GEOCHRONOMETRIA Vol. 21, pp 97-108, 2002 – *Journal on Methods and Applications of Absolute Chronology*

$\delta^{13}C$ and $\delta^{18}O$ TIME RECORD AND PALAEOCLIMATIC IMPLICATIONS OF THE HOLOCENE CALCAREOUS TUFA FROM SOUTH-EASTERN POLAND AND EASTERN INDIA (ORISSA)

ANNA PAZDUR[1], RADOSŁAW DOBROWOLSKI[2], TOMASZ DURAKIEWICZ[3], NATALIA PIOTROWSKA[1], MANMOHAN MOHANTI[4] and SRIKANTA DAS[4]

[1]Department of Radioisotopes, Institute of Physics, Silesian University of Technology, Krzywoustego 2, 44-100 Gliwice, Poland
(e-mail: anna.pazdur@radiocarbon.gliwice.pl)
[2]Department of Physical Geography and Palaeogeography, Maria Curie-Skłodowska University, Akademicka 19, 20-033 Lublin, Poland
[3]Mass Spectrometry Laboratory, Maria Curie-Skłodowska University, Plac Marii Curie-Skłodowskiej 1, 20-031 Lublin, Poland;
Los Alamos Laboratory, Condensed Matter and Thermal Physics Group, Los Alamos, Mailstop K764, NM 87545, USA
[4]Department of Geology, Utkal University Bhubaneswar - 751004 (Orissa) India

Key words: CALCAREOUS TUFA, STABLE ISOTOPES, PALAEOCLIMATE, HOLOCENE, POLAND, INDIA

Abstract: **Measurements of $\delta^{18}O$ and $\delta^{13}C$ in tufa samples dated by ^{14}C method have been used to reconstruct climatic changes in Southern and Eastern Poland and in Eastern India (Orissa) for the last *ca* 13,500 years. Stable isotope time record $\delta^{18}O$ in calcareous tufa profiles can be interpreted as palaeoclimatic record if dependence between oxygen isotope composition and temperature for the specific climatic region is known. Estimated sedimentation temperatures of calcareous tufas from Polish sites indicate the mean year of air temperatures during the last 12,000 years and mean winter and summer temperature for Orissa state, using stable isotope analysis for calcareous tufa from Indian sites. The estimated temperatures have real values, comparable with contemporaneous sedimentation temperature. The characteristic trend of the temperature changes increasing for Poland and decreasing for Orissa, since the beginning of the Holocene till today, can be observed with climatic optimum *ca* 5000-6000 BP synchronous in both countries.**

1. INTRODUCTION

Calcareous tufa and speleothems appear to be significant indicators of palaeoenvironmental and palaeoclimatic changes. These deposits reflect the combined effects of karst processes, controlled to a great extent by climatic factors, especially temperature and humidity. Freshwater tufas in continental realm, deposited by physicochemical and/or biochemical processes are also considered as reliable recorders of palaeoclimatic and environmental change (Andrews *et al.*, 1994 and Pazdur *et al.*, 1988b). Stable isotopes, like ^{18}O and ^{13}C, and chemical analysis, frequency distribution of U/Th and ^{14}C dates have frequently been used as a tool for analysis of sedimentological processes and reconstruction of palaeoclimatic conditions, as well as for stratigraphic purposes. Measurements of $\delta^{18}O$ and $\delta^{13}C$ in tufa samples dated by ^{14}C method have been used to reconstruct Holocene climatic changes in southern and eastern Poland (Pazdur, 2000).

Precise dating of speleothems by ^{14}C and other dating methods along with $\delta^{13}C$ and $\delta^{18}O$ measurements have been used to interpret palaeoclimatic changes (Pazdur *et al.*, 1995). The frequency distribution of ^{14}C and U/Th dates has been successfully applied to palaeoclimatic studies using speleothems (Goslar *et al.*, 2000; Hercman, 2000).

Interpretation of isotopic investigations in lacustrine carbonates is much more sophisticated and difficult because of the complex nature of sedimentation, influenced by a number of physicochemical and biological factors. Palaeolake level changes of the Gościąż Lake (Central Poland) have been studied from the lake and lake-margin sediments with help of deposits constituted of laminated sediments, peat, lacustrine gyttja and beach sediments together with radiocarbon chronology and carbon isotope content interpretation. The behaviour of this lake during the last 12 ka reflects global climate change in the temperate zone fairly well (Pazdur *et al.*, 1994 and 1995b).

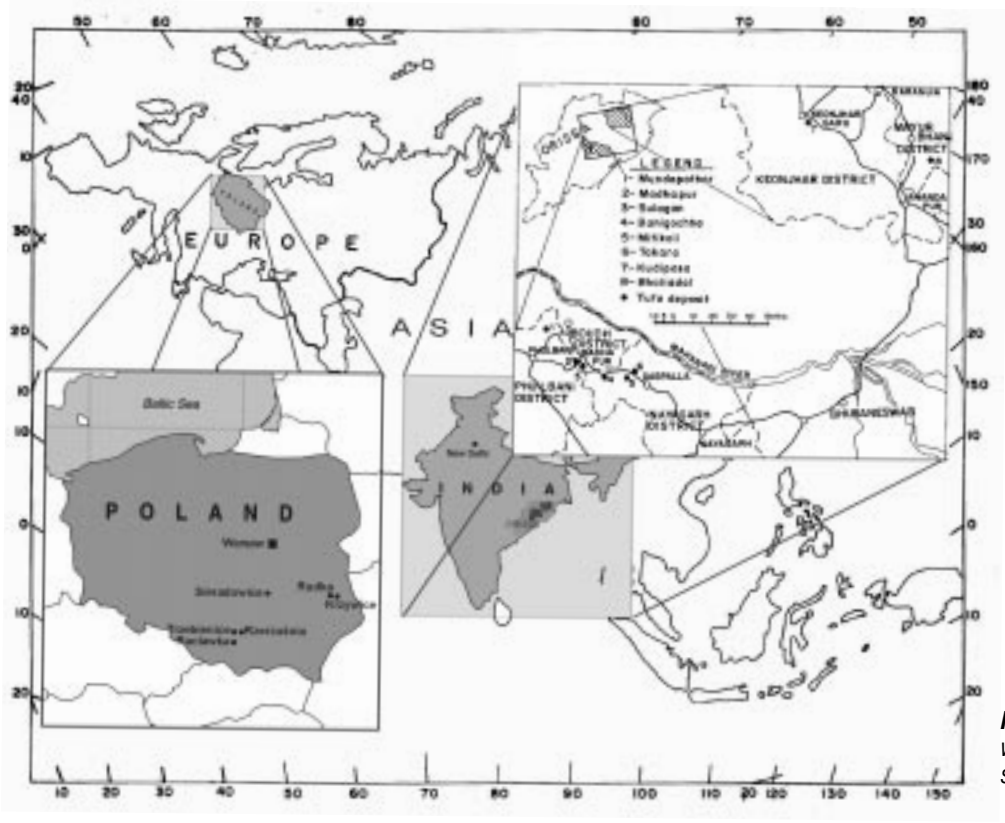

Fig. 1. *Map of Europe and Asia where tufa samples have been studied in Poland and India (Orissa).*

The significance of undisturbed lacustrine calcareous sediments as potential geochemical archives of isotopic records of palaeoenvironmental changes has been recognized. Isotopic studies of pedogenic carbonates (caliche, concretions) and cements provide information related to circulation of groundwater and precipitation, and, indirectly, lead to palaeoclimatic conclusions (Pazdur *et al.*, 1995a).

