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HOLOCENE CALCAREOUS TUFA IN SIERADOWICE - GEOLOGY, MALACOLOGY, RADIOCHRONOLOGY AND STABLE ISOTOPES

Summary. Three types of lithostratigraphic sequences of calcareous sediments were distinguished in the studied site. Results of field studies prove the episode of vertical erosion followed by slope processes, next the dominance of mechanical denudation gradually replaced with chemical denudation, and, finally, the second phase of vertical erosion in the Subboreal phase. Precise ^{14}C age measurements of both calcareous tufa and organic matter indicate constant value of the apparent age of tufa carbonate, equal to 910±120 yr. Sedimentation of tufa series has occured from the beginning of Holocene till the end of the Atlantic phase. Results of malacological studies indicate that since the Late Glacial till the beginning of Neoholocene the valley floor was periodically overflooded and drained. Values of $\delta^{13}C$ of carbonate samples reveal systematical changes, indicating that sedimentation of calcareous tufa took place in semilimnic conditions, while measured values of $\delta^{18}O$ indicate abrupt warming at ca 9500 BC and relatively high temperature till ca 5000 BP.

1. INTRODUCTION

Among already described sites of Holocene sediments in the Holy Cross Mts area the Sieradowice site is the only one with occurence of calcareous tufa. First information on this site was published by Filonowicz (1962). Calcareous sediments were described by cited author as intercalation of tufa in loess. Further field studies led to modifications of opinions concerning genetical interpretation and stratigraphical position of tufa (Klatka, 1969; Jersak, Klatka and Snieszko, 1983). These studies, based on detailed mapping and radiocarbon datings have proved Holocene age of calcareous series and their overlying stratigraphic position with respect to the loess series. Malacological studies of Zajączkowska (1983) and Alexandrowicz (1984) provided evidence for reconstruction of environmental changes during early and middle Holocene (Eo- and Mesoholocene) in investigated region. Since 1983 complementary stu-

lies were started on this site, including more detailed ^{14}C datings and stable isotopes measurements. The results obtained enable us to present more complete and detailed description of environmental changes in uppermost parts of valleys in the Holy Cross Mts area.

2. GEOLOGICAL STUDIES

The outcrop of late Quaternary calcareous sediments in Sieradowice is situated in the NE part of the Bodzentyn syncline of Paleozoic massif of the Holy Cross Mts. In the axis of syncline there occur limestones, marls and shales of Middle Devonian, while near the synclinal flancs there are dolomites and dolomitic limestones, as well as lower Devonian sandstones, quartzites, shales and conglomerates. Now sandstones and shales form ranges of hills while in marls, dolomites and limestones valleys are developed. In the Sieradowice region the older bedrock is covered with tills, gravels and sands of the Middle Polish glaciation (Riss), which are overlain by Vistulian loess series up to 20 cm thick. In the axis of small river valleys occurs a series of sediments of loess-like muds, travertines, and tufa, intercalated with fossil soil levels. These sediments form wide terraces of height 4 - 7 m above the present day level of streams. Studies of geological features of terraces enables us to distinguish three different types of lithostratigraphical sequences:

A. First type of deposits is represented as filling of dry valley above present spring. In the axis of the valley occur laminated noncalcareous muds of thickness up to 4 m, which overlie up to 1 m thick humus accumulation level of bog soil developed on loessy deluvium. Whole pedolithic complex is deposited on errosional surface. This type of deposits is illustrated by profile Sieradowice I:

0-4.0 m - laminated loess-like mud, straw-colored, gleyey at base - deluvium.

4.0-5.2 m - structureless noncalcareous black muds with numerous iron concretions - humus accumulation level of meadow soil.

5.2-6.5 m - noncalcareous gleyey mud with traces of lamination - deluvium.

6.5- m - straw-colored calcareous loess, cut at top - younger Vistulian loess (IIb).

Similar sequence of deposits was found in dry valleys in Małopolska Upland of southern Poland covered with loess (Snieszko, 1985). In this area the beginning of humus accumulation coincides with Vistulian-Holocene boundary.

B. Second type of deposits is represented by sequence in upper part of Sieradowice valley. Overflooded terrace, 7 m high, of recently drained valley, is built of calcareous tufa and travertines with intercalations

of peat and humus levels. Maximum thickness of these deposits was found near the present axis of the valley. Differentiation of geological structure of deposits is illustrated by the profile Sieradowice II:

0 - 0.75 m - laminated light-grey mud, at top structureless - deluvium.

0.75 - 1.10 m - structureless black-grey mud, locally black. At top pottery from XII century found in situ. Basal part is ^{14}C - dated to 4870±70 BP - upper meadow soil.

1.10 - 1.50 m - chips of travertine, light-grey and white.

1.50 - 1.55 m - psammitic tufa and calcareous mud with organic matter (dated to 5100±80 BP).

