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Radiocarbon in freshwater carbonates as tool of Late Quaternary studies

ANNA PAZDUR

Silesian University of Technology, Institute of Physics,
Radiocarbon Laboratory of the Department of Radioisotopes,
Krzywoustego 2, 44-100 Gliwice

Abstract: Different methods of radiometric dating (^{14}C, U/Th, TL) and stable isotopes composition (^{13}C and ^{18}O) in freshwater carbonates are used for analysis of sedimentologic process and reconstruction of paleoclimatic conditions as well as for stratigraphic purposes. Calcareous tufa and speleothems deposited in karst areas seem to be fightly significant indicators of the past changes because of their direct relation to the environment of deposition. Some important methodical and interpretation problems for Quaternary research in Poland were solved during the last *ca.* 20 years in Gliwice Radiocarbon Laboratory.

Synthetic approach to ^{14}C dating of calcareous tufa from Southern Poland, based on statistical analysis of correlation between lithologic type of tufaceous sediment, carbon isotope composition and apparent age was done. Results of measurements of $\delta^{18}O$ and $\delta^{13}C$ in tufa samples dated with ^{14}C method are used to reconstruct Holocene climatic changes in southern and Eastern Poland. The stable isotope composition was used to estimate the mean annual temperatures in the interval 9500–2000 yr BP.

On the basis of statistical analysis of several hundred ^{14}C dates for speleothems from Kraków–Wieluń Upland caves warm and cold climate periods were indicated during the last 50,000 years BP. Distribution of the dates indicate that growth of speleothems between 30 and 20 ka BP may be interpreted as reflecting changes of paleoclimatic conditions.

Comparison of measured ^{14}C activities in carbonate fractions of lake marl from Gościąż Lake with their varve ages allowed for accurate determination of secular changes of ^{14}C dilution factor of total dissolved inorganic carbon. Basing on the geochemical model developed by Broecker and Walton it was possible to reconstruct mean lake level during the Late Glacial and Holocene. Basing on ^{14}C dates of lithological boundaries in the cores from Gościąż lake basin the changes of lake level during the last 12 ka BP were reconstructed.

Paleokarst forms known as "pipes" from Southwest England and South Wales were dated by ^{14}C, U/Th and TL methods. ^{14}C ages were obtained from carbonate cements within sandrock and on the pipe walls. Statistical analysis of dates and geochemical considerations indicate on periods of pipes pipes and pipes infillings.

Key words: radiocarbon dating, stable isotopes, palaeoclimate.

Introduction

The isotopic investigations of freshwater carbonate (stable isotope ^{18}O and ^{13}C, chemical analysis, frequency distribution of ^{14}C and U/Th dates) have frequently been used as tool for analysis of sedimentologic processes and reconstruction of paleoclimatic conditions, as well as stratigraphic purposes. The stable isotope method has been successfully applied to studies of speleothems. Interpretation of stable isotope measurements in lacustrine carbonates is much more sophisticated and difficult because of the complex nature of sedimentation, influenced by number of physicochemical and biological factors. Isotopic studies of pedogenic carbonates (caliche, concretions, cements) give information connected with circulation of groundwater and thus indirectly lead to paleoclimatic conclusions. Some papers have been devoted to isotopic studies of spring tufas deposited from hot and/or mineral springs. Because of their endogenic origin, such waters weakly reflect surficial environmental changes. Calcareous tufa deposited from normal surface water in karstic areas seems to be a highly significant indicator of past changes because of its direct relation to the environment of deposition. These deposits, like as speleothems, reflect the combined effects of karst processes, controlled to a great extent by climatic factors, especially temperature and humidity.

For reconstruction of time record of paleoenvironmental conditions of the sedimentary processes reconstruction of the time scale of carbonate deposition should be done. Usually ^{14}C, U/Th, TL and AAR – dating methods may be used.

Radiocarbon dating of carbonates is sophisticated because to interpret ^{14}C results some information about geochemical cycle of carbon in dependent karst area should be known. Both theoretical considerations, based on geochemical processes involved in formation of the secondary carbonate sediments (Pearson 1992) and numerous experimental data (Gascoyne 1992; Holmgren *et al.* 1994; Pazdur *et al.* 1995, 1999) lead to the conclusion that all carbonate sediments are depleted in radiocarbon with respect to contemporary biosphere. The magnitude of the depletion in isotope ^{14}C is connected with so-called reservoir correction (sometimes called the reservoir age). The true ages of the dated samples are younger than the conventional radiocarbon ages.

The large number of dating results obtained by different methods enable to interpret results using probabilistic methods (Baker *et al*. 1993; Geyh 1970; Smart & Richards 1992; Srdoc *et al*. 1983). Frequency distributions of dates may be compared with results of investigations obtained by other methods, such as changes temperature and precipitation in the past reconstructed from pollen analyses of peat-bog profiles and lake sediments of unglaciated areas, and with paleoclimatic records from deep sea cores (Guiot *et al.* 1989; Schackleton 1967).

Radiocarbon dating and reservoir effect

Radiocarbon activity of freshwater carbonate sediment at the moment of precipitation (A_0) is obviously influenced by isotopic composition of carbon compounds dissolved in water. Radiocarbon studies of groundwater have resulted in the formulation of different models which estimate initial ^{14}C activity of HCO_3^- ions dissolved in water (Mook 1976; Pearson 1992). However, physicochemical processes involved in precipitation of tufa are complex and numerous environmental factors may influence them (Friedman 1970; Usdowski *et al.* 1979; Pazdur *et al.* 1988a, b; Pazdur & Pazdur 1990). Direct application of such models in ^{14}C dating of tufa has led to unsatisfactory results.

The conventional radiocarbon age (T_C) of carbonate, determined by the ratio of measured ^{14}C activity (A) in a sample to ^{14}C activity of the contemporary biosphere (A_{ox}), defined as 95% of the activity of NBS oxalic acid standard (Stuiver & Polach 1977), *i.e*,

$$T_C = -8033 \times \ln(A/A_{0x}) \tag{1}$$

is greater than the real age of sediments because of depletion of initial ^{14}C activity in precipitated carbonate with respect to biosphere. Difference between T_C and real age is characterised by so called "reservoir age" T_R (or apparent age T_{app}, Pazdur 1988). The value of T_R is related to initial ^{14}C activity of carbonate (A_0) and reservoir dilution factor (q) through the equation

$$T_R = -\ 8033 \times \ln(A_0/A_{0x}) = -8033 \times \ln q. \tag{2}$$

The real radiocarbon age T is obviously described by

$$T = T_C - T_R. \tag{3}$$

T_R value for different freshwater carbonates

The quantity of reservoir age T_R observed for calcerous tufa, lake marl and lacustrine gyttja, cements is characteristic for deposition environment of carbonate: geographical locality of the karst area, type of vegetation, type of bedrock and contain information about sources of carbon and its geochemical cycle in environment. Observed T_R values for these sediments range from several hundred to several thousand years and sometimes more (Pazdur 1988a; Pazdur

& Pazdur1991; Pazdur *et al*. 1995a, b). Speleothems have reservoir age relatively constant determined by stable sedimentation conditions in caves (Holmgren *et al.* 1994; Pazdur *et al.* 1995c, 1999).

Calcareous tufa

The scatter of the values of T_R observed by various authors could be explained by the dependence of T_R on the bedrock type (which is a source of ^{14}C-free carbon) and the type of sediment. The type of calcareous sediments depends strongly on hydrodynamic conditions of water flow. Detailed classification of tufaceous deposits, based on their lithological properties and geochemical conditions of sedimentation, has been described by Pazdur *et al.* (1988b, see Fig. 1). A slightly simplified classification is:

– Spring tufa: precipitated in turbulent water flow (oncoids, stromatolites, moss travertines).

– Tufas (oncoids, moss travertines) and peloidal calcareous muds: precipitated in streams with low or variable water flow.

– Calcareous muds: precipitated in shallow, stagnant-water basins in conditions of semilimnic sedimentation.

Observed values of q in both recent and ancient tufas lie from 0.5 to 0.95 (Srdoc *et al.* 1983; Thorpe *et al.* 1981; Pazdur 1988a; Pazdur *et al.* 1988c; Pazdur

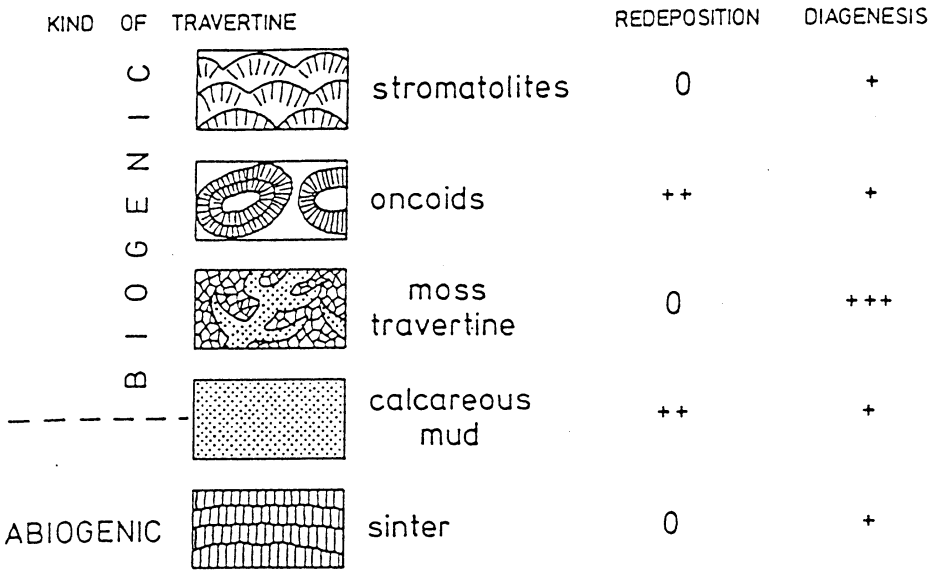

Fig. 1. Possible errors in ^{14}C dating of tufa deposits caused by postdepositional changes. Qualitative scale: 0 = null, + = weak, ++ = moderate, +++ = high (after Pazdur *et al.* 1988b).

& Pazdur 1991) and consequently the values of T_R are included in interval from 500 to 5500 yr. They can receive extremely high value *ca* 11 kyr (Pazdur 1988a).

The magnitude of reservoir age can be determined experimentally by measuring the age of organic matter associated with the layer of carbonate sediment, or detritical organic matter dispersed in the carbonate, itself. Assuming that the age of organic remnants reflects the actual age of carbonate precipitation, we can define the T_R of carbonate

$$T_R = T_C - T_{ORG.} \qquad (4)$$

This value determined for tufa profile with known values of δ^{13}C across profile, can be used to estimation of real age of tufa horizons on the base T_C measurements (Pazdur 1988a; Dobrowolski *et al.* 1996, 1999).

The factors determining the precipitation of freshwater carbonates should be reflected by isotopic composition of carbon ($\delta^{13}C$, A_0) in carbonate samples and should influence the T_R value. The measured values are T_C and some dependence between δ^{13}C and T_C is expected. To estimate magnitude of reservoir age the relation between T_R and δ^{13}C can be used in the shape of equation characteristic for spring tufa precipitated from high energy water (Pazdur 1988a)

$$T_R = (13.50 \pm 3.27) + (0.96 \pm 0.34) * \delta^{13}\mathrm{C}\ [\mathrm{kyr}] \qquad (5)$$

or characteristic for tufas precipitated from average and low energy water

$$T_R = (4.41 \pm 0.98) + (0.25 \pm 0.11) * \delta^{13}\mathrm{C}\ [\mathrm{kyr}]. \qquad (6)$$

The T_R and T values may be determined on the base of both relation (5) and (6) for each measured pair T_C and δ^{13}C in tufa samples. For reconstruction of the time scale sedimentary processes and paleoclimatic interpretation of stable isotope results we assume, that the best calculated ages T are those which give the correct stratigraphy of investigated sediment levels in profiles.

