

Calcareous tufas in the soligenous mires of eastern Poland as an indicator of the Holocene climatic changes

RADOSŁAW DOBROWOLSKI¹, TOMASZ DURAKIEWICZ^{2,3} & ANNA PAZDUR⁴

¹ *Institute of Earth Sciences, UMCS, Akademicka 19, PL - 20-033 Lublin, Poland. E-mail: rdobro@biotop.umcs.lublin.pl*

² *Institute of Physics, UMCS, pl. M. Curie-Skłodowskiej 1, PL - 20-031 Lublin, Poland*

³ *Los Alamos Laboratory, Condensed Matter & Thermal Physics Group, Los Alamos, Mailstop K764, NM 87545, USA.*

E-mail: tdur@uswest.net

⁴ *Institute of Physics, Silesian Technical University, Krzywoustego 2, PL - 44-100 Gliwice, Poland*

E-mail: pazdur@zeus.polsl.gliwice.pl

ABSTRACT:

DOBROWOLSKI, R., DURAKIEWICZ, T. & PAZDUR, A. 2002. Calcareous tufas in the soligenous mires of eastern Poland as an indicator of the Holocene climatic changes. *Acta Geologica Polonica*, **52** (1), 63-73. Warszawa.

Measurements of stable carbon and oxygen isotope composition and radiocarbon datings of sediments of soligenous mires from the Lublin Upland (E Poland) were used for reconstruction of palaeoenvironmental changes during the last 10 ka. Six depositional phases of the Holocene calcareous tufas were recognized: 10.3-9.9; 8.0-7.5; 6.7-6.5; 6.0-5.6; 2.5-1.7; 1.0-0.6 ka BP. They corresponded to the periods of relatively warm and humid climatic conditions.

Key words: Calcareous tufa, Soligenous mire, Climate change, Holocene, Eastern Poland.

INTRODUCTION

Soligenous mires belong to the rare group of fens supplied with groundwaters of distinct flow, generally of ascending nature (SJÖRS 1948). They usually form raised knolls up to several metres high and 10-20 m in diameter and are characterized by a specific lithology of deposits. Layers of slightly consolidated calcareous tufas with various grain-sizes occur within reed and sedge fen peats (DOBROWOLSKI 1996). Such beds are excellent for detailed palaeoenvironmental studies because of their continuous peat-tufa sedimentation. Carbonates can be a very important indicator of humidity-thermic changes because their deposition is closely connected with the environmental conditions (BAKALOWICZ 1990). Continental carbonate deposits like tufa were used as

such indicators in many karst areas of Europe (among others GEUERTS 1976; SRDOC & *al.* 1980, 1982, 1983; THORPE & *al.* 1980, 1981; LÉCOLLE & LÉCOLLE 1990; ANDREWS & *al.* 1994; HLADKOWA & *al.* 1996; PAZDUR & *al.* 1988a, b; SANCZO & *al.* 1997). Soligenous mires are suitable for estimation of the reservoir effect as both carbonate and organic fractions can be radiocarbon dated (PAZDUR 1988).

From among five sites of the soligenous mires found in eastern Poland (Text-fig. 1) which are characterized by similar lithological sequences, the Krzywice-1 and Rudka-2 sections were selected for palaeoenvironmental and chronostratigraphic reconstructions. The Krzywice and Rudka mires represent the so-called open artesian type with raised peat-tufa knolls, clearly visible in relief. In both of the examined sections the depositional conditions

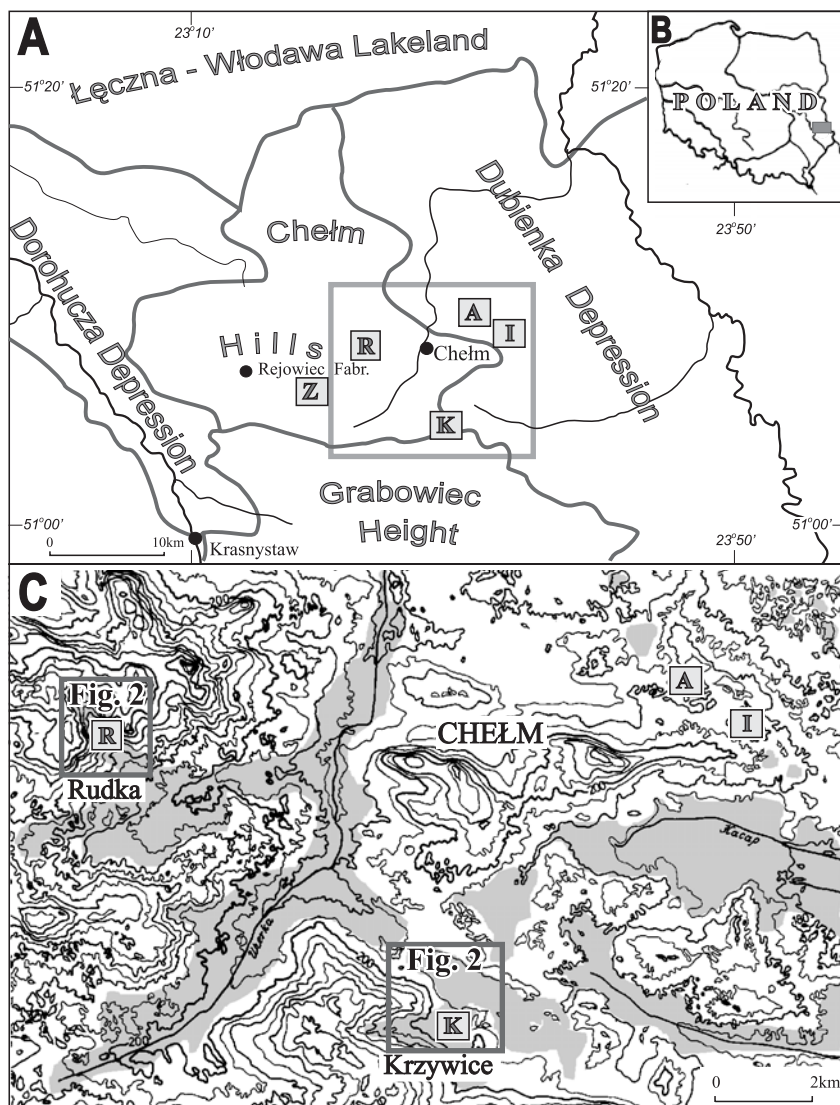


Fig. 1. Location map; A - Distribution of soligenous mires in eastern Poland (after DOBROWOLSKI & *al.* 1999, completed); A - Antonin site, I - Ignatów site, K - Krzywice site, R - Rudka site, Z - Zawadówka site; B - General location in Poland; C - Topographic situation in the environs of the Rudka and Krzywice soligenous mires

were similar and the stratigraphically correlated main tufa layers were sedimented simultaneously. Therefore, the differences between the successive key horizons were considered to be a result of regional changes.

