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Reconstitution climatique et environnementale au Tardiglaciaire et à l'Holocène à partir de l'étude des isotopes stables dans une séquence de tuf du Pays de Galles

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LATE-GLACIAL AND EARLY HOLOCENE CLIMATE AND ENVIRONMENT FROM STABLE ISOTOPES IN WELSH TUFA

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ABSTRACT

The Caerwys tufa in North Wales (UK) contains basal deposits thought to represent carbonate precipitation during the Late-glacial interstadial. These deposits are used to test whether stable isotope data record all or part of a warming-cooling-warming trend through the transition of the Late-glacial interstadial, Younger Dryas stadial and early Holocene. The $\delta^{18}O$ values and molluscan abundance data suggest that deposition of the Late-glacial tufa occurred mainly during a relatively warm period (? GL-1c or 1e) followed by cooling, the latter likely to be the transition into the Younger Dryas stadial. Tufa deposition is not recorded in the coldest part of the stadial: it is replaced by a sandy horizon. $\delta^{13}C$ values around –8.5‰ in the basal Late-glacial interstadial tufas show there was a significant influence from isotopically light soil-zone CO_2, consistent with development of birch scrub and woodland further south in North Wales. During climatic cooling into the Younger Dryas stadial a 1‰ decrease in tufa $\delta^{13}C$ is interpreted to represent decreasing phytoplankton photosynthetic activity in pools causing less isotopic enrichment of the tufa $\delta^{13}C$. In the (pre-9000 cal. years BP) early Holocene tufas at Caerwys, palaeo-water temperatures calculated from $\delta^{18}O$ in tufa calcite and from shell carbonate of *Lymnaea peregra* agree well and suggest summer water temperatures in the range 13 to 16.5°C. $\delta^{13}C$ data from these early Holocene pool-micrite tufas demonstrate that phytoplanktonic photosynthetic activity within the water column resumed under the warmer conditions causing isotopic enrichment of the tufa $\delta^{13}C$ values.

Key-words: Tufa, Late-glacial, early Holocene, *Lymnaea peregra*, stable isotopes, palaeoclimate, UK

RÉSUMÉ

RECONSTITUTION CLIMATIQUE ET ENVIRONNEMENTALE AU TARDIGLACIAIRE ET À L'HOLOCÈNE À PARTIR DE L'ÉTUDE DES ISOTOPES STABLES DANS UNE SÉQUENCE DE TUF DU PAYS DE GALLES.

Le tuf de Caerwys situé au nord du Pays de Galles (Grande-Bretagne) contient, à sa base, des dépôts à précipitations carbonatées, attribués à l'interstade du Tardiglaciaire. Ces dépôts sont utilisés pour tester la validité des isotopes stables dans l'enregistrement d'une séquence de température chaud-froid-chaud au cours de la transition Interstade du Tardiglaciaire-Dryas récent– début Holocène. Les valeurs de $\delta^{18}O$ ainsi que la courbe d'abondance des malacofaunes indiquent que le tuf tardiglaciaire s'est déposé au cours d'une phase tempérée (GL-1c ou 1e ?) suivie par un refroidissement qui pourrait correspondre à la transition vers le Dryas récent. Au cours de la phase la plus froide de cet épisode stadiaire la formation du tuf cesse et la sédimentation devient sableuse. Les valeurs de $\delta^{13}C$ qui se placent autour de –8.5‰ dans le tuf interstadiaire de base montrent une influence significative de la zone CO_2 du sol isotopiquement faible qui est cohérente avec l'extension vers le sud de forêts de bouleaux dans la partie nord du Pays de Galles. Pendant le refroidissement du Dryas récent, la baisse de 1‰ du $\delta^{13}C$ du tuf est interprétée comme la représentation de la diminution de l'activité photosynthétique du phytoplancton dans les mares qui est la cause d'un enrichissement isotopique plus faible du $\delta^{13}C$ du tuf. Au sein des tout premiers niveaux de tuf holocènes (pré-9000 cal.an BP) à Caerwys, les paléo-températures de l'eau calculées à partir du $\delta^{18}O$ de la calcite du tuf et des carbonates des coquilles de *Lymnaea peregra* sont en bon accord et suggèrent des estimations des températures estivales de l'eau situées entre 13 et 16.5°C. Les données de $\delta^{13}C$ obtenues dans ces tufs de mare-micrite du début de l'Holocène démontrent que l'activité photosynthétique du phytoplancton à l'intérieur de la colonne d'eau reprend quand les conditions sont plus chaudes et provoquent un enrichissement isotopique des valuers de $\delta^{13}C$ du tuf.

Mots-clés : Tuf, Tardiglaciaire, début Holocène, *Lymnaea peregra*, isotopes stables, paléoclimat, Grande-Bretagne.

1 - INTRODUCTION

It is now generally accepted that the stable isotope geochemistry of riverine tufa carbonates is a potentially valuable palaeoclimatic and palaeoenvironmental archive (Andrews, 2006; Andrews & Brasier, 2005). Highly resolved sub-sampling of annual layers in active/sub-recent and Holocene tufas, show conclusively that seasonal records of temperature ($\delta^{18}O$) and relative recharge intensity ($\delta^{13}C$) are recorded (Matsuoka *et al.*, 2001; Andrews, 2006). At decadal-scale sampling resolution, tufa deposits record (mostly) variation in $\delta^{18}O$ of meteoric recharge, which depending on locality may reflect source or amount effects (particularly continentality), or temperature change (Andrews, 2006). For example, in some NW European early Holocene tufas, a clear $\delta^{18}O$ minimum at about 8.2 ka has been recorded from a number of sites (Andrews, 2006;

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Garnett *et al.*, 2004; Maknach *et al.*, 2000; 2004), suggesting that the temperature anomaly of the global 8.2 ka cold event (Dansgaard *et al.*, 1993; Alley *et al.*, 1997) is recorded in the tufa $\delta^{18}O$.

In this context the Caerwys tufa in North Wales (Preece, 1978; Preece *et al.*, 1982) is an exciting site because it contains basal deposits thought to represent carbonate precipitation during the Late-glacial (Preece & Turner, 1990). These deposits are thus ideally suited to test whether stable isotope data from the tufa record all or part of a warming-cooling-warming trend through the transition of the Late-glacial interstadial, Younger Dryas stadial and early Holocene. In addition, some of the early Holocene carbonate deposits at Caerwys consist of well-preserved laminated micrites formed in small pools containing the freshwater gastropod *Lymnaea peregra*. The presence of *L. peregra* is particularly useful, as this mollusc has an experimentally calibrated fractionation factor for aragonite-water $\delta^{18}O$ equilibrium as a function of temperature (White, 1998; White *et al.*, 1999). These tufas are thus ideal for testing equilibrium relationships, based on comparison of the *L. peregra* aragonite and contemporaneous tufa calcites, and for demonstrating whether microenvironmental variability in pool deposits are recorded isotopically.

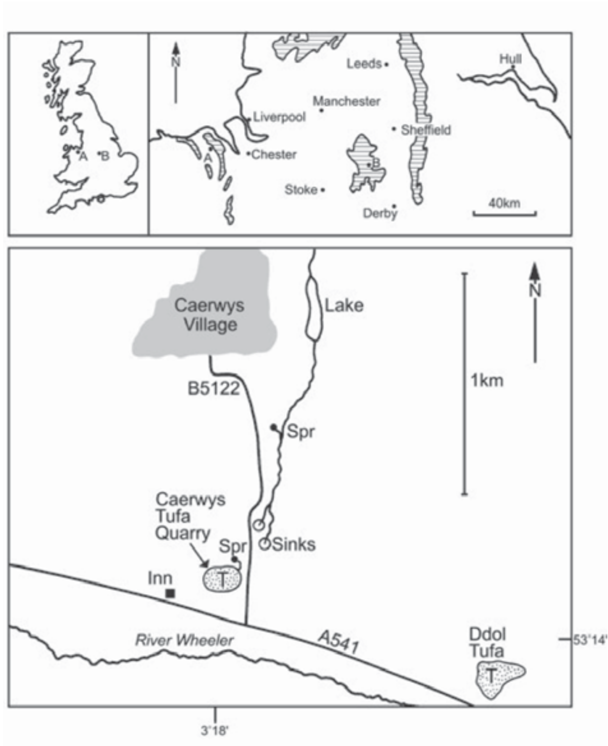

Fig. 1: Location of the Caerwys tufa (A in top panels). Hatched areas in top panels indicate outcrops of Carboniferous and Permian bedrock limestones. Locality B is the river Lathkill in North Derbyshire. Bottom panel shows detailed locality map with main roads, rivers and tufa localities. Spr denotes presence of springs. Top panel after Pedley *et al.*, 1996.

