Environmental Archaeology
The Journal of Human Palaeoecology
ISSN: 1461-4103 (Print) 1749-6314 (Online) Journal homepage: http://www.tandfonline.com/loi/yenv20

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To cite this article: Melanie J. Leng & Jonathan P. Lewis (2016) Oxygen isotopes in Molluscan shell: Applications in environmental archaeology, Environmental Archaeology, 21:3, 295-306, DOI: 10.1179/1749631414Y.0000000048

To link to this article: http://dx.doi.org/10.1179/1749631414Y.0000000048

Published online: 19 Nov 2014.

Oxygen isotopes in Molluscan shell: Applications in environmental archaeology

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Oxygen isotope geochemistry of Molluscan shell is an essential part of environmental archaeology and over the last decade has contributed significantly to the understanding of the past inhabitants of our planet. From the analysis of collected (and disposed of) shells we can gain information on environmental data from the species assemblages and also from the shell chemistry. In particular, intra-seasonal information can be gained from shells by analysing the isotope composition of the shell from successive growth increments. Here, we describe some of the recent developments in the use of oxygen isotopes in environmental archaeology. In particular, we consider preservation and sampling and describe how $\delta^{18}O$ can provide us with information on seasonal climate, season of collection as well as changes in global climate.

Keywords: Environmental archaeology, Mollusc shells, Oxygen isotopes, Environmental reconstructions, Subsistence strategy

Introduction

Mollusca are invertebrates whose soft bodies are protected by a hard calcium carbonate shell. Mollusc shells are common components of archaeological sites, collected by the past inhabitants as a source of food, ornamentation or decoration (e.g. Stiner *et al.* 2002; Bailey and Milner 2008; Bar-Yosef Mayer *et al.* 2010; Çakirlar 2011 and papers therein). Gastropods and bivalves are among the most common types of Mollusca and live in marine, freshwater (both) and terrestrial (gastropods only) environments and preserve well in the sedimentary record. Molluscs provide environmental data from species assemblages and also from the chemistry of their shells (Antczak and Cipriani 2008; Andrus 2011). In particular, intra-seasonal information can be gained from shells by analysing the oxygen (and carbon) isotope composition of successive growth increments of calcium carbonate along the direction of growth (known as sclerochronology), although it should be noted that shell growth is often not continuous and there may be significant seasonal cessations in growth.

Oxygen Isotopes

The use of oxygen isotope ratios ($^{18}O/^{16}O$, from which we derive $\delta^{18}O$) from molluscan carbonate is an established method to derive environmental information from daily (Goodwin *et al.* 2001) to centennial scale (Schöne *et al.* 2004; Scourse *et al.* 2006) time periods (although some studies use whole shells thus integrating the whole growth period). The $\delta^{18}O$ of pristine (non-diagenetically altered) molluscan carbonate, if precipitated in isotopic equilibrium, is a function of the formation water $\delta^{18}O$ and the temperature at the time of the shell formation. In marine bivalves and gastropods these are sea water (controlled by salinity near coast and Global Ice Volume in more open water; Sharp 2007) and sea water temperature where the animal lived (Craig 1965) (Fig. 1A). Molluscs living in normal marine salinity tend to respond to the latter, i.e. to seasonal seawater temperature change, assuming a constant seawater $\delta^{18}O$. Equilibrium oxygen isotope precipitation of calcium carbonates decreases by about 0·24‰ for each 1°C increase in temperature (Craig 1965). A number of studies have determined the empirical relationship between the temperature, the oxygen isotope composition of different carbonate minerals (calcite, aragonite) and the composition of the water from which they formed. Many so-called palaeotemperature studies utilise the empirical relationship of Epstein *et al.* (1953) which was famously turned into a palaeotemperature equation by Craig (1965). More recent attempts to determine fractionation behaviour for inorganic and biogenic calcites (Grossman and Ku 1986; Kim and O'Neil 1997) involving careful laboratory experiments have yielded more precise equilibrium relationships. There are now a number of palaeotemperature equations for the equilibrium precipitation of carbonates. Studies of aragonite Mollusca material

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DOI 10.1179/1749631414Y.0000000048