DESCRIPTION OF THE STUDY SITES

The examined soligenous mires occur in the north-eastern, marginal part of the Lublin Upland, near the border of the Lublin Polesiye (Text-fig. 1). In spite of local differences, especially in the lithology of the surface deposits near the sites, the existence conditions of the mires are similar. It concerns, among other things, strong relationships between groundwater circulation and structure of the Upper Cretaceous rock massif. These conditions directly influence the character of

water supply to the mires, and indirectly the sedimentation type within the mires.

Krzywice site

This site is situated in the borderland of three distinctly differentiated morphostructural regions: Chełm Hills, Grabowiec Height and Dubienka Depression (Text-fig. 1). The soligenous mire set is composed of two neighbouring peat-tufa knolls (Krzywice-1 and Krzywice-2) 25-30 m in diameter, raised about 1 m over the peat plain. They occur in the central part of the broad (about 1.2 km²) karst depression; its accumulation floor reaches 195-200 m a.s.l. This form is surrounded by low hills built of marly opokas overlain in places by a thin cover of the Pleistocene sands (Text-fig. 2).

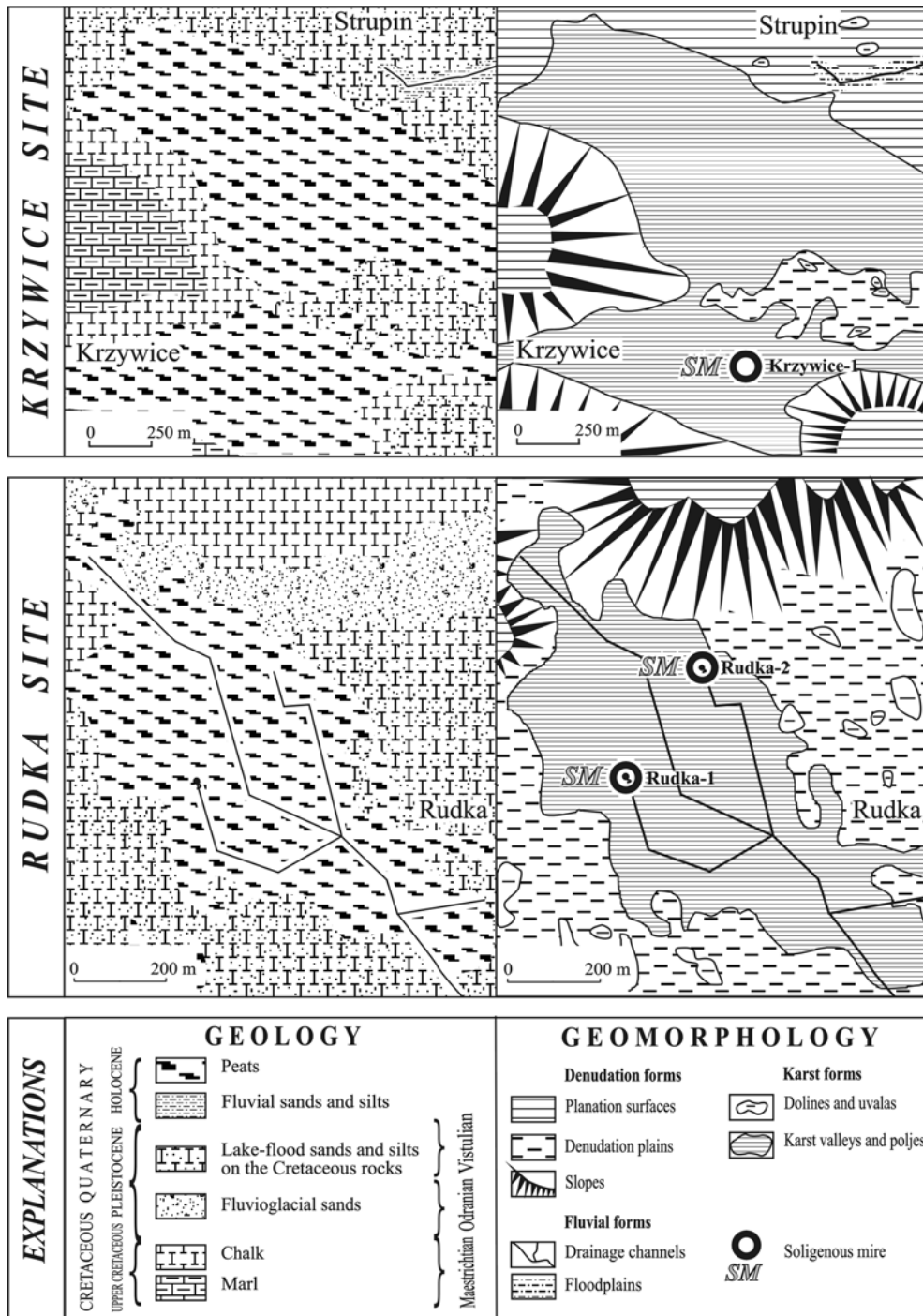


Fig. 2. Geological and geomorphological conditions of the occurrence of soligenous mires in Krzywice and Rudka (after DOBROWOLSKI 1998)

The Upper Cretaceous aquifer, related to the Maastrichtian fissured rocks, is the only one occurring in Krzywice. It is supplied mainly with rainwater infiltrating directly into the carbonate substratum, or indirectly through the Quaternary unconsolidated

deposits and the cover of weathered carbonate rocks. The groundwater table is free within the hills and confined in the depression. In its central part, the artesian waters feeding the soligenous mire flow out under hydrostatic pressure.

