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

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Abstract

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

Keywords: Late Quaternary, Mediterranean, lake, stable isotopes, Rock Eval pyrolysis, geochemistry
1. Introduction

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

2. General setting

Lake Prespa is situated in SE Europe between Albania, Macedonia and Greece (Fig. 1). The lake drains into the larger Lake Ohrid through a karst system within the Mali Thate (2,287 meters above sea level (m.a.s.l.)) and Galicica (2,262 m.a.s.l.) mountains, which form the topographical divide between the two lakes. The lake is thought to have been formed within a tectonic graben during the Alpine Orogeny in the Pliocene (Aliaj et al., 2001). Owing to the lakes position within the rain shadow of the surrounding mountains and the proximity to the Adriatic Sea, the lake catchment is under the influence of a sub-
Mediterranean climate with continental influences (Watzin et al., 2002; Panagiotopoulos, in press). Mean July and January temperatures are +21°C and +1°C respectively, with a mean annual temperature of +11°C. Precipitation peaks in winter (when snowfalls are frequent) and drops in summer, varying from 750 mm in the lowlands to over 1,200 mm on the mountains (Hollis and Stevenson, 1997). The diverse topography, the exposure of slopes and valleys, as well as the presence of a large water body create a complex patchwork of microclimates in the catchment that is also reflected in the vegetation. As such we expect that Mediterranean type changes seen across the circum-Mediterranean will also be recorded in Lake Prespa (Roberts et al., 2008).

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

3. Material and Methods

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

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

3.1. Stable isotope analysis of modern waters

Water isotope data include data from a monitoring period between 1984-2000 published by Anovski et al. (1992) and Anovski (2001) and data from waters reported in Matzinger et al. (2006a), data collected between August 2008 – October 2009 (Leng et al., 2010), and new data from June 2011 (Fig. 2a). The new data (June 2011) were measured at NIGL, the waters were equilibrated with CO$_2$ using an Isoprep 18 device for oxygen isotope analysis with mass spectrometry using a VG SIRA. For hydrogen isotope
analysis, an on-line Cr reduction method was used with a EuroPyrOH-3110 system
coupled to a Micromass Isoprime mass spectrometer. Isotopic ratios ($^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$)
are expressed in delta units, $\delta^{18}\text{O}$ and $\delta\text{D}$ ($\%$, parts per mille), and defined in relation to
the international standard, VSMOW (Vienna Standard Mean Ocean Water). Analytical
precision is typically $<0.2\%$ for $\delta^{18}\text{O}$ and $\pm1.0\%$ for $\delta\text{D}$.
Total dissolved inorganic carbonate (TDIC) was precipitated from the June 2011 water
collection (Fig. 2b), ca. 85 ml of water was reacted with c. 15 ml of NaOH-BaCl$_2$ solution
soon after collection. The resultant barium carbonate was filtered in the laboratory under
$\text{N}_2$, and rinsed with deionised water. The carbon isotope analysis ($\delta^{13}\text{C}_{\text{TDIC}}$) followed the
method described below for the sedimentary calcite.

3.2. Stable isotope and Rock Eval analysis of organic matter
The core from Lake Prespa was sampled for carbon isotopes on organic matter at 2 cm
intervals from the surface to a correlated depth of 168 cm, and ca. 10 cm from 170 cm to
the base at 1,575 cm. The samples were dried at 40°C and powdered. The powders
were treated with 10% HCl to remove calcite, washed several times with distilled water to
neutral pH, and then dried again at 40°C. $\text{CO}_2$ was evolved by combustion using a Carlo
Erba 1108 elemental analyser, interfaced to a Finnigan DeltaPlusXL via the Finnigan
MAT Conflo II interface. Organic carbon isotope values ($\delta^{13}\text{C}_{\text{org}}$) are reported as per
mille ($\%$) deviations of the isotopic ratios ($^{13}\text{C}/^{12}\text{C}$) calculated to the VPDB scale using a
within-run laboratory standards (graphite and ANU-sucrose) and international NBS
standards. Overall analytical reproducibility for the standards was $<0.1\%$ for $\delta^{13}\text{C}$. Note
that any siderite (see section 3.4) present below 168 cm would not be removed with 10%
HCl. In any case, the TIC spikes seen in the TIC data do not correspond to spikes in the
$\delta^{13}\text{C}_{\text{org}}$ data, the calculated 1-2% of siderite with an $\delta^{13}\text{C}$ composition of ca. $+10\%$
changes the $\delta^{13}\text{C}_{\text{org}}$ data by $<1\%$, and within the high frequency (not interpreted)
variability of the $\delta^{13}\text{C}_{\text{org}}$ record (Fig. 3).
Samples for Rock Eval analysis were selected at 5 cm resolution from correlated depths
ranging from 10 to 1563 cm. Pyrolysis was performed on approximately 60 mg of
powdered sediment (dry/wt) using a Rock-Eval 6 analyser (Vinci Technologies) in
standard configuration (pyrolysis and oxidation as a serial process). Samples were
heated from 300ºC to 650ºC at 25ºC/min in an inert atmosphere of N2. The residual
carbon was then oxidised at 300ºC to 850ºC at 20ºC/min (hold 5 min). Hydrocarbons
released during the two stage pyrolysis were measured using a flame ionization detector.
The CO and CO2 released during thermal cracking of the bound organic matter (OM)
were monitored using an IR cell. The performance of the instrument was checked every
10 samples against the accepted values of Institut Français du Pétrole (IFP) standard
(IFP 160 000, S/N1 5-081840). Classical Rock-Eval parameters were calculated by
integration of the amounts of HC (Thermo-vaporized free hydrocarbons) expressed in
mg/HC/g rock (S1) and hydrocarbons released from cracking of bound OM expressed in
mg/HC/g rock (S2) as well as CO and CO2. During analysis thirteen acquisition
parameters are determined from integration of the amounts of OM, CO and CO2. Here
the data presented are the Hydrogen Index (HI) calculated from S2x100/TOC and the
Oxygen Index (OI), S3x100/TOC (Fig. 3 and 4).