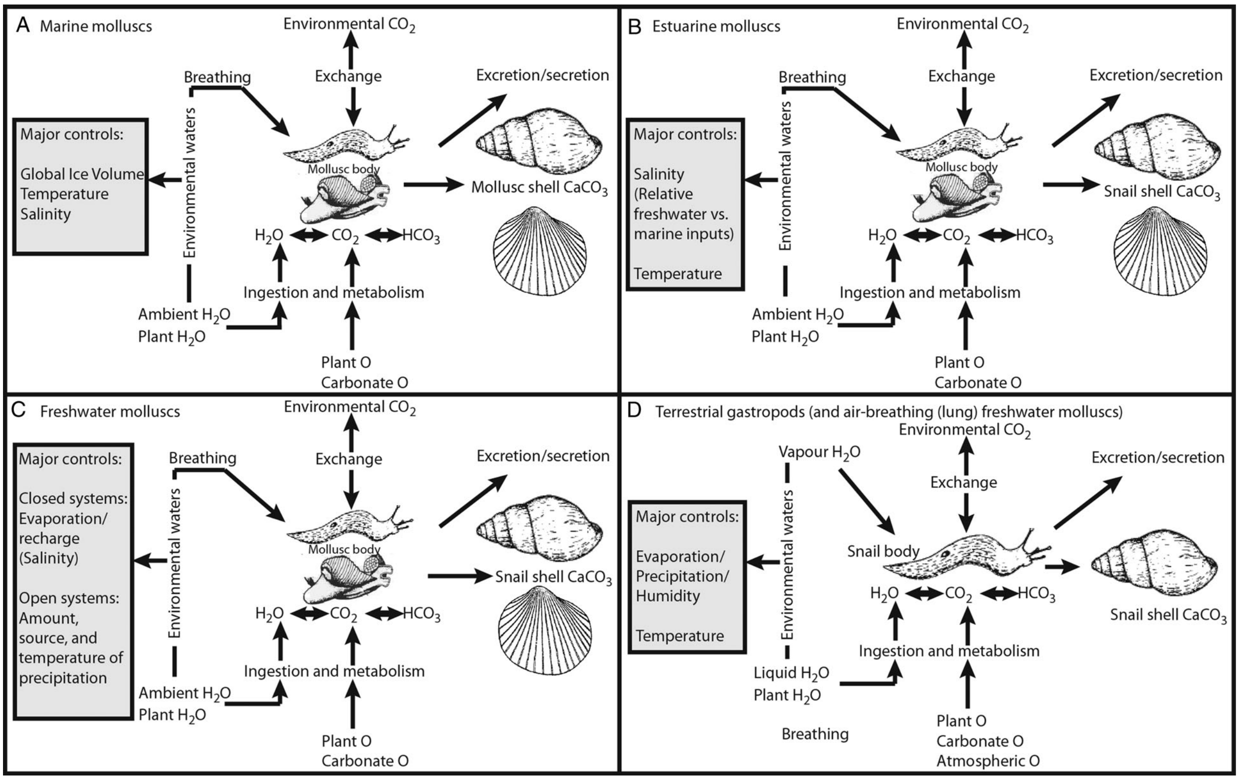

Figure 1 Controls on the oxygen isotope ratios within molluscan carbonate, in each type of mollusc the environmental waters are thought to be the most dominant influence: (A) marine molluscs, where the major controls are salinity, temperature and over longer time scale the Global Ice Volume; (B) estuarine molluscs, where the major controls are salinity and temperature; (C) freshwater molluscs, where major controls are whether the lakes are closed (the signal will be evaporation) or open (the signal will be some aspect of precipitation); (D) terrestrial and lung breathing freshwater molluscs, where the major controls are evaporation, precipitation (humidity) and temperature.

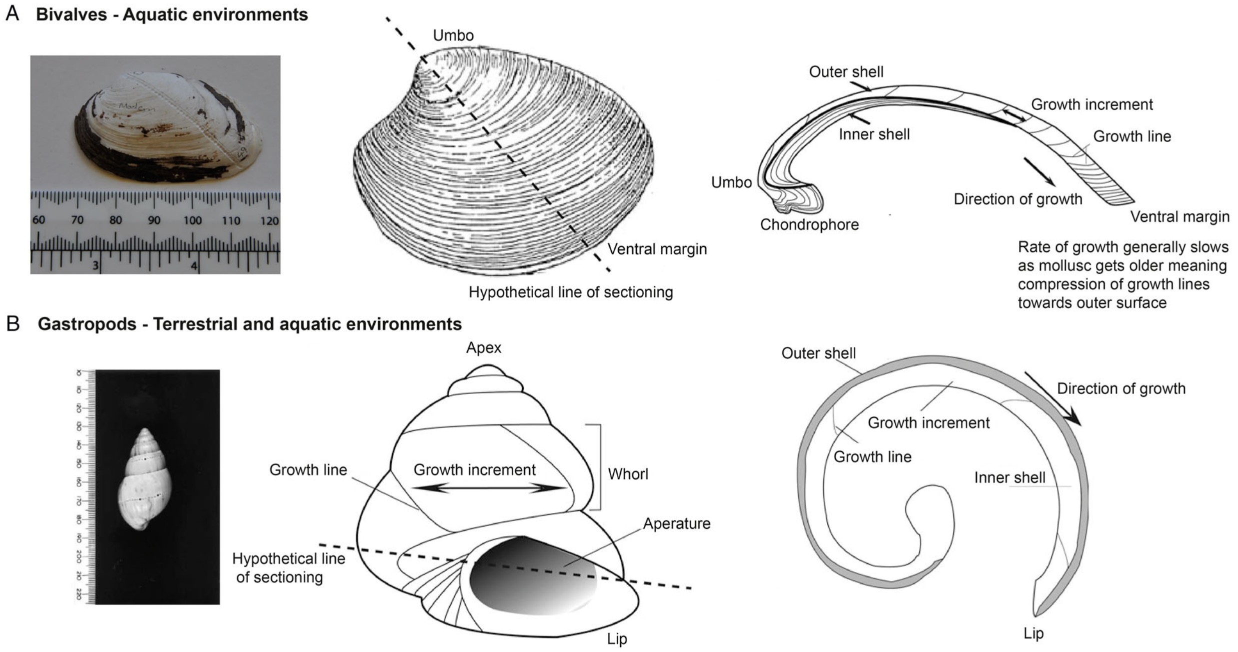

Figure 2 Mollusc sampling protocols: top left, modern freshwater bivalve specimen of *Unio* sp. from Çatalhöyük, Turkey (Bar-Yosef Mayer *et al.* 2012) and bottom left, terrestrial gastropod Limicolaria kambeul chudeaui Germain from margins of Lake Tilo, Ethiopia (Leng *et al.* 1998) showing sampled cross sections (i.e. holes along the/whorl) for $\delta^{18}O$ analysis. Drawings represent morphology of a bivalve (top centre and top left) and gastropod (top centre and top left) shell (modified from Prendergast and Stevens 2013).

tend to use (Grossman and Ku 1986):

$$t = 20.60 - 4.34(c - (w - 0.27))$$

where t is the temperature (°C), c is the $\delta^{18}O$ carbonate (to Vienna – PeeDee belemnite (V-PDB) in ‰) and w is the $\delta^{18}O$ water (to Vienna – standard mean oceanic water (V-SMOW) in ‰).

With estuarine Mollusca, the difference between marine and freshwater $\delta^{18}O$ (salinity) is often the largest effect on $\delta^{18}O$ (Leng and Pearce 1999), there being a significant (several per mil) difference between freshwater and marine water $\delta^{18}O$ (Fig. 1B) (Sharp 2007). In freshwater molluscs $\delta^{18}O$ often preserve changes in the lake water, low latitude (closed) lakes tend to have lake water oxygen isotope variations that are dominated by dry season evaporation (high $\delta^{18}O$) and wet season recharge (low $\delta^{18}O$), while at high latitudes in open lake systems lake water $\delta^{18}O$ is often controlled by the amount, source and temperature of precipitation (Leng *et al.* 2001; Bar-Yosef *et al.* 2012) (Fig. 1C).

The $\delta^{18}O$ of terrestrial gastropod carbonate is thought to be controlled by the $\delta^{18}O$ of the water that was ingested by the snail. This is often meteoric water with variations that are variable across latitudes and altitudes (Goodfriend *et al.* 1989) (Fig. 1D). These variations must be determined for different regions through a modern calibration. Calibration studies show that, in general, humidity (Yapp 1979; Yanes *et al.* 2011), source and the amount of rainfall are important (Leng *et al.* 1998), but no straightforward global relationship exists (see review in Zanchetta *et al.* 2005). For example, in the Mediterranean and lower latitudes, there is a good relationship between $\delta^{18}O$ and local precipitation (e.g. Zanchetta *et al.* 2005), while at high latitudes water vapour $\delta^{18}O$ (e.g. Goodfriend *et al.* 1989) is important. Studies have also observed the effect of relative humidity on the isotopic fractionation of body fluid, which seems in turn to be transmitted to the shell (Balakrishnan and Yapp 2004). Balakrishnan and Yapp (2004) developed a model which predicts the interaction of humidity, temperature and oxygen isotope composition of atmospheric vapour in equilibrium with that of precipitation during the season of snail activity (flux balance model). The model has been to some extent validated by studies on snail shells from mid-latitude (Colonese *et al.* 2013, 2014) to low-latitude (Yanes and Romanek 2013) areas. Other potential influences on shell $\delta^{18}O$ of terrestrial molluscs are the isotope composition of plant-derived water and species-specific fractionation (vital effects), though studies have also shown that land snails in general do not have intra-species fractionation differences (Zanchetta *et al.* 2005).

Carbon Isotopes

Carbon isotope ratios ($^{13}C/^{12}C$, from which we derive $\delta^{13}C$) are collected alongside $\delta^{18}O$ from molluscan carbonate. In aquatic (marine and freshwater) environment, CO_2 and the dissolved inorganic carbon (DIC) ion are often the main source of carbon for Mollusca. Shell $\delta^{13}C$ is typically a few ‰ lower than ambient $\delta^{13}C$ DIC, which can reflect processes such as changes in salinity (in coastal and estuarine environments) (McConnaughey and Gillikin 2008). In terrestrial molluscs, $\delta^{13}C$ will be influenced by carbon from several sources including ingested organic matter and carbonates as well as atmospheric CO_2. Previous studies have mainly found that the primary variable affecting $\delta^{13}C$ in terrestrial snail shells is diet. Therefore, in herbivorous species, $\delta^{13}C$ is often thought to be a proxy for changes in palaeovegetation mainly in terms of the distribution of C3 and C4 plants and changes due to water stress (Yapp 1979; Francey 1983; Goodfriend and Ellis 2002; Stott 2002; Metref *et al.* 2003; Balakrishnan *et al.* 2005a, 2005b; Baldini *et al.* 2007). Other studies have observed consistent inter-specific variability in $\delta^{13}C$ likely reflecting species-specific feeding behaviour (e.g. Goodfriend and Ellis 2002; Colonese *et al.* 2010). In some calciophilous species, the contribution of soil carbonates to the diet seems to be important (Yanes *et al.* 2009).

Preservation and Analytical Methods

Both bivalves and gastropods are widespread in archaeological deposits through the Quaternary although may not occur continually through sedimentary sequences. Freshwater and marine shells often comprise thermodynamically unstable aragonite, which can convert to calcite and effectively 'reset' the isotope signal. The mineralogy of the shell can be tested using X-ray diffraction (XRD) or Raman spectroscopy. There are several other tests of preservation which include examination of the ultrastructure of the shell carbonate and examination of the carbonate under cathodoluminescence to check for signs of recrystallisation (Angiolini *et al.* 2008, 2012), and major element chemistry (Stephenson *et al.* 2012), although these tend to be applied to geological (rather than archaeological) aged material.

Intra-shell samples from molluscs (to investigate seasonality in $\delta^{18}O$) are usually taken from polished, unstained cross sections through the longitudinal growth axis of the shell. Samples are taken using either a hand- (dentist type-drill) or a computer-driven micromill depending on the resolution required. Drill bits can go down to a fraction of a millimetre. Holes are drilled either sequentially or into individual growth increments (if these are visible) to a depth of a few hundred micrometres, or shell material can be 'shaved' off pushing the drill bit in a trough. Sample weights are usually small, <100 μg. Care needs to be taken that only the prismatic layer of the shell is sampled. Prendergast (2013) recommends staining the sections with Mutvei's solution after drilling so that sample locations can be retrospectively matched to individual growth increments.

For season of collection analysis, a few sequential samples are usually drilled from the outer edge along the axis of growth (Mannino *et al.* 2003, 2011; Prendergast 2013). In a study of modern shells from Sicily, Mannino *et al.* (2003) analysed the last-deposited growth increments of shells (in the context of data from a whole year) and compared to environmental data. They removed the outer calcite layer with a manual drill, and then samples were drilled from the last-deposited growth increments. Post-sampling, the shells were checked for diagenesis by XRD and by staining with Feigl's solution (Kato *et al.* 2003).

Isotope ratios (water $\delta^{18}O$ and shell $\delta^{18}O$ and $\delta^{13}C$) are measured using isotope ratio mass spectrometry. Samples are introduced to the mass spectrometer as pure gases, achieved through combustion, chemical reaction (carbonate) or equilibration (water oxygen). By comparing the isotopic ratios of the sample (i.e. ^{18}O and ^{16}O) to a measured standard of known isotope composition (see below), a very accurate determination of the isotopic composition of the sample is obtained.

Notation and Standardisation

A short summary on notation and standardisation is given here, full descriptions can be found in Bowen (1988), Coleman and Fry (1991), Clark and Fritz (1997), Hoefs (1997) and Criss (1999). Isotope ratios from mollusc carbonate ($^{18}O/^{16}O$, $^{13}C/^{12}C$) are expressed in terms of delta values (δ), because the isotope ratios are more easily measured as relative differences, rather than absolute values. We describe δ values in units of per mille (per mil, ‰). The δ value is defined as

$$\delta = \left(R_{\text{sample}}/R_{\text{standard}} - 1\right)*1000$$

where R is the measured ratio of the sample and standard, respectively. Since the ratio of a sample may be either higher or lower than that of the standard, δ values can be positive or negative. The δ value is dimensionless, so where comparisons are made between samples (e.g. where $\delta A < \delta B$) the δ value of A, is said to be 'lower' than that of B (and B 'higher' than A). Where reference is made to absolute ratios, A may be said to be 'depleted' in the heavier isotope compared to B (and B 'enriched' compared to A).

