**Last glacial-Holocene temperatures and hydrology of the Sea
of Galilee and Hula Valley from clumped isotopes in
Melanopsis shells**

Shikma Zaarur¹, Hagit P. Affek^{1,2}, and Mordechai Stein³

¹ Department of Geology and Geophysics, Yale University (shikmaz@gmail.com
, hagit.affek@yale.edu)

² Now at The Institute of Earth Sciences, The Hebrew University of Jerusalem
(hagit.affek@mail.huji.ac.il).

³ Geological Survey of Israel (motistein@gsi.gov.il)

Submitted: February 2015; Revised version submitted: September 2015, second revision
submitted: November 2015

25 pages, 2 tables, 4 figures.

Supplementary Information includes 1 document and 5 tables

Abstract

The carbonate clumped isotope (Δ_{47}) thermometer was applied to fresh water snails (*Melanopsis* spp.) grown in the waters of the Sea of Galilee and Hula Valley, in the north of Israel. Modern shells, grown at known temperatures agree with the Δ_{47} - T calibration of Zaarur et al. (2013). Fossil *Melanopsis* shells from 2 locations, Gesher Bnot Ya'aqov (at the southern tip of the Hula Valley) and the Sea of Galilee provide a temperature record for the region during the time interval of the past 20 kyrs. Glacial temperatures are ~ 5 °C cooler than mid-Holocene and ~ 3 °C cooler than modern, similar to other records in the region. These Δ_{47} -derived temperatures are combined with $\delta^{18}\text{O}$ of the shell carbonate to calculate the oxygen isotopic composition of the habitat waters. Contrary to global trends and other regional records, reconstructed $\delta^{18}\text{O}_{\text{water}}$ values increase from the late glacial through the Holocene. This reversed signal reflects a decrease in the relative contribution of snow-melt to the watershed post-LGM and a transition to a more rain dominated inflow. A fairly constant difference in $\delta^{18}\text{O}_{\text{water}}$ values between the Hula Valley and Sea of Galilee waters, suggests that the hydrological relationship of the two water bodies had remained constant, with the temperature changes playing only a minor role in the extent of evaporation of the Sea of Galilee relative to the Hula.

1. Introduction

Oxygen isotope compositions in lake carbonates provide important constraints on the paleolimnological, hydrological, and environmental conditions in terrestrial environments (Gat, 1995; Kolodny et al., 2005; Leng, 2006; Li and Ku, 1997). The oxygen isotope composition of a mineral, when precipitated at isotopic equilibrium, depends on both the temperature of mineral formation and the isotopic composition of the water in which it grows. Due to the complexity of hydrological variations controlling the oxygen isotopic composition of the relevant waters, $\delta^{18}\text{O}$ has an inherent limitation in its application to paleoclimate in the terrestrial environments. To deduce water $\delta^{18}\text{O}$ values, independent estimates of temperature are required. In some cases these may be obtained from other paleothermometers such as Mg/Ca or Sr/Ca in calcium carbonates or by the alkenone unsaturation method. These proxies, however, were designed primarily for marine settings and their use in lacustrine environments is not straightforward. Alternatively, inferring water temperature requires an independent estimate of the isotopic composition of the water. In the oceans, estimates of variations in continental ice volume provide a constraint on ocean water $\delta^{18}\text{O}$ values, and hence on surface or deep water temperatures at the glacial-interglacial time scale. On land, however, ice volume has only an indirect and partial control on freshwater $\delta^{18}\text{O}$. Carbonate clumped isotopes paleothermometry allows to derive the temperature of mineral formation and is independent of the isotopic composition of the water. These independent constraints on water temperatures allow to calculate $\delta^{18}\text{O}$ values of the respective waters.

The Quaternary climate of the Eastern Mediterranean, or Levant, has been the subject of many studies (as reviewed by Rambeau, 2010; Roberts et al., 2008; Robinson et al., 2006). Terrestrial climate in this region is directly influenced by the Mediterranean Sea and is thought

to have been so in the past (Bar-Matthews et al., 2003; Begin et al., 2004; Enzel et al., 2008; Roberts et al., 2008). This sea-land relationship therefore provides a concrete framework for the understanding of the terrestrial response to climate change.

This region is of particular interest in the context of Early Human behavior, response and adaptation to environmental change, as the Levant has been inhabited by Early Humans and is thought to have been the main route for the migration of Early Humans out of Africa (Bar-Yosef and Belfer-Cohen, 2013; Frumkin et al., 2011). It is generally thought that water availability plays a key role in human habitation, past and present, making the study of hydrological response to climate change relevant to both archeological studies in the region and to future climate change.

Today, precipitation in the Eastern Mediterranean occurs predominantly during the winter months. The Mediterranean Sea is the main vapor source with most rainstorms resulting from air derived from North East Atlantic fronts, that pass over Europe and then accumulate moisture from the warm waters of the Mediterranean Sea (Rindsberger et al., 1983). Occasionally precipitation is associated with sub-tropical air passing directly over the Mediterranean Sea (Dayan, 1986). A minor source of moisture that mostly affects Southern Israel, is the Red Sea Trough which is part of a Southern Indian Ocean low-pressure thermal system (Tsvieli and Zangvil, 2005). These modern climatic systems provide the framework for thinking of variations in the Late Quaternary climate system with the understanding that specific storm trajectories and rainfall patterns might have been different during glacial times.

Paleoclimate studies in this region include reconstructions based on foraminifera oxygen isotopes and alkenone unsaturation records in the Mediterranean Sea (Almogi-Labin et al., 2009; Martrat et al., 2004), speleothems (Affek et al., 2008; Bar-Matthews et al., 2003), lake sediments

(e.g., Kolodny et al., 2005), and pollen (Cheddadi and Rossignolstrick, 1995; Langgut et al., 2011; Rossignol-Strick and Paterne, 1999). Here we use carbonate clumped isotopes of fresh water gastropod shells (*Melanopsis* spp.) collected from Gesher Bnot Ya'aqov, at the southern tip of the Hula Valley and from the Sea of Galilee (Figure 1) to reconstruct the last glacial-Holocene temperatures and hydrological conditions in this region.

2. Methodology

2.1 Geological and hydrological settings

The modern Sea of Galilee is a fresh water monomictic lake in the Northern Jordan River Valley, Israel (Figure 1). The lake is a remnant of larger water-bodies that occupied the Kinnarot Basin during the Late Pleistocene-Early Holocene (Stein, 2014). Surface water temperatures range between 15 °C in winter and 29 °C in summer, with a mean annual temperature of ~24 °C (Serruya, 1978). The Sea of Galilee evolved as a flow-through lake with its most important inlet being the Jordan River that drains the Hula Valley, and flows into the Sea of Galilee from the north. Today, the Jordan River contributes about half of the total water input to the Sea of Galilee with the rest being direct rainfall and underwater springs (Gvirtzman, 2002). The Jordan River is predominantly fed by three karst springs: Dan (~50%), Banias (~25%) and Hatzbani (~25%) that are recharged by rainfall and snow melt from the Trans-Lebanon mountains (Gvirtzman, 2002). The Sea of Galilee is shallow (40 m at the deepest location) with a large surface area and is therefore subject to a high degree of water loss by evaporation (35% of input to the lake; Gvirtzman, 2002). The only natural outflow from the Sea of Galilee is through the Southern Jordan River outlet that flows towards the terminal Dead Sea. This southern outlet has been dammed since 1932, such that the modern-day lake is essentially terminal.

During the late Quaternary the Sea of Galilee was a freshwater lake that co-existed with hypersaline lakes filling the Dead Sea basin (e.g., Stein, 2001; Stein, 2014). The surface water elevation and the size of these lakes were determined by inflow/evaporation and local topography with topographic sills at the Yarmouk River delta and Wadi Malih (40 km south of the modern Sea of Galilee) at ~ 200 and ~ -260 m below sea level (bsl), respectively (Bartov et al., 2002; Hazan et al., 2005) separating the lakes when water levels dropped below these elevations. High water stands during the last glacial period led to the expansion of the Sea of Galilee and Lake Lisan (the precursor of the Dead Sea) so that they overflowed the sills (Hazan et al., 2005). Sea of Galilee water level reconstruction, performed by radiocarbon dating of paleo-lake shorelines, indicates fluctuations between ~220 and 175 m bsl during the past 40 kyrs (Hazan et al., 2005; Stein, 2014). The highest lake levels occurred between ~26 and ~24 ka BP when Lake Lisan and the Sea of Galilee converged. Two events of water level drop, at ~23.8 ka BP (the onset of Heinrich event H2), and at ~17 ka BP, resulted in lakes separation and a retreat to the approximate size and elevation of the modern lakes (Hazan et al., 2005). Abrupt events of smaller lake level change occurred also during the Bolling-Allerod and at the mid-Holocene (Stein, 2014).

Particularly relevant for this study is the dating of lake levels from the Ohalo-II archeological site to ~22 ka BP (Nadel et al., 2001), as we analyzed materials from the nearby Tel Beit Yerach and Shaldag Beach sites. The high quality of the preservation of both the structures and fragile materials at the Ohalo-II archeological site had been suggested to result from a quick and gentle burial shortly after human occupation at the site, leading to its abandonment (Nadel et al., 2001). The quick and gentle submergence hints to its proximity to the lake waters, and suggests a shallow water, evaporative environment. The depositional

environment during the H2 lake retreat was studied by Lev et al. (2014), who described the area as “lake margin”. We refer to samples of similar age from the nearby Shaldag Beach and Tel Beit Yerach as belonging to the “Sea of Galilee”, bearing in mind that they are not necessarily representative of the bulk lake waters, but rather the lake shore.

Lake Hula occupies the northern part of the Jordan River Valley, north of the Sea of Galilee at ~70 m asl (Figure 1). The shape of the lake is thought to have been approximately constant since its formation at the early Pleistocene (Horowitz, 1978). Prior to the artificial drainage of Lake Hula in 1957 the Jordan River flowed through the Hula Valley and created a shallow, marsh-like, lake environment. The paleo-hydrological setting of the Hula Valley has not been well studied such that it is not clear whether our sampling site (see below) belonged in the past to a shallow lake or to a slow flowing river; in either case, the geographical location implies that these water served as input to the Sea of Galilee. Here we refer to these samples according to their modern-day location, as collected from Gesher Bnot Ya’aqov, at the southern tip of the Hula Valley.

2.2 *Melanopsis* snails

Melanopsis snails are fresh water gastropods that are widespread in the entire Near East, including isolated springs in the deserts (Tchernov, 1975). They inhabit rivers, lakes and marshes, and are particularly abundant in habitats that are rich in succulent aquatic vegetation (Moshkovitz and Magaritz, 1987). They are rock dwellers and can be found at depths of up to ~10 m. In anaerobic muddy environments such as the Sea of Galilee they are restricted to the water surface at the shore (Tchernov, 1975). *Melanopsis* snails live for several years and feed on algae. Their aragonitic shell (roughly 0.5 x 1.5 cm in size) is coated by an organic layer that

erodes shortly after the snail dies (Lev et al., 2007). Two species were investigated in this study
Melanopsis costata (Olivier, 1804) and *Melanopsis buccinoidea* (Olivier, 1801). One sample,
from Gesher Yossef, was identified as a hybrid of *Melanopsis buccinoidea* x *costata* (also
described as *M. saulcy*; Bourguignat, 1853).

2.3 Sample collection

Modern *Melanopsis* snails were collected live together with their habitat water from the
Sea of Galilee, and from springs and streams along the Jordan River Valley (Figure 1). Water
temperatures measured at time of collection, spanned between 16 - 26 °C (Table 1). Note that
these water temperatures are summer temperatures and do not necessarily reflect the mean
temperature that the snails were exposed to during growth. Fossil shells were collected in 2 main
locations: The Jordan River banks (north of Gesher Bnot Ya'aqov, at the southern tip of the Hula
Valley), and the shores of the Sea of Galilee (a trench dug at Shaldag Beach at the Southern
shore of the Sea of Galilee, near the old lake outlet of the southern Jordan River, and from the
nearby shore deposits at the northern side of Tel Beit Yerach). The samples from the Sea of
Galilee were collected by Hazan et al. (2005). Additionally, a number of modern and fossil
bivalve shells (*Corbicula* sp. and an unknown species) were collected from the Jordan River and
Gesher Hapkek (Tables 1 and 2).

2.3. Analytical methods

High-resolution $\delta^{18}\text{O}$ analysis was performed in order to examine inner-shell variability
and potential biases due to growing season preferences. Shell material was sub-sampled for $\delta^{18}\text{O}$
analysis by continuous-drilling (using a New Wave Research Micromill) along the growth axis

of the shell from the aperture towards the apex. Sampling distance was defined by the powder fraction size of ~200 μg , required for the $\delta^{18}\text{O}$ measurements. The carbonate was digested using 103% H_3PO_4 at 25 °C using standard procedures for GasBench carbonate analysis. Water $\delta^{18}\text{O}$ was also analyzed using a GasBench system, through equilibration with 0.3% CO_2 in Helium. Water and shell $\delta^{18}\text{O}$ and shell $\delta^{13}\text{C}$ were measured using a Thermo DeltaPlus XP mass spectrometer. Typical precision per measurement is $\pm 0.10\text{‰}$, $\pm 0.08\text{‰}$ and $\pm 0.11\text{‰}$ for carbonate $\delta^{13}\text{C}$, carbonate $\delta^{18}\text{O}$, and water $\delta^{18}\text{O}$, respectively.

Bulk shells were used for carbonate clumped isotope analyses, using a procedure described previously (Affek and Eiler (2006); Huntington et al. (2009); Zaarur et al. (2011)). Briefly, each shell was sliced along the growth axis. One half was ground to powder using an agate mortar and pestle, providing more than enough powder for all replicate analyses. Aliquots (3-4 mg) of the powdered shell material were digested overnight in 103% H_3PO_4 at 25 °C. CO_2 was extracted cryogenically on a vacuum line and cleaned by passing through a GC column (Supelco Q-Plot, 30m x 0.53mm) at -20 °C. Measurements were performed using a Thermo MAT253 mass spectrometer. Each measurement consisted of 90 cycles of a sample-standard comparison, with an ion integration time of 20 seconds. Samples were measured in 3-7 replicates (aliquots of powdered shell). $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ were measured together with Δ_{47} and are reported using the VPDB scale (using a 25 °C acid digestion fractionation of 10.25‰ for $\delta^{18}\text{O}$; Kim et al., 2007a) as determined by a pre-calibrated Oztech CO_2 reference working gas, having $\delta^{13}\text{C}$ of -3.64‰ VPDB and $\delta^{18}\text{O}$ of 25.02‰ VSMOW, as confirmed by NBS19 IAEA standard analysis.

Standardization of Δ_{47} values was performed using analyses of a set of CO_2 gases that were heated at 1000 °C for 2 hours, resulting in random distribution of the heavy isotopes ($\Delta_{47}=0.027\text{‰}$; Wang et al., 2004), and regular analysis of in-house standards (Carrara marble,

cylinder CO₂, and CO₂ equilibrated with water at 25 °C and 50 °C) (see Supplementary Material for standardization details). Values are reported in the text using the absolute reference frame (Dennis et al., 2011). Additionally, Δ_{47} values in the original reference frame (Ghosh et al., 2006) are given in Tables 1 and 2 to facilitate comparison with previous studies. We apply the Peirce elimination criterion (Peirce, 1852; Ross, 2003), to the measured data to screen for replicate outliers (replicated measurements of a sample that are significantly different from the mean). Using this criterion we eliminate 3% of the measurements (5 out of 171). Unless otherwise noted, all reported uncertainties are standard errors based on the number of independent replicated sample aliquots. We reference our samples to the Δ_{47} –Temperature calibration of Zaarur et al. (2013); the calibration error is ± 2 °C. The uncertainties of $\delta^{18}\text{O}_{\text{carbonate}}$ are negligible relative to those of the Δ_{47} derived temperatures; we therefore calculate the $\delta^{18}\text{O}_{\text{water}}$ uncertainties (sections 4.2) based on the Δ_{47} derived temperature uncertainties.

Fossil sample ages were determined by ¹⁴C dating at the W.M. Keck Carbon cycle Accelerator Mass Spectrometry Laboratory, UC Irvine (following the methods described by Xu et al., 2007). All reported ages are calibrated using CalPal online program (<http://www.calpal-online.de>; Danzeglocke et al., 2012) and we refer to them in the text as ka BP. Shell mineralogy was determined by XRD (at the X-ray Crystallographic Facility, Yale University).

3. Results

3.1. ¹⁴C dating

Fossil samples were dated using radiocarbon measurements of the shells material; measured and calibrated ages are given in Table 2. Calibrated ages for samples of the Gesher Bnot Ya'aqov site range between $\sim 21.7 \pm 0.4$ ka BP and 0.7 ± 0.01 ka BP. One sample, from the

Musteric terrace, has a ^{14}C age greater than 50 ka BP, which is beyond the radiocarbon detection limit. Fossil samples from the Sea of Galilee, have calibrated ages of 5.6 ± 0.02 to 22.5 ± 0.3 ka BP, and the sample from Gesher Sheikh Hussaein (GSH) has an age of ~ 40.5 ka BP. A reservoir age of 2 kyrs for the Jordan River was determined through radiocarbon measurements of two modern shells (these specimens were not analyzed for Δ_{47}), Consistent with Lev et al. (2007). We use a reservoir age of 750 years for the Sea of Galilee, following Lev et al. (2007). Sea of Galilee samples had been previously dated by Hazan et al. (2005) using radiocarbon measurements of organic material that provide an independent constraint on the reservoir age. For the Hula valley, such materials were not available, but there is no evidence that the source of water and bedrock through which it flows was different in the past (e.g., basaltic versus limestone aquifer). We therefore assume that the reservoir ages in these locations are constant for the time period discussed.

The ages of the samples from the Sea of Galilee are consistent with the ^{14}C age measurements of Hazan et al. (2005) for these sites, and are related to the time intervals of relatively high water stands in the lake (Hazan et al., 2005). This implies, that although these samples represent a lake shoreline environment, making them more prone to evaporation than bulk lake water (see section 2.1), the environment captured by these samples is likely broadly representative of lake waters during high stand conditions.

3.2. Modern *Melanopsis* shells

Modern shell data is given in Table 1. Measured water $\delta^{18}\text{O}$ values and temperatures from the different sampling sites range between -4.97 to $+0.50$ ($\pm 0.11\text{‰}$) and 16 to 25 ± 0.5 $^{\circ}\text{C}$, respectively. Shell aragonite isotopic values range between $-1.31 \pm 0.04\text{‰}$ and $-6.94 \pm 0.05\text{‰}$

for $\delta^{18}\text{O}$ and between $-3.855 \pm 0.02\text{‰}$ and $-14.17 \pm 0.06 \text{‰}$ for $\delta^{13}\text{C}$. Δ_{47} values range between $0.758 \pm 0.012\text{‰}$ and $0.695 \pm 0.011\text{‰}$. As is common in these types of studies, this set of samples does not cover a temperature range that is sufficiently large to create an independent geochemical thermometer calibration. Instead, we use these samples in concert with the existing calibration, to test the applicability of the clumped isotopes thermometer to this material; we compare Δ_{47} - T relationship of modern shells that grew at known temperatures to the clumped isotopes thermometer calibration of Zaarur et al., (2013). For snail growth temperatures, we use our measured temperatures for spring grown shells, as spring water is expected to be constant year round due to the long residence time in the bedrock that allows for thermal equilibrium. The Sea of Galilee, has a large seasonal temperature variability (15-29 °C), hence, for this location we use the mean annual temperature. Within error, modern *Melanopsis* shells are consistent with the Zaarur et al., (2013) Δ_{47} - T calibration (Figure 2a), and we therefore conclude that this calibration can be used for fossil shells. Note that none of our shells, either modern or fossil, is likely to have grown at a temperature that is low enough to suffer from large uncertainty due to the choice of calibration (e.g., Zaarur et al., 2013 versus Henkes et al., 2013).

To test for variability among individual shells of the same species in the same location and over time, we compare 3 specimens from Gesher Bnot Ya'aqov (GBY) that were collected together in 2009, to a specimen collected (and therefore living) 6 years earlier at the same location (GBY 2003), and to a specimen collected in 2009 at Gesher Hapkak (GHP) ~4.5 km upstream of Gesher B'not Ya'aqov (GBY). Four of the five samples have Δ_{47} values that are indistinguishable from each other ($0.702 \pm 0.011\text{‰}$ to $0.709 \pm 0.015\text{‰}$, corresponding to 24-25 °C) and one sample, GBY-a, has a value of $0.695 \pm 0.011\text{‰}$ (corresponding to 27 °C). Even though this difference is within the average sample measurement uncertainty ($\pm 0.01\text{‰}$), it is

flagged as an outlier by the Peirce elimination criteria. No significant difference in $\delta^{18}\text{O}$ is observed, however, between these specimens.

To examine the potential for bias due to seasonal preference in shell secretion, we conducted high-resolution $\delta^{18}\text{O}$ analyses in individual shells. $\delta^{18}\text{O}$ values of the sample from the Sea of Galilee (*M. costata*) are high ($-0.80 \pm 0.55\text{‰}$) and show a strong seasonal variability; the shell $\delta^{18}\text{O}$ seasonality encompasses 2 annual cycles (Figure 2). $\delta^{18}\text{O}$ values of a shell (*M. costata*) from the Jordan River are ^{18}O -depleted relative to the Sea of Galilee ($-7.0 \pm 0.5\text{‰}$), also showing cyclic seasonal variability (Figure 2). $\delta^{18}\text{O}$ values of a shell (*M. buccinoidea*) from the Dan Spring are fairly constant with $\delta^{18}\text{O}$ values of $-6.5 \pm 0.3\text{‰}$, showing no evidence of seasonal variability; this is consistent with the stable spring water temperature and $\delta^{18}\text{O}$ composition (Figure 2). Shells from different habitats exhibited different patterns that reflect the environmental variability they were exposed to. The cyclical nature of the $\delta^{18}\text{O}$ signal suggests year round growth and that individual gastropod lives for about 2 years, such that bulk shell composition may be interpreted as reflecting mean annual conditions. We cannot exclude the possibility of a minor seasonal growth preference, in particular as a shell that lived ~2 years may have been collected after less (or slightly more) than a full growth cycle.

Shell carbon isotopes have been suggested to be in equilibrium with dissolved inorganic carbon (DIC) of the habitat water (Lev et al., 2007). Shells $\delta^{13}\text{C}$ values from most sites range between -8.1 and -9.3‰ . The DIC in these locations is dominated by the association of the water with a carbonate bedrock. The shell from the Gonen Spring, in which water is associated with basaltic rocks, has a lower $\delta^{13}\text{C}$ value (-14.2‰). Geinosar Beach, at the Sea of Galilee, has a higher $\delta^{13}\text{C}$ value (-3.9‰) that is likely associated with the substantial ^{12}C uptake by primary producers in the lake (Dubowski et al., 2003). The shell from Ein Tamar has a relatively high

$\delta^{13}\text{C}$ value (-5.3‰) that could reflect the local bedrock or the effect of primary productivity within the small pool where the spring water accumulate. $\delta^{13}\text{C}$ values are given in Table 1 but are not discussed further.

3.3 Last glacial-Holocene shells

Data of fossil shells are given in Table 2. The oxygen isotopic composition of *Melanopsis* shells from the Hula Valley range from -4.1 to -6.4‰, and in the Sea of Galilee from -4.8 to -0.5‰. Δ_{47} values of the Hula Valley indicate that water temperature in the late glacial (21.7-17.6 ka BP) was 23 ± 2 °C; temperatures then increase to 28 ± 1 °C in the early to mid-Holocene (10.2-5.9 ka BP). Two early Holocene (12.1 and 10.0 ka BP) Hula Valley bivalves have Δ_{47} values (0.686‰ and 0.705‰) that agree with those of the *Melanopsis* shells, providing further support for the consistency of these fresh water mollusks with the clumped isotope thermometer calibration. The temperatures derived from Δ_{47} in the Sea of Galilee are 21 ± 3 °C for the late glacial (22.5-22.0 ka BP) and 24 ± 4 °C in early-mid Holocene (7.6-5.6 ka BP). Sea of Galilee and Hula Valley temperatures are mostly consistent with each other; the regional temperatures derived from combining the data from the two water bodies are: 22 ± 2 °C for late glacial (22.5-17.6 ka BP), 27 ± 2 °C in the early to mid-Holocene (12.1-5.9 ka BP). One late Holocene (0.7 ka BP) sample has a temperature of 22 ± 2 °C.

One sample dated to ~40.5 ka BP was available from the Central Jordan River, at Gesher Sheikh Hussein, ~25 km south of the Sea of Galilee. This location is at the southern outlet of the Sea of Galilee and thus, is expected to be closely related in temperature to Sea of Galilee water, with perhaps a slight enrichment of $\delta^{18}\text{O}$ due to additional evaporation. One fossil shell was collected from the Mousterian terrace at the Gesher Bnot Ya'akov archaeological site;

radiocarbon measurements suggest that it is older than of 50 ka BP, beyond the range of radiocarbon dating. Due to the lack of continuity and age uncertainty of these samples, we report the data in Table 2 but do not discuss the data further.

4. Discussion

Paleoclimate in the Eastern Mediterranean-Levant region has been studied in the marine environment and in several terrestrial records (as reviewed by Rambeau, 2010; Roberts et al., 2008; Robinson et al., 2006). In comparing our data to these records the following patterns emerge (as discussed in detail in the following sections):

1) The amplitude of Glacial to Holocene temperature changes at the Hula Valley and Sea of Galilee are consistent with estimated sea surface temperature (SST) changes in the nearby Mediterranean Sea between these time intervals (Almogi-Labin et al., 2009; Martrat et al., 2004) as well as with terrestrial estimates from speleothems (Affek et al., 2014; McGarry et al., 2004). The absolute temperatures at the sites of this study are, however, significantly higher.

2) The late Glacial to Holocene trend in carbonate and water $\delta^{18}\text{O}$ compositions in our study area is opposite to the global deglaciation trend observed in Mediterranean Sea foraminifera (Almogi-Labin et al., 2009) or in the terrestrial records of Soreq Cave speleothems (Bar-Matthews et al., 2003) and Lake Lisan sediments (Kolodny et al., 2005).

4.1. Modern shells - seasonality and habitat

High-resolution $\delta^{18}\text{O}$ profiles of modern shells vary amongst the three sampled sites in a way that reflects the expected variability of water isotopic composition at the different types of habitats. The shell from Dan Spring has low $\delta^{18}\text{O}$ values and only little variability. This is

expected as the Dan Spring is fed by ^{18}O -depleted snow melt with a long residence time within the bedrock, yielding a stable temperature and water $\delta^{18}\text{O}$ composition which are not affected by individual precipitation events or by seasonality. *Melanopsis* shells were collected near the spring outlet in a shaded area, minimizing the possibility of temporal variations in $\delta^{18}\text{O}$ due to evaporation.

The Jordan River is fed by Dan, Banias, and Hatzbani springs and is therefore expected to reflect a combination of these waters. The high-resolution $\delta^{18}\text{O}$ of a shell from Gesher Bnot Ya'aqov has on average similar $\delta^{18}\text{O}$ values to that of the Dan Spring but exhibits some cyclical variations that likely reflect seasonal changes in evaporation from the Jordan River. The sampling site at Gesher Bnot Ya'aqov is not fully shaded and specimens were collected in shallow water. Temporal variations in temperature and $\delta^{18}\text{O}$ are expected due to the relative contribution of the several water sources, local surface water evaporation, and warming due to direct exposure to solar heating.

The Jordan River is a major water source to the Sea of Galilee (50%). Lake waters, however, are strongly affected by evaporation and the modern setting is practically that of a terminal lake (due to a dam at the main outlet). The shell from the Sea of Galilee has $\delta^{18}\text{O}$ values that are higher than Gesher B'not Ya'aqov and Dan Spring, and exhibit a strong seasonal signal. As typical for either terminal or flow-through lakes, the Sea of Galilee $\delta^{18}\text{O}$ water values are higher than its water source due to evaporation from the lake surface.

The high-resolution isotopic profiles thus reflect the type of seasonality characteristic of each hydrological setting and the full cycles suggest that *Melanopsis* shells grow year round. As clumped isotope measurements require a bulk shell analysis, the continuous secretion of shell material year round suggests that Δ_{47} would reflect mean annual conditions.

4.2. Clumped isotopes in modern *Melanopsis*

Δ_{47} values of modern *Melanopsis* shells grown at known temperatures are consistent, within error, with the carbonate clumped isotope thermometer calibration (Zaarur et al., 2013). The variability observed in *Melanopsis* shells around the thermometer calibration is similar to the variability of other biogenic carbonates (see figure 4 of Zaarur et al., 2013). Five specimens from the same location (GBY a,b,c, GBY 2003 and GHP), have Δ_{47} values that are indistinguishable from one another, indicating that the snails reliably record the same conditions and have similar shell growth patterns. No difference in Δ_{47} is observed between the two species, *M.costata* and *M. buccinoidea*.

We combine the temperatures derived from Δ_{47} with the $\delta^{18}\text{O}$ of the carbonate shell to calculate the isotopic composition of the water in which the shells grew, using the Kim et al. (2007b) aragonite-water fractionation calibration (Table 1). Calculated $\delta^{18}\text{O}_{\text{water}}$ values are generally consistent with measured $\delta^{18}\text{O}_{\text{water}}$ at the collection sites (Table 1). Isotopic fractionations (α) vary somewhat between the two species, with *M.costata* exhibiting fractionations that are closer to the Kim et al. (2007b) calibration and *M. buccinoidea* exhibit more variability and an average offset of $\sim 1.2 \pm 0.6\text{‰}$ from the Kim et al. (2007b) calibration (Figure 3b). The difference in $\delta^{18}\text{O}$ between the two species could result from differences in growth rates that effect the $\delta^{18}\text{O}$ but not Δ_{47} (Affek and Zaarur, 2014; Kluge et al., 2014; Tang et al., 2014), or perhaps from a vital effect associated with differences in $\delta^{18}\text{O}_{\text{water}}$ between the calcifying fluid and environmental water. While natural variability, measurement uncertainty, and the small size of our data set prevent us from creating an independent calibration for *Melanopsis* shells, the observations are sufficient to indicate that temperatures derived from

clumped isotopes can be used to derive water $\delta^{18}\text{O}_{\text{water}}$ with an estimated species specific oxygen isotope fractionation. Due to the apparent ^{18}O -depletion relative to Kim et al. (2007b), 1.2‰ is added to $\delta^{18}\text{O}_{\text{water}}$ calculated from fossil *M. buccinoidea* albeit with a relatively large uncertainty.

4.3. Late Glacial to Holocene temperatures

The amplitude of the late Glacial to Holocene warming we observe is of 5 °C increase between the late glacial and early- to mid-Holocene, consistent with Mediterranean Sea surface temperatures, as derived from alkenone unsaturation (Almogi-Labin et al., 2009; Martrat et al., 2004), and with Soreq Cave speleothems (Affek et al., 2008; Affek et al., 2014). In absolute terms, however, the temperatures we observe are 7-10 °C warmer than either the Mediterranean Sea surface or Soreq Cave. Similar temperature difference is also observed at present-day and is related to the different geographic setting, mostly elevation. Whereas Soreq Cave is at 400 m asl with mean annual temperatures of 18-19 °C, the Sea of Galilee is at ~212 m bsl, with a modern mean annual temperature of ~24 °C. A temperature gap similar to that in modern-day thus has been present also at the end of the last glacial period.

A glacial-interglacial warming of 5 °C is larger than that in the eastern tropical Atlantic (3.5 °C; Schneider et al., 1995). The larger amplitude is explained by the semi-enclosed basin effect of the Mediterranean Sea and the reduced moderating effect of the Atlantic Ocean during the glacial, compared to the Holocene (Almogi-Labin et al., 2009). Similar to the amplification of the Mediterranean Sea relative to the Atlantic Ocean, the amplitude of temperature change observed in our data can also be explained by an amplification effect of terrestrial surface water. Alternatively, higher temperatures may be the result of the *Melanopsis* recording lake waters that in some cases are warmer than air temperatures (Hren and Sheldon, 2012). In a survey of

multiple lakes, Hren and Sheldon (2012) noted that the mean annual temperature of lake surface water is typically higher than the respective mean annual air temperature; the effect being most pronounced in cold regions, and is small when air temperature is above 10 °C. This effect is likely insignificant in the relatively warm Levant, and may only be somewhat relevant in the Glacial. If so, the expectation would be a reduced glacial-interglacial temperature difference, contrary to our observations.

4.4. Paleohydrology

Changes in the isotopic composition of water can provide information about the hydrological evolution of the region. The temperatures derived from Δ_{47} are combined with the $\delta^{18}\text{O}$ of the aragonitic shells to calculate the isotopic composition of the water in which the snails grew (Figure 4). $\delta^{18}\text{O}_{\text{water}}$ values of Hula Valley water are $\sim -5.0 \pm 0.3\text{‰}$ in the late Glacial and increase to $\sim -2.9 \pm 0.8\text{‰}$ in the early to mid-Holocene. Sea of Galilee $\delta^{18}\text{O}_{\text{water}}$ values are $\sim -2.6 \pm 0.7\text{‰}$ in the late Glacial and are much more ^{18}O -enriched, up to $+1.5\text{‰}$, in the early to mid-Holocene. Two main features are apparent in the isotopic evolution of the two water bodies. First, unlike the uniformity of water temperatures in the two locations, but similar to the modern-day water composition, Sea of Galilee waters are ^{18}O -enriched relative to the Hula waters. Considering the coarse time resolution, the difference is fairly constant over time, at $\sim 4 \pm 1\text{‰}$, reflecting evaporative enrichment of the lake relative to the incoming water. Second, the $\delta^{18}\text{O}_{\text{water}}$ values in both locations are lower during the late Glacial relative to the Holocene. This is contrary to what would be expected if these waters followed the global trends in the oceans or the regional trends of the Mediterranean Sea and associated rainfall, in which glacial $\delta^{18}\text{O}_{\text{water}}$ values are higher than those in the Holocene, as a result of continental ice buildup.

4.4.1. $\delta^{18}\text{O}_{\text{water}}$ of Hula and Sea of Galilee

In the geological past, our sampling location at Gesher Bnot Ya'akov, may have resembled its modern hydrological setting of the slow flowing Jordan River; alternatively, it may have been a shallow lake or a swampy environment, similar to the early 20th century Lake Hula. Irrespective of its specific form, however, it has been a main water source to the Sea of Galilee (Horowitz, 1978). In the modern setting, the Sea of Galilee is ~5‰ more ^{18}O -enriched relative to the Hula water. This enrichment results from it being downstream of the Hula Valley and is due to a high evaporation flux from the lake surface. The damming of the lake in 1932 converted the Sea of Galilee from a flow-through to a terminal lake with enhanced evaporation (~35% of inflowing waters; Gvirtzman, 2002). Similarly, our data suggest that from the late Glacial through the Holocene, Sea of Galilee waters were $\sim 4 \pm 1$ ‰, more enriched relative to the Hula waters. The roughly constant difference in $\delta^{18}\text{O}_{\text{water}}$ between the two implies that their hydrological relationship had remained constant, with the glacial-interglacial increase in temperature playing only a minor role in enhancing evaporation of the Sea of Galilee relative to the Hula waters.

4.4.2. The direction of isotopic change

In comparing to global and regional glacial-interglacial $\delta^{18}\text{O}$ trends, our record shows a reverse signal with an isotopically depleted glacial relative to post-glacial. When considering potential causes for the reverse trend in $\delta^{18}\text{O}_{\text{water}}$ in our records, it is important to consider local hydrology and the different processes that can affect the $\delta^{18}\text{O}$ of the water. The Mediterranean Sea is the main source of moisture in this region today and was so also during glacial times, in

spite of a southward shift in the shoreline and storm trajectories, due to lower sea levels (Enzel et al., 2008). This is evident from the general shape of $\delta^{18}\text{O}$ trends in several regional terrestrial records that follow the trends and magnitude of Mediterranean Sea water (e.g., Bar-Matthews et al., 2003; Frumkin et al., 1999; Kolodny et al., 2005).

Carbonate $\delta^{18}\text{O}$ in marine (Almogi-Labin et al., 2009), speleothem (Bar-Matthews et al., 2003; Bar-Matthews et al., 2000), and lake (Kolodny et al., 2005) records in the region are consistent with the global trends of Glacial-Interglacial transition, with an amplification that is characteristic of the semi-enclosed Mediterranean basin. Kolodny et al. (2005) showed that for the past ~70 ka the differences in $\delta^{18}\text{O}$ between Mediterranean Sea foraminifera, Soreq Cave speleothems, and Lake Lisan sediments are constant leading to the conclusion that the terrestrial records are governed by the changes in Mediterranean Sea water that are transcribed into rainfall composition, albeit with local modifications. Furthermore, the $\delta^{18}\text{O}_{\text{carbonate}}$ record of the Yammoûneh Lake, in Lebanon (in the northern Levant) exhibits an isotopic trend similar to the global and regional Glacial-Interglacial changes, with late Glacial values being ~2‰ more ^{18}O -enriched than the Holocene (Develle et al., 2010). Our record is unique at displaying an opposite trend, namely of increasing $\delta^{18}\text{O}$ values through the Glacial to Holocene transition in both $\delta^{18}\text{O}_{\text{carbonate}}$ and calculated $\delta^{18}\text{O}_{\text{water}}$; this is observed more strongly in the Sea of Galilee record (Figure 4). Note that when examining the Glacial to Holocene transition in $\delta^{18}\text{O}_{\text{carbonate}}$, the change is a combination of variations in both temperature and $\delta^{18}\text{O}_{\text{water}}$. Δ_{47} -derived temperatures enable the isolation of the $\delta^{18}\text{O}_{\text{water}}$ component and in our case do not eliminate the opposite trend observed in the waters.

Paleo- $\delta^{18}\text{O}_{\text{water}}$ values of both sites in this study follow the same trend as the $\delta^{18}\text{O}_{\text{carbonate}}$, with Holocene waters that are isotopically enriched relative to the late Glacial waters (as

determined by a student-t test; Figure 4). Develle et al. (2010) used a compilation of literature temperature estimates to assess $\delta^{18}\text{O}_{\text{water}}$ composition in the Yammoûneh Lake, resulting in ^{18}O -enriched Holocene water relative to the late Glacial, similar to our observations. In contrast, $\delta^{18}\text{O}_{\text{water}}$ in Soreq Cave has Holocene waters that are ^{18}O -depleted relative to the late Glacial, but reflecting an attenuation of the trend observed in $\delta^{18}\text{O}_{\text{carbonate}}$ (Affek et al., 2008). A $\delta^{18}\text{O}_{\text{water}}$ reconstruction of Soreq Cave waters, as estimated by Develle et al. (2010), suggests Holocene values that are similar to the late Glacial (excluding the time period of the last Sapropel event) implying that the observed signal in the speleothem carbonate is driven predominantly by temperature changes rather than a change in the isotopic composition of the water.

As the Mediterranean Sea has been the main source of moisture throughout this time period in all 3 locations, any scenario explaining the opposite change in $\delta^{18}\text{O}_{\text{water}}$ observed in our record must reside within the local hydrological setting. We therefore suggest that the late Glacial-Holocene $\delta^{18}\text{O}_{\text{water}}$ shift is the result of a change in the form of precipitation and/or in evaporation fluxes.

Today, local precipitation in the Jordan River (which flows through the Hula Valley and into the Sea of Galilee) and in the Soreq Cave area is almost exclusively in the form of rain. Most of the water inflow into the Jordan River, however, is sourced in several springs that are fed by snowmelt from mountains to the north. Given the glacial temperatures, local precipitation was probably still predominantly in the form of rain but the relative contribution of snowmelt to the tributaries flowing into the Jordan River may have been larger. Snow is typically ^{18}O -depleted relative to rain, leading to lower $\delta^{18}\text{O}_{\text{water}}$ values during the Glacial without the need to invoke a change in either precipitation amount or moisture source. As temperatures increased in the Holocene, rain is likely to have become more dominant in the river inflow, such that the

reversed signal observed between the late Glacial and Holocene waters could reflect a transition from a snow dominated system to the snow-rain mixture observed today.

This scenario would also explain the Yammoûneh Lake $\delta^{18}\text{O}_{\text{water}}$ record that exhibits late Glacial values that are $\sim 3\text{‰}$ lower than Holocene and modern waters (Develle et al., 2010). Develle et al. (2010) interpret this reverse signal as reflecting one of several alternatives: an increased “continental effect” due to lower sea levels, increased amounts of rain during the late Glacial with the “amount effect” controlling the isotopic signal, or a steeper glacial lapse rate. A steeper lapse rate would result in colder precipitation and hence an increased proportion of precipitation in the form of snow, consistent with our interpretation. The Soreq Cave water input is expected to have been in the form of rain with no significant snow input also in the Glacial, as it is located further south and at low elevation; its water $\delta^{18}\text{O}$ values therefore follow the Mediterranean Sea and global $\delta^{18}\text{O}$ trends. A speleothem record from Mizpe Shelagim Cave, on Mount Hermon, the Southern end of the trans-Lebanon mountain range (Figure 1) and a source of snowmelt in the region, is similar to the Soreq Cave record (Ayalon et al., 2013). However, speleothems in this cave were not deposited during the LGM suggesting sub-freezing temperatures that again support a snow dominated system and increased snowmelt contribution at somewhat lower elevation in the Jordan River watershed. Speleothem data in Mizpe Shelagim Cave are available shortly after the LGM (~ 18 ka), such that the direction of post LGM isotopic change is observed, and is similar to that in Soreq Cave. This similarity is not surprising as the form of precipitation in the high elevation Mizpe Shelagim Cave is not expected to have shifted throughout this time period, and has been snow dominated both today and in the past.

A sensitivity test suggests that at least 10% decrease in snow contribution during the Holocene relative to the late Glacial is required to yield the observed reversed $\delta^{18}\text{O}_{\text{water}}$ trend. We

use the isotopic composition of modern-day precipitation on Mount Hermon (at Mitzpe Shelagim; Ayalon et al. 2013) to estimate the modern mass balance of water sources in the region. Precipitation $\delta^{18}\text{O}$ values range between -5‰ and -10.5‰ for the time period of 02/2001 – 04/2009; we infer these to be the rain and snow end-members of local precipitation. The balance is then derived by comparing these end-member values with the modern-day Dan spring water, which is fed directly from Mt. Hermon precipitation, and is the main tributary to the Jordan River.

The Dan Spring, with $\delta^{18}\text{O}$ value of -6.9‰, reflects an input of approximately 65% rain and 35% snow. Average modern Upper Jordan River waters have a $\delta^{18}\text{O}$ value of -4.8‰. The Jordan River water $\delta^{18}\text{O}$ is similar or slightly more ^{18}O -enriched than rainwater, and significantly more enriched than snow. The enrichment relative to the Dan spring must therefore indicate evaporative enrichment within the river system. To estimate the relative rain versus snow contribution during the glacial period, we assume the same sea-to-land isotopic difference as today (following Almogi-Labin et al, 2009), with marine carbonates being 2.5‰ more enriched during the late Glacial (Bar-Matthews et al, 2003). If the trend in marine carbonates is transcribed into an equivalent trend in the isotopic composition of precipitation (both rain and snow), resulting in estimated rain and snow values of -2.5‰ and -8‰, then the same relative contribution of snow and rain as modern would result in spring water of ~ -4.4 ‰. Mean water $\delta^{18}\text{O}$ value in the Jordan River between 17.6-21.7 ka BP, however, is -5.0‰, similar to the modern-day value, and similar or lower than the assumed spring waters. For river $\delta^{18}\text{O}$ value to have remained constant, it had to have been fed by a larger relative contribution of ^{18}O -depleted water from snowmelt. With no evaporative enrichment between spring and river waters, paleo-river waters of -5.0‰ thus require a minimum of 10% increase in snow contribution. Lower

glacial temperatures would have reduced the degree of water evaporation relative to today, but no evaporation at all is unlikely, such that the snowmelt contribution is likely to have been even higher.

The approximately constant difference between Hula and Sea of Galilee waters $\delta^{18}\text{O}$ values suggests that the Glacial to Holocene warming had a minimal effect on the evaporation flux out of the Sea of Galilee, relative to the incoming water from the Jordan River. The reversed Glacial-Interglacial $\delta^{18}\text{O}_{\text{water}}$ signal could, however, reflect the evolution of regional hydrology, with surface waters being more evaporated during the Holocene relative to the Glacial in both the Sea of Galilee and the Jordan River that feeds it.

Our Sea of Galilee samples are dated to time periods of relatively high water levels in the Sea of Galilee, during the last Glacial MIS2 and Holocene, although they all postdate the separation of Lake Lisan and Sea of Galilee, and hence represent a small lake. Evaporation from the small and shallow Sea of Galilee would result in further isotopic enrichment. Whereas a minor shift in precipitation form can easily explain the reverse signal in Glacial-Holocene (and modern) $\delta^{18}\text{O}_{\text{water}}$, increased evaporation from a smaller lake may serve to amplify the signal generated by a shift in precipitation form, and can also provide an alternative explanation to the observed isotopic trend.

5. Summary

In summary, our $\delta^{18}\text{O}$ and Δ_{47} measurements of modern *Melanopsis* shells suggests that the clumped isotope thermometer calibration is relevant to these materials, and that *Melanopsis* shells can be used in the fossil record to reconstruct terrestrial temperatures as well as paleo-water $\delta^{18}\text{O}$. We find that the amplitude of temperature change from the late Glacial to the present

is consistent with other regional records. Contrary to global and regional trends, however, our Glacial to Holocene $\delta^{18}\text{O}_{\text{water}}$ trend exhibit an increase in values, with an isotopically enriched Holocene relative to the Glacial. We interpret this reverse signal to represent a transition from a snowmelt to a rain dominated system.

Acknowledgments

We thank Einot Tzukim and Ein Gedi Israel National Parks for providing water and shell materials; Eric Lazo-Wasem and Lourdes Rojas from the Yale Peabody Museum of Natural History, Henk Mienes from Steinhardt National Collections of Natural History Department of Zoology Tel Aviv University and Adam Baldinger from the Harvard University Museum of Comparative Zoology for assistance in snail species identification. We thank Gerard Olack, Dominic Colosi, Glendon Husinger of the Earth System Center for Stable Isotope Studies for technical support. The work was supported by the National Science Foundation Grant NSF-EAR-0842482 to Hagit Affek.

References

- Affek, H.P., Bar-Matthews, M., Ayalon, A., Matthews, A., Eiler, J.M., 2008. Glacial/interglacial temperature variations in Soreq cave speleothems as recorded by 'clumped isotope' thermometry. *Geochimica et Cosmochimica Acta* 72, 5351-5360.
- Affek, H.P., Eiler, J.M., 2006. Abundance of mass 47 CO₂ in urban air, car exhaust, and human breath. *Geochimica et Cosmochimica Acta* 70, 1-12.
- Affek, H.P., Matthews, A., Ayalon, A., Bar-Matthews, M., Burstyn, Y., Zaarur, S., Zilberman, T., 2014. Accounting for kinetic isotope effects in Soreq Cave (Israel) speleothems. *Geochimica et Cosmochimica Acta* 143, 303-318.
- Affek, H.P., Zaarur, S., 2014. Kinetic isotope effect in CO₂ degassing: insight from clumped and oxygen isotopes in laboratory precipitation experiments. *Geochimica et Cosmochimica Acta* 143, 319-330.
- Almogi-Labin, A., Bar-Matthews, M., Shriki, D., Kolosovsky, E., Paterne, M., Schilman, B., Ayalon, A., Aizenshtat, Z., Matthews, A., 2009. Climatic variability during the last similar to 90 ka of the southern and northern Levantine Basin as evident from marine records and speleothems. *Quaternary Science Reviews* 28, 2882-2896.
- Ayalon, A., Bar-Matthews, M., Frumkin, A., Matthews, A., 2013. Last Glacial warm events on Mount Hermon: the southern extension of the Alpine karst range of the east Mediterranean. *Quaternary Science Reviews* 59, 43-56.
- Bar-Matthews, M., Ayalon, A., Gilmour, M., Matthews, A., Hawkesworth, C.J., 2003. Sea-land oxygen isotopic relationships from planktonic foraminifera and speleothems in the Eastern Mediterranean region and their implication for paleorainfall during interglacial intervals. *Geochimica Et Cosmochimica Acta* 67, 3181-3199.
- Bar-Matthews, M., Ayalon, A., Kaufman, A., 2000. Timing and hydrological conditions of Sapropel events in the Eastern Mediterranean, as evident from speleothems, Soreq cave, Israel. *Chemical Geology* 169, 145-156.

589 Bar-Yosef, O., Belfer-Cohen, A., 2013. Following Pleistocene road signs of human dispersals
590 across Eurasia. *Quaternary International* 285, 30-43.

591 Bartov, Y., Stein, M., Enzel, Y., Agnon, A., Reches, Z., 2002. Lake levels and sequence
592 stratigraphy of Lake Lisan, the late Pleistocene precursor of the Dead Sea. *Quaternary Research*
593 57, 9-21.

594 Begin, Z.B., Stein, M., Katz, A., Machlus, M., Rosenfeld, A., Buchbinder, B., Bartov, Y., 2004.
595 Southward migration of rain tracks during the last glacial, revealed by salinity gradient in Lake
596 Lisan (Dead Sea rift). *Quaternary Science Reviews* 23, 1627-1636.

597 Bourguignat, J., 1853. *Catalogue raisonné des mollusques terrestres et fluviatiles recueillis par*
598 *M. F. de Saulcy pendant son voyage en Orient.*, Paris: Gide & Baudry.

599 Cheddadi, R., Rossignolstrick, M., 1995. Eastern Mediterranean Quaternary paleoclimates from
600 pollen and isotope records of marine cores in the Nile cone area. *Paleoceanography* 10, 291-300.

601 Danzeglocke, U., Jöris, O., Weninger, B., 2012. CalPal-2007^{online} (online version), CalPal-
602 2007^{online}. <http://www.calpal-online.de/>.

603 Dayan, U., 1986. Climatology of back trajectories from Israel based on synoptic analysis. *Journal*
604 *of Climate and Applied Meteorology* 25, 591-595.

605 Dennis, K.J., Affek, H.P., Passey, B.H., Schrag, D.P., Eiler, J.M., 2011. Defining an absolute
606 reference frame for 'clumped' isotope studies of CO₂. *Geochimica Et Cosmochimica Acta* 75,
607 7117-7131.

608 Develle, A.-L., Herreros, J., Vidal, L., Sursock, A., Gasse, F., 2010. Controlling factors on a
609 paleo-lake oxygen isotope record (Yammouneh, Lebanon) since the Last Glacial Maximum.
610 *Quaternary Science Reviews* 29, 865-886.

611 Dubowski, Y., Erez, J., Stiller, M., 2003. Isotopic paleolimnology of Lake Kinneret. *Limnology*
612 *and Oceanography* 48, 68-78.

613 Enzel, Y., Arnit, R., Dayan, U., Crouvi, O., Kahana, R., Ziv, B., Sharon, D., 2008. The climatic
614 and physiographic controls of the eastern Mediterranean over the late Pleistocene climates in the
615 southern Levant and its neighboring deserts. *Global and Planetary Change* 60, 165-192.

616 Frumkin, A., Bar-Yosef, O., Schwarcz, H.P., 2011. Possible paleohydrologic and paleoclimatic
617 effects on hominin migration and occupation of the Levantine Middle Paleolithic. *Journal of*
618 *Human Evolution* 60, 437-451.

619 Frumkin, A., Ford, D.C., Schwarcz, H.P., 1999. Continental oxygen isotopic record of the last
620 170,000 years in Jerusalem. *Quaternary Research* 51, 317-327.

621 Gat, J.R., 1995. Stable Isotopes of Fresh and Saline Lakes, in: Lerman, A., Imboden, D.M., Gat,
622 J.R. (Eds.), *Physics and Chemistry of Lakes*. Springer Berlin Heidelberg, pp. 139-165.

623 Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W.F., Schauble, E.A., Schrag, D., Eller, J.M.,
624 2006. $^{13}\text{C}^{18}\text{O}$ bonds in carbonate minerals: A new kind of paleothermometer. *Geochimica Et*
625 *Cosmochimica Acta* 70, 1439-1456.

626 Gvirtzman, H., 2002. Israel water resources. *Chapters in Hydrology and Environmental*
627 *Sciences*. Yad Ben-Zvi Press, Jerusalem.

628 Hazan, N., Stein, M., Agnon, A., Marco, S., Nadel, D., Negendank, J.F.W., Schwab, M.J., Neev,
629 D., 2005. The late quaternary limnological history of Lake Kinneret (Sea of Galilee), Israel.
630 *Quaternary Research* 63, 60-77.

631 Henkes, G.A., Passey, B.H., Wanamaker, A.D., Jr., Grossman, E.L., Ambrose, W.G., Jr., Carroll,
632 M.L., 2013. Carbonate clumped isotope compositions of modern marine mollusk and brachiopod
633 shells. *Geochimica Et Cosmochimica Acta* 106, 307-325.

634 Horowitz, A., 1978. The Quaternary evolution of the Jordan Valley, in: Serruya, C. (Ed.), *Lake*
635 *Kinnerat, Monografiae Biologicae*.

636 Hren, M.T., Sheldon, N.D., 2012. Temporal variations in lake water temperature:
637 Paleoenvironmental implications of lake carbonate $\delta^{18}\text{O}$ and temperature records. *Earth and*
638 *Planetary Science Letters* 337, 77-84.

639 Huntington, K.W., Eiler, J.M., Affek, H.P., Guo, W., Bonifacie, M., Yeung, L.Y., Thiagarajan,
 640 N., Passey, B., Tripathi, A., Daeron, M., Came, R., 2009. Methods and limitations of 'clumped'
 641 CO₂ isotope Δ_{47} analysis by gas-source isotope ratio mass spectrometry. *Journal of Mass*
 642 *Spectrometry* 44, 1318-1329.

643 Kim, S.-T., Mucci, A., Taylor, B.E., 2007a. Phosphoric acid fractionation factors for calcite and
 644 aragonite between 25 and 75 degrees C: Revisited. *Chemical Geology* 246, 135-146.

645 Kim, S.T., O'Neil, J.R., Hillaire-Marcel, C., Mucci, A., 2007b. Oxygen isotope fractionation
 646 between synthetic aragonite and water: Influence of temperature and Mg²⁺ concentration.
 647 *Geochimica Et Cosmochimica Acta* 71, 4704-4715.

648 Kluge, T., Affek, H.P., Dublyansky, Y., Spoetl, C., 2014. Devils Hole paleotemperatures and
 649 implications for oxygen isotope equilibrium fractionation. *Earth and Planetary Science Letters*
 650 400, 251-260.

651 Kolodny, Y., Stein, M., Machlus, M., 2005. Sea-Rain-Lake relation in the Last Glacial East
 652 Mediterranean revealed by a $\delta^{18}\text{O}$ $\delta^{13}\text{C}$ in Lake Lisan aragonites. *Geochimica Et Cosmochimica*
 653 *Acta* 69, 4045-4060.

654 Langgut, D., Almogi-Labin, A., Bar-Matthews, M., Weinstein-Evron, M., 2011. Vegetation and
 655 climate changes in the South Eastern Mediterranean during the Last Glacial-Interglacial cycle
 656 (86 ka): new marine pollen record. *Quaternary Science Reviews* 30, 3960-3972.

657 Leng, M.J., 2006. *Isotopes in palaeoenvironmental research*. Springer, Dordrecht.

658 Lev, L., Almogi-Labin, A., Mischke, S., Ito, E., Ben-Avraham, Z., Stein, M., 2014.
 659 Paleohydrology of Lake Kinneret during the Heinrich event H2. *Palaeogeography*
 660 *Palaeoclimatology Palaeoecology* 396, 183-193.

661 Lev, L., Boaretto, E., Heller, J., Marco, S., Stein, M., 2007. The feasibility of using *Melanopsis*
 662 shells as radiocarbon chronometers, Lake Kinneret, Israel. *Radiocarbon* 49, 1003-1015.

663 Li, H.C., Ku, T.L., 1997. $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ covariance as a paleohydrological indicator for closed-basin
 664 lakes. *Palaeogeography Palaeoclimatology Palaeoecology* 133, 69-80.

665 Martrat, B., Grimalt, J.O., Lopez-Martinez, C., Cacho, I., Sierro, F.J., Flores, J.A., Zahn, R.,
 666 Canals, M., Curtis, J.H., Hodell, D.A., 2004. Abrupt temperature changes in the Western
 667 Mediterranean over the past 250,000 years. *Science* 306, 1762-1765.

668 McGarry, S., Bar-Matthews, M., Matthews, A., Vaks, A., Schilman, B., Ayalon, A., 2004.
 669 Constraints on hydrological and paleotemperature variations in the Eastern Mediterranean region
 670 in the last 140 ka given by the delta D values of speleothem fluid inclusions. *Quaternary Science*
 671 *Reviews* 23, 919-934.

672 Moshkovitz, S., Magaritz, M., 1987. Stratigraphy and isotope records of middle and late
 673 Pleistocene mollusks from a continuous corehole in the hula basin, northern Jordan Valley,
 674 Israel. *Quaternary Research* 28, 226-237.

675 Nadel, D., Belitzky, S., Boaretto, E., Carmi, I., Heinemeier, J., Werker, E., Marco, S., 2001. New
 676 dates from submerged Late Pleistocene sediments in the Southern Sea of Galilee, Israel.
 677 *Radiocarbon* 43, 1167-1178.

678 Olivier, G., 1801. *Voyage dans l'Empire Ottoman, l'Egypte et la Perse*, Paris: Agasse.

679 Olivier, G., 1804. *Voyage dans l'Empire Ottoman, l'Egypte et la Perse*, Paris: Agasse.

680 Peirce, B., 1852. Criterion for the rejection of doubtful observations. *Astronomical Journal* 45,
 681 161-163.

682 Rambeau, C.M.C., 2010. Palaeoenvironmental reconstruction in the Southern Levant: synthesis,
 683 challenges, recent developments and perspectives. *Philosophical Transactions of the Royal*
 684 *Society a-Mathematical Physical and Engineering Sciences* 368, 5225-5248.

685 Rindsberger, M., Magaritz, M., Carmi, I., Gilad, D., 1983. The relation between air-mass
 686 trajectories and the water isotope composition of rain in the Mediterranean-Sea area.
 687 *Geophysical Research Letters* 10, 43-46.

688 Roberts, N., Jones, M.D., Benkaddour, A., Eastwood, W.J., Filippi, M.L., Frogley, M.R., Lamb,
 689 H.F., Leng, M.J., Reed, J.M., Stein, M., Stevens, L., Valero-Garces, B., Zanchetta, G., 2008.

690 Stable isotope records of Late Quaternary climate and hydrology from Mediterranean lakes: the
691 ISOMED synthesis. *Quaternary Science Reviews* 27, 2426-2441.

692 Robinson, S.A., Black, S., Sellwood, B.W., Valdes, P.J., 2006. A review of palaeoclimates and
693 palaeoenvironments in the Levant and Eastern Mediterranean from 25,000 to 5000 years BP:
694 setting the environmental background for the evolution of human civilisation. *Quaternary*
695 *Science Reviews* 25, 1517-1541.

696 Ross, S.M., 2003. Peirce's criterion for the elimination of suspect experimental data. *Journal of*
697 *Engineering Technology* 20, 38-41.

698 Rossignol-Strick, M., Paterne, M., 1999. A synthetic pollen record of the eastern Mediterranean
699 sapropels of the last 1 Ma: implications for the time-scale and formation of sapropels. *Marine*
700 *Geology* 153, 221-237.

701 Schneider, R.R., Muller, P.J., Ruhland, G., 1995. Late Quaternary surface circulation in the East
702 Equatorial South-Atlantic - evidence from alkenone sea-surface temperatures. *Paleoceanography*
703 10, 197-219.

704 Serruya, C., 1978. *Lake Kinneret*. W. Junk, The Hague ; Boston.

705 Stein, M., 2001. The sedimentary and geochemical record of Neogene-Quaternary water bodies
706 in the Dead Sea Basin - inferences for the regional paleoclimatic history. *Journal of*
707 *Paleolimnology* 26, 271-282.

708 Stein, M., 2014. Late Quaternary limnological history, in: Zohary, T., Sukenik, A., Berman, T.,
709 Nishri, A. (Eds.), *Lake Kinneret, ecology and management*. Springer.

710 Tang, J., Dietzel, M., Fernandez, A., Tripathi, A.K., Rosenheim, B.E., 2014. Evaluation of kinetic
711 effects on clumped isotope fractionation (Δ_{47}) during inorganic calcite precipitation. *Geochimica*
712 *Et Cosmochimica Acta* 134, 120-136.

713 Tchernov, E., 1975. The molluscs of the Sea of Galilee. *Malacologia* 15, 147-184.

714 Tsvieli, Y., Zangvil, A., 2005. Synoptic climatological analysis of 'wet' and 'dry' Red Sea
715 Troughs over Israel. *International Journal of Climatology* 25, 1997-2015.

716 Wang, Z.G., Schauble, E.A., Eiler, J.M., 2004. Equilibrium thermodynamics of multiply
717 substituted isotopologues of molecular gases. *Geochimica Et Cosmochimica Acta* 68, 4779-
718 4797.

719 Xu, X., Trumbore, S.E., Zheng, S., Southon, J.R., McDuffee, K.E., Luttgen, M., Liu, J.C., 2007.
720 Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets:
721 Reducing background and attaining high precision. *Nuclear Instruments & Methods in Physics*
722 *Research Section B-Beam Interactions with Materials and Atoms* 259, 320-329.

723 Zaarur, S., Affek, H.P., Brandon, M.T., 2013. A revised calibration of the clumped isotope
724 thermometer. *Earth and Planetary Science Letters* 382, 47-57.

725 Zaarur, S., Olack, G., Affek, H.P., 2011. Paleo-environmental implication of clumped isotopes in
726 land snail shells. *Geochimica et Cosmochimica Acta* 75, 6859-6869.

727

728

729 Table 1. Isotopic data of modern *Melanopsis* shells

730

731 GBY are samples from Gesher Bnot Ya'aqov, GHP is Gesher Hapkak, BIV is a bivalve sample.

732 * Published mean annual value (Serruya, 1978).

733 Ghosh and abs refers to the Ghosh et al. (2006) and absolute reference frame (Dennis et al.,
734 2011), respectively.

735 Carbonate and water values are references to the VPDB and VSNOW standards respectively.

736 Table 2. Isotopic data of fossil *Melanopsis* samples.

737

738 GBY are samples from Gesher Bnot Ya'aqov, BY and JR samples are from the Sea of Galilee
739 and GSH is the sample from Gesher Sheikh Huseain. BIV are bivalve samples.

740 Ghosh and abs refers to Ghosh et al. (2006) and absolute reference frame (Dennis et al., 2011),
741 respectively.

742 Carbonate and water values are references to the VPDB and VSNOW standards respectively.

743

Figure captions:

Figure 1. Map of study area and sample collection sites. (1) Mount Hermon; (2) Dan Spring; (3) Gesher Yosef; (4) Hula Basin; (5) Gesher B'not Ya'akov and Gesher Hapkek; (6) Gonen Spring; (7) Geinosar Beach; (8) Beit Yerach; (9) Ma'agan Beach; (10) Soreq cave; (11) Ein Gedi; (12) Ein Tamar.

Figure 2. High resolution $\delta^{18}\text{O}$ of modern *Melanopsis* shells from the Sea of Galilee (a), Gesher Bnot Ya'aqov (b) and Dan Spring (c). Black lines are running mean of the data of a 5 points average.

Figure 3. Δ_{47} (a) and $\delta^{18}\text{O}$ (b) of *Melanopsis* shell aragonite compared to the temperature dependence of the carbonate clumped isotope thermometer calibration (Zaarur et al., 2013) and of the oxygen isotope fractionation ($1000\ln^{18}\alpha$) thermometer calibration (Kim et al., 2007b). Average error bars given are $\pm 2\sigma$. All Δ_{47} are given in the absolute reference frame.

Figure 4. A comparison of (a) temperature records from *Melanopsis* (Mel.) and from the Hula Valley and sea of Galilee to temperature records from the Mediterranean Sea (Almogi-Labin et al., 2009) and Soreq Cave (Affek et al., 2014); (b) $\delta^{18}\text{O}_{\text{carbonate}}$ of *Melanopsis* (Mel.) shells and speleothem from Soreq Cave (Bar-Matthews et al., 2003); (c) $\delta^{18}\text{O}_{\text{water}}$ of calculated paleo-waters of the Hula and Sea of Galilee. Red diamonds and blue circles represent *Melanopsis* samples from the Sea of Galilee and the Jordan River respectively. Small green circles in (a) and black line in (b) and (c) represent Soreq cave data.

Table 1

Sample	Species	n	$\delta^{18}\text{O}_c$ [‰]	$\delta^{13}\text{C}_c$ [‰]	Δ_{47} (Ghosh) [‰]	Δ_{47} , abs [‰]	Temp. (Δ_{47}) °C	Temp. Measured °C	$\delta^{18}\text{O}_{\text{water}}$ Calculated [‰]	$\delta^{18}\text{O}_{\text{water}}$ Measured [‰]
Ein Gedi	<i>Melanopsis buccinoidea</i>	5	-6.05 ± 0.02	-9.23 ± 0.05	0.647 ± 0.006	0.707	24.3 ± 1.5	23	-4.59 ± 0.3	-2.99
Ein Tamar	<i>Melanopsis buccinoidea</i>	3	-6.94 ± 0.05	-5.32 ± 0.01	0.655 ± 0.003	0.716	22.2 ± 0.8	25	-5.91 ± 0.2	-3.50
Ma'agan Beach*	unidentified	5	-1.31 ± 0.04	-3.85 ± 0.02	0.651 ± 0.015	0.711	23.6 ± 3.6	24	0.01 ± 0.7	0.50
Gonen Spring	<i>Melanopsis buccinoidea</i>	5	-6.20 ± 0.02	-14.17 ± 0.06	0.653 ± 0.013	0.713	23.0 ± 3.2	22	-5.02 ± 0.6	-4.19
Dan Spring	<i>Melanopsis buccinoidea</i>	5	-6.02 ± 0.03	-8.87 ± 0.05	0.695 ± 0.012	0.758	13.1 ± 2.6	16	-6.91 ± 0.6	-4.97
Gesher Yosef	<i>Melanopsis buccinoidea</i> x <i>costata</i>	7	-6.41 ± 0.04	-8.80 ± 0.06	0.654 ± 0.004	0.714	22.6 ± 1.0	21	-5.30 ± 0.2	-3.50
GHP	<i>Melanopsis costata</i>	3	-6.33 ± 0.06	-8.78 ± 0.03	0.645 ± 0.008	0.705	24.7 ± 2.0	22	-4.79 ± 0.4	-4.58
GBY 2003	<i>Melanopsis buccinoidea</i>	3	-6.48 ± 0.03	-12.58 ± 0.02	0.642 ± 0.011	0.702	25.6 ± 2.8		-4.77 ± 0.6	
GBY 1 c	<i>Melanopsis costata</i>	6	-6.33 ± 0.04	-9.08 ± 0.06	0.649 ± 0.015	0.709	24.1 ± 3.6	21	-4.91 ± 0.7	-4.42
GBY 1 b	<i>Melanopsis costata</i>	4	-6.86 ± 0.03	-8.73 ± 0.04	0.645 ± 0.007	0.705	24.7 ± 1.7	21	-5.32 ± 0.3	-4.42
GBY 1 a	<i>Melanopsis costata</i>	5	-6.40 ± 0.02	-9.32 ± 0.03	0.636 ± 0.011	0.695	27.2 ± 2.7	21	-4.37 ± 0.5	-4.42
GHP BIV	unidentified	3	-6.66 ± 0.01	-14.42 ± 0.09	0.624 ± 0.005	0.683	30.2 ± 1.4	22	-4.04 ± 0.3	-4.58

Table 2

Sample	Species	^{14}C yr BP	Calibrated Age Ka	n	$\delta^{18}\text{O}_e$ [‰]	$\delta^{13}\text{C}_e$ [‰]	Δ_{47} (Ghashk) [‰]	$\Delta_{47, \text{abs}}$ [‰]	Temp [°C]	$\delta^{18}\text{O}$ (water) [‰]
GBY 8	<i>Melanopsis costata</i>	2740 ± 15	0.7 ± 0.01	4	-4.48 ± 0.03	-1.27 ± 0.04	0.657 ± 0.010	0.717	22.0 ± 2.4	-3.5 ± 0.5
GBY 7	<i>Melanopsis costata</i>	7180 ± 15	5.9 ± 0.01	4	-5.40 ± 0.03	-4.13 ± 0.03	0.634 ± 0.009	0.693	27.7 ± 2.2	-3.3 ± 0.4
GBY 5b	<i>Melanopsis costata</i>	7315 ± 20	6.1 ± 0.07	5	-4.10 ± 0.04	-3.24 ± 0.06	0.625 ± 0.008	0.684	29.9 ± 2.1	-1.5 ± 0.4
GBY 9b	<i>Melanopsis costata</i>	8610 ± 25	7.5 ± 0.02	5	-5.62 ± 0.03	-1.79 ± 0.05	0.636 ± 0.011	0.696	27.1 ± 2.8	-3.6 ± 0.5
GBY 5a	<i>Melanopsis costata</i>	10375 ± 20	9.4 ± 0.05	4	-5.67 ± 0.04	-2.50 ± 0.12	0.635 ± 0.009	0.694	27.5 ± 2.3	-3.6 ± 0.4
GBY 4b	<i>Melanopsis costata</i>	10940 ± 25	10.1 ± 0.09	6	-5.41 ± 0.05	-3.72 ± 0.06	0.644 ± 0.009	0.704	25.1 ± 2.3	-3.8 ± 0.5
GBY 4a	<i>Melanopsis costata</i>	10985 ± 25	10.1 ± 0.09	5	-4.67 ± 0.08	-2.55 ± 0.03	0.632 ± 0.012	0.691	28.3 ± 3.2	-2.4 ± 0.6
GBY 9a	<i>Melanopsis costata</i>	11050 ± 25	10.2 ± 0.01	4	-4.64 ± 0.05	-1.07 ± 0.08	0.632 ± 0.007	0.691	28.1 ± 1.9	-2.4 ± 0.4
GBY 6	<i>Melanopsis costata</i>	16485 ± 40	17.6 ± 0.24	4	-6.41 ± 0.02	-6.71 ± 0.02	0.656 ± 0.012	0.716	22.2 ± 2.8	-5.4 ± 0.6
GBY 3b	<i>Melanopsis costata</i>	19270 ± 60	20.7 ± 0.28	6	-6.17 ± 0.05	-7.34 ± 0.06	0.647 ± 0.009	0.707	24.6 ± 3.5	-4.7 ± 0.7
GBY 3a	<i>Melanopsis costata</i>	20030 ± 70	21.7 ± 0.36	5	-5.89 ± 0.03	-7.49 ± 0.03	0.660 ± 0.009	0.721	21.1 ± 2.2	-5.1 ± 0.5
GBY MT	<i>Melanopsis corrugata</i>	>48500 ± 0	50.0 ± 0.00	4	-7.22 ± 0.02	-6.47 ± 0.03	0.640 ± 0.008	0.700	26.1 ± 2.0	-5.4 ± 0.4
BY 1-5b	<i>Melanopsis costata</i>	5700 ± 20	5.6 ± 0.02	5	-0.64 ± 0.03	-1.64 ± 0.04	0.634 ± 0.010	0.693	27.7 ± 2.5	1.5 ± 0.5
JR 8-1	<i>Melanopsis costata</i>	7540 ± 20	7.6 ± 0.02	5	-0.51 ± 0.03	-0.98 ± 0.04	0.665 ± 0.009	0.726	20.1 ± 2.3	0.1 ± 0.5
JR 8-1 b	<i>Melanopsis costata</i>	7540 ± 20	7.6 ± 0.00	3	-1.70 ± 0.07	-2.42 ± 0.09	0.646 ± 0.002	0.706	24.6 ± 0.6	-0.2 ± 0.1
BY 1-4	<i>Melanopsis buccinoidea</i>	19020 ± 60	22.0 ± 0.32	5	-4.79 ± 0.04	-7.28 ± 0.02	0.671 ± 0.008	0.732	18.6 ± 1.9	-3.3 ± 0.8
BY 1-1	<i>Melanopsis buccinoidea</i>	19510 ± 60	22.5 ± 0.29	5	-4.11 ± 0.05	-7.34 ± 0.06	0.656 ± 0.02	0.716	22.5 ± 4.4	-1.8 ± 0.3
GSH	<i>Melanopsis buccinoidea</i>	36390 ± 400	40.5 ± 0.89	5	-2.80 ± 0.14	-4.80 ± 0.07	0.661 ± 0.010	0.721	21.1 ± 2.5	-0.8 ± -0.7
GBY 4 BIV	unidentified	11195 ± 25	10.0 ± 0.09	3	-6.67 ± 0.03	-7.39 ± 0.09	0.646 ± 0.018	0.705	24.9 ± 4.4	-5.1 ± 0.9
GBY 5 BIV	<i>Corbicula spec.</i>	12605 ± 30	12.1 ± 0.17	3	-6.72 ± 0.04	-7.49 ± 0.07	0.627 ± 0.012	0.686	29.6 ± 3.2	-4.2 ± 0.6

Figure 1

Figure 2

Figure 3

Figure 4