Several authors dealing with freshwater carbonates assumed that kinetic effects during isotopic fractionations are small (except at spring heads) and used the isotopically derived temperature for studying local and regional palaeoclimatic and palaeoenvironmental records (Andrews *et al.* 1993 and 1994; Pazdur *et al.* 1988b). Usdowski *et al.*, (1979) and Dandurand *et al.,* (1982), while studying calcite precipitation at springs and streams, attributed the variations in isotopic composition to disequilibrium condition due to kinetic effects. Turi (1986) noted that isotopic equilibrium is seldom attained in the deposition of travertines mainly as a consequence of kinetic effects. Recently, Chafetz and Lawrence (1994) demonstrated that $\delta^{18}O$ values of the precipitates can change drastically within a travertine system and stressed that the overall changes with water flow, microenvironmental controls and disequilibrium precipitation determine the isotopic signatures of these freshwater deposits. It is, therefore, necessary to stress the depositional conditions before establishing the isotopic signatures and reconstructing the palaeoclimatic change.

Generally, tufa deposits, for example European tufas, involve headwaters, which contain dissolved calcium carbonate derived from marine (isotopically heavy) carbonates. In contrast to these deposits, tufas of Orissa State are formed in a Precambrian terrain of crystalline and metasedimentary rocks. Due to the absence of any marine limestone or dolomite, the tufa depositional system forms an interesting geochemical system. Das and Mohanti (1997) recently presented the fabrics of microbial tufas and discussed depositional processes. In this paper, we have attempted to date the tufa carbonates and apply the stable isotopic signatures to understand the implications of climatic changes in Orissa during the Holocene.

For reconstruction of time record of palaeoenvironmental conditions of the sedimentary processes the time scale of carbonate deposition should be reconstructed. Radiocarbon, U/Th, TL and AAR dating methods may be usually used.

The large number of dating results obtained by different methods enable interpretation of results with use of probabilistic methods (Baker *et al.,* 1993; Smart and Richards, 1992; Srdoc *et al*., 1983; Hercman, 2000). Frequency distributions of dates may be compared with results obtained by other methods, like changes of temperature and precipitation in the past, reconstructed from pollen analyses of peat-bog profiles and lake sediments of non-glaciated areas, and with palaeoclimatic records from deep sea cores (Guiot *et al*., 1989; Schackleton, 1967).

2. INVESTIGATED SITES IN POLAND AND IN INDIA

The radiocarbon time scale record of $\delta^{13}C$ and $\delta^{18}O$ from sites situated in the Cracow-Wieluń Upland (Racławka, Rzerzuśnia, Trzebienice; southern Poland) and the Holy Cross Mountains (Sieradowice; south-

eastern Poland) and their palaeoclimatic interpretation was given by Pazdur *et al.* (1988b). In this paper the results are used for comparison of those from Krzywice-1 and Rudka-2 (Lublin Upland, eastern Poland; Dobrowolski *et al.*, 1996) with Mundapathar, Kudipasa and Sulagan (Orissa, eastern India). Dobrowolski *et al.* (1999 and 2002), presenting $\delta^{13}C$ and $\delta^{18}O$ record in time related to Holocene stratigraphical division, but without detailed radiocarbon time scale. Das and Mohanti (1997) and Pazdur *et al.* (2002) described results of radiocarbon dating, $\delta^{13}C$ and $\delta^{18}O$ measurements, and sedimentological description for sites in India.

Poland

Sedimentological and isotopic studies were made for profiles from the following geographical regions:

- Cracow-Wieluń Upland (southern Poland): 27 samples of calcareous tufa of biogenic origin (autochthonous calcareous muds, stromatolites, oncoids, and moss travertines; Pazdur *et al.,* 1988a) from three sites (Racławka, Rzerzuśnia and Trzebienice). The sites represent different hydrodynamic conditions of tufa sedimentation. They are situated in small valleys entrenched in carbonate rocks of Lower Carboniferous (Racławka), Jurassic and Cretaceous (Trzebienice and Rzerzuśnia).
- Holy Cross Mountains (south-eastern Poland): 11 samples of fine-grained calcareous muds, rich in organic matter, precipitated in shallow stagnant water basin (Pazdur *et al.,* 1988a). The Sieradowice profile is situated in a small valley cut in Devonian carbonate rocks.
- Lublin Upland (eastern Poland): both sediment profiles, Krzywice-1 and Rudka-2, consist of calcareous muds rich in organic matter precipitated, like tufa from Sieradowice, in low-energy water conditions. They are situated on Upper Cretaceous rocks (Dobrowolski *et al.,* 1999 and 2002).

Radiocarbon chronology of sedimentation was made on the basis of 8 organic and the same number of carbonate ^{14}C dates for Krzywice-1, and 6 organic and 9 carbonate ^{14}C dates for Rudka-2 profiles (Dobrowolski *et al.,* 2002). Sixty three carbonate samples for stable isotope ^{13}C and ^{18}O analyses were taken (37 from Krzywice-1 and 26 from Rudka-2 profile) and radiocarbon time scale for $\delta^{13}C$ and $\delta^{18}O$ time record was reconstructed (Pazdur *et al.,* 2002). The construction of similar time scale for other profiles from Poland and India was based on dependence between reservoir age and $\delta^{13}C$ values in tufa samples. The methodology and details of the reconstruction are given by Pazdur (1988) and Pazdur *et al.* (2002).

India (Orissa)

Detailed description of profiles and classification of tufa samples is given by Pazdur *et al.* (2002). Sedimentological and isotopic studies are based on:

- Mundapathar: 13 tufa samples from one profile, including stromatolic tufa, moss (phytohermal) tufa, phytoclastic tufa, pisoid and sinter. The deposit of about 7 m in thickness is situated at a small waterfall formed on charnockite under high-energy conditions.
- Kudipasa: 8 tufa samples from one profile, including stromatolic tufa, moss tufa, phytoclastic tufa and sinter. The deposit measuring about 6 m in vertical thickness is located on a hill slope. Streams depositing the tufa drain basic lava, tuff and quartzite under moderate hydrodynamic conditions.
- Sulagan: 7 tufa samples including stromatolic tufa and moss tufa. The deposit is about 6 m in vertical thickness. It is located at a small waterfall formed on charnockite under high-energy conditions.
- Single tufa samples from various sites (regional samples). Miticoli and Mundapathar represent high-energy conditions, Madhapur and Bhaliadal represent moderate energy conditions, Takara and Banigochha represent low hydrodynamic conditions.

Fig. 2. *Stromatolitic crusts draping over moss-rich pockets on the lower part (close to the hammer). Upper part shows stromatolitic crusts alternating with phytohermal (moss-rich) deposits. Central region of the photograph shows speleothemic crusts. Locality: Mundapathar.*

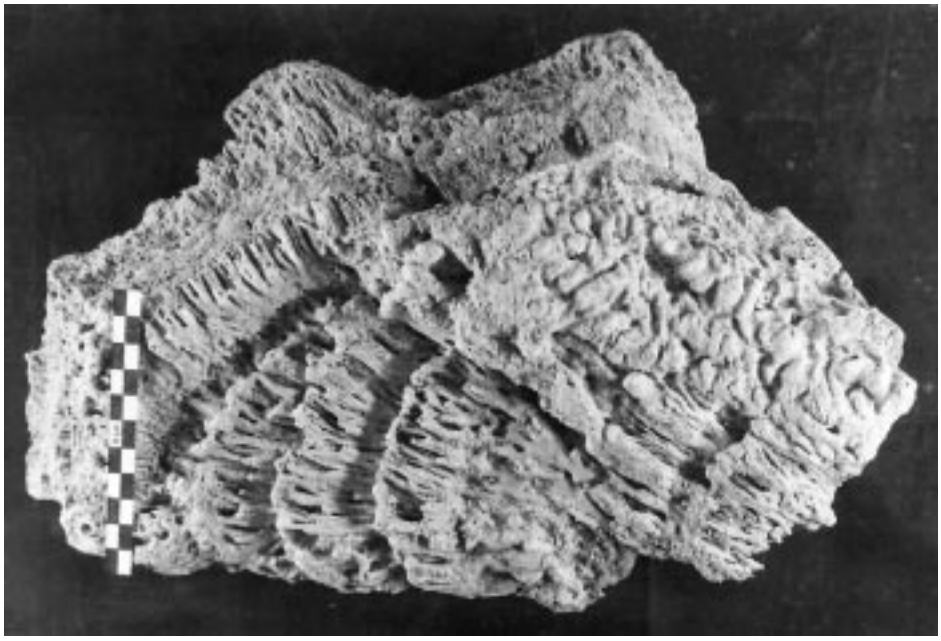

Fig. 3. *Phytohermal tufa (calcified moss) showing several stages of growth and high porosity. The unidirectional orientation of the moss indicate hydrodynamic control on phytoherms. Sample from Mundapathar. Each division of the scale is 1 cm.*

Fig. 4. *Stromatolitic crusts showing alternate dark and light laminae. The darker laminae are thicker at the lower parts and appear convex due to growth over small bushy mosses. Sample from Bhaliadal.*

Radiocarbon time scale of sedimentation of the tufa profiles was made on the basis of 11 carbonate and 2 organic ^{14}C dates for Mundapathar, 6 carbonate and 2 organic ^{14}C dates for Kudipasa, and 4 carbonate and 2 organic ^{14}C dates for Sulagan. Radiocarbon dating of the regional samples was made for the carbonate fractions. Thirty three carbonate samples were taken for stable ^{13}C and ^{18}O analysis from all sites together (Pazdur *et al.*, 2002).

3. PRESENT CLIMATIC BACKGROUND

Sites from Poland

Sedimentation of biogenic calcareous tufa occurs mostly during spring months. In the southern and south-eastern Poland, the temperature of spring water at this time is equal to mean annual air temperature; therefore, the mean annual temperature of meteoric water coincides with temperature of tufa sedimentation. Climatic data from the Cracow Upland show that the mean annual temperature varies from 7 to 8°C and mean temperature of springs from 7 to 9°C (after Pazdur *et al.,* 1988b). The temperature of streams fluctuates between 7 and 12°C.

Studied tufas from the Cracow Upland were sampled with a thickness less than 5 cm. It means that each sample covers 10- to 20-yr time interval according to determined sedimentation rate (several mm/yr). This intervals are insignificant when compared to errors of the age determination. Sampling of Krzywice-1 and Rudka-2 sites was made across profiles, with small (ca 30 mg) amounts of carbonate. The results of $\delta^{18}O$ analysis present mean values in a shorter period of time than in the case of samples from the Cracow Upland profiles, even though the sedimentation rate is about several or more mm per year.

Sites from India (Orissa)

The warm and humid tropical climate of Orissa is characterised by seasonal southwest monsoon rainfall. The annual mean precipitation is *ca* 150-200 mm. Major part of the rainfall is concentrated in the monsoon season (Mid-June to Mid-October, with an average of *ca* 200-350 mm of rainfall).

The ranges of air temperature change are as follows: in winter 8-12°C minimum and 25-28°C maximum and in summer 25-28°C and 36-42°C, respectively. Water temperatures when tufa precipitates are influenced by general thermal conditions. Water temperatures are as follows: 19-20.5°C in winter (December-January) and 27.5-29°C in summer (April-May).

The deposition of tufas takes place mostly during spring (February-March) and summer (April-May) periods. Presently, summer deposition is negligible – possibly due to the groundwater table fall and limited or missing surface flow. The sparitic and micritic laminae in stromatolitic tufa indicate seasonal deposition (spring-summer and rainy-winter periods). Thickness of laminae couplets suggests a depositional rate of 1 mm to a little more than 1 cm per year.

Stream waters depositing the tufa show a pH value of 8.0 to 8.6. Concentrations of Ca^{2+}, Mg^{2+} and HCO^-_3 vary within the range of 30-80 mg/l, 9-28 mg/l and 200-310 mg/l respectively (Das and Mohanti, 2001).

4. TIME RECORD OF $\delta^{13}C$

The enrichment of carbonate in heavy carbon isotope, in comparison to water solution, may be induced by partial disequilibrium between HCO^-_3 in water and atmospheric CO_2 during precipitation. This is attributed to kinetic effects during $CaCO_3$ precipitation from highly supersaturated solution in which the rate of carbonate precipitation is faster than equilibrium fractionation with the respect to the stable isotopes (Usdowski *et al.,* 1979; Dandurand *et al.,* 1982; Turi, 1986; Chafetz *et al.,* 1991). In natural environments, the exchange of CO_2 can only lead to equilibrium if sufficient residence time is available, which can be attained in standing water bodies like lakes. The geomorphic setting of our tufa deposits indicates a very low residence time and great water turbulence. This situation favours the idea of partial disequilibrium precipitation.

We believe that dominant part of the carbon has been derived from biogenic sources and may be partly from the atmosphere. The range of $\delta^{13}C$ values indicates relative enrichment of tufa in heavy isotopes. The enrichment in heavy isotopes may be determined by photosynthesis of plants, which preferentially use lighter carbon (^{12}C) leaving the remaining HCO^-_3 enriched in ^{13}C (Pentecost and Spiro, 1990; Merz, 1992; Casanova and Hillaire-Marcel, 1993; Guo *et al.,* 1996). But the photosynthetical removal of CO_2 requires relatively longer residence time. Tufas in the Orissa State originate in discharge basins with low residence time of water. Even though profuse amount of cyanobacteria, diatoms and mosses are involved, the rate of photosynthetic removal of CO_2 by these plants is small in comparison to the rate of physical degasation due to turbulence of water. Photosynthesis may be locally significant, depending on the amount of biomass, especially where cyanobacteria or algae and moss thrive together.

The range of $\delta^{13}C$ of tufa from Poland sites is *ca* from -10.5 ‰ to -6 ‰ for the last 10,600 years (Pazdur, 1988). The significantly higher values are observed for the Krzywice-1 site, with the longest time record, in the time of 11,800-10,800 BP (**Fig. 5**). The $\delta^{13}C$ values from the Orissa sites receive *ca* -2.5 to -11.7 ‰ in the whole investigated period between 13,500 BP and the present time. The range of $\delta^{13}C$ values of tufa from the Polish and Orissa sites is in accordance with a deposition from freshwater and suggest the presence of isotopically lighter organic carbon.

As there is no marine limestone and/or dolomite in the studied area of Orissa, we believe that the carbonates have originated mostly from organic matter. Ca^{++} ions are derived from weathering of silicates, mostly plagioclase and pyroxene. Kalsotra and Prasad (1979) and Pawar *et al.* (1988) have reported tufa deposits from sandstones and shales and basaltic areas in India. Augustithis (1982) also noted the formation of carbonate nodules from disintegration of olivine basalts in Duncan, south of Addis-Ababa.

Tufas are depleted in heavy isotope ^{18}O in all Polish and Indian sites (see **Fig. 7**), when compared to $\delta^{18}O$ values expected for equilibrium sedimentary processes. The low and negative $\delta^{18}O$ values suggest a low rate of evaporation.

Individual $\delta^{13}C$ values of tufa samples shown in **Fig. 5** as time records reveal short-time fluctuations and increase/decrease trends, different in detail from a profile to profile. The co-variation of oxygen isotope data with the carbon isotope ones (**Fig. 6**) indicate similar trend of changes in disequilibrium condition for all the India samples; correlation coefficient is equal to r = 0.73 (22 pairs of $\delta^{13}C$ and $\delta^{18}O$). For all Polish samples, the dependence between both delta values is positive (r = 0.20), if we remove 6 extreme points with $\delta^{13}C > -4$ ‰ and $\delta^{18}O > -6$ ‰ (Krzywice-1 profile) from period older than 10,000 BP. It means high confidence level and confirm disequilibrium sedimentary conditions and presence of isotopic kinetic fractionation effect. The relations indicate, that organic consumption of CO_2 may be significant because of the presence of chemo- and heterotrophic bacteria (Pazdur *et al.,* 1988b) observed for tufa sites in the southern Poland. Enrichment of tufas in the heavier carbon isotope (^{13}C) during the warmer periods may be connected to some extent with activation of plant consumption.

5. TIME RECORD OF $\delta^{18}O$ AND TUFA SEDIMENTATION TEMPERATURE

$\delta^{18}O$ of tufa in palaeoclimatic studies

Isotopic investigations of tufa from Poland deals with sites of spring tufa deposition in variable conditions of river water energy (southern Poland; Pazdur *et al.*, 1988a) and semi-limnic conditions (south-eastern Poland; Pazdur *et al.*, 1988a; Dobrowolski *et al.*, 1999). The palaeotem-

perature curve was constructed (Pazdur *et al.*, 1988b) on the basis of the time scale reconstruction using radiocarbon dating and interpretation of stable isotope carbon and oxygen composition in sedimentary processes. The curve describes the annual mean temperature changes for the southern Poland in the period of 2000-9600 BP, *i.e.*, in which sedimentation of tufa took place in Racławka, Rzerzuśnia, Trzebienice and Sieradowice (see **Figs 5** and **7**). Thirty eight results of ^{14}C dating and stable isotope analysis were used for palaeoclimatic reconstruction. Dobrowolski *et al.*, (1999) carried out isotopic investigations on two eastern Polish sites, Krzywice-1 and Rudka-2. Radiocarbon time scale of tufa sedimentation was constructed for those sites (Pazdur *et al.*, 2002) and palaeoclimatic interpretation of 61 new results of stable isotope analyses can be done together with the previous results. Time record of $\delta^{18}O$ measurements in individual and all tufa sites from Poland and India is shown in **Fig. 7**.

The variation in $\delta^{18}O$ values indicates differences in isotopic composition of tufa depositing waters controlled by water temperature. The temperature of cold spring waters in continental conditions is influenced by rainfall and atmospheric temperature, *i.e.*, climate controls the tufa deposition.

Temperature precipitation of tufaceous sediments in Poland and India

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 for the reconstruction of the approximate thermal condition of sedimentation, or strictly speaking, the temperature of water, from which carbonate precipitated. Reconstruction of palaeotemperature changes for a given geographical region may be based on known seasonal dependence of $\delta^{18}O$ in meteoric water upon temperature (Van der

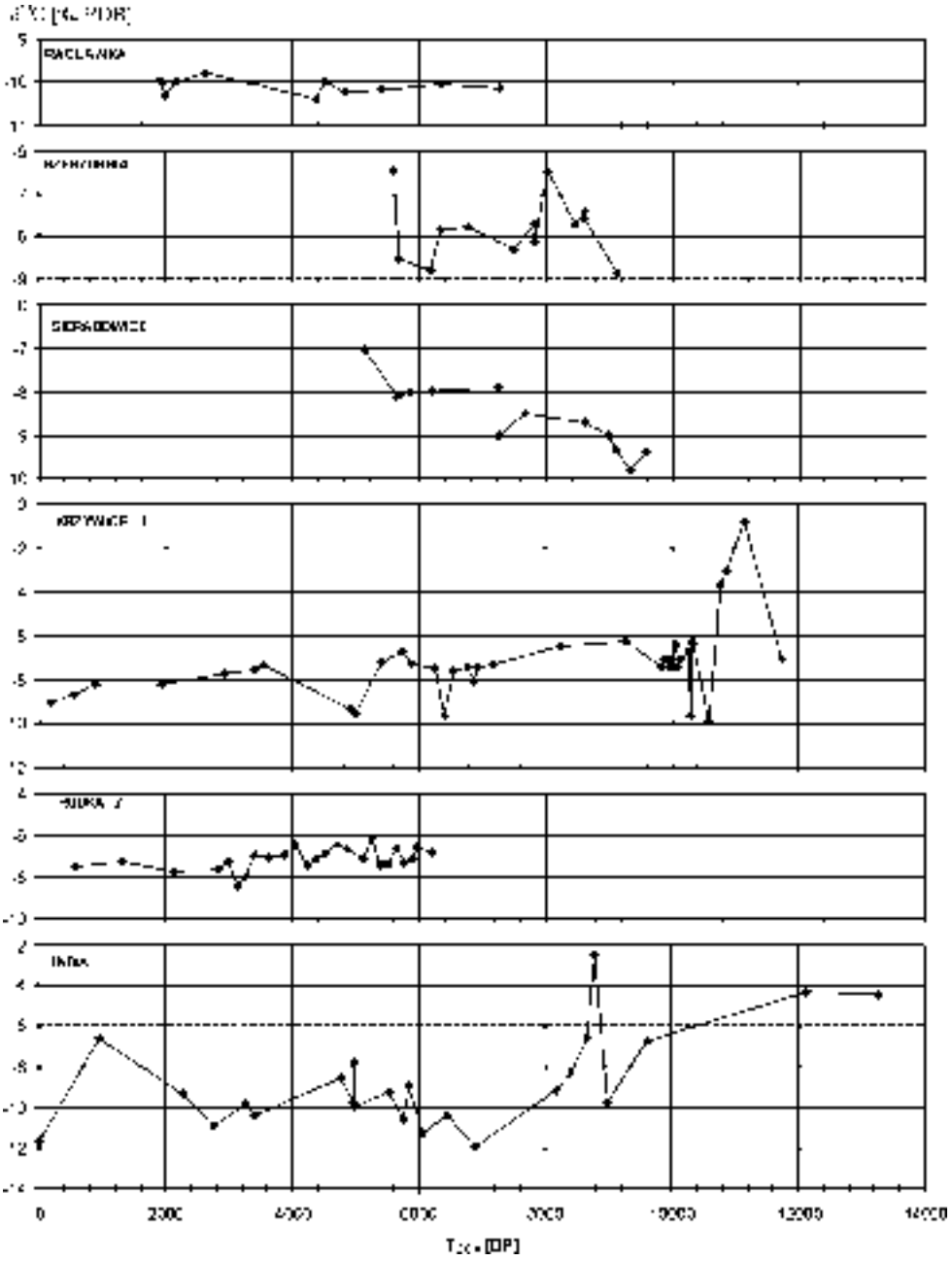

Fig. 5. *Time record of $\delta^{13}C$ in separate tufa sites of Poland and all sites together from India.*

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 the results of investigation of recent tufas (Pazdur *et al.*, 1988b). One of this is that 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 precipitation and stream water, and second – kinetic fractionation effect of oxygen isotopes is independent on sedimentation temperature. To reconstruct temperature record for the Late Glacial and Holocene, the constant values of temperature oxygen gradient and kinetic effect in the whole period must be assumed (Pazdur *et al.*, 1988b). It means that in this whole time period the circulation of air mass was the same (Różański, 1985). The temperature t of tufa sedimentation may be estimated on the basis of simple equation (Pazdur *et al.*, 1988b):

$$(\delta^{18}O)_C = \left[\frac{d(\delta^{18}O)}{dt}\right]_w \cdot t + A + \Delta, \qquad (5.1)$$

where A means extrapolated $\delta^{18}O$ value of water in 0 °C, equal to -13.0±0.4 ‰ (Pazdur *et al.*, 1988b) and Δ – the value of kinetic fractionation effect for oxygen isotopes in sedimentary processes of carbonates, *i.e.*, the difference between the $\delta^{18}O$ value in carbonate (vs. PDB) and the same value in water solution, from which the sediment was deposited (vs. SMOW).

The global temperature gradient for coastal region in meteoric water is equal to 0.72 (Van der Straaten and Mook, 1983) and 0.37 ‰ /°C for continental climatic area (Pazdur *et al.*, 1988b). The estimation Δ (Pazdur *et al.*, 1988b) receive values between -1.7 and -2.5 ‰ for recent tufa from the southern England (Thorpe *et al.*, 1980) and change from +0.26 to -0.04 ‰ for Germany, Central Europe (Usdowski *et al.*, 1979).

To estimate the temperature time record in Poland, the mean 500-year $\delta^{18}O$ values were used for calculations of t, on the basis of Eq. (5.1); the maximal and minimal values of Δ like for Germany were applied. Such values of Δ give correct value of present water spring temperature in the southern Poland (*ca* 8 °C) if the measured value

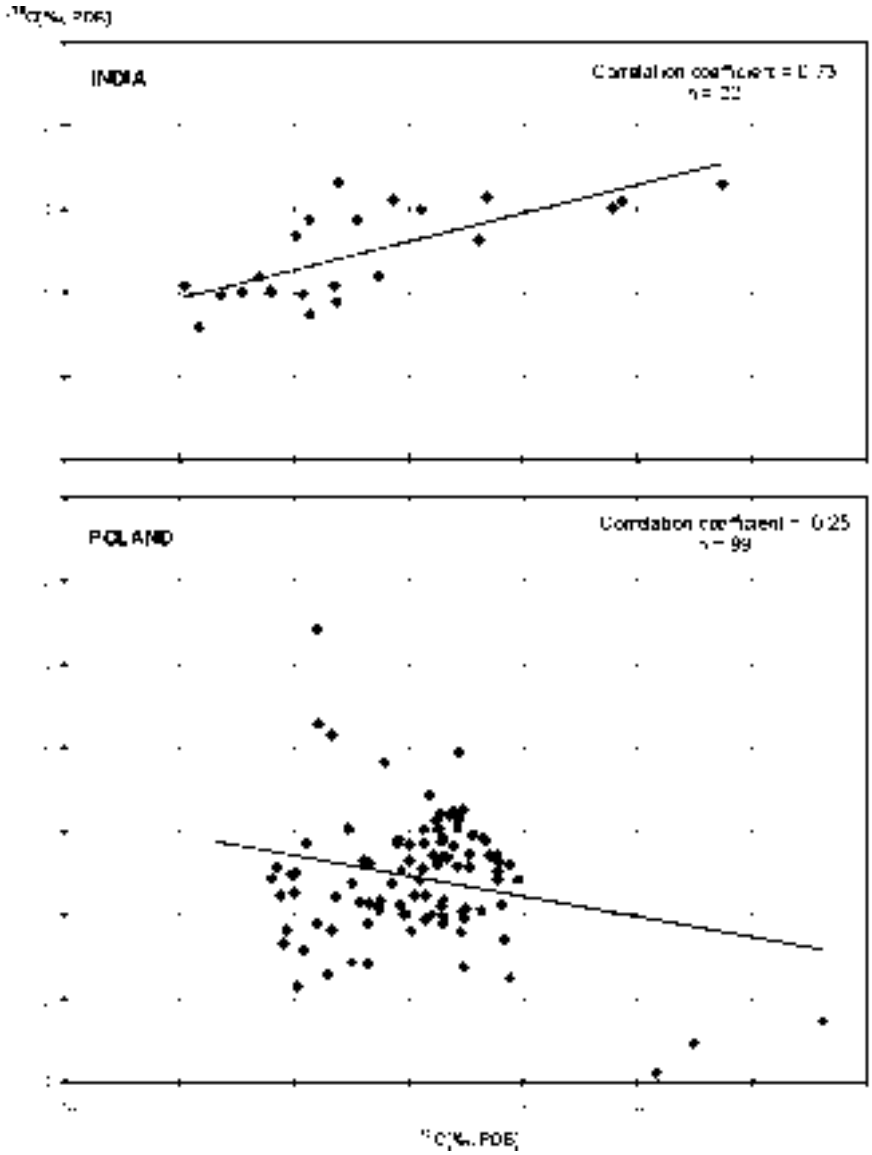

Fig. 6. *Dependence between $\delta^{13}C$ and $\delta^{18}O$ for all tufa profiles of India and Poland. Correlation between both delta values is negative for Polish samples and positive for samples from India.*

of $\delta^{18}O$ in contemporaneous spring water (*ca* 10 ‰) is taken into account. It confirms assumed way of temperature reconstruction in the past.

The estimation of temperature time record for India is more problematic, as the dependence between $\delta^{18}O$ and temperature of precipitation and spring water is unknown. If we assume the gradient temperature of $\delta^{18}O$ the same as in Poland and Δ values characteristic for the southern England (-1.7 and -2.5 ‰), the precipitation temperature at present, estimated on the basis of $\delta^{18}O$ in modern tufa sample, would be *ca* 22°C. This value is too low in comparison with 28-29°C of water in streams, if deposition of tufa took place in summer time mainly, when biogenic processes are intensive. The other combinations of model parameters (grad $\delta^{18}O$ and Δ values) give lower temperature values in every case.

The reconstructed temperature curves in ca 500-12,000 for Poland and 0-13,400 BP for India are shown in **Fig. 8**. The width of both curves is bordered by temperature values calculated for maximum and minimum Δ values.

6. WARM/DRY AND WET/HUMID PHASES IN THE HOLOCENE OF POLAND AND INDIA

The time records of $\delta^{18}O$ and estimated temperature cover 500-12,000 BP for Poland and 0-13,500 BP for Orissa (India). Periods of carbonate sedimentation started in different times in the southern and south-eastern Poland, *i.e.* at 9600 BP in Cracow and at 11,800 BP in the Lublin Upland. This difference is determined by environment of sedimentation, which determined the type of tufas: high-energy water tufas in the Cracow Upland

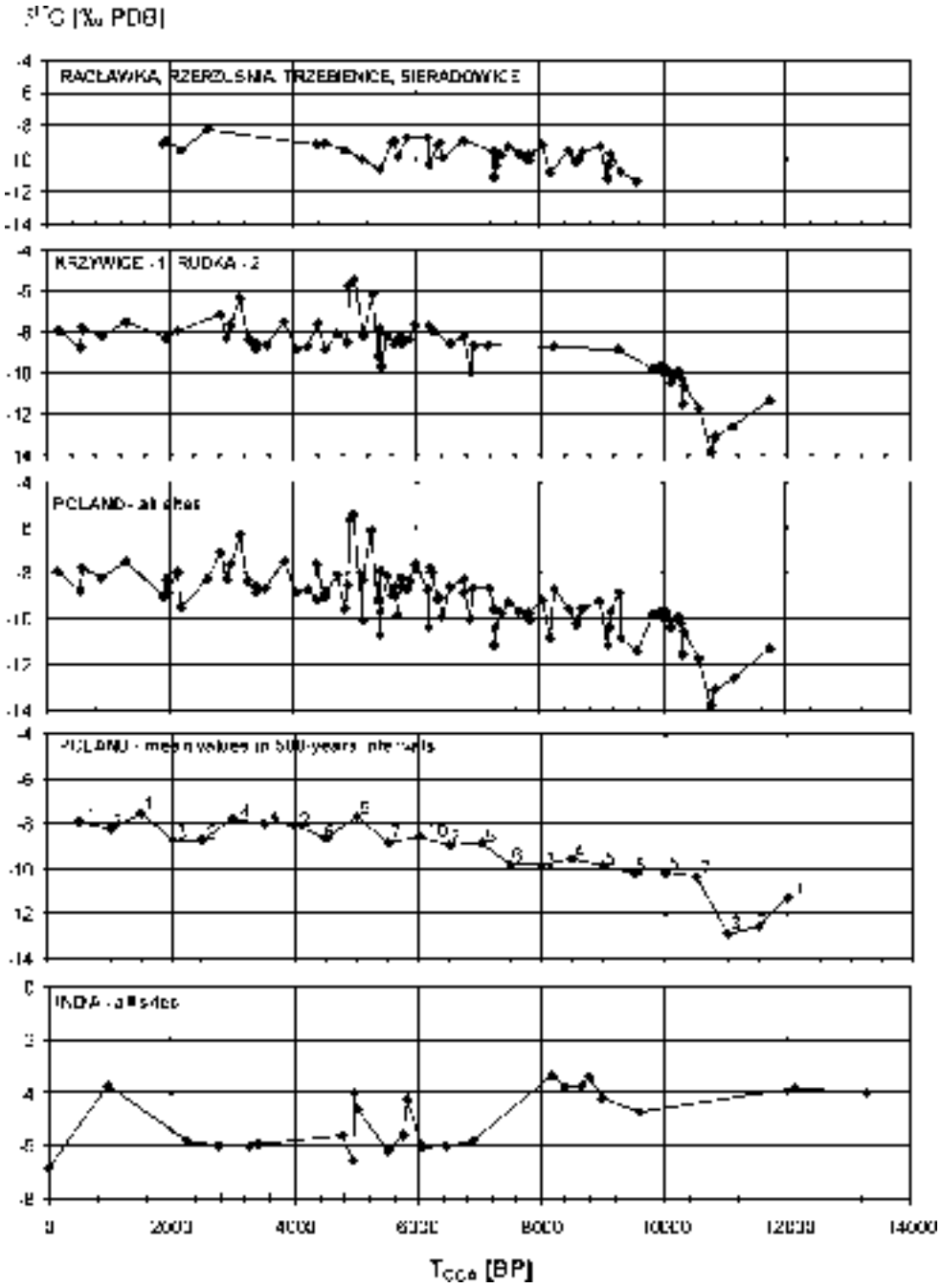

Fig. 7. *Time record of $\delta^{18}O$ of southern (Racławka, Rzerzuśnia, Trzebienice and Sieradowice), south-eastern Poland (Krzywice-1 and Rudka-2), all sites of Poland together and all India sites. Additionally, curve of mean values of $\delta^{18}O$ in 500-years intervals is given, which was used for estimation of temperature ranges shown in Fig. 8. The numbers near points on the Figure give the numbers of $\delta^{18}O$ results in 500-years intervals.*

(Racławka, Rzerzuśnia and Trzebienice) and low-energy water in the Lublin Upland (Krzywice-1, Rudka-2 and Sieradowice). The longest time records of $\delta^{18}O$ and $\delta^{13}C$ are observed for Krzywice-1 (**Figs. 5** and **7**) depending also on possibility of more detailed sampling of semilimnic sediments. The processes of tufa deposition have been still observed both in Poland and in Orissa, although no isotope analysis of Polish sites for the last 500 years has been made.