In the laboratory it is necessary to use 'working standards' with values calibrated against recognised standard materials, thus all values are quoted relative to the latter according to Craig (1957) and Deines (1970). For waters (oxygen and hydrogen) we use V-SMOW an average ocean water, for carbonate we use V-PDB, see discussions in Bowen (1988), Coleman and Fry (1991), Clark and Fritz (1997), Hoefs (1997) and Criss (1999). Stable isotope data are presented as per mille (‰) deviations from the relevant international standard (e.g. ‰ V-PDB).

Environmental Archaeology

Reconstructing Seasonal Climate and Environmental Change Using $\delta^{18}O$

The measurement of $\delta^{18}O$ along the growth of molluscs is a widely used technique in palaeoclimate and archaeological science, enabling very high-resolution (daily to interannual) reconstruction of a wide variety of environmental/climatic parameters such as temperature and rainfall amount over several annual cycles. This is particularly advantageous for studying short-term climate variability (e.g. interdecadal phenomena such as El Niño Southern Oscillation (ENSO); Carré *et al.* 2005a, 2005b) and for filling in the gaps often left by other commonly used proxies such as diatoms, ostracods and foraminifera that can be biased towards an average of a particular season over decades. Furthermore, this level of detail is essential when trying to assess cultural–climatic links in the past, as changing seasonal conditions can be extremely detrimental to societies, often leading to long-term climate stress and in extreme cases abandonment of settlements, migration or societal collapse (e.g. Patterson *et al.* 2010).

A modern example of the type of information that can be obtained is a study by Leng *et al.* (1998) who measured the $\delta^{18}O$ variations within shells of the African land snail *Limicolaria kambeul*, demonstrating cyclic variations in $\delta^{18}O$ with regular periodicity, but fluctuating amplitude, driven by changes in the source and isotopic composition of rainfall (Fig. 3). Cycles are characterised by a sudden rise in $\delta^{18}O$ as the snail becomes active with the onset of spring rains, decreasing $\delta^{18}O$ throughout the wet season as the isotopic composition of rainfall decreases during the summer rains, followed by a period of dormancy over the dry season. Another study is of the gastropod *Melanoides tuberculata,* a snail that is widespread in modern (Abell 1985) and Quaternary deposits throughout Africa and Asia and is ubiquitous in both fresh and highly evaporated lakes.

In the study of both whole shells and incremental growth of shell material, Leng *et al.* (1999) analysed both modern and fossil *Melanoides* from lakes in the Ethiopian Rift Valley, and showed that the $\delta^{18}O$ values in the modern shells precipitates in isotopic equilibrium with modern waters and that $\delta^{18}O$

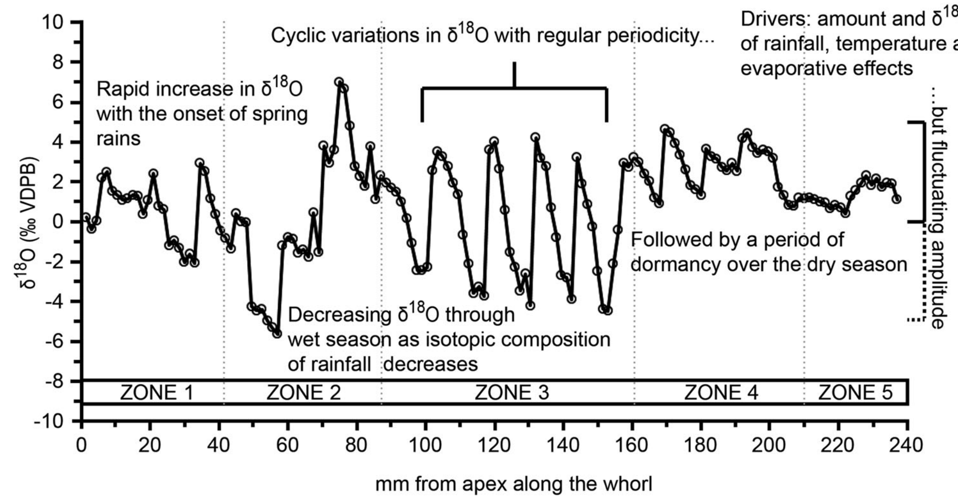

Figure 3 Annotated δ^{18}O profile (plotted at intervals of 1·5 mm) from a modern land snail Limicolaria kambeul chudeaui Germain collected from the margins of Lake Tilo, Ethiopian Rift Valley near Awassa (Leng *et al.* 1998), showing annual climate cycles from the shell δ^{18}O. Ten cycles are present spanning the lifetime of the individual shell.

values are currently very stable over the organism's life. However, measurement of δ^{18}O in fossil shells, clearly documented much wetter conditions with periodic flooding in the early Holocene, followed by a transition to drier conditions from the mid-Holocene to present day (marked by higher salinity and much lower lake levels). Other studies of seasonality in shells include for example Yanes *et al.* (2012) and Hallmann *et al.* (2013).

In an example of the use of mollusc from the world famous Çatalhöyük archaeological site (in south central Turkey), Bar-Yosef Mayer *et al.* (2012) used shells of the freshwater *Unio* spp. to explore changing seasonal contrasts in evaporation/precipitation over the occupation phase (~9400–8000 cal years BP) (Bar-Yosef Mayer *et al.* 2012; Lewis *et al*. unpublished data) (Fig. 4). The intra-shell δ^{18}O profiles generally span between 2 and 4 years, identifiable via clear wet–dry seasonal cycles marked by low winter δ^{18}O (close to estimated modern rainfall values; Bar-Yosef Mayer *et al.* 2012) and high summer δ^{18}O due to evaporation. This is consistent with regional palaeoclimate records which demonstrate highly seasonal climate over the study period with most precipitation falling during the winter/spring months, followed by extremely dry evaporative summers (Ayalon *et al.* 1999; Brayshaw *et al.* 2010). Between shells, there is a temporal trend towards reduced seasonality, broadly coinciding with millennial cooling (beginning ~8600 years ago; Rohling and Pälike 2005) and the 8·2 k event, manifested in the isotope signal as a drop in summer δ^{18}O (Lewis *et al.* unpublished data). Due to the low summer precipitation yields, this has been interpreted as a reduction in summer evaporation due to climatic cooling. While a drop in winter evaporation is likely during a cold-dry period, it seems to have had little impact upon winter δ^{18}O. Reduced seasonality and changing climate likely affected the timing and duration of the growing season (closely associated with the flood pattern of the Çarşamba river) and subsequently resource scheduling, and was perhaps a contributing forcing factor behind societal changes (e.g. settlement abandonment) evident in the archaeological record (Lewis *et al*. unpublished data).

δ^{18}O from marine mollusc growth increments is a method particularly widely used for both environmental and archaeological studies. Intra-shell variations are thought to record past seawater salinity and/or temperature (e.g. Kennett and Voorhies 1996; Klein *et al.* 1997; Aguire *et al.* 1998; Carré *et al.* 2005a, 2005b; Mannino *et al.* 2008; Stephens *et al.* 2008; Patterson *et al.* 2010; Azzoug *et al.* 2012), with some studies using modern environment–shell δ^{18}O relationships to quantify changes in these parameters (discussed below). This technique is of great importance in archaeological investigations as marine fossil shells are very common from archaeological sites (e.g. Burman and Schmitz 2005; Andrus 2011), which means that environmental and climatic inferences are directly applicable to the period of site occupation and often form the major drivers of marine resource availability and subsequently patterns of human subsistence (e.g. Kennett and Voorhies 1996; Mannino *et al.* 2011). Carré *et al.* (2005a, 2005b) demonstrate the potential of δ^{18}O from molluscan growth increments for studying short-term, high-frequency events such as ENSO over the Holocene, using the surf clam *Mesodesma donacium*, present in Peruvian coastal archaeological deposits. Carré *et al.* (2005a) demonstrate a close relationship between local sea surface temperature (SST) data and high-resolution shell δ^{18}O data in modern specimens, enabling monthly SSTs to be reconstructed with ±1·5°C precision. Another study used δ^{18}O of marine and

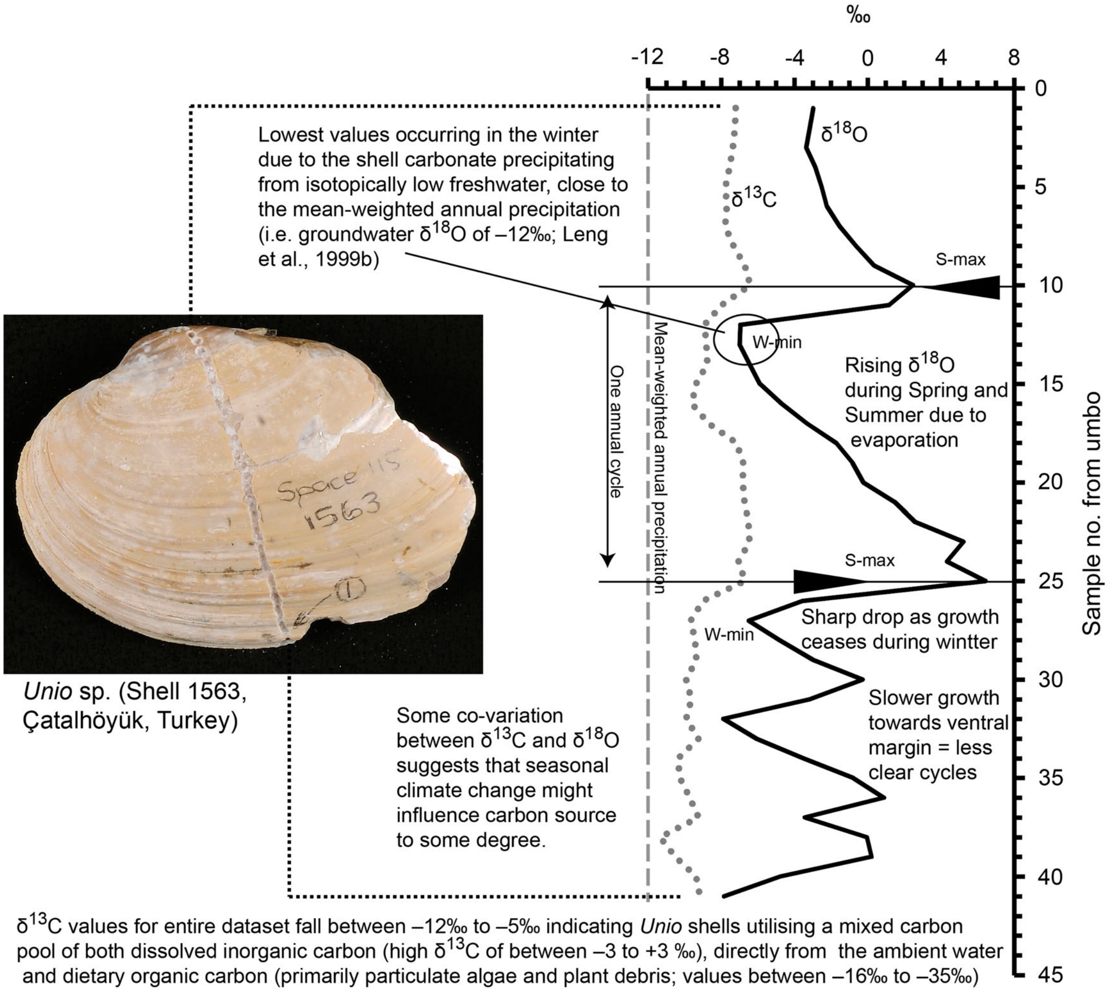

Figure 4 Example of seasonal δ^{18}O and δ^{13}C data from the shell of a fossil freshwater bivalve (*Unio* sp.) collected from Çatalhöyük, Central Anatolia, Turkey (Bar-Yosef Mayer *et al.* 2012). This bivalve likely lived between 4 and 5 years ca. 8500 cal years BP, providing insight into annual climate cycles during the early Holocene (see annotations) during the occupation phase of Çatalhöyük. Dotted lines refer to maximum (summer; S-max) δ^{18}O.

