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Research Report

Interpreting stable isotope records from freshwater snail shell carbonate: a Holocene case study from Lake Gölhisar, Turkey.

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Abstract

The oxygen and carbon stable isotope ratios from fossil snail shells within a small intramontane lake in Southwest Turkey are used to highlight the potential, and problems, of using freshwater snail carbonate as a palaeoenvironmental proxy. Two species (*Gyraulus piscinarum* and *Valvata cristata*) yielded different isotope ratios at the same sampling intervals, probably due to differences in water isotope composition between different microhabitats. Isotope ratios from a number of individual shells from the same sampling intervals (representing ~7-25 years), show large ranges (up to 8 ‰ for δ^{18} O) for each species. Only by analysis of a significant number of species specific shells (>5) from each sampling interval can a true understanding of environmental change be obtained. Averages of the data provide an insight into longer-term climatic variation whilst the ranges provide an estimate of short-term (decadal) environmental variability.

Keywords

Freshwater snails, oxygen isotopes, carbon isotopes, Turkey, lakes.

Introduction

Fossil freshwater mollusc shells are widespread in Quaternary lacustrine deposits. As the oxygen and carbon stable isotope values of snail-shell carbonate ($\delta^{18}O_{snail}$, $\delta^{13}C_{snail}$) generally reflect the isotopic composition of lake-water (Fritz & Poplawski 1974, Leng *et al.*, 1999a), they are potentially a powerful tool for palaeoenvironmental reconstruction (Siegenthaler and Eicher, 1986). In practice however, freshwater snail carbonate has been generally underused in contrast to other materials for stable isotope studies, with relatively few published records (e.g. Abell, 1985; Gasse *et al.*, 1987). Some investigations (e.g. Abell and Williams, 1989) have raised concerns over inter-species fractionation differences, although records which have been published using multiple species have considered such variability insignificant (Abell and Hoelzmann, 2000). Some records use only one or two individual values from a given depth (e.g. Bonadonna and Leone, 1995; Zanchetta *et al.*, 1999) while other studies show considerable ranges from individual sample levels (Abell and Hoelzmann, 2000).

 $\delta^{18}O_{snail}$ values are primarily dependent on the temperature and oxygen isotope composition of the water ($\delta^{18}O_w$) in which the snail grew (Fritz and Poplawski, 1974). $\delta^{18}O_w$, in turn, is controlled by factors including the isotopic composition of the inflowing water and the degree of evaporation. Controls on $\delta^{13}C_w$ (the isotope composition of dissolved inorganic carbon (DIC) in the lake-water) include the amount of carbon derived from exchange with atmospheric CO₂ and the amount of carbon produced in metabolic processes by the snail (Fritz and Poplawski 1974; Tanaka *et al.* 1986).

Here, isotope data from <u>Gyraulus piscinarum</u> (Bourguignat, 1852) and <u>Valvata cristata</u> Müller, 1774, two dominant species from a Holocene lake sequence in SW Turkey, are compared. The whole-shell δ^{18} O and δ^{13} C data, provide an integration of seasonal change over the life span of the snail, and demonstrate that past environmental conditions have changed substantially through the Holocene with a trend to increased aridity and increased lake-water

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residence times. However, variation over decadal time scales may have been almost as large.

The study aims to increase understanding of variation in isotope values between different snail species. The number of individual shells required for analysis from a given sample level for robust palaeoenvironmental inferences is investigated. The variability of oxygen and carbon isotopes between and within sample levels is discussed with a view to understanding climate variability at different time scales.

Site description

Gölhisar Gölü (37°8'N, 29°36'E, elevation 930 m) is a small (~4 km²), shallow (~2.5 m) lake located in a NW-SE orientated intramontane valley in the West Taurus Mountains, Southwest Turkey. Average annual precipitation for Gölhisar is ~600 mm, of which ~50% falls during the winter and ~12% during the summer (Eastwood *et al.*, 1999a). Annual mean δ^{18} O of precipitation in Turkey lies between -6 and -8 ‰ (Gat, 1996).

The slopes around the south and east of the basin consist mainly of Mesozoic limestone; ultra-basic igneous rocks are exposed to the east and Neogene marls outcrop to the southwest. There are no major rivers in the catchment so allogenic input into the lake basin is thought to be minimal. The lake is fed by numerous small springs around the margin and losses are through groundwater seepage.

Materials and Methods

An 8 m sediment core (GHA92) was taken in the summer of 1992, the collection of which is described in Eastwood *et al.* (1999a). The radiocarbon chronology was established from conventional radiocarbon ages on total organic matter (see Eastwood *et al.*, 1999a for details). Ages are given here as calibrated years BP, using the CALIB 4.2 calibration

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programme (Stuiver and Reimer, 1993). A tephra layer from the mid-second millennium eruption of Santorini (Eastwood et al., 1998: 1999b) further supports the chronology of the site.

Lake-water samples for isotopic analyses were collected in July 1999 and 2000 in leak-tight polyethylene bottles, sealed with PVC tape. Total dissolved inorganic carbon (TDIC) for ${}^{13}C/{}^{12}C$ analysis was precipitated on site by addition of BaCl₂ + NaOH solution; untreated water was collected for ${}^{18}O/{}^{16}O$ and D/H analysis. Samples were stored in a refrigerator (at $4^{\circ}C$) prior to laboratory analysis by standard techniques.

For molluscan analysis, 1 cm slices of core sediment (aprox. 20 cm³) were removed at approximately 8 cm vertical intervals. Sediment samples were air dried for 48 hours and then wet-sieved using a 0.5 mm mesh (Lozek, 1986). Shells were picked after drying and then sorted and counted under a low power binocular microscope. Whole individuals and apical fragments were counted, such that one apex equals one individual (Sparks, 1964).

Ideally, a single species would have been analysed for isotope ratios throughout the entire sequence. However, due to species occurrence, this was not possible and two species of fresh-water snails (*G. piscinarum* and *V. cristata*) were chosen due to their relatively high abundance through the sequence. The two species partially overlap stratigraphically, thus enabling assessment of any interspecific variation in isotope ratios. Individual snail shells were washed in deionised water. The larger species, *G. piscinarum*, were placed in an ultrasonic bath to loosen and remove sediment. The smaller species, *V. cristata*, were hand brushed as they were found to disintegrate in the ultrasonic bath. The washed shells were individually crushed to a fine powder in an agate pestle and mortar for XRD and isotope analysis.

As the shells of many freshwater snails are composed of thermodynamically unstable

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aragonite, some shells were tested for aragonite and calcite content by XRD in the Department of Geology, Royal Holloway, University of London. The shells correlated well to both laboratory aragonite standards and to published aragonite XRD values (Moor and Reynolds, 1997), showing conversion to calcite to be negligible. An aragonite correction of 0.6‰ was subtracted from the values derived for oxygen isotope ratios (following Tarutani *et al.*, 1969; Abell & Williams, 1989), to report the δ^{18} O values of the shells as calcite.

A number of individual shells (10 where available) were analysed, for oxygen and carbon isotope ratios, from a number of sample levels. Conventional methods were followed for isotope analysis (cf. McCrea, 1950). The shell powders were reacted with anhydrous phosphoric acid *in vacuo* overnight, at a constant 25°C. The liberated CO₂ was separated from water vapour and collected for analysis. The majority of the G. piscinarum and some of the V. cristata were analysed on a Provac upgraded Micromass 903 mass spectrometer. Where sufficient carbonate was available, duplicate analyses were run from the same shell to check the homogeneity of the samples. Overall, analytical reproducibility for the standard materials was normally better than 0.02 % for both isotope ratios (1 SD), and < 0.1 % for the mean of the duplicate snail shells. Single shells < 2 mg were analysed on an Optima mass spectrometer with Isocarb facility together with similarly sized samples of a laboratory calcite standard. Analytical precision (1 SD), based on the laboratory standard, was typically < 0.07 ‰ for both oxygen and carbon isotope ratios. Consistency of results was achieved by comparing laboratory standards against NBS-19 for each mass spectrometer. Isotope values $(\delta^{13}C \text{ and } \delta^{18}O)$ are reported as per mil (‰) deviations of the isotope ratios ($^{13}C/^{12}C$, $^{18}O/^{16}O$) from standards (VPDB for carbonates, VSMOW for water samples).

Results

Species abundance

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The snail shell count shows a major change in predominant species around 700 cm (Fig. 1), although the exact nature of this transition is not recorded due to a gap in the snail record between 700 and 620 cm. Below 700 cm, the fauna consists of numerous <u>V. cristata</u> and Planorbidae, such as <u>Gyraulus crista</u> (Linné, 1758) and <u>Segmentina</u> sp. (Jones, 2000), which are known from ponds with a strong growth of macrophytes and a silty organic substrate. They are usually restricted to water depths of less than 1-2 m. Above 620 cm this fauna is replaced by one dominated by <u>G. piscinarum</u> and <u>Valvata macrostoma</u>, Mörch, 1864 and with <u>Valvata piscinalis</u> (Müller, 1774) also common. This latter taxon occurs in well-oxygenated water, either in rivers or lakes, in water depths of 2-5 m, although occasionally being found up to 10 m depth (Kerney, 1999). <u>G. piscinarum</u> is found in lake shores, marshes, swamps and other shallow water environments (Germain, 1921-1922) through Asia and the Near East.

Most freshwater gastropods of this size (< 7 mm) are able to grow to adult in a single summer, so are effectively annual species. Shells grow from eggs in 30-40 days (Graham 1988), and add increments to their shells to grow to full adult size when conditions are favorable. All of these molluscan species breed annually in summer (Økland, 1990).

Shell $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$

The 177 individual shells analysed produced a large range of both δ^{18} O and δ^{13} C values. δ^{18} O values range from -9.7‰ to +1.3‰, δ^{13} C from -10.7‰ to +2.8‰. Trends in the isotope data (Fig. 1) are picked out by a line running through the mid point of each level. The isotope data have been divided into three zones based on the occurrence of molluscs in the record.

Isotope zone 1 (695 cm – 765 cm): The trend in isotope values from <u>*V. cristata*</u>, analysed from all six levels, shows that means of δ^{18} O and δ^{13} C are similar through the lowest three levels (δ^{18} O ~ -6‰, δ^{13} C ~ -7‰), then fluctuate between these and heavier values (δ^{18} O ~ -2‰, δ^{13} C ~ -4‰). Shells of <u>*G. piscinarum*</u> were also sampled at the top of this section for comparison between the two species. δ^{18} O and δ^{13} C values for both species co-vary (Fig. 2),

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the Pearson correlation coefficient (r) giving a value of 0.81.

Isotope zone 2 (491 cm – 605 cm): There is a considerable variation in the mid-points of δ^{18} O (~ 0 ‰ to -7 ‰) and δ^{13} C (-1 ‰ to -8 ‰) ranges from <u>*G. piscinarum*</u>, through the nine levels analysed in this section. The two records again co-vary (Fig. 2), r = 0.62.

Isotope zone 3 (287 m – 334 cm). δ^{18} O values of <u>*G. piscinarum*</u> vary between -5‰ and approximately +2‰, δ^{13} C between -6‰ and 0‰. δ^{18} O and δ^{13} C show a slight negative correlation between the two data sets (r = -0.03). <u>*V. cristata*</u> and <u>*G. piscinarum*</u> were both analysed, from the same sample level, for species comparison at the base of this section. Molluscs are rare in the upper two sample levels.

Isotope zone 1 shows more depleted δ^{18} O and δ^{13} C with means of -5.3‰ and -7.1‰ respectively, δ^{18} O ranges from -9.7 to +0.3 and δ^{13} C from +0.7 to -2.4. In Isotope zone 2 both curves are highly variable with a range of +1.7 to -7.9 for δ^{18} O and +1.5 to -9.4 for δ^{13} C, mean values are -3.64 and -4.69 respectively. Isotope zone 3 shows more positive values with mean values of -2.3‰ for δ^{18} O and -1.7‰ for δ^{13} C and ranges of -4.51 to 1.27 (δ^{18} O) and - 6.22 to +2.83 (δ^{13} C).

Discussion

$\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values

The δ^{18} O and δ^{13} C values of the snail shells show great variation throughout the core. δ^{13} C versus δ^{18} O from Isotope zones 1, 2 and 3 (Fig. 2) show different degrees of co-variation. Isotope zones 1 and 2 show a very close relationship between δ^{18} O and δ^{13} C with r-values of 0.81 and 0.62 respectively. It is evident from this degree of co-variation that both elements were governed by some common controlling mechanism. Detailed accounts of the

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mechanisms influencing δ^{18} O and δ^{13} C in lake-waters are given elsewhere (Talbot, 1990; Li and Ku, 1997) and are summarised on Fig. 2.

Co-variation suggests that carbon incorporated into the shells was not substantially derived from metabolic carbon but from DIC in the lake-water. It is difficult to say whether there is a fractionation effect as the shell carbonate δ^{13} C (total range: -10.7 to +2.8 ‰) has values which include the values for present day carbonate (-5.7 ‰, July 2000). By using monospecific records, and taking the essential palaeoecological assumption that species environmental needs are constant with time, it may be assumed that any metabolic or fractionation effects are constant through the record. Thus, shifts in δ^{13} C values are taken to reflect changes in lake residence time, catchment vegetation cover and lake productivity i.e. controls on DIC.

The more positive δ^{18} O values are taken to reflect more evaporation i.e. greater aridity, as modern water data have established the presence of an evaporative control on δ^{18} O (Fig.3). The more negative values reflect more positive water balance within the lake system and, probably, higher humidity. Periods in the record where measured levels are isotopically heavier (e.g. Isotope zones 2 and 3) appear to be related to periods when lake-water was more strongly evaporated and lake-water residence times longer. Based on the isotope data the early Holocene (Isotope zone 1) appears to be the wettest of the three zones covered by the molluscs, with the greatest biogenic productivity. Large fluctuations in lake isotope hydrology occur within Isotope zone 2, suggesting climatic instability. A period of greater aridity and an increase in lake residence time is inferred from Isotope zone 3.

Inter species variation

There are three levels in the sequence where both <u>*G. piscinarum*</u> and <u>*V. cristata*</u> were analysed in significant (\geq 4) numbers (Fig. 1). δ^{13} C and to a lesser extent δ^{18} O values for <u>*V.*</u> <u>*cristata*</u> are more positive than those of <u>*G. piscinarum*</u> at all three levels. The difference in the isotope ratios could be a physiological fractionation (vital) effect although other studies have

shown that fresh water snails exhibit minor, if any, vital effects (e.g. Leng *et al.*, 1999a). The difference in the data is therefore most likely to be a spatial (i.e. habitat) or temporal (time of calcification) effect. We only have contemporary lake-water δ^{18} O data from the centre of Lake Gölhisar, but in arid and semi-arid regions, marginal waters are often warmer and may become isotopically enriched through evaporation during the summer or dry months (Lamb, 2000). Temperature at the margins of Gölhisar in July 2000 was 6°C warmer than the lake centre waters. Conductivity, often an indicator of the degree of evaporation, was also found to be higher (0.70 mS/cm lake centre, 0.95 mS/cm edge), and it has been shown that similar lakes in Turkey evolve isotopically through the year (Leng *et al.*, 1999b). Differences in δ^{18} O of the two species are therefore likely to be related to changes in water temperature (a function of water depth), evaporation (enhanced in the marginal waters), and the specific period of shell calcification.

Range in δ^{13} C and δ^{18} O from each level

Duplicate isotope analyses show that individual shells, when crushed, produce a homogenous sample (\pm 0.1 ‰). The samples provide an average value, weighted toward the optimum growth in the summer months, over the lifetime of the snail. Since these snails are able to grow to adult size in a single summer, their shell isotope composition effectively represents single summer lake-water composition. However, as each stratigraphic level sampled for snails will span anywhere between 7 and 25 years (Eastwood et al., 1999a), a number of points require consideration:

1) Modern $\delta^{18}O_w$ values change from year to year; there having been a 1 ‰ increase in $\delta^{18}O_w$ between July 1999 and July 2000 (Fig.3). This trend has also been observed in other lakes in Southwest Turkey (N. Roberts, unpublished data).

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2) Changes in sedimentation rate may also affect the ranges of δ^{18} O from a single level. Slower sedimentation will represent a longer time, and may potentially show greater ranges in isotope composition.

3) Reworking of the sediment may mix shells of different ages.

Two of the isotope sample levels (576 cm and 695 cm) show ranges in oxygen isotope values much greater than the average (around 3 or 4 ‰; Table 1). The ratio between opercula and <u>Bithynia</u> shells has been used as a proxy for reworking of lake sediments elsewhere (Hammarlund and Keen, 1994). The sample at 576 cm depth has six <u>Bithynia</u> opercula to every whole <u>Bithynia</u> shell, suggesting at this level the greater range in values may be due to reworking of the sediment. In contrast, the ratio at 695 cm is 0.9, suggesting other processes, probably climate, have caused the increased δ^{18} O range.

Number of individuals sampled at each level

Interpretations of δ^{18} O range variability between different depths can only be significant if the sample range can be shown to be a close representation of the true range. Fig. 4 shows how the ranges at different depths change as the number of individual shells analysed increases. It appears that in this case study five or six shells are required for analysis before the maximum range is reached.

An optimal range is reached in most of the samples after six individuals have been analysed. Only the curves of samples at 493.5 cm and 514.5 cm show no signs of flattening. This suggests that analysing six shells at this site gives a good (87 %) representation of the true range. Levels where only five shells were analysed, due to shell abundance, may still be compared (representing 79 % of the true range) although any inferences may not be as reliable.

Conclusions

Two co-existing species yield different δ^{18} O and δ^{13} C values, probably due to habitat differences within the lake system. It cannot be assumed that, although all species may be precipitating carbonate in equilibrium with the water in which they are living, δ^{18} O_w is constant in different microhabitats. If multi-species records are necessary, due to the nature of the fossil mollusc record, overlapping species should be chosen allowing comparison of the species through time.

Reliable interpretations of palaeoenvironmental change can be produced from the stable isotope ratios of snail shell carbonate if a sufficient number of individual shells can be analysed from each level in a given sequence (in this case, six). Studies where only one or two shells per level are analysed are unlikely to provide a true indication of the variability within the period represented by the sample. This is especially true in small lakes where there are potentially large changes in lake-water isotope values.

In this study up to 10 individuals per level were analysed. The resulting range in isotope ratios is probably due to snails living in different years as lake-water δ^{18} O and δ^{13} C has been shown to change annually. By measuring the stable isotope ratios of a number of individual shells an estimate can be made of short-term climatic variability. However, sufficient and constant numbers of shells need to be analysed from each level, representing the true range, for any strict comparisons to be made.

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Figure 1. Shell carbonate δ^{18} O and δ^{13} C and selected mollusc taxa from GHA.92. The range of values for <u>*G. piscinarum*</u> (squares) and <u>*V. cristata*</u> (triangles) at each sample level are shown with a trend line running through the mid point of each level for isotope zones 1-3 (Iz 1-3). Sample levels where significant numbers (≥ 4) of both species were analysed are bracketed. Ages are calibrated years BP, bracketed values are one standard deviation either side of the given values.



Figure 2. δ^{18} O v. δ^{13} C for snail carbonate from Gölhisar Gölü. Increased lake water residence time would increase exchange with the atmosphere and the potential for evaporation, leading to more positive δ^{18} O and δ^{13} C values.



Figure 3. δ^{18} O v. δ D from modern waters at Gölhisar Gölü. The five springs that directly feed the lake lie on or near the Global Meteoric Water Line (GMWL). The composition of lakewater in July 1999 and July 2000 was enriched in both heavy isotopes and lies on a Local Evaporation Line (LEL), suggesting an evaporative control on $\delta^{18}O_{snail}$.



Figure 4. Plot demonstrating the number of individual shells required for analysis to represent the true range at one sample level from Lake Gölhisar. Taking the true range to be that when all individuals have been analysed (usually the range has become constant by this point), analysing six samples from this site would represent, on average, 87 % of the true range (five samples would represent 79 %).