The shells of molluscs from all over the world – on land, in lakes, and in the ocean – contain very detailed imprints of past climate change. Using isotope analysis, we can extract these signals and start to piece together long-term climate variations. You will never look at a garden snail in the same way again!

What are molluscs?

Molluscs are soft-bodied (invertebrate) organisms that are widespread in terrestrial, freshwater, and marine habitats. We can split them into two basic groups:

- Gastropods: Molluscs with up to one shell or 'valve' (such as snails or slugs)
- Bivalves: Molluscs with two-sided shells or 'valves' (such as clams, oysters, and mussels)

Many molluscs (both gastropods and bivalves) build hard shells that are rich in calcium carbonate. We call these 'calcareous shells'. Such shells are formed in distinct bands (like tree rings) growing outwards along the direction of growth – the oldest shell is at the edge. Over time, more bands are added to the shell as it grows and the organism is enlarged (Figure 1a-c). The environmental conditions in which the organism live are reflected in the types of isotopes that are present in its shell. This means that the shell contains a 'geochemical' signature of the mollusc's habitat and lifestyle. When the organism dies, its shell can become buried and preserved in sediments at the bottom of the lake or ocean (Figure 1d-f). Once preserved, these shells provide us with a valuable record of environmental conditions at the time that the organism lived. We can analyse the isotopes within the shells to build up a picture of environmental conditions in the past.

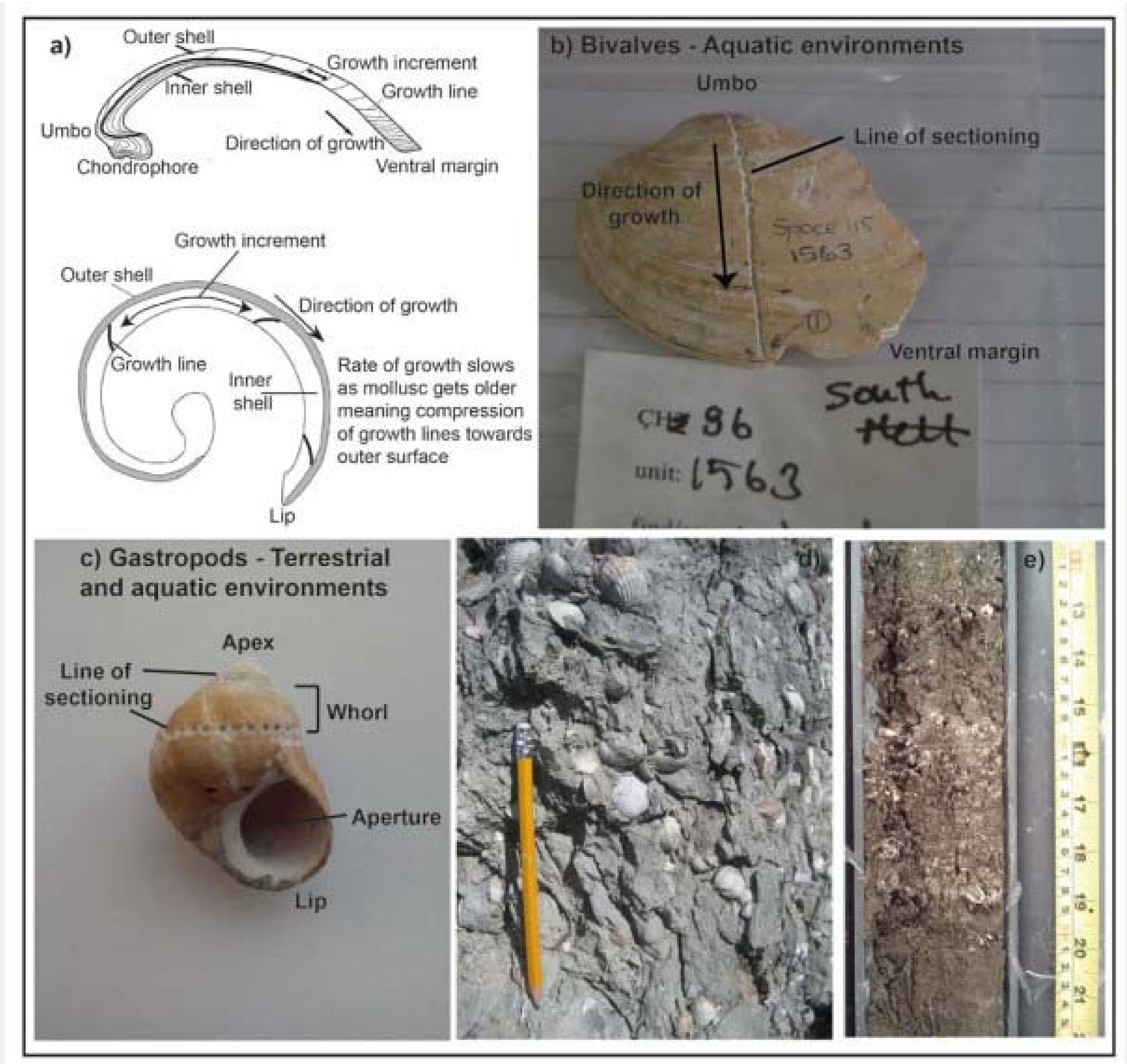

Figure 1. (a) Patterns of mollusc growth and δ18O sampling protocols for bivalves and gastropods (modified from Prendergast and Stevens, 2013 in Encyclopaedia of Global Archaeology). (b) Sequential δ18O sampling in bivalves and (c) gastropods. (d, e) Molluscs preserved in different settings in Jutland, Denmark: d, Whole bivalves preserved in an uplifted sedimentary deposit (formerly marine). e, Abundant mollusc remains present in a sedimentary core sequence from Sebbersund in the Limfjord region of northern Jutland (Denmark). Molluscs can be also directly radiocarbon (14C) dated to provide geochronological context. However, this can be problematic in carbonate rich catchments and shallow marine/coastal sites such as Sebbersund due to reservoir effects (carbon sourced from an 'older' reservoir out of equilibrium with the atmosphere, thereby yielding excessively 'old' dates).

Here we focus on the oxygen isotope ($\delta^{18}O$) record from bivalve and gastropod mollusc shells. We explore how samples of calcium carbonate from individual bands can be used to measure $\delta^{18}O$ (and carbon; $\delta^{13}C$) isotopes. We also look at how such detailed (or 'high resolution') sampling can provide annual or even seasonal environmental records of the mollusc's lifespan.

Oxygen isotopes in mollusc shells

Isotopes are variants of a chemical element, containing equal numbers of protons, but different numbers of neutrons. For example, three isotopes exist for oxygen:

- ^{16}O
- ^{17}O
- ^{18}O

^{16}O has the fewest neutrons and we call this the 'lightest' isotope (its atomic number is lower than the other isotopes of oxygen). It is the most abundant in nature, and the heavier isotopes, ^{17}O and ^{18}O, are extremely rare in comparison. For oxygen isotope analysis in mollusc shells, we are interested in the ratio between ^{18}O and ^{16}O, as ^{17}O is the least abundant and therefore of limited use for isotope analysis.

For shell building, molluscs utilise oxygen (and carbon) either from:

- The atmosphere (in the case of lung breathing terrestrial and freshwater molluscs).
- Or from water (in the case of aquatic gill breathing molluscs from the oceans and freshwaters).

Therefore, for a lung breathing mollusc, for example, the 18-oxygen isotope composition of its shell (or $\delta^{18}O_{shell}$ for short) depends largely on local/regional atmospheric $\delta^{18}O$ – which is mainly controlled by temperature. Likewise, $\delta^{18}O_{shell}$ of aquatic molluscs depends on the $\delta^{18}O$ of the water body in which it lives. This is determined by the relative isotopic difference between inputs (e.g. precipitation and run off), outputs (e.g. evaporation), and temperature in both fresh and marine waters. All the controls on $\delta^{18}O$ are driven by global, regional, or local climate (see summary diagram in Figure 2). This means that the major controls on the isotopic composition of mollusc shells vary between habitats. This is helpful as it allows us to differentiate between different environmental conditions:

- In oceanic environments, water temperature, salinity and (on longer timescales) global ice volume are the major factors influencing isotope values.
- In estuaries, salinity is often the dominant driver due the existence of large salinity gradients, though temperature is also influential.
- In lakes the signal is often due to evaporation (terminal lakes) or precipitation in open lakes where water flows freely through it.
- Finally, for terrestrial and lung breathing freshwater molluscs, $\delta^{18}O_{shell}$ mainly reflects changes in evaporation, precipitation (humidity), and temperature.

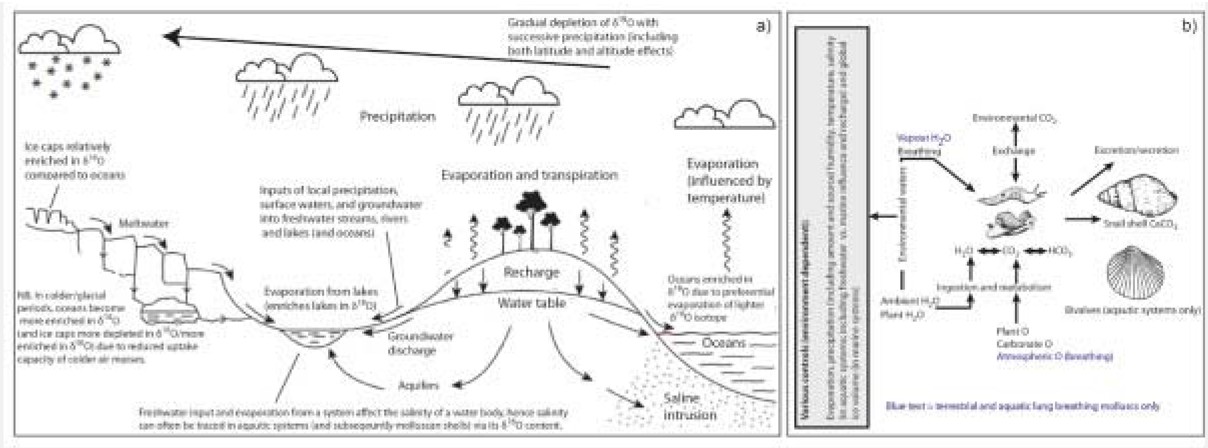

Figure 2. (a) Cartoon of some of the major processes that might affect the ambient δ18O of terrestrial and aquatic systems, from which molluscs take in the oxygen used in shell synthesis. Modified from (original source): Darling et al. 2004, in Isotopes in Palaeoenvironmental Research, Leng, M.J. (Ed.) DPER series volume 10, Springer. (b) Major controls on the δ18O composition of molluscan shells. Modified from: Leng et al. 1998. The Holocene, vol. 8, pp. 407-412.

We can also analyse the carbon isotopes within mollusc shells (e.g. $\delta^{13}C_{shell}$) alongside $\delta^{18}O_{shell}$. This provides us with additional information such as mollusc diet, local vegetation change, salinity (in coastal and estuarine systems), and carbon cycling.

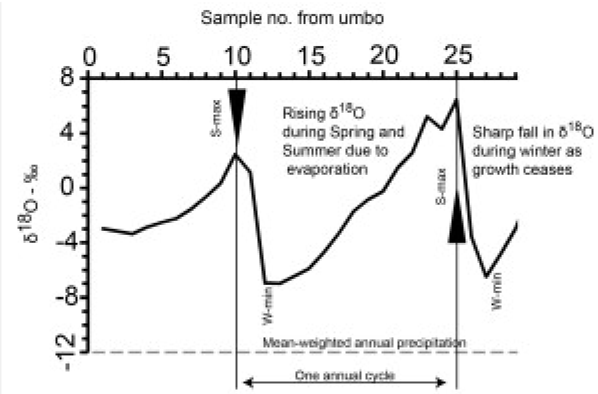

Figure 3. Example of the 'saw-tooth' pattern often exhibited in seasonal δ18O mollusc data from arid or semi-arid regions (this data is from a bivalve collected from Çatalhöyük, Turkey).

So how can we use oxygen isotopes in shells to explore past environments?

In arid regions with distinct seasonal climate (wet and dry), $\delta^{18}O$ data from mollusc shell bands shows a cyclical 'saw-tooth' pattern (Figure 3) with:

- Low $\delta^{18}O$ in the wet season – due to re-charge of regional water bodies.
- Higher $\delta^{18}O$ throughout the dry season – due to evaporation (as the lighter ^{16}O isotope is more easily evaporated, and the heavier $\delta^{18}O$ gets left behind).

Analysis of seasonal data of multiple shells spread through a stacked sequences of deposits – at the bottom of a lake, say – can reveal how seasonal patterns (or 'seasonality') has changed over time. For example, δ18O analysis of modern and fossil freshwater African snail shells (Melanoides tuberculata) from Ethopian Rift Valley lakes indicate that the early Holocene (around 10,000 years ago) saw much wetter conditions than the present day and there is evidence of periodic flooding. It wasn't until the mid-Holocene (around 5,000 years ago) that conditions began to resemble those of the present day – dry conditions with much lower water levels and higher salinity within the lakes.

Elsewhere, seasonal $\delta^{18}O$ data from multiple fossil Unio shells from the world famous Çatalhöyük archaeological site in south central Turkey has shown that there was a reduction in seasonality at around 9,000 to 8,000 years ago. This trend coincides with other records of climate change at the same time, where there was a shift towards drier and cooler conditions and a reduction in winter precipitation and summer evaporation.

Some molluscs (such as *Glycymeris glycymeris* and *Arctica islandica)* can have a lifespan of several hundred years. In fact, the oldest recorded specimen lived to 507 years! If we take several samples of these kinds of shells, then we can match up their growth bands to create much longer environmental records stretching back over 1,000 years. These kinds of records are very valuable for the study of climate change. This is because, as we know, mollusc shells preserve continuous, seasonal records of the environments in which they lived. Piecing together many shells allows us to study short-term climate variations in great detail. This includes interdecadal phenomena such as El Niño Southern Oscillation (ENSO) and the North Atlantic Oscillation (NAO)).

How can we use these shells, and their isotopes, to quantify seasonal climate change?

When studying past environments, we often use qualitative descriptions of the climate (e.g. 'it got warmer'; 'it got drier'). But we also need to produce more quantitative measures of the climate changes by assigning more meaningful numbers/values to our qualitative inferences (*How many* degrees warmer? *How much* drier?). The oxygen isotope composition of mollusc shells allow us to produce such quantitative measures of past environmental conditions. To do this, we first need to study the modern day relationship between a species and the environment in which it lives. For example, if we wanted to use $\delta^{18}O$ isotopes from freshwater snail shells, we would need to measure the isotopic composition of present day snails as well as the $\delta^{18}O$ in the water or atmosphere. We would also measure other conditions in the environment, such as water temperature and salinity, so that we can begin to establish a relationship between the environment and the isotopic value of the snail's shell. We call this method a 'transfer function'. Once established, the transfer function can be applied to *fossil* specimens by using the modern shell-environment relationship and assuming that this hasn't changed over time. We can then turn measured $\delta^{18}O_{shell}$ data into useful environmental units (e.g. if there is a change in the oxygen isotope composition of the shell, how many degrees (°C) of temperature or per mil (‰) of salinity has the lake water changed?).

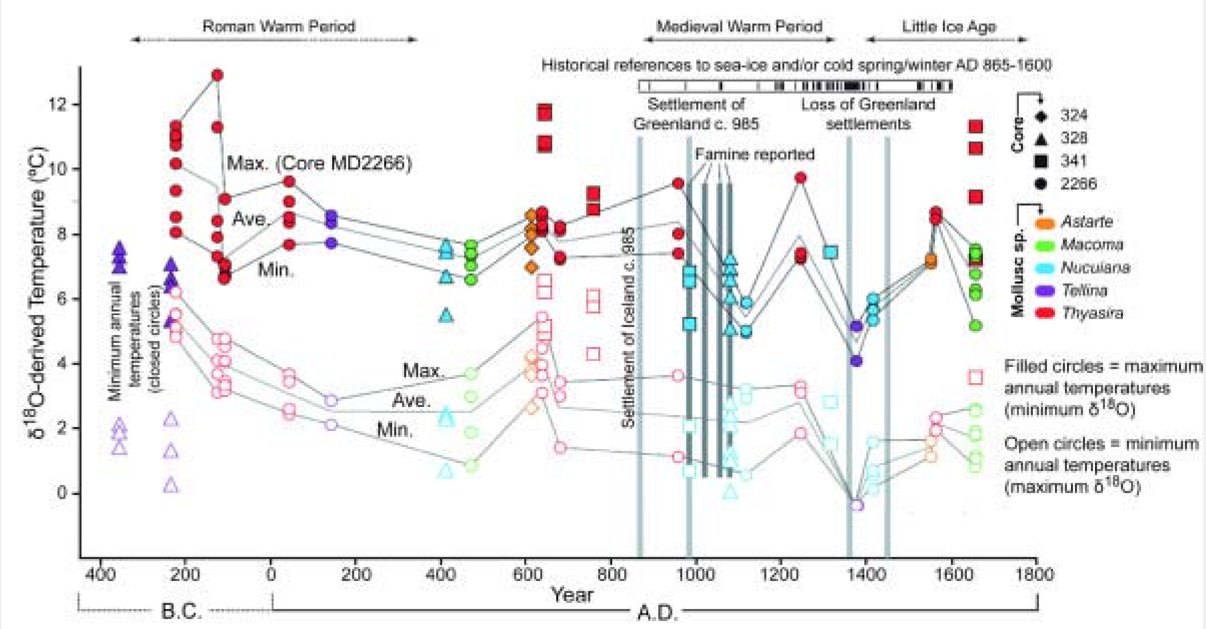

Figure 4. Quantitative reconstruction of North Atlantic sea surface temperatures inferred from seasonal δ18Oshell in Arctic molluscs, demonstrating that changes in seasonality coincide with key archaeological events in Norse history (i.e. site settlement and abandonment and documented cold spring/winters and recorded sea ice). Filled symbols = minimum δ18O values (maximum annual temperatures), open symbols = maximum δ18O values (minimum annual temperatures) for each shell. Modified from (original source): Patterson et al. (2010), PNAS, doi: 10.1073/pnas.0902522107

For ocean sediments the relationship between temperature, the oxygen isotope composition of different carbonate minerals (calcite, aragonite) and the composition of the water from which they formed is well established. As there is already a large dataset, new studies on $\delta^{18}O$ mollusc-based sea surface temperature can apply a 'common' palaeotemperature equation from the existing transfer functions. For example, quantitative sea surface temperature inferences (SST's) from Arctic molluscs have been used in the North Atlantic to study the impacts of seasonal climate change on Norse colonies between 360 BC to AD 1660. Seasonal $\delta^{18}O_{shell}$ and inferred SSTs suggest that Norse settlement of Iceland and Greenland occurred during favourable climatic conditions for sea voyages (reduced sea ice) and (later) crop growing (i.e. high summer and winter temperatures), whilst deterioration of seasonal climate (particularly decreasing summer temperatures and colder, more variable winters) has been linked with famine and settlement abandonment (Figure 4).

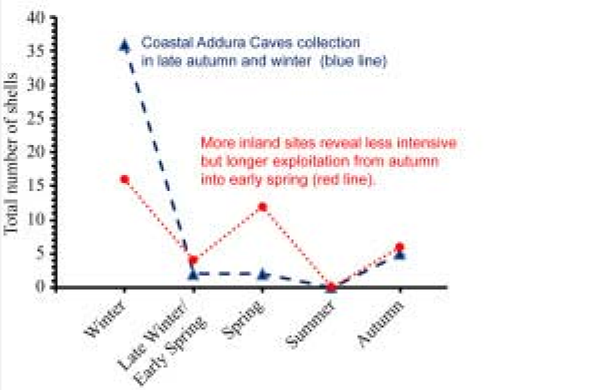

Figure 5. Seasonal mollusc collection patterns inferred from δ18O 'time of death' analyses from Late Pleistocene deposits from northwest Sicily; cumulative data for all inland sites (red line), and all coastal sites (blue line) analysed in this study. The δ18O data has revealed differential mollusc collection patterns of Patella (limpet) and Oscilinus (top snail) molluscs by Lateglacial/Early Holocene (16-9 kyrs BP) hunter-gatherer communities. Based on data from Manino et al. 2011, Quaternary International, vol. 244, pp. 88-104

Using mollusc shells in archaeology

Molluscs can be preserved within archaeological deposits. They also formed an important human resource (collected for food, decoration, and ornamentation) and are often abundant at sites of prehistoric settlements. This means that they provide a very valuable opportunity to reconstruct the past environmental conditions of the local area. In fact, $\delta^{18}O$ from growth bands of molluscs is increasingly being used in environmental (or geo-) archaeology to assess past human-environment interactions and human response/adaptation to palaeoclimatic change. A number of studies have now shown that there are long-term links between seasonal climate variation and social change (e.g., Figure 4).

This research now forms part of a publication for the journal Environmental Arcaheology, which can be downloaded here.

Dr Jonathan Lewis is a Post Doctoral Research Associate based at the Centre of Hydrological and Ecosystem Science at Loughborough University. His research focuses on using diatoms, molluscs, and isotopes to reconstruct palaeoenvironmental conditions in coastal, estuarine and freshwater habitats in Denmark and the Mediterranean Basin. Twitter: @lewis_jp

Professor Melanie Leng is the Director of the Centre of Environmental Geochemistry based at the University of Nottingham and a Science Director at the British Geological Survey where she manages the Stable Isotope Facility, part of the National Facilities, a role which involves a collaborative service role for the UK academic geosciences community. Her research focus is in using isotopes to assess climate and environmental change in the Antarctic Ocean over Northern Europe, the Mediterranean and East Africa. Twitter: @MelJLeng