estuarine shells to detect archaeological foraging ranges due to changes in salinities across the foraging range (e.g. Andrus and Thompson 2012). Application to fossil specimens inferred a general warming trend in Peruvian SSTs over the Holocene (Carré *et al.* 2005b). Additionally, several warm (El Niňo) events were identified, within an overall trend of cooler mean temperatures indicating an intense ocean upwelling system in the early Holocene, followed later by a period of reduced seasonality and weaker ENSO variability in the mid-Holocene. ENSO variability is an extremely important component of the Pacific climate system, influencing oceanic upwelling, atmospheric pressure systems, precipitation trend and temperatures, and has been shown to have significant impact on cultures and societies living in the South Pacific region (e.g. McGowan *et al.* 2012).

Recently, very long, continuous sequences of isotope data have been produced by matching-up growth pattern histories in long-living molluscan species (e.g. *Arctica islandica* and *Glycymeris glycymeris*). Butler *et al.* (2013) produced a continuous chronological sequence from annual growth increments in *A. islandica* extending back over 1300 years covering the Medieval Climate Anomaly and the Little Ice Age, while Wanamaker *et al.* (2011) demonstrated the potential of using seasonal δ^{18}O from fossil specimens of *A. islandica* for enhanced palaeoclimatic reconstruction. These deep sea clams are seldom present in archaeological deposits, but such well dated and high-resolution climate data will inevitably prove useful for investigating environmental–cultural links in coastal and marine archaeology.

Season of Collection Using δ^{18}O

The δ^{18}O composition of the final shell growth has been used since the early work of Shackleton (1973) who showed that the last deposited carbonate (at the ventral margin in bivalves, and the aperture in gastropods) reflects the environmental conditions at the time of the animal's death, which in archaeological deposits is often assumed to be the season of collection, if a change in the environmental conditions occurs between seasons. This might be temperature in temperate coastal settings, rainfall composition in terrestrial snails or summer evaporation in freshwater lakes. The timing of human foraging is of interest because it informs on the use of a particular archaeological site and subsistence behaviour (e.g. Mannino and Thomas 2001; Culleton *et al.* 2009; Mannino *et al.* 2011). The number of growth increments (representing time) or sample spots analysed for δ^{18}O in season-of-collection studies must balance the need to analyse enough shells per archaeological context to detect meaningful foraging patterns with the need to characterise the pattern of growth to accurately determine season of collection (Mannino *et al.* 2003). Early studies measured only the outermost growth increment which seems to work when identifying seasonal extremes (i.e. summer and winter). However, it is more difficult to disentangle signatures from shells collected during transitional conditions, as autumns and spring conditions may have similar δ^{18}O. Sequential analyses covering a few weeks/months of growth allow for a more accurate determination of the season of collection as it shows the direction of change (i.e. progressive colder/warmer conditions in the autumn/spring) (Kennett and Voorhies 1996; Mannino *et al.* 2003; Hallmann *et al.* 2013).

Quantitative Information of Environmental Change from δ^{18}O in Archaeological Shells

Measurement of modern shell isotopic ratios across an environmental gradient can enable quantification of environmental/climatic conditions from archaeological deposits and sedimentary sequences (e.g. Burman and Schmitz 2005; Patterson *et al.* 2010). This so-called 'transfer function' can be based on established environmental–$\delta^{18}O_{shell}$ relationships (Grossman and Ku 1986), though often requires the development of local calibration datasets due to local/regional climatic conditions. A wide range of environmental variables have been quantitatively reconstructed depending on the type of environment (see above for major controls on shell δ^{18}O in each environment). The majority of quantitative δ^{18}O shell growth studies come from coastal and marine settings, for reconstruction of past SST following the pioneering work of Emiliani *et al.* (1964). In freshwater and terrestrial environments most δ^{18}O shell growth studies remain only qualitative, but quantification is becoming more common as modern δ^{18}O shell–environment relationships become better understood and key problems tackled. For example, Yanes *et al.* (2011) quantitatively reconstructed relative humidity from archaeological snails from Los Catillejos, SE Spain, demonstrating markedly wetter conditions in the early (particularly before 7200 years BP) and mid-Holocene compared to present day. Dettman *et al.* (1999; 2004), Versteegh *et al.* (2011) and Andrus and Thompson (2012) have all demonstrated the potential of using estuarine and freshwater molluscs to quantify changes in river discharge and glacial meltwater, respectively, and subsequently climate-driven precipitation/drought events. Quantification of river discharge or glacial meltwater requires the production of a modern (locally applicable) calibration dataset, calculated by measuring the relative isotopic offset of modern shells subjected to variable inputs of river discharge or glacial meltwater (both indirect variables of salinity of the ambient water), from end-member values for specimens precipitated in fully marine (or 'no flow' conditions).

Patterson *et al.* (2010) provide a good example of archaeological application from the marine environment. They demonstrate that key events in Norse history (e.g. settlement, famine, societal collapse; Fig. 5) coincide with climatic extremes in the North Atlantic evident in subseasonal δ^{18}O data from Arctic molluscs. A 2000 years (360 BC to AD 1660) quantitative record of North Atlantic seasonal SSTs around Iceland was produced from 26 shells (using several Arctic molluscs species) spanning a series of warm and cold intervals over the study period (Fig. 5). Each shell provided a snapshot of seasonal climate history (spanning ~2–9 years), with modern $\delta^{18}O_{shell}$–temperature–$\delta^{18}O_{water}$ relationships being used to quantitatively infer palaeotemperatures. Seasonal climate was evaluated via differences between δ^{18}O-derived summer and winter temperatures and overall seasonal temperature variability (in Fig. 5), with results demonstrating that settlement of Iceland and Greenland occurred during conditions favourable to sea voyages (i.e. lack of sea ice, warm temperatures) and after successful cropping years (i.e. high summer and winter temperatures). When climate deteriorated (decreasing summer temperatures and colder, more variable winters), several great famines occurred in Iceland (between AD 975 and AD 1056), and later, rapid average temperature decline (~2°C in 70 years; AD 1250–1320) caused increased sea-ice, severe spring/winter weather and abandonment of Greenland settlements (eastern settlement in AD 1360 and west AD 1450) and sailing routes. This study successfully highlights the importance of seasonal climatic extremes on the societies living in difficult environments such as the North Atlantic and how high-resolution δ^{18}O data from molluscs can help better establish causal links between seasonal climate variation and societal response.