1.55 - 2.25 m - chips of travertine, gradual transition at topmost part.

2.25 - 2.30 m - calcareous tufa with peat admixture.

2.30 - 2.75 m - highly broken light-grey travertine.

2.75 - 2.80 m - peat with chips of travertine (^{14}C-dated to 7110±160 BP).

2.80 - 3.75 m - highly broken travertine, changing to psammitic calcareous tufa at top.

3.75 - 3.80 m - peat with calcareous mud (^{14}C-dated to 8080±80 BP).

3.80 - 4.60 m - light-grey tufa

4.60 - 5.60 m - dense, porous travertine with secondary iron sinters.

5.60 - 6.50 m - calcareous mud with thin peat layers.

6.50 - 6.80 m - structureless black-grey loessy mud with carbonate and wood fragments at base (dated to 9860±60 BP) - lower meadow soil.

6.80 - 7.75 m - loessy mud with wood fragments. Concentration of organic remnants at depth 7.5 m (^{14}C-dated to 11,360±220 BP) - deluvium.

7.75 m - Devonian limestone with the erosional surface on the top.

C. This type of deposits is represented by tufa of younger Holocene age, which in Sieradowice were documented by drillings. They were found in exposure in Sniadka site, situated in lower part of valley. In this site overflooded terrace is only ca 4 m high. Sequence of sediments is illustrated by the Sniadka profile:

0 - 1.8 m - calcareous mud with fine laminations, consisting of yellow and dark-grey laminae - alluvium, extrachannel faci

1.8 - 2.6 m - fine-laminated mud with organic matter - alluvium, extrachannel facies.

2.60 - 2.65 m - fragments of wood (^{14}C dated to 600±60 BP).

2.65 - 3.0 m - structureless dark-grey calcareous mud - alluvium. extrachannel bog facies.

3.0 - 3.10 m - dense travertine.

3.10 - 3.25 m - structureless grey calcareous mud -alluvium, extrachannel bog facies.

3.25 - 3.70 m - peaty mud, black, calcareous -alluvium, extrachannel bog facies.

3.70 - dense travertine.

Lowermost part of profile was not available for detailed studies because of high ground water level. In exposed upper part of profile are clearly visible breaks in deposition of travertine, caused by silting of valley floor with flooded deposits.

In the present stage of field work the Eo- and Mesoholocene calcareous tufa deposits were most completely recognized and described. These sediments were then subjected to detailed isotopic and malacological studies.

3. MOLLUSCAN ASSEMBLAGES

Calcareous tufa and silts representing the second type of Quaternary deposits in Sieradowice are available in a few outcrops. They comprise rich and differentiated molluscan assemblages described by Zajączkowska (1983) with some supplements of S. W. Alexandrowicz (1983). More detailed malacological studies have been carried out in recent years simultanously with the field studies of Z. Śnieszko. Shells of molluscs occur in calcareous silts, tufa, travertines and muds with intercalations of fossil soil. More than 40 taxa of snails and bivalves are found in the profile in question. They are divided into five ecological types, defined by Lozek: A - forest snails, B - open habitat snails, C - mesophile snails, D_1 - hygrophile snails, D_2 - water molluscs. Eight molluscan assemblages are distinguished with respect to stratigraphical range of particular species representing the mentioned ecological types, as well as to its percentage (Fig. 1).

I. Calcareous silts and muds with wood fragments from the lowermost part of the profile (S) comprise an assemblage with numerous shells of: *Punctum pygmaeum*, *Vallonia costata*, *Vallonia pulchella*, *Nesovitrea hammonis*, *Euconulus fulvus*, *Succinea oblonga*, *Carychium minimum* and *Lymnaea truncatula*. The occurence of *Vertigo genesii* and *Vertige geyeri* reaching a considerable content in the upper part of the described layer is noteworthy. Mesophile snails (ecotype C) are the dominant component of the mentioned fauna, but in the uppermost part of silts the number of hygrophile snails increases markedly.

II. In the fossil soil (LS) and the lower part of calcareous tufa (Tt) an assemblage with *Discus ruderatus* and *Vertigo substriata* can be distinguished. The population of the first mentioned snail appears earlier than the population of the second one. Some other taxa are also represented by a considerable number of shells, e.a.: *Vitrea crystallina*, *Perforatella bidentata*, *Vallonia costata*, *Vallonia pulchella*, *Nesovitrea hammonis*, *Euconulus fulvus*, *Vertigo angustior* and *Carychium*

minimum. The content of snails preferring shady habitats increases markedly, but species belonging to the ecological types B, C, and D_1 are the main components of the fauna described.

