Palaeo-seasonality of the last two millennia reconstructed from the oxygen isotope composition of carbonates and diatom silica from Nar Gölü, central Turkey

Jonathan R. Dean [a,*], Matthew D. Jones [a], Melanie J. Leng [b,c], Hilary J. Sloane [b], C. Neil Roberts [d], Jessie Woodbridge [d], George E.A. Swann [a], Sarah E. Metcalfe [a], Warren J. Eastwood [e], Hakan Yiğitbaşıoğlu [f]

[a] School of Geography, University of Nottingham, University Park, Nottingham NG7 2RD, UK
[b] NERC Isotope Geosciences Laboratory, British Geological Survey, Nottingham NG12 5GG, UK
[c] Department of Geology, University of Leicester, Leicester LE1 7RH, UK
[d] School of Geography, Earth and Environmental Sciences, University of Plymouth, PL4 8AA, UK
[e] School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, UK
[f] Department of Geography, Ankara University, Ankara, Turkey

ARTICLE INFO

ABSTRACT

Carbonates and diatoms are rarely deposited together in lake sediments in sufficient quantities for the oxygen isotope composition ($\delta^{18}O$) to be investigated simultaneously from both hosts. Here, $\delta^{18}O_{carbonate}$ are compared to $\delta^{18}O_{diatom}$ data from the varved sediments of Nar Gölü, a closed lake in central Turkey, over the last 1710 years. Lake monitoring suggests carbonate is probably precipitated during May—June and $\delta^{18}O_{carbonate}$ is a proxy for regional water balance. Diatom activity is mainly weighted towards the spring. At times between ~301 and 561 AD, while $\delta^{18}O_{carbonate}$ values are the highest for the entire 1710 year period, suggesting summer drought, $\delta^{18}O_{corrected-diatom}$ values are among the lowest. $\delta^{18}O_{lakewater}$ values estimated for the times of diatom growth and carbonate precipitation show large differences. We suggest this could be explained by increased snowmelt that formed a freshwater lid on the lake at the time of peak diatom growth. Increased snowmelt is also inferred ~561—801 AD. From 801 AD to the present, precipitation is less winter-dominated, although increased snowmelt is inferred 921—1071 AD and in the latter part of the Little Ice Age (i.e. the mid to late 1800s AD). By combining oxygen isotope data from hosts that form in lakes at different times of the year, we show that such analyses can provide insights into palaeo-seasonality.

© 2012 Elsevier Ltd. Open access under CC BY license.

1. Introduction

Water in the Near East is a politically sensitive resource (Issar and Adar, 2010) and water stress in the region is projected to increase during the 21st century (Cruz et al., 2007), so an improved understanding of hydrological variability over long timescales is required. It has been proposed that changes in water availability have influenced the rise and fall of civilisations over the past 2000 years in the region (Issar and Zohar, 2007). While studies such as Jones et al. (2006) have provided high resolution and well dated proxy records of shifts in water balance, there are few reconstructions of seasonal variation in precipitation, despite its importance for human societies (Rosen, 2007). Precipitation in the region today is markedly seasonal, with dry summers and wetter winters and

springs (Türkeş, 2003), and shifts in seasonality are anticipated globally in a warming world (Meehl et al., 2007). There is consequently a requirement for the development of methods that allow past seasonality changes to be reconstructed at an adequate temporal resolution for understanding change on human timescales.

Seasonality change analysis requires climate proxies that are sensitive to different seasons. Several reconstructions of seasonality using isotope analysis of lake sediments have recently been published (Henderson et al., 2010; Anderson, 2011; Barker et al., 2011). In the Near East, Stevens et al. (2001, 2006) suggested that Holocene changes in isotope records from Iranian lake sediments were driven by changes in the seasonality of precipitation and Orland et al. (2009, 2012) and Rowe et al. (2012) investigated past seasonality using the oxygen isotope composition of speleothems from the Soreq Cave, Israel and a cave in northeast Turkey respectively. Here we consider how to best compare the oxygen isotopic composition of carbonate and diatom components in lacustrine

sediments from central Turkey to give insights into changing seasonality.

Oxygen isotope analysis (δ^{18}O) of lake sediments is most commonly carried out on carbonates. If precipitated in equilibrium, δ^{18}O$_{carbonate}$ is dependent upon the temperature and isotopic composition of the lake water in which it is precipitated, with the degree of fractionation at $-0.24‰ °C^{-1}$ (Leng et al., 2006). In hydrologically open lakes, temperature and the δ^{18}O of precipitation entering the lake will be the most important drivers of final δ^{18}O values. In closed lakes with long residence times, the effect of evaporation will usually be far more important (Li and Ku, 1997; Leng and Marshall, 2004; Leng et al., 2006). δ^{18}O analysis can also be carried out on diatom silica. The controls on δ^{18}O$_{diatom}$ are very similar to those on δ^{18}O$_{carbonate}$ (Leng and Barker, 2006) and the fractionation factor between diatom silica and the water from which it is precipitated has been shown as being similar (ca. $-0.2‰ °C^{-1}$) to calcite-water fractionation (Brandriss et al., 1998; Moschen et al., 2005; Crespin et al., 2010). Under some circumstances, if the pH of lake waters is between 7 and 8, and if silica is not limited, carbonates and diatoms may be preserved in sufficient quantities for δ^{18}O analysis to be carried out on both hosts.

Leng et al. (2001) first suggested that if carbonates and diatom silica are precipitated at different times of the year, comparing δ^{18}O from the two hosts would provide information on seasonality. Working on a Late Pleistocene sediment sequence from Lake Pınarbaşı (37°28′N, 33°07′E) in Turkey and assuming carbonates were precipitated in the summer and diatoms grew throughout the year but especially in the spring and autumn, they suggested δ^{18}O$_{carbonate}$ was a proxy for mean summer temperature and δ^{18}O$_{diatom}$ a proxy for spring snowmelt, accounting for the substantial differences between δ^{18}O trends from the two hosts. Large differences in δ^{18}O were also seen in the record from Lake Gościąż (52°35′N, 19°21′E) in Poland (Rozanski et al., 2010), again thought to be because of differences in the time of deposition of diatoms and carbonates. In contrast, a study by Lamb et al. (2005) using the sediments of Lake Tilo in the Ethiopian Rift Valley (7°03′N, 38°05′E), for the period 9.0—5.7 ka, found that while δ^{18}O$_{diatom}$ was more variable (ascribed by the authors to be largely the result of tephra contamination) and did not pick up two arid events seen in the δ^{18}O$_{carbonate}$ record, the general trends were the same because diatom growth and carbonate precipitation occurred at similar times of the year. However, these studies lack the detailed limnological monitoring required for a full understanding of the lake isotope system. Also, they did not rigorously quantify contamination of diatom δ^{18}O samples. As such, it is unclear whether differences in trends between carbonate and diatom δ^{18}O are due to shifts in lake conditions or changes in the amount of contamination in the samples, although it should be acknowledged that in these studies the authors thought they were analysing relatively pure diatom material.

Here, we develop a robust methodology for comparing carbonate and diatom δ^{18}O data, including: (1) monitoring of the modern lake to identify firstly the drivers of δ^{18}O$_{lakewater}$ and secondly what time of the year the two hosts form; (2) diatom species analysis of the sediment to aid with the δ^{18}O$_{diatom}$ interpretation; and (3) quantification of contamination allowing mass balancing of δ^{18}O$_{diatom}$ data following the methodology developed over the past decade (Morley et al., 2005; Brewer et al., 2008; Mackay et al., 2011). We apply this to the study of sediments from Nar Gölü, central Turkey, from where the carbonate (a mixture of endogenic calcite and aragonite) δ^{18}O (Jones et al., 2005, 2006) and the diatom species (Woodbridge and Roberts, 2010, 2011; Woodbridge et al., 2010) records have already been published.

2. Site description

Nar Gölü (38°20′24″N, 34°27′23″E; 1363 m a.s.l.; Fig. 1) is a small ($\sim$0.7 km^2) but relatively deep ($>$20 m) maar lake in Cappadocia, central Turkey. The east and west sides of the crater are rimmed by basalt, with the southern side dominated by exposures of ignimbrite (Gevrek and Kazancı, 2000). Consequently, there is no potential for problems associated with detrital carbonate contamination (cf. Leng et al., 2010). The climate of the region is continental Mediterranean (Kutiel and Türkeş, 2005) with annual precipitation at Niğde, 45 km from Nar, averaging 339 mm between 1935 and 2010. July, August and September are very dry, receiving only 6% of the total precipitation, while April and May are the wettest months, accounting for 27% of the total (Fig. 1). The hottest months are July and August, when temperatures average +23 °C, while from December to February temperatures average +0.7 °C. Measured evaporation at Niğde between 1935 and 1970 was 1547.6 mm per year (Meteoroloji-Bulteni, 1974).

