THE ISOTOPE HYDROLOGY OF QUATERNARY CLIMATE CHANGE

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Abstract

Understanding the links between climate change and human migration and culture is an important theme in Quaternary archaeology. While oxygen and hydrogen stable isotopes in high-latitude ice cores provide the ultimate detailed record of palaeoclimate extending back to the Middle Pleistocene, groundwater can act as a climate archive for areas at lower latitudes, permitting a degree of calibration for proxy records such as lake sediments, bones and organic matter. Not only can oxygen and hydrogen stable isotopes be measured on waters, but the temperature of recharge can be calculated from the amount of the noble gases neon, argon, krypton and xenon in solution, while residence time can be estimated from the decay of the radioisotopes carbon-14, chlorine-36 and krypton-81 over timescales comparable to the ice core record. The Pleistocene–Holocene transition is well characterised in aquifers worldwide, and it is apparent that isotope–temperature relationships of the present day are not necessarily transferable to past climatic regimes, with important implications for the interpretation of proxy isotope data. Groundwaters dating back to one million years, i.e. to beyond the Middle Pleistocene, are only found in major aquifer basins and information is relatively sparse and of low resolution. Speleothem fluid inclusions offer a way of considerably increasing this resolution, but both speleothem formation and large-scale groundwater recharge require humid conditions which may be relatively infrequent for areas currently experiencing arid climates. Both types of record therefore require caution in their interpretation when considering a particular archaeological context.

Introduction

An important element in understanding human evolution is the reaction of hominins to climate change. A powerful technique for doing this is to use the stable isotopic values of proxies associated with hominins and their activities. Some stable isotope ratios ($^{13}C/^{12}C$, $^{15}N/^{14}N$) are primarily used to assess dietary changes or developments, but these are not necessarily linked to climate change. The isotope ratios associated with water, $^{18}O/^{16}O$ and $^{2}H/^{1}H$, are on the other hand much more likely to have a direct link. The basic requirement for the understanding of water isotope proxies is then to have a conception of how climatic change affects environmental water isotope values.

At the present day the largest reservoir of 'old' environmental fresh water is the ice of glaciated regions, with an estimated volume of 24×10^6 km^3, but liquid groundwater at 11×10^6 km^3 still represents a substantial store (Gleick, 1996). When compared to the long, highly-detailed records provided by ice cores from the polar regions (Johnsen et al., 2001; EPICA, 2004), groundwater can only be viewed as a coarse-resolution climate archive. Nevertheless, from an archaeological point of view it has the advantage of being much more widely distributed than ice, and is potentially of more use in low-latitude palaeoenvironmental reconstruction. Three fundamental methods for interpreting groundwater as an archive exist: stable isotopes, noble gases, and residence-time indicators.

It is established that there is generally a strong correlation between surface air temperature and the oxygen or hydrogen stable isotope ratios of rainfall at locations across the globe (Dansgaard, 1964; Rozanski et al., 1992; Fricke and O'Neil 1999). The precise numerical value of the 'δ–T' coefficient for a particular location may be somewhat difficult to assign, depending on the way the relationship is derived (e.g. from seasonal measurements or inter-annual variation: see Darling et al., 2005), but the relationship is robust enough to ensure that stable isotopes play a major part in palaeoclimate reconstructions.

However, there are instances where the isotopic ratios of rainfall have changed significantly over time owing to alterations in the meteorological regime brought about by climate change. These isotopic changes are not simply temperature-related, but are the product of profound alterations in atmospheric circulation patterns. A major example of this is found in the Sahara Desert, where palaeo-recharge to the Nubian Sandstone aquifer is very different in isotopic composition from that of present-day rainfall in the region (Sonntag et al., 1978; Issar, 1985). Fortunately for such instances, an independent way of measuring recharge temperature exists in the form of the dissolved noble gases neon, argon, krypton and xenon (Mazor, 1972; Andrews and Lee, 1979; Stute et al., 1992).

Palaeotemperature information by itself is of comparatively little value without a reasonably secure dating framework. The agents used to date long-residence groundwaters are exclusively radioisotopes: for example ^{14}C, ^{36}Cl and ^{81}Kr but, unlike the short-term age indicator ^{3}H, none of these forms part of the water molecule and therefore there are usually constraints on interpretation.

While all three techniques have been applied mainly to groundwaters in aquifer basins, they are also being increasingly used to investigate waters trapped in fluid inclusions within speleothems. The purpose of this paper is to review progress in both areas with regard to climatic conditions in the later Quaternary. The importance of such reconstruction in a general archaeological context is clear: the "relationship between Plio-Pleistocene climate change and key events in hominin evolution has been a long-term research interest in palaeoanthropology" (Petraglia, 2005: 305). Perhaps this is of greatest significance in East Africa (e.g., Trauth et al., 2007), the location of many key hominin discoveries in Neogene and Quaternary deposits. However, the subsequent dispersal of *Homo* species could be viewed as the point where archaeology begins to acquire a more complex cultural dimension. Waves of migration into the Levant, NW Africa, the northern side of the Mediterranean and elsewhere from 1.8 M yr. onwards (e.g., Bar-Yosef and Belfer-Cohen, 2001; Sahnouni et al., 2002; Carbonell et al., 2008) were undoubtedly climate-mediated to a large extent, mainly via compression of the inter-tropical convergence zone or ITCZ (Trauth et al., 2007), and therefore require a palaeoenvironmental context to aid further understanding.

The narrow Levantine corridor, confined between the desert and the Mediterranean Sea, was particularly important in early hominin migrations and the importance of well-characterised Middle Pleistocene archaeological sites like Gesher Benot Ya'aqov (GBY) is difficult to overstate. The general scarcity of water in the Middle East of the present day has made it one of the first areas where isotope hydrological techniques have been widely applied (Gat and Tzur, 1967; Issar et al., 1972). Inevitably this led to the desire to know more about 'palaeo-groundwaters' and therefore palaeo-climates. The Levant and wider Middle East is a region that has encountered some dramatic climate shifts which have been reflected in major changes in the isotopic composition of environmental water (Geyh et al.,1985; Issar, 1985; Weyhenmeyer et al., 1990), and such changes need to be taken into account when considering the significance of isotope values derived from floral or faunal proxies (Leng, 2005). The application of knowledge about climate change derived from palaeo-groundwaters to Holocene human history was an obvious step (e.g. Issar and Zohar, 2004). To extend this further back in time by one or two orders of magnitude, to encompass migrating *Homo sapiens* and hominins respectively, is undoubtedly more of a challenge.

Palaeohydrological techniques for studying groundwater

Stable isotopes

Oxygen and hydrogen stable isotope ratios are expressed in ‰ with respect to Vienna Standard Mean Ocean Water (VSMOW) on the delta scale:

$$\delta = [(R_{sample}/R_{standard})-1] \times 10^3 \tag{1}$$

where R_{sample} is the $^{18}O/^{16}O$ or $^{2}H/^{1}H$ ratio of the samples, and $R_{standard}$ the corresponding ratio in VSMOW.

Stable isotopes in water are considered powerful tools in palaeoclimatology because strong apparent links exist between some relevant meteorological parameters, such as surface air temperature or amount of rainfall, and the distribution patterns of stable isotopes in rainfall observed for present-day climatic conditions. Based on this link, there have been many attempts to reconstruct past climatic conditions from records of the isotopic composition of ancient precipitation preserved, often via proxies, in various environmental archives (glacier ice, sediments, groundwater, organic matter, and others: see Leng, 2005). However, quantitative reconstruction of past climatic changes from proxy records requires that the isotope palaeothermometer or palaeopluviometer be adequately calibrated for the timescales of interest.

An apparent link between isotopic composition of precipitation and surface air temperature is most important for palaeoclimate reconstructions (e.g., Fricke and O'Neil, 1999). Much present-day data has been accumulated by the IAEA-WMO Global Network for Isotopes in Precipitation (GNIP, see http://nds121.iaea.org/wiser) and various δ–T coefficients have been proposed depending on climate type (Rozanski et al., 1993) and the different ways (seasonal, inter-annual or long-term) of quantifying the δ–T relationship (Darling et al., 2005). However, doubts have arisen as to whether present-day δ–T coefficients are wholly appropriate to interpret isotopic records of past precipitation preserved in various environmental archives (e.g., Darling et al., 2005). The implication is that it is always desirable to obtain some 'real' water from the general location recharged during the climatic period in question. Clearly, direct preservation of palaeo-precipitation is impossible away from polar regions, but fortunately groundwater $\delta^{18}O$ and $\delta^{2}H$ values usually closely reflect the bulk isotopic composition of the rainfall giving rise to them (Clark and Fritz, 1997; Darling et al., 2005). Within certain limitations, speleothem fluid inclusion water may provide the same function (McDermott et al., 2005).

Most rainfall originates from evaporation of the ocean in tropical latitudes. Craig (1961) proposed that the relationship between O and H isotopes in rainfall over most of the Earth's surface could be approximated by the equation

$$\delta^{2}H = 8\delta^{18}O + 10 \tag{2}$$

The validity of this 'world meteoric line' (WML) is surprisingly widespread (Rozanski et al., 1993) given the great variations in climate world-wide. However, while for the most part $\delta^{18}O$ and $\delta^{2}H$ are highly correlated in rainfall, some variation can occur as a result of

atmospheric conditions. A useful index of this is the deuterium excess or d-value (Dansgaard, 1964), defined as:

$$d = \delta^2H - 8\delta^{18}O \tag{3}$$

Deuterium excess is considered to be largely controlled by conditions of atmospheric humidity during the oceanic vapour forming process. For the WML in Eqn.(2), d has a value of 10‰. Much temperate-zone rainfall has similar d-values (Rozanski et al. 1993), though these may show usually modest seasonal variation mainly owing to changes in humidity in the moisture source area. Under certain conditions however, particularly evaporation of seawater into very low-humidity air, d-values exceeding 20‰ can be produced (e.g. Gat, 1980). Such conditions are likely to be restricted to seas adjacent to arid zones such as in the eastern Mediterranean Sea.

Deuterium excess can therefore be a good indicator of moisture provenance. However, both $\delta^{18}O$ and δ^2H values are required (unlike for temperature, when either isotope is sufficient), and few proxies provide reliable data for both isotopes, leaving groundwater as the most likely source of d-value data.

Noble gas recharge temperatures

The solubilities of the noble gases He, Ne, Ar, Kr and Xe are temperature dependent, though significant amounts of ^4He can be produced in aquifers by radioactive decay of uranium and its daughter products, so in practice the technique is restricted to Ne, Ar, Kr and Xe. Nevertheless the existence of four gases still permits a degree of 'redundancy,' effectively leading to greater accuracy in the calculation of recharge temperatures (RTs).

The technique has a minor drawback in that recharge altitude has to be assumed, but provided relief does not exceed 1000 m or so, any error is likely to be small compared to factors such as measurement precision. A more important disadvantage is due to the phenomenon of 'excess air' (EA). This arises from the forcible dissolution of air bubbles during the recharge process, and is present in all groundwaters to varying extents, related to factors such as the nature of matrix porosity, amount of fracturing, and magnitude of seasonal variations in the elevation of the water table. The effect of these factors may change with rainfall intensity, and EA has therefore been proposed as a palaeopluviometer (Wilson and McNeill, 1997; Kipfer et al, 2002), but EA is generally viewed as a factor for which correction is needed. This is because the excess gas means that the measured noble gas concentrations are no longer solely the product of equilibrium at the recharge temperature.

Several different calculation methods exist to extract reliable RTs from EA 'noise'. They tend to rely on reaching a 'best fit' between the different noble gases. The two methods mainly used are iterative optimisation (e.g., Stute et al., 1995), and inverse modelling (e.g., Aeschbach-Hertig et al., 1999). It is not always possible to calculate a realistic RT from noble gas data – specific instances include perturbations from very high EA contents due to glacial overpressuring (e.g., Raidla et al., 2009), or where recharge-derived noble gases have been diluted by a large amount of terrestrial outgassing of CO_2 (e.g., Gilfillan et al, 2008) – but in general the noble gas RT method provides a temperature yardstick against which secular changes in stable isotopes can be compared. Typical precision on calculated RTs would be within ±1°C.

Recently the use of noble gases to investigate the RT of speleothem fluid inclusions has commenced (Kluge et al., 2008; Scheidegger et al., 2010). As with the stable isotopes,

this promises to increase profoundly the resolution of palaeo-information about water because of the great increase in time resolution potentially obtainable via uranium-series dating of the rock matrix (see next section).

Residence time indicators

Any information derived from stable isotopes and noble gases is of little use for palaeoclimate studies unless constrained by age. The coarse resolution of groundwater as a climate archive, resulting from dispersion and advection effects (Stute and Schlosser, 1993), means that only long-range dating techniques are relevant. Radioisotopes dissolved in groundwater are generally recognised as being satisfactory for an age range covering about six half-lives; for example ^{14}C, with a half-life ($t_{1/2}$) of 5730 years, can be used for ages up to around 35 k yr. Other principal age indicators are ^{36}Cl ($t_{1/2}$ 300 k.yr.) and ^{81}Kr ($t_{1/2}$ 230 k.yr.); clearly either of these isotopes has the potential to cover large parts, if not all of the Pleistocene. The isotope ^{4}He, mentioned above in connection with noble gas RTs also has potential as a long-range age indicator (Mazor and Bosch, 1992), but by accumulation rather than decay. Since individual aquifers behave very differently in their helium production rates, ^{4}He requires careful calibration against other age indicators and is not considered further here.

Each of the isotopes ^{14}C, ^{36}Cl and ^{81}Kr has various constraints on its use. These may be practical, e.g., the necessity to outgas several cubic metres of water for ^{81}Kr (Sturchio et al., 2004), or geochemical, e.g., uncertainties about subsurface augmentation for ^{36}Cl (Phillips et al., 1986), or dilution for ^{14}C (Clark and Fritz, 1997). Analysis, especially of ^{36}Cl and ^{81}Kr, is also relatively costly. Nevertheless, they remain the only feasible options for Pleistocene groundwater dating.

Speleothem fluid inclusion waters are far too low in volume to date directly by ^{14}C, ^{36}Cl or ^{81}Kr techniques. Even if this were possible, the dates would be subject to the same uncertainties as for groundwaters. However, on the assumptions that fluid inclusions are well-sealed against post-depositional modification, the use of uranium-series dating of the speleothem matrix (Schwarcz, 1992) is not only less costly but also clearly offers the prospect of very much higher resolution. Using current analytical methods the technique is satisfactory up to 600 k yr.

Uncertainties

<u>Stable isotopes</u> Based on data from numerous studies, δ^{18}O and δ^{2}H in groundwater usually reflect the weighted mean of local precipitation to within quite close tolerances (about ±0.5‰ for δ^{18}O and ±5‰ for δ^{2}H [Darling et al., 2005]). However, while this seems to be a useful rule of thumb for temperate and tropical humid climates, it may apply less successfully to semi-arid or strongly seasonal climates. In the former case there is often simply a lack of long term rainfall data, making any comparison difficult. In the latter case, winter snow cover or very seasonal recharge could upset the balance. For example, snowmelt runoff might exceed aquifer recharge capacity, or the isotopic composition of strongly seasonal recharge might reflect winter or summer air temperature rather than mean annual temperature. However, the available evidence for these proposed effects is restricted to isolated examples (see references in Darling, 2004), and it seems unlikely that a major groundwater body would not be closely representative of the precipitation giving rise to it. That said, there are cases of groundwaters recharged via lakes where large positive isotopic fractionations are possible (Darling et al., 2005). However, such modification would

normally be detected by changes in the relationship between $\delta^{18}O$ and δ^2H compared to the world meteoric line (Craig, 1961), and by hydrochemical indicators.

At least two potential isotope effects arise with regard to dripwaters before they reach the site of speleothem formation. Firstly, the altitude of recharge may not be known with certainty, secondly, there may be selection of recharge by season, individual precipitation event or other factor (see discussion in Darling et al., 2005 and references therein). The first would cause isotopic depletion increasing with rise in recharge altitude, while the second could have some unpredictable effects, depending on residence time in the soil zone and during further percolation. Maximum deviations from weighted precipitation might be expected for dripwaters under cold or arid climates, though in general it appears that the effects are not serious enough to hinder the reconstruction of palaeoclimate, as demonstrated in the much-studied Soreq Cave of Israel (e.g., Ayalon et al., 1998). Isotopic fractionation effects during speleothem growth are probably more significant in this regard. While they lie beyond the scope of this review they have been amply covered (e.g., McDermott et al., 2005; Lachniet, 2009).

<u>Noble gases</u> The recharge temperature information provided by noble gases dissolved in groundwater is considered related to conditions at the water table. Unless the unsaturated zone is very thick, at least many tens to hundreds of metres, the temperature at the water table (RT) is likely to be very similar to mean annual air temperature (MAAT). Furthermore, beneath depths of around 1–1.5 m the temperature of the soil is almost completely damped in relation to surface variations. Most water tables lie at greater depths so it is likely that strongly seasonal recharge becomes equilibrated to soil temperature and therefore reflects MAAT. Indeed the use of noble gas RTs in palaeoenvironmental reconstruction is predicated on this link.

However, under certain circumstances there may be departures of RT from MAAT. If seasonal rainfall is high enough in amount, full temperature equilibration may not be achieved until below the water table, though in general this effect will be well within ±1°C of MAAT. More significant changes are likely to occur in areas with significant seasonal snow cover, where the snow insulates the soil against winter air temperature changes. According to Cey (2009), this could lead to RT being up to ~1.5°C warmer than MAAT. Clearly this is a factor that needs consideration if climate change is likely to have caused major changes in the amount of snow in a particular recharge area.

<u>The δ–T relationship</u> Several processes have been identified which may lead to long-term alterations in the δ–T link over time in a given area: changes in the source region of moisture, changes in the isotopic composition of the ocean, changes of atmospheric circulation patterns shifting the sources and/or routes of the air masses causing precipitation, and changes in seasonality of precipitation (see references in Darling et al., 2005). In theory at least, all four of these factors could be operating concurrently, making it difficult to unravel the magnitude of one particular effect. The interpretation of δ–T data therefore requires as much circumstantial evidence as possible (e.g., the ocean isotopic composition at the time from foraminiferal evidence, GCM estimates of air flow patterns) to narrow down the options.

<u>Residence time indicators</u> There are significant uncertainties associated with groundwater age indicators. Rock dilution of ^{14}C and subsurface augmentation of ^{36}Cl have already been mentioned, but there are others of equal or greater importance. For example, unlike for the stable isotopes and noble gases, where measurement precisions remain effectively the same across their ranges, radioisotope relative standard deviations become much larger as the detection limits are approached, although this can always be acknowledged in the age error bars for a particular sample.

A more fundamental problem is what a water age actually represents. In ideal terms the residence time of groundwater is a simple function of its distance from the point of

surface recharge. Figure 1a depicts a thin porous sandstone aquifer where water age will be in proportion to the distance from outcrop down the flowline – so-called 'piston flow'. Figure 1b however shows a perhaps more common situation where the aquifer is thicker and has some stratification, leading to number of flow horizons. Depending on where and how much of the aquifer is penetrated by a screened borehole, the same mean residence time (masking different age distributions) could be measured on samples from different parts of the aquifer. While this can be addressed to some extent by a knowledge of borehole construction details, records of these are commonly either difficult to access or not available. In the case of fractured aquifers (Fig 1c), simple intergranular flow is overtaken by significantly faster flow along conduits of varying size, conceivably accompanied by mixing of waters of different ages. A knowledge of inflow horizons from borehole geophysics can help to some extent, but for the most part fractured aquifers are better avoided as palaeoclimate archives (Darling et al., 1997).

FIGURE 1

The effects of climate change on groundwater at the basin scale

Aquifer characteristics and groundwater residence time

In order for groundwater to be in residence long enough to preserve evidence of recharge under different climatic conditions, an aquifer must be confined by under- and overlying impermeable rocks (aquicludes). Then residence time ideally becomes a function of piston flow through the aquifer, the velocity of which is governed by a combination of aquifer size and discharge rate. The implication of this is that while aquifers relatively small in areal terms (and therefore flowpath length) may contain waters in excess of 50 k.yr. old (e.g., some of the aquifers in the UK: Darling et al., 1997), only very large systems are likely to contain water in the age range 100–1000 k.yr. (e.g., the Great Artesian Basin of Australia: Bentley et al., 1986).

The small aquifers tend to be relatively well characterised in terms of age and palaeo-recharge conditions. The sheer size of the major aquifer basins, and sparse networks of the deep boreholes necessary to sample groundwater from different points along the assumed flowpaths makes such characterisation more difficult, but these basins present the only opportunity to measure 'active' groundwaters in the age range 10^5–10^6 yrs (as opposed to waters trapped in speleothems, whose origins may be obscured by pre- or post-depositional diagenetic processes).

By far the best documentation of climate change effects on groundwater recharge comes from studies of aquifers in which groundwater age spans the interval from modern to ~30 k.yr., in other words from the Holocene to the late Pleistocene, and including the Last Glacial Maximum (LGM). Examples of such aquifers will be considered first, followed by a necessarily briefer treatment of the much less well-understood major basins containing older groundwaters.

Recording climate change over the LGM and the Pleistocene-Holocene transition

Figure 2 shows plots of $\delta^{18}O$ versus radiocarbon age for a number of sandstone aquifers in Europe (limestone aquifers tend to be rather worse archives: Darling et al., 1997). Immediately prior to the Holocene there is evidence for a time interval in the late Devensian during which there was little or no groundwater recharge over much of Europe, and indeed this is reflected (at least in the UK) by the lowest speleothem growth rate in the past 300 k.yr.

(Gordon et al., 1989). The 'recharge gap' is best developed in the more northerly aquifers where it apparently may have lasted for several thousands of years, but even in the Aveiro aquifer of northern Portugal, the closest to a supply of rainfall (i.e. the tropical ocean), there are signs of a hiatus in recharge. This absence of recharge has been attributed to the existence of permafrost conditions, but since the effect can be discerned to varying extents in localities such as the Levant (Geyh et al., 1985) and North Africa (Edmunds et al., 2004) it may simply be related to low moisture supply, or in other words a general aridity resulting from the sequestration of additional water in the icecaps of the LGM.

FIGURE 2

In all the cases in Figure 2, and others across the world (e.g., Kimmelmann e Silva et al., 1989; Zhu, 2000; Chen et al., 2003), there is a shift in stable isotopic composition between Holocene and older groundwaters. The magnitude of the shifts is variable and usually positively correlated with temperature (the negative correlation from Portugal is simply the result of temperature-related isotopic depletion being outweighed by enrichment of the ocean moisture source by the 'ice effect': Condesso de Melo et al., 2001). The question therefore arises as to the nature of the δ–T link during recharge. There have been fewer studies where noble-gas RTs have been measured, but sufficient research exists to permit some discussion of temperature effects. Three widely-separated examples are considered in detail: the aquifers underlying the North China Plain, the Hungarian Plain, and the Uitenhage basin of southeastern South Africa.

FIGURE 3

North China Plain Kreuzer et al. (2009) measured samples along a flowline in the confined aquifer system in the area south of Beijing (area location in Figure 3). As with the European examples considered above, a recharge gap during the LGM is apparent (Figure 4), so possible minimum isotope and RT values may not be represented. However, a difference of approximately 4.5°C between present (13°C) and pre-LGM recharge conditions is observed, accompanied by an isotopic depletion of about 2‰ $\delta^{18}O$. This would be equivalent to a δ–T coefficient of 0.44‰, higher than the δ–T relationship currently observed for rainfall in this region of China, which lies in the range 0.11–0.15‰. However, Kreuzer et al. (2009) concluded that only about half the isotopic change was due to rising temperature, the other half being due to a weakening in monsoon strength (with implications for moisture source and/or humidity changes) as the Holocene progressed. This conclusion was based on stable isotope compositions, which had a higher deuterium excess value at the beginning of the Holocene (Figure 5). Assuming the purely temperature-related rise in $\delta^{18}O$ has been only 1°C, a δ–T coefficient of 0.22‰ is indicated, significantly closer to the modern rainfall value.

FIGURE 4

FIGURE 5

Hungarian Plain The Quaternary ('Q') aquifer was sampled by Stute and Deak (1989) along a section of 150 km broadly increasing in age southwestward of Fehergyarmat in northeastern Hungary (area location in Figure 3). Some of the interest in this dataset lies in the minimum RTs with very late glacial ages around 15 k.yr. (Figure 6). These interrupt what would otherwise seem to be a long recharge gap (though this could simply be a function of sample availability). However, further samples of this apparent cool recharge would be necessary to

give a more robust confirmation of a cold-but-humid episode. In considering the δ–T relationship in relation to other cases reviewed here, it is more consistent to take the pre-25 k.yr. recharge temperatures. These show that for a decrease of 5°C from present values, there is a depletion of ~2.5‰ in $\delta^{18}O$. This suggests a δ–T coefficient of 0.5‰, which is typical of continental interiors at the present day. There is evidence for reduced d-excess during the apparently coldest period (Figure 5), which implies high humidity in the moisture source area, though as with the recharge temperatures, more confirmation is desirable.

FIGURE 6

Uitenhage Basin The Uitenhage aquifer (area location in Figure 3) consists of fractured quartzites which dip to the SSE beneath a confining layer of shales (Heaton et al., 1986). The sampled flowline is relatively short (about 30 km) but flow through the quartzite is slow and corrected radiocarbon ages of up to ~30 k.yr. have been measured. Figure 7 shows plots of $\delta^{18}O$ and RT versus corrected age. The $\delta^{18}O$ change is well-defined and shows a depletion of 1‰ between the present and the period 20–30 k.yr. Over the same period, RT also falls, and though the scatter is greater, it is clear that a difference of some 6°C is involved. As before, the size of the coefficient needs to be considered in the context of possible humidity variations, but in this case proximity to the ocean is also a factor. Heaton et al. (1986) demonstrated that d-excess values in the Uitenhage groundwaters remained very constant (Figure 5), suggesting that moisture source tracks remained similar over time. The relatively high values of the d-excess imply that the present 'Mediterranean' climate of the area has existed for at least 30 k.yr. Therefore, no correction to the δ–T coefficient is required for humidity. As far as ocean proximity is concerned, the 1‰ rise in oceanic $\delta^{18}O$ is likely to have affected weighted mean rainfall to a similar extent. If this rise is added to the 1‰ change observed in the aquifer, a δ–T coefficient of 0.33‰ for $\delta^{18}O$ is indicated.

FIGURE 7

It is clear from the three diverse examples considered above that the combination of stable isotopes and noble gas RTs in groundwater at the basin scale can provide information on various aspects of large-scale climatic changes, which can provide a context for the interpretation of more-detailed proxy isotope data. However, these studies have been based on the relatively secure foundation of radiocarbon dating. Moving beyond this age range provides some challenges.

The major aquifer basins: groundwater ages of up to a million years

The inference of palaeoclimatic conditions derived from groundwater in large basins is compromised both by a shortage of sampling points and the relatively large errors on water dates. Nevertheless progress has been made with three major systems: the Great Artesian Basin of central–eastern Australia, the Continental Intercalaire of Algeria and Tunisia, and the Nubian sandstone of northeast Africa. A fourth system, the Guarani aquifer of Argentina, Brazil, Paraguay and Uruguay is being investigated (Sracek and Hirata, 2002; Bonotto and Jiménez-Rueda, 2007), but to date there are insufficient data to attempt any palaeoclimatic interpretation.

The Great Artesian Basin of Australia The GAB has provided a test-bed sufficiently large for the application of ^{36}Cl, ^{81}Kr and other dating techniques (Bentley et al., 1986; Lehmann et al., 2003; Kulongoski et al., 2008). However, the size and complexity of the basin makes sampling along a particular flowpath a difficult proposition so there are few instances where

RT, stable isotope composition and age are known for the same sampling points. The results of one such study (Lehmann et al., 2003; study location in Figure 3) are shown in Figure 8a. Owing to the extremely low concentrations of ^{81}Kr, the error bars on individual ages are relatively much larger than for radiocarbon ages. The δ^{18}O values of the four samples lie within the range of modern to sub-recent groundwaters in the recharge area in eastern Australia (Radke et al., 2000). Noble gas RTs measured on the same samples gave temperatures in the range 23–27°C, which is only slightly above temperature measurements in shallow boreholes in the recharge area. There is no evidence for long-term changes in the nature of moisture supply to the GAB.

FIGURE 8

The Continental Intercalaire of the northern Sahara This aquifer underlies a significant area of northern Algeria and extends into Tunisia (study location in Figure 3), where its groundwater eventually discharges into saline lakes (chotts) or directly into the Mediterranean in the Gulf of Gabes. Slow flow through the formation suggests hydraulic ages of up to ~1 M.yr., and this appears to be confirmed by ages based on ^{36}Cl (Guendouz and Michelot, 2006). Figure 8b shows a plot of δ^{18}O versus residence time. While the dataset shows no significant variation with time, it is known that modern recharge to the Continental Intercalaire is 3‰ enriched (Edmunds et al., 2003). This indicates that the present climate of the area is inconsistent with the long-term mean.

The Nubian sandstone of the Western Desert, Egypt The Nubian is a vast groundwater resource underlying 2 million km^2 of northeast Africa (Thorweihe, 1990), with slow-moving waters likely to be of great age simply on hydraulic grounds. As Sturchio et al. state, "The age of groundwater is one of the most elusive geologic parameters to quantify…" (2004: 1). Nevertheless the results from that paper and a related one by Patterson et al. (2005) show reasonably good agreement between the ^{36}Cl and ^{81}Kr techniques (Figure 8c; study location in Figure 3). The figure also shows a considerable difference between isotope ratios of modern and palaeo-recharge. While this was already known from waters of radiocarbon age in the general area (e.g., Gat and Issar, 1974; Sonntag et al., 1978; Darling et al., 1987; Vengosh et al., 2007) and attributed to changes in the ITCZ, the Sturchio et al. (2004) and Patterson et al. (2005) studies suggest a recurring predominant Atlantic source of rainfall for at least the past million years.

Groundwater at the micro-scale and its potential as a palaeoclimate resource

Fluid inclusion waters

Stable isotopes (especially δ^2H) have been measured on fluid inclusions or waters of crystallisation formed under temperature and pressure conditions ranging from near-atmospheric to hydrothermal. While some applications have been investigated (e.g., Sofer, 1978; Bath et al., 1987; Buck and Van Hoesen, 2005), the palaeoclimatic information obtainable from hydrated minerals or hydrothermal inclusions is likely to be limited owing to exchange reactions, so in general, greater credence has been given to speleothem inclusion waters as being more likely to reflect ambient atmospheric conditions. As with groundwaters, supporting evidence of temperature and age are important.

Noble gas thermometry of speleothem inclusions is at a very early stage but Kluge et al. (2008) demonstrated the possibility of obtaining precisions not far off those achieved for

basin groundwaters. Limiting factors include the need to obtain an adequate separation of air and water inclusions, and the fact that lattice-trapping of He and Ne restricts the gases useable for RT purposes to Ar, Kr and Xe (Scheidegger et al., 2010). So far the technique has been tried for Holocene speleothems only, and it remains to be seen whether it is robust enough to be extended back in time by two orders of magnitude. As a form of validation the method could be checked using the clumped-isotope approach (Affek et al., 2008).

The dating of speleothems by uranium-series decay (also known in this context as uranium-thorium dating) is a well-tested method (e.g., van Calsteren and Thomas, 2006), relying on the degree to which equilibrium has been restored between ^{230}Th and its parent ^{234}U within an individual sample. While there can be problems when detrital material is present (e.g., Schwarcz, 1992) or the system is too open, in general no correction is required (unlike radiocarbon or, for that matter, the ^{36}Cl and ^{81}Kr methods of water dating). The length of speleothem required for a U-Th date is generally equivalent to a deposition time of 5–50 years, far less than the analytical error of the dating method. Using current analytical techniques, U-Th dating is limited to dates of up to ~600 k.yr. Other than this, perhaps the main limitation on speleothems as a source of stable isotopic information is that they tend not to grow during arid periods whether warm or cold (but then, as shown in Figures 2, 4, 6 and 7, groundwater recharge is also restricted for the same reason).

Although some δ^{18}O measurements have been made on fluid inclusion waters (e.g., Dennis et al., 2001, McDermott et al., 2005), the main object is usually to obtain δ^2H values which can then be compared with water δ^{18}O values inferred from carbonate δ^{18}O measurements. The latter can be performed by micro-milling (Spötl and Mattey, 2006), giving far higher resolution than could be provided by the relatively large samples needed to provide sufficient inclusions for a δ^{18}O measurement (between one and two orders of magnitude higher than the amount required for a δ^2H determination). Once inclusion δ^2H values are known, these can be combined with the inferred water δ^{18}O values to obtain the palaeoclimatic 'holy grail' of d-excess (discussed earlier), with its implications for change (or lack of it) in moisture source area and therefore in air mass movements over time. Generally the precision on direct δ^2H measurements is good. Figure 9 shows a typical example based on a study of a cave in Oman (Fleitmann et al., 2003; location in Figure 3). Although the spread of samples at around 120 k yr. certainly exceeds δ^2H measurement precision, the measured age range is actually greater than 10 k.yr. Even after factoring in the resolution of the U-Th method (averaging ±2.4 k.yr. in this age range), the changes could still be reflecting changes in climate taking place over intervals of ~5 k.yr.

FIGURE 9

Unsaturated zone pore waters

Another micro-scale phenomenon with the potential to record isotopic changes over long time periods is the existence of pore waters in thick unsaturated zones. The unsaturated zone, also sometimes referred to as the vadose zone, is that part of an aquifer formation which overlies the water table. Depending on a combination of geology and the humidity of the climate, unsaturated zone thicknesses can range from a meter or less to many hundreds of metres. Unsaturated zone profiles up to tens of metres thick have often been measured for purposes of estimating aquifer recharge rates, but residence times based on tritium measurements have only been of the order of 10^1–10^2 years (Cook et al., 1992).

In a sufficiently deep profile, however, traces of recharge water of much greater age may be preserved. Because of the resources required, few of these ultra-deep unsaturated zones have been investigated, but a good example is provided by a study carried out at the

Nevada Test Site by Tyler et al. (1996). Here, pore-water samples from three unsaturated zone profiles extending to more than 230 m deep were analysed for stable isotopes and ^{36}Cl. Pore waters found at depth in the profiles ranged from 20 k.yr.–120 k.yr. in age, with isotope depletions of up to ~3‰ in δ^{18}O compared to modern precipitation. However, d-excess values were similar to those of the present day, suggesting that recharge was derived from the same type of air mass movement, but at a lower temperature.

Inevitably, processes of diffusion and dispersion limit the resolution of these profiles compared to those available from speleothems or high-latitude ice cores. There is also currently no way of extracting information on recharge temperature. Nevertheless the technique provides a possible way of checking on speleothem isotope values in the more arid areas.

Discussion

The combination of three different approaches to investigating groundwater as an archive – stable isotopes, recharge temperature and water age – is paying dividends in palaeoclimate studies; evidence dating back to the Early–Middle Pleistocene boundary and beyond can now be obtained. However, there is nearly always some room for improvement in investigation techniques, whether field- or laboratory-based. The following are areas where some progress can be anticipated.

The dating of aquifer basin waters will improve. Coupled transport and geochemical models will make radiocarbon dating more secure, though with the proviso that 'calibration' (i.e., allowing for secular changes in cosmic ray flux) is inherently difficult with groundwater. There will be lower-volume sampling for ^{81}Kr (Yokochi et al., 2008), and perhaps cheaper analysis for ^{36}Cl. Noble gas analysis will become more precise and recharge temperature modelling will become ever more sophisticated.

Despite such improvements, however, it is debatable whether this will benefit palaeoenvironmental characterisation in an archaeological context compared to a situation with less demanding time-resolution requirements, such as the assessment of nuclear repository potential. The reason for this is of course the increasing blurring of the groundwater record with increase in residence time (also a factor in the interpretation of deep unsaturated zone moisture profiles). A comparison of Figures 8b and 8c with Figure 9 illustrates the problem. While the palaeoclimatic shifts in North Africa and the Arabian Peninsula may not be directly comparable, it seems likely that major recharge periods in North Africa would have been as episodic as those indicated by the Oman cave data, but this is simply not discernable from the low temporal resolution of the available groundwater data.

The above implies that fluid inclusion studies will be more important than groundwaters for archaeology, problems of cave recharge derivation or modification notwithstanding (e.g., recharge altitude, mixing, kinetic fractionation: Lachniet, 2009; Meyer et al., 2009). It remains to be seen whether noble gas RT measurements are going to be widely employable on speleothems, but even if relatively few turn out to have sufficiently low gas/water ratios, the information obtained would still be an advance over the present situation. More rapid ways of processing and measuring inclusion δ^2H values are likely to be devised, leading to higher-resolution d-excess records. However, this supposes that inclusion sealing times are not excessive, and that inclusions remain sealed off for up to 1 M.yr. and beyond. Neither of these may be easy to demonstrate conclusively, though the data of Fleitmann et al. (2003) in Figure 9 suggest that satisfactory sealing on such timescales is at least sometimes achieved. U-Th dating of speleothems (and hopefully therefore their inclusion fluids) has been pursued with great success, but while better measurement

techniques may push the limit a little further towards 1 M.yr., Early Pleistocene investigations require different dating techniques such as ESR (electron spin resonance) or U-Pb, both of which have so far proved rather more challenging than U-Th when applied to speleothems and tufas (e.g., Skinner, 2000; Woodhead et al., 2006).

However, even the potentially high resolution obtainable from speleothem inclusions can provide only a partial picture of the palaeoenvironment because only the wetter climatic phases tend to be represented. What of drier conditions, such as those of present day deserts? It rains periodically over at least some parts of the North African desert, as well as in Oman, but does not recharge the aquifer basins or contribute to speleothem formation to any significant degree. Despite this, human communities exploiting shallow water resources manage to exist in the areas. The relatively enriched isotopic compositions of modern rainfall and recharge (e.g., Figures 8b, 8c and 9) are only known from direct measurements at the present day. While proxies other than speleothems may retain evidence of past low-recharge episodes in isotopic terms, RT will have to be inferred using other means. Archaeological investigations need to take this into consideration when dealing with hominin sites active under more arid conditions.

For example, although the long (100 k.yr.) sedimentary record from the GBY site provides no evidence that the palaeolake Hula ever dried out completely, changes in sediment type indicate some fluctuation in lake level (Feibel, 2004). Since there is no reason to believe that the basic hydrological context of the valley (situated between Mount Hermon and the Golan Heights) was fundamentally different from that of the present day, the sedimentary record can be interpreted very largely in terms of water supply and therefore palaeoclimate. Based on the presence or absence of various fauna and flora, and the $\delta^{18}O$ values of Viviparids, Spiro et al. (2009) inferred a cold and dry start to the sequence, but a trend towards warmer conditions more or less coinciding with the Early–Middle Pleistocene boundary. Only once these warmer conditions had settled down in terms of intensity of wet/dry fluctuations, about halfway (chronologically) through the sequence, are hominin relics widely recorded (Goren-Inbar et al., 2000). But such relics are also known from the preceding cold dry period, and recharge temperature(s) inferred from isotope proxies alone would be subject to all the uncertainties regarding δ–T that have been considered earlier, hence the use of complementary floral and faunal evidence by Spiro et al. (2009).

Conclusions

Although high-latitude ice cores provide an isotopic record of unequalled resolution for much of the Quaternary, there is always likely to be a displacement between their isotope values and those of contemporaneous precipitation away from the polar regions. Therefore at lower latitudes proxy records become important, but require a degree of calibration against 'real' water to realise their full potential.

Groundwater in either free or trapped form can act as an archive of palaeoclimate. To access this, age and recharge temperature need to be measured in addition to oxygen and hydrogen stable isotope ratios. Recharge temperature can be calculated from the solubility of the noble gases neon, argon, krypton and xenon, while residence time since recharge (i.e., groundwater age) can be assessed by the use of the radioactive isotopes of carbon, chlorine and krypton.

Confined aquifers commonly contain waters whose age extends back into the Late Pleistocene. In particular, the transition between the Pleistocene and the Holocene – colloquially the 'end of the ice age,' a critical period in archaeology – is characterised reasonably well across the world. Using the above investigation techniques, it has been demonstrated that present-day relationships between recharge temperature and groundwater

stable isotope ratios do not always apply under past precipitation regimes; therefore caution is necessary in interpreting proxy isotope data in terms of palaeotemperature.

Major aquifer basins such as those underlying North Africa or eastern Australia have been shown to contain waters up to 1 M.yr., i.e., dating back to Middle Pleistocene times. However, sparsely-distributed boreholes and technical challenges in the water dating process have meant these groundwater bodies are less well understood than the smaller basins.

Groundwaters from basins large or small form a low-resolution archive. Speleothem fluid inclusion waters have the potential to provide much higher resolution, and efforts are underway to measure temperatures of formation. While it seems unlikely that inclusion waters will ever be directly datable, uranium-series dating of the speleothem matrix offers a way of assigning an age to the waters. Deep unsaturated zone pore waters are something of a 'halfway house' between aquifers and speleothems, but require rather specific conditions to be preserved.

It must always be remembered that both aquifer basins and speleothems are only recharged or formed under reasonably humid conditions. Present-day evidence shows that human communities can exist naturally under more arid conditions. Archaeological investigations of dry-climate sites need to bear in mind that proxy isotope data may be difficult to relate to the climatic regime prevailing at the time because of the lack of information about recharge temperature.

Acknowledgments

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Figure captions

Figure 1. Schematics to illustrate the effect of aquifer type on groundwater flow and residence time: (a) simple sandstone aquifer with good intergranular permeability acting as a single conduit ('piston flow') with separate narrow age distributions around the mean for groundwaters from boreholes 1 and 2, (b) a thicker sandstone aquifer with layering leading to stacked flow lines, with water residence time depending on the average of flows intercepted by each borehole (flowlines A and B are the same length, so boreholes 1 and 2 would provide groundwater with the same mean age even though 2 is 50% further away from outcrop); age distributions vary depending on the proportion of the aquifer penetrated by the borehole, (c) a fractured limestone aquifer where groundwater flow can 'bypass' intergranular flow by flowing more rapidly along fractures, thus indicating a lower mean residence time than BH 1 in case (b), but with a broad age distribution.

Plots of $\delta^{18}O$ versus ^{14}C age for selected sandstone aquifers in Europe, illustrating the change in stable isotope composition accompanying the transition from Pleistocene to Holocene climate. Note the evidence for the late-Pleistocene 'recharge gap'. Typical radiocarbon age precisions are indicated by error bars on samples from the East Midlands aquifer. Based on data from Darling (2004) and references therein.

Figure 3. Map showing the location of areas used as examples in this paper. 1 – Aveiro Cretaceous aquifer of N Portugal; 2 – Miocene aquifer of the South of France; 3 – Cretaceous aquifers of the Paris Basin, France; 4 – Triassic aquifer of southern Germany; 5 – Triassic aquifer of the East Midlands, UK; 6 – Pliocene–Quaternary aquifer of the Hungarian Plain; 7 – Quaternary aquifer of the North China Plain; 8 – Ordovician aquifer of the Uitenhage area; S Africa; 9 – Continental Intercalaire aquifer of Algeria and Tunisia; 10 – Nubian aquifer of Egypt; 11 – Great Artesian Basin aquifer of Australia; 12 – Hoti Cave in Oman.

Figure 4. Plots of $\delta^{18}O$ and noble gas (NG) recharge temperature versus ^{14}C age for waters from the aquifer system underlying the North China Plain (based on data of Kreuzer et al, 2009).

Figure 5. δ-plots of groundwaters from (a) the North China Plain, (b) Hungarian Plain and (c) the Uitenhage aquifers. Values in brackets refer to ^{14}C ages in ka. Departures from the WML (World Meteoric Line) are interpreted as differing humidity. Data sources as for Figs 4, 6 and 7.

Figure 6. Plots of $\delta^{18}O$ and noble gas (NG) recharge temperature versus ^{14}C age for waters from the aquifer system underlying the Hungarian Plain (based on data of Stute and Deak, 1989).

Figure 7. Plots of $\delta^{18}O$ and noble gas (NG) recharge temperature versus ^{14}C age for waters from the Uitenhage aquifer, South Africa (based on data of Heaton et al, 1986).

Figure 8. Plot of stable isotope composition ($\delta^{18}O$ or δ^2H as appropriate) versus age (^{36}Cl or ^{81}Kr as appropriate) for waters from (a) the Great Artesian Basin of eastern–central Australia (data from Lehmann et al, 2003), (b) the Continental Intercalaire of Tunisia and northern Algeria (data from Guendouz and Michelot, 2006), and (c) the Nubian sandstone of western Egypt (data from Sturchio et al, 2004; Patterson et al, 2005).
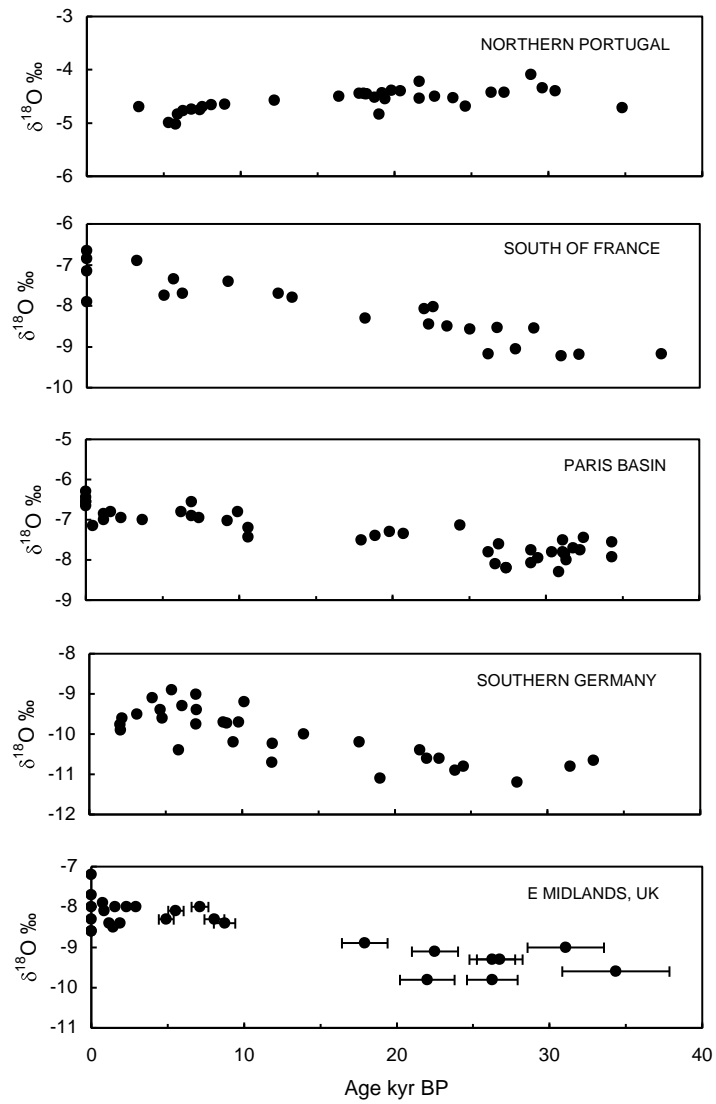
Figure 9. Plot of δ^2H versus U-Th age for inclusion waters taken from speleothems in the Hoti Cave of Oman (data from Fleitmann et al, 2003). Error bars shown for the H4 stalagmite samples only.
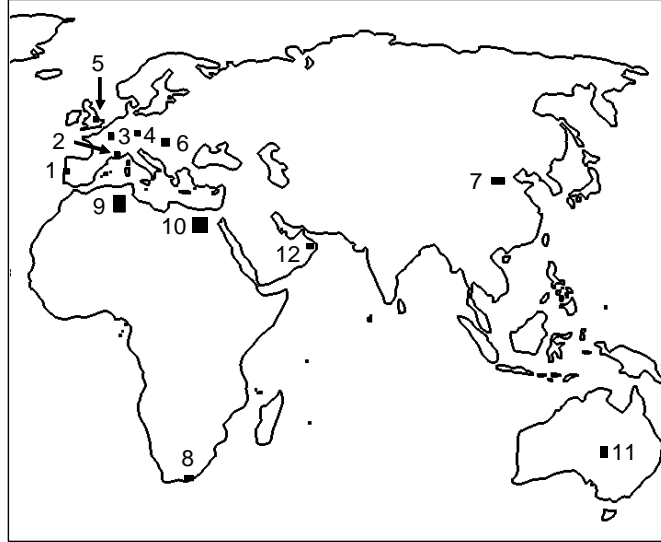
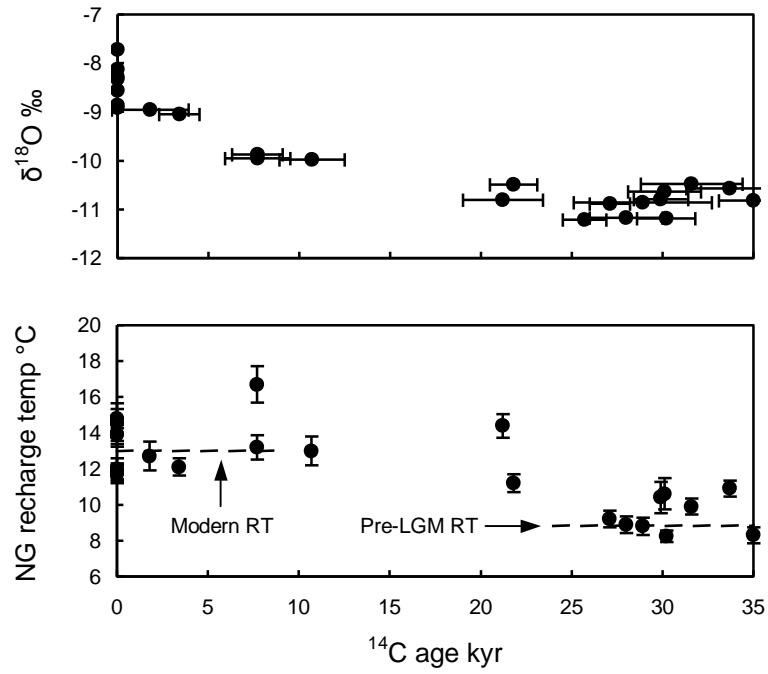**The isotope hydrology of Quaternary climate change – Figure 1**
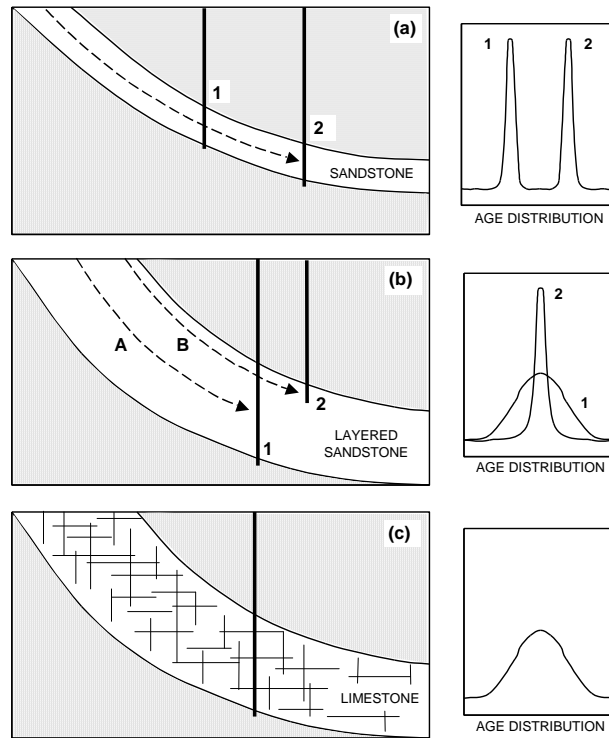
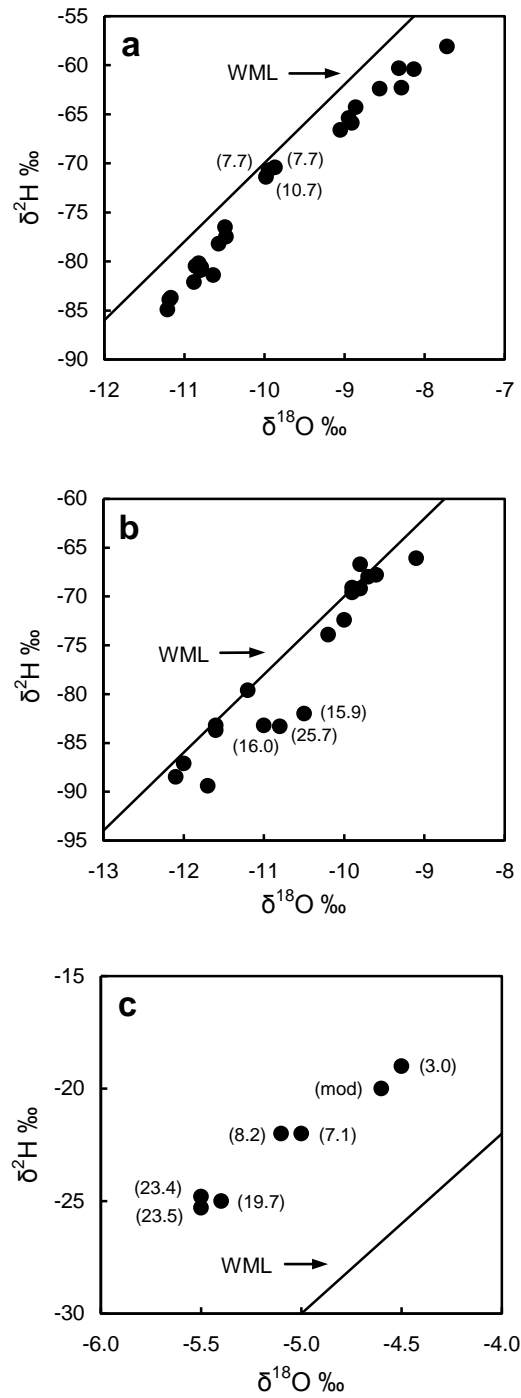**The isotope hydrology of Quaternary climate change – Figure 2**

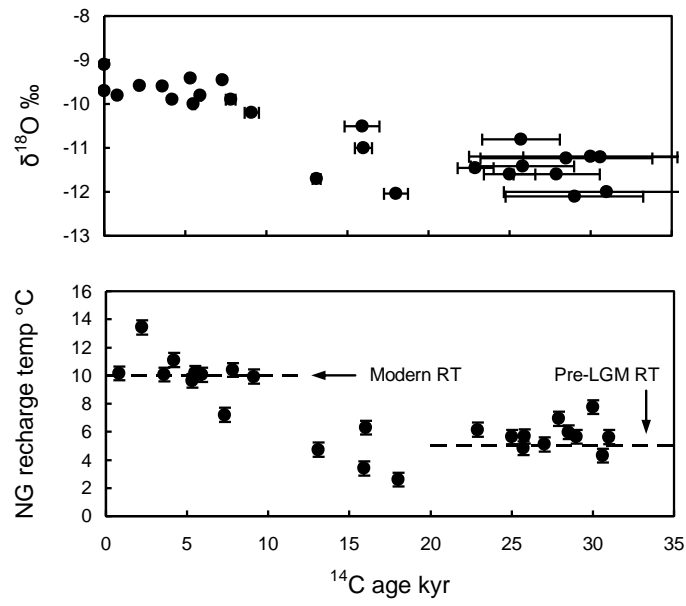**The isotope hydrology of Quaternary climate change – Figure 3**

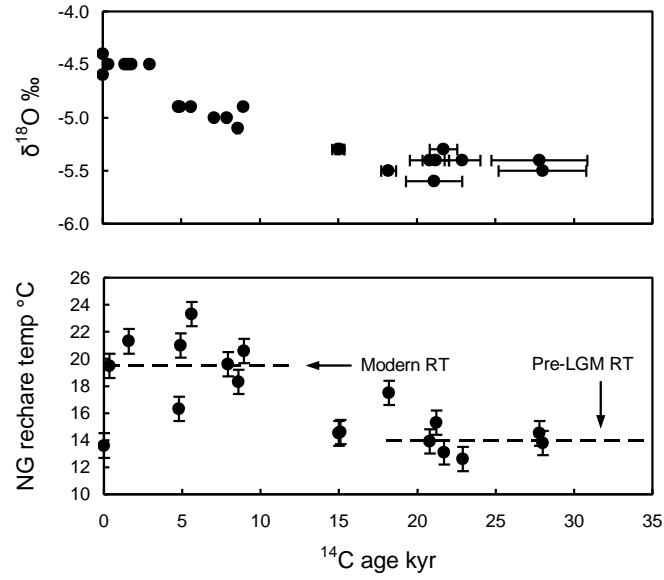**The isotope hydrology of Quaternary climate change – Figure 4**

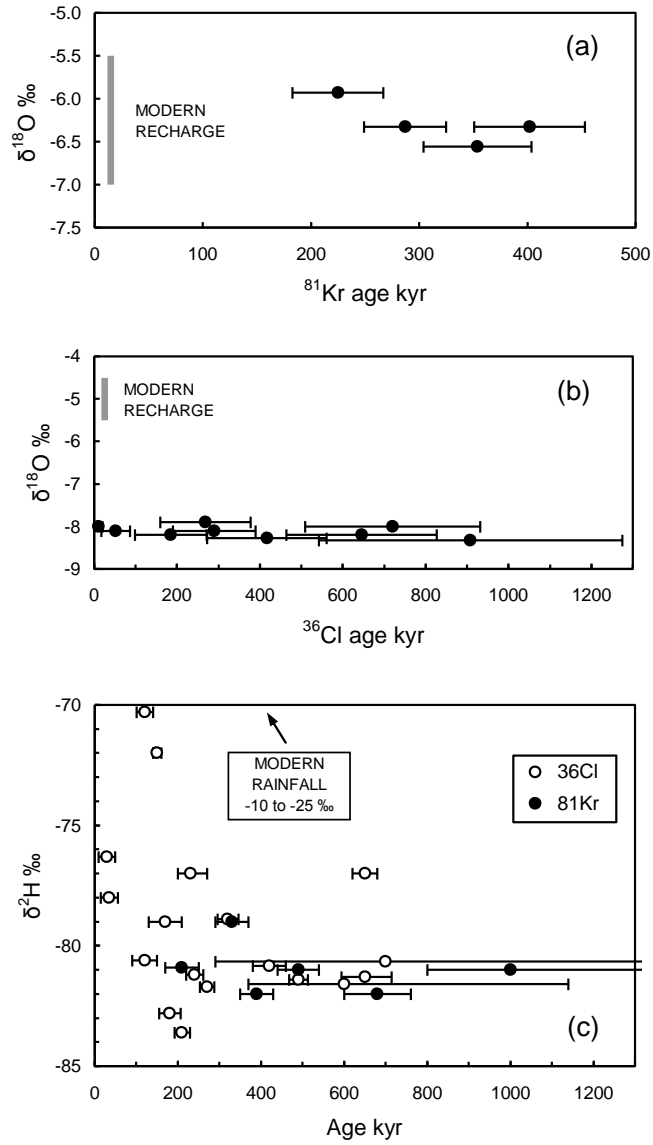**The isotope hydrology of Quaternary climate change – Figure 5**

The isotope hydrology of Quaternary climate change – Figure 6

The isotope hydrology of Quaternary climate change – Figure 7

The isotope hydrology of Quaternary climate change – Figure 8

The isotope hydrology of Quaternary climate change – Figure 9