Experimental Calibration and Field Investigation of the Oxygen Isotopic Fractionation Between Biogenic Aragonite and Water

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Marine molluscs have long been recognised as potential records of palaeoclimate change using the patterns and differences in the stable isotopic composition of the carbonate shells. The aim of this study is to improve the robustness of this approach for aragonitic molluscs by completing the first experimental calibration of the fractionation between water and biogenic aragonite. Fractionation factors were calibrated by growing specimens of the freshwater mollusc Lymnaea peregra under controlled conditions of water temperature and isotopic composition.

Fifteen populations of L. peregra were maintained at constant temperature and isotopic conditions for five months (at five different temperatures and using three different water compositions). Water samples and temperature measurements were taken regularly throughout the experiment. The temperature dependence of the fractionation factor, between 8 and 24°C, is given by:

$$1000 \ln \alpha = 16.74 \times (1000T^{-1}) - 26.39 \quad (T \text{ in Kelvin})$$

and the relationship between temperature ($T$), $\delta^{18}O_{\text{carb}}$ and $\delta^{18}O_{\text{wat}}$ is given by:

$$T = 21.36 - 4.83 \times (\delta^{18}O_{\text{carb}} - \delta^{18}O_{\text{wat}})$$

($T$ is in °C, $\delta^{18}O_{\text{carb}}$ is with respect to Vienna Pee Dee Belemnite (PDB), the International Atomic Energy Agency (IAEA) replacement standard for PDB, and $\delta^{18}O_{\text{wat}}$ is with respect to Vienna standard mean ocean water (VSMOW))

The outcome of the controlled experiment is compared with previous studies on synthetic, and biogenic, calcite and aragonite from field and laboratory investigations. These comparisons suggest that although a vital offset exists between the fractionation of isotopes in synthetic and biogenic aragonite for molluscs in general, there is no vital effect that is specific either to freshwater, or to individual, genera. Therefore, the calibrated relationship may be used for any freshwater or marine mollusc to derive palaeotemperatures providing the isotopic composition of the environmental water can be reliably constrained. Copyright © 1999 John Wiley & Sons, Ltd.

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Analyses of the oxygen isotope ratios of numerous marine organisms have been investigated in order to extract palaeoclimatic information pertaining to the time when the organism grew. However, the materials currently available for interpreting continental palaeoclimates using similar oxygen isotope methodology have various limitations. Although freshwater molluscs may be a source of palaeoenvironmental data an accurate method of interpreting this resource is required in order to reconstruct palaeoenvironments with confidence. In order to do this the oxygen isotope fractionation between the biogenic aragonite and environmental water must be quantified for the range of relevant temperatures. In addition, data from a variety of modern environments is needed to give information regarding the relationships between water composition, temperature and resulting snail shell composition in the natural environment.

OUTLINE OF LABORATORY METHODOLOGY

Experimental design

After one year’s experimental design and testing, a glass condensing unit was prepared which could be easily attached to a small glass jar (referred to as a habitat cell). The result of this experimental setup was that water bodies (~1.5 L) could be continuously aerated with only minimal isotopic enrichment for up to 7 weeks.

The culture experiment was carried out in a controlled temperature laboratory using water baths heated with elements in copper cases with proportional/derivative temperature controllers and platinum resistance temperature sensors. The experiments were carried out at five different constant temperatures between 8 and 24°C (±0.5°C) and using three water types of different isotopic composition ranging from −4.43 to −8.25‰ (±0.2‰ in the worst case and 0.05‰ in the best). Juveniles from a laboratory breeding population of Lymnaea peregra were used to provide snails for the experiment. After a few days individuals were visible on the lettuce leaves in the breeding
aquarium and could be transferred to each habitat cell. These populations, of approximately ten individuals, were cultured for five months before the snails were culled and prepared for isotope analysis.

**Analytical Procedures**

(a) **Snails.** Analysis of procedures employed to prepare biogenic carbonates for isotopic analysis, cited in the literature, indicated that ultrasonic rinsing followed by crushing would be sufficient preparation (grinding is to be avoided as this appears to cause a definite enrichment even of a more thermodynamically stable mineral such as marble\(^2\)). Sub-samples of each snail were analysed by the standard McCrea method;\(^3\) reaction with orthophosphoric acid under vacuum to produce CO\(_2\) followed by cryogenic purification before analysis on a double collecting mass spectrometer.

(b) **Water.** Water samples were analysed following the equilibration with CO\(_2\) of known isotopic composition.\(^4\) An aliquot of this CO\(_2\) was cryogenically cleaned to remove water and other volatile contaminants before analysis on a double collecting mass spectrometer.

**LABORATORY STUDY: RESULTS AND CONCLUSIONS**

After five months snail specimens were culled, sub-sampled and isotopically analysed. Each sub-sample was used in conjunction with temperature and water isotopic measurements to derive values of 1000 ln \(\alpha\) and [\(\delta^{18}O_{\text{arag}} - \delta^{18}O_{\text{wat}}\)]. This information was plotted against 1/T (T in Kelvin) and \(T\) (°C), respectively, to give the relationships described below. The temperature dependence of the fractionation factor, \(\alpha\), between 8 and 24°C is given by (refer to Fig. 1)

\[
1000 \ln \alpha = 16.74 \times (1000T^{-1}) - 26.39
\]

where \(T\) is in Kelvin, and the relationship between temperature, \(\delta^{18}O_{\text{wat}}\) and \(\delta^{18}O_{\text{arag}}\) is given by (refer to Fig. 2)

\[
T = 21.36 - 4.83 \times (\delta^{18}O_{\text{arag}} - \delta^{18}O_{\text{wat}})
\]

where \(T\) is in °C, \(\delta^{18}O_{\text{arag}}\) is with respect to VPDB and \(\delta^{18}O_{\text{wat}}\) is with respect to VSMOW.

The outcome of the controlled experiment is compared with previous studies on synthetic, and biogenic, calcite and aragonite from field and laboratory investigations (Fig. 3). These comparisons suggest that, although a vital offset exists between the fractionation of isotopes in synthetic and biogenic aragonite, for molluscs in general there is no vital effect that is specific either to freshwater, or to individual, genera. Therefore, the calibrated relationship may be used for any freshwater or marine mollusc to derive palaeotemperatures providing the isotopic composition of the environmental water can be reliably constrained.

**OUTLINE OF FIELD METHODOLOGY**

**Introduction**

In parallel with this laboratory study a programme of monitoring local natural environments was devised and completed between April 1996–April 1997. The sites chosen were two rivers, two ponds and a ditch. The survey consisted of collecting snails, water samples and temperature measurements on a weekly or fortnightly basis. In the
past similar field studies have been completed, as an alternative to laboratory calibrations, to determine the relationship between shell and water isotopic composition and temperature in the natural environment. Mollusc specimens were isotopically analysed and the values compared with water temperature records and water isotopic composition. A drawback of this approach is that even sampling at regular intervals may not adequately

**Figure 2.** Graph of temperature against the values for the water corrected snail shell isotopic composition.

**Figure 3.** Comparison of $1000(1/T)$ against $1000\ln a$ for data from this and previous studies. (See Refs 7 to 9).

define the variability of the natural environment and the variation in the mollusc shell composition as a result. The aim of the field survey in the research outlined in this paper was not to define an empirical field calibration as in earlier studies, but to determine the potential of the laboratory results for interpreting the isotopic composition of freshwater snail shells for palaeoclimatic reconstruction.

Collection and analytical procedures

(a) Snails. A weekly or fortnightly search was made for snails at each site by collecting a bucket of water and substrate and examining this carefully, as well as checking the leaves and stems of aquatic plants. Individuals were culled, cleaned and stored (in distilled water, as this improves the effect of ultrasonic rinsing) until required for analysis. The samples were then sub-sampled and analysed using the same procedure as for the laboratory snails.