The modern limnology has been investigated over the past decade. The lake has no surface outflow and lake waters are evaporatively enriched in ^{18}O compared to spring waters (Table 1), plotting off the Ankara Meteoric Water Line (as discussed in detail in Jones et al., 2005; Woodbridge and Roberts, 2010). This evaporative enrichment leads to the concentration of sodium, chloride and bicarbonate ions, with high pH values $\sim$8, which aids the preservation of both diatoms and carbonates. Using sediment traps, and comparing these data to thin section analysis of the sediment cores, it is estimated that carbonate is presently precipitated in May—June and diatom activity is weighted towards the spring, with a secondary growth peak in the autumn (Jones et al., 2005; Woodbridge and Roberts, 2010). Data loggers have been used to record temperature through the water column (Eastwood et al., unpublished data) and suggest that through 2009—2011 lake
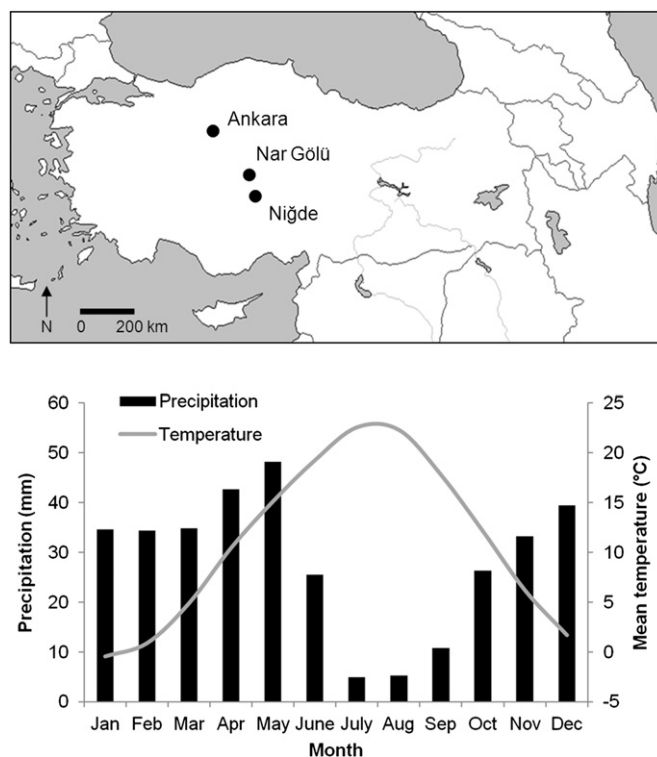

Fig. 1. Location of Nar Gölü and climate record from Niğde collected by Turkish Meteorological Service showing monthly average temperatures and precipitation totals averaged 1935—2011.

Table 1
Water isotope data showing increase in $\delta^{18}O_{lakewater}$ and lake level fall between June 2001 and September 2011, and intra-annual increases in $\delta^{18}O_{lakewater}$ between May and July 2009 and June and September 2011. Spring waters are significantly lower in $\delta^{18}O$ than lake waters highlighting the evaporative enrichment of the lake. * indicates data previously published in Jones et al. (2005).

	Lake centre surface water $\delta^{18}O$ ‰ VSMOW	Max. lake depth (m)	Upper spring water $\delta^{18}O$ ‰ VSMOW
June 2001*	−2.60	25	−10.55
June 2002*	−2.40	24	−10.70
July 2003	−2.50		−10.58
May 2004	−2.73		
September 2006	−0.87	23	−10.56
July 2008	−0.57	23	−10.60
May 2009	−1.17	22.5	
July 2009	−0.56		−10.63
July 2010	−0.24	22	−10.65
June 2011	−0.81	22	−10.55
September 2011	−0.19	22	−10.63

waters were stratified from early March to late November, and mixed during December, January and February. Based on these data, we suggest a likely epilimnion temperature range of $+15-+20$ °C at the time of carbonate precipitation and $+5-+15$ °C at the time the majority of diatom growth occurred.

3. Methods

3.1. Fieldwork and chronology

A 376 cm core sequence was obtained in 2001/2 (NAR01/02) using Glew (Glew et al., 2001) and Livingstone (Livingstone, 1955) corers from the deepest part of the lake (25 m water depth at the time). The cores were laminated throughout and ^{210}Pb and ^{137}Cs dating on the top 50 cm of the core and the analysis of sediment trap material indicates the couplets are annual (Jones et al., 2005; Woodbridge and Roberts, 2010). A maximum age uncertainty of 2.5% for the varve counting was calculated from counting replicate cores, although true dating precision is likely to be better than this (Jones et al., 2005). Additionally, a 36 cm core (NAR06, as described in Woodbridge and Roberts, 2010) and a 44 cm core (NAR10), both collected using a Glew corer, were used to provide samples for the 20th and 21st centuries, including recent sediments deposited since the collection of NAR01/02 core. The three core sequences were stratigraphically tied through counting varve couplets and identifying matching sediment patterns between cores. Water samples were collected from springs and the centre or edge of the lake and maximum lake depths were estimated using a Garmin® Fish Finder and a weighted tape during field visits between 1997 and 2012.

3.2. $\delta^{18}O$ analysis of waters and carbonates

Water samples were analysed for $\delta^{18}O$ using an equilibration method on a VG SIRA mass spectrometer at the NERC Isotope Geosciences Laboratory (NIGL), with data presented as ‰ deviations from VSMOW. Analytical reproducibility was 0.05‰. On the NAR01/02 core sequence each of the uppermost 900 carbonate layers were individually analysed for $\delta^{18}O_{carbonate}$ at NIGL using classic vacuum techniques and an Optima dual-inlet mass spectrometer, with the following 825 analysed from contiguous bulk samples at a 5 year resolution (Jones et al., 2006). Every carbonate layer from the top of the NAR10 core was analysed in the same way. The data are presented here as ‰ deviations from VPDB and analytical reproducibility was 0.1‰.

3.3. Diatom isotope sample preparation

For diatom oxygen isotope analysis, bulk samples consisting of 3 varve years were taken at 10 varve year intervals from 301 AD to 1921 AD on the NAR01/02 core sequence, with $\delta^{18}O_{diatom}$ analysis on samples from the same varve years from different cores in the sequence confirming the core overlaps. The NAR06 and NAR10 cores were used to provide additional sample material for the past 100 years, with 4 and 5 varve year bulk samples taken respectively.

Samples need to be as free as possible of contamination since the method for analysing $\delta^{18}O_{diatom}$ will liberate oxygen from minerogenic material. The cleaning process was similar to that of Morley et al. (2004), with the use of hydrogen peroxide, nitric acid, hydrochloric acid, differential settling and sieving stages. Although sieving at 10 μm meant that small diatom frustules, including those of the endemic species *Clipeoparvus anatolicus* (Woodbridge et al., 2010), were lost from the sample, SEM-EDS (Scanning Electron Microscopy-Energy-Dispersive X-ray Spectroscopy) showed that unsieved samples were significantly more contaminated than sieved samples because of the presence of clays. Samples from the last 100 years from NAR06 and NAR10 ($n = 16$) underwent a final density separation stage using sodium polytungstate (SPT) to help remove minerogenic material. This stage can be problematic as SPT needs to be removed from the samples otherwise it will itself become a contaminant. SPT was therefore flushed away from samples by filtering them with distilled water at 0.45 μm.

3.4. EDS estimations of contamination, $\delta^{18}O$ analysis of diatom silica and mass balance corrections

The process described above can sometimes yield samples of a sufficient purity that contamination is not an issue (e.g. Swann et al., 2010). However, even when SPT is used, diatom samples can remain significantly contaminated, especially when minerogenic material is attached to diatoms by electrostatic charges or trapped within diatoms (Fig. 2) and where there is no significant density contrast between diatoms and the contaminants (Brewer et al., 2008). Even the samples from NAR06 and NAR10 on which

Fig. 2. SEM image of *Campylodiscus clypeus* highlighting the difficulties of producing a contaminant-free diatom sample when minerogenic matter attaches to diatoms. Mass balance corrections can be used to correct for the effect of this on $\delta^{18}O_{diatom}$ data.

SPT was used contain an average of 10% non-diatom silicate material. Contamination in samples from Lake Baikal, initially analysed by Morley et al. (2005) and reanalysed by Mackay et al. (2011), averaged 29.2% despite the use of SPT. In these difficult sediments, mass balancing is the only way to remove the effects of contamination on $\delta^{18}O_{diatom}$. Morley et al. (2005) and Mackay et al. (2008) estimated percentage contamination using light microscopy on randomly selected areas. However, point counting gives a surface area, not volumetric, and only a semi-quantitative assessment of contamination. Lamb et al. (2007) and Brewer et al. (2008) used XRF, Chaplighin et al. (2012) used Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Swann and Patwardhan (2011) used Fourier Transform Infrared Spectroscopy (FTIR) to provide more accurate contamination estimates. The abundance of elements such as aluminium is typically used to represent the level of contamination (Brewer et al., 2008). However, conventional XRF and ICP-OES require fairly large amounts of material. Therefore, in this study an EDS probe in a SEM, which can make measurements on very small amounts (<0.5 mg) of material, was used instead.

To test the accuracy of the EDS probe in measuring contamination, a series of samples with known mineralogy were analysed following the methodology described below. The Al content of 8 samples from Lake Baikal, previously analysed for $\delta^{18}O_{diatom}$ and XRF (Mackay et al., 2011), and 10 samples with known mixtures of mica, montmorillonite, kaolinite and chlorite, were compared to Al measured on the EDS. This exercise gave an error for the Al reading from the EDS of ±0.5%. Chaplighin et al. (2012) found EDS underestimated the amount of contamination in diatom samples. Our analyses show a similar underestimation and we therefore divide our measured contamination by 0.64 (identical to Chaplighin et al.'s correction). This led to some samples reporting over 100% contamination, which is clearly impossible, so the values were again adjusted, dividing by the overall range after the 0.64 correction, to restrict the contamination to a range from 0 to 100%.

Prepared samples were viewed at 100× magnification under SEM, and EDS was used to detect oxygen, sodium, magnesium, aluminium, silicon, phosphorus, sulphur, potassium, calcium, titanium, manganese and iron. Since most clay-sized minerogenic material should have been removed by sieving at 10 μm and carbonates and organics by chemical processes, most of the contamination in 'clean' samples was assumed to be from minerogenic material presumably washed in from the catchment and

similar in size, shape and specific gravity to the diatoms. Oxygen isotope analysis of the 'cleaned' diatom samples was carried out at NIGL using the stepwise fluorination technique as described in Leng and Sloane (2008), a method that has been verified through an inter-laboratory comparision exercise (Chaplighin et al., 2011). The data are presented as ‰ deviations from VSMOW and analytical reproducibility was 0.3‰.

Following Brewer et al. (2008) and Mackay et al. (2011), the amount of contamination in samples as a percentage of overall content was calculated by:

$$\%_{contamination} = (sample_{Al} / contamination_{Al}) \times 100 \tag{1}$$

where $sample_{Al}$ is the measured Al concentration in each sample analysed for $\delta^{18}O_{diatom}$ and $contamination_{Al}$ is the average percentage of Al in Nar silt samples from the core ($8.6\% \pm 0.5$, $n = 7$; similar to that found in Mackay et al., 2011) that were prepared and run as $\delta^{18}O_{diatom}$ samples. These silt samples were taken from turbidite layers throughout the core sequence, to ensure that contaminant values did not vary significantly with time. Following Mackay et al. (2011), a mass balance correction was used to account for the impact of silt contamination on the $\delta^{18}O$ values:

$$\delta^{18}O_{corrected-diatom} = \left(\delta^{18}O_{diatom} - \delta^{18}O_{contamination} \times \right.$$
$$\left. [\%_{contamination}/100]\right) \Big/ (\%_{diatom}/100) \tag{2}$$

where $\delta^{18}O_{diatom}$ is the original isotope value of the 'cleaned' diatom sample, $\%_{contamination}$ and $\%_{diatom}$ (i.e. $100 - \%_{contamination}$) are estimated by EDS and $\delta^{18}O_{contamination}$ is the isotope value of contamination. The latter can be estimated in a number of ways. Measuring $\delta^{18}O$ of the contamination directly is difficult, as much of the minerogenic material is removed during the processing of samples, such that the end member contaminant left is the minerogenic material that has been through chemical and physical separation processes. We kept this effect to a minimum by preparing silt samples in the same way as the diatom samples prior to $\delta^{18}O$ analysis, but to ensure this had no effect we use a modified version of the linear regression method of Chaplighin et al. (2012). By plotting measured $\delta^{18}O_{diatom}$ against $\%_{diatom}$ (the inverse of $\%_{contamination}$), an estimated end member contamination $\delta^{18}O$ value of $+16.5‰$ (Fig. 3) is calculated, which we use in Eq. (2). The
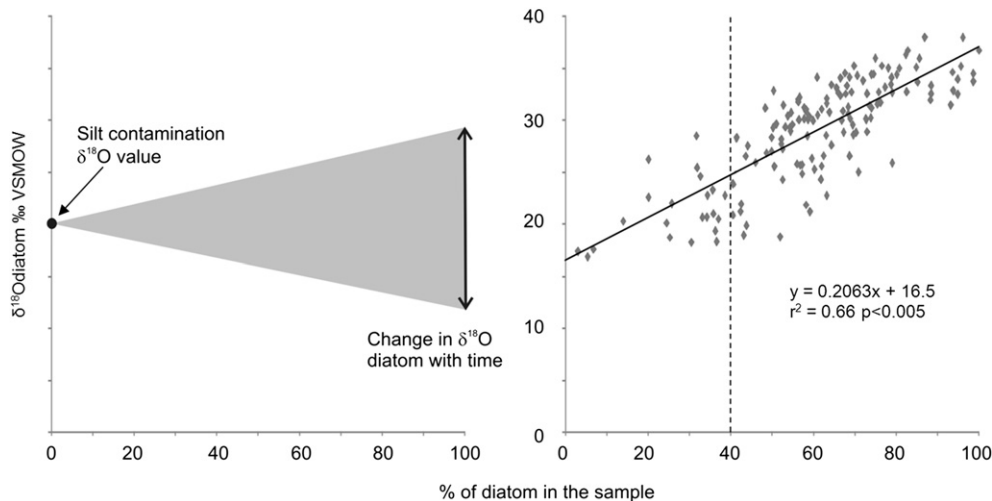

Fig. 3. Theoretically, in $\%_{diatom} - \delta^{18}O_{diatom}$ space, all samples will fall in a cloud within the shaded area (left), between a single contamination value and changing values of $\delta^{18}O$ through time. At Nar (right) the samples describe a line, showing the $\delta^{18}O$ of contamination is 16.5‰. Samples containing <40% diatom (i.e. >60% contamination), as indicated by the dotted line, were removed from subsequent analyses.

uncertainty associated with mass balancing was calculated by combining the errors associated with the various components of Eq. (2), as discussed above.

It should be noted that two factors will likely have led to an overestimation of %$_{contamination}$. Firstly, some minerogenic material will be removed by the first fluorination stage before $\delta^{18}O$ measurements are made (Swann and Leng, 2009). Secondly, diatom frustules can incorporate Al into their skeletons and therefore Al% in the samples will not just reflect minerogenic contamination (Beck et al., 2002; Koning et al., 2007; Swann, 2010). However, because of the difficulties and uncertainties of correcting for these components, these two factors were not accounted for in this study.

3.5. Calculation of $\delta^{18}O_{lakewater}$

To allow for direct comparison of the $\delta^{18}O$ data from carbonate and diatoms, removing the effects of temperature fractionation, we estimate $\delta^{18}O_{lakewater}$ at the time of diatom growth and carbonate precipitation. We took into account changes in carbonate mineralogy between calcite and aragonite (Jones, 2004), which has an effect on $\delta^{18}O_{carbonate}$ (Grossman, 1984; Abell and Williams, 1989), and re-express the calcite (Leng and Marshall, 2004), aragonite (Grossman and Ku, 1986) and diatom (Crespin et al., 2010) palaeotemperature equations respectively to provide estimates of $\delta^{18}O_{lakewater}$:

$$\delta^{18}O_{lakewater} = \delta^{18}O_{calcite} - \left(4.58 \pm \sqrt{[4.58^2 - 4 \times 0.08 \times (13.8 - T)]} \right) \Big/ 2 \times 0.08 \tag{3}$$

$$\delta^{18}O_{lakewater} = \delta^{18}O_{aragonite} - (T - 19.7)/-4.34 \tag{4}$$

$$\delta^{18}O_{lakewater} = \delta^{18}O_{corrected-diatom} - (T - 245)/-6.25 \tag{5}$$

where $\delta^{18}O_{lakewater}$ and $\delta^{18}O_{diatom}$ are expressed on the VSMOW scale, $\delta^{18}O_{calcite}$ and $\delta^{18}O_{aragonite}$ against VPDB and T in °C.

4. Results

4.1. Water, core top and sediment trap $\delta^{18}O$ data

Nar Gölü has been monitored during field seasons for over a decade so the modern isotope limnology is fairly well understood. There is a strong relationship between lake depth and $\delta^{18}O_{lakewater}$ over the past decade (Fig. 4, Table 1), with values increasing by 2.45‰ (−2.64‰ June 2001 to −0.19‰ September 2011, measured against VSMOW) as lake levels have fallen (~25 m June 2001 to ~22 m September 2011). This increase is also seen in $\delta^{18}O_{carbonate}$ values from the past decade (NAR10 core), which have increased from −3.3‰ (VPDB) in 2001 to −0.5‰ in 2010. $\delta^{18}O_{corrected-diatom}$ values from core top material vary by 9.6‰ over the past 30 years (between +34.0‰ and +43.6‰, standard deviation + 3.5‰, $n = 10$) but there is no substantial increase matching that of $\delta^{18}O_{carbonate}$ over the past decade and isotopic shifts are not outside cumulative errors. Sediment trap $\delta^{18}O_{corrected-diatom}$ values (between +34.0‰ and +37.0‰ in the last decade) are similar to those from core top sediments.

4.2. Contamination

The mean percentage of contamination assessed by EDS across all diatom isotope samples was 40% ($n = 149$). Samples with >60% contamination were removed from subsequent analyses ($n = 22$); while this is a fairly arbitrary point, it is around this level that errors increase to >10‰. Fig. 5 shows that while some periods on the whole have more contaminated samples than others, high and low %$_{contamination}$ values are found throughout the record.