Fig. 1 : Localisation du tuf de Caerwys (A dans les cartouches supérieurs). Les zones hachurées indiquent les sections ouvertes dans les calcaires du Carbonifère et du Permien. La localité B est la rivière Latthkill dans le Derbyshire nord. Cartouche inférieur : carte détaillée de la localisation du tuf avec notation des sources (Spr). Le cartouche supérieur est tiré de Pedley et al.*, 1996.*

2 - DEPOSITIONAL ENVIRONMENT AND AGE

The Caerwys tufa is situated in the Wheeler Valley, North Wales, 7km SW of Holywell and 0.75km south of the village of Caerwys (British National Grid Reference SJ 129 719; fig. 1). The tufa has precipitated from springs that drain a Carboniferous Limestone aquifer to the northeast. The tufa formed on glacio-fluvial siliciclastic sands that mantle a flat-bottomed valley. Before removal by quarrying the tufa covered an area of approximately 200 m by 250 m, being at least 12 m thick in places (Pedley, 1987). Quarrying has progressively revealed much of the internal tufa architecture allowing detailed sedimentological and palaeontological study (Preece, 1978; Preece *et al.*, 1982; Pedley, 1987; Pedley *et al.*, 1996).

The tufa was deposited as a barrage system (Pedley, 1987; Pedley *et al.*, 1996), specifically a spring-fed riverine tufa with vertical accretions (buttresses) of carbonate that caused impoundment of water, creating small pools that accumulated carbonate muds and organic matter. The Caerwys buttresses consist of downstream inclined carbonate sheets that intermingle with pool deposits on the upstream side, and merge into fluvial oncoidal and detrital tufa facies downstream (Pedley *et al.*, 1996). The buttresses are typical phytoherm build-ups with primary porosity, and extensive plant macrofossil moulds. The pools were shallow, typically not deeper than 1 m and in many places even shallower: the deposits consisted primarily of micrite and peloidal aggregates often containing freshwater gastropods (Preece, 1978; Pedley, 1987; Preece & Turner, 1990; Pedley *et al.*, 1996). The edges of the pools contained semi-aquatic plants, leading to sapropelitic and peaty organic matter and vertical tube facies (Ordoñez & Garcia del Cura, 1983) that consist of reed stem encrustations. Truncation surfaces occur throughout the tufa and some are marked by thin palaeosols. The more widespread palaeosols represent valley-wide terminations in tufa accumulation (Pedley, 1987; Preece & Turner, 1990). Palaeosols in the lower sequences consist of thin, pale to dark grey, humic-rich micritic layers (Preece *et al.*, 1982).

Tufa deposition at Caerwys began during the Late-glacial based on a radiocarbon age of $13,806 \pm {}^{1346}_{384}$ cal. years BP (tab. 1 and fig. 2) and the molluscan biostratigraphy (fig. 3; Preece & Turner, 1990). A sedge-peat (~0.4m thick) under the northern part of the tufa gave an age of 11,225 cal. years BP (tab. 1; Preece & Turner, 1990) and contained pollen indicative of birch scrub. An early Holocene age of 9104 cal. years BP was obtained from charcoal from the major valley-wide palaeosol (fig. 2; Preece *et al.*, 1982; Bowman *et al.*, 1990; Preece & Turner, 1990). Cessation of widespread tufa deposition is harder to date (Preece & Turner, 1990), although tufa deposition at nearby Ddol (1.5km SW; fig. 1) ceased sometime after 7198 cal. years BP (tab. 1; Preece & Turner, 1990).

Lab. Ref.	Site	Material	^{14}C age (BP)	Calib. age (BP)†
Q-2376	Caerwys	Palaeosol	11,725 ±120	$13,806 \pm ^{1346}_{384}$
Q-2396	Caerwys	Sedge-peat	9840 ±100	$11,225 \pm ^{328}_{131}$
BM-1736R	Caerwys	Charcoal	8100 ±180	$9014 \pm ^{476}_{551}$
Q-1533	Ddol	Wood	6260 ±120	$7198 \pm ^{228}_{393}$

Tab. 1: Radiocarbon dates and calibrated ages from the Caerwys and Ddol tufas, North Wales (from Bowman *et al*., 1990; Preece & Turner, 1990). The calibrated ages shown are the age ranges which contain 95.4 % of the area under the probability curve. All ages in this table were calibrated with CALIB 4.3 (Stuiver & Reimer, 2000) using the bidecadal atmospheric curve (Stuiver & Reimer, 1993, and references therein).

Tab. 1 : Datations radiocarbone et âges calibrés des tufs de Caerwys et Ddol, nord du Pays de Galles (d'après Bowman et al*., 1990 ; Preece & Turner, 1990). Les âges calibrés correspondent à 95,4 % de l'aire couverte par la courbe de probabilité. Tous les âges de ce tableau ont été calibrés avec CALIB 4.3 (Stuiver & Reimer, 2000) en utilisant la courbe atmosphérique bidécennale (Stuiver & Reimer, 1993, et références incluses)*

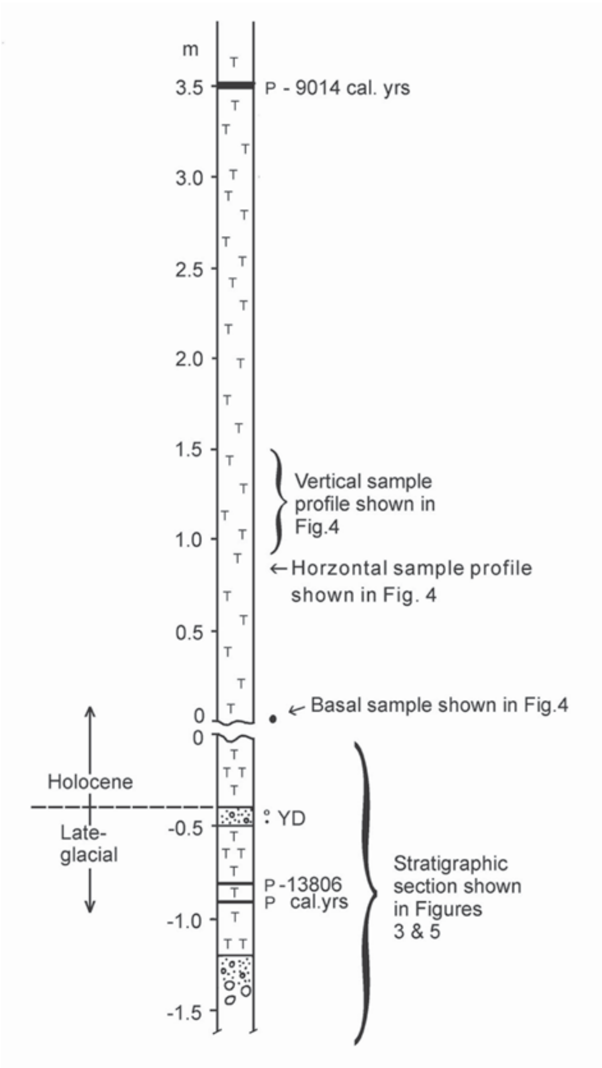

Fig. 2: Composite stratigraphic section showing Late-glacial and very early Holocene deposits below 0 m datum (sampled in 1983 when temporarily exposed), and early Holocene deposits above 0 m datum (sampled in 2000). The discontinuity at 0 m is not likely to represent more than 10s of centimetres of deposit. The two calibrated radiocarbon dated horizons are marked (see Table 1 for details) as are the positions of the samples from which data are presented in Figures 3-5. 'T' = tufa, stipple = red sand and 'P' = palaeosol. ?YD marks likely deposits of Younger Dryas stadial.

