

Palaeoclimatic records from stable isotopes in riverine tufas: Synthesis and review

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Abstract

It has been known for some time that viable palaeoclimatic information should be recorded in groundwater-fed riverine tufas, particularly barrage, paludal or spring-line deposits. Stable isotope variation in active tufa-depositing systems is well understood. Variability in $\delta^{18}\text{O}$ is driven mainly by changes in water temperature and the $\delta^{18}\text{O}$ value of the recharging water. Variability in $\delta^{13}\text{C}$ reflects principally the relative contribution of isotopically light CO_2 from soil organic matter, and isotopically heavier carbon derived from the dissolution of the aquifer limestone, modulated by equilibration of the aquifer, spring and stream water with atmospheric CO_2 (degassing) and by in-aquifer or in-stream calcite precipitation. In fast-flowing riverine systems the effects of evaporation and in-stream biological activity are negligible. Disequilibrium isotope effects away from actively degassing springs are probably very small, although this can be difficult to demonstrate, especially for $\delta^{13}\text{C}$. Highly resolved sub-sampling of annual layers in active/sub-recent and Holocene tufas show conclusively that seasonal records of temperature ($\delta^{18}\text{O}$) and relative recharge intensity ($\delta^{13}\text{C}$) are recorded. At decadal-scale sampling resolution tufa deposits record (mostly) variation in $\delta^{18}\text{O}$ of meteoric recharge, which depending on locality may reflect source or amount effects (particularly continentality), or temperature change. In Holocene tufas from NW Europe, centennial-scale climatic cooling, culminating in a sharp 8.2 ka minimum is recorded. At one site a detailed $\delta^{13}\text{C}$ record suggests progressive dryness accompanying coldness at 8.2 ka. Although cementation of void space, micritization and aggrading neomorphism all occur in sub-recent and older tufas, there is no unequivocal evidence that diagenesis is either pervasive or that it seriously changes depositional stable isotope values. As tufa deposits accumulate rapidly, where annually laminated they offer an excellent opportunity to study seasonality in Quaternary palaeoclimates. Tufa stable isotope records should be considered complementary to the longer-term palaeoclimatic data provided by speleothems, particularly as these terrestrial carbonates are often closely associated geographically.

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1. Introduction

Tufas are terrestrial carbonates that form under open-air conditions in streams, rivers and lakes. Tufa carbonates precipitate at ambient temperature from calcium-

bicarbonate waters derived from dissolution of carbonate bedrock; in this respect they are similar to cave speleothem deposits, in effect above-ground expressions of speleothems. Following the definitions of [Pedley et al. \(2003\)](#) the term tufa (not travertine) is preferred here as this review deals exclusively with ambient temperature deposits: the term travertine is used by some workers to denote hydrothermal deposits. Tufa calcites precipitate when dissolved CO_2 in karst

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groundwater outgases at a spring, or due to further CO₂ degassing downstream of springs when rapids, waterfalls (Fig. 1; Zhang et al., 2001) or other obstructions such as fallen trees cause water turbulence. Because tufas form in the light, unlike speleothems, they almost always contain microbial (bacterial and cyanobacterial) and sometimes other algal components; many tufas encrust higher plants that live on the margins of streams, waterfalls and wetlands.

Extracting palaeoclimatic and palaeoenvironmental information from terrestrial deposits is now an important area of Quaternary environmental science research. It is therefore desirable to establish both the quality and availability of as many terrestrial climatic and environmental proxies as possible. Research on terrestrial carbonate sediments, typically speleothems and lake sediments, has shown that long and detailed palaeoclimate records can be constructed from stable isotopes (see e.g. Bar-Matthews et al., 1997; Von Grafenstein et al., 2000; Leng and Marshall, 2004; McDermott, 2004; Fleitmann et al., 2004). As shown in this review, tufa carbonates can also record palaeoclimatic information in their geochemical records (e.g. see Garnett et al., 2004a; Smith et al., 2004). The thickest well-dated tufa depositional sequences are much shorter (typically <5000 yrs, although a site in the Czech Republic spans some 7000 yrs; Zak et al., 2002) than many speleothem records, where timescales of >100,000 yrs are achievable (see e.g. McDermott, 2004). However, the rapid accumulation of tufas means that, particularly where

annually laminated, they offer an excellent opportunity to study seasonality in Quaternary palaeoclimates (Matsuoka et al., 2001; Ihlenfeld et al., 2003; Andrews and Brasier, 2005) and potentially to provide high resolution records of relatively short-lived climatic events such as the Holocene 8.2 ka cold event (Makhnatch et al., 2000, 2004; Garnett et al., 2004a). In this way, tufa records should be considered complementary to the longer-term palaeoclimatic data provided by speleothems.

There has been substantial research addressing the types of tufa deposits that might be best studied to recover palaeoclimatic information. Much of this work has addressed fundamental issues about the way stable isotope systems vary in different modern environments. It was well established by the late 1990s that viable palaeoclimatic information should be sought in groundwater-fed riverine tufa systems (Andrews et al., 1993, 1997, 2000) and that waterfall, lake-shoreline and lacustrine spring-fed tufa bioherms were not suitable, for a variety of deposit geometry and geochemical reasons (Andrews et al., 1997, 2000; Rosen et al., 2004). Riverine barrage tufa, or paludal springline deposits (e.g. Garnett et al., 2004a) offer the best hope of long and continuous tufa sequences (Fig. 2), preferably with evidence of autochthonous carbonates such as reed stem encrustations (Andrews et al., 2000). Reliable chronologies in ancient tufa sequences are also crucial, and while some Quaternary tufa deposits have been dated satisfactorily (e.g. Eikenberg et al., 2001;



Fig. 1. Fontaine Petrifiante (E of Le Freney de O'sions, French Alps), a perched spring-line tufa forming at 1700 m altitude with recharge above 2000 m. Tufa deposits have built out to form a small bench over which water cascades, creating a thin apron of tufa on bedrock mudstones in the foreground. $\delta^{18}\text{O}$ of the active tufa is -10.9‰ VPDB and reflects the isotopically negative recharge at this altitude ($\delta^{18}\text{O}$ of -11.1‰ VSMOW). $\delta^{13}\text{C}$ of the active tufa is -0.2‰ VPDB, reflecting sparse input of soil carbon. Although isotope data at sites like these record palaeoenvironmental parameters (Andrews et al., 1997) the deposits are too thin and the geometry is too complicated to use for palaeo-records.



Fig. 2. Late Pleistocene paludal tufa deposit at Ruguilla in central Spain (Pedley et al., 2003). These paludal deposits are ~10 m thick and clearly formed in a valley bottom setting. They have predictable geometry, simple low-angle layered stratigraphy and in situ reed stem encrustations (autochthonous deposits) and are thus excellent targets as palaeoclimatic and palaeoenvironmental archives. Stream incision has inverted the landscape and the tufa deposits are now capping low hills. These hill-top deposits can be susceptible to karstification although other diagenesis is limited and not pervasive (Pedley et al., 2003).

Soligo et al., 2002), others have not (e.g. Arenas et al., 2000), and it is not yet proven that high resolution chronologies are routinely achievable, particularly in Holocene deposits (Garnett et al., 2004b).

This paper reviews palaeoclimatic records derived from stable isotopes in recent (i.e. active)/sub-recent (i.e. <10 yrs since active) and older riverine tufas. The emphasis is on describing the principal driving processes that control the stable isotope records and assessing problems of interpreting the signals and possible diagenetic effects.

1.1. Sensitivity and reproducibility of stable isotope data

Before discussing palaeo-records it is worthwhile considering achievable sensitivity and reproducibility of isotope data. Data produced over the last 30 yrs has normally had levels of precision (based on pure calcite laboratory samples) of <0.1‰ for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. In the last decade the main technological advance has been routine analysis of <300 μg samples, rather than sample masses of 2 mg or more. It is also possible to sample using laser and ion microprobe techniques (Fairchild et al., 2005—this volume), although in both cases precision is reduced (no better than 0.25‰ for ion probe and between 0.1‰ and 0.3‰ for laser-IRMS (Fairchild et al., 2005—this volume; O'Brien et al., in press), the latter also potentially subject to decrease by ~0.1‰ in accuracy due to uncertainties regarding corrections (Sharp and Cerling, 1996). Sampling of smaller masses by whatever methods mean that sub-millimetre resolution sampling can be achieved (e.g. Matsuoka et al., 2001) although sample inhomogeneity could also complicate interpre-

tations. Nonetheless, sensitivity better than 0.1‰ using physically separated μg samples means that palaeo-water temperature variation is theoretically resolvable to <0.5 °C, based on the Craig palaeotemperature relationship (see below). In practice this precision is compromised in palaeo-tufas because precise values (and variability) in $\delta^{18}\text{O}_{\text{water}}$ cannot be demonstrated (Andrews et al., 1994, 2000). Sensitivity of $\delta^{13}\text{C}$ values of about $\pm 0.2\text{‰}$ for palaeo-tufas is much smaller than inherent variability in environmental $\delta^{13}\text{C}$ variation (see below), such that robust records of $\delta^{13}\text{C}$ are assured.

2. Stable oxygen isotopes in tufas

Stable oxygen isotopes in tufa carbonates, along with other terrestrial carbonates (speleothems, lake sediments) are principally a function of: (1) the water temperature in which the tufa calcite forms; (2) the $\delta^{18}\text{O}$ value of the water from which the tufa calcite precipitates, plus or minus (3), other environmental factors, mainly evaporation in the case of $\delta^{18}\text{O}$.