4.3. Comparing the diatom and carbonate oxygen isotope records 301–2010 AD

$\delta^{18}O_{corrected-diatom}$ values for the sediment core samples follow the same general trend as $\delta^{18}O_{diatom}$ but are on average increased by 6.9‰ (Fig. 5). For parts of the last 1710 years, there is a marked contrast between $\delta^{18}O_{corrected-diatom}$ and $\delta^{18}O_{carbonate}$ trends. For example, the increase in the latter at ~1400 AD and decreases at ~561 AD and 1960 AD are not seen in the $\delta^{18}O_{corrected-diatom}$ record (Fig. 5). Minima in the $\delta^{18}O_{corrected-diatom}$ record centred on 341 AD, 521 AD, 691 AD and 1831 AD are likewise not seen in the $\delta^{18}O_{carbonate}$ record. On the other hand, $\delta^{18}O$ trends from both hosts are similar 801–921 AD with both records increasing to a peak 861–871 AD before decreasing again. To compare $\delta^{18}O$ trends directly, Eqs. (3)–(5) are applied to take into account likely temperature differences and produce estimates of $\delta^{18}O_{lakewater}$

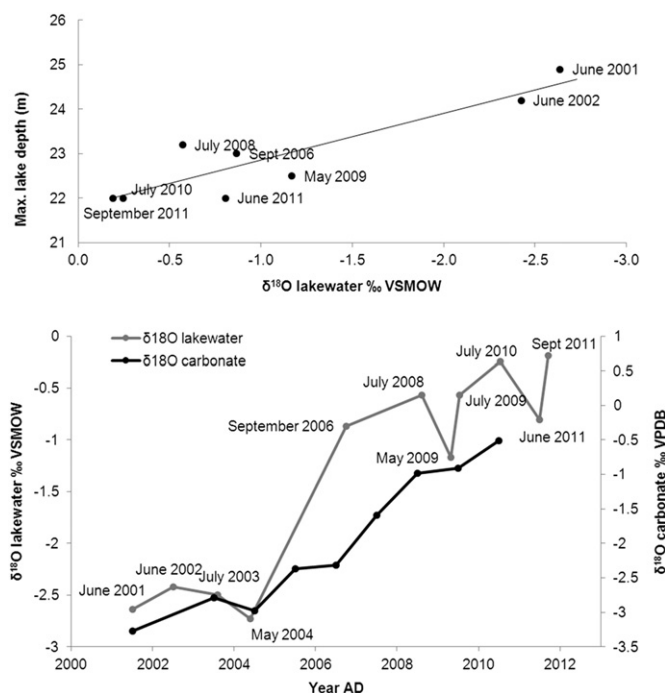**Fig. 4.** Relationship between lake depth and $\delta^{18}O_{lakewater}$ over the past decade (top), with linear regression line fitted through data. $\delta^{18}O_{carbonate}$ values (plotted to reflect their probable formation in May–June) follow a similar trend to $\delta^{18}O_{lakewater}$ values (dates of collection shown) (bottom). This adds support to the interpretation of Jones et al. (2005) that $\delta^{18}O_{carbonate}$ at Nar is a proxy for water balance.
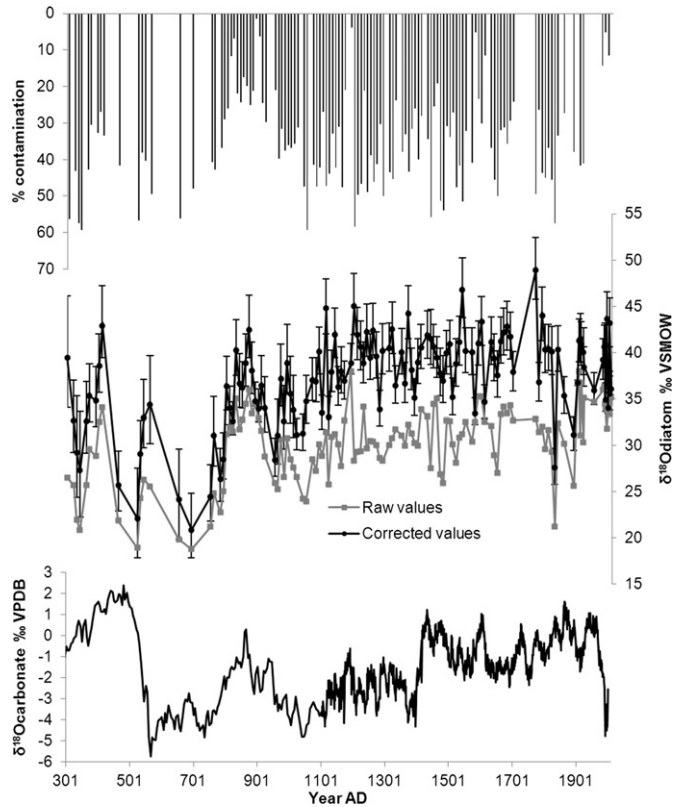
Fig. 5. $\delta^{18}O_{diatom}$ and $\delta^{18}O_{corrected-diatom}$ (middle) with error bars showing the combined uncertainty associated with analytical error and the process of estimating %contamination. The trend of $\delta^{18}O_{corrected-diatom}$ clearly differs from that of $\delta^{18}O_{carbonate}$ (bottom). High %contamination values of diatom isotope samples (top) coincide with both high and low $\delta^{18}O_{diatom}$ values, suggesting contamination is not the main driver of $\delta^{18}O$.

Fig. 6. Estimates of $\delta^{18}O_{lakewater}$ at time of diatom growth (grey area) and carbonate precipitation (black area) calculated using Eqs. (3)–(5) and based on a range of temperatures (+5−+15 °C for diatoms and +15−+20 °C for carbonates) (middle). $\Delta\delta^{18}O_{lakewater}$ (bottom) = $\delta^{18}O_{lakewater}$ at time of diatom growth minus $\delta^{18}O_{lakewater}$ at time of carbonate precipitation. Odd numbered zones represent increased seasonality (more negative $\Delta\delta^{18}O_{lakewater}$), when there was probably sufficient snowmelt to form a freshwater lid on the lake, whereas even numbered zones represent times of less winter-dominated precipitation. *Cyclotella meneghiniana* biovolume as a % of total biovolume is also shown (top), with greatest biovolume at times of more negative $\Delta\delta^{18}O_{lakewater}$.

(Fig. 6). As discussed in Section 2, we estimate that carbonate formed in lake surface water temperatures between +15 and +20 °C and diatoms grew in waters of +5−+15 °C. The average difference between estimated $\delta^{18}O_{lakewater}$ values at the time of diatom growth and carbonate precipitation ($\Delta\delta^{18}O_{lakewater}$) is also shown. Six key zones are identified. From 301 to 561 AD (zone 1a), $\delta^{18}O_{carbonate}$ is the highest for the entire record (reaching >2‰ VPDB) while for parts of this period $\delta^{18}O_{corrected-diatom}$ is low (reaching a minimum value of +22.1‰ VSMOW, at which time $\Delta\delta^{18}O_{lakewater}$ reaches −15‰). In zone 1b (561−801 AD), $\delta^{18}O_{carbonate}$ is lower while $\delta^{18}O_{corrected-diatom}$ is still low, with very negative $\Delta\delta^{18}O_{lakewater}$ for most of the period. In zone 2 (801−921 AD) $\delta^{18}O_{carbonate}$ and $\delta^{18}O_{corrected-diatom}$ both increase, following the same trend, and $\Delta\delta^{18}O_{lakewater}$ is nearer to 0. Two short-lived periods of negative $\Delta\delta^{18}O_{lakewater}$ are seen in zone 3 (921−1071 AD), although $\Delta\delta^{18}O_{lakewater}$ here is not as negative as during zone 1. Following this there is a long period where $\Delta\delta^{18}O_{lakewater}$ is fairly constant, within error and closer to 0 (zone 4, 1071−1821 AD). $\Delta\delta^{18}O_{lakewater}$ again becomes notably negative in zone 5 (1821−1898 AD), before approaching 0 again in zone 6 (1898−2008 AD).

5. Discussion

5.1. Drivers of $\delta^{18}O$

Previously, Jones et al. (2005) used calibration with the meteorological record and modelling to show the $\delta^{18}O_{carbonate}$ record from Nar can be considered a strong proxy for regional water

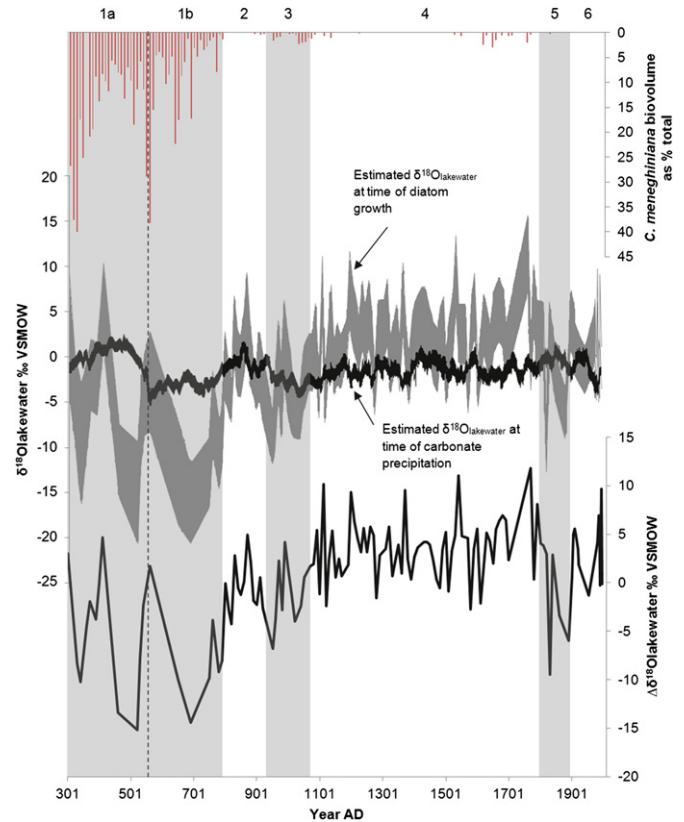balance. Here we add support to this interpretation. An increase in $\delta^{18}O_{lakewater}$ has occurred over the past decade as lake levels have fallen, a signal that is transferred to the carbonate oxygen isotope record from core top material (Fig. 4). However, unlike for $\delta^{18}O_{carbonate}$ analysis, the amount of core material available to us from a single varve year does not yield sufficient material for $\delta^{18}O_{diatom}$ analysis. It is therefore difficult to draw any firm conclusions from core top $\delta^{18}O_{corrected-diatom}$. To work out what could be driving down-core variations in $\delta^{18}O_{corrected-diatom}$, we have to consider all the variables that could influence it, and in particular which variables have the potential to account for the large magnitude (>15‰) shifts seen in Fig. 5.