Fig. 2 : Profil stratigraphique composite des séquences Tardiglaciaire et début Holocène sous le niveau actuel à 0 m (échantillonnage de 1983 lors d'une exposition temporaire des dépôts), et des dépôts holocènes au dessus de 0 m (échantillonnage en 2000). La discontinuité à 0 m ne représente pas plus de 10 cm de sédiment. Les deux datations radiocarbone calibrées sont signalées (Voir tabl. 1 pour le détail) ainsi que les positions des échantillons d'où sont extraites les données présentées sur les figures 3 à 5. 'T' = tuf, pointillés = sable rouge et 'P' = paléosol. YD indique les depots correspondent probablement au stade Dryas récent.

3 - MATERIAL STUDIED

3.1 - THE LATE-GLACIAL BASAL TUFA

Ten samples of soft white to grey to brown (sandy) tufa were taken from the basal 1.3 m of the Caerwys tufa deposit (fig. 2) when it was exposed during excavation of a drainage ditch in the quarry floor in 1983. The exact relationship of these samples to the Holocene deposits sampled in 2000 (see below) is not clear, but probably only a few tens of centimetres of section are missing. The discontinuity between the two sections is assigned 0 m as a datum (fig. 2) with the samples below the discontinuity assigned a negative value and those above a positive value (fig. 2). Mollusc evidence (fig. 3) suggests these soft carbonate muds were deposited as shallow pool and marsh micrites (marsh species are well-represented). The upper sample (–0.3 to –0.4 m) is assigned an early Holocene age on the basis of the occurrence of *Carychium minimum* and *Vertigo substriata* (fig. 3). Although *C. minimum* has been found in Late-glacial sediments, it is extremely rare in such contexts (Preece & Bridgland, 1999), whereas *V. substriata* is not known from the British Late-glacial. The upper three samples are quite pure tufas containing relatively little acid insoluble residue (fig. 5). A conventional radiocarbon date from organic matter in a palaeosol at –0.8 m gave an age of $13,806 \pm ^{1346}_{384}$ cal. years BP (tab. 1; fig. 2; Preece & Turner, 1990). This age is probably a few hundred years too old when compared to the mollusc assemblage (fig. 3), presumably because of contamination with dead carbon (Lowe *et al*., 1988). The palaeosol may be equivalent to the Allerød' (or Pitstone) soil seen in Kent (southern Britain), which has produced similar, or slightly younger, ^{14}C dates (Preece, 1994). The intervening sandy horizon between –0.4 and –0.5 m demonstrates cessation in tufa deposition, probably during the Younger Dryas stadial. However, the tufa samples between –0.5 to –0.8 m show a dramatic reduction in shell numbers (fig. 3) that might also have been caused by cooler conditions. The increasing insoluble residue (including sand) content of the tufa below –0.7 m, particularly associated with the palaeosols (fig. 5) is thought to indicate Late-glacial deposition, based on the molluscan assemblage and the ^{14}C age. The basal tufa is

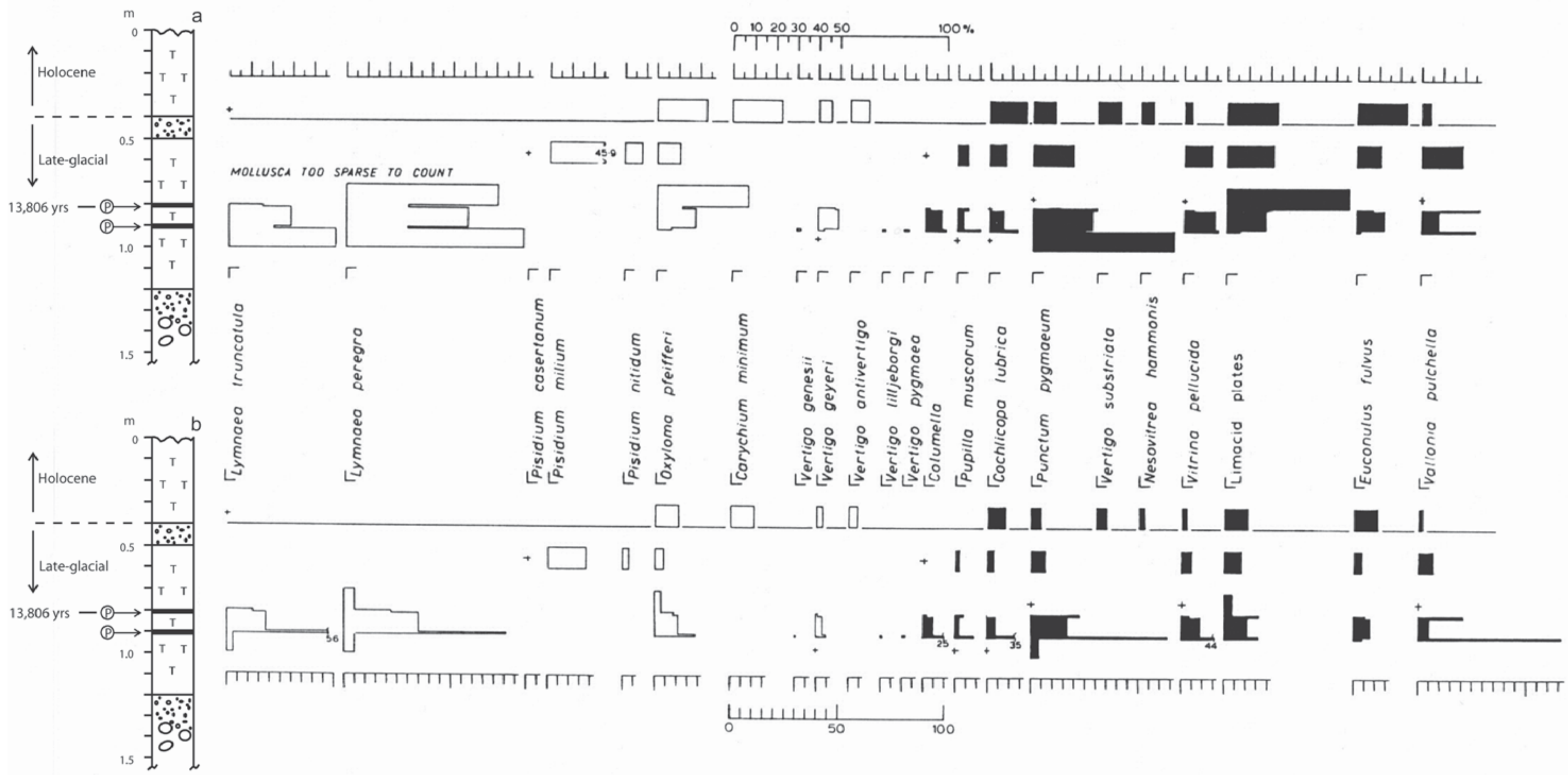

Fig. 3: Mollusc diagram from the Late-glacial part of the Caerwys tufa, showing both percentage frequency (a) and absolute abundance (b). Aquatic species are shown as open histograms, which in (a) have been calculated as a percentage of the terrestrial taxa (in black). The lower of the two organic horizons yielded the greatest number of shells. The assemblages below 50 cm are typical of marshland communities that existed during the Devensian Late-glacial and include several species (e.g. *Vertigo genesii* and *V. geyeri*) with modern arctic-alpine ranges. The tufa above –0.40 m is early Holocene, since it contains a few taxa (e.g. *Carychium minimum* and *Vertigo substriata*) that are either rare or completely unknown in the British Late-glacial. 'T' = tufa, stipple = red sand and 'P' = palaeosol. Age is calibrated radiocarbon years BP (see Table 1).