III. The next assemblage can be distinguished in a thin layer of white and light grey tufa. Water snails: *Armiger crista nautileus*, *Hippeutis complanatus* and *Lymnaea peregra* are the dominant elements of this assemblage. Some mesophile and hygrophile species occur in a considerable number of specimens: *Cochlicopa lubrica*, *Nesovitrea hammonis*, *Euconulus fulvus*, *Carychium minimum* and *Succinea putris*. The presence of *Vertigo moulinsiana*, a taxon rarely cited from the Holocene sediments of Poland but reported from Sieradowice by Zajączkowska (1983) is noteworthy.

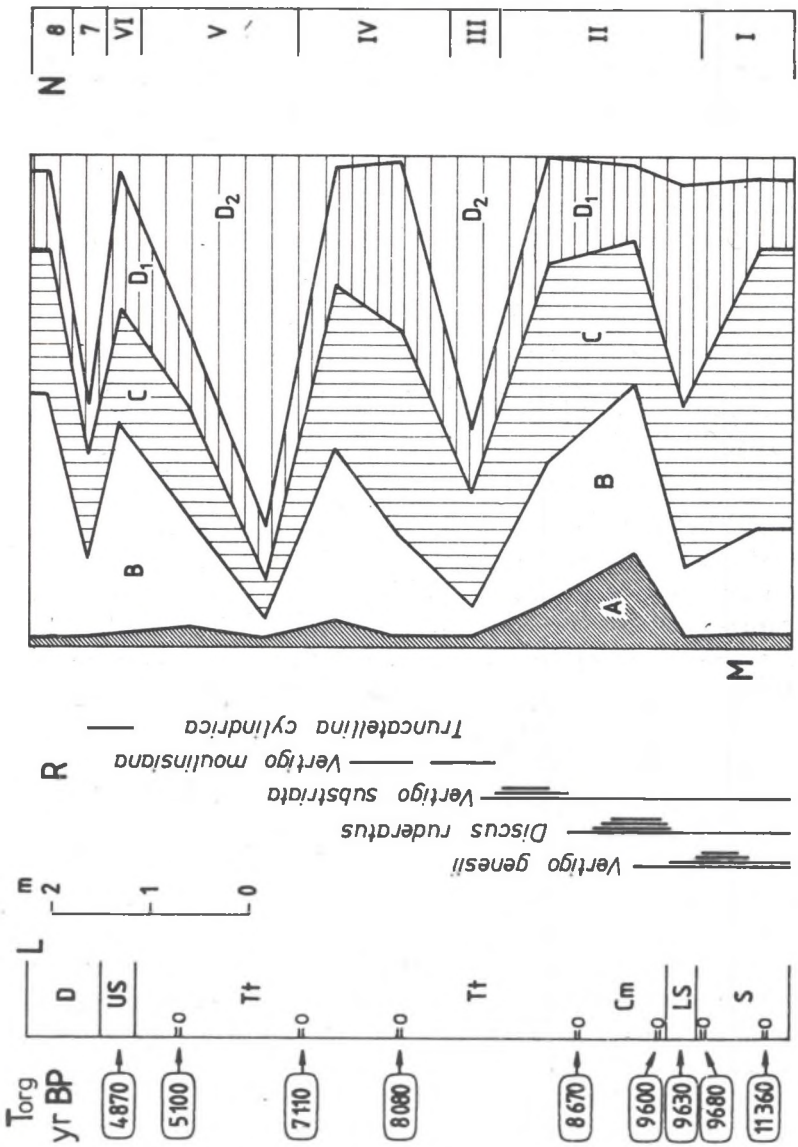
IV. In the middle part of tufa and travertines the molluscan fauna comprises mainly snails representing ecological types B, C, and D_1. The first of them includes *Vallonia pulchella* and *Vallonia costata*, the second one - *Cochlicopa lubrica*, *Punctum pygmaeum*, *Nesovitrea hammonis*, *Euconulus fulvus* and *Vertigo angustior*, while the third one - mainly *Carychium minimum*.

V. The upper part of calcareous tufa is characterised by an assemblage with the predominance of water molluscs (ecotype D_2: *Armiger crista nautileus*, *Hippeutis complanatus*, *Anisus leucostomus* and *Lymnaea truncatula*, as well as *Pisidium casertanum*. Land snails are represented by species regarded as typical of open environment (*Vallonia pulchella*), mesophile snails (*Cochlicopa lubrica*, *Euconulus fulvus*) and a hygrophile species - *Carychium minimum*.

VI. The fossil soil covering calcareous sediment (US) contains a fauna of meadow snails (ecotyp B). Besides the dominant species - *Vallonia pulchella*, mesophile snails known from the tufa and travertines are present here. The occurence of taxa living in dry, sunny habitats: *Truncatellina cylindrica* and *Cochlicopa lubricella* is worth noting.

7 - 8. In grey mud lying at the top of the described profile two molluscan assemblages can be distinguished. The first one comprises a considerable number of amphibiotic species - *Lymnaea truncatula*, and the second one - mixed fauna with *Vallonia costata*, *Vallonia pