Investigating the environmental interpretation of oxygen and carbon isotope data from whole and fragmented bivalve shells

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ABSTRACT

Sclerochronological data from whole bivalve shells have been used extensively to derive palaeoenvironmental information. However, little is known about the relevance of shell fragments more commonly preserved in the sediment record. Here, we investigate the oxygen and carbon isotope composition of *Dreissena carinata* fragments from a core recovered from Lake Dojran (FYRO Macedonia/Greece) to identify their relevance and efficacy as a proxy in palaeoenvironmental studies. We use a modern *Dreissena* shell to calibrate the relationship between the bivalve and its contemporary environment, which suggests their isotope composition is primarily a function of temperature and water balance. The range of fragment isotope data from the core overlaps with that of unbroken fossil shells, suggesting the fragments broadly record lakewater conditions across the time of deposition. A comparison of the isotope composition of shell fragments and endogenic carbonate shows an offset between the two sets of data, which is likely due to temperature differences between surface and bottom waters, the timing of carbonate precipitation, and productivity-controlled stratification of the dissolved inorganic carbon pool. Shell fragment isotope data seem to reflect the signal of environmental change recorded in other proxy data from the same core and may potentially be used (like endogenic carbonate) to provide information on past changes in lake level.

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1. Introduction

The isotope composition of carbonate from the sequential analysis of intact fossil bivalves is being increasingly utilised in palaeoenvironmental reconstructions (Schöll-Barna et al., 2012; Lewis et al., 2017). However, little is known about the relevance of the isotope composition of shell fragments, which are commonly preserved in the sedimentary record (Wagner et al., 2014; Marcano et al., 2015). To better understand the efficacy of shell fragments as proxy in palaeoenvironmental studies, we utilise sediment cores recovered from Lake Dojran (Balkan Peninsula) that have been previously investigated using multi-proxy techniques and contain both whole shells and fragments of the bivalve *Dreissena carinata*.

The bivalve genus *Dreissena* is renowned for including two of the most invasive of all freshwater organisms, *Dreissena polymorpha* and *Dreissena rostriformis*, but also comprises species restricted to their native distribution (Albrecht et al., 2007). Lake Dojran is thought to exclusively contain *D. carinata* (Wilke et al., 2010). Although information on the ecological tolerances of *D. carinata* is limited, they will be similar to *D. polymorpha* as the two species have a close phylogenetic relationship. *Dreissena* spp. typically live for 2—19 years and their shells are characterised by external rings that form when growth slows or stops due to

changes in environmental conditions (e.g. temperature, water depth, trophic conditions, current strength, turbidity; Karatayev et al., 2006). Shell growth typically starts at ~10 °C and if temperatures exceed ~32 °C most mussels die (Karatayev et al., 2006). Within Lake Dojran, young *D. carinata* are mainly found on the littoral lakebed and adults typically occur attached to sublittoral hard substrates, such as empty shells and pebbles, and often form small clusters (Šapkarev, 1980; Griffiths et al., 2002; our observations).

The oxygen isotope composition ($\delta^{18}O$) of bivalve carbonate (typically aragonite) is a function of the temperature and $\delta^{18}O$ of lakewater ($\delta^{18}O_{lake}$; Leng and Marshall, 2004; Goewert et al., 2007), assuming isotopic equilibrium and no diagenetic alteration, as there are limited vital effects on $\delta^{18}O$ in freshwater bivalves (Dettman et al., 1999; Geist et al., 2005). Equilibrium precipitation of biogenic aragonite is subject to a temperature-dependent fractionation between the carbonate and water, where $\delta^{18}O$ decreases by 0.23‰ for every $+1$ °C (Grossman and Ku, 1986; Dettman et al., 1999). The carbon isotope composition ($\delta^{13}C$) of bivalves typically reflects the $\delta^{13}C$ of the dissolved inorganic carbon pool (DIC), where any disequilibrium between the shell and DIC is relatively constant (Apolinarska, 2013). Consequently, changes in $\delta^{18}O_{lake}$, $\delta^{13}C_{DIC}$, and temperature will be recorded in subsequent layers of the shell during growth.

Here we test the potential of using the isotope composition of bivalve shell fragments in palaeoenvironmental studies by investigating: 1) how $\delta^{18}O$ and $\delta^{13}C$ of modern whole *D. carinata* shells relates to present day lakewater, 2) if shell fragments from sediment cores reflect the isotope range of fossil whole shells, and 3) the relationship between shell $\delta^{18}O$ and $\delta^{13}C$ and other proxy data. We provide a modern calibration using stable isotope data from a recent shell and monitoring data from Lake Dojran, and present sequential isotope data from whole shells from the early Holocene. The fossil whole shell data are combined with isotope data from shell fragments, which occur in variable quantities through the Holocene, and are compared with previous palaeoenvironmental investigations on the same core sequence.

