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

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Abstract

Carbonates and diatoms are rarely deposited together in lake sediments in sufficient quantities for the oxygen isotope composition (δ18O) to be investigated simultaneously from both hosts. Here, δ18Ocarbonate are compared to δ18Odiatom 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 δ18Ocarbonate is a proxy for regional water balance. Diatom activity is mainly weighted towards the spring. At times between ~301 and 561 AD, while δ18Ocarbonate values are the highest for the entire 1710 year period, suggesting summer drought, δ18Ocorrected-diatom Values are among the lowest. δ18Owater 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.

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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 (Türkø, 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 changes 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 ($\delta^{18}O$) of lake sediments is most commonly carried out on carbonates. If precipitated in equilibrium, $\delta^{18}O_{\text{carbonate}}$ is dependent upon the temperature and isotopic composition of the lake water in which it is precipitated, with the degree of fractionation at $-0.24^{\circ}\text{C}^{-1}$ (Leng et al., 2006). In hydrologically open lakes, temperature and the $\delta^{18}O$ of precipitation entering the lake will be the most important drivers of final $\delta^{18}O$ 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). $\delta^{18}O$ analysis can also be carried out on diatom silica. The controls on $\delta^{18}O_{\text{diatom}}$ are very similar to those on $\delta^{18}O_{\text{carbonate}}$ (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. $-0.2^{\circ}\text{C}^{-1}$) 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O_{\text{carbonate}}$ was a proxy for mean summer temperature and $\delta^{18}O_{\text{diatom}}$ a proxy for spring snowmelt, accounting for the substantial differences between $\delta^{18}O$ trends from the two hosts. Large differences in $\delta^{18}O$ were also seen in the record from Lake Gosciaž (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 $\delta^{18}O_{\text{diatom}}$ 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 $\delta^{18}O_{\text{carbonate}}$ 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 $\delta^{18}O$ samples. As such, it is unclear whether differences in trends between carbonate and diatom $\delta^{18}O$ 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 $\delta^{18}O$ data, including: (1) monitoring of the modern lake to identify firstly the drivers of $\delta^{18}O_{\text{lakewater}}$ and secondly what time of the year the two hosts form; (2) diatom species analysis of the sediment to aid with the $\delta^{18}O_{\text{diatom}}$ interpretation; and (3) quantification of contamination allowing mass balancing of $\delta^{18}O_{\text{diatom}}$ 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) $\delta^{18}O$ (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 (~0.7 km²) 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 Nigde, 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 Nigde 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 ~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
water samples were collected from springs and the centre or edge of the lake and maximum lake depths were estimated using a Garmin depth sounder and a weighted tape during June 2001 and September 2011, and intra-annual increases in $\Delta$18O between May and July 2009 and June and September 2011. Spring waters are significantly lower in $\Delta$18O than lake waters highlighting the evaporative enrichment of the lake. * indicates data previously published in Jones et al. (2005).

### 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 210Pb and 137Cs 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 ±100 years, with 4 and 5 varve year bulk samples taken respectively. 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. 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 *C. 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.

#### 3.2. $\delta^{18}O$ 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 $\delta^{13}C_{carbonate}$ 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 $\delta^{18}O$ 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 *C. 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...
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 $\delta^{18}O_{\text{diatom}}$. 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, Chapligin 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 $\delta^{18}O_{\text{diatom}}$ 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%. Chapligin 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 Chapligin 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 mineralogic material should have been removed by sieving at 10 μm and carbonates and organic 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 comparison exercise (Chapligin et al., 2011). The data are presented as $\%_{\text{contam}}$ 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:

$$%_{\text{contamination}} = \left( \frac{\text{sample Al}}{\text{contamination Al}} \right) \times 100 \quad (1)$$

where sample Al is the measured Al concentration in each sample analysed for $\delta^{18}O_{\text{diatom}}$ and contamination Al is the average percentage of Al in Nar silt samples from the core (8.6% ± 0.5, n = 7; similar to that found in Mackay et al., 2011) that were prepared and run as $\delta^{18}O_{\text{diatom}}$ 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:

$$\delta^{18}O_{\text{corrected-diatom}} = \left( \delta^{18}O_{\text{diatom}} - \delta^{18}O_{\text{contamination}} \times \left( \frac{%_{\text{contamination}}}{100} \right) \right) / \left( \frac{%_{\text{diatom}}}{100} \right) \quad (2)$$

where $\delta^{18}O_{\text{diatom}}$ is the original isotope value of the ‘cleaned’ diatom sample, $%_{\text{contamination}}$ and $%_{\text{diatom}}$ (i.e. 100 – $%_{\text{contamination}}$) are estimated by EDS and $\delta^{18}O_{\text{contamination}}$ 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 Chapligin et al. (2012). By plotting measured $\delta^{18}O_{\text{diatom}}$ against $%_{\text{diatom}}$ (the inverse of $%_{\text{contamination}}$), an estimated end member contamination $\delta^{18}O$ value of +16.5‰ (Fig. 3) is calculated, which we use in Eq. (2).
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 \( \%_{\text{contamination}} \). 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 \( \delta^{18}O_{\text{lakewater}} \)

To allow for direct comparison of the \( \delta^{18}O \) data from carbonate and diatoms, removing the effects of temperature fractionation, we estimate \( \delta^{18}O_{\text{lakewater}} \) 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 \( \delta^{18}O_{\text{carbonate}} \) (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) paleotemperature equations respectively to provide estimates of \( \delta^{18}O_{\text{lakewater}} \):

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

\[
\delta^{18}O_{\text{lakewater}} = \delta^{18}O_{\text{aragonite}} - (T - 19.7)/-4.34
\]  

\[
\delta^{18}O_{\text{lakewater}} = \delta^{18}O_{\text{corrected-diatom}} - (T - 245)/-6.25
\]

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

### 4. Results

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

Nar Göllü 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 \( \delta^{18}O_{\text{lakewater}} \) 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 \( \delta^{18}O_{\text{carbonate}} \) values from the past decade (NAR10 core), which have increased from −3.3‰ (VPDB) in 2001 to −0.5‰ in 2010. \( \delta^{18}O_{\text{corrected-diatom}} \) values from core top material vary by 9.6‰ over the past 30 years (between +34.0‰ and +37.0‰, standard deviation +3.5‰ n = 10) but there is no substantial increase matching that of \( \delta^{18}O_{\text{carbonate}} \) over the past decade and isotopic shifts are not outside cumulative errors. Sediment trap \( \delta^{18}O_{\text{corrected-diatom}} \) 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). For parts of the last 1710 years, there is a marked contrast between \( \delta^{18}O_{\text{corrected-diatom}} \) and \( \delta^{18}O_{\text{carbonate}} \) trends. For example, the increase in the latter at ∼1400 AD and decreases at ∼561 AD and 1960 AD are not seen in the \( \delta^{18}O_{\text{corrected-diatom}} \) record (Fig. 5). Minima in the \( \delta^{18}O_{\text{corrected-diatom}} \) record centred on 341 AD, 521 AD, 691 AD and 1831 AD are likewise not seen in the \( \delta^{18}O_{\text{carbonate}} \) 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 \( \delta^{18}O_{\text{lakewater}} \):

\[
\delta^{18}O_{\text{lakewater}} = \delta^{18}O_{\text{carbonate}}(\text{NAR10}) - (T - 245)/-6.25
\]

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

\( \delta^{18}O_{\text{corrected-diatom}} \) values for the sediment core samples follow the same general trend as \( \delta^{18}O_{\text{diatom}} \) but are on average increased by 6.9‰ (Fig. 5). For parts of the last 1710 years, there is a marked contrast between \( \delta^{18}O_{\text{corrected-diatom}} \) and \( \delta^{18}O_{\text{carbonate}} \) trends. For example, the increase in the latter at ∼1400 AD and decreases at ∼561 AD and 1960 AD are not seen in the \( \delta^{18}O_{\text{corrected-diatom}} \) record (Fig. 5). Minima in the \( \delta^{18}O_{\text{corrected-diatom}} \) record centred on 341 AD, 521 AD, 691 AD and 1831 AD are likewise not seen in the \( \delta^{18}O_{\text{carbonate}} \) 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 \( \delta^{18}O_{\text{lakewater}} \):

\[
\delta^{18}O_{\text{lakewater}} = \delta^{18}O_{\text{carbonate}}(\text{NAR10}) - (T - 245)/-6.25
\]
and biological record and modelling to show the difference between estimated high and low \(\delta^{18}O\) values, suggesting contamination is not the main driver of \(\delta^{18}O\).

(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 \(\delta^{18}O_{\text{lakewater}}\) values at the time of diatom growth and carbonate precipitation (\(\Delta\delta^{18}O_{\text{lakewater}}\)) is also shown. Six key zones are identified. From 301 to 561 AD (zone 1a), \(\delta^{18}C\) for carbonate is the highest for the entire record (reaching >2‰ VPDB) while for parts of this period \(\delta^{18}O_{\text{corrected-diatom}}\) is low (reaching a minimum value of +22.1‰ VSMOW, at which time \(\Delta\delta^{18}O_{\text{lakewater}}\) reaches ~15‰). In zone 1b (561—801 AD), \(\delta^{18}O\) carbonate is lower while \(\delta^{18}O_{\text{corrected-diatom}}\) is still low, with very negative \(\Delta\delta^{18}O_{\text{lakewater}}\) for most of the period. In zone 2 (801—921 AD) \(\delta^{18}O\) carbonate and \(\delta^{18}O_{\text{corrected-diatom}}\) both increase, following the same trend, and \(\Delta\delta^{18}O_{\text{lakewater}}\) is nearer to 0. Two short-lived periods of negative \(\Delta\delta^{18}O_{\text{lakewater}}\) are seen in zone 3 (921—1071 AD), although \(\Delta\delta^{18}O_{\text{lakewater}}\) here is not as negative as during zone 1. Following this there is a long period where \(\Delta\delta^{18}O_{\text{lakewater}}\) is fairly constant, within error and closer to 0 (zone 4, 1071—1821 AD). \(\Delta\delta^{18}O_{\text{lakewater}}\) 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 \(\delta^{18}O_{\text{carbonate}}\) record from Nar can be considered a strong proxy for regional water balance. Here we add support to this interpretation. An increase in \(\delta^{18}O_{\text{lakewater}}\) 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 \(\delta^{18}O_{\text{carbonate}}\) analysis, the amount of core material available to us from a single varve year does not yield sufficient material for \(\delta^{18}O_{\text{diatom}}\) analysis. It is therefore difficult to draw any firm conclusions from core top \(\delta^{18}O_{\text{corrected-diatom}}\). To work out what could be driving down-core variations in \(\delta^{18}O_{\text{corrected-diatom}}\), 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 \(\delta^{18}O_{\text{diatom}}\) and while contamination is high in parts of zone 1 where \(\delta^{18}O_{\text{diatom}}\) is low, it is also high in parts of the record where \(\delta^{18}O_{\text{diatom}}\) is high (Fig. 5). This suggests other factors are more important drivers of \(\delta^{18}O_{\text{diatom}}\) than contamination. In any case, mass balance corrections have been applied to remove the effect of contamination to produce \(\delta^{18}O_{\text{corrected-diatom}}\). While there are uncertainties associated with mass balance corrections, the shifts in \(\delta^{18}O_{\text{corrected-diatom}}\) 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 Chaplin 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 δ18O_lake-water) that δ18O_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, Synechococcus 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 δ18O_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 μC m⁻¹; Juggins, 2012), it tolerates a wide range of alkalinity (Gasse, 1986), with a conductivity optimum of 912 μC m⁻¹ and a tolerance of 218–4168 μC m⁻¹ in a Ugandan crater lake training set (Mills and Ryves, 2012) and an optimum of 2000 μC m⁻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. δ18O_lake-water values also increase through the year (e.g. 1 May 2009 epilimnion δ18O_lake-water 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 δ18O_lake-water values, leading to lower δ18O_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 δ18O_lake-water 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 δ18O_corrected-diatom (negative δ18O_lake-water) values in Nar are conditions that arefavoured by C. meneghiniana.

5.4. Temperature effect on δ18O_corrected-diatom

If the temperature at the times of diatom growth and/or carbonate precipitation changed significantly, this would shift calculated δ18O_lake-water 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 δ18O_corrected-diatom ~800 AD if δ18O_lake-water was kept constant. While temperature will have some effect on isotope values, it alone cannot account for the size of the shifts seen in δ18O_corrected-diatom. Intra-annual temperature differences are taken into account to produce estimates of δ18O_lake-water at the times of diatom growth and carbonate precipitation (Fig. 6) to try to remove this variability.

5.5. Changes in lake water δ18O and the freshwater lid hypothesis

If the large shifts in δ18O_lake-water calculated from δ18O_corrected-diatom are not due to contamination, temperature or species effects, what is driving them? The other potentially significant variable is the δ18O of the lake water itself. Changes in δ18O_lake-water can occur due to shifts in the source of precipitation, the δ18O 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 δ18O_corrected-diatom seen in this record (Roberts et al., 2008, δ18O_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 δ18O_corrected-diatom trends closely follow δ18O_carbonate and where inferred δ18O_lake-water 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 δ18O_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 δ18O_lake-water at the time of diatom growth estimates are considered more reasonable, as today δ18O_lake-water in Nar is much more realistic, as today δ18O_lake-water 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, δ18O_lake-water values inferred for a temperature range of +5−+15 °C from core material from the late 2000s using this equation were unreasonable (~−3.5‰−~−11‰) when compared to measured δ18O_lake-water on 1 May 2009 of ~−11.7‰. Fig. 6 indicates that for most of the period since ~1000 AD, apart from the end of the Little Ice Age (LIA), δ18O_lake-water is near to 0 and could be explained by the small seasonal δ18O_lake-water variations discussed in Section 5.3. Intra-annual variability of δ18O_lake-water 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 δ18O_lake-water shifts at times in Nar to be greater than would be expected for a closed lake with a long residence time.

Snowfall δ18O is significantly lower than rain δ18O 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 δ18O_precipitation would be far outweighed by evaporative effects. However, an input of low δ18O 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 δ18O 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 δ18O_lake-water 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; Willemsen et al., 2004; McGowan et al., 2008; Pieters and Lawrence, 2009). Fig. 6 shows that the lowest δ18O_corrected-diatom values of ~−20‰ would represent δ18O_lake-water values of ~−15‰. A fresh snow sample taken in late February 2012 from the Nar catchment had a δ18O value of ~−16.9‰ (IAEA data for Ankara (400 m lower in elevation than Nar) add support to this, with snow δ18O values commonly below ~10‰. IAEA/WMO, 2012). However, it is difficult to imagine that the average δ18O 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 δ18Ocorrected-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 δ18Ocorrected-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 Δδ18Olakewater is more negative and C. meneghiniana dominates biovolume calculations and times such as the present, when Δδ18Olakewater is closer to 0 and N. paleacea and S. acus are the dominant bloom species, could be much larger inputs of low δ18O 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 Δδ18Olakewater, with ancient texts from the first half of the first millennium AD, for example, describing the people of Cappadocia as “reeling from snow” and roads impassable until April (Van Dam, 2002). Significant snowfalls in other parts of Anatolia were also reported at this time (Stathakopoulos, 2004). Ngide, 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 Δδ18O closer to zero and no C. meneghiniana blooms. Therefore, since the other factors that could influence δ18Ocorrected-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 δ18Ocorrected-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, δ18Ocorrected-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 δ18Ocarbonate but δ18Ocorrected-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 δ18O and diatom species records suggest wetter conditions (Jones et al., 2006; Woodbridge and Roberts, 2011) and δ18Ocorrected-diatom suggests less severe winters than during zone 1. δ18Ocarbonate 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). Δδ18Olakewater suggests a less seasonal climate at this time (zone 4). However, towards the end of the LIA, a period of increased Δδ18Olakewater 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 δ18Ocorrected-diatom alongside δ18Ocarbonate 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), δ18Ocarbonate 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 δ18Ocarbonate here responds to water balance. Therefore, the insights provided by comparing δ18O 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 δ18Ocarbonate is easier to interpret than δ18Ocorrected-diatom because of the many factors that can influence the latter, not least changes in species assemblages shifting the time of year to which δ18Ocorrected-diatom is weighted and the error associated with mass balance corrections. As a result, and as found in other carbonate-diatom δ18O comparison studies, the δ18Ocorrected-diatom record is significantly noisier than the δ18Ocarbonate record.

This study draws attention to the value of δ18O analysis from multiple hosts. Had only the δ18Ocorrected-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 δ18Ocarbonate 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 δ18O 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 δ18O 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 δ18Ocarbonate record is seen as a proxy for water balance, we suggest δ18Ocorrected-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 δ18Ocarbonate 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.
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