5.2. Contamination of samples

Minerogenic contamination has an effect on $\delta^{18}O_{diatom}$, and while contamination is high in parts of zone 1 where $\delta^{18}O_{diatom}$ is low, it is also high in parts of the record where $\delta^{18}O_{diatom}$ is high (Fig. 5). This suggests other factors are more important drivers of $\delta^{18}O_{diatom}$ than contamination. In any case, mass balance corrections have been applied to remove the effect of contamination to produce $\delta^{18}O_{corrected-diatom}$. While there are uncertainties associated with mass balance corrections, the shifts in $\delta^{18}O_{corrected-diatom}$ in the Nar record are far greater than these (Fig. 5). In less sensitive lakes, this issue will be more of a problem as isotopic shifts may not

be outside of error, leading Chapligin et al. (2012) to suggest that the mass balance method is only valid up to 15% contamination.

5.3. Changes in species assemblage composition

While species vital effects in diatoms have been shown to be of limited importance (Brandriss et al., 1998; Schmidt et al., 2001; Moschen et al., 2005; Swann et al., 2006; Schiff et al., 2009), down-core changes in the time of year that diatoms are growing in Nar would change the lake conditions (i.e. temperature and $\delta^{18}O_{lakewater}$) that $\delta^{18}O_{corrected-diatom}$ is recording. Uncertainties in diatom ecology make it difficult to reconstruct how the seasonality of diatom growth changed through the record. Freshwater species *Nitzschia paleacea*, *Synedra acus* and *Stephanodiscus parvus* were identified as bloom species from thin section analysis between 1100 AD and present (Woodbridge and Roberts, 2010, 2011). Based on sediment trap data and thin section analysis, *N. paleacea* and *S. parvus* probably bloom immediately prior to carbonate formation, while *S. acus* blooms in the autumn or early spring (Woodbridge et al., 2010).

In contrast, *Cyclotella meneghiniana* dominates biovolume calculations before 800 AD during the periods of significantly lower $\delta^{18}O_{corrected-diatom}$ (Fig. 6) and it may also have been a bloom species (thin sections are not available for this period so this cannot be confirmed). While *C. meneghiniana* has a high conductivity optimum in the European diatom database (6600 μS cm^{-1}; Juggins, 2012), it tolerates a wide range of alkalinity (Gasse, 1986), with a conductivity optimum of 912 μS cm^{-1} and a tolerance of 218–4168 μS cm^{-1} in a Ugandan crater lake training set (Mills and Ryves, 2012) and an optimum of 2000 μS cm^{-1} in the Turkish training set (Reed et al., 2012). In the Ugandan lakes, nutrient input, not salinity, is seen as the most important driver of changes in the abundance of this species (Ryves et al., 2011; Mills and Ryves, 2012). With species such as *C. meneghiniana*, the importance of salinity relative to nutrients can be difficult to unravel (Fritz et al., 2010).

From temperature monitoring data 2009–2011 we know epilimnion temperature changes in Nar through the spring from ~+5 °C in March to ~+15 °C in May. $\delta^{18}O_{lakewater}$ values also increase through the year (e.g. 1 May 2009 epilimnion $\delta^{18}O_{lakewater}$ was −1.17‰ but it had risen to −0.56‰ by 16 July 2009). However, it is possible that *C. meneghiniana* grew at times when there was a greater intra-annual range of $\delta^{18}O_{lakewater}$ values, leading to lower $\delta^{18}O_{corrected-diatom}$ values than recorded by the modern bloom species. Whatever the driver of *C. meneghiniana*, it is interesting to note that its appearance is closely linked to $\Delta\delta^{18}O_{lakewater}$ in Nar. As well as dominating zone 1, it returns to the diatom record in zone 3 (Fig. 6), suggesting the lake conditions that lead to low $\delta^{18}O_{corrected-diatom}$ (negative $\delta^{18}O_{lakewater}$) values in Nar are conditions that are favoured by *C. meneghiniana*.

5.4. Temperature effect on $\delta^{18}O_{corrected-diatom}$

If the temperature at the times of diatom growth and/or carbonate precipitation changed significantly, this would shift calculated $\delta^{18}O_{lakewater}$ values. However, assuming a temperature coefficient of ~−0.2‰°C^{-1} (Brandriss et al., 1998; Moschen et al., 2005; Crespin et al., 2010), it would take an unrealistic temperature change of 75 °C to explain the ~15‰ increase in $\delta^{18}O_{corrected-diatom}$ ~800 AD if $\delta^{18}O_{lakewater}$ was kept constant. While temperature will have some effect on isotope values, it alone cannot account for the size of the shifts seen in $\delta^{18}O_{corrected-diatom}$. Intra-annual temperature differences are taken into account to produce estimates of $\delta^{18}O_{lakewater}$ at the times of diatom growth and carbonate precipitation (Fig. 6) to try to remove this variability.

5.5. Changes in lake water $\delta^{18}O$ and the freshwater lid hypothesis

If the large shifts in $\delta^{18}O_{lakewater}$ calculated from $\delta^{18}O_{corrected-diatom}$ are not due to contamination, temperature or species effects, what is driving them? The other potentially significant variable is the $\delta^{18}O$ of the lake water itself. Changes in $\delta^{18}O_{lakewater}$ can occur due to shifts in the source of precipitation, the $\delta^{18}O$ of the source water, the water balance of the lake and the type of precipitation. The effect of the first two is not considered large enough through this time period to have caused the large shifts in $\delta^{18}O_{corrected-diatom}$ seen in this record (Roberts et al., 2008). $\delta^{18}O_{carbonate}$ has already been shown to be a strong proxy for water balance at Nar (Jones et al., 2005; also Fig. 4), so at times where $\delta^{18}O_{corrected-diatom}$ trends closely follow $\delta^{18}O_{carbonate}$ and where inferred $\delta^{18}O_{lakewater}$ values (Fig. 6) from the two hosts only show an offset of a few per mil due to differences in the time of year they grow/precipitate and error from mass balancing, it would be reasonable to assume that $\delta^{18}O_{corrected-diatom}$ is also responding to changes in water balance. While the temperature range and minimum and maximum errors from the mass balance correction are plotted on Fig. 6 to give the shaded areas, values at the lower end of the $\delta^{18}O_{lakewater}$ at the time of diatom growth estimates are considered much more realistic, as today $\delta^{18}O_{lakewater}$ at the time of diatom growth is lower than at the time of carbonate precipitation. Although the appropriateness of using the Crespin et al. (2010) equation at Nar could be questioned and further work should be undertaken to derive a diatom palaeotemperature equation for Nar itself, $\delta^{18}O_{lakewater}$ values inferred for a temperature range of +5−+15 °C from core material from the late 2000s using this equation were not unreasonable (−3.5‰−+1.1‰) when compared to measured $\delta^{18}O_{lakewater}$ on 1 May 2009 of −1.17‰. Fig. 6 indicates that for most of the period since ~1000 AD, apart from the end of the Little Ice Age (LIA), $\Delta\delta^{18}O_{lakewater}$ is near to 0 and could be explained by the small seasonal $\delta^{18}O_{lakewater}$ variations discussed in Section 5.3. Intra-annual variability of $\delta^{18}O_{lakewater}$ today is in the order of 2‰, which is not as much as estimated for parts of zone 1 on Fig. 6. However, here we propose one mechanism that would allow intra-annual $\delta^{18}O_{lakewater}$ shifts at times in Nar to be greater than would be expected for a closed lake with a long residence time.