3.3. Pollen data

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

3.4. Stable isotope and XRD analysis of carbonates

The core from Lake Prespa was sampled for oxygen and carbon isotopes on carbonate
at 2 cm intervals from the surface to a correlated depth of 168 cm, where after carbonate
content becomes negligible, although small (0.5-2%) TIC spikes occur (Fig. 3). The
identification of carbonate species was undertaken using X-Ray Diffraction (XRD) using a
Bruker D8 Advance powder diffractometer equipped with a LynxEye linear position
sensitive detector and using CuKα radiation over the scan range 4 to 90° 2θ. The step size was 0.015° 2θ, with 0.8 s per step. Phase identification (calcite and siderite) was performed using Bruker DIFFRAC$$^\text{plus}$$ EVA search/match software interfaced with the PDF-4+ database from the International Centre for Diffraction Data (ICDD). The Ca,Mg-substituted siderite pattern 04-009-7660 (Heiss, 1988) offers a better match than pure siderite. Calcite is the only carbonate mineral present above 168 cm, thereafter the carbonate is substituted siderite, except for a layer at depth 1458 - 1463 cm which contains shelly fragments (and no siderite).

1 cm³ subsamples (from 0-168 cm and from the TIC spikes below 168 cm) were disaggregated in 5% sodium hypochlorite solution for 24 hours to oxidise reactive organic material. Samples were then washed three times in distilled water and sieved at 85 μm to remove any potential biogenic carbonate. The <85μm fraction was filtered, washed with deionised water and dried at 40°C and ground in agate. Prior to the carbonate isotope analysis, the form of the carbonate was investigated using SEM. Calcite crystals in Lake Prespa are of mixed form, some fragments are platy while others are in the form of fine (partially redissolved) calcite rhombs. The siderite crystals were not found using SEM. For the calcite isotope analysis (0-168 cm and 1,462 cm) the CO₂ was evolved by reaction with anhydrous phosphoric acid within a vacuum overnight at a constant 25°C. For the siderite isotope analysis (TIC spikes between 170 – 1,575 cm, except 1,462 cm) the CO₂ was evolved by reaction with anhydrous phosphoric acid within a vacuum for 72 hours at 90°C. For both the calcite and siderite, the CO₂ was cryogenically separated from water vapour under vacuum and collected for analysis using a VG Optima dual inlet mass spectrometer. The mineral-gas fractionation factors for calcite and siderite used were 1.01025 and 1.01006 (derived from Rosenbaum and Sheppard, 1986). Carbon and oxygen isotope values (δ¹³C(calcite/siderite), δ¹⁸O(calcite/siderite)) are reported as per mille (‰) deviations of the isotopic ratios (¹³C/¹²C, ¹⁸O/¹⁶O) calculated to the VPDB scale using within-run laboratory standards (calcite = MCS, siderite = CHH8) and international NBS standards. Overall analytical reproducibility for MCS and CHH8 was <0.1‰ for δ¹³C and δ¹⁸O.

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

5. Results

5.1. Modern waters

The oxygen and hydrogen isotope composition of present day waters from a variety of springs around Lakes' Prespa (Mikri and Megali), as well as the lakes themselves are given in Figure 2a (alongside the Global Meteoric Water Line (GMWL) and Mediterranean Meteoric Water Line (MMWL)). In addition there are 3 spot rainfall samples which fall on or close to the MMWL. These data are from samples taken between 1984 and 2009 (described in Leng et al., 2010), and new data (from springs/rivers entering Lake Prespa as well as the lake itself) from June 2011. Also plotted are monthly modelled rainfall isotope compositions (using 41.17°N, 20.75°E, average altitude of precipitation 1500 m) and mean weighted annual rainfall isotope 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 δ\(^18\)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 δ\(^18\)O –8.8‰ and δD –57‰ (Bowen et al., 2005) and is
302 above the vast majority of the spring/river data. Therefore the data suggests that the
303 springs/rivers 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/rivers 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‰ for δ\(^18\)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 δ\(^18\)O = –8.8‰ and δD = –60.6‰, is ca.
313 2‰ in δ\(^18\)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
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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 δ\(^13\)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 δ\(^{13}\)C\(_{\text{siderite}}\) and δ\(^{18}\)O\(_{\text{siderite}}\) are
327 generally high in comparison to the majority of calcite δ\(^{13}\)C and δ\(^{18}\)O. During MIS 4-2
328 several individual peaks of AP values exceed 70%, pollen from aquatic macrophytes and
algae are present but in low numbers. The Pleistocene/Holocene transition is likely between 292 and 204 cm based on dating and a change in the proxies, i.e. a return to brown sediments, increasing HI, TOC, TOC/N, TIC, and decreasing OI, $\delta^{13}$C$_{\text{organic}}$. The Holocene (MIS 1) sediments in the upper 204 cm have high HI, TOC, TOC/N, TIC and low OI, $\delta^{13}$C$_{\text{organic}}$. High TIC is due to calcite precipitation, $\delta^{13}$C is consistent around +1.1 ± 0.4‰, while $\delta^{18}$O is generally low (−4.6 ± 0.8‰) except for two high phases in the early and late Holocene. Arboreal pollen as well as aquatic macrophytes and algae dominate in the Holocene.

6. Discussion

6.1. Modern water oxygen and hydrogen isotope composition

Over the lakewater collection period (1984 - 2011) the two Prespa lakes (Megali and Mikri Prespa) had an almost identical range in water isotope composition ($\delta^{18}$O ca. –7 to +1‰; $\delta^D$ ca. −47 to −13‰). $\delta^{18}$O and $\delta^D$ fall on a Local Evaporation Line (LEL) and as such are evaporated (compared to spring waters), the similarity in the isotope data for the two lakes reflects their hydrological connection (Fig. 2a). The range in isotope data for the lakes suggests that the Prespa lakes are very sensitive to moisture balance (winter precipitation versus summer evaporation) and as such respond dramatically too seasonally (i.e. their isotope composition changes through the season due to winter recharge and summer evaporation). However, large seasonal ranges in lake level (up to 1.5 m) have been recorded (Hollis and Stephenson, 1997), so another explanation is that the samples with the intermediary isotope compositions were collected close to rivers or subaqueous springs that flow into the lake (Matzinger 2006a). We know from Lake Ohrid that subaqueous springs result in lakewaters with intermediary isotope compositions (Leng et al., 2010), and that lakes at steady state change very gradually in their isotope composition based on successive, seasonally averaged, either dry or wet conditions at time scales longer than the residence time of the lake water. In addition, Megali Prespa has no surface outlet, although there is subaqueous water outflow through the karst aquifer into Lake Ohrid (Matzinger et al., 2006b). The isotope composition of Lake Ohrid which is very stable with $\delta^{18}$O and $\delta^D$ values around −4 and −32‰ since 1989 (Leng et al., 2010). The difference in the isotope composition of Ohrid and Prespa lake water is
probably a function of lake size. The volumetrically much larger Lake Ohrid (55.4 km$^3$) compared to 3.6 km$^3$ of Lake Prespa, Matzinger et al., 2006a) with its longer residence time (70 and 11 years respectively, Matzinger et al., 2006a) makes Lake Ohrid much better buffered and less responsive (on a decadal scale) against high frequency hydrological change compared to Lake Prespa. Overall, in terms of understanding past lake water balance from the oxygen isotope composition of lacustrine carbonates, the modern water isotope data suggest that we should interpret $\delta^{18}$O variation in Lake Prespa as mainly representing changes of the amount of winter rainfall water contribution (recharge), winter ice cover (reducing winter evaporation), summer aridity (enhancing evaporation), and changes in lake water residence time at a decadal resolution.

6.2. Modern water carbon isotope composition

$\delta^{13}$C$_{TDIC}$ of bicarbonate from the Lake Prespa springs, inflowing rivers, and lake waters taken in June 2011 provide a range in $\delta^{13}$C$_{TDIC}$ values between –15.7‰ and –4.7‰ (Fig. 2b). Dissolved bicarbonate is derived from dissolution and weathering of catchment rocks, soils and atmospheric CO$_2$. The geology around Prespa is largely old basement rocks and Triassic limestones although there are large areas with Quaternary glacial and volcanic deposits (Aufgebauer et al., in press). Geological sources of bicarbonate tend to have high $\delta^{13}$C (Andrews et al., 1993; 1997; Hammarlund, 1993) and so are not likely the major source of the isotopically light ion in the springs and rivers. In contrast organic derived C has $\delta^{13}$C values generally between –25 and –35‰ (higher up to –16‰ where there is a greater contribution from C4 taxa). Isotopically light CO$_2$ liberated by decay of terrestrial organic matter in the soil infiltrates springs and rivers by shallow groundwater flow. Under alkaline conditions, and mid range annual temperatures (+10°C), HCO$_3^-$ derived solely from soil CO$_2$ with $\delta^{13}$C$_{organic}$ of ca. –25‰ should have $\delta^{13}$C$_{TDIC}$ of ~ –15‰. This is remarkably consistent with the measured spring and river water $\delta^{13}$C (–15.7‰, see also Leng et al., 2001), although once the bicarbonate enters rivers and lakes other processes change $\delta^{13}$C. Prespa lakewater has high $\delta^{13}$C$_{TDIC}$ (Fig. 2b). High $\delta^{13}$C$_{TDIC}$ is common in lakes which do not have a surface outlet (so called closed lakes) where dissolved bicarbonate has time to exchange with atmospheric CO$_2$ (Leng and Marshall, 2004) or in lakes with a large biomass, so long as there is sedimentation of organic
matter (ie removal of $^{12}$C, and not recycling of $^{12}$C) (Meyers and Teranes, 2001). Both processes (exchange and productivity) are likely in Lake Prespa.

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

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

The van Krevelen-type HI-OI diagram distinguishes three main types of organic matter (Types I, II, III) but also can provide information on the amount of oxidation and diagenetic alteration of the organic matter (Talbot and Livingstone, 1989). The data from Lake Prespa shows both Type II and Type III organic matter, which is either a source function or an oxidation artefact (Fig. 4). Type II organic matter corresponds to
moderately rich hydrocarbons, and suggests that the sedimentary organic matter is predominantly derived from algae, whereas Type III is poor in hydrocarbon-generating materials and more typical of woody plant material. However, the data fall on a curve of changing OI suggesting that the organic matter has undergone differential amounts of oxidation (which is climate or hydrology related and not time dependent). The down core HI, TOC and N data show that Lake Prespa sediments have changed in their Rock Eval and elemental characteristics through time. Type II sediments with high HI are more typical of the sediments from the Holocene, MIS 3 and MIS 5; whereas Type III with low HI are more common in MIS 2 and 4.

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

In MIS 3, HI and TOC are intermediary between MIS 1 and 2/4, while OI is generally low apart from some spikes. The most likely explanation of the intermediary values is that of a mixed source (samples from this interval also span the kerogen Type II and III boundary), likely being partially altered terrestrial plant matter but also containing a component of aquatic organic matter which is reflected in the rise in TOC and TOC/N. In MIS 1, HI, and TOC peak, and suggest lake sediments containing significant amounts of aquatic organic material (Jacob et al., 2004; Hetényi et al., 2005; Lojka et al., 2009). High algal productivity is indicated by high TIC, which is fine grained calcium carbonate. Similar <30 µm idiomorphic calcite crystals occur in Lake Ohrid and are typical of photosynthetic phytoplankton endogenic precipitation (Leng et al., 2010; Matter et al., 2010). The high rates of organic material preservation suggest more limited mixing with longer periods of O-depleted bottom waters and might imply less seasonal (i.e. from dimictic to monomictic) overturning. Within MIS 1 there are spikes to lower HI, TOC, TIC
(i.e. at 140 cm) which might suggest short perturbations back to cold conditions and better lake mixing. The highest TOC/N ratios of the entire profile occur in MIS 1 (up to 9) but are still suggestive of aquatic productivity and perhaps less decomposition/degradation.

6.4. Carbon isotope composition of organic matter from Lake Prespa

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

Lacustrine algae utilise dissolved HCO$_3^-$ in hard water lakes so variations in the isotope composition of the dissolved HCO$_3^-$ and changes in $\delta^{13}C$ related to productivity and nutrient supply are both possible. The modern TDIC data suggest that the main source of carbon ions to the lakes is soil derived CO$_2$. The ion will be utilised by the plants growing in the lake. Phytoplankton tend to have $\delta^{13}C$ that is 20‰ lower than the $\delta^{13}C$ of the bicarbonate ion (Leng et al., 2005). In Lake Prespa $\delta^{13}C_{org}$ is consistent around –25‰ and so could be derived from $\delta^{13}C_{TDIC}$ with a value similar to the modern lake (of ca. –4.7‰) through MIS 5, 4, 3, 2. These stages also have low TOC, except MIS 5. In contrast the Holocene has lower $\delta^{13}C_{org}$ (–28‰) and high TOC relative to the other stages. The higher $\delta^{13}C_{org}$ in the pre-Holocene sediments suggests high productivity, but in the presence of low TOC suggests productivity under a more limited carbon input, possibly due to more limited recharge of soil-CO$_2$ leached from the catchment. If soil development is critical that it would follow that the lower $\delta^{13}C$ in the Holocene could just be a function of greater supply of soil derived CO$_2$ and an improving climate. Pollen evidence suggests well developed soils during the Holocene inferred from rising amounts of AP pollen types and increasing total pollen concentration values culminating during the Middle and Late Holocene (Fig. 5; Panagiotopoulos et al., in press). Other pollen data from the region suggest a cold climate during MIS 4 and 2 (e.g. Allen et al., 1999, 2000; Wagner et al.,
2009; Lézine et al., 2010). During MIS 5 (and to a lesser extend during MIS 3) the total pollen concentration and percentages of AP suggest favourable climate conditions for plant growth (warmer and/or sufficient moisture).

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

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

The modern water isotope composition of Lake Prespa shows that the lake is sensitive to the winter recharge (input) versus the summer evaporation ratio (I/E). We assume that the oxygen isotope composition of the lakewater is captured in the carbonates that are precipitated within the lake (Leng and Marshall, 2004). The TIC spikes through MIS 4-2 comprise siderite. Siderite is a common early diagenetic mineral in many lake sediments, forming in porewaters close to the sediment-water interface (Giresse et al., 1991), its geochemistry is often used as a indicator of sediment water redox. Siderite precipitation usually occurs under reducing conditions (Berner, 1971) in slightly to strongly reducing methanogenic zones because of relatively low sulphate and high organic carbon concentrations (Coleman, 1985). We do not know why the siderite only occurs sporadically, although the siderite spikes correlate with highs in the OI and low values in
the HI, so perhaps the siderite forms under particular environmental conditions, likely involving a more acidic environment where oxides and hydroxyl ferric-oxides are dissolved (Giresse et al., 1991). The formation of siderite over other carbonates suggests low Ca and Mg. The mean $\delta^{13}C$ values for the Prespa siderites is +11.9‰. Similar high $\delta^{13}C$ values have been reported elsewhere for other lake carbonates (Mozley and Wersin, 1992) and their formation is described as a function of low sulphate concentrations being consumed at shallower levels in the sediments fairly rapidly leaving a greater quantity of organic matter for decomposition by methanogenic bacteria. The heavy $\delta^{13}C$ forms as a result of $^{13}C$ enriched bicarbonate derived from methanogenesis (Berner, 1980). Indeed methane and/or CO$_2$ gas occur trapped within the Lake Prespa sediments because when the cores were retrieved there was core swelling due to gas expansion and release. There is no evidence to support other causes of high $\delta^{13}C$, for example $^{13}C$-enriched volcanic gas, dissolution of $^{13}C$ enriched carbonate, and high planktonic productivity (Bahrig, 1988).

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

Even allowing for lower glacial $\delta^{18}$O precipitation it seems likely that the lake was less evaporative in the glacial, probably as a consequence of cooler summers and longer winter ice cover.

Within the Holocene we assume that the mechanism for calcite precipitation is likely the same as described for Ohrid whereby phytoplankton productivity assimilate CO$_2$ as long as there is a supply of bicarbonate (Matzinger et al., 2006b) which will be replenished via surface run-off into the lake and concentrated by evaporation. There is likely some seasonal dissolution of calcite in the bottom waters triggered by aerobic decomposition of organic matter, higher CO$_2$ and lower pH (Vogel et al., 2010b). Indeed, Löffler et al. (1998) have shown that pH in the surface waters (pH = 8.3) is generally higher than at depth (pH = 7.3). Endogenic calcite preservation is coincident with high organic matter and suggests high primary productivity likely as a result of the transition from the former glacial to interglacial together with more ion input due to soil development and weathering. In addition the OI, HI and TOC/N suggest better preservation of organic matter possibly due to less lakewater mixing and due to longer periods of bottom water anoxia.

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

Lake Prespa $\delta^{18}$O$_{\text{calcite}}$ shows similarities to $\delta^{18}$O$_{\text{calcite}}$ from Lake Ohrid cores (Leng et al., 2010). The basal portions of Co1215 from Prespa and Co1202 from Ohrid show higher
values, although the highest values in Prespa between 10 and 8 ka are not evident in Co1202. From ca 6 ka the Ohrid cores show a general trend toward higher $\delta^{18}O$, although Lake Prespa has low and fairly consistent $\delta^{18}O$ between 8-2 ka. High $\delta^{18}O$ between 2 to 0.5 ka appear in both cores although the magnitude of variation is significantly different. Prespa $\delta^{18}O_{\text{calcite}}$ range is $-7$ to $+6\%o$, while Ohrid is $-7$ to $-3\%o$. The enhanced response to lakes level changes in Lake Prespa is not surprising given the difference in water volumes and residence between the lakes.

Lakes that are sensitive to moisture balance (I/E) often have some hydrological closure and/or longer residence time and precipitate carbonates with high $\delta^{13}C_{\text{calcite}}$, despite having much more $^{12}C$-enriched inflowing waters (Andrews et al., 1993). Evaporating lakes tend to have a covariant relationship between $\delta^{13}C_{\text{calcite}}$ and $\delta^{18}O_{\text{calcite}}$ (Talbot, 1990; Leng and Marshall, 2004), this is not the case for Lake Prespa ($r^2 = 0.25$). $\delta^{13}C_{\text{calcite}}$ values in Prespa will reflect $\delta^{13}C_{\text{TDIC}}$ at the time of calcite formation, and like the composition of aquatic organic material the $\delta^{13}C_{\text{TDIC}}$ is likely a function of equilibration of the bicarbonate ion with atmospheric CO$_2$. High algal productivity is unlikely to explain these values because during MIS 2-4 the algae peaks in our diagram are not synchronous with peaks in TIC (Fig. 3). However, during MIS 1 and 5 algal and TIC peaks are synchronous. Isotopic equilibrium with atmospheric CO$_2$ will result in lake water $\delta^{13}C$ having values between $+1$ to $+3\%o$ (Usdowski and Hoefs, 1990), values similar to the core values within Lake Prespa ($\delta^{13}C_{\text{calcite}}$ values through the Holocene $= +1.1\%o +/− 0.4\%o$) perhaps suggesting the bicarbonate has reached a steady state due to the long water residence time. One explanation for the lack of a co-variation between $\delta^{13}C_{\text{calcite}}$ and $\delta^{18}O_{\text{calcite}}$ is perhaps low bicarbonate concentration, unlike changes in $\delta^{18}O$ which will be driven by hydrological balance.

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

6.6.1. Late Glacial to Holocene transition

The Late Glacial to Holocene transition in Prespa Co1215 initiates at ca.15 ka (Fig. 2) with a gradual increase in organic matter content (interpreted as increased productivity; Aufgebauer et al., in press), increased TOC/N (less decomposition). There is little or poor
evidence that a similar change occurs in the existing Lake Ohrid cores. This gradual transition to the Younger Dryas is often marked in Mediterranean lake records by an increase in $\delta^{18}O_{\text{calcite}}$ (Roberts et al., 2008), this phase and other Pleistocene carbonate isotopic enrichment events seen in Mediterranean lakes may be linked to the North Atlantic Heinrich cold events (Roberts et al., 2008), although chronological imprecision means this suggestion is currently not verifiable. In Lake Prespa the low carbonate content prior to 10 ka cannot confirm this transition from the isotope perspective (the carbonate is too low to analyse for isotopes), although the absence of significant amounts of carbonate perhaps implies a lake with low evaporation. Within this transition, immediately post the harsh climate of the Lateglacial/Oldest Dryas, the pollen show a retreat of steppe herb communities (e.g., *Artemisia* and Chenopodiaceae) coupled with a gradual rise of pine and oak suggest rising moisture availability within the Prespa catchment. This trend is interrupted by an abrupt millennial vegetational setback (likely the Younger Dryas chronozone) which is characterized by increasing aridity and lower temperatures. Around Prespa this is marked by a major restructuring of the vegetation including a descending treeline and/or a thinning of existing tree stands (Panagiotopoulos et al., in press).

### 6.6.2. Early Holocene

In the early Holocene, Lake Prespa shows a small peak in $\delta^{18}O_{\text{calcite}}$ between 10-8 ka while Lake Ohrid shows a small $\delta^{18}O_{\text{calcite}}$ peak between 10-9 ka. Other lakes in the Eastern and Central Mediterranean show that the early Holocene carbonates are isotopically depleted at this time (Roberts et al., 2008; their figure 5; Fig. 6). The magnitude of evaporative enrichment in Lake Prespa during the early Holocene is less than the later Holocene (see below). It is difficult to compare directly the $\delta^{18}O_{\text{calcite}}$ from the early and late Holocene because there are isotope complications, for example, the source composition of precipitation would have likely been different partly because of changes in the Mediterranean Sea at that time. Other lakes around the Eastern Mediterranean show an early Holocene oxygen isotope depletion, which Roberts et al. (2008) ascribe as most likely a function of regional water balance and a difference in the source isotope composition of precipitation due to the formation of sapropel in the Mediterranean Sea. The sapropel formation was thought to be initiated by increased
rainfall and runoff from the Nile into the Eastern Mediterranean Sea, which would have contributed significantly to the creation of a freshwater lid and subsequently bottom water anoxia between 9.5 ka and 6.5 ka (Rohling, 1994; Ariztegui et al., 2000). The pollen record shows the gradual formation of closed oak forests and their diversification, with the establishment of thermophilous and drought-sensitive trees after approximately 10 ka which suggests the absence of summer droughts and thus confirms sufficient precipitation for forest growth during this period. Moreover, the parallel appearance and establishment of important maquis constituents exclude the existence of intense late winter and spring droughts. In light of the above, the pollen record suggests a rather even distribution of annual precipitation, which appears to be in agreement with the sapropel formation in the eastern Mediterranean (Panagiotopoulos et al., in press).

6.6.3. Middle Holocene humidity

Lake Prespa records the lowest $\delta^{18}O_{\text{calcite}}$ values for the period (8-2 ka), while Lake Ohrid clearly shows a progressive enrichment in $\delta^{18}O_{\text{calcite}}$ over this time interval (Fig. 6). This difference could be a function of hydrology and the different lake sizes. Recharge into Lake Prespa was presumably sufficient to counter summer evaporation, whereas in Ohrid with its much larger lake water volume to surface area in comparison to catchment area may mean that Lake Ohrid may be less responsive to winter recharge. The pollen records from the two sites (Wagner et al., 2009; Panagiotopoulos et al., in press) are almost identical during the Holocene implying similar climate regimes in both catchments. Overall, the low and stable $\delta^{18}O$ values in both Prespa and Ohrid through the middle Holocene is a general feature observed in other eastern and central Mediterranean lakes and speleothems (Bar-Matthews et al., 2000; Zanchetta et al., 2007b; Roberts et al., 2008; Develle et al., 2010), although not always over exactly the same time periods notwithstanding dating issues. Lakes Van and Frassino have a low and stable $\delta^{18}O$ period from 9-4 ka (Baroni et al., 2006), while Eski is low only till about 6 ka (Roberts et al., 2001). The much smaller Golhisar Golu appears to respond very rapidly to moisture balance although values are generally low between 7-5 ka (Eastwood et al., 2007; Fig. 6). This mid-Holocene humidity has been interpreted in different ways, for example it has been attributed to increased amounts of precipitation related to an increase in winter precipitation of Atlantic origin (Zanchetta et al., 2007; Zhornyak et al., 2011) or a
significant (especially for eastern Mediterranean) freshening of surface marine water of
the eastern Mediterranean at that time resulting in lower $\delta^{18}O$ of precipitation (e.g.,
Kolodny et al., 2005; Develle et al., 2010). The Middle Holocene Prespa pollen record
suggests similar climatic and environmental conditions to the early Holocene.

6.6.4. Late Holocene

The higher $\delta^{18}O_{\text{calcite}}$ in Lake Prespa (and Lake Ohrid) from 2 ka suggests drier
conditions, and probably a significant lake level drop in Prespa, as $\delta^{18}O_{\text{calcite}}$ values are
the highest of the entire record. Over this time there is a general trend towards higher
$\delta^{18}O_{\text{calcite}}$ in many other Mediterranean isotopic records both in lakes (e.g. Roberts et al.,
2008; Develle et al., 2010) and in speleothems (e.g., Bar-Matthews et al., 2000; Zanchetta
et al., 2007b; Verheyden et al., 2008). Lake Van, Eski and Frassino show consistently
high values from 4 ka (the latter 2 showing hiati from between 2-1 ka; Fig. 6). In Golhisar
Golu there are high values also from 4 ka but the hydrology likely changes around 3 ka
with the effect of the Santorini tephra on the lake catchment (Eastwood et al., 2007; Fig.
6). This regional drying has previously been described as related to progressive
reduction in moisture advection from the Atlantic linked to a reduction in summer
insolation, which also resulted in a decrease in monsoon activity on tropical Africa and
progressive aridification of the Sahara (e.g. Gasse, 2000). Isotopically this increase could
also be related to progressive increase in isotopic composition in the Mediterranean Sea
(Emeis et al., 2000) and the related effect on rainfall amount. Very low lake levels (and
highest $\delta^{18}O_{\text{calcite}}$) at Lake Prespa occur around ca. 1 ka and are thought to correspond
with the occurrence of ruins of several buildings at 840-842 m.a.s.l. (Sibinović,1987).
These buildings were constructed at the end of the 10th/beginning of the 11th century AD
and it is unlikely that they were formed in the water. There is a rapid reversal in the last
500 years as $\delta^{18}O_{\text{calcite}}$ declines to some of the lowest values ($-7$‰) in the most recent
sediments (also seen in Ohrid core Lz1120; Leng et al., 2010; Fig. 6). Why Co1215
shows a consistent wet phase (low $\delta^{18}O$) in the last 500 years is unclear but there is
some evidence in Lake Ohrid for very recent (apparent) freshening driven by
anthropogenic change including the Roman and recent forest clearance (Wagner et al.,
2009).
Finally, in the modern lakewater, assuming peak precipitation of calcite occurs during the warmer summer months when mean monthly temperatures are high (summer temperatures between 2001 and 2004 averaged between +20 and +22°C, Matzinger et al., 2007), calcite precipitating in Lake Prespa with a lakewater value of −1‰ will have a δ₁⁸O_{calcite} of around −2‰, i.e. an oxygen isotope composition that is higher than most of the Holocene calcite δ₁⁸O except for the early and late Holocene arid phases. However, the isotopic composition of modern lake water is perhaps as much to do with anthropogenic activities as climate. Indeed the recent receding woodlands and the development of agriculture (cereals and crop trees) occurring alongside the increased accumulation rates of algae suggests that Lake Prespa is undergoing substantial changes that point to intensive anthropogenic activities (Panagiotopoulos et al., in press). In Lake Prespa as with in many other lakes disentangling natural from human impact over the very recent past is challenging.

7. Conclusions

The current Lake Prespa waters are evaporated compared to the inflowing spring waters. The hydrological balance in Lake Prespa is a function of summer aridity and winter precipitation, on a decadal scale. The spring water bicarbonate ion is likely derived from soil CO₂ which once incorporated into the lakewater likely equilibrates with atmospheric CO₂.

The Lake Prespa sediments broadly fall into zones based on their sedimentology, geochemistry, palynology and the existing chronology; these zones roughly equate to Marine Isotope Stages 5 to 1. The Glacial sediments are grey, contain low TOC and TOC/N and high δ¹³C_{organic} suggesting low supply of carbon to the lake, but high summer productivity. Through this period there are spikes in OI and siderite, which suggest that although the lake was likely to have mixed regularly leading to enhanced oxidation of organic matter, there must have been within sediment reducing conditions and methanogenesis. In contrast the MIS 5 sediments have relatively high TOC, TOC/N, HI while TIC, OI, and δ¹³C_{org} are low, similar to MIS 1 although the Holocene sediments contain high calcite. MIS 5 and 1 sediment suggest much more productivity, higher rates
of organic material preservation possibly due to more limited mixing with longer periods of O-depleted bottom waters.

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

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

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The project was funded by the British Geological Survey. Leng and Wagner undertook the main interpretation of all the data sets. Boehm provided the geochemical concentration data (and intellectually via Aufgebauer et al. in press). Panagiotopoulos provided the pollen data and interpretation of the pollen (and intellectually via Panagiotopoulos et al. in press). Vane provided the Rock Eval data and interpretation. Snelling, Haidon, Woodley and Baneschi provided the isotope and mineralogy data. Vogel and Zanchetta contributed intellectually to the discussions of the data.
Figures

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

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

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

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

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

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

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


8200–7100 ka from Renella Cave (Central Italy). Quaternary Science Reviews, 30, 409–417.

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

<table>
<thead>
<tr>
<th>Property</th>
<th>Prespa</th>
</tr>
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<tbody>
<tr>
<td>Altitude (masl)</td>
<td>849</td>
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<tr>
<td>Catchment area (km²)</td>
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<tr>
<td>Lake area (km²)</td>
<td>254</td>
</tr>
<tr>
<td>Mean lake depth (m)</td>
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</tr>
<tr>
<td>Volume (km³)</td>
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</tr>
<tr>
<td>pH (surface/bottom)</td>
<td>8.4-7.3</td>
</tr>
</tbody>
</table>
Type I, waxy organic matter
Type II, algal organic matter
Type III, vascular plant organic matter

HI (mg HC/TOC)

OIRe6 (mgO2/TOC)

0 - 10ka
10ka - 30ka
30ka - 55ka
55ka - 70ka
70ka - bottom