isola, I., Gagan, M.K.,
1112 Pareschi, M.T., 2007. Enhanced rainfall in the Western Mediterranean during deposition
1113 of sapropel S1: stalagmite evidence from Corchia cave (Central Italy).
1114 *Quaternary Science Reviews*, 26, 279–286.
1115

1116 Zhang, C.L., Horita, J., Cole, D.R., Zhou, J., Lovley, D.R., Phelps, T.J., 2001.
1117 Temperature-dependent oxygen and carbon isotope fractionations of biogenic siderite.
1118 *Geochimica et Cosmochimica Acta*, 65, 2257–2271.
1119

1120 Zhornyak, L.V., Zanchetta, G., Drysdale, R.N., Hellstrom, J.C., Isola, I., Regattieri, E.,
1121 Piccini, L., Banerjee, S., 2011. Stratigraphic evidence for a “pluvial phase” between ca.

1122 8200-7100 ka from Renella Cave (Central Italy). Quaternary Science Reviews, 30, 409-
1123 417.
1124
1125
1126
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Property	Prespa
Altitude (masl)	849
Catchment area (km ²)	1300
Lake area (km ²)	254
Mean lake depth (m)	14-19
Volume (km ³)	3.6
pH (surface/bottom)	8.4-7.3

1128
1129 Table 1. Characteristics of Lake Prespa (data from Matzinger et al., 2006a; Wilke et al.,
1130 2010)