Similarly, Ferguson *et al.* (2011) used δ^{18}O (together with shell Mg/Ca ratios as an independent proxy for SSTs) from archaeological (i.e. human-collected) limpet shells (*Patella vulgata*, *Patella caerulea* and *Patella ferruginea*) present in cave deposits in

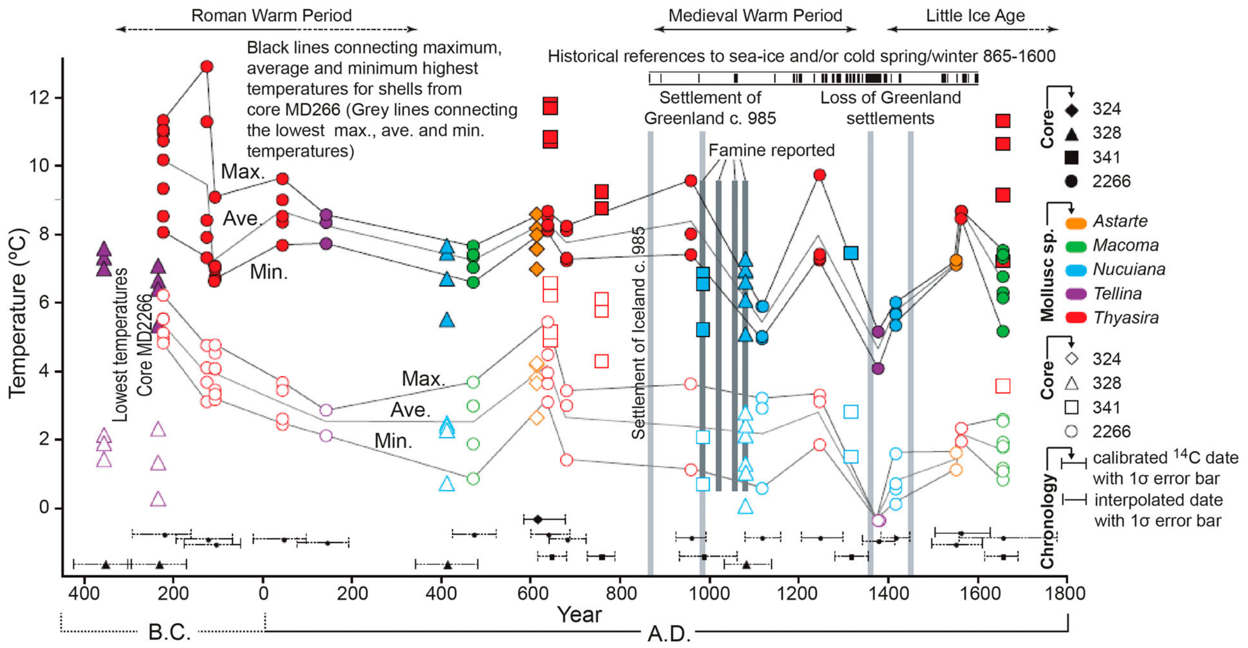

Figure 5 **$\delta^{18}O_{shell}$ derived variation of seasonality in temperature (360 BC to AD 1660) from North-West Iceland (Patterson *et al.* 2010). Filled symbols = minimum $\delta^{18}O$ values (maximum annual temperatures), open symbols = maximum $\delta^{18}O$ values (minimum annual temperatures) for each shell. Temperatures were calculated using local aragonite fractionation equation based on regional salinity-temperature $\delta^{18}O$ relationships applying a constant water $\delta^{18}O$ value of 0·1‰. Key archaeological events (i.e. site settlement and abandonment and documented cold spring/winters and recorded sea ice) and major climate periods are also shown on the diagram. Figure from Patterson *et al.* (2010) with modifications.**

Gibraltar, to quantitatively reconstruct seasonal SSTs in the West Mediterranean during the last Glacial. This is a climatically interesting region due to its high seasonal variability (warm-dry subtropical summers and wet, cooler winters due to southward migration of circulation cells) and ideal location for reconstructing past North Atlantic SSTs and seawater inputs into the Mediterranean Sea. Furthermore, in archaeological terms, Gibraltar is an important locality for studies of human evolution (inhabited by Neanderthals up until ~28 k years BP and early modern anatomical humans) and past societal development. Modern day $\delta^{18}O_{water}$–temperature relationships were investigated via comparison of SSTs derived from modern limpets and measured $\delta^{18}O$ in coastal water samples (using the O'Neil *et al.* (1969) calcite–water $\delta^{18}O$ relationship, and a 0·72‰ positive constant carbonate correction to convert to SSTs), with NOAA (National Oceanic and Atmosphere Administration) optimum interpolation SST data. Almost all fossil specimens exhibited clear $\delta^{18}O$ (and Mg/Ca) seasonal cycles, though summer SSTs were shown to gradually decrease between 40 and 19 k years BP, following the trend of summer insolation and consistent with other regional palaeoclimate records (with the exception of Heinrich event 4). Ferguson *et al.* (2011) also show that the seasonal range in SSTs were ~2°C greater than present day during the last glacial, attributed to the southward extension of the polar front and winter sea-ice at lower latitudes.