The changes of oxygen isotope composition as the function of the age can be transformed on temperature time record. The frequency distribution of tufa samples, in division on time ranges, should be connected with intense precipitation and, because of this, with humid climatic phases. Warm and humid phases are especially favourable environmental conditions for tufa deposition.

Both climatic curves for Poland and India (**Figs 7** and **8**) indicate trends of temperature changes. They are opposite – increasing for Poland and decreasing for India in the whole period of 12,000 years. Numerous warmer and cooler fluctuations are visible on curves. The confidence level of fluctuations for Poland is higher owing to a greater number of experimental points (99) than for India (24).

The shape of both temperature curves at their beginning is completely different. The Holocene warming is visible before 10,000 years BP on the Polish curve, immediate decrease of temperature to this time is clear on the Indian curve. The similar directions of changes of $\delta^{18}O$ (and temperature) for both curves are shown in time periods:

- Lower values, indicating cooler climatic conditions, are observed at *ca* 9600-9400, 8000-7500, 5800-5200, 4500-4200, and 2500-1800 BP;
- Higher values, dependant on warmer periods, are visible at *ca* 9200-8200, 6200-4500 (with several relatively high fluctuations on both curves), and 1800-500 BP. After *ca* 1000 BP until present, the temperature decreased to final 23 in India and 9°C in Poland.

It may be noticed that frequency of samples in warmer periods are the highest, which means humid climatic conditions. Because of difference in geographical position of India and Poland, we can assume, that indicated warm and cool periods have global character.

7. CONCLUSIONS

$\delta^{18}O$ time records, based on the radiocarbon time scale, in calcareous tufa provide information on temperature changes during the last *ca* 12,000 years in the south-eastern Poland and 13,500 years in India (Orissa). Reconstructed temperature values are realistic and reflect mean annual temperature of air in Poland and mean annual temperature of water in streams for Orissa. The mean annual water temperature is several degrees lower than the mean annual air temperature. The general trends of temperature changes in both countries are opposite; starting at *ca* 13,500 BP the mean annual temperature is decreasing in Orissa until present. In the range of 12,000-11,000 BP the temperature decreased, and after this time increased again in Poland. Observed temperature fluctuations, with different amplitudes, have been correlated in time. Some warmer and cooler phases of the same age ranges occurred in Poland and India, indicating their global character.

ACKNOWLEDGEMENTS

The interpretation and preparation results of isotope analyses to print has been made within the projects BW and BK sponsored by Silesian University of Technology, Poland, during the last 2 years and Scientific Research Committee, Poland, within grant No. 6 P04E 007 17

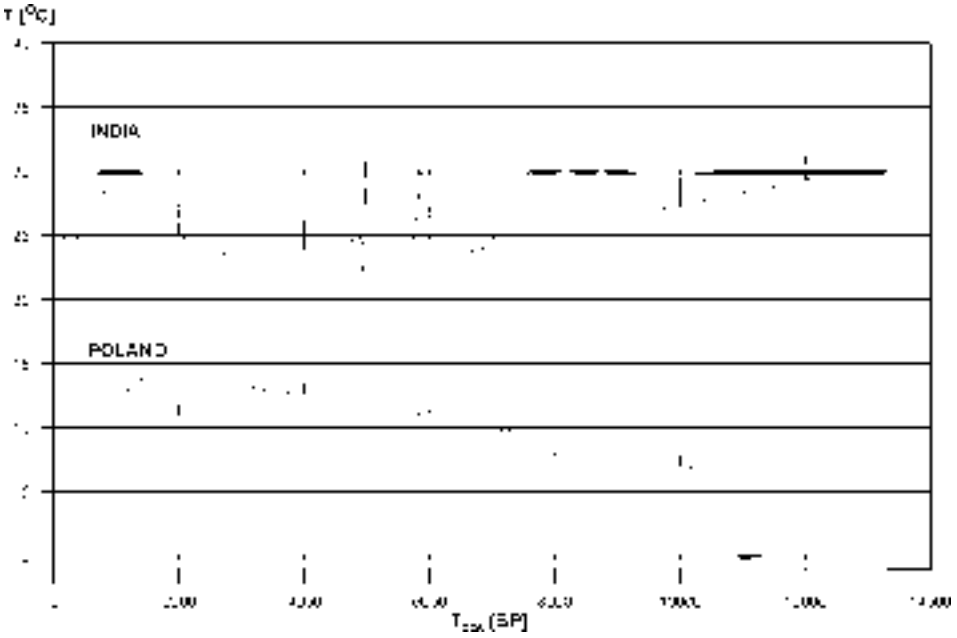

Fig. 8. *Temperature time record for Poland and India estimated with assumption of isotope kinetic fractionation effect in sedimentary processes of tufa. The ranges of temperature were determined for minimal and maximal values of Δ according to (5.1) Equation.*

REFERENCES

Andrews J.E., Pedley H.M. and Dennis P.F., 1994: Stable isotope record of palaeoclimatic change in a British Holocene tufa. *The Holocene* 4: 349-355.

Andrews J.E., Riding R. and Dennis P.F., 1993: Stable isotopic compositions of Recent freshwater cyanobacterial carbonates from British Isles: local and regional environmental controls. *Sedimentology* 40: 303-314.

Augustithis S.S., 1982: *Atlas of sphaeroidal textures and structures and their genetic significance.* Theophrastus Publ., S.A., Athens: 329.

Baker A., Smart P.L. and Ford D.C., 1993: Northwest European palaeoclimate as indicated by growth frequency variations of secondary calcite deposits. *Palaeogeography, Palaeoclimatology, Palaeoecology* 100: 291-301.

Casanova J. and Hillaire-Marcel C., 1993: Carbon and Oxygen isotopes in African stromatolites: palaeo-hydrological interpretation. *American Geophysical Union, Geophysical Monograph* 78: 123-133.

Chafetz H.S. and Lawrence J.R., 1994: Stable isotopic variability within modern travertine. *Geographie Physique et Quaternaire* 48(3): 257-273.

Chafetz H.S., Rush P.F. and Utech, N.M., 1991: Microenvironmental controls on mineralogy and habit of $CaCO_3$ precipitates: an example from an active travertine system. *Sedimentology* 38: 107-126.

Dandurand J.L., Guirt R., Hoefs J., Menschell G., Schott J. and Usdowski E., 1982: Kinetically controlled variations of major components and carbon isotopes in calcite precipitating spring. *Chemical Geology* 36: 299-315.

Das S. and Mohanti M., 1997: Holocene Microbial tufas: Orissa State, India. *Carbonates and Evaporites* 12(2): 204-219.