Rudka site

This site is situated in the SE part of the Chelm Hills (Text-fig. 1), in a broad plain of mire (0.4 km²) filling the large karst depression. Two peat-tufa knolls (Rudka-1 and Rudka-2) rise about 1 m over the accumulation floor of this karst form which is at 205-215 m a.s.l. (Text-fig. 2). Ascending springs occur on both knolls. The carbonate complex of Upper Maastrichtian chalk, in places with interbeds of marls and opokas, predominates among the surface deposits surrounding the site. The Quaternary sediments differ in respect of thickness and lithology in the vicinity of the site. Odranian fluvioglacial sandy and sandy-silty deposits and Vistulian lacustrine-flood sands and silts predominate.

Fissured chalk deposits form the regional aquifer, generally with a free groundwater table. However, the groundwater is confined in places because a clayey residuum of Upper Cretaceous rocks overlies the water-bearing horizon. This situation results in the occurrence of ascending springs in the floor of the karst depression, and formation of the spring soligenous mires.

MATERIAL AND METHODS

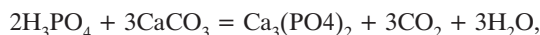
Geology of the sites was studied in detail and two cores of undisturbed structure were taken from the soligenous mires (Krzywice-1 and Rudka-2 sections). The thicknesses and lithological sequences were similar in both profiles. Detailed sedimentological, malacological and pollen analyses were carried out for both the sections (ALEXANDROWICZ & *al.* 1994, DOBROWOLSKI & *al.* 1999). Samples for radiocarbon dating and measurements of oxygen and carbon isotope contents were selected from the lithofacial key horizons representing peat and tufa sedimentation cycles (DOBROWOLSKI & *al.* 1996, 1999).

In both the Krzywice-1 and in the Rudka-2 sections the tufas occur as pale coloured, weakly consolidated calcareous deposits encrusting hydrophilous plants in the outflow zone of the ascending spring. Tufa layers are from 0.5 to 40 cm thick, their grain-size varies; coarse-grained tufas occur in the top parts of the sections, fine-grained and silty tufas in the bottom parts (DOBROWOLSKI 1998 a, b). Young tufa is usually strongly porous because it represents the structure of non-transformed plant material, mainly calciphilous mosses, sedge and reed roots. Older tufas have lost this structure as a result of compaction.

Measurements of stable carbon and oxygen isotope composition

The analytical material used for carbon and oxygen stable isotope measurements in the soligenous mires were the authigenic carbonates precipitated in the oxidizing environment as calcareous tufa. Basically, in this type of sediment, the oxygen isotopic composition, $\delta^{18}\text{O}$, depends primarily on the isotopic composition of the groundwaters as well as on the temperature of the deposition/crystallization (MCCREA 1950). 41 carbon-oxygen pairs of measurements were made for the Krzywice-1 (DOBROWOLSKI & *al.* 1996) and 20 pairs for the Rudka-2 section (Text-fig. 3).

Measurements of the oxygen and carbon isotopic composition were made by use of gaseous CO₂ obtained from carbonate samples in accordance with the standard procedure based on the reaction with phosphoric acid (MCCREA 1950). Reaction of 5 to 10 mg of sample with concentrated acid (103.3%) was performed in a glass vacuum extraction line adapted to work on-line with the mass spectrometer. Samples of carbonates of grain size < 0.1 mm were placed in separate glass containers. The temperature of both the acid and the samples was stabilized at 25°C. Sample and acid were evacuated and degassed. When the pressure was constant at 10⁻³ mbar, the glass reaction vessels were sealed and the samples were flushed with phosphoric acid. CO₂ from carbonates was obtained according to the reaction:



which was continued for 24 hours. The vessels were placed in a thermostatic chamber with forced air convection, at 25°C. The CO₂ gas obtained from each sample was dried (purified from water) by use of the P₂O₅ water trap and, when purified, the CO₂ was trapped on a medium volume cold finger. The isotopic composition of the CO₂ gas was measured by use of the modified triple collector mass spectrometer MI1305 (HAŁAS 1979; HAŁAS & SKÓRZYŃSKI 1980; DURAKIEWICZ & HAŁAS 1994; DURAKIEWICZ 1996). Measurement of each sample was performed 13 times, by the common sample/reference switching method. 800 voltage samples were measured for each switching period, each of the samples representing the 44, 45 and 46 ion currents converted to voltage by use of the I/U converter. The unnormalized 'delta' values in per mil reference were obtained by use of the following formulae:

$$\delta^{18}\text{O}_{\text{app}} = \{[(16/144)\text{sample}/(16/144)\text{reference}] - 1\} * 1000,$$

$$\delta^{13}\text{C}_{\text{app}} = \{[(15/144)\text{sample}/(15/144)\text{reference}] - 1\} * 1000,$$

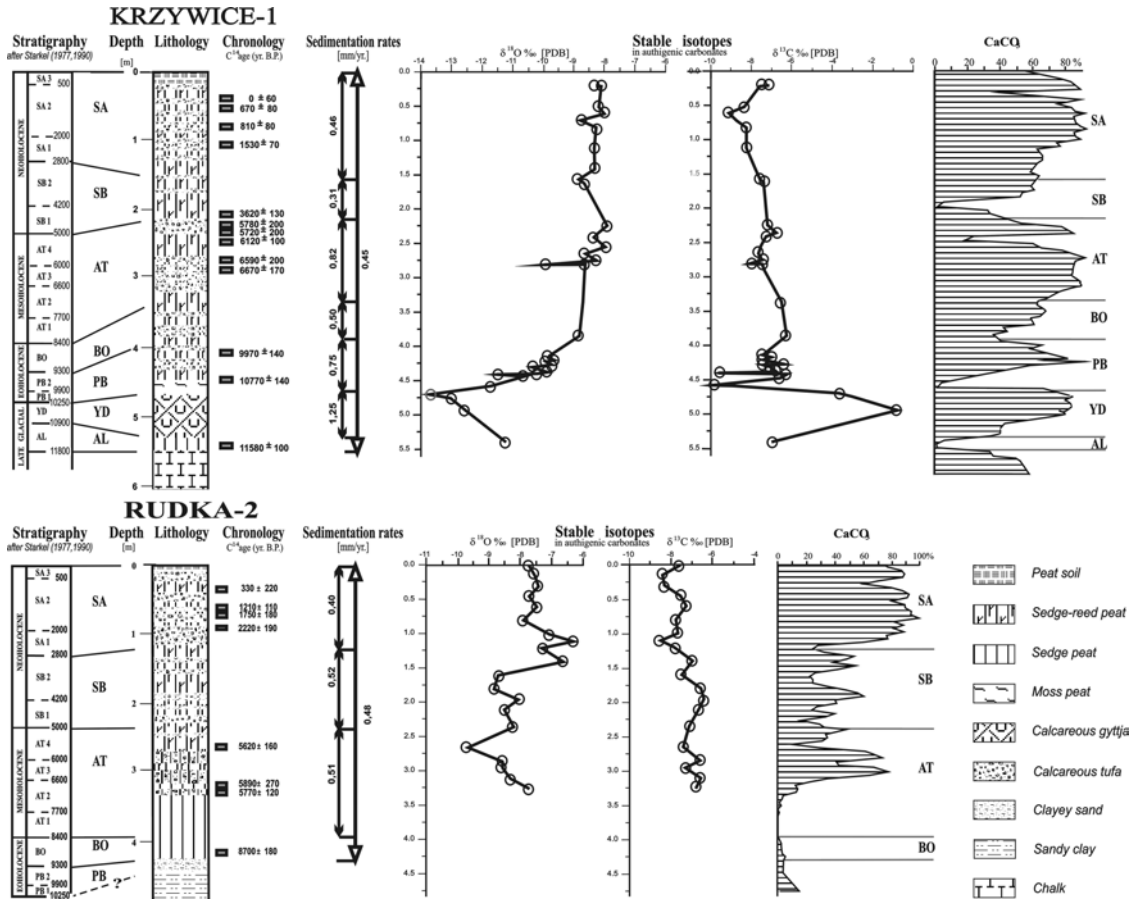


Fig. 3. Correlation of the lithostratigraphic horizons in the Krzywice-1 and Rudka-2 profiles of soligenous mires

and subsequently the $\delta^{18}O_{app}$ and $\delta^{13}C_{app}$ values were normalized. The normalization procedure includes the corrections for the mass spectrometer internal fractionation.

Analytical error was calculated as a square root of the sum of squares of deviations from the mean value, divided by $n-1$, where n is the number of measurements. The standard analytical error does not exceed 0.08 ‰.

Carbonate crystallization temperature was calculated by use of the formula (EPSTEIN & *al.* 1953):

$$T = 16.5 - 4.3(\delta c - \delta w) + 0.14(\delta c - \delta w)^2,$$

where δc is the isotopic composition of the carbonate, expressed in delta notation (‰), δw - isotopic composition of modern water.

Radiocarbon dating and reservoir effect

Thirty one radiocarbon datings of tufas from the soligenous mires were performed (16 datings from the

Krzywice-1 and 15 datings from the Rudka-2 sections). Radiocarbon age of either the carbonate or organic fraction was determined for each tufa sample, but in several samples both fractions were dated (Table 1). Thus, the values of the reservoir effect could be estimated. The $\delta^{13}C$ values determined in the carbonate deposits were used for correction of the radiocarbon ages.

All of analyzed samples were dated using CO_2 -filled proportional counters. T values in Table 1 mean ^{14}C ages of carbonate (T_C) and organic matter (T_{ORG}) normalized to $\delta^{13}C = -25\text{‰}$, according to the recommendation of STUIVER & POLACH (1977).

The 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 the 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 & *al.* 1979, PAZDUR & *al.* 1988a). Direct application of such models in ^{14}C dating of tufa has led to unsatisfactory results.

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

$$T_C = -8033 \cdot \ln(A/A_0), \quad (1)$$

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

$$T_R = -8033 \cdot \ln(A_0/A_{ox}) = -8033 \cdot \ln q. \quad (2)$$

Observed values of q in both recent and ancient tufas range from 0.5 to 0.95 (SRDOC & *al.* 1983, THORPE & *al.* 1981, PAZDUR & *al.* 1988, PAZDUR 1988) and consequently the values of T_R range from 500 to 5500 yr. Extremely high values ca 11 kyr, have been recorded elsewhere (PAZDUR 1988). The scatter of the T_R values could be explained by dependence of T_R on the bedrock type and the type of sediment, which depends strongly on hydrodynamic conditions of water flow (spring tufa; tufas: oncoids, moss travertines; peloidal calcareous muds; calcareous muds *vide* PAZDUR & *al.* 1988a).

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

$$T_R = T_C - T_{ORG}. \quad (3)$$

This value determined for a tufa section with known values of $\delta^{13}\text{C}$ throughout the profile, can be used for estimation of the real age of tufa horizons on the basis of T_C measurements. Small changes of $\delta^{13}\text{C}$ or a constant value indicate a constant value of T_R (PAZDUR 1988): the maximum changes of $\delta^{13}\text{C}$ in the samples from the Krzywice-1 section are from -6.71‰ to -9.04‰ ; in the Rudka-2 section the corresponding changes are from -6.57‰ to -8.27‰ (Table 1). It was

found that a constant T_R value indicates the type of calcareous sediment named silty tufa, precipitated from stagnant or low-energy water, such as the sediments from the the Krzywice-1 and Rudka-2 sites (DOBROWOLSKI & *al.* 1996, 1998).

RESULTS OF ANALYSES

Analyses of stable isotopes

The analytical results obtained so far for the calcareous tufas from the soligenous mires Krzywice-1 and Rudka-2 allow us to present the following conclusions:

- Comparison of the isotopic trends during the Holocene from both locations reveals similarities in the long-term changes of isotopic composition (Text-fig. 3). Values increasing with time are observed for oxygen (from -8.5 to -7.5‰), and decreasing for carbon (from -6.5 to -8‰).

- The relative stability of the groundwater isotopic composition is confirmed in both locations in the period from 9000 BP up to present.

- Isotopic data for the bottom parts of the Krzywice mire reveal a fundamental change in the character of the water source at the boundary of the Late Glacial and Holocene. Isotopically light waters ($\delta^{18}\text{O} \approx -15\text{‰}$), corresponding to groundwaters from degrading permafrost, are gradually replaced by isotopically heavier waters ($\delta^{18}\text{O} \approx -10.50 \div -10.15\text{‰}$). This, in the present authors' view, is related directly to the activation of the ascending spring, with change of the water supply to ascending, as soon as the vertical circulation was triggered by lack of permafrost. The oxygen isotope curve shows also, that, in the period from 10250 BP to 9900 BP, mixing of waters of different isotopic composition took place, with a gradually decreasing input of isotopically light waters.

The isotopic composition of meteoric water depends on numerous factors, e.g. air temperature, distance from coastline, geographic location etc. As was shown empirically by DANSGAARD (1964), there exists a positive correlation between $\delta^{18}\text{O}$ in H_2O and air temperature. Extrapolation of the Dansgaard's formula into the past seems useless, considering the empirical and modern character of his data and the number of unknown factors influencing $\delta^{18}\text{O}$ in H_2O other than air temperature in our area of interest. But the general idea of positive correlation, even one of unknown slope, may be applied to the entire Holocene. We therefore conclude that, in agreement with palaeogeographic predictions, the initial

negative excursion in $\delta^{18}\text{O}$ of our data corresponds mostly to degradation of isotopically light permafrost waters.

The isotopic record was also used as a source of information about the directions of changes of the palaeoenvironmental conditions in the vicinity of the mires, especially in the estimation of the relative changes in the temperature. Estimation of palaeotemperatures of the calcareous tufa on the basis of isotopic composition is possible (BAKALOWICZ 1990), but requires knowledge about the isotopic composition of the water. In practice, this knowledge is not available and therefore the *a priori* assumptions are made, assuming various water compositions for various points in the profile. In the authors' view, it is clearer to present data calculated for only one *a priori* assumed value of $\delta^{18}\text{O}$ in H_2O , and then treat the data obtained as a signal of relative changes of temperature only. Therefore it was found convenient to treat the temperature value from the top of the section, which represents modern water and modern temperature, as a reference point T_{ref} , and then calculate the relative temperature factor RT_x at each point x in the section as:

$$RT_x = T_x / T_{\text{wz}}$$

The dimensionless values of RT_x may be treated as generalized and relative temperature changes in the section. As may be seen in Fig. 4 these values are in good concordance with earlier palaeogeographic interpretations of environmental changes, especially temperature changes (*vide* ALEKSANDROWICZ & *al.* 1994; DOBROWOLSKI & *al.* 1999), up to the mid-Atlantic. Carbonates from the lower parts of the section represent, in the authors' view, precipitates formed under conditions of varying isotopic composition of the water. This might be due to the influence of degrading, isotopically light permafrost.

Radiocarbon dating

T_R values and corrected carbonate ages for the reservoir effect (T_{CCA}) of tufa carbonate itself ($T_{\text{CCA}} = T_C - T_R$) are listed in Table 1.

ENVIRONMENTAL HISTORY

Sedimentological analysis of the tufas, including the results of radiocarbon datings, isotope, malacological and pollen analyses, allowed us to reconstruct a sequence of events during the existence of the soligenous mires at Krzywice and Rudka.

Development of the mire at Krzywice started in the Alleröd, when non-carbonate sedge peats were deposited under permafrost conditions in a cold temperate climate. Their variety evidenced a limited supply of carbonates from the surroundings though Upper Cretaceous carbonate rocks were exposed over vast areas. It should be related to low precipitation and the occurrence of permafrost. During the Younger Dryas the floors of the deepest depressions were occupied by small, intermittent water bodies in which calcareous gyttja and lacustrine chalk accumulated. Signs of climate warming are visible at the top of the shallow-water deposits (Text-fig. 3). A distinct change of the sedimentation conditions and type occurred at the beginning of the Holocene. The water bodies gradually diminished and declined. During the Preboreal, under rather dry climatic conditions, a fen started to develop once again, but now as a soligenous mire. At first, the succession of the calciphilous moss species *Calliergon giganteum* and *Scorpidium scorpioides* (PB-1) appeared, then the communities of reeds and sedges developed, and calcareous tufas accumulated. It was connected with a complete transformation of groundwater circulation after degradation of permafrost, resulting in a change of water supply to the mire, and in a rise of ascending springs. The isotope signal record in the carbonate deposits suggests that the process of permafrost deterioration finished at the beginning of the PB-2 phase. At that time a long-lasting development of typical soligenous mire started. A period of rather stable environmental conditions began in the Preboreal phase. It was characterized by cyclic organic (reed-sedge and sedge-reed peats) and carbonate (calcareous tufas) sedimentation. A gradual humidity decrease occurred in the end of the Preboreal and during the whole Boreal period, resulting in a rather slow peat accumulation (Text-fig. 3). However, occurrences of single, thin (up to a dozen or so millimetres) interbeds of carbonate sediments (silty calcareous tufas) evidenced wetter episodes. Air humidity and temperature increased at the beginning of the Atlantic period. Distinctly cyclic organic and carbonate sedimentation indicated the occurrence of alternating episodes. Tufas were deposited during the warmer episodes (AT-1, first stage of AT-3, AT-4), and peats formed during the colder ones (AT-2, late stage of AT-3). Such an interpretation is indirectly confirmed by changes in the molluscan associations (ALEKSANDROWICZ & *al.* 1994) and by the isotope record. A distinct decrease in humidity followed by a decrease in temperature, occurred in the Subboreal period. Carbonate sedimentation was significantly reduced, and the rate of organic material growth was slow (0.31 mm/year). Humidity increased at the beginning of the Subatlantic period (SA-1). This was evidenced by a higher rate of peat growth

Krzywice-1								
Name of sample	Depth [m]	F	Lab. No. Gd-	T _{ORG} [BP]	T _C [BP]	T _R [years]	T [BP]	δ ¹³ C [‰, PDB]
KRZ 1/94	5,37-5,50	O	10280	11530±100			11530±100	
KRZ 2/94	4,37-4,60	O	10070	10770±140			10770±140	
KRZ 4/94	4,00-4,10	C	7516		10590±80		9970±140	-7,43
KRZ 4/94	4,00-4,10	O	10072	9970±140			9970±140	
KRZ 5/94	2,80-2,95	O	9237	6670±170			6670±170	
KRZ 5/94	2,80-2,95	C	7517	10620±50			6670±170	-7,32
KRZ 6/94	2,70-2,79	C	7518		10540±70	3950±250	6590±200	-8,08
KRZ 7/94	2,42-2,55	O	10073	6120±100			6120±100	
KRZ 8/94	2,31-2,43	C	7519		9670±60	3950±250	5720±200	-6,71
KRZ 9/94	2,16-2,31	C	7522	9730±70		3950±250	5780±200	-6,71
KRZ 10/94	2,00-2,15	O	10074	3620±130			3620±130	
KRZ 11/94	1,00-1,12	O	10079	1530±70			1530±70	
KRZ 12/94	0,79-0,92	C	7524		4340±60	3530±60	810±100	-8,17
KRZ 13/94	0,56-0,66	C	7525		4200±50	3530±60	670±80	-9,04
KRZ 14/94	0,56-0,43	C	7520		3530±60	3530±60	0±60	-8,28
KRZ 14/94	0,56-0,43	O	9231	MODERN			0±60	
Rudka-2								
R2-1	4,20-4,10	O	10655	8700±180			8700±180	
R2-2	3,21-3,09	C	10642		7130±190	1360±130	5770±120*	-6,57
R2-3	3,09-3,01	C	10651		6980±180	1360±130	5620±160	-6,57
R2-3	3,09-3,01	O	10649	5620±160			5620±160	
R2-4	2,80-2,70	C	10645		7670±150	1780±220	5890±270	-7,39
R2-4	2,80-2,70	O	9816	5890±270			5890±270	
R2-5	0,92-0,87	C	10646	2720±140		500±140	2220±190	-7,74
R2-5	0,92-0,87	O	9801	2220±190			2220±190	
R2-6	0,87-0,82	C	10659		2870±140	?		-7,74
R2-7	0,82-0,74	C	7980		3080±70	?		-7,74
R2-8	0,74-0,71	C	9797		3530±210	1780±150	1750±180	-7,25
R2-8	0,74-0,71	O	9807	1750±180			1750±180	
R2-9	0,71-0,65	C	10663		2980±140	1780±150	1200±110*	-7,25
R2-10	0,48-0,37	C	7983		2190±60	1860±120	330±220	-8,27
R2-10	0,48-0,37	O	9809	330±220			330±220	

Table 1. Results of ¹⁴C dating of carbonate (C) and organic (O) fractions (F) of tufa samples (T_C, T_{ORG}), δ¹³C measurements and estimation of reservoir (T_R) and “true” conventional radiocarbon ages (T) of the tufa horizons. T value means T_{ORG} if was dated organic fraction of tufa and T_{CCA} for tufas without organic matter.

and the succession of molluscan assemblages. A temperature rise was recorded in the phases of carbonate sedimentation during SA-2.

The soligenous mire at Rudka started to develop in the Boreal period of the Holocene (Text-fig. 3). Sedimentation of sedge peats, in a reducing environment with low pH and lack of carbonate precipitation, was connected with progressive swamping of the area, and lasted until the mid-Atlantic period. The change in the character of the water supply to an ascending one at the boundary of the AT-2 and AT-3 phases was evidenced by sedimentation of carbonates (interbeds of silty tufa). The

amount of carbonate material in the peat increased gradually during the Younger Mesoholocene and reached its maximum in the initial stage of the AT-4 phase. Sedge peat was replaced by sedge-reed simultaneously with the appearance of calcareous tufas in the section. The gradual increase in carbonate content in the latter part of the Atlantic period resulted from progressive climatic changes – an increase in humidity and temperature – which caused intensive leaching of carbonates from the Upper Cretaceous bedrock.

The Subboreal period was characterized by cyclic biogenic and carbonate sedimentation (Text-fig. 3).

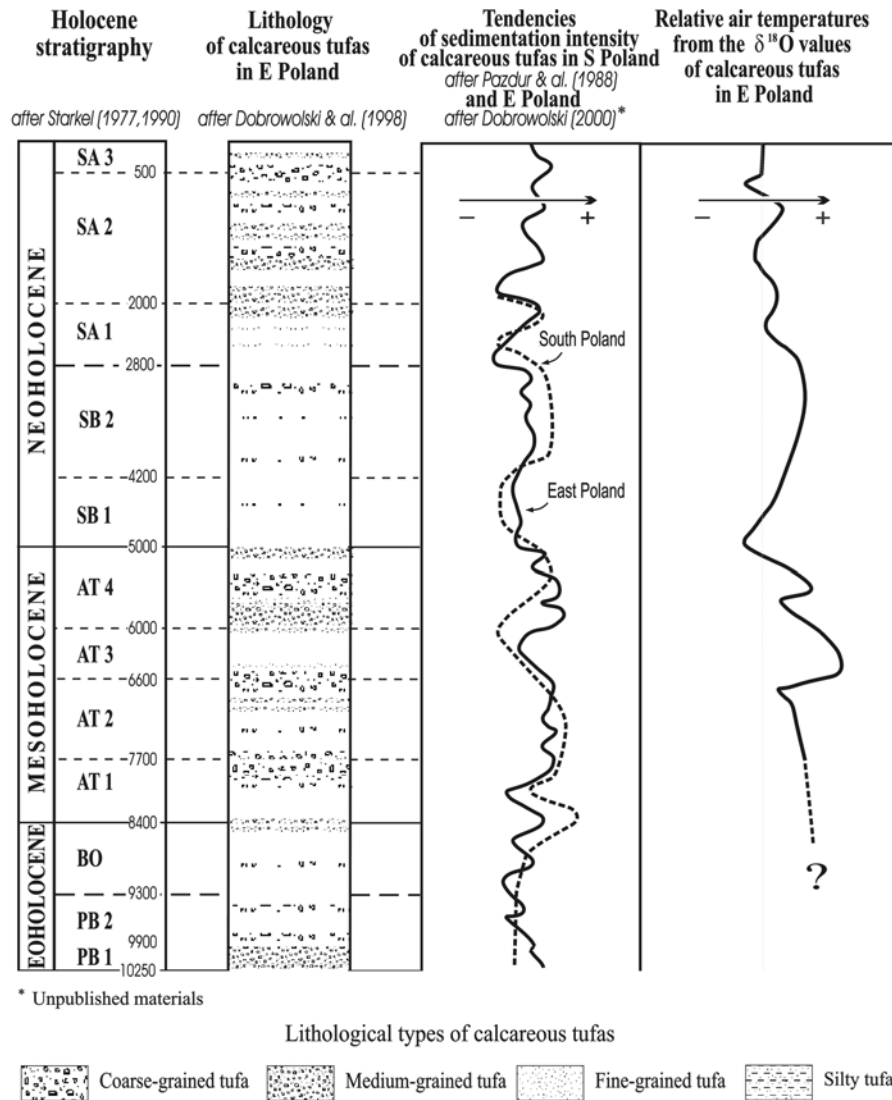


Fig. 4. Chronology of sedimentation of calcareous tufas in eastern Poland in relation to the Holocene temperature changes

However, the carbonate material did not form distinct lithostratigraphic horizons, but was usually dispersed. Including the results of isotope analyses we think that this type of sedimentation was a record of air humidity changes (alternating dryer and less dry periods) with rather stable air temperatures.

Repeated, considerable increases in the amount of carbonate in the soligenous mire started from the beginning of the Subatlantic period, with a maximum between 2500 and 1700 years BP. Distinct layers of calcareous tufas were formed as a result. One episode of climate cooling about 330 ± 220 years BP (Little Ice Age?) was evidenced by a substantial decrease in carbonate content, which is visible in both the Rudka-2 and

Krzywice sections. We suppose that during the Subatlantic period (mainly in the SA-3 phase) the character and course of sedimentation in the mire was influenced not only by climatic change but also by local factors, especially those connected with human impact on water conditions (deforestation followed by agricultural drainage).

Sedimentation rates (determined from the radiocarbon datings) of the organic-carbonate deposits in both of the examined soligenous mires (Text-fig. 3) were similar to the average values for peat growth in the Holocene fens in Poland (ŻUREK 1986). However, the course of this process was rather uniform in the Rudka mire during the whole period of its existence, while at

the Krzywice site there were marked distinct 'accelerations' during rather wet intervals and 'decelerations' during dry ones (Text-fig. 3). It seems that these differences resulted from the overlapping of regional changes (climatic conditions) and local changes (geological and hydrogeological conditions, human influences).

When comparing the two sections we find great similarity of the Meso- and Neoholocene lithostratigraphical sequences, and also synchronous deposition of carbonates (calcareous tufas) and biogenic accumulation. However, the timing of the beginning of the development of the spring knolls was different at Krzywice (Preboreal) from that at Rudka (Boreal). Rates and courses of sedimentation during the Subboreal were also different at these two sites. This was probably caused by local factors, especially hydrological and hydrogeological ones, affecting the transformation of the groundwater system to ascending conditions in the Eoholocene, and later influencing the course of water supply during the whole Holocene.

CONCLUSIONS

The results of our studies show synchronous sedimentation of the main tufa layers in the sections of the examined soligenous mires in eastern Poland. As the conditions of tufa deposition and the lithological sequences of deposits in the sections were similar, we think that the differences between the successive key horizons were a result of regional changes (Text-fig. 4). Therefore, palaeoclimatical and palaeohydrological generalizations can reasonably be, though the course of sedimentation was locally modified at various times during the existence of the mires. Radiocarbon datings allow us to distinguish the main phases of intensified carbonate deposition, separated by phases of biogenic sedimentation. This cyclicity of sedimentation was connected with regional variability of humidity and temperature. Carbonate deposition occurred in the following periods:

- 10250-9900 years BP (PB-1). Progressive climatic warming caused complete permafrost degradation during this period. Activation of vertical groundwater circulation favoured intensive leaching of the carbonate from the exposed surfaces of Upper Cretaceous rocks, followed by their secondary precipitation in the outflow zones of the ascending springs.

- 8000-7500 years BP (AT-1). This period was characterized by a considerable increase in temperature and relatively slower increase in humidity. Great variability of both components is reflected in the sec-

tions by distinctly 'laminated' carbonate-organic sedimentation.

- 6700-6500 years BP (first stage of AT-3). Intensified sedimentation of calcareous tufas was connected with repeated, distinct increase in temperature and humidity during this period.

- 6000-5600 years BP (first stage of AT-4). This was the main deposition phase of calcareous tufas during the optimum of the Atlantic period, but was preceded by a distinct decrease in humidity and temperature in the late stage of AT-3.

- 2500-1700 years BP (late stage of SA-1 and first stage of SA-2). A relative increase in temperature and also humidity occurred at the beginning of the Subatlantic period (after the distinctly cooler and drier Subboreal period). The amount of carbonate deposits in the spring knoll sections increased considerably, reaching a maximum between 1800 and 1700 years BP.

- 1000-650 years BP (SA-2). During this period, the course of tufa sedimentation was affected not only by favourable climatic conditions but probably also by progressive deforestation, which indirectly influenced the hydrological and hydrogeological conditions.

The main phases of tufa deposition in the soligenous mires corresponded to warm and rather wet periods. Cool climatic conditions were unfavourable for carbonate precipitation. Distinct hiatuses connected with such climatic conditions occurred mainly in the latter part of the AT-3 phase of the Atlantic period, at the beginning of the Subboreal period (SB-1) and at the boundary of the Subboreal and Subatlantic periods (SB-2/SA-1).

Acknowledgements

The investigations were partially supported by the State Committee for Scientific Research (Grant 6 PO4E 026 10). The authors thank Prof. Teresa MADEYSKA and Prof. Tim ATKINSON for their helpful comments, which improved this paper significantly.

REFERENCES

- ALEXANDROWICZ, S.W., BAŁAGA, K. & DOBROWOLSKI, R. 1994. Etapy rozwoju torfowiska kopolowego Krzywice w okolicach Chełma Lubelskiego. *Zeszyty Naukowe AGH, Geologia*, **20** (3), 259-273.
- ANDREWS, J.E., PEDLEY, H.M. & DENNIS, P.F. 1994. Stable isotope record of paleoclimatic change in a British Holocene tufa. *The Holocene*, **4**, 349-355.
- BAKALOWICZ, M. 1990. Geochimie des eaux incrustantes, formation des travertins et neotectonique: l'exemple des