(b) Water. Water samples were collected (weekly or fortnightly) in 125mL glass bottles that had airtight McCartney screw caps with rubber seals. Samples were collected by rinsing the bottle then submerging it fully and replacing the lid under water to prevent entrapment of air. Samples were stored at $\pm 5^\circ$C until required for analysis and were analysed using the same method as for the laboratory water samples.

(c) Temperature. Wet and dry bulb air temperature measurements were taken upon visiting each site using a hygrometer. Water temperature measurements were also...
taken, using a standard thermometer, at roughly the same position that the water samples were taken from.

FIELD STUDY: RESULTS AND CONCLUSIONS

The most significant results of this field campaign are twofold; firstly the isotopic composition of a freshwater snail shell is an accurate recorder of an environmental signal that mixes temperature variation with changes in the $\delta^{18}O_{\text{wat}}$. This outcome was derived by comparing the observed snail shell isotopic composition with that calculated by inputting the water isotopic composition and temperature measurements into the relationship derived from the laboratory experiment (Fig. 4). The second conclusion from the field study is that fossil snails from only specific types of hydrological locality will be useful for palaeoclimate reconstruction. From the field campaign hydrological localities could be classified, by the patterns in temperature and water fluctuations, as one of three types of site.

(1) Water isotopic composition remains relatively constant whilst water temperature fluctuates significantly. The river sites showed this pattern. In this case the temperature changes are the dominant control on snail shell composition and the $\delta^{18}O_{\text{arag}}$ is a record of temperature changes through the growth period of the organism (Fig. 5(a)).

(2) Temperature changes result in significant fluctuations in the water isotopic composition due to increased evaporation. The ponds showed this behaviour, drying up completely and achieving very enriched heavy isotope compositions while doing so. This enrichment in the $\delta^{18}O_{\text{wat}}$ is the dominant control on snail shell isotopic composition. However, the fluctuations in temperature affect the isotopic fractionation factor in the opposite sense to the enrichment. Therefore the final snail shell composition records the effect of the changing water composition ‘dampened’ by an opposing effect resulting from the temperature fluctuations (Fig. 5(b)).

(3) Water temperature fluctuations cause changes in the water isotopic composition due to evaporative effects. Neither parameter is dominant but each acts to dampen the effect of the other.

The types of site from which the snail shells would be reliable recorders of environmental conditions are those where the water isotopic composition remains relatively constant throughout the year and therefore temperature fluctuations are the dominant control on snail shell isotopic composition. The accompanying field study on the patterns in water isotopic composition and temperature for hydrologically different sites indicates that groundwater-dominated fluvial systems and, potentially, large lacustrine environments, have a small range in water isotopic composition. The accompanying field study on the patterns in water isotopic composition and temperature for hydrologically different sites indicates that groundwater-dominated fluvial systems and, potentially, large lacustrine environments, have a small range in water isotopic composition. The accompanying field study on the patterns in water isotopic composition and temperature for hydrologically different sites indicates that groundwater-dominated fluvial systems and, potentially, large lacustrine environments, have a small range in water isotopic composition. The accompanying field study on the patterns in water isotopic composition and temperature for hydrologically different sites indicates that groundwater-dominated fluvial systems and, potentially, large lacustrine environments, have a small range in water isotopic composition.
climatic factors. However, fossils from fluvial and/or lacustrine environments may be useful as palaeoclimate tools.

SUMMARY

A detailed laboratory experiment to calibrate the relationship between freshwater molluscs and water temperature and isotopic composition has, until now, been lacking.

The existence of an offset between synthetic and biogenic carbonates is supported by this experiment although there appears to be no separate vital effect specific to Lymnaea peregra. The vital offset attributable to metabolic processes appears to be general to all molluscs and this suggests that species-by-species calibration of freshwater or marine molluscs may not be necessary.

In the natural environment the patterns of mollusc shell isotopic composition are dominated by either changes in water temperature or water composition or a combination of both. The isotopic composition of L. peregra is a good recorder of the environmental conditions in which it lived.

The patterns in the isotopic composition of molluscs shells could be used to determine changes in palaeotemperature provided the specimens grew in an environment of near constant water isotopic composition and that this water composition can be quantified.

REFERENCES