Speleothems

Several studies (Holmgren *et al.* 1994; Pazdur *et al.* 1999a) made measurements of modern radiocarbon activity in recent cave calcite. Holmgren *et al.* (1994) suggests that a droplet hanging on stalactite tip or dripping onto a stalagmite equilibrates relatively quickly with the ambient atmosphere, and, if the cave is well-ventilated (as caves with archaeological site), it is likely that the speleothems were deposited with a radiocarbon concentration in equilibrium with the ambient surface atmosphere. Measurements of carbon isotope contents in contemporaneous karst environment of Southern Poland (Pazdur *et al.* 1999a, b) proved that the karst area Kraków–Wieluń Upland establish the closed geochemical system for carbon. We assume the sedimentation model of calcium carbonate in caves with carbon sources from limestones and biogenic CO_2 in

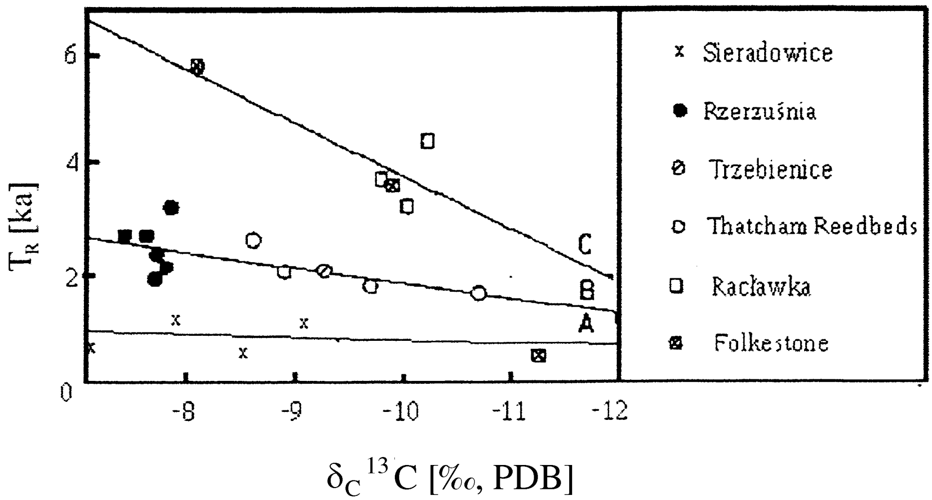

Fig. 2. Relation between experimentally determined values of T_{app} (T_R) and $\delta^{13}C$ for all described profiles from S Poland and UK (after Pazdur *et al.* 1988a).

equilibrium conditions. In this case the ^{14}C concentration in contemporaneous carbonates should be around 85 percent of modern carbon, what makes 1350 years of reservoir age. ^{14}C concentration in the group of recent carbonate samples from Kraków–Wieluń Upland caves ranged from *ca.* 73 to *ca.* 88 pMC (Pazdur *et al.* 1999a).

If we know that the karst area is closed geochemical system for carbon, carbon sources are from limestones and biogenic CO_2 and in caves speleothems were deposited with a ^{14}C concentration in equilibrium with the ambient surface atmosphere, we can assume that reservoir age is constant during the period of the carbonate sedimentation.

Lacustrine gyttja

As the sedimentation of lake marls and lacustrine gyttja in the region of of the temperate zone is limited to the time interval covering the last 15 000 years, the most suitable time scale for sedimentary processes is provided by radiocarbon method. The method is used especially widely for dating either bulk organic and/or carbonate fraction of sediment using conventional counting methods (Pazdur *et al.* 1994; Goslar *et al.* 1998a) or selected macrofossils separated from the sediment with AMS techniques (Goslar *et al.* 1998b).

Interpretation of conventional ^{14}C dating of both carbonate and organic fraction is difficult because initial ^{14}C activity (A_0) of sediment is as a rule unknown and may differ significantly from the corresponding value of contemporary biosphere. Dissolved inorganic carbon in water, as in calcereous tufa and speleo-

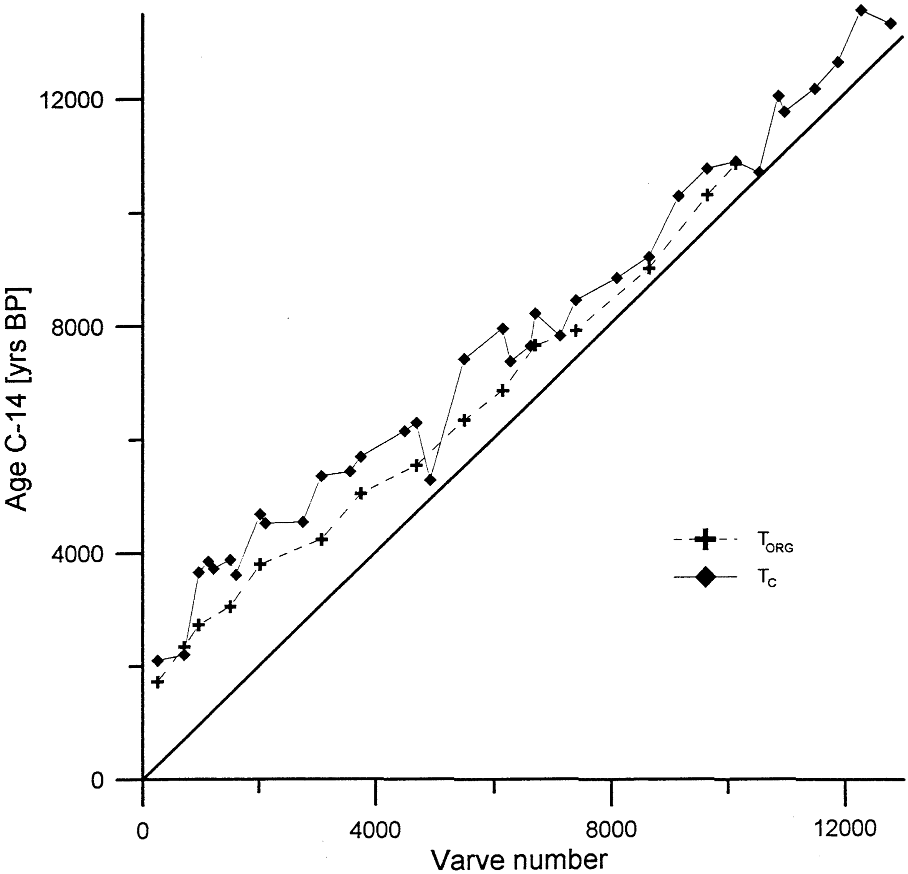

Fig. 3. Relation between ^{14}C age of organic (T_{org}) and carbonate (T_C) fractions and varve number in G1/85 and G2/87 cores from Gościąż Lake. The varve number depends calendar age of sample. The straight line means the line of equal radiocarbon and calendar ages (after Pazdur *et al.* 199b).

thems, oncorporates from different reservoirs. Moreover, the sedimentation of the lacustrine gyttja is influenced in different ways by the presence of water plancton and bacteria and higher water plants. All these factors determine finally the fractionation of carbon isotopes, which is revealed by variable values of δ^{13}C and A_0 in both organic and carbonate fraction.