Fig. 3 : Diagramme malacologique de la sequence tardiglaciaire du tuf de Caerwys, montrant les pourcentages de fréquence (a) et les abondances absolues (b). les espèces aquatiques sont figurées par des histogrammes blancs qui en (a) ont été calculés comme des pourcentages par rapport aux taxons terrestres (en noir). L'horizon organique inférieur est celui qui livre le plus grand nombre de coquilles. Les assemblages à 50 cm de profondeur sont typiques des communautés de marécage qui ont existées durant le Tardiglaciaire Weichsélien et comprennent plusieurs espèces (par exemple Carychium minimum *et* Vertigo substriata*) qui sont aujourd'hui rares voire absentes dans les îles britanniques. 'T' = tuf, pointillés = sable rouge et 'P' = paléosol. Dates en années radiocarbone calibrées BP (voir tabl. 1).*

dominated by insoluble detritus containing only 20-25 wt % $CaCO_3$ (fig. 5).

3.2 - EARLY HOLOCENE POOL ENVIRONMENTS

At the western margin of the Caerwys tufa, a 12 m wide and 4.5 m thick pool deposit (fig. 2) comprises laminated micrites with abundant *Lymnaea peregra,* an aquatic freshwater gastropod. This deposit, sampled in 2000, lies above the Late-glacial deposits (see section 3.1) but below the valley wide palaeosol dated at 9014 cal. years BP (fig. 2; tab. 1). The pool deposits must therefore be of early Holocene age (around 10,500 cal. years BP), an interpretation corroborated by the persistence of arctic-alpine snails. These pool deposits are thus too old to contain a stable isotope record of later intra-Holocene climatic events such as the 8.2 ka event (see above) which might explain why other workers have apparently failed to identify any meaningful correlation between isotope values and climatic changes in this deposit (Pentecost, 2005, p. 280).

The pool laminae are made of alternating 3-4 cm thick pale and more carbonate-rich layers, and 5-11 cm thick darker less carbonate-rich layers, the latter perhaps representing summer precipitation associated with increased planktonic algal activity. The pool edge was colonised by larger plants, the stems of which were encased in tufa encrustations. Many of these stem encrustations are upright and preserve the external stem morphology of *Sparganium erectum* L., or Burreed (R. Boar, pers. comm. 2003) The vertical compactional displacement between the pool margin reed encrustations' and centre is of the order of 20 cm. The shells of *L. peregra* are still composed of original pure aragonite (checked by x-ray diffraction) and the total lack of cementation of the micrites suggests these deposits have suffered little or no diagenetic alteration.

The pool tufas were sampled in a horizontal array at +0.9 m (fig. 2) at six equally spaced points along an individual pool lamina from the reed stem encrustations (margin) to the pool centre to test for isotopic variability along one time horizon (fig. 4). In addition, pool carbonate and associated *L. peregra* (where available), were sampled vertically between +0.95 and +1.5 m (fig. 2) through five pairs of pool lamina, with an additional tufa sample taken at the stratigraphically lowest point (0 m: fig. 2).

4 - STABLE ISOTOPES: ANALYTICAL METHODS

Bulk tufa samples were dried overnight at 110 °C and then ground to a fine powder. Volatile organic matter was removed by low temperature (<80°C) oxygen plasma ashing for three hours at 300 W forward power in a Bio-Rad PT 7300 plasma barrel etcher. Stable isotope analyses were performed on CO_2 derived from 3-5 mg samples that were reacted with anhydrous H_3PO_4 at 25 °C overnight. Isotope ratios were measured on a VG Sira Series II mass spectrometer at the University of East Anglia. Replicate analyses of the laboratory standard (n = 9) gave a 2σ precision of 0.13‰ for oxygen and 0.07‰ for carbon.

The aragonitic shells of *L. peregra* were broken to remove any carbonate inside the whorls and then cleaned with a fine paint brush and ultra-pure Milli-Q™ water. The laboratory methods were otherwise similar to those for the bulk tufas, although the shell fragments were not plasma ashed. The $\delta^{18}O$ value for aragonite from CO_2 evolved during phosphoric acid reaction was corrected using the fractionation factor of 1.01034 (Sharma & Clayton, 1965).

5 - RESULTS AND INTERPRETATION

Interpretation of stable isotope data in modern and Holocene tufas is now quite robust and various studies, e.g. (Andrews, 2006; Andrews *et al*., 1993, 1997, 2000; Matsuoka *et al.*, 2001; Garnett *et al*. 2004) have shown that many tufa calcites record isotopic values that represent equilibrium, or near equilibrium conditions. There is no reason to doubt that the Caerwys tufa calcites also formed under equilibrium isotopic conditions, although we accept that short-term variations in a number of parameters could have disrupted the equilibrium from time to time.

It has also been shown that $\delta^{18}O$ and $\delta^{13}C$ data from shallow, fast-flowing riverine tufas are potential recorders of climate and environmental change (e.g. Andrews, 2006; Andrews *et al*., 1993, 1997, 2000; Matsuoka *et al*., 2001; Garnett *et al*., 2004). Holocene timescale variations in $\delta^{18}O$ in temperate climates are likely to be controlled by the temperature of moisture condensation in the air mass (± some source/amount effects; see Garnett *et al*., 2004). $\delta^{13}C$ is primarily controlled by the relative proportion of isotopically light CO_2 derived from soil organic matter, mixed with isotopically heavier carbon derived from (1) dissolution of the aquifer limestone, and (2) equilibration of the aquifer and spring water with atmospheric CO_2. The isotopic composition is also modulated by within-aquifer and within-pool processes (Andrews, 2006; Garnett *et al*., 2004).

Because more has been published on the stable isotopic compositions of Holocene tufas (Andrews *et al*., 1994, 2000; Garnett *et al*., 2004) we start by discussing the younger material first.

5.1 - STABLE ISOTOPE ANALYSIS OF EARLY HOLOCENE POOL DEPOSITS

5.1.1 - Oxygen isotopes

Isotopic data from calcitic micrites and shell aragonite of the aquatic gastropod *Lymnaea peregra* from Early Holocene Caerwys pool deposits are shown in Figure 4. $\delta^{18}O$ values from a single lamina of the Early Holocene micritic pool deposit (fig. 4a) show little