In more open ocean environments, where changes in salinity are insignificant, temperature will exert the greatest control on shell $\delta^{18}O$. In coastal and estuarine systems, salinity is often important due to local effects, primarily freshwater flux and evaporation (particularly in lagoon systems). Burman and Schmitz (2005) explored the potential for using the common periwinkle *Littorina littorea* (abundant within these world famous Danish shell middens), for quantitative reconstruction of salinity and temperature, believed to be key environmental parameters driving ecosystem change and subsequently marine resource availability (e.g. Andersen 2007). Modern isotopic–salinity–temperature relationships (and vital effects) for *L. littorea* were established by measuring seasonal $\delta^{18}O$ isotope variations in modern *L. littorea* shells, collected across a salinity gradient (in the Danish Limfjord, from ~30‰ in the west at the opening to the North Sea to ~20‰ in the east where it flows out into the Kattegat) along with seawater $\delta^{18}O$, temperature and salinity. This relationship was then applied to periwinkle specimens present in the Ertebølle shell midden (spanning ~1000 years from ~7100 to 6100 BP), inferring that salinity and temperature in the central Limfjord were ~4–6 psu and 2–4°C higher, respectively during the mid-late Ertebølle archaeological period. This transfer function has also been applied to fossil *L. littorea* specimens from two Eemian sites (in the Kattegat and English channel), inferring that both higher salinity and temperatures than present existed during the Eemian (Burman and Påsse 2008).

Quantification of environmental conditions using $\delta^{18}O$ from molluscan shells has great potential for improving our understanding of past climate/environmental change and cultural linkages. Key problems still exist though, for example, variable $\delta^{18}O_{water}$ in some environments can affect SST (and salinity) reconstructions (see reviews in Andrus 2011; Prendergast 2013). $\delta^{18}O_{water}$ can be evaluated by additional proxies (e.g. fish otoliths, foraminifera, ostracods, water chemistry), but normally only at annual average estimates not at seasonal resolution. Shanahan *et al.* (2005) demonstrated that in nearly constant environmental conditions inter-species and intra-shell isotopic variations in both aquatic and terrestrial mollusc often exceeds that predicted by environmental conditions alone (i.e. offset from isotopic equilibrium even in constant environments). In some cases these offsets can be explained by seasonality effects, meaning that both behavioural and physiological factors need to be considered. New studies are increasingly overcoming these problems (e.g. Burman and Schmitz 2005; Walker and Surge 2006; Wang *et al.* 2011) and other problems such as local effects on the $\delta^{18}O$ signal and variable species vital effects, to produce high-quality, meaningful quantitative climate inferences from palaeoarchives. As with all isotope based studies, the most successful application occurs when used in conjunction with other proxies, particularly if accompanying proxies can provide information on key isotope controls so multiple forcings can be deconvoluted.

Global Scale Climate Controls on Human Population Dynamics from $\delta^{18}O$ in Shells

Studies of global forcings on human population dynamics can be gained from the isotopic composition of shells. For example, from North African and Levantine archaeological records Prendergast (2013) contributes to the investigation of the late Pleistocene dispersal of anatomically modern humans out of Africa as well as the emergence of behavioural modernity. One hypothesis is that these cultural and behavioural developments were forced by major shifts in climate and environment, which can be tested with independent climate records against well dated archaeological sequences. Archaeological cave sites in Libya (Haua Fteah) and Lebanon (Ksar Akil) contain some of the longest and most complete sequences of human occupation in the southeast Mediterranean as well as abundant mollusca (Ewing 1947; McBurney 1967; Barker *et al.* 2010). Prendergast (2013) used $\delta^{18}O$ of marine and freshwater molluscs to assess snippets of time for palaeoenvironmental windows from around the last interglacial to the Neolithic (~130,000 to 5000 years ago). The modern studies showed that $\delta^{18}O$ of modern marine molluscs recorded submonthly SST, while terrestrial molluscs have $\delta^{18}O$ variations linked to the amounts of rainfall. Combined marine and terrestrial stable isotope records from Haua Fteah show that the initial Middle Stone Age (marine isotope stage (MIS)-5) occupation of the site occurred during warm and wet conditions, but the environment became cooler and more arid during MIS-4 coincidental with a reduction in population density. Mollusc oxygen isotope data from Ksar Akil suggested a variable climate through the MIS-3 perhaps as a result of northern hemisphere millennial-scale climate oscillations. There is archaeological evidence of an Upper Palaeolithic change in technologies at this time and one suggestion is that this might have been as a result of populations adapting to rapidly changing environmental conditions (Prendergast 2013 and refs therein). In Libya, the population size remained low through MIS-3 until late MIS-3 and into MIS-2 isotope data indicate a cool and arid environment suggesting that Gebel Akhdar probably served as an environmental refugium for Late Stone Age populations. Through MIS-1 the environment became warmer and wetter but punctuated by arid events. Seasonal shellfish foraging data show year-round occupation of the cave at this time. Overall, the integration of environmental change data from the isotope composition of molluca material with archaeology enable an assessment of the climate controls on human population dynamics during one of the most critical periods of late Pleistocene to Holocene environmental change when anatomically modern humans were thought to have dispersed out of Africa.

Summary

Oxygen isotope geochemistry of Molluscan shell is an essential part of environmental archaeology and over the last decade has contributed significantly to the understanding of the past inhabitants of our planet. Molluscs provide environmental data from the species assemblages and also from the chemistry of their shells. In particular, intra-seasonal information can be gained from shells by analysing the oxygen (and carbon) isotope composition of successive growth increments of calcium carbonate along the direction of growth. The use of $\delta^{18}O$ from molluscan carbonate is an established method to derive environmental information over a range of time scales. The $\delta^{18}O$ of pristine molluscan carbonate, if precipitated in isotopic equilibrium, is a function of the formation water $\delta^{18}O$ and the temperature at the time of the shell formation in the marine environment. With estuarine Mollusca, the difference between marine and freshwater $\delta^{18}O$ (salinity) is often the largest effect on

δ^{18}O, in freshwater molluscs δ^{18}O often preserve changes in the lake water, which might be a function of evaporation or amount, source and temperature of precipitation. The δ^{18}O of terrestrial gastropod carbonate is thought to be controlled by the δ^{18}O of meteoric water. There are excellent examples, some of which we describe, of where δ^{18}O can provide information on reconstructing seasonal climate, season of collection (death of the animal) and environmental change using δ^{18}O. We also provide examples of how this type of data is increasingly becoming more quantitative and how shell isotope data can help with global climate reconstructions. However, preservation testing and sampling methods are still areas that work is needed and are often shell-type specific.

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