Snowfall $\delta^{18}O$ is significantly lower than rain $\delta^{18}O$ because snow reflects equilibrium conditions in the cloud rather than being in isotopic equilibrium with near-ground water vapour (Darling et al., 2006; IAEA/WMO, 2012). Normally in closed lakes, it would be expected that the effects of changes in $\delta^{18}O_{precipitation}$ would be far outweighed by evaporative effects. However, an input of low $\delta^{18}O$ water may not immediately mix with the bulk of the lake water. Large amounts of snowmelt in the spring could form a freshwater lid on the lake surface because of the density contrast with the saline waters left over from the previous summer. If the majority of diatom growth occurred in this low $\delta^{18}O$ water and if by the time of carbonate formation this freshwater lid had mixed with the rest of the lake water, large intra-annual differences in epilimnion $\delta^{18}O_{lakewater}$ could occur. In Canada and Greenland, freshwater lids form after large inputs of snow into lakes that have underlying saline waters (McGowan et al., 2003; Willemse et al., 2004; McGowan et al., 2008; Pieters and Lawrence, 2009). Fig. 6 shows that the lowest $\delta^{18}O_{corrected-diatom}$ values of ~+20‰ would represent $\delta^{18}O_{lakewater}$ values of ~−15‰. A fresh snow sample taken in late February 2012 from the Nar catchment had a $\delta^{18}O$ value of −16.98‰. IAEA data for Ankara (400 m lower in elevation than Nar) add support to this, with snow $\delta^{18}O$ values commonly below −10‰ (IAEA/WMO, 2012). However, it is difficult to imagine that the average $\delta^{18}O$ of lake waters in which diatoms grew was this low, especially since some diatom species are likely

to have grown at other times of the year. Any such relationship between $\delta^{18}O_{corrected-diatom}$ and climate is complicated, in this case with a threshold required above which there is sufficient snowmelt to form a freshwater lid. This means it is difficult to test the hypothesis.

However, there is some support from other proxies. As discussed in Section 5.3, the appearance of C. meneghiniana in the record appears to roughly coincide with low $\delta^{18}O_{corrected-diatom}$ values (Fig. 6), suggesting there were indeed noteworthy changes in lake conditions at this time. We suggest that the difference between lake conditions at times when $\Delta\delta^{18}O_{lakewater}$ is more negative and C. meneghiniana dominates biovolume calculations and times such as the present, when $\Delta\delta^{18}O_{lakewater}$ is closer to 0 and N. paleacea and S. acus are the dominant bloom species, could be much larger inputs of low $\delta^{18}O$ snowmelt in the former that were sufficient to form freshwater lids, possibly with associated increases in the inwash of nutrients. While we acknowledge the limitations of the available documentary sources, it does appear there may have been significantly more snowfall in the region at times of increased $\Delta\delta^{18}O_{lakewater}$, with ancient texts from the first half of the first millennium AD, for example, describing the people of Cappadocia as "reeking of snow" and roads impassable until Easter (Van Dam, 2002). Significant snowfalls in other parts of Anatolia were also reported at this time (Stathakopoulos, 2004). Niğde, 45 km from Nar, saw on average from 1935 to 2010 AD only 33 snowy days per year, perhaps explaining why a significant freshwater lid does not seem to have formed over the past few decades, with $\Delta\delta^{18}O$ closer to zero and no C. meneghiniana blooms. Therefore, since the other factors that could influence $\delta^{18}O_{corrected-diatom}$ (namely contamination and temperature) would not be able to cause the magnitude of the shifts seen, and based on our present understanding of Nar, we propose that increased snowmelt that formed a freshwater lid is the best explanation for low $\delta^{18}O_{corrected-diatom}$ values.

5.6. Implications for Near East palaeoclimatology

Previous studies have shown that summers in the Near East were dry in Late Antiquity, i.e. 300–560 AD at Nar (Jones et al., 2006) and 100–700 AD in Israel (Orland et al., 2009). Increased climate variability and a decline in precipitation were also inferred for central Europe around this time (Buntgen et al., 2011). However, reconstructions of the severity of winters were lacking. Here, $\delta^{18}O_{corrected-diatom}$ is interpreted as indicating significantly increased snowfall for much of the period 301–801 AD (zone 1). The period 301–561 AD (zone 1a) coincided with a time of lower water balance, suggesting increased seasonality with winter-dominated precipitation and dry summers. In zone 1b (561–801 AD), there seems to be less significant summer droughts with lower $\delta^{18}O_{carbonate}$ but $\delta^{18}O_{corrected-diatom}$ is still very low suggesting significant winter snow at this time too. This period of unfavourable climate for people ~300–700 AD (the 'Dark Ages') is seen across Europe. Bond event 1 is dated to around this time (Bond et al., 1997) and a decline in agriculture in NW Europe has been linked to the cooler conditions (Berglund, 2003). The fact climate shifts seem to have been broadly synchronous from the North Atlantic to the Near East suggests a common climate driver and indeed Jones et al. (2006) showed how the winter climate of Nar is influenced by the North Atlantic Oscillation and the North Sea-Caspian Pattern Index.

Links between the climates of the North Atlantic and central Turkey are also seen in later parts of the Nar record. As described in Roberts et al. (2012), during the Medieval Climate Anomaly (950–1350 AD) carbonate $\delta^{18}O$ and diatom species records suggest wetter conditions (Jones et al., 2006; Woodbridge and

Roberts, 2011) and $\delta^{18}O_{corrected-diatom}$ suggests less severe winters than during zone 1. $\delta^{18}O_{carbonate}$ at Nar indicates increased aridity ~1400–1900 AD during the LIA, with drought independently recorded in tree ring and historical sources from Anatolia 1580–1610 AD (Kuniholm, 1990; Touchan et al., 2007; White, 2011). $\Delta\delta^{18}O_{lakewater}$ suggests a less seasonal climate at this time (zone 4). However, towards the end of the LIA, a period of increased $\Delta\delta^{18}O_{lakewater}$ is seen (zone 5), which coincides, within the dating error, with the reported freezing of the Black Sea 1823 AD (Yavuz et al., 2007) and the Dalton Sunspot Minimum 1790–1830 AD (Wagner and Zorita, 2005).

5.7. Implications for the stable isotope community

Using $\delta^{18}O_{corrected-diatom}$ alongside $\delta^{18}O_{carbonate}$ data we are therefore able to provide insights into the seasonality of Near East precipitation over the past 1710 years. This was possible because, as in the studies of Leng et al. (2001) and Rozanski et al. (2010), the climate of the study site is seasonal and the two hosts apparently record conditions in the lake at different times of the year. At Pınarbaşı (Leng et al., 2001), $\delta^{18}O_{carbonate}$ is seen as a proxy for summer temperature because of the short residence time of the lake, but Nar has a long residence time meaning that $\delta^{18}O_{carbonate}$ here responds to water balance. Therefore, the insights provided by comparing $\delta^{18}O$ from carbonates and diatoms are likely to depend on the hydrological residence time of the lake and what time of the year each host grows/precipitates, emphasising the requirement for detailed limnological monitoring and acknowledgement that precipitation/growth times could vary down core. We also highlight how $\delta^{18}O_{carbonate}$ is easier to interpret than $\delta^{18}O_{corrected-diatom}$ because of the many factors that can influence the latter, not least changes in species assemblages shifting the time of year to which $\delta^{18}O_{corrected-diatom}$ is weighted and the error associated with mass balance corrections. As a result, and as found in other carbonate-diatom $\delta^{18}O$ comparison studies, the $\delta^{18}O_{corrected-diatom}$ record is significantly noisier than the $\delta^{18}O_{carbonate}$ record.

This study draws attention to the value of $\delta^{18}O$ analysis from multiple hosts. Had only the $\delta^{18}O_{corrected-diatom}$ record been produced from the Nar sediments, the large shifts may have been interpreted as showing large changes in water balance. However, because of the $\delta^{18}O_{carbonate}$ record, we have been able to show this could not be the case. Thus, as first highlighted by Leng et al. (2001), rather than being direct substitutes for each other, comparing $\delta^{18}O$ records from hosts that form at different times of the year can provide additional information to aid palaeohydrological reconstructions.

6. Conclusions

Building on previous carbonate-diatom $\delta^{18}O$ comparison studies, we highlight the necessity for an understanding of the modern limnology of the lake, diatom species work and a thorough assessment of error to support interpretations of oxygen isotope records. In particular, we demonstrate the potential of EDS to provide quantitative assessments of contamination in diatom isotope samples. While the $\delta^{18}O_{carbonate}$ record is seen as a proxy for water balance, we suggest $\delta^{18}O_{corrected-diatom}$ may be driven by changes in the amount of spring snowmelt. Thus, we tentatively propose increased snowmelt (more severe winters) for much of the periods 301–801 AD, 921–1071 AD and 1821–1898 AD. Combining this record with the $\delta^{18}O_{carbonate}$ record, we are therefore able to highlight the potential for oxygen isotope analysis from different hosts in lake sediments to provide insights into palaeo-seasonality.

Acknowledgements

References

Abell, P., Williams, M., 1989. Oxygen and carbon isotope ratios in gastropods shells as indicators of paleoenvironments in the Afar region of Ethiopia. Palaeogeography, Palaeolimnology, Palaeoecology 74, 265–278.

Anderson, L., 2011. Holocene record of precipitation seasonality from lake calcite delta(18)O in the central Rocky Mountains, United States. Geology 39, 211–214.

Barker, P.A., Hurrell, E.R., Leng, M.J., Wolff, C., Cocquyt, C., Sloane, H.J., Verschuren, D., 2011. Seasonality in equatorial climate over the past 25 k.y. Revealed by oxygen isotope records from Mount Kilimanjaro. Geology 39, 1111–1114.

Beck, L., Gehlen, M., Flank, A.M., Van Bennekom, A.J., Van Beusekom, J.E.E., 2002. The relationship between Al and Si in biogenic silica as determined by PIXE and XAS. Nuclear Instruments & Methods in Physics Research Section B — Beam Interactions with Materials and Atoms 189, 180–184.

Berglund, B.E., 2003. Human impact and climate changes — synchronous events and a causal link? Quaternary International 105, 7–12.