- Corbieres. *Bull. Centre de Géomorphologie du CNRS*, 38, *Travaux du Groupe Seine*, 5, 67-78. Paris.
- DANSGAARD, W. 1964. Stable isotopes in precipitation. *Tellus*, 16, 436-468.
- DOBROWOLSKI, R. 1998a. Development conditions of calcareous tufas from the karst area of the Chełm Hills (Lublin Upland). *Kras i Speleologia*, 9 (18), 194-206.
- 1998b. Strukturalne uwarunkowania rozwoju współczesnej rzeźby krasowej na międzyrzeczu środkowego Wieprza i Bugu. 88 pp. *Wydawnictwo UMCS*; Lublin.
- DOBROWOLSKI, R., DURAKIEWICZ, T., PAZDUR, A. & PAZDUR, M.F. 1996. Chronostratigraphy and development stages of the spring peat – knoll at Krzywice near Chełm, Lublin Upland, SE Poland. *Zeszyty Naukowe Politechniki Śląskiej, Matematyka-Fizyka*, 80, *Geochronometria*, 17, 19-30.
- DOBROWOLSKI, R., ALEXANDROWICZ, S.W., BAŁAGA, K., DURAKIEWICZ, T. & PAZDUR, A. 1999. Badania martwic wapiennych w obrębie śródliskowych torfowisk kopułowych we wschodniej Polsce. In: PAZDUR A., BLUSZCZ A., STANKOWSKI W. & STARKEL L. (Eds), *Geochronologia górnego czwartorzędu Polski w świetle datowań radiowęglowych i luminescencyjnych*, pp. 179-197. Wrocław.
- DURAKIEWICZ, T. 1996. Electron emission controller with pulsed heating of filament, *Int. J. Mass Spectr. Ion Proc.*, 156, 31-40.
- DURAKIEWICZ, T. & HAŁAS, S. 1994. Triple collector system for isotope ratio mass spectrometer. *IF UMCS Report*, 131-132.
- FRIEDMAN, I. 1970. Some investigations of the deposition of travertine from hot springs-I. The isotopic chemistry of a travertine depositing spring. *Geochimica and Cosmochimica Acta*, 34, 1303-1315.
- HAŁAS, S. 1979. An automatic inlet system with pneumatic changeover valve for isotope ratio mass spectrometer. *J. Phys. E.: Sci. Instrum.*, 18, 417-420.
- HAŁAS, S. & SKÓRZYŃSKI Z. 1980. An inexpensive device for digital measurements of isotopic ratios. *J. Phys. E.: Sci. Instrum.*, 13, 346-349.
- HLADIKOVA, J., ZAK, K., KADLEV, J., CILEK, V. & LOZEK, V. 1996. Holocene climatic record in the calcareous tufa mound in Svaty Jan pod Skalou, Bohemian Karst (Czech Republic). In: *Climate Change: The Karst Record*, 59-61. Bergen.
- LÉCOLLE P. & LÉCOLLE R. 1990. Paléotempératures déduites de la composition isotopique des tests de Gastéropodes terrestres et des travertins de la vallée de la Seine. *Bull. Centre de Géomorphologie du CNRS*, 38, *Travaux du Groupe Seine*, 5, 79-92. Paris.
- MCCREA, J.M. 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.*, 18, 849-857.
- MOOK, W.G. 1976. The dissolution-exchange model for dating groundwater with ^{14}C . In: *Interpretation of environmental and isotope data in groundwater hydrology*: IAEA, Vienna, 213-225. Vienna.
- PAZDUR, A. 1988. The relations between carbon isotope composition and apparent age of freshwater tufaceous sediments. *Radiocarbon*, 30 (1), 7-18.
- PAZDUR, A., PAZDUR, M.F. & SZULC J. 1988a. Radiocarbon dating of Holocene calcareous tufa from south Poland. *Radiocarbon*, 30 (2), 133-146.
- PAZDUR A., PAZDUR M.F., STARKEL, L. & SZULC, J. 1988b. Stable isotopes of the Holocene calcareous tufa in Southern Poland as paleoclimatic indicators. *Quaternary Research* 30, 177-189.
- PEARSON F.J., Jr. 1992. Effects of Parameter Uncertainty in Modelling ^{14}C . In: TAYLOR R.E., LONG A. & KRA R.S. (Eds), *Radiocarbon After four Decades. An Interdisciplinary Perspective*, pp. 262-275. Springer-Verlag; New York.
- SANCHO, C., PENA, J.L. & MELENDEZ, A. 1997. Controls on Holocene and present-day travertine formation in the Guadalaviar River (Iberian Chain, NE Spain). *Z. Geomorph. N.F.*, 41 (3), 289-307.
- SJÖRS, H. 1948. Myrvegetation i bergslagen. *Acta Phytogeographica Suecica*, 21, Uppsala.
- SRDOC, D., HORVATINCIC, N., OBELIC, B. & SLIEPCEVIC, A. 1982. Rudjer Boskovic Institute radio-carbon measurements VII. *Radiocarbon*, 24 (3), 352-371.
- SRDOC, D., HORVATINCIC, N., OBELIC, B. & SLIEPCEVIC, A. 1983. Radiocarbon dating of tufa in paleoclimatic studies. In: STUIVER, M. & KRA, R.S. (Eds), *International ^{14}C Conference, 11th, Proceedings*. *Radiocarbon*, 25 (2), 421-427.
- SRDOC, D., OBELIC, B., HORVATINCIC, N. & SLIEPCEVIC, A. 1980. Radiocarbon dating of calcareous tufa: How reliable results can we expect? In: STUIVER, M. & KRA, R. S. (Eds), *International ^{14}C Conference 10th, Proceedings*. *Radiocarbon*, 22 (3), 858-862.
- STUIVER, M. & POLACH, H. 1977. Discussion: Reporting of ^{14}C data. *Radiocarbon*, 19, 355-363.
- THORPE, P.M., HOLYDAK, D.T., PREECE, R.C. & WILLING, M.J. 1981. Validity of corrected ^{14}C dates from calcareous tufa, In: *Formations carbonates externes, tufas et travertines. Actes Colloques AGF*, 151-156. Paris.
- THORPE, P.M., OTLET, R.L. & SWEETING, M.M. 1980. Hydrological implications from ^{14}C profiling of UK tufa, In: STUIVER, M & KRA, R.S. (Eds), *International ^{14}C Conference, 10th, Proceedings*. *Radiocarbon*, 22 (3), 897-908.
- USDOWSKI, E., HOEFS, J. & MENSCHER, 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 Letter*, 42, 267-276.
- ŻUREK, S. 1986. Szybkość akumulacji torfu i gytii w profilach torfowisk i jezior Polski (na podstawie danych ^{14}C). *Przegląd Geograficzny*, 58 (3), 459-475.

Manuscript submitted: 10th May 2001

Revised version accepted: 15th September 2001