Das S. and Mohanti M., 2001: The geochemistry of a tufa – depositing stream of Mayurbanj (Orissa), India: possible controls on calcite and dolomite precipitation. In preparation to print.

Dobrowolski R., Durakiewicz T., Pazdur A. and Pazdur M.F., 1996: Chronostratygrafia i fazy rozwoju źródliskowego torfowiska kopułowego Krzywice kolo Chełma (Wyżyna Lubelska) (Chronostratigraphy and development stages of the spring peat – knoll at Krzywice near Chełm, Lublin Upland, South-eastern Poland). *Zeszyty Naukowe Politechniki Śląskiej, Seria Matematyka- Fizyka, Zeszyt 80, Geochronometria* Nr 17: 19-30.

Dobrowolski R., Alexandrowicz S.W., Bałaga K., Durakiewicz T. and Pazdur A., 1999: Badania martwic wapiennych w obrębie źrodliskowych torfowisk kopułowych we wschodniej Polsce (Studies of tufa within spring cupola peatbogs in eastern Poland). In: Pazdur A., Bluszcz A., Stankowski W. and Starkel L., eds, *Geochronologia górnego czwartorzędu Polski w świetle datowania radioweglowego i luminescencyjnego (Geochronology of the Upper Quaternary in Poland in the light of radiocarbon and luminescence dating).* WIND-J. Wojewoda, Wrocław: 179-197.

Dobrowolski R., Durakiewicz T. and Pazdur A., 2002: Calcareous tufas in the soligenous mires of Eastern Poland as an indicator of the Holocene climatic changes. *Acta Geologica Polonica*, in print.

Goslar T., Hercman H. and Pazdur A., 2000: Comparison of U-Series and radiocarbon dates of speleothems. *Radiocarbon* 42: 403-414.

Guiot J., Pons A., Bealieu J.L. and Reille M., 1989: A 140,000 year continental climate reconstruction from two European pollen records. *Nature* 338: 309-313.

Guo L., Andrews J., Riding R., Dennis P. and Dresser Q., 1996: Possible microbial effects on stable carbon isotopes in hot-spring travertines. *Journal of Sedimentary Research* 66(3): 468-473.

Hercman H., 2000: Reconstruction of palaeoclimatic changes in Central Europe between 10 and 200 thousand years B, based on analysis of growth frequency of speleothems. *Studia Quaternaria* 17: 35-70.

Kalsotra M.R. and Prasad S., 1979: Calc-tufa deposit of the Vindhyan scarp and its utilization. Geological Survey of India, *Indian Minerals* 33: 16-21.

Merz M.U.E., 1992: The biology of carbonate precipitation by cyanobacteria. *Facies* 26: 81-102.

Pawar N.J., Kale V.S., Atkinson T.C. and Rowe P.J., 1988: Early Holocene waterfall tufa from semi-arid Maharastra Plateau, India. *Journal of Geological Society of India* 32: 513-515.

Pazdur A., 1988: The relations between carbon isotope composition and apparent age of freshwater tufaceous sediments. *Radiocarbon* 30(1): 7-18.

Pazdur A., 2000. Radiocarbon in freshwater carbonates as tool of Late Quaternary studies. *Geologos* 5: 136-154.

Pazdur M. F., Bluszcz A., Pazdur A. and Morawiecka I., 1995a: Radiocarbon and thermoluminescence studies of the karst pipe systems in southwest England and South Wales. In: Cook G. T., Harkness D. D., Miller B. F. and Scott E. M., eds, *Proceedings of the 15th International ^{14}C Conference. Radiocarbon* 37: 111-117.

Pazdur A., Fontugne M. R., Goslar T. and Pazdur M. F., 1995b: Late Glacial and Holocene water-level changes of the Gosciąż Lake, Central Poland, derived from carbon isotope studies of laminated sediments. *Quaternary Science Reviews* 14: 125-135.

Pazdur A., Pazdur M. F., Goslar T., Wicik B. and Arnold M., 1994: Radiocarbon chronology of Late Glacial and Holocene sedimentation and water-level changes in the area of the Gościąż Lake Basin. *Radiocarbon* 36: 187-202.

Pazdur A., Pazdur M. F., Pawlyta J., Górny A. and Olszewski M, 1995: Palaeoclimatic implications of radiocarbon dating of speleothems from Cracow-Wieluń Upland, southern Poland. In: Cook G. T., Harkness D. D., Miller B. F. and Scott E. M., eds, *Proceedings of the 15th International ^{14}C Conference. Radiocarbon* 37: 103-110.

Pazdur A., Pazdur M.F. and Szulc J., 1988a: Radiocarbon dating of Holocene calcareous tufa from south Poland. *Radiocarbon* 30(2): 133-146.

Pazdur A., Pazdur M.F. , Starkel L. and Szulc J., 1988b: Stable isotopes of the Holocene calcareous tufa in southern Poland as palaeoclimatic indicators. *Quaternary Research* 30: 177-189.

Pentecost A. and Spiro B., 1990: Stable carbon and oxygen isotope composition of calcites associated with modern freshwater cyanobacteria and algae. *Geomicrobiology Journal* 8: 17-26.

Różański K., 1985: Deuterium and oxygen-18 in European groundwaters links to atmospheric circulation in the past. *Chemical Geology* 52: 349-363.

Schackleton N.J., 1967: Oxygen isotope analyses and Pleistocene temperatures re-assessed. *Nature* 215: 15-17.

Smart P.L. and Richards D, 1992: Age estimates for the Late Quaternary sea-stands. *Quaternary Science Review* 11: 687-696.

Srdoc D., Horvatincic N., Obelic, B. and Sliepcevic A., 1983: Radiocarbon dating of tufa in palaeoclimatic studies. In: Stuiver M. and Kra R.S., eds., *Proceedings of 11th International ^{14}C Conference*: *Radiocarbon* 25(2): 421-427.

Thorpe P.M., Otlet R. L. and Sweeting M.M., 1980: Hydrological implications from ^{14}C profiling of UK tufa. In: Stuiver M. and Kra R. S., eds., *Proceedings of 10th International ^{14}C Conference. Radiocarbon* 22(3): 897-908.

Turi, B., 1986: Stable isotope geochemistry in travertines. In: Fritz P. and Frontes J. C., eds., *Handbook of Environmental Isotope Geochemistry* 2. Elsevier, Amsterdam: 207-235.

Usdowski E., Hoefs J. and Menschel G., 1979: Relationship between ^{13}C and ^{18}O fractionation and changes in major elements composition in a recent calcite-depositing spring - a model of chemical variations with inorganic $CaCO_3$ precipitation. *Earth and Planetary Science Letters* 42: 267-276.

Van der Straaten C. M. and Mook W. G., 1983: Stable isotope composition of precipitation and climatic variability. In: *Palaeoclimates and Palaeowaters: A collection of environmental isotope studies.* IAEA, Vienna: 53-64.