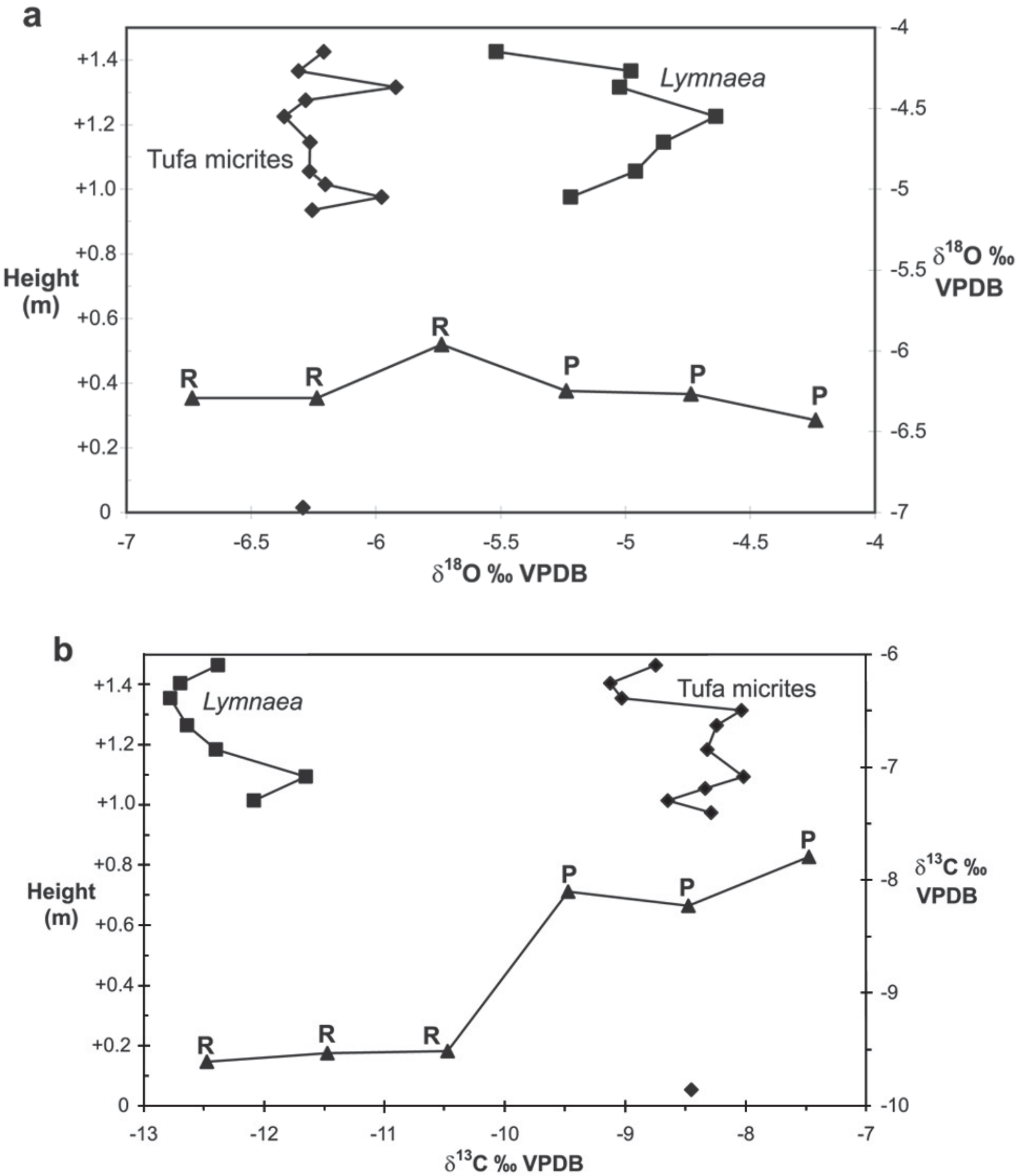

Fig. 4: $\delta^{18}O$ (a) and $\delta^{13}C$ (b) values for Holocene pool tufa micrites (diamonds and triangles) and *Lymnaea peregra* (squares) located in Fig. 2. Error bars are effectively the width of the symbols. Diamonds and squares are samples from vertical profiles, and triangles are samples from an individual horizontal lamina sampled at +0.9 m (Fig. 2). $\delta^{18}O$ values (a) from a single lamina show little variation and there are no discernable differences in $\delta^{18}O$ from reed stem encrustations (R) and pool micrites (P). $\delta^{13}C$ values (b) from the single lamina show a distinct difference between the reed stem encrustations (R) and pool micrites (P). The offset between *L. peregra* and contemporaneous pool micrite $\delta^{18}O$ values in (a) is caused by mineralogical and species specific kinetic fractionation (see text). The offset between *L. peregra* and contemporaneous pool micrite $\delta^{13}C$ values in (b) is due to either microenvironmental photosynthetic effects, or molluscan metabolic effects (see text).

Fig. 4 : Valeurs de $\delta^{18}O$ (a) et $\delta^{13}C$ (b) pour les micrites de mare holocène (losanges et triangles) et Lymnaea peregra (carrés) localisés sur la figure 2. Les barres d'erreur correspondent effectivement à la largeur des symboles. Les losanges et les carrés sont des échantillons provenant des profils verticaux, et les triangles sont des échantillons provenant d'un horizon laminé à 0,9 m (Fig. 2). Les valeurs de $\delta^{18}O$ (a) d'une seule lamine montrent peu de variations et il n'y a pas de différences notables par rapport aux $\delta^{18}O$ des incrustations de racines de roseaux (R) et des micrites de mares (P). Les valeurs de $\delta^{13}C$ (b) d'une seule lamine montrent une différence notable entre les incrustations de racines de roseaux (R) et les micrites de mares (P). Le décalage entre L. peregra *et les valeurs de $\delta^{18}O$ des micrites de mare contemporaine (a) est causé par la minéralogie et la vitesse de fractionnement spécifique de l'espèce (voir texte). Le décalage entre* L. peregra *et les valeurs de $\delta^{13}C$ des micrites de mare contemporaine (b) est dû à des effets de photosynthèse microenvironnementaux ou à des effets métaboliques des mollusques (voir texte).*

variation (mean = –6.3‰, range of 0.47‰, largely due to one outlying point; fig. 4a). Moreover, there are no discernable differences in $\delta^{18}O$ from reed stem encrustations and pool micrites. $\delta^{18}O$ from the vertical array of the banded pool micrite samples (fig. 4a) vary between –5.9 to –6.4‰ (mean –6.2‰).

Overall these $\delta^{18}O$ values are close to the mean values in modern British riverine tufas (Andrews *et al.*, 1993) and similar to other early Holocene data from northern upland England (Andrews *et al.*, 1994). Within this shallow pool, $\delta^{18}O$ of the water apparently did not vary significantly from the edge to the centre of the pool, and $\delta^{18}O$ was not controlled by the type or location of tufa precipitation. $\delta^{18}O$ variability does not correspond with lamina type (light vs. dark) and so does not appear to record seasonal change. The negative values suggest that evaporation effects on $\delta^{18}O$ were not substantial, presumably because the water was continually replenished from an isotopically invariant groundwater source.

$\delta^{18}O$ values for the shell aragonite of *L. peregra* range between –4.7 and –5.5‰ (mean –5.0‰; fig. 4a). *L. peregra* shell aragonite $\delta^{18}O$ is on average 1.2‰ more positive than coexisting pool micritic calcite, an offset very close to that expected from combined mineralogical and kinetic effects. About +0.6‰ of this offset is due to mineralogical fractionation (Tarutani *et al.*, 1969) and there is probably a constant non-species specific kinetic offset as a result of biological processes during aragonitic shell calcification (+0.74‰ between inorganic and biogenic aragonite at 25 °C (Grossman & Ku, 1986; Tarutani *et al.*, 1969)).

The combined *L. peregra* and micritic calcite $\delta^{18}O$ values can be used to test the idea that palaeo-tufa calcites record a temperature signature using the experimental relationship for *L. peregra* defined by White (1998) and White *et al.* (1999);

$$T\ (^{o}C) = 21.36 - 4.83\ (\delta^{18}O_{aragoniteVPDB} - \delta^{18}O_{waterVSMOW}) \quad (1)$$

and that defined for meteoric calcite cements (Hays & Grossman 1991);

$$T\ (^{o}C) = 15.7 - 4.36\ (\delta^{18}O_{calciteVPDB} - \delta^{18}O_{waterVSMOW}) + 0.12\ (\delta^{18}O_{calciteVPDB} - \delta^{18}O_{waterVSMOW})^{2} \quad (2)$$

The mean recent $\delta^{18}O$ composition of groundwater in this part of North Wales is around –6.5‰ VSMOW (Darling, 2004). This author also demonstrated that groundwater $\delta^{18}O$ resembled the weighted mean rainfall input. We can therefore suggest that the likely $\delta^{18}O$ of the spring-waters that precipitated the Holocene tufas was around –6.5‰ VSMOW. Using this value for $\delta^{18}O_{water}$ in both equations, and inputting the range of measured carbonate $\delta^{18}O$ (fig. 4a), the resulting rounded temperature ranges are between 13 and 16.5°C (*L. peregra*) and 13-15°C from the micritic pool calcites. These temperature ranges compare well with one another and with those from modern groundwater-fed rivers with barrage tufa systems in northern England, e.g. the Lathkill in Derbyshire (fig. 1, location B), where the annual temperature range is 7-15°C (Pedley *et al.*, 1996). The Caerwys system was probably more sluggish than the Lathkill, and the pools were much smaller and shallower, explaining the slightly warmer temperature range. It is important to note that these calculated water temperature values are only a guide to actual early Holocene water temperatures because the $\delta^{18}O_{water}$ value is only an estimate and the calculated temperatures are very sensitive to small changes in the $\delta^{18}O_{water}$ value. Despite this, these water temperatures are consistent with early Holocene ($T^{o}C_{max}$) air temperature estimates based on beetle remains (Atkinson *et al.*, 1987).

The reason for larger variability in $\delta^{18}O$ of the shell aragonite (and hence the derived temperatures) is not clear, although the 0.8‰ variability is comparable to that recorded by modern *L. peregra* (White *et al.*, 1999). The micrites almost certainly record snapshots of water isotopic composition and temperature, and yet are remarkably constant. The snail shells, however, record those variables over at least a few months during spring and summer (White *et al.*, 1999). Apparently, either temperature or the isotopic composition of the recharge varied significantly over the time the snails were calcifying their shells.

5.1.2 - Carbon isotopes

$\delta^{13}C$ values from the single lamina of the Early Holocene pool deposit have a mean of –8.9‰, ranging between –7.9 and –9.7‰ (fig. 4b), but with distinct difference between the reed stem encrustations (mean $\delta^{13}C$ = –9.7‰) and the pool micrites (mean $\delta^{13}C$ = –8.2‰).

$\delta^{13}C$ from the vertical array of the banded pool micrite samples (fig. 4b) vary between –8.0 to –9.1‰ (mean –8.5‰), values similar to pool micrites from the single lamina (fig. 4b). These values are a little less negative than typical riverine modern and Holocene tufas (Andrews *et al.*, 1993, 1994; Garnett *et al.*, 2004), although similar to modern and Holocene lacustrine tufas (Andrews *et al.*, 1993; Andrews *et al.*, 2000), suggesting that within pool processes, including degassing and biology have an impact on $\delta^{13}C$ (see below).

The difference in $\delta^{13}C$ between the reed encrustations and the pool micrites may result from phytoplanktonic photosynthetic activity within the water column that controlled the microenviromental $\delta^{13}C$ of the precipitating pool micrites. Biological activity typically increases $\delta^{13}C_{DIC}$ in a water body, due to plants preferentially utilising $^{12}CO_2$ rather than $^{13}CO_2$ during photosynthesis (Anderson & Arthur, 1983). This results in more positive $\delta^{13}C$ in the DIC of the microenvironment around the precipitating micrite and is recorded in the pool micrite sediments. $\delta^{13}C$ of the pond margin reed stem encrustations are, however, probably representing the composition of inorganically degassed running water. Variability of $\delta^{13}C$ in the micrites does not correspond to lamina type (light vs. dark) and so does not obviously reflect seasonal changes. There is, however, a weak negative relationship between $\delta^{18}O$ and $\delta^{13}C$ (r = –0.45) suggesting that this shallow pool had a strong input of groundwater recharge that was not influenced too strongly by residence time effects or evaporation (Andrews *et al*., 1993).

$\delta^{13}C$ values for the shell aragonite of *Lymnaea peregra* range between –11.7 and –12.8‰ (mean –12.4‰; fig. 4b), about 3.8‰ more negative than contemporaneous micritic calcite. There is a weak positive relationship (r = 0.66) between $\delta^{13}C$ of the micritic calcites and the coexisting *L. peregra* shell aragonites, which suggests that *L. peregra* $\delta^{13}C$ is at least in part controlled by the variation in the DIC $\delta^{13}C$, although other factors including metabolism and microhabitat will be significant too (e.g. Grossman & Ku, 1986; Tanaka *et al*., 1986; Veinott & Cornett, 1998). Temperature can influence biogenic aragonite $\delta^{13}C$ (Grossman & Ku, 1986), although this may be linked to increased vital effects as temperatures rise (Romanek *et al*., 1992; Veinott & Cornett, 1998).

The mean negative 3.8‰ offset between *L. peregra* shell aragonite and calcite micrite (fig. 4b), is in the wrong direction to be caused by the mineralogical difference (aragonite should be isotopically enriched by +1.7‰ relative to calcite at temperatures between 10-40°C (Romanek *et al*., 1992)). Similar negative offsets are, however, known from other lacustrine deposits (e.g. von Grafenstein *et al*., 2000). Andrews *et al*. (1997, 2000) attributed similar offsets in tufa-precipitating systems to microenvironmental effects. They thought the aragonite shell carbonate $\delta^{13}C$ was representing the DIC $\delta^{13}C$ while the microbial (micritic) carbonate $\delta^{13}C$ was modified by microenvironmental effects caused by phytoplankton photosynthesis preferentially extracting $^{12}CO_2$ from micrometer-millimetre-scale packages of water. In the case of Caerwys, if the *L. peregra* $\delta^{13}C$ (-12.4‰) is reflecting $\delta^{13}C_{DIC}$, then the isotopically heavier reed stem encrustation $\delta^{13}C$ (–9.7‰) cannot simply be representing inorganic calcite precipitation resulting from degassing (see above). This either suggests that the reed stem encrustation $\delta^{13}C$ was also affected to some extent by photosynthetic enrichment (although less so than the pool micrites) or the $\delta^{13}C$ of *L. peregra* shell aragonite is strongly affected by metabolic effects (see above).

5.2 - STABLE ISOTOPES FROM LATE-GLACIAL TO EARLY HOLOCENE TUFA

5.2.1 - Oxygen isotopes

The $\delta^{18}O$ values from the Late-glacial-early Holocene deposits (fig. 5) increase upward from the basal value of –6.7‰ reaching a maximum of –5.7‰ at –0.86 m. The $\delta^{18}O$ values then decline over a lesser range until –0.55 m. The upper sample, above the sandy horizon, is not significantly different to the samples below the sand, although less negative than the sample immediately below the sand (fig. 5).

Long-term (>millennial) changes in late Pleistocene tufa and lake carbonate $\delta^{18}O$ have so far been shown to represent changes in air temperature that control the $\delta^{18}O$ of rainfall and hence recharge to the aquifers that feed tufa-forming streams (e.g. see discussions in Andrews, 2006; Andrews *et al*., 1994, 2000; Marshall *et al*., 2002; Garnett *et al*., 2004). At temperate latitudes today a 0.58‰ increase in water $\delta^{18}O$ reflects a 1°C increase in air temperature (Rozanski *et al*., 1993), although it is not proven that this relationship is constant in the past; it may have been lower (Jouzel *et al*., 2000). In addition, the tufa calcite record of this relationship is dampened (decreased) because calcite precipitation from water has a smaller but inverse relationship between $\delta^{18}O$ and temperature (see e.g. Andrews, 2006; Marshall *et al*., 2002; Garnett *et al*., 2004). These uncertainties, coupled with the problem that it is not possible to know the exact isotopic composition of either Late-glacial spring-water at Caerwys, or the temperature of calcite precipitation, mean that the $\delta^{18}O$ records in tufa carbonate are probably thus an estimate of *relative* minimum changes in air temperature.

Interpreted on this basis the 0.98‰ increase in $\delta^{18}O$ with time from the base of the Caerwys tufa until –0.86 m (fig. 5) suggests an air temperature rise of no more than 2-3°C (Andrews, 2006). Two thin palaeosol horizons (-0.9 to –0.92 and –0.8 to –0.82 m) recording temporary cessation of tufa accumulation occur close to the acme of this warming trend (fig. 5) and these palaeosols also record an increase in wetland molluscs (fig. 3). Above –0.86 m until –0.55 m the $\delta^{18}O$ values decrease by 0.65‰ suggesting a 1-1.5°C cooling (fig. 5) and molluscan abundance is low (see above). Above the break in tufa deposition, marked by the sandy horizon (–0.4 to –0.5 m) the basal Holocene $\delta^{18}O$ value at –0.35 m is slightly less negative than the value immediately below the sand, perhaps suggesting the start of a recovery (rise) in temperature.

The only age control we have in this sedimentary sequence is the radiocarbon date from the upper palaeosol 13,806 $\pm\,^{1346}_{384}$ cal. years BP at –0.8 to –0.82 m. Given the large calibration error for the date, and the molluscan evidence suggesting the date is slightly too old (see above), we can be confident only that the tufa formed during Greenland Interstadial 1 (GI-1; terminology of Johnsen *et al*., 1992; Björck *et al*., 1998). It is *possible* the tufa sequence developed during the warming from GL-1d into GL-1c (Johnsen *et al*., 1992; Dansgaard *et al*., 1993; Björck *et al*., 1998) but we acknowledge that direct comparisons with Greenland Ice cores are not straightforward (Lowe *et al*., 1999). This correlation is consistent with the $\delta^{18}O$ values which are least negative around the palaeosols, indicating warm conditions (GL-1c?) which appear to have been identified at this time by other palaeoclimatic proxies in UK Late-glacial sequences (Lowe *et al*., 1999). However, the presence of palaeosols suggest that breaks in sedimentation occurred below the dated horizon, so this interpretation is not concrete and it is equally possible the warming trend relates to the earlier warming in GL-1e. We note that the highest reconstructed Late-glacial temperatures from Llanilid in south Wales (200 km S of our site) occur between 15,000-14,500 cal. years BP

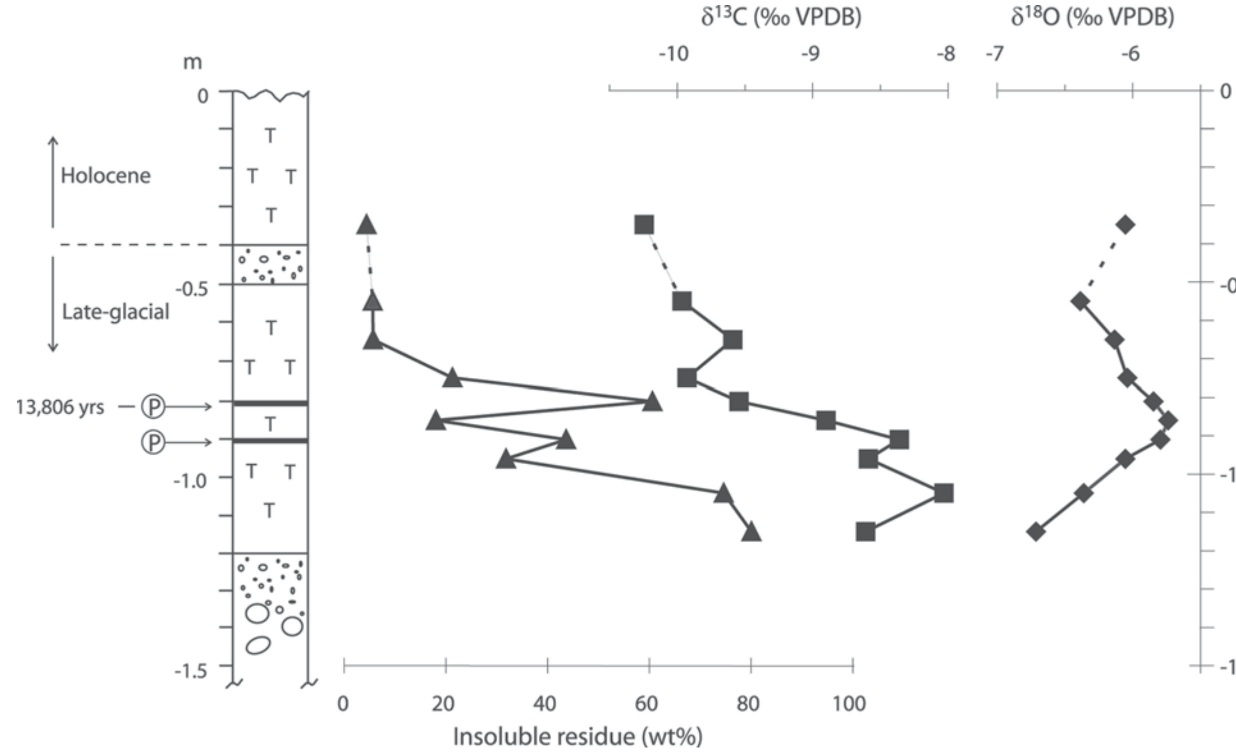

Fig. 5: $\delta^{18}O$ and $\delta^{13}C$ values and insoluble residue content for the Late-glacial part of the Caerwys tufa, plotted against depth and tufa stratigraphy (key as Figs 2 and 3). Age is in calibrated radiocarbon years BP (Table 1). Error bars are effectively the width of the symbols. The $\delta^{18}O$ values (diamonds) increase upward from the basal value of –6.7‰ reaching a maximum of –5.7‰ at –0.86 m and then decline over a lesser range until –0.55 m, interpreted as a climatic warming and then cooling trend (see text). The $\delta^{13}C$ values (squares) decrease markedly between –0.82 & –0.50 m perhaps due to decreasing phytoplankton photosynthetic activity under the colder conditions, and less isotopic enrichment of the tufa $\delta^{13}C$ (see text).

Fig. 5 : Valeurs de $\delta^{18}O$ et $\delta^{13}C$ et résidu insoluble pour la partie tardiglaciaire du tuf de Caerwys en regard de la stratigraphie (même légende que Figs 2 et 3). La date est donnée en années radiocarbone calibrée BP (Tabl. 1). Les barres d'erreurs correspondent effectivement à la laergeur des symboles. Les valeurs de $\delta^{18}O$ (losanges) augmentent de la base vers le sommet de –6.7‰ et atteignent un maximum de –5.7‰ à –0.86 m puis un déclin jusqu'à –0.55 m, interprété comme un réchauffement climatique suivi par une tendance au refroidissement (voir texte); Les valeurs de $\delta^{13}C$ (carrés) diminuent fortement entre –0.82 et –0.50 m peut-être à cause d'une diminution de l'activité photosynthétique du phytoplancton sous les conditions les plus froides et de moindre enrichissement isotopique du tuf en $\delta^{13}C$ (voir texte).

(during GL-1e), with maximum lacustrine calcium carbonate production occurring around 13,300 cal. years BP; Mayle *et al.*, 1999; Walker *et al.*, 2003); this latter parameter might reasonably be expected to relate to tufa formation at Caerwys, which within the limits of dating, it does.

The ensuing cooling (above the dated horizon; –0.5 to –0.86 m in fig. 5), suggested by the $\delta^{18}O$ and low molluscan abundance, is consistent with cooling in the Llanilid record after 13,100 cal. years BP (Mayle *et al.*, 1999; Walker *et al.*, 2003) and could be part of the transition into the Younger Dryas stadial (GS-1 of Johnsen *et al.*, 1992; Björck *et al.*, 1998), with the sandy horizon (–0.4 to –0.5 m) representing cessation of tufa precipitation during the coldest part of this stadial. If this is correct Gl-1a is not clearly represented in the tufa. It is, however, unlikely that the 0.65‰ decline in $\delta^{18}O$ seen at Caerwys represents the full cooling trend into the Younger Dryas stadial because a 2‰ decline was observed in a lake carbonate record in NW England (Jones *et al.*, 2002; Marshall *et al.*, 2002), and because tufa precipitation is thought generally to be linked to relatively warm climate (e.g. Hennig *et al.*, 1983; Pentecost, 1995; Dramis *et al.*, 1999). The 0.65‰ decline in tufa might thus represent the early stages of cooling in the Younger Dryas stadial until low temperatures caused cessation of tufa deposition and truncation of the record. The higher $\delta^{18}O$ seen in the uppermost sample, along with the early Holocene molluscs appear to represent the re-commencement of tufa precipitation with climate amelioration at the beginning of the early Holocene. Without better dating it is not possible to be more confident about these interpretation, particularly as four distinct warm to cold fluctuations have been documented within the Late-glacial from the GRIP record (Johnsen *et al.*, 1992; Taylor *et al.*, 1993), marine records (Hughen *et al.*, 1996) and lacustrine/bog records from Europe (von Grafenstein *et al.*, 1999; Ammann, 2000; Brooks & Birks, 2000; Marshall *et al.*, 2002).

The inferred Late-glacial temperatures from the Caerwys tufa $\delta^{18}O$ should be considered in the context of other palaeotemperature estimates for northern England based on marl lake isotopic data (Marshall *et al.*, 2002) and chironimids (Brooks & Birks, 2000). These studies suggest a decline of 6.5°C and 3.7°C respectively towards the coldest part of the Younger Dryas stadial. Best estimate coleopteran-inferred temperatures suggest a $T°C_{max}$ temperature decrease into the Younger Dryas stadial of between 6°C (Atkinson *et al.*, 1987; Walker *et al.*, 2003) and ~3°C (Coope *et al.*, 1998), the latter estimate from North Wales, 75 km SW of our site. This comparison again implies that if Younger Dryas cooling is represented at Caerwys, it is only showing the initiation of climate deterioration.

5.2.2 - Carbon isotopes

The $\delta^{13}C$ values from the Late-glacial-early Holocene deposits range from around –8.0 to around –10‰ (mean of –9.2‰; (fig. 5) comparable to the values for the later Holocene samples (fig. 5). The five basal samples have $\delta^{13}C$ values around –8.5‰ whereas above –0.86 m the values mainly decrease with time (up profile).

Values around –8.5‰ in the basal samples (fig. 5) suggests there was a significant influence from isotopically light soil-zone CO_2 before 13,806 ± +1346 –384 cal. years BP, (11,725 ± 120 ^{14}C years BP: Table 1) a finding that concurs with development of birch scrub and woodland between 13,000 and 12,000 ^{14}C years BP 70 km SSW of our site in North Wales (Lowe & Lowe, 1989) and further south in the Llanilid record (Mayle *et al.*, 1999; Walker *et al.*, 2003). Moreover, if increasing $\delta^{18}O$ from the base of the Caerwys tufa until –0.86 m (fig. 5) represents warming (see above) we might expect this to be accompanied by increased vegetation and more input of isotopically-light soil-zone CO_2 (unless conditions were dry): $\delta^{18}O$ and $\delta^{13}C$ would thus be inversely related, which they clearly are not (fig. 5). The $\delta^{13}C$ values are apparently not influenced by the presence of two palaeosol horizons either. This decoupling of expected $\delta^{18}O$ and $\delta^{13}C$ relationships is probably related to the pool depositional environment of the tufas. The five basal samples (mean $\delta^{13}C$ = –8.5‰), when temperature was increasing (fig. 5), probably formed in a productive pool environment where photosynthetic removal of CO_2 by phytoplankton caused isotopic enrichment of the $\delta^{13}C$ of the precipitating calcite (Andrews *et al.*, 1997), just as it appears to have done in the early Holocene pool micrites (see above). During the subsequent climatic cooling above –0.86 m, four samples between –0.82 and –0.50 m show a 1‰ decrease in $\delta^{13}C$ (fig. 5) that might represent decreasing phytoplankton photosynthetic activity under the colder conditions, and therefore less isotopic enrichment of the tufa $\delta^{13}C$. The uppermost early Holocene sample (figs. 3 and 5) does not contain fully aquatic molluscs (*L. truncatula* is amphibious), and has a depleted $\delta^{13}C$ composition. This suggests the pool environment had not fully re-established and the photosynthetic effects had not re-initiated control over $\delta^{13}C$, perhaps because climate amelioration had only just started.

6 - NW EUROPEAN LATE GLACIAL TUFA DEPOSITS: OBSERVATIONS

Given the success in identifying a tufa $\delta^{18}O$ record of marked cooling events such as the Holocene 8.2 ka event (Andrews, 2006; Garnett *et al.*, 2004), it was expected that a more dramatic cooling event, such as that associated with the Younger Dryas stadial might be recorded by tufa $\delta^{18}O$. However, as demonstrated above, the Caerwys $\delta^{18}O$ record is at best only a partial record of the cooling. The main problem seems to be that in NW Europe generally, at least north of 50ºN latitude (Andrews, 2006), tufa deposition did not occur during the coldest part of the stadial (Gedda *et al.*, 1999; Žák *et al.*, 2002). Other than Caerwys, only three other studies of NW European tufa have reported possible Late-glacial tufa deposition (Preece & Bridgland, 1998; Makhnach *et al.*, 2004; Boch *et al.*, 2005). Travertine and tufas from southern England (Preece & Bridgland, 1998) and the Eastern Tyrol in Austria (Boch *et al.*, 2005) both have ages around 13,500 cal. years BP implying formation during GI-1 as with the Caerwys deposit. More controversial is an impure and possibly detrital tufa deposit described from Pitch in Belarus that has been assigned to the Younger Dryas stadial based on pollen (Makhnach *et al.*, 2004). As the authors admit, the tufa chronology is poorly constrained by dating and no significant decrease in tufa $\delta^{18}O$ – that might be expected with cooling in the Younger Dryas stadial – was detected, whereas nearby marl-lake data show $\delta^{18}O$ decreases of ~5‰ (Makhnach *et al.*, 2004). The Belarus chronology and tufa facies are thus not yet well enough constrained to make further interpretations, although the site is clearly an important one for future work.

7 - CONCLUSIONS

New stable isotope data from Late-glacial and early Holocene tufa deposits at Caerwys in North Wales demonstrate the following key points.

1. Based on $\delta^{18}O$ values, deposition of Late-glacial tufa probably occurred mainly during a climatic warming (probably GL-1c or 1e) and the ensuing cooling suggested by $\delta^{18}O$ values and low molluscan abundance, could be the transition into the Younger Dryas stadial, with a sandy horizon representing cessation of tufa precipitation during the coldest part of the stadial. It is, however, unlikely that a 0.65‰ decline in $\delta^{18}O$ seen at Caerwys represents the full cooling trend into the Younger Dryas stadial because a 2‰ decline was observed in lake carbonates from NW England. This finding is consistent with observations from most other tufa sites in NW Europe, where tufa deposition is not recorded in the coldest part of the stadial.
2. $\delta^{13}C$ values around –8.5‰ in the basal Late-glacial tufas show there was a significant influence from isotopically light soil-zone CO_2, a finding that concurs with development of birch scrub and woodland at this time further south in NorthWales. During climatic cooling into the Younger Dryas stadial a 1‰ decrease in tufa $\delta^{13}C$ is interpreted to represent decreasing phytoplankton photosynthetic activity under the colder conditions causing less isotopic enrichment of the tufa $\delta^{13}C$.

3. The (pre-9000 cal. years BP) early Holocene tufas at Caerwys contain well-preserved laminated micrites formed in small pools containing the freshwater gastropod *Lymnaea peregra*. Palaeo-water temperatures calculated from $\delta^{18}O$ values using the Hay & Grossman (1991) calcite palaeotemperature equation (tufa), and those based on an experimentally calibrated fractionation factor for *L. peregra* (White *et al.*, 1999) show quite good agreement and suggest that summer water temperatures were in the range 13 to 16.5°C, consistent with air temperatures inferred from beetle remains.
4. The combined $\delta^{13}C$ data from the early Holocene pool micrites and contemporary *L. peregra* shells suggest that $\delta^{13}C_{DIC}$ could have been as negative as –12.4‰ (based on *L. peregra* values) in which case pool micrites and pool marginal reed stem encrustations were affected to a greater or lesser extent (respectively) by phytoplanktonic photosynthetic activity within the water column. Photosynthesis increased $\delta^{13}C_{DIC}$ by preferentially utilising $^{12}CO_2$ rather than $^{13}CO_2$ resulting in more positive $\delta^{13}C$ in the DIC of the microenvironment around the precipitating micrite. Even if the isotopically negative *L. peregra* values reflect, in part, metabolic effects of the gastropod, photosynthetic effects on the pool micrites are still implicated because the tufa $\delta^{13}C$ values are less negative than other early Holocene riverine tufa sites in the UK.

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