Bond, G., Showers, W., Cheseby, M., Lotti, R., Almasi, P., deMenocal, P., Priore, P., Cullen, H., Hajdas, I., Bonani, G., 1997. A pervasive millennial-scale cycle in North Atlantic Holocene and glacial climates. Science 278, 1257–1266.

Brandriss, M.E., O'Neil, J.R., Edlund, M.B., Stoermer, E.F., 1998. Oxygen isotope fractionation between diatomaceous silica and water. Geochimica et Cosmochimica Acta 62, 1119–1125.

Brewer, T.S., Leng, M.J., Mackay, A.W., Lamb, A.L., Tyler, J.J., Marsh, N.G., 2008. Unravelling contamination signals in biogenic silica oxygen isotope composition: the role of major and trace element geochemistry. Journal of Quaternary Science 23, 321–330.

Buntgen, U., Tegel, W., Nicolussi, K., McCormick, M., Frank, D., Trouet, V., Kaplan, J.O., Herzig, F., Heussner, K.U., Wanner, H., Luterbacher, J., Esper, J., 2011. 2500 Years Of European climate variability and human susceptibility. Science 331, 578–582.

Chapligin, B., Leng, M.J., Webb, E., Alexandre, A., Dodd, J.P., Ijiri, A., Lücke, A., Shemesh, A., Abelmann, A., Herzschuh, U., Longstaffec, F.J., Meyer, H., Moschen, R., Okazaki, Y., Rees, N.H., Sharp, Z.D., Sloane, H.J., Sonzogni, C., Swann, G.E.A., Sylvestre, F., Tyler, J.J., Yam, R., 2011. Inter-laboratory comparison of oxygen isotope compositions from biogenic silica. Geochimica et Cosmochimica Acta 75, 7242–7256.

Chapligin, B., Meyer, H., Bryan, A., Snyder, J., Kemnitz, H., 2012. Assessment of purification and contamination correction methods for analysing the oxygen isotope composition from biogenic silica. Chemical Geology 300–301, 185–199.

Crespin, J., Sylvestre, F., Alexandre, A., Sonzogni, C., Pailles, C., Perga, M.E., 2010. Re-examination of the temperature-dependent relationship between delta O-18(diatoms) and delta O-18(lake water) and implications for paleoclimate inferences. Journal of Paleolimnology 44, 547–557.

Cruz, R.V., Harasawa, H., Lal, M., Wu, S., Anokhin, Y., Punsalmaa, B., Honda, Y., Jafari, M., Li, C., Huu Ninh, N., 2007. Asia. In: Parry, M.L., Canziani, O.F., Palutikof, J.P., van der Linden, P.J., Hanson, C.E. (Eds.), Climate Change 2007: Impacts, Adaptation and Vulnerability. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, pp. 469–506.

Darling, W.G., Bath, A.H., Gibson, J.J., Rozanski, K., 2006. Isotopes in water. In: Leng, M.J. (Ed.), Isotopes in Palaeoenvironmental Research. Springer, Dordrecht, pp. 1–66.

Fritz, S.C., Cumming, B.F., Gasse, F., Laird, K.R., 2010. Diatoms as indicators of hydrologic and climatic change in saline lakes. In: Smol, J.P., Stoermer, E.F. (Eds.), The Diatoms: Applications for the Environmental and Earth Sciences. Cambridge University Press, Cambridge, pp. 186–208.

Gasse, F., 1986. Bibliotheca Diatomologica: East African Diatoms. Gebrüder Borntraeger, Berlin.

Gevrek, A.I., Kazancı, N., 2000. A Pleistocene, pyroclastic-poor maar from central Anatolia, Turkey: influence of a local fault on a phreatomagmatic eruption. Journal of Volcanology and Geothermal Research 95, 309–317.

Glew, J.R., Smol, J.P., Last, W.M., 2001. Sediment core collection and extrusion. In: Last, M., Smol, J.P. (Eds.), Tracking Environmental Change Using Lake Sediments. Basin Analysis, Coring and Chronological Techniques. Kluwer Academic Publishers, Dordrecht, pp. 73–105.

Grossman, E.L., Ku, T.L., 1986. Oxygen and carbon isotope fractionation in biogenic aragonite — temperature effects. Chemical Geology 59, 59–74.

Grossman, E.L., 1984. Carbon isotopic fractionation in live benthic foraminifera — comparison with inorganic precipitate studies. Geochimica et Cosmochimica Acta 48, 1505–1512.

Henderson, A.K., Nelson, D.M., Hu, F.S., Huang, Y.S., Shuman, B.N., Williams, J.W., 2010. Holocene precipitation seasonality captured by a dual hydrogen and oxygen isotope approach at Steel Lake, Minnesota. Earth and Planetary Science Letters 300, 205–214.

IAEA/WMO, 2012. Global Network of Isotopes in Precipitation. http://www.iaea.org/water (accessed 10.01.12.).

Issar, A., Adar, E., 2010. Progressive development of water resources in the Middle East for sustainable water supply in a period of climate change. Philosophical Transactions of the Royal Society A 368, 5339–5350.

Issar, A., Zohar, M., 2007. Climate Change: Environment and History of the Near East. Springer, Berlin.

Jones, M.D., Leng, M.J., Roberts, C.N., Turkes, M., Moyeed, R., 2005. A coupled calibration and modelling approach to the understanding of dry-land lake oxygen isotope records. Journal of Paleolimnology 34, 391–411.

Jones, M.D., Roberts, C.N., Leng, M.J., Turkes, M., 2006. A high-resolution late Holocene lake isotope record from Turkey and links to North Atlantic and monsoon climate. Geology 34, 361–364.

Jones, M.D., 2004. High-resolution Records of Climate Change from Lacustrine Stable Isotopes Through the Last Two Millennia in Western Turkey. Ph.D thesis, Plymouth University.

Juggins, S., 2012. European Diatom. Database Online. http://craticula.ncl.ac.uk/Eddi/jsp/index.jsp (accessed 10.01.12.).

Koning, E., Gehlen, M., Flank, A.M., Calas, G., Epping, E., 2007. Rapid post-mortem incorporation of aluminum in diatom frustules. Evidence from chemical and structural analyses. Marine Chemistry 106, 208–222.

Kuniholm, P.I., 1990. Archaeological evidence and nonevidence for climatic-change. Philosophical Transactions of the Royal Society A 330, 645–655.

Kutiel, H., Turkes, M., 2005. New evidence for the role of the North Sea — Caspian pattern on the temperature and precipitation regimes in continental central Turkey. Geografiska Annaler Series A 87A, 501–513.

Lamb, A.L., Leng, M.J., Sloane, H.J., Telford, R.J., 2005. A comparison of the palaeoclimate signals from diatom oxygen isotope ratios and carbonate oxygen isotope ratios from a low latitude crater lake. Palaeogeography, Palaeoclimatology, Palaeoecology 223, 290–302.

Lamb, A.L., Brewer, T.S., Leng, M.J., Sloane, H.J., Lamb, H.F., 2007. A geochemical method for removing the effect of tephra on lake diatom oxygen isotope records. Journal of Paleolimnology 37, 499–516.

Leng, M.J., Barker, P.A., 2006. A review of the oxygen isotope composition of lacustrine diatom silica for palaeoclimate reconstruction. Earth Science Reviews 75, 5–27.

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

Leng, M.J., Sloane, H.J., 2008. Combined oxygen and silicon isotope analysis of biogenic silica. Journal of Quaternary Science 23, 313–319.

Leng, M.J., Barker, P.A., Greenwood, P., Roberts, N., Reed, J., 2001. Oxygen isotope analysis of diatom silica and authigenic calcite from Lake Pinarbasi, Turkey. Journal of Paleolimnology 25, 343–349.

Leng, M.J., Lamb, A.L., Heaton, T.H.E., Marshall, J.D., Wolfe, B., Jones, M.D., Holmes, J.A., Arrowsmith, C., 2006. Isotopes in lake sediments. In: Leng, M.J. (Ed.), Isotopes in Palaeoenvironmental Research. Springer, Dordrecht, pp. 147–184.

Leng, M.J., Jones, M.D., Frogley, M.R., Eastwood, W.J., Kendrick, C.P., Roberts, C.N., 2010. Detrital carbonate influences on bulk oxygen and carbon isotope composition of lacustrine sediments from the Mediterranean. Global and Planetary Change 71, 175–182.

Li, H.C., Ku, T.L., 1997. Delta C-13-delta O-18 covariance as a paleohydrological indicator for closed-basin lakes. Palaeogeography, Palaeoclimatology, Palaeoecology 133, 69–80.

Livingstone, D.A., 1955. A lightweight piston sampler for lake deposits. Ecology 36, 137–139.

Mackay, A.W., Karabanov, E., Leng, M.J., Sloane, H.J., Morley, D.W., Panizzo, V.N., Khursevich, G., Williams, D., 2008. Reconstructing hydrological variability in Lake Baikal during MIS 11: an application of oxygen isotope analysis of diatom silica. Journal of Quaternary Science 23, 365–374.

Mackay, A.W., Swann, G.E.A., Brewer, T.S., Leng, M.J., Morley, D.W., Piotrowska, N., Rioual, P., White, D., 2011. A reassessment of late glacial — Holocene diatom oxygen isotope record from Lake Baikal using a geochemical mass-balance approach. Journal of Quaternary Science 26, 627–634.