2. Study site

Lake Dojran (41°12′N, 22°44′E; 144 m asl) is located on the border between the Former Yugoslav Republic of Macedonia and Greece (Fig. 1) in an elliptical karst basin of Neogene age. The lake is 8.9 km long and 7.1 km wide. The lake has a volume of 0.3 km³ with gently inclined slopes, a surface area of 42 km², and an average water depth of 6.5 m (Francke et al., 2013). Water inflow is primarily derived from small rivers, creeks, and groundwater sourced from precipitation over the catchment. Outflow is dominated by summer evaporation, and also via groundwater, irrigation, and water supply to local populations (Gesovska, 2016). The lake has no natural outflow, however, during times of higher lake level, the River Doiranitis connects Dojran to the Vardar River and the Aegean Sea (Sotiria and Petkovski, 2004). The lake is monomictic, experiencing thermal stratification in summer months, with overturn likely occurring during winter (Temponeras et al., 2000; Zacharias et al., 2002; Lokoska et al., 2006). The lakewater is eutrophic with a pH of 7.6–9.5, an electrical conductivity of 0.8–1.5 mS/cm (Sotiria and Petkovski, 2004) and total phosphorous of 50–520 μ/l (measured during 2004–2006; Tasevska et al., 2012).

The climate of the local area is characterised by hot and dry summers and mild, humid winters (Popovska et al., 2005). Temperature and precipitation are influenced by Aegean Sea through the Thessaloniki Plain and continental influences from the north. The average air temperature is 14.3 °C, ranging between 26.1 °C and 3.7 °C, and annual precipitation is 630 mm (Sotiria and Petkovski,

2004; Popovska et al., 2005). The mean weighted annual isotope composition of precipitation has $\delta^{18}O = -7.4‰$ and $\delta D = -48‰$, ranging between $-10.6‰$ in winter and $-3.2‰$ in summer for $\delta^{18}O$ (calculated on-line at waterisotopes.org; Bowen et al., 2005). Inflow $\delta^{18}O$ plots close to the Global Meteoric Water Line (GMWL; Craig, 1961), whereas $\delta^{18}O_{lake}$ defines a local evaporation line (LEL; Fig. 2). Therefore, $\delta^{18}O_{lake}$ is controlled primarily by the water balance of the lake (Leng and Marshall, 2004), for example a decrease in $\delta^{18}O_{lake}$ of $-2.9‰$ between 1997 and 2011 coincided with a lake level increase of ~4 m (Griffiths et al., 2002; Francke et al., 2013). Spring inflows have $\delta^{13}C_{DIC}$ between $-13.0‰$ and $-7.9‰$, which is lower than lakewater values of between $-5.9‰$ and $-0.6‰$ (Fig. 2; Griffiths et al., 2002; Francke et al., 2013). There is negligible impact from geological carbonate within the basin and $\delta^{13}C_{DIC}$ is mainly influenced by in-lake processes, such as exchange with atmospheric CO_2 and/or the preferential uptake of ^{12}C by algae during photosynthesis (Leng and Marshall, 2004).

3. Material and methods

A ~7 m sediment core (Co1260; Fig. 1) was recovered in June 2011 using gravity and percussion piston corers from a site of undisturbed, horizontally-bedded sediments (water depth = 6.6 m). Cores were recovered in 3 m-long sections, cut to 1 m, and then split lengthways and subsampled continuously at 2 cm intervals (a full overview of coring, sampling, sedimentology, and chronology is described in Francke et al. (2013)).

Subsamples were sieved (63 μm) to separate larger shelly material from fine-grained clays and endogenic carbonate. Intact shells were rare in the subsamples. Alongside a modern shell collected from the littoral zone in June 2011 (Fig. 3), two fossil shells from 447.9 cm to 470.9 cm core depth were recovered and appeared well preserved. The whole shells were sampled sequentially along the ridge of the shell from the umbo to ventral margin using a Dremel rotary hand drill with a 1 mm bit, which produced a fine powder. Fragmented shells occurred in varying proportions throughout the core (Fig. 3). Only those subsamples which contained at least five individual fragments between 0.5 and 1 mm (sizeable enough to provide >50 μg of carbonate) were selected for isotope analysis. Individual fragments were crushed to a fine powder prior to analysis. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX), X-ray Diffraction (XRD), and X-ray fluorescence (XRF) were used to confirm that the dominant carbonate species forming the shell material is aragonite, with no evidence of calcite.

Stable isotope analysis was conducted at the British Geological Survey. Approximately 50–200 μg of powder was analysed using an Isoprime dual inlet mass spectrometer coupled to a Multiprep device, by reaction with concentrated phosphoric acid for 15 min at 90 °C. Carbon and oxygen isotope values for the whole shells ($\delta^{13}C_{shell}$ and $\delta^{18}O_{shell}$) and shell fragments ($\delta^{13}C_{frag}$ and $\delta^{18}O_{frag}$) are reported as parts per mil (‰) calculated to the Vienna Pee Dee Belemnite (VPDB) scale using a within-run laboratory standard (KCM) calibrated to international NBS standards. Analytical reproducibility for KCM was <0.1‰ for both $\delta^{13}C$ and $\delta^{18}O$. The mineral-gas fractionation factor used for aragonite was 1.00854 (derived from Kim et al., 2007a).

4. Results

The modern shell (24.9 mm long) has average $\delta^{18}O_{shell} = -0.3 \pm 1.0‰$ (1σ), ranging between $+2.3‰$ and $-1.3‰$, and average $\delta^{13}C_{shell} = -1.7 \pm 1.0‰$ (1σ), ranging between $+0.3‰$ and $-3.4‰$ (Fig. 4). There is a strong correlation between $\delta^{18}O_{shell}$