Under equilibrium conditions, temperature and water isotope composition are related to the isotope composition of calcite (the main tufa carbonate) by the 'Craig palaeotemperature equation' (Craig, 1965) where a 1 °C temperature change equates to 0.24‰ change in $\delta^{18}\text{O}$ of precipitating calcite. A number of derivatives of this equation are used, commonly either the Anderson and Arthur (1983) version:

$$T^{\circ}\text{C} = 16.0 - 4.14(\delta^{18}\text{O}_{\text{calcite}}(\text{PDB}) - \delta^{18}\text{O}_{\text{water}}(\text{SMOW})) + 0.13(\delta^{18}\text{O}_{\text{calcite}}(\text{PDB}) - \delta^{18}\text{O}_{\text{water}}(\text{SMOW}))^2$$

or the Hays and Grossman (1991) version, proposed specifically for meteoric cements:

$$T^{\circ}\text{C} = 15.7 - 4.36(\delta^{18}\text{O}_{\text{calcite(PDB)}} - \delta^{18}\text{O}_{\text{water(SMOW)}}) + 0.12(\delta^{18}\text{O}_{\text{calcite(PDB)}} - \delta^{18}\text{O}_{\text{water(SMOW)}})^2$$

In tufa research the Hays and Grossman (1991) version has often been used (e.g. Andrews et al., 1993, 1997, 2000) as tufa calcites are arguably types of meteoric cement. For all practical purposes the PDB and SMOW notations are the same as using the Vienna standardized VPDB and VSMOW (Leng and Marshall, 2004). It is, however, important to know which version of these equations has been used in a particular study; the Hays and Grossman (1991) version yielding slightly cooler temperatures than the Anderson and Arthur (1983) version for most temperate tufa system $\delta^{18}\text{O}_{\text{calcite}}/\delta^{18}\text{O}_{\text{water}}$ combinations. Equilibrium isotope compositions at active tufa sites can be demonstrated (or otherwise) by comparing measured temperatures with those derived from the isotope data and palaeotemperature equation (Uzdowski et al., 1979).

Water temperature in most tufa depositing streams is a direct function of the local climate, in particular groundwater temperature. Groundwater temperature

controls spring and stream water temperature, the latter modulated by solar insolation which causes downstream warming. This means that downstream of springs, water temperature may vary predictably over climatic seasons (Kano et al., 2003), a signal that has been—at least partially—recorded in the precipitating tufa (e.g. see Matsuoka et al., 2001) as discussed further below.

As most tufa depositing systems are spring-fed, the isotope composition of the tufa depositing water is essentially karst groundwater, the composition of which is fed by recharging meteoric water. It is thus expected that the main controls on the isotope composition of water in tufa depositing systems stem from controls on meteoric water (Fig. 3). It is well known that global variation in the $\delta^{18}\text{O}$ value of meteoric water is latitude dependent (Craig, 1961): excepting tropical regions, it also varies systematically with mean annual air temperature (Clark and Fritz, 1997) the global relationship being $d\delta^{18}\text{O}/dT \sim +0.2\text{‰}$ to $0.7\text{‰}/^{\circ}\text{C}$. As mean annual air temperature is mainly a function of latitude and ground surface altitude, at a given tufa depositing site, latitude and altitude (Fig. 3) are the primary controls on $\delta^{18}\text{O}$ of meteoric water: modern microbial tufas can record these influences as

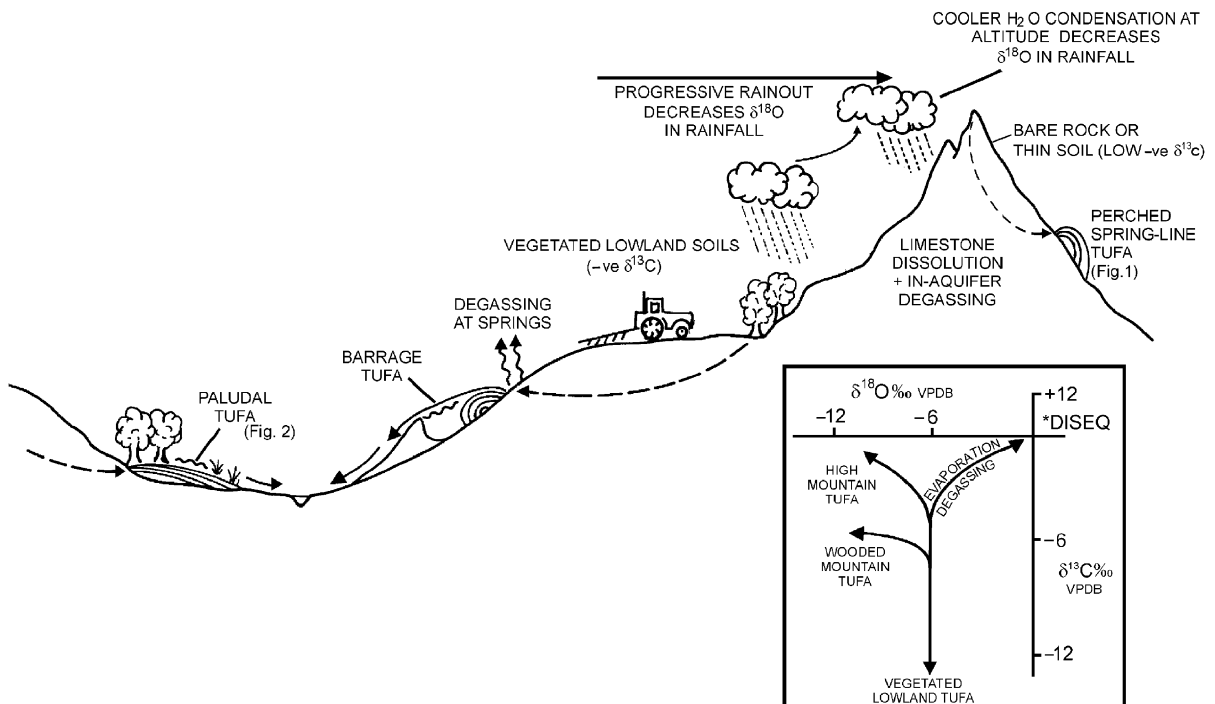


Fig. 3. Cartoon to show main regional-scale environmental factors that affect $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of temperate riverine tufas. Perched spring-line tufas, which may occur at altitude, barrage tufas and paludal tufas, which tend to form at <500 m, are likely to record useful palaeoclimatic data. The inset is an isotope cross plot with typical trajectories likely in maritime NW European data. More continental sites will tend to have lower $\delta^{18}\text{O}$ due to increased rainout effects. Intense degassing at springs may result in low positive disequilibrium (DISEQ) values.

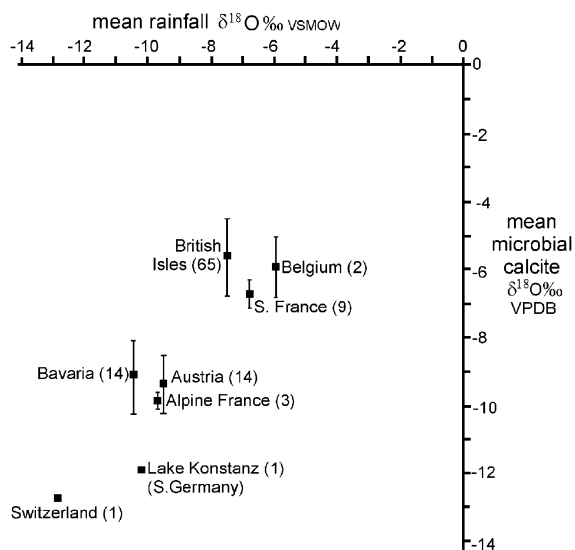


Fig. 4. Mean $\delta^{18}\text{O}$ value for active microbial carbonate for various sites in NW Europe (Andrews et al., 1997), plotted against mean $\delta^{18}\text{O}$ values for rainfall in that area (rainfall data from the synthesis of Rozanski et al., 1993). Use of only actively precipitating microbial calcites means that diagenetic effects are eliminated. Values in brackets represent number of samples and range bars represent one standard deviation from the mean. The British Isles mean is an updated value from Andrews et al. (1993). The best fit line for these data (not plotted) has an r^2 value of 85%. Diagram after Andrews et al. (1997).

shown by Andrews et al. (1997) in a Europe wide spatial survey (Fig. 4). In temperate and humid latitudes the $\delta^{18}\text{O}$ of the groundwater is similar to that of the recharging meteoric water (Gat, 1971; Darling, 2004). In a study of Tertiary sediments from northern Spain, Zamarreño et al. (1997) suggested that a 2.5‰ negative shift in calcite $\delta^{18}\text{O}$ from Late Palaeocene to Middle–Late Eocene tufa stromatolites, was caused by change in recharge $\delta^{18}\text{O}$ driven by a 1000 m increase in catchment altitude over this time, a neat example of the altitude effect developed at one location over millions of years.

At a given site a number of other factors can cause short-term variation in the $\delta^{18}\text{O}$ of meteoric water. These include intense precipitation events (common in the tropics and monsoonal areas), causing ‘amount effects’ (Dansgaard, 1964), and seasonal variability which intensifies in polar (Lawrence and White, 1991) and continental settings (Leng and Marshall, 2004) leading to isotopically more negative rainfall in the cooler winter months. Variation in air mass source direction can also be important: for example in the UK most air masses arrive from the W or SW bringing warm maritime air, whereas the arrival of cold polar airflow brings isotopically more negative $\delta^{18}\text{O}$ meteoric water. Most of these effects are short-lived, lasting

for hours, days or weeks and are thus not seen in groundwater-fed streams due to long residence times and mixing in aquifers. Most tufa-depositing streams reflect the stability of groundwater $\delta^{18}\text{O}$ compositions with remarkably constant $\delta^{18}\text{O}_{\text{water}}$ values over time (Chafetz et al., 1991a,b; Matsuoka et al., 2001) and predictable $\delta^{18}\text{O}_{\text{tufa}}$ values within a region (Andrews et al., 1993; Arenas et al., 2000).

Groundwater $\delta^{18}\text{O}$ in semi-arid and desert regions can have more complicated relationships with $\delta^{18}\text{O}$ of meteoric water due to evaporation before recharge, and due to mixing with older groundwaters recharged under different climatic regimes (Gat and Issar, 1974). Increase in the $\delta^{18}\text{O}$ value of surface streams can also occur due to evaporation; although this effect is likely to be small in temperate groundwater-fed streams (Andrews et al., 1997), it is a problem that will affect tufa $\delta^{18}\text{O}$ values in semi-arid regions (Zamarreño et al., 1997; Smith et al., 2004) or climates with pronounced dry seasons (Fig. 5; see also Ihlenfeld et al., 2003). Significant covariation of tufa $\delta^{18}\text{O}$ with $\delta^{13}\text{C}$ is likely



Fig. 5. Dried-out stream bed coated with bright-white tufa crusts, Montpellier area of southern France (Notre Dame des Londres). The semi-arid climatic setting means that spring flow is seasonal, restricted to wetter winter conditions; evaporation will affect $\delta^{18}\text{O}$ values in dry seasons. Robert Riding for scale.

to arise from combined evaporation and degassing (Smith et al., 2004), just as it does in hydrologically closed lakes (Talbot, 1990).

The issue of whether tufa carbonates record equilibrium or disequilibrium isotope compositions is an important one and early work identified clear disequilibrium effects in high calcite-supersaturation streams within 300–500 m of the groundwater discharge at springs (Usdowski et al., 1979; Dandurand et al., 1982). These authors suggested that isotope disequilibrium occurred because the tufa calcite precipitation rate was faster than isotope equilibration in the calcite–water system (see also Zhou and Zheng, 2002). Although disequilibrium isotope effects in tufas near limestone-hosted springs are clear (Turi, 1986; Portman et al., 2005), disequilibrium effects diminish downstream as the system re-equilibrates to ambient surface conditions (Andrews et al., 1993). The exact distance at which this occurs in a particular stream depends on initial supersaturation and the amount of out-gassing and could be hundreds of metres to kilometres.

Even in streams where equilibrium conditions are likely, it is difficult to *prove* precise equilibrium conditions because water samples are never truly cogenetic with the sampled tufa carbonate: each water sample being an instantaneous ‘snapshot’, whereas calcite samples represent weeks or months of deposition (Chafetz et al., 1991a,b; Chafetz and Lawrence, 1994; Lojen et al., 2004). The practical approach is to study tufa-precipitating streams with demonstrably invariant water isotope composition (by multiple sampling). In the most convincing study of this type Chafetz et al. (1991a,b), working on two streams in Oklahoma (USA), demonstrated no significant differences in tufa $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ on different artificial substrates: they also showed that individual tufa $\delta^{18}\text{O}$ values were close to expected equilibrium values some kilometres from the springs. Near-equilibrium $\delta^{18}\text{O}$ tufa values in other European and N. American streams have also been demonstrated using this approach (Arp et al., 2001; Garnett et al., 2004a; O’Brien et al., in press). Most of the evidence thus suggests that tufa carbonates sampled away from springs will record close to equilibrium $\delta^{18}\text{O}$, although Lojen et al. (2004) report some contradictory data, perhaps because the hydrogeology of their system was not constrained adequately.

2.1. Evidence for climatically driven $\delta^{18}\text{O}$ variability in sub-recent tufas?

The potential for palaeo-tufas to record $\delta^{18}\text{O}$ variability is best tested on recent (active) to sub-recent (i.e.

<10 yrs since active) tufas. Many recent freshwater tufas contain millimetre-scale, alternating laminae of dense micrite and more porous or sparry crystalline calcites (see review in Andrews and Brasier, 2005). These alternating laminae (tufa stromatolites) have been interpreted to represent seasonally controlled differences in the biotic activity of microbes, and/or seasonally controlled changes in the rate of calcification. Either way, couplets of these microbially mediated alternating calcified laminae are generally agreed to represent annual seasonality (Andrews and Brasier, 2005). In recent/sub-recent deposits these seasonal laminae can thus be related directly and confidently to age; moreover these recent deposits will have had least chance to undergo post-depositional diagenetic alteration. Matsuoka et al. (2001) achieved 0.2 mm resolution sampling through ~5 cm (about 10 yrs) of recent/sub-recent Japanese tufa. Their stream water had an

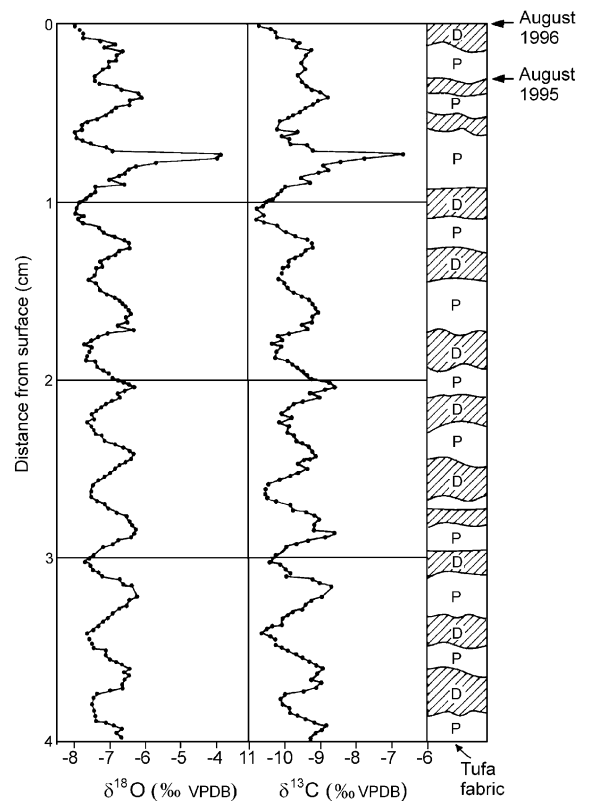


Fig. 6. Positive covariation (r^2 value of 77%) in recent to sub recent tufa calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ at Shirokawa, SW Japan, modified from Matsuoka et al. (2001). The 1.5‰ cyclical variability in tufa $\delta^{18}\text{O}$ values records a total water temperature change of about 6 °C, which is approximately half the measured range in the water (see text). $\delta^{13}\text{C}$ cycles are controlled by stronger wintertime ventilation of the aquifer conduit air, decreasing subsurface air $p\text{CO}_2$, which causes degassing of isotopically light $^{12}\text{CO}_2$ from the groundwater, leaving remaining DIC in the groundwater-fed stream isotopically heavier.

essentially invariant $\delta^{18}\text{O}$ value during the year, allowing comparison of observed water temperature change (caused by seasonal solar heating) with temperatures calculated from tufa $\delta^{18}\text{O}$ variation using a palaeotemperature equation (see above: the exact equation used is given in Matsuoka et al., 2001, p. 38). The 1.5‰ cyclical variability (Fig. 6) in their tufa $\delta^{18}\text{O}$ values represents a total calculated water temperature change of about 6 °C, approximately half of the measured 12 °C change in water temperature. This suggests that the sampling was imperfect, each sample including calcite precipitated over several months (Matsuoka et al., 2001), causing a time-averaging or ‘damping’ effect on the temperature signal. The only other significant study using coupled $\delta^{18}\text{O}$ values from laminated recent/sub recent tufa deposits and their depositing waters was by Ihlenfeld et al. (2003). Their 14 yr record of $\delta^{18}\text{O}$ values from laminated barrage tufa in monsoonal northern Australia is complicated by variability in $\delta^{18}\text{O}$ of the recharge and dry-season evaporation. However, statistically significant, although modest anticorrelation of $\delta^{18}\text{O}$ with Mg ($r^2=29\%$), an element that has temperature dependence during substitution in calcite, suggests that at least a component of the $\delta^{18}\text{O}$ record is controlled by temperature. The rest of the $\delta^{18}\text{O}$ variability was attributed to seasonally variable evaporation, highlighting the importance of this effect in semi-arid climatic settings.

3. Stable carbon isotopes in tufas

Tufa calcite $\delta^{13}\text{C}$ from ambient temperature surface streams will principally reflect the relative sources of carbon that contribute to the dissolved inorganic carbon (DIC) of groundwater, these being CO_2 with low $\delta^{13}\text{C}$ derived from soil organic matter, and higher $\delta^{13}\text{C}$ carbon derived from the dissolution of the aquifer limestone (Fig. 3; Andrews et al., 1993); involvement of even small amounts of thermal waters will typically intensify aquifer limestone contributions due to deeper circulation and longer residence times, leading to less negative $\delta^{13}\text{C}$ (e.g. Arenas et al., 2000). The isotope composition of the DIC is then modulated by equilibration of the aquifer, spring and stream water with atmospheric CO_2 (Usdowski et al., 1979; Matsuoka et al., 2001), by in-aquifer or in-stream calcite precipitation (Andrews and Brasier, 2005), and also potentially by biological activity in the stream.

Preferential degassing of $^{12}\text{CO}_2$ results in higher $\delta^{13}\text{C}$ values of DIC and tufa downstream. Within a few hundred metres of springs this degassing results in rapid calcite precipitation and disequilibrium of the

carbon isotope system (Usdowski et al., 1979; Dandurand et al., 1982). As the isotope system evolves toward equilibrium further downstream, rates of degassing and calcite deposition decline. However, continued progressive CO_2 degassing carries on increasing $\delta^{13}\text{C}$ values of DIC and tufa downstream (Pentecost and Spiro, 1990); this means the distance of a tufa deposit from a spring will be an important relative control on its $\delta^{13}\text{C}$.

Tufa precipitated downstream of sites where disequilibrium effects finish still tend to have rather variable $\delta^{13}\text{C}$ when compared to expected equilibrium values (Emrich et al., 1970; Romanek et al., 1992). In a few studies, near equilibrium has been demonstrated (Arp et al., 2001; Garnett et al., 2004a), whereas in others disequilibrium effects are clear (Chafetz et al., 1991a,b; Lojen et al., 2004). This rather unpredictable outcome is almost certainly due to instability of environmental influences on the $\delta^{13}\text{C}$ system, which is affected by water flow rate, degassing, up stream calcite precipitation and potential microenvironmental effects of photosynthesis, particularly cyanobacterial photosynthesis (see below).

The relative amount and type of soil carbon contributing to groundwater DIC will potentially affect DIC $\delta^{13}\text{C}$ (Fig. 3). It has been shown that $\delta^{13}\text{C}$ from mountainous Alpine microbial carbonates and tufas are between 2‰ and 6‰ higher than lowland sites due to smaller soil-zone carbon inputs where mountain soils are thin or poorly vegetated (Figs. 1 and 3; Andrews et al., 1997). Change in topography and altitude over millions of years, during orogenic events, could lead to development of rugged, less-well vegetated catchments and concomitant decrease of soil-zone influence on $\delta^{13}\text{C}$. Such events seem to have been recorded by an 8‰ shift toward less negative $\delta^{13}\text{C}$ values in tufa stromatolites from Late Palaeocene to Middle–Late Eocene times in northern Spain during up-building of the Catalan Coastal Ranges (Zamarreño et al., 1997).

Similarly, the type of plant metabolism (C3 vs. C4 photosynthetic pathways; Deines, 1980) will affect DIC $\delta^{13}\text{C}$. In most temperate systems studied to date C3 plants have dominated, leading to tufa $\delta^{13}\text{C}$ typically below -8% (see below), whereas in semi-arid and desert regions where C4 vegetation is more common, tufa $\delta^{13}\text{C}$ values are markedly less negative, e.g. between -6% and $+2\%$ (Smith et al., 2004).

The role of in-stream biology affecting tufa $\delta^{13}\text{C}$ is debated: although some workers hint that $\delta^{13}\text{C}$ might be affected by vegetation (Pavlović et al., 2002a,b; Horvatinčić et al., 2003) the data are not convincing, and the general view is that plants (mosses, algae) provide a framework on which diatoms and cyanobac-

teria largely act as sticky surfaces that aid calcite nucleation, particularly on entrapped seed crystals (Emeis et al., 1987; Pentecost, 1993, 1998; Zhang et al., 2001; Pavlović et al., 2002a,b) and perhaps by helping remove kinetic inhibitors (Bosak and Newman, 2005). Early work showed that effects of higher plant photosynthesis on DIC $\delta^{13}\text{C}$ were negligible in open-system flowing streams (Uzdowski et al., 1979; Dandurand et al., 1982) although effects can become significant in small stagnant pools (Liu et al., 2005). Encrustation of moss and other plants by tufa is in most cases essentially abiogenic and photosynthetic effects on tufa $\delta^{13}\text{C}$ are small (Pentecost and Spiro, 1990; Arp et al., 2001). The exception to this is when cyanobacteria and other algae are present in large numbers; under these conditions microenvironmental effects of photosynthesis *within the colonies* (i.e. partially isolated from the bulk DIC) can remove isotopically light $^{12}\text{CO}_2$ to leave microbial tufas calcites enriched in ^{13}C (Pentecost and Spiro, 1990; Arp et al., 2001; Lojen et al., 2004). These microenvironmental effects are not yet widely proven (see discussion in Arp et al., 2001) and their signal in riverine tufa deposits is likely to be small, except perhaps in semi-arid systems prone to seasonal drought (Andrews and Brasier, 2005).

3.1. Evidence for climatically driven $\delta^{13}\text{C}$ variability in sub-recent tufas?

Recent/sub-recent Japanese tufas show a very highly resolved cyclical record of seasonal $\delta^{13}\text{C}$ variation over 10 yrs (Fig. 6; Matsuoka et al., 2001), with values apparently close to equilibrium (\pm possible small photosynthetic effects) with the DIC. This suggests that at a given site $\delta^{13}\text{C}$ can be more predictable than spatial studies have suggested so far. Corroborating this, the modern DIC $\delta^{13}\text{C}$ values also showed seasonal variation, being lowest in summer and highest in winter (Matsuoka et al., 2001). As the tufa calcite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values co-varied positively (Fig. 6, $r^2=77\%$), the seasonal change in $\delta^{13}\text{C}$ of both the modern DIC and tufa calcites appeared to be linked to temperature. Matsuoka et al. (2001) argued that the principal control was winter degassing of CO_2 in the groundwater that feeds the spring and tufa depositing stream. This effect is strongest in winter when the subsurface karst conduit air is warmer (less dense) than air in the atmosphere. The resulting instability (warm air below cold air) promotes mixing and ventilation of the conduit air, decreasing its $p\text{CO}_2$, and promoting further degassing of $^{12}\text{CO}_2$ from the groundwater, leaving the remaining DIC in the groundwater-fed stream with a higher $\delta^{13}\text{C}$

value. These interpretations were broadly corroborated by Ihlenfeld et al. (2003) in a study of recent/sub-recent laminated tufa from northern Australia. Their 14-yr tufa record showed statistically significant co-variation between Sr and Ba ($r^2=64\%$) and between Sr and $\delta^{13}\text{C}$ ($r^2=46\%$). The only process capable of causing this co-variation was precipitation of calcite (forced by CO_2 degassing) upstream in the karst aquifer and stream (Ihlenfeld et al., 2003), i.e.:



a process that increases $\delta^{13}\text{C}$ of the residual DIC (see above) and increases dissolved Sr/Ca, and Ba/Ca in the remaining water, because these trace elements have partition coefficients $\ll 1$. If degassing in aquifer air pockets is enhanced during decreased recharge when groundwater levels are low, sympathetic variation in $\delta^{13}\text{C}$ and element/Ca ratios may represent an index of recharge and therefore precipitation intensity (Ihlenfeld et al., 2003; Andrews and Brasier, 2005).

4. Stable isotope proxies for palaeoclimate in late Quaternary tufas

The preceding section has outlined the likely controls on $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in tufa deposits, and the evidence from time-resolved short stratigraphies of recent/sub-recent tufa (Matsuoka et al., 2001; Ihlenfeld et al., 2003) shows that high quality stable isotope information is recorded. These encouraging results suggest that older Quaternary tufas could record important palaeoclimatic data, particularly *relative* temperature change ($\delta^{18}\text{O}$) and moisture availability (linked to biomass type/abundance) and recharge ($\delta^{13}\text{C}$): available Late Quaternary data are compiled in Fig. 7 to illustrate this point.

To date, only one study has been published with seasonal-scale $\delta^{18}\text{O}$ resolution in an ancient tufa (O'Brien et al., in press). Their results showed for the first time that a seasonal temperature signal, as described from sub-recent deposits (see above) is resolvable from $\delta^{18}\text{O}$ in a 7000 yr old deposit. However, the sampling resolution for long-term isotope records in ancient tufas has more typically been at centimetre scale, each sample probably representing decadal time-scales of tufa accumulation (Pazdur et al., 1988; Andrews et al., 1994; Zak et al., 2002; Garnett et al., 2004a; Makhnach et al., 2000, 2004). With this coarser sampling resolution, seasonal-scale environmental variations are 'averaged out' and only longer term changes in isotopic composition recorded.

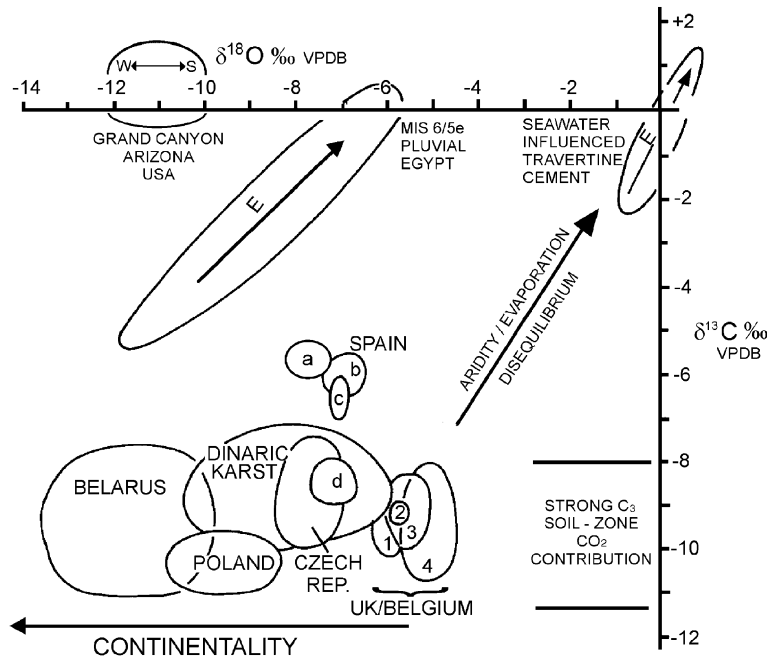


Fig. 7. Combined $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ plot for well-dated late Quaternary tufa calcites. The temperate NW European data show strong influence from C_3 plant/soil-zone CO_2 in $\delta^{13}\text{C}$ and increasing effects of isotopically lighter winter rainfall with increased continentality (see also Fig. 8). The expected trajectory from UK-type values with increased aridity and evaporation should follow the marked arrow, $\delta^{13}\text{C}$ decreasing as soil C input decreases or changes from C_3 to C_4 plants. However, although evaporation effects may be marked within a data set (e.g. arrow marked 'E' in MIS 6/5e pluvial data from Egypt), the starting $\delta^{18}\text{O}$ value will be influenced by local airmass source, rainout effects due to continentality, or processes such as monsoonal rainout. The Grand Canyon data are the only ones collected with high enough resolution to differentiate a seasonal temperature signal between winter (W) and summer (S). In all other cases where evaporation is not important the horizontal width of the data envelope represents changes in recharge $\delta^{18}\text{O}$ over decadal or longer time-scales. Disequilibrium processes will move data toward less negative values (arrow), as will sea-spray contribution to meteoric water in coastal settings. Data sources: Belarus (Makhnach et al., 2004); Poland (Pazdur et al., 1988); Dinaric Karst (Horvatinčić et al., 2003); Czech Republic (Zak et al., 2002); UK/Belgium (1. Andrews et al., 1994; 2. Thorpe et al., 1980; 3. Janssen and Swennen, 1997; 4. Garnett et al., 2004a); Spain (a. Peña et al., 2000; b. Sancho et al., 1997; c. Arenas et al., 2000; d. Andrews et al., 2000); Egypt (Smith et al., 2004); USA (O'Brien et al., in press) sea-spray influenced travertine (Flinn and Pentecost, 1995). The data from Flinn and Pentecost (1995) pertains to mixed carbonate (aragonite+calcite+hydromagnesite), ambient temperature 'travertine' cementing screens on seacliffs: it is included as a guide to likely effects of sea-spray and evaporation.