McGowan, S., Ryves, D.B., Anderson, N.J., 2003. Holocene records of effective precipitation in West Greenland. Holocene 13, 239–249.

McGowan, S., Juhler, R.K., Anderson, N.J., 2008. Autotrophic response to lake age, conductivity and temperature in two West Greenland lakes. Journal of Paleolimnology 39, 301–317.

Meehl, G.A., Stocker, T.F., Collins, P., Friedlingstein, P., Gaye, A.T., Gregory, J.M., Kitoh, A., Knutti, R., Murphy, J.M., Noda, A., Raper, S.C.B., Watterson, I.G., Weaver, A.J., Zhao, Z.C., 2007. Global climate Projections. In: Solomon, S., Qin, D.,

Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, pp. 748—845.

Meteoroloji-Bulteni, 1974. State Meteorological Services. Ankara.

Mills, K., Ryves, D.B., 2012. Diatom-based models for inferring past water chemistry in western Ugandan crater lakes. Journal of Paleolimnology 48, 383—399.

Morley, D.W., Leng, M.J., Mackay, A.W., Sloane, H.J., Rioual, P., Battarbee, R.W., 2004. Cleaning of lake sediment samples for diatom oxygen isotope analysis. Journal of Paleolimnology 31, 391—401.

Morley, D.W., Leng, M.J., Mackay, A.W., Sloane, H.J., 2005. Late glacial and Holocene environmental change in the Lake Baikal region documented by oxygen isotopes from diatom silica. Global and Planetary Change 46, 221—233.

Moschen, R., Lucke, A., Schleser, G.H., 2005. Sensitivity of biogenic silica oxygen isotopes to changes in surface water temperature and palaeoclimatology. Geophysical Research Letters 32, L07708.

Orland, I.J., Bar-Matthews, M., Kita, N.T., Ayalon, A., Matthews, A., Valley, J.W., 2009. Climate deterioration in the Eastern Mediterranean as revealed by ion micro-probe analysis of a speleothem that grew from 2.2 to 0.9 ka in Soreq Cave, Israel. Quaternary Research 71, 27—35.

Orland, I.J., Bar-Matthews, M., Ayalon, A., Matthews, A., Kozdon, R., Ushikubo, T., Valley, J.W., 2012. Seasonal resolution of Eastern Mediterranean climate change since 34 ka from a Soreq Cave speleothem. Geochimica et Cosmochimica Acta 89, 240—245.

Pieters, R., Lawrence, G.A., 2009. Effect of salt exclusion from lake ice on seasonal circulation. Limnology and Oceanography 54, 401—412.

Reed, J.M., Mesquita-Joanes, F., Griffiths, H.I., 2012. Multi-indicator conductivity transfer functions for Quaternary palaeoclimate reconstruction. Journal of Paleolimnology 47, 251—275.

Roberts, C.N., Jones, M.D., Benkaddour, A., Eastwood, W.J., Filippi, M.L., Frogley, M.R., Lamb, H.F., Leng, M.J., Reed, J.M., Stein, M., Stevens, L., Valero-Garcés, B., Zanchetta, G., 2008. Stable isotope records of Late Quaternary climate and hydrology from Mediterranean lakes: the ISOMED synthesis. Quaternary Science Reviews 27, 2426—2441.

Roberts, C.N., Moreno, A., Valero-Garcés, B.L., Corella, J.P., Jones, M.D., Allcock, S., Woodbridge, J., Morellón, M., Luterbacher, J., Xoplaki, E., Türkes, M., 2012. Palaeolimnological evidence for a bipolar climate see-saw in the Mediterranean since AD900. Global and Planetary Change 84-85, 23—34.

Rosen, A., 2007. Civilizing Climate. AltaMira Press, Plymouth.

Rowe, P.J., Mason, J.E., Andrews, J.E., Marca, A.D., Thomas, L., van Calsteren, P., Jex, C.N., Vanhof, H.B., Al-Omari, S., 2012. Speleothem isotopic evidence of winter rainfall variability in northeast Turkey between 77 and 6 ka. Quaternary Science Reviews 45, 60—72.

Rozanski, K., Klisch, M.A., Wachniew, P., Gorczyca, Z., Goslar, T., Edwards, T.W.D., Shemesh, A., 2010. Oxygen-isotope geothermometers in lacustrine sediments: new insights through combined delta O-18 analyses of aquatic cellulose, authigenic calcite and biogenic silica in Lake Gosciaz, central Poland. Geochimica et Cosmochimica Acta 74, 2957—2969.

Ryves, D.B., Mills, K., Bennike, O., Brodersen, K.P., Lamb, A.L., Leng, M.J., Russell, J.M., Ssemmanda, I., 2011. Environmental change over the last millennium recorded in two contrasting crater lakes in western Uganda, eastern Africa (Lakes Kasenda and Wandakara). Quaternary Science Reviews 30, 555—569.

Schiff, C., Kaufman, D., Wolfe, A., Dodd, J., Sharp, Z., 2009. Late Holocene storm-trajectory changes inferred from the oxygen isotope composition of lake diatoms, south Alaska. Journal of Paleolimnology 41, 189—208.

Schmidt, M., Botz, R., Rickert, D., Bohrmann, G., Hall, S., Mann, S., 2001. Oxygen isotope of marine diatoms and relations to opal-A maturation. Geochimica et Cosmochimica Acta 65, 201—211.

Stathakopoulos, D., 2004. Famine and Pestilence in the Late Roman and Early Byzantine Empire: a Systematic Survey of Subsistence Crises and Epidemics. Ashgate, Aldershot.

Stevens, L.R., Wright, H.E., Ito, E., 2001. Proposed changes in seasonality of climate during the Lateglacial and Holocene at Lake Zeribar, Iran. Holocene 11, 747—755.

Stevens, L.R., Ito, E., Schwalb, A., Wright, H.E., 2006. Timing of atmospheric precipitation in the Zagros Mountains inferred from a multi-proxy record from Lake Mirabad, Iran. Quaternary Research 66, 494—500.

Swann, G.E.A., Leng, M.J., 2009. A review of diatom delta O-18 in palae-oceanography. Quaternary Science Reviews 28, 384—398.

Swann, G.E.A., Patwardhan, S.V., 2011. Application of Fourier Transform Infrared Spectroscopy (FTIR) for assessing biogenic silica sample purity in geochemical analyses and palaeoenvironmental research. Climate of the Past 7, 65—74.

Swann, G.E.A., Maslin, M.A., Leng, M.J., Sloane, H.J., Haug, G.H., 2006. Diatom delta(18)O evidence for the development of the modern halocline system in the subarctic northwest Pacific at the onset of major Northern Hemisphere glaci-ation. Paleoceanography 21, 1—12.

Swann, G.E.A., Leng, M.J., Juschus, O., Melles, M., Brigham-Grette, J., Sloane, H.J., 2010. A combined oxygen and silicon diatom isotope record of Late Quaternary change in Lake El'gygytgyn, North East Siberia. Quaternary Science Reviews 29, 774—786.

Swann, G.E.A., 2010. A comparison of the Si/Al and Si/time wet-alkaline digestion methods for measurement of biogenic silica in lake sediments. Journal of Paleolimnology 44, 375—385.

Touchan, R., Akkemik, U., Hughes, M.K., Erkan, N., 2007. May-June precipitation reconstruction of Southwestern Anatolia, Turkey during the last 900 years from tree rings. Quaternary Research 68, 196—202.

Türkeş, M., 2003. Spatial and temporal variations in precipitation and aridity index series of Turkey. In: Bolle, H.J. (Ed.), Mediterranean Climate — Variability and Trends. Regional Climate Studies. Springer-Verlag, Heidelberg, pp. 181—213.

Van Dam, R., 2002. Kingdom of Snow: Roman Rule and Greek Culture in Cappa-docia. University of Pennsylvania Press, Philadelphia.

Wagner, S., Zorita, E., 2005. The influence of volcanic, solar and the Dalton Minimum (1790—1830): CO_2 forcing on the temperatures in a model study. Climate Dynamics 25, 205—218.

White, S., 2011. The Climate of Rebellion in the Early Modern Ottoman Empire. Cambridge University Press, Cambridge.

Willemse, N.W., van Dam, O., van Helvoort, P.J., Dankers, R., Brommer, M., Schokker, J., Valstar, T.E., de Wolf, H., 2004. Physical and chemical limnology of a subsaline athalassic lake in West Greenland. Hydrobiologia 524, 167—192.

Woodbridge, J., Roberts, C.N., 2010. Linking neo- and palaeolimnology: a case study using crater lake diatoms from central Turkey. Journal of Paleolimnology 44, 855—871.

Woodbridge, J., Roberts, C.N., 2011. Late Holocene climate of the Eastern Mediter-ranean inferred from diatom analysis of annually-laminated lake sediments. Quaternary Science Reviews 30, 3381—3392.

Woodbridge, J., Roberts, C.N., Cox, E.J., 2010. Morphology and ecology of a new Centric diatom from Cappadocia (Central Turkey). Diatom Research 25, 195—212.

Yavuz, V., Akçar, N., Schlüchter, C., 2007. The frozen Bosphorus and its paleoclimatic implications based on a summary of the historical data. In: Yanko-Hombach, V., Gilbert, A.S., Panin, N., Dolukhanov, P.M. (Eds.), The Black Sea Flood Question: Changes in Coastline, Climate and Human Settlement. Springer, Berlin, pp. 633—650.