The most accurate chronostratigraphy of lake sediments may be obtained on profiles of laminated sediments with annual lamination as for Gościąż Lake (Goslar *et al.* 1998a, b). Laminated sediments of the Gościąż Lake, containing *ca.* 12 500 couplets is the longest known sequence, covering significant part of the Late Glacial and whole Holocene, and offers therefore the unique opportunity for detailed palaeoecologic and palaeoclimatic reconstruction (Pazdur *et al.* 1995b; Starkel *et al.* 1996). ^{14}C dates of both organic (T_{ORG}) and carbonate (T_C) fractions are presented on Fig. 3 as function of the number of varves N. The number N denote calendar age of the sample. In this case the quantity of the reservoir age T_R is determined by difference between T_C or T_{ORG} and the number of varves N. The value of T_R for organic fraction was estimated as amounting to 1600 years in the upper part of core G1/85 and to 1400 years in its lower part. These values are confirmed by available AMS radiocarbon dates of macrofossils separated from the laminated sediment (Pazdur *et al.* 1994). The changing of T_R values with age of sediments for both organic and carbonate fractions can be noted.

Cements

Determination of the reservoir effect and possibility of the evaluation of ^{14}C data depend strongly on geochemical conditions of sedimentary processes and can be individually done in the sediments which contain cements. Geochemical considerations on carbon isotope composition in sediments from karst pipe systems in Southwest England and South Wales have been proved to evaluation of the ages of raised beach calcareous sandrock and secondary cements of the pipe wall deposits (Pazdur *et al.* 1995a).

Dated by ^{14}C method carbonate samples may be divided into two groups: (1) samples collected from walls of natural outcrops, (2) the samples collected from pipe walls. In the first group the carbonate present in the sample contains old (radiocarbon-free) shell detritus and carbonate cement 1 formed by dissolution of shell and subsequent carbonate precipitation. The carbonate present in the samples of the second group, contains old shell detritus, carbonate cement of the first generation (cement 1) and carbonate cement of the second generation (cement 2), formed by dissolution of both shells and primary cement. In both primary and secondary cements the main source of ^{14}C isotope is atmospheric carbon dioxide dissolved in water infiltrating the sandrock.

Both groups of dated carbonate samples contain, in approximately the same proportion old shell detritus and cements. Mean composition of carbonates indicate that for samples collected from pipe walls the dilution factor $q = 0.4$. This value correspond to reservoir correction of *ca* $T_R = 5000$ years. The T_R corresponding value for sandrock samples is 5500 years.

^{14}C and stable isotopes in freshwater carbonates as paleoclimatic indicators

$\delta^{18}O$ and $\delta^{13}C$ in calcareous tufa dated with ^{14}C method for reconstruction the Holocene climatic changes

The stable isotopes ^{18}O and ^{13}C of continental carbonate sediments have frequently been used as a tool for analysis of sedimentologic processes and reconstruction of paleoclimatic conditions, as well as for stratigraphic purposes. The stable isotope method has been successfully applied to studies of speleothems (Baker *et al.* 1993; Gascoyne 1992; Geyh & Schleicher 1990; Pazdur *et al.* 1995c, 1999). Interpretation of stable isotope measurements in lacustrine carbonates is much more sophisticated and difficult because of the complex nature of sedimentation, influenced by a number of physicochemical and biological processes (Kuc *et al.* 1998). Istotopic studies of the spring tufas are devoted papers Friedman (1970), Thorpe *et al.* (1981), Michaelis *et al.* (1985), Pazdur *et al.* (1988b).

Tufa sediments, unlike speleothems and lacustrine marl, are deposited under conditions that strongly violate isotopic equilibrium. Despite difficulties caused by disequilibrium precipitation of $CaCO_3$, it may be expected that the isotopic composition of oxygen of Holocene tufa might be useful in reconstructing the approximate thermal condition of sedimentation, or, strictly speaking, the temperature of water from which carbonate has been precipitated. Reconstruction of paleotemperature changes for given geographic region may be based on known seasonal dependence of $\delta^{18}O$ in meteoric water upon temperature (Van der Straaten and Mook 1983). Any attempt to estimate temperatures of sedimentation from measured values of $\delta^{18}O$ in calcareous tufa requires several simplifying assumptions, which are based on results of investigation of recent tufas (Pazdur *et al.* 1988b): (1) isotopic composition of oxygen in meteoric water is preserved in spring waters; (2) the temperature gradient of $\delta^{18}O$ is not changed in the process of deposition, i.e., the temperature gradient of $\delta^{18}O$ in the sediment is the same as in water; (3) the kinetic effect causing differentiation of isotopic composition of oxygen in water and precipitated carbonate is constant and independent

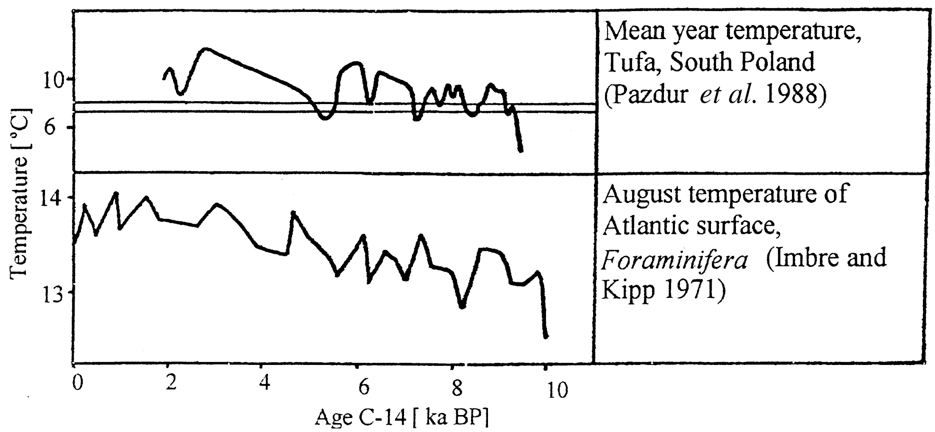

Fig. 4. Mean annual temperature for Southern Poland and August temperature for Atlantic Ocean surface obtained on the basis of stable isotope investigation of tufa samples (Pazdur *et al.* 1988c) and *Foraminifera* (Imbre & Kipp 1971) in the Holocene (after Pazdur 1990).

on temperature; (4) the isotopic composition of oxygen in sediment is independent on the type of tufa; (5) assumptions (1)–(4) are fulfilled over the whole time interval of interest (whole Holocene). The temperature sedimentation of the biogenic tufa (mean year temperature of air) from sites situated in Kraków–Wieluń Upland (Racławka, Rzerzuśnia, Trzebienice) and Holy Cross Mountains (Sieradowice) for the Holocene period was estimated. The record of temperature during Holocene estimated on the basis of the above assumptions is shown in Fig. 4 (Pazdur 1990). We can see the comparison of the Holocene August temperature record of Atlantic surface reconstructed by Imbre and Kipp (1971) on the base of the investigations of *Foraminifera* from deep ocean core sediments and mean year temperature record for Southern Poland.

Late Glacial and Holocene water-level changes of the Gościąż Lake derived from carbon isotope studies of laminated sediments

Changes of lake levels during the Late Quaternary have been studied at numerous localities in the temperate zone, including Europe and North America, in arid and tropical areas and in subarctic zone. The methods which may be used to reconstruct past lake levels including geomorphological mapping of shorelines and analysis of lacustrine sediments.

Cores of the sediments taken in the litoral zone of lake basin, or along the present-day lake shore of the Gościąż Lake, contains as a rule a variety of lithologically differentiated sediments, such as beach sands, peat, lacustrine gyttja, which gave direct evidence of lake level changes (Pazdur *et al.* 1994). Cores taken in the deep central part of the lake basin represent lithologically almost uniform and undisturbed sediment consisting lacustrine gyttja with variable proportion of lake carbonate, reduced organic matter, and fine-grained terrigenous organic material (clay), with some admixture of sulphuric or iron compounds. It should be pointed out that the significance of undisturbed lacustrine calcareous sediments as potential geochemical archives of isotopic records of past environmental changes had been recognised.

Detailed studies of cores G1/85, G1/87 and G2/87 comprising exact counting of the number of varves have led to a floating varve chronology, which covers the last 10 000 years (Goslar *et al.* 1993, 1998) and it was therefore possible to determine the values of the reservoir age of the carbonate fraction and respective dilution factor (q_L) of ^{14}C isotope for all samples dated with conventional techniques, with errors approximately equal to the laboratory errors of ^{14}C age measurements (Pazdur *et al.* 1995b). It may be assumed, that q value determine content of radiocarbon in water lake in the moment of sedimentation of carbonate. The mass balance equations in steady state describing the amount of carbon

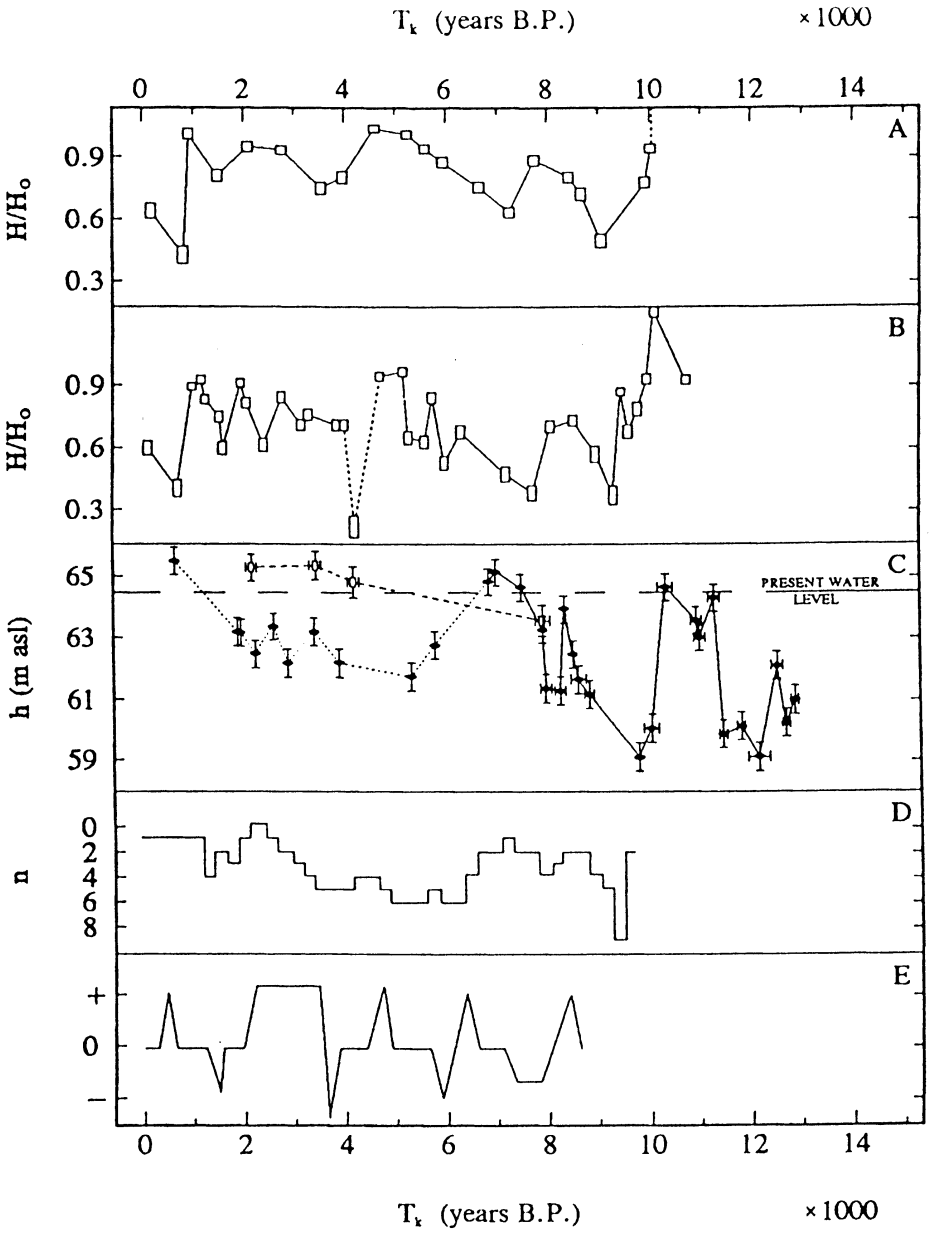

Fig 5. Comparison of lake-level changes at Gościąż Lake in the Late Glacial and Holocene: **A** – modelled changes based on data from G1/85 core; **B** – the same plot obtained for varve chronology based on data from G1/85 and G2/87 cores; **C** – changes reconstructed from ^{14}C dating of lithological boundaries marking high and low lake stands in cores taken at lake shoreline;
D – number of lakes showing low water stands in southern Sweden;
E – transgression (+) and regression (–) of lakes in Jura and northern subalpine ranges in France (after Pazdur *et al.* 1995b).

and the ^{14}C content in the lake may be written on the basis of model described by Broecker and Walton (1959). The q value depends on the model parameters: rates at which CO_2 enters and leaves the lake surface (R), linear evaporation rate from lake surface (l_E), concentration of the total carbon in water entering the lake (k_R), concentration of the total carbon in the lake (k_L), dilution factor of ^{14}C isotope in water entering the lake (q_R) and the ratio of the lake volume to its surface ($H = V_L/A_L$). The last parameter is equal to mean depth of the water in the lake and may be estimated for the moment of sedimentation of carbonate samples on the basis of q_L values and all the remaining parameters. For the studies of the history of the lake it is sufficient to evaluate the relative changes of the mean lake depth, H/H_0

$$H/H_0 = Aq^{-1} - B, \tag{7}$$

where H_0 is the ratio of the lake volume to its surface at present, A and B are combinations of model parameters listed above.

The results of calculation based on different data sets are shown as curves A and B in the upper part of the Fig. 5. Curve C shows reconstruction of changes of the water level based on ^{14}C datings of lithological boundaries between lacustrine and terrestrial biogenic sediments (peat, gyttja, soil with charcoals) observed in 16 cores taken in the nearest vicinity of the lake (Pazdur *et al.* 1994; Starkel *et al.* 1996).

Developing of the karst pipe systems in Southwest England and South Wales

Geochemical considerations on carbon isotope composition and ^{14}C, TL and U/Th dating of sediments from karst pipe systems in Southwest England and South Wales have been proved to reconstruction of the time scale for developing of the systems (Pazdur *et al.* 1995a). The semi-lithified calcareous sandstones and arenaceous limestone (known generally as "sandrock") of the Pleistocene raised beaches contain some developments of karst, principally vertical pipes. They are present in Quaternary cliffs of Cornwall (Newquay, Trebetherick, Godrevy), Devon (Saunton, Croyde, Prawle Point) and S Wales (Fresh-

Table 1. The main forming stages of karst pipe system from SW England and S Wales (after Pazdur *et al.* 1995a).

Processes	Periods and dating methods
Dunes formation	>80 ka BP (TL)
Raised beach deposition	*ca.* 70–80 ka BP (U/Th)
Raised beach primary cementation	*ca.* 35–20 ka BP (^{14}C)
Pipe formation, secondary cementation	*ca.* 30–2 ka BP (^{14}C)
Pipe infills	*ca.* 40 ka BP (TL)

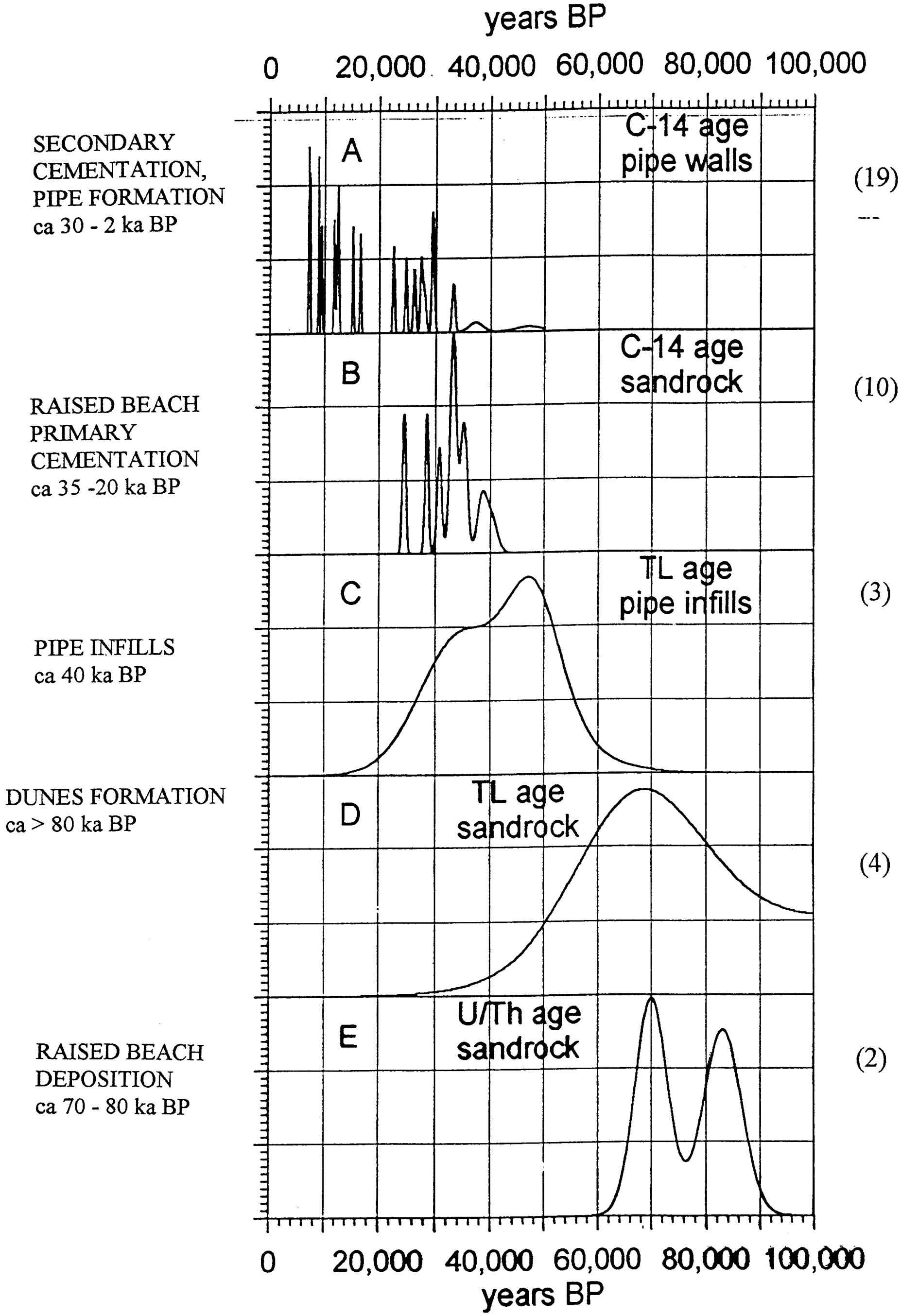

Fig. 6. A record of ^{14}C, TL and U/Th ages for speleothems. Maxima of the distribution determine periods on the time axis. The numbers in brackets in the right mean number of dates (after Pazdur *et al.* 1995a).

water West). According to geological studies (Bowen *et al*. 1985) the pipes are paleokarst forms developed in periglacial conditions of the late Devensian.

Apart of ^{14}C dating the TL method was applied to determine the age of quartz grains forming the raised beaches collected from sandrock and pipe walls. Few U/Th age determinations were also made on carbonate cements from sandrock.

The TL ages of the quartz grains separated from sandrock samples range from about 50 to 120 ka BP (see Fig. 6). Corresponding TL results on sandy material from pipe infills are centered around 40 ka BP. Radiocarbon dates of carbonate cements from sandrock and pipe walls indicate the range of primary cementation (ages of cement 1) between 35 and 20 ka BP, and secondary cementation (ages of cement 2) between 30 and 2 ka BP with break during the climate deterioration caused by the last ice sheet advancement (Fig. 6A). Time record of the developing of karst pipe systems is described in the Fig. 6 and Table 1.

Statistical analysis of tufas and speleothems ^{14}C dates. Paleoclimatic implications

Analysis of the frequency distributions of ^{14}C-dated samples in a time scale have been carried out for different geographic regions (Baker *et al.* 1993; Geyh & Schleicher 1990; Goździk & Pazdur 1987; Pazdur & Pazdur 1986; Pazdur *et al*. 1995a, c; Smart & Richards 1992; Srdoc *et al*. 1983; Tomczak *et al*. 1999). Distinct correlation was noted between observed frequency of ^{14}C dates and variations of specific geological features controlled by climatic changes. The ^{14}C dating method, used simply to determine the absolute age of sediment containing dated samples, becomes therefore an important source of information on the course of some geological processes in the past.

The accuracy of climatic interpretation of the frequency distributions of ^{14}C dates is limited by a number of factors of various origin, which, in general may be grouped in two classes (Goździk & Pazdur 1987): (1) factors connected with nature of dated sediment (depletion of initial radiocarbon concentration, contamination with younger matter, postdepositional processes leading to destruction of the sediment, technical reasons) and (2) factors connected with sampling (decreasing availability of older deposits, subjective causes).

Calcareous tufa

Some papers have been devoted to isotopic studies of spring tufas deposited from hot and/or mineral springs. Because of their endogenic origin, such waters weakly reflect surficial environmental changes. Calcareous tufa deposited from normal surface water in the karst areas seems to be a highly significant indicator of past changes because of its direct relation to the environment

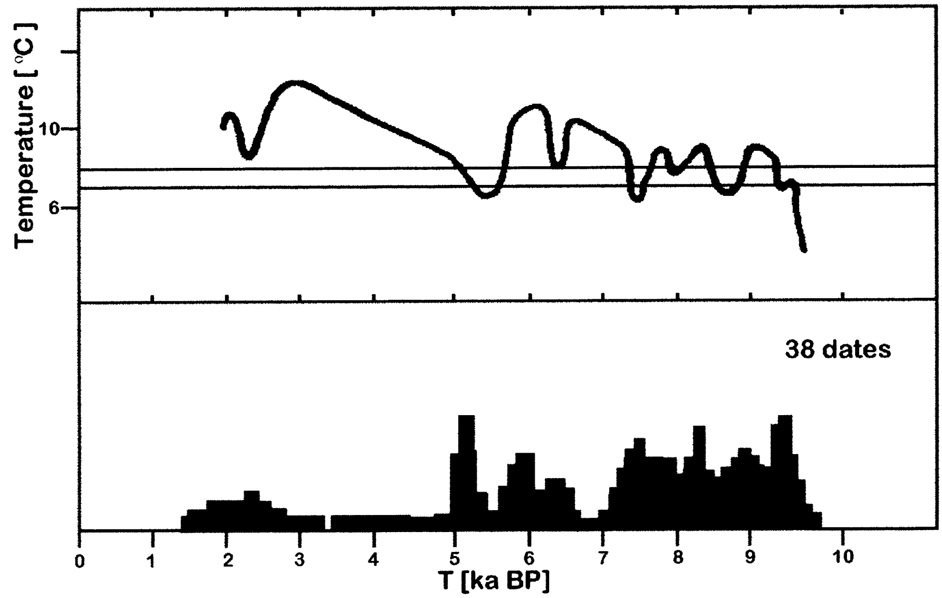

Fig. 7. Distribution of ^{14}C dates and Holocene temperature record obtained on the basis of stable isotope investigation of tufa samples. The horizontal straight lines indicate present range of mean annual temperature in Kraków–Wieluń Upland (7–8°C, after Pazdur 1987).

of deposition. These deposits, like as speleothems, reflect the combined effects of karst processes, controlled to a great extent by climatic factors, especially temperature and humidity.

The frequency distribution of 38 radiocarbon dates for tufas from South and Eastern Poland is shown in Fig. 7 (Pazdur 1987). For comparison the temperature curve from stable isotope analysis of oxygen ($\delta^{18}O$) in the same tufas (Pazdur *et al.* 1988b) deduced is enclosed. The correlation between warm periods in Holocene and maxima in the frequency distribution may be observed.

Speleothems

The frequency distribution of ^{14}C dates is based on a set of 125 radiocarbon results obtained for speleothems from caves of Kraków–Wieluń Upland karst area (Pazdur *et al.* 1995c, 1999b). The results enable to draw some conclusions about climatic changes in the study area during the last glacial-interglacial cycle. Figures 9a and 9b show the main set of ^{14}C results. The ^{14}C dates for Holocene speleothems used for analysis are conventional ages calculated according to Stuiver and Polach (1977) and corrected for reservoir age T_R = 1650 years (Pazdur *et al.* 1999b).

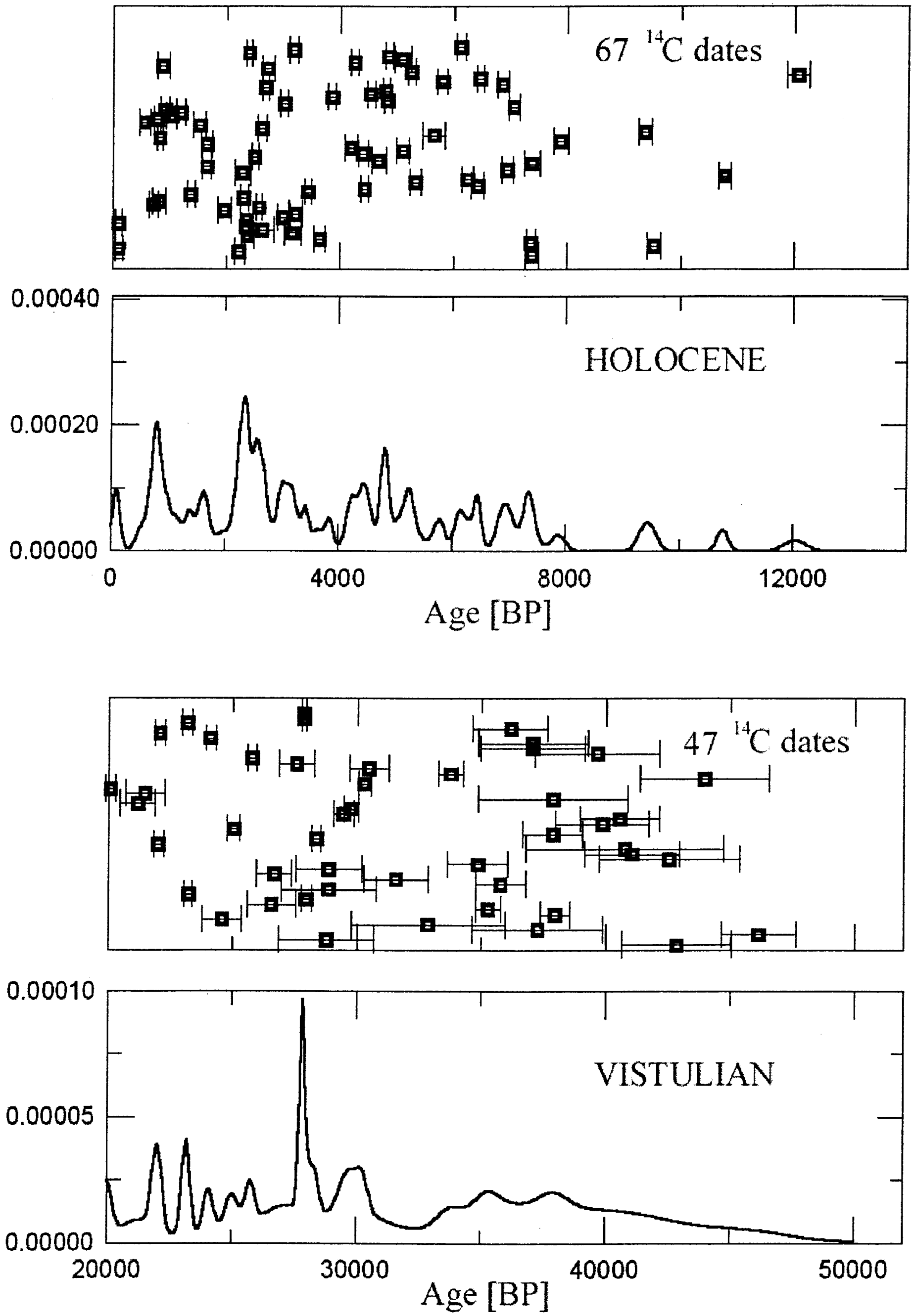

Fig. 8. Distribution of ^{14}C dates, corrected for reservoir effect (1650 years), for speleothems from Kraków–Wieluń Upland caves (after Pazdur *et al.* 1999b). On vertical axis the note number of dates per year.

The group of older dates range from 48 to 20 ka BP (Fig. 8). The boundaries, determined by the presence of speleothems, coincide almost exactly with the Interplenivistulian climatostratigraphic unit, determined from paleogeographic studies in the foothills of the Carpathian Mountains (Starkel 1980). The period approximately overlaps the duration of the Jerzmanowice culture, discovered at numerous sites in Jerzmanowice area (Madeyska 1982). The results also show an interruption in speleothem formation between 20 and 10 ka BP, which may be interpreted as serious climatic deterioration associated with the maximum extent of the last glaciation (Younger Plenivistulian, incorporating the Late Glacial period). The principal period of speleothem deposition falls within the Holocene. The oldest dates of these group (around *ca* 9000 BP) were obtained on speleothems from the Ciemna and Straszykowa Caves. In particular, the highest peak of the distribution plot approximately fit the climatic optimum of the Holocene, i.e. Atlantic period.

Conclusions

Processes of isotopic differentiation that occur during sedimentation of carbonates and lead to different initial values of ^{14}C concentration depend on environmental conditions. Reliable radiocarbon dating is the key to successful application of method to climatic reconstruction during the last 50 000 years. Results of ^{14}C measurements of tufa from several sites in southern Poland indicated significant variability of initial ^{14}C activity and its dependence on sedimentologic and geochemical processes. Ageing of ^{14}C dates of calcareous tufas, organic and carbonate fraction of lake marl, calcite forming speleothems and carbonate cements, commonly described by the reservoir age of sediment, change from hundred to many thousands years and its estimation need knowledge about sedimentary conditions. The isotopic composition of oxygen in tufa seems to be a sensitive indicator of temperature and humidity changes in the past. Comparative analysis of lake-level changes of the Gościąż lake reconstructed from model considerations with those obtained from radiocarbon-dated sedimentologic features indicates coincidence of both records during Late Glacial and Holocene. The ^{14}C, TL and U/Th dating of the sandrock, pipe wall and pipe infill samples help to construct time scale for the following sequence of paleoenvironmental events in Southwest England and South Wales: raised beach formation, raised beach cementation and formation of karst pipes within the raised beach deposition. Statistical analysis of carbonate ^{14}C dates is tool of investigations of environmental accidents. A group of older ^{14}C dates obtained on speleothem samples indicate on interval of the Interplenivistulian. An interruption occurred in speleothem formation between 20 and 10 ka BP, caused by serious climatic deterioration associated with the last glacial maximum. The younger dates span the Holocene, the broad maximum falling within the Atlantic phase.

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