Reproducibility of ancient decadal-scale isotope data can be demonstrated by re-coring and reanalysis at a site. Dr. Martyn Pedley and the author have re-cored and re-sampled early to mid Holocene tufas from Alport (central England; site E core of Andrews et al., 1994). Samples taken from a core—within a few metres of the original—at exactly the same depth, have identical $\delta^{18}\text{O}$ values and $\delta^{13}\text{C}$ values within $-0.1/+0.3$ (Table 1). This level of reproducibility confirms findings of Garnett et al. (2004a) who also demonstrated coherence of re-cored data: this allows a high degree of confidence in Holocene and older Quaternary tufa stable isotope profiles.

4.1. Evidence for climatically driven $\delta^{18}\text{O}$ variability in late Quaternary tufas?

In their ground-breaking study of Polish Holocene tufas, Pazdur et al. (1988) assumed that most tufa

calcite precipitated during the spring months, when groundwater-fed spring temperatures were equal to mean air temperature. They thus concluded that temperature of in-stream tufa calcite formation was the same as mean air temperature, and would be measured

Table 1
Reproducibility of re-cored Holocene tufa data at the same site

Depth (m)	$\delta^{13}\text{C}$ ‰ VPDB	$\delta^{18}\text{O}$ ‰ VPDB
4.55–4.62	-10.4 (-10.4)	-6.0 (-6.0)
5.60–5.67	-10.1 (-10.4)	-6.4 (-6.4)
6.20–6.25	-10.4 (-10.3)	-6.0 (-6.0)
7.33–7.50	-10.2 (-10.3)	-6.2 (-6.2)
(Plus/minus error)	(-0.1/+0.3)	(0/0)

Original data from Alport (England) reported in Andrews et al. (1994), re-cored and reanalysed data (shown in brackets) was taken about 4 m from the original. Stratigraphy below a marked erosion surface at about 4.5 m was directly comparable.

by $\delta^{18}\text{O}$ calcite. Having attempted to calibrate their record with the local modern $\delta^{18}\text{O}_{\text{calcite-water}}$ and temperature relationship, their resulting calculated mean water temperatures, although believable, had a $\sim 7^\circ\text{C}$ range, much bigger than the $1\text{--}3^\circ\text{C}$ temperature variability reported from various early–middle Holocene palaeoclimate proxies from Greenland and NW Europe (e.g. Huntley and Prentice, 1988; Grootes et al., 1993; Rousseau et al., 1998; Von Grafenstein et al., 1999).

In the next interpretation of a Holocene tufa $\delta^{18}\text{O}$ record, Andrews et al. (1994) suggested that the 0.9‰ variability in their UK deposit was explained (mostly) by variation in $\delta^{18}\text{O}$ of the meteoric water recharge, which was itself controlled principally by climatic (air temperature) change. They rejected stream water temperature change as the main driver, because, as in the Polish study, resulting temperature changes were unrealistically large. It is now known that for NW Europe the mean empirical spatial relationship between $\delta^{18}\text{O}$ in meteoric water and surface air temperature is $+0.58\text{‰}/^\circ\text{C}$ (Rozanski et al., 1993): on this basis a 0.9‰ change in $\delta^{18}\text{O}$ (range reported by Andrews et al., 1994) translates to about 1.5°C . The air temperature record ($\delta^{18}\text{O}$ increases with warming) will however, be ‘damped’ by the opposing signal of temperature dependence of calcite precipitation in water ($-0.24\text{‰}/^\circ\text{C}$, Craig, 1965), such that the measured $\delta^{18}\text{O}$ signal will record about 40% of the actual change in air temperature (i.e. $+0.58\text{‰}/^\circ\text{C} - 0.24\text{‰}/^\circ\text{C}$), suggesting that a 1‰ change in tufa $\delta^{18}\text{O}$ actually corresponds to about a 3.5°C change in air temperature and broadly consistent with other indicators of European Holocene temperature change. Interpreted on this basis the 2.5‰ range in the Polish $\delta^{18}\text{O}$ data (Pazdur et al., 1988) records around 8.5°C air temperature variation, which is too large to be credible (Andrews et al., 1994). This suggests that water temperature was not the principal driver for changing $\delta^{18}\text{O}$, and it is interesting to note that at another continental Holocene site in Belarus (Makhnach et al., 2000; 2004; Fig. 7) a similarly large range has been demonstrated, suggesting that palaeoclimatic changes were here accompanied by changes in moisture source that significantly altered the recharge $\delta^{18}\text{O}$ (see below). This could explain why the *apparent* temperature ranges calculated by Pazdur et al. (1988) were so extreme.

It is also important to stress that these relationships are a guide to *relative* temperature change because it is not possible to be definitive about the relationship between timing of meteoric water recharge (nor its precise $\delta^{18}\text{O}$ value) and temperature of calcite formation. Aquifer recharge probably occurs mainly in winter

(see below), whereas the bulk of calcification might occur during the wettest seasonal periods when supply of dissolved CaCO_3 is highest (Kano and Fujii, 2000; Kano et al., 2003) or when cyanobacterial activity dictates (Andrews and Brasier, 2005), which may not always be in spring as assumed by Pazdur et al. (1988).

Despite these problems the directions of relative temperature changes recorded at both the Polish and UK sites (Pazdur et al., 1988; Andrews et al., 1994) were sensible, particularly the temperature rise in the early Holocene, punctuated by colder and warmer phases, some of which correlated with other palaeoclimatic proxies. These types of $\delta^{18}\text{O}$ records have subsequently been produced from well-dated Late Quaternary (mainly Holocene) tufa sequences in Spain (Andrews et al., 2000), the Czech Republic (Zak et al., 2002), southern England (Garnett et al., 2004a), Belarus (Makhnach et al., 2000, 2004) and Egypt (Smith et al., 2004). These data are summarised in Fig. 7, and in all cases it is clear that the principal driver for overall $\delta^{18}\text{O}$ value has been $\delta^{18}\text{O}$ of the meteoric water recharge. Thus in NW Europe, increased continentality at a given latitude leads to progressively more negative $\delta^{18}\text{O}$ (Figs. 7 and 8). Mean $\delta^{18}\text{O}$ for early Holocene tufa deposits in an E–W transect across NW Europe between latitudes 50 and 54°N show a clear W to E change in $\delta^{18}\text{O}$ from around -6‰ in the UK and Belgium, to around -11‰ in Belarus (Fig. 8), demonstrating the ‘amount effect’ as air masses moved from W to E. The total W–E difference (Δ) in tufa $\delta^{18}\text{O}$ is 5.5‰ (Fig. 8), essentially the same as the expected difference in modern winter rainfall $\delta^{18}\text{O}$ (December to February) and much bigger than the 3‰ $\Delta^{18}\text{O}$ for modern *mean annual* rainfall. As UK groundwater $\delta^{18}\text{O}$ is similar to UK mean annual rainfall $\delta^{18}\text{O}$ (Darling et al., 2003), the total $\delta^{18}\text{O}$ between the UK and Belarus (Fig. 8) suggests that, at least in Belarus, and perhaps in this part of eastern Europe as a whole, $\delta^{18}\text{O}$ of *winter rainfall* (which presumably forms the bulk of the recharge) is the key parameter controlling tufa $\delta^{18}\text{O}$ at a site. Amount effects associated with recharge derived from an Atlantic source (Sultan et al., 1997) also explain negative $\delta^{18}\text{O}$ values for marine isotope stage (MIS) 6/5e tufas in the Egyptian desert (Fig. 7; Smith et al., 2004). Moisture sourced from the high latitude Pacific during winter explains the isotopically negative $\delta^{18}\text{O}$ for the Grand Canyon data (Fig. 7; O’Brien et al., in press). Evaporation effects are only apparent *within* arid or semi-arid zones data sets (Fig. 7), while disequilibrium processes (exceptionally rapid calcification and vigorous degassing of CO_2) will move data toward less negative values (Uzdowski et al.,

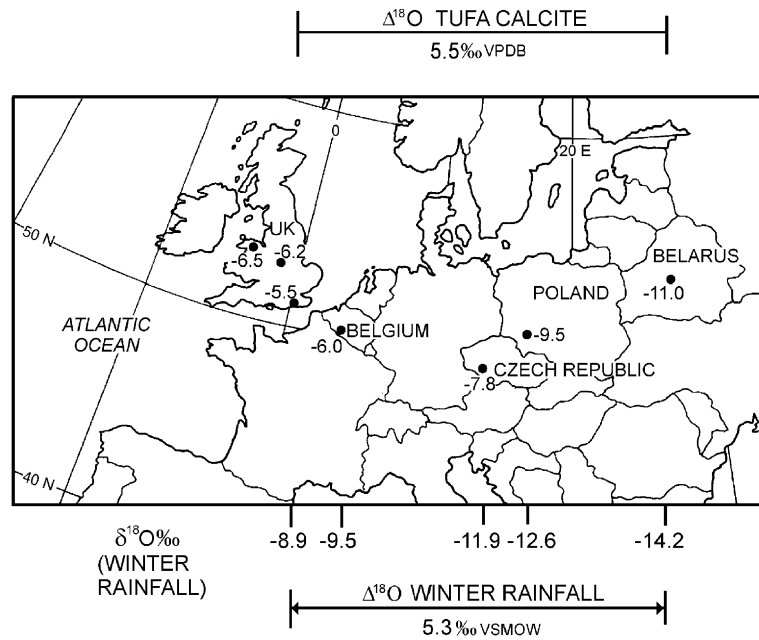


Fig. 8. Mean $\delta^{18}\text{O}$ for early Holocene tufa deposits in an E–W transect across NW Europe between latitudes 50 and 54°N. The tufa $\delta^{18}\text{O}$ values are taken only from sites with good chronology and represent mean values in the time period 8500–9500 calibrated yrs BP. The data show a clear W to E change in $\delta^{18}\text{O}$ from around -6‰ in the UK and Belgium, to around -11‰ in Belarus, demonstrating the ‘continental effect’ as air masses move from W to E. The total W–E difference (Δ) in tufa $\delta^{18}\text{O}$ is 5.5‰ (upper bar), essentially the same as the expected difference in modern winter rainfall $\delta^{18}\text{O}$ (December to February) shown below the map and calculated based on latitude and altitude of the sites using OPIC (Online Isotopes in Precipitation Calculator at <http://www.waterisotopes.org/>, courtesy of Dr Gabriel Bowen: see also Bowen and Wilkinson, 2002; Bowen and Revenaugh, 2003; Bowen et al., 2005). Note that the $\Delta^{18}\text{O}$ for modern mean annual rainfall is only 3‰ , emphasising that $\delta^{18}\text{O}$ of winter rainfall is the key parameter controlling tufa $\delta^{18}\text{O}$ at the Belarus site (see text). The data sources for the UK were from Wateringbury (Garnett et al., 2004a), Alport (Andrews et al., 1994) and Caerswys (Garnett, 2003). Other data were from a Belgian site at Treignes (Janssen and Swennen, 1997), a Polish site from Ractawka (Pazdur et al., 1988) a Czech Republic site at Svatý Jan (Zak et al., 2002) and Belarus sites at Ptich (Makhnach et al., 2004).

1979; Dandurand et al., 1982), as will sea-spray contribution to meteoric water in coastal settings.

If the position of data envelopes in Fig. 7 is controlled by overall recharge characteristics, the width of the envelope in a non-evaporated tufa system records either progressively larger changes in temperature or variability in recharge $\delta^{18}\text{O}$ (i.e. air mass source) with time. Comparison of early Holocene NW European tufas (where chronology is reasonably well constrained; but see also Section 6) with the GISP2 (Greenland Ice Sheet Project) $\delta^{18}\text{O}$ profile demonstrates similarity in the first order structure of the profiles (Fig. 9), and suggests that climatic temperature is an important driver for bulk tufa $\delta^{18}\text{O}$ variation over time. At the southern English site (Wateringbury; Fig. 9) where chronology is well-constrained with both radiocarbon ages and biostratigraphy (Garnett et al., 2004a), tufa accumulation began around 11,500 calibrated yrs BP, recording early Holocene warming (as had a site further north (Andrews et al., 1994)) and suggesting a relatively mild maritime climate. By contrast the more continental sites of Svatý Jan (Czech Republic) and Ptich (Belarus)

did not start accumulating pure carbonate tufa before about 9500 to 10,000 calibrated yrs BP (Zak et al., 2002; Makhnach et al., 2004) probably due to colder conditions.

In all three tufa profiles (and probably in GISP2 also) a long-term cooling trend began around 9500 calibrated yrs BP (Fig. 9), culminating with minima that appear to correlate with a well defined cold event at 8200 calibrated yrs BP (the so-called 8.2 ka event) in the Holocene, originally detected in GISP2 and GRIP (Dansgaard et al., 1993; Alley et al., 1997) and subsequently identified in a wide range of marine and terrestrial sediments (see e.g. Rohling and Pälike, 2005).

In the UK and Czech Republic (Fig. 9) the $\delta^{18}\text{O}$ values decline by about 1‰ over 1500 yrs (between 9500 and 8200 calibrated yrs BP) assuming constant tufa accumulation rates: a temperature decline of up to 3.5 °C (see above) could thus have occurred during this time. In the Belarus record the isotope decline is more like 3‰ , suggesting either a more intense cooling, or perhaps a change in air mass source to more

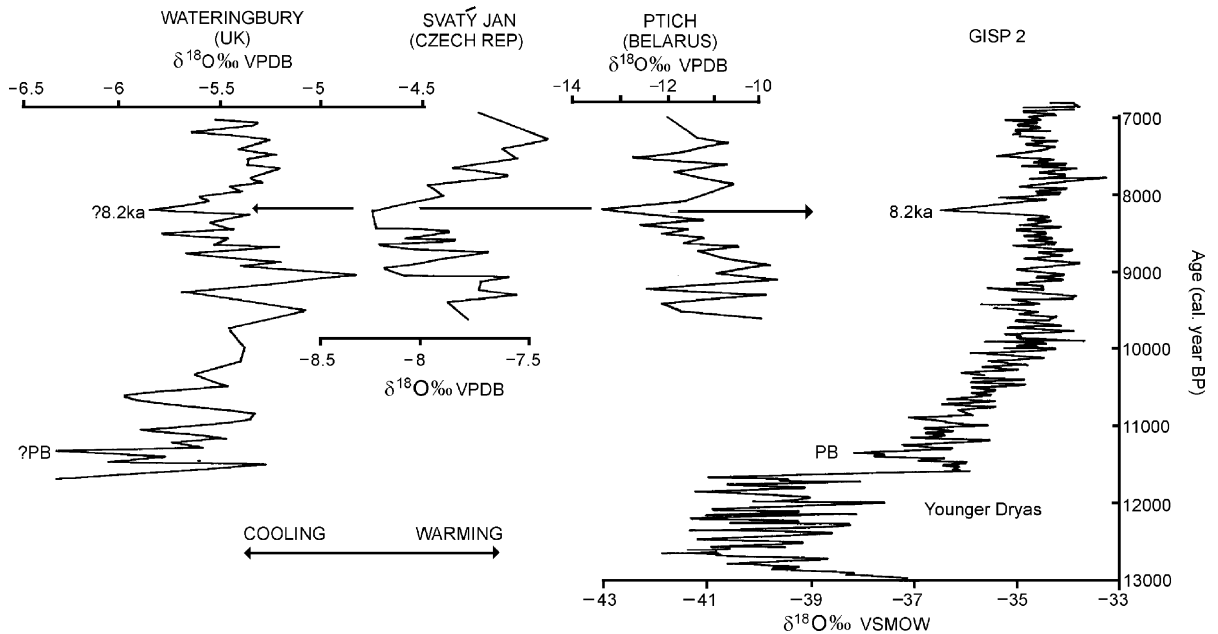


Fig. 9. Early Holocene (11,500 to 7000 calibrated yrs BP) tufa $\delta^{18}\text{O}$ profiles from the UK, Czech Republic and Belarus (data sources and map in Fig. 8) correlated with the GISP2 ice core $\delta^{18}\text{O}$ (Stuiver et al., 1995, 1997; Steig et al., 1994). The calendar ages from GISP2 are from annual ice layer counting (Messe et al., 1994) and are related directly to the age models for Wateringbury and Svátý Jan. The correlation between the Ptich deposit and the other sites is less secure as the age model is less robust (Makhnach et al., 2004). Here the Ptich profile is for pure carbonate tufa, which probably began accumulation in the late Pre-Boreal around 10,500 calibrated yrs BP (Makhnach et al., 2004); this suggests the base of the Ptich correlation here could be 500 yrs adrift. Despite these uncertainties the 8.2 ka event in GISP 2 appears to correlate with the minimum tufa $\delta^{18}\text{O}$ between 11,000 and 7000 calibrated yrs BP in all three tufa profiles. It is also apparent that in all three tufa profiles (and probably in GISP2 also) a long-term cooling trend began around 9500 calibrated yrs BP, culminating with the 8.2 ka event (probably superimposed on the longer-term trend) and followed by warming to about 7800 to 7500 calibrated yrs BP. The continental sites of Svátý Jan and Ptich (see Fig. 8) did not start accumulating pure carbonate tufa before about 9500 to 10,000 calibrated yrs BP (Zak et al., 2002; Makhnach et al., 2004), whereas at Wateringbury the milder maritime location (Fig. 8) allowed tufa accumulation to begin around 11,500 calibrated yrs BP, recording the early Holocene climatic warming and possibly the Pre-Boreal Oscillation (PB).

isotopically negative arctic sourced air? It has been suggested recently that the ‘sharp’ 8.2 ka event is superimposed on centennial-scale cooling (Rohling and Pälike, 2005) and these tufa records are consistent with this. The rapid decrease in $\delta^{18}\text{O}$ to the 8.2 ka spike in the GISP2 (Fig. 9) seems to correspond to $\sim 0.4\text{‰}$ decline to the minimum value in both the UK and Czech Republic records and $\sim 1.5\text{‰}$ decline to minimum in the Belarus record, suggesting maximum temperature decreases of around 1.5 °C and 5.0 °C respectively. In all three tufa records $\delta^{18}\text{O}$ ‘temperatures’ apparently recovered soon after 8000 calibrated yrs BP and were followed by warming to about 7500 to 7800 calibrated yrs BP (Fig. 9). These temperature estimates are presented as a guide to possible palaeoclimatic changes: the key point is that tufa $\delta^{18}\text{O}$ does appear to be recording relative changes in regional palaeo-temperature in much the same way as speleothems do, contrary to the conclusions of Horvatinčić et al. (2003).

Given these interpretations it might be expected that even bigger cooling events, such as that associated with the Younger Dryas stadial might be recorded by tufa $\delta^{18}\text{O}$. To date, stable isotope data for late glacial to early Holocene tufas is very poorly known. In Belarus the tufa chronology is not well constrained (Makhnach et al., 2004) and the tufa designated to Younger Dryas age is impure and possibly detrital. No significant decrease in tufa $\delta^{18}\text{O}$ —that might be expected with cooling in the Younger Dryas stadial—was detected, whereas nearby marl-lake data show $\delta^{18}\text{O}$ decreases of $\sim 5\text{‰}$ (Makhnach et al., 2004). At this time the Belarus chronology and tufa facies are not well enough constrained to make further comment, but the site could be an important one for future work. At Caerwys in North Wales, impure sandy tufas of late Glacial age (Preece et al., 1982; Preece and Turner, 1990) record a $\delta^{18}\text{O}$ decrease of 0.65‰ (approximately 25% of the 2‰ ‘Younger Dryas signal’ seen in NW England marl lakes by Marshall et al., 2002). The tufa $\delta^{18}\text{O}$ data are

probably recording the beginning of climatic change to cold stadial conditions, while in the coldest part of the stadial, tufa deposition appears to have ceased (Garnett, 2003). The exact details of this sequence are still being worked on, so at present we have no convincing record of Younger Dryas climatic change in tufa deposits.

A feature of the Watringbury study in southern England (Fig. 9; Garnett et al., 2004a) was the comparison between $\delta^{18}\text{O}$ in the bulk tufa and the shell calcite of the ostracod *Psychrodromus olivaceus*. The ostracod data were positively displaced by about 1‰ relative to the bulk tufa consistent with vital effects shifting ostracod shell $\delta^{18}\text{O}$ from equilibrium values. Although the ostracod record was more ‘spiky’ it

showed similarity to the bulk tufa, and the minimum (8.2 ka) bulk tufa value corresponded exactly with a marked minimum in the ostracod record. Lack of strong statistical correlation was not a surprise as the tufa samples represent time-averaged decadal records (see above), whereas the ostracods data are specific to the timing of shell calcification, representing specific ‘snapshots’ of relatively short (years) duration.

4.2. Evidence for climatically driven $\delta^{13}\text{C}$ variability in Late Quaternary tufas?

Ancient temperate riverine tufa $\delta^{13}\text{C}$ values published to date are all less than -8‰ (Fig. 7) indicating

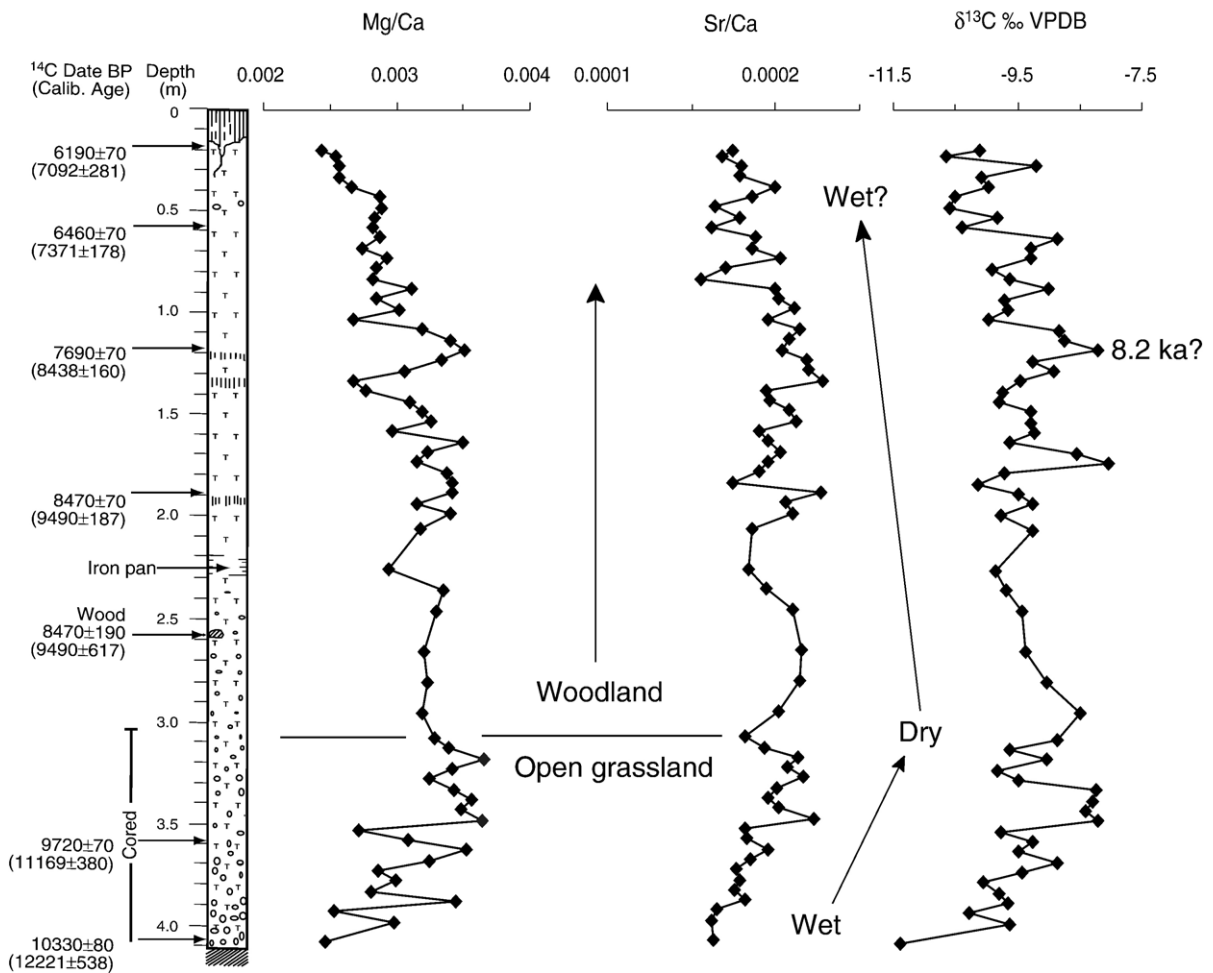


Fig. 10. $\delta^{13}\text{C}$, Mg/Ca, and Sr/Ca molar ratios for early Holocene bulk tufa plotted against the tufa profile and chronology from Watringbury, southern England, modified from Garnett et al. (2004a,b): full details of the chronology are given in these references. 1 sigma errors are smaller than data points. The $\delta^{13}\text{C}$, Mg/Ca and Sr/Ca all have increasing values from the base of the deposit until c.10,400 calibrated yrs BP, suggesting increased aquifer-water residence time due to drier conditions. A short episode of apparently dry stable conditions (ca. 10,300–9050 calibrated yrs BP) is followed by increasingly negative $\delta^{13}\text{C}$ and decreasing Mg/Ca and Sr/Ca ratios in the upper 2 m of the tufa, suggesting increased wetness and development of woodland at the expense of grassland and corroborated by molluscan data in Kerney et al. (1980). ‘T’=soft white tufa, ‘O’=oncoids, vertical lines=grey tufa ?soil horizon, horizontal lines=iron pan, diagonal lines=Atherfield Clay.

strong soil-zone influence (Andrews et al., 1993; 1997). Variability in $\delta^{13}\text{C}$ principally reflects changes in vegetation type that affect the contribution of isotopically light CO_2 derived from soil organic matter (Andrews et al., 1994). Climatic effects, for example change in moisture availability due to aridity or fridity, are likely to be the principal driver of changes in plant communities and the rate of soil respiration, both factors that could cause changes in $\delta^{13}\text{C}$ of tufa calcites (Andrews et al., 2000). Increased aridity leads to either less soil-zone input and less negative $\delta^{13}\text{C}$, or change toward C4-dominated vegetation, explaining why data from Egypt and Arizona have low negative to low positive $\delta^{13}\text{C}$ (Smith et al., 2004; O'Brien et al., in press). Recent studies have combined $\delta^{13}\text{C}$ data with palynological and palaeontological data (Zak et al., 2002; Makhnach et al., 2004) which also respond to vegetation change and moisture availability.

In the most complete treatment of Holocene tufa $\delta^{13}\text{C}$ variation to date, Garnett et al. (2004a) discovered statistically significant positive correlations between bulk tufa $\delta^{13}\text{C}$, Mg/Ca and Sr/Ca molar ratios (Fig. 10). As $\delta^{13}\text{C}$ fractionation during calcite precipitation from dissolved bicarbonate is insensitive to precipitation rate and temperature (Romanek et al., 1992), this positive covariation is likely controlled by in-aquifer processes (see also above). Decreased recharge (dry conditions) increases aquifer water residence time, allowing longer contact and dissolution of aquifer limestone increasing $\delta^{13}\text{C}$. Lower recharge can also increase aquifer conduit air space at the saturated/unsaturated zone boundary, encouraging CO_2 degassing and calcite precipitation, a process that increases $\delta^{13}\text{C}$, Mg/Ca and Sr/Ca of the remaining water (see above and Ihlenfeld et al., 2003). The Mg/Ca, Sr/Ca and $\delta^{13}\text{C}$ show a trend towards increasing values from the base of the deposit until ca. 10,400 calibrated yrs BP (Fig. 10), suggesting increased aquifer-water residence time due to drier conditions. A short episode of apparently dry stable conditions (ca. 10,300–9050 calibrated yrs BP) was then followed by decreasing Mg/Ca and Sr/Ca ratios and increasingly negative $\delta^{13}\text{C}$, from -8.5‰ to -10.5‰ (Fig. 10), in the upper 2 m (ca. 9050–6700 calibrated yrs BP) of the tufa. These changes indicate increased wetness, strengthening spring flow and increasing development of woodland vegetation at the expense of grassland (Kerney et al., 1980) consistent with changes in the molluscan fauna. Woodland provided leaf litter and allowed humus development, increasing root respiration and microbial organic decay, which in turn increased the generation of isotopically light soil carbon. This trend is also recorded by $\delta^{13}\text{C}$

values in shell calcite of the ostracod *P. olivaceus*, albeit displaced on average by about 0.6‰ to more positive values due to vital effects (Garnett et al., 2004a). The 8.2 ka cold event, seen in the $\delta^{18}\text{O}$ record (see above), corresponds to distinct peaks in Mg/Ca and $\delta^{13}\text{C}$ (Fig. 10) suggesting drier conditions with lower spring flow rates and increased aquifer-water residence time. Cold and dry conditions, especially in wintertime, are now known broadly for the northern-hemisphere at this time (Alley and Ágústsdóttir, 2005).

5. Effects of diagenesis on stable isotope records in palaeo-tufas

There is very little data on the effects of diagenesis on stable isotope records in palaeo-tufas, it being extremely difficult to confidently separate syndepositional fabrics from later diagenetic ones (e.g. see Heimann and Sass, 1989). Where cyanobacteria are present even more complications arise. For example *Rivularia haematites* is associated with quite complex tufa calcification fabrics (Monty, 1976), dominated by intense calcification in winter (December–February), essentially cement growing on and penetrating into the colony surface (Pentecost, 1987). Less intensely calcified summer bands (July and September) may be prominent, separated by weakly calcified summer layers (Pentecost, 1987). In some of the summer bands calcification could be directly associated with photosynthetic activity of *Rivularia* itself, accounting for up to 20% of the calcification (Pentecost, 1987). Although these syndepositional microenvironmental photosynthetic effects might increase $\delta^{13}\text{C}$ in the ‘photosynthetic-calcites’ by up to 0.7‰, relative to the bulk calcite, their small mass means the isotope effect will hardly be discernable in the bulk tufa calcites. More pervasive wintertime calcification or cementation growing into pre-existing fabrics might have more serious effects on isotopic records, at best ‘blurring’ the quality of palaeoclimatic signals (Andrews and Brasier, 2005), but isotope data are not available to verify this.

Presence of sparry calcite may not be diagnostic of alteration or diagenesis in the way it is in marine limestones (see e.g. James and Choquette, 1990), because spar is a primary calcite tufa fabric, particularly in barrier and waterfall facies (Heimann and Sass, 1989; Pedley, 1993; Chafetz et al., 1994). In active or sub-recent tufas, primary spar crystals appear to form around cyanobacterial bushes (Love and Chafetz, 1988) and *R. haematites*, *Phormidium foveolarum*, *Phormidium incrustatum* and *Schizothrix calcicola* have all been associated with the formation of primary

sparry calcite laminae or radial palisades (Monty, 1976; Love and Chafetz, 1988; Janssen et al., 1999; Freydet and Verrecchia, 1999).

Tufa calcites, including primary spar crystals, can be altered by aggrading neomorphism (Love and Chafetz, 1988; Freydet and Verrecchia, 1999; Janssen et al., 1999; Pavlović et al., 2002a,b; Pedley et al., 2003; Andrews and Brasier, 2005), by microbial micritization (Chafetz et al., 1994) and by vadose and phreatic cementation (Janssen and Swennen, 1999; Pavlović et al., 2002a,b). However, the isotope effects of neomorphic alteration or simple cementation in tufa calcites are very poorly known; even where isotope data are available it is not easy to distinguish environmental changes at the time of deposition, from later effects of isotopic exchange or neomorphism (e.g. tufa stromatolite data in Lojen et al., 2004). Early diagenetic effects on geochemical systems will not be as obvious as in marine systems (see e.g. James and Choquette, 1990) because the waters involved in neomorphism of pre-existing tufa fabrics and cementation of void space will be similar to the water that deposited the tufa originally.

In a study of Belgian tufas both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are higher (by about 1.5‰ and 0.5‰ respectively) in the fossil tufas relative to the active ones (Janssen and Swennen, 1997; Janssen et al., 1999). Dissolution of pre-existing tufa calcites by rainwater and subsequent reprecipitation of sparry calcites could have yielded the slightly less negative $\delta^{13}\text{C}$ values than tufas precipitated directly from soil-zone associated karst river water. Diagenetic differences in $\delta^{18}\text{O}$ value could be caused by temporal changes in water temperature/isotope composition during dissolution–reprecipitation or void cementation, but there are no unambiguous published data, and quantification of the masses of diagenetic calcite have not been attempted. Limited data in Horvatinčić et al. (2003) and Andrews and Brasier (2005) show no significant difference between Holocene and Pleistocene isotope data from the same site. This suggests similar catchment characteristics of recharge, climate and vegetation in the two most recent interglacials. The lack of clear difference in stable isotope values of recent, Holocene and older tufas, does not necessarily indicate lack of diagenesis; it simply shows the isotopes are not diagnostic.

Aggrading neomorphism to form sparry calcite layers *within* tufas certainly takes years (Arp et al., 2001) and probably decades. This slow neomorphism must result in some time-averaging effect on geochemical signatures, although simple cementation of pore spaces may not affect the isotope compositions of the depositional calcites. Approximately 250 yr old tufas

on the surface of a now inactive tufa mound in Northern England (Harry's Screen, Gordale Scar; Pentecost, 1981) contain abundant sparry calcites, whereas older tufas below this horizon, possibly up to 5000 yrs old (Pentecost et al., 1990) are still soft and friable with little or no sparry calcite cementation (Pentecost, 1981), consistent with other assessments of well-preserved depositional fabric in Holocene and Tertiary tufas (Zamarreño et al., 1997; Pedley et al., 2003). These findings are also consistent with the clear palaeoclimatic signals recorded in Holocene and older tufas (discussed above), and demonstrate that sparry calcite cementation and neomorphism are not simply a function of age. In many tufas, sparry cementation is best developed in the bed of active channels (Andrews and Brasier, 2005) and macropores (Pedley et al., 2003), such that cementation and diagenesis is related to focussed through-flow of water and not pervasive alteration. Tufa stromatolites from the Upper Palaeocene (i.e. >50 Ma) of northern Spain preserve pristine depositional fabrics, and apparently stable isotopic values, with no major evidence of pervasive diagenetic alteration (Zamarreño et al., 1997). This demonstrates that tufas can be reliable archives of climatic and environmental information over Quaternary and much longer timescales.

6. Establishing chronologies in tufa carbonates

Although this review has concentrated on stable isotope records of palaeoclimatic change in tufas it is clear that reliable chronologies are crucial to allow such climate proxies to be used more widely in Quaternary climatic reconstructions. With recent/sub-recent annually laminated tufas it is possible to count seasonal laminae back from the active surface (Matsuoka et al., 2001; Ihlenfeld et al., 2003) although so far this has not achieved high resolution records longer than 14 yrs, and even laminae counting has to be done with care, particularly with older tufa sequences (Andrews and Brasier, 2005).

On Holocene timescales, tufa deposits can be dated using radiocarbon techniques, preferably on interbedded organic deposits such as peats (often basal peats), sapropel or wood fragments (e.g. Andrews et al., 2000; Garnett et al., 2004a). Direct dating of tufa carbonates has been done (Garnett et al., 2004a), but there are problems, particularly the well known 'hard water/dead carbon' effects (e.g. see Genty et al., 1999), that result in older than expected ages. It is thus crucial to support radiocarbon dates with detailed molluscan and pollen data wherever possible (e.g. see Kerney et

al., 1980; Garnett et al., 2004a): even then chronologies can be problematic (Makhnach et al., 2004). In most published studies of Holocene tufas, dated horizons at a site are so stratigraphically separated (if present at all) that it is impossible to make meaningful interpretations of tufa accumulation rates. While it is possible to date Holocene tufas using $^{230}\text{Th}/^{234}\text{U}$ (Eikenberg et al., 2001) significant detrital contamination, combined with low initial U concentrations, and short time for ingrowth of radiogenic ^{230}Th , make routine high resolution U series dating of Holocene tufa very challenging (Garnett et al., 2004b). For Holocene tufas younger than 7000 yrs, the decay of excess ^{226}Ra normalized to the initial ^{226}Ra can also be used (Eikenberg et al., 2001) when correction of a detrital component limits precision of the $^{230}\text{Th}/^{234}\text{U}$ chronometer.

For older Quaternary tufas, dating has tended to rely on $^{230}\text{Th}/^{234}\text{U}$ (e.g. Soligo et al., 2002) which in theory can date deposits back to about 400,000 yrs. However, detrital contamination is still an important issue affecting quality of dates (see e.g. Garnett et al., 2004b). It is also possible to date these older tufa deposits using amino acid racemization, specifically D/L ratios of aspartic acid and glutamic acid in ostracod valves (Torres et al., 2005).

Perhaps the most exciting prospect for future work is to locate a thick pre-Holocene paludal tufa, preferably with at least some seasonally laminated sequences, that can be dated to a specific, probably interglacial (Soligo et al., 2002; Torres et al., 2005), period. Such a site will allow a number of key questions to be addressed. For example, (1) were earlier interglacial tufas more active early on, as they seem to have been at least in the NW European Holocene, and if so why? Moreover, (2) is it possible to discover seasonal climatic variability on a similar scale to that seen in sub-recent tufas, and (3) are longer-term (centennial–millennial) climatic anomalies, such as the Holocene 8.2 ka event, evident in older tufa records? Such a site, particularly where complemented by nearby speleothem or lacustrine data, could provide exceptionally high quality regional terrestrial palaeoclimatic data for the Quaternary community.

7. Conclusions

This review demonstrates clearly that stable oxygen and carbon isotope data in active to Pleistocene riverine tufas record palaeoclimatic information. The key points to stress are:

1. The drivers for stable isotope variation in recent tufa systems are well understood. For $\delta^{18}\text{O}$, variability is driven by (1) the water temperature, (2) the $\delta^{18}\text{O}$

value of the water, plus or minus (3), other much smaller environmental factors, mainly evaporation. For $\delta^{13}\text{C}$, variability reflects principally the relative contribution of isotopically light CO_2 from soil organic matter, and isotopically heavier carbon derived from the dissolution of the aquifer limestone: values are modulated by equilibration of the aquifer, spring and stream water with atmospheric CO_2 and by in-aquifer or in-stream calcite precipitation. Effects of in-stream biological activity are small, as are disequilibrium isotope effects away from actively degassing springs.

2. Highly resolved sub-sampling of annual layers in recent/sub-recent and Holocene tufas, show conclusively that seasonal records of temperature ($\delta^{18}\text{O}$) and relative wetness/dryness ($\delta^{13}\text{C}$ and some trace elements) are recorded in tufa calcites. There is still some work required to fully understand why the $\delta^{18}\text{O}$ ‘temperatures’ are damped when compared to measured temperature variation. We need to look more critically at the petrography of annually laminated deposits.
3. At decadal-scale sampling resolution there is little doubt that tufa deposits record (mostly) variation in $\delta^{18}\text{O}$ of meteoric recharge, which depending on locality may reflect source or amount effects (particularly continentality), or temperature change. In Holocene tufas from NW Europe, centennial-scale climatic cooling, culminating in a sharp 8.2 ka minimum are recorded at three widely spaced localities. Moreover, at one site a detailed $\delta^{13}\text{C}$ record suggests progressive dryness, culminating at 8.2 ka.
4. Although cementation of void space and aggrading neomorphism undoubtedly occur in sub-recent and older tufas, there is almost no unequivocal evidence that this is either pervasive or that it seriously changes depositional stable isotope values, at least on Holocene timescales.
5. Tufa deposits accumulate rapidly, and where annually laminated, offer an excellent opportunity to study seasonality in Quaternary palaeoclimates. Well dated tufa stable isotope records should be considered complementary to the longer-term palaeoclimatic data provided by speleothems, particularly as they are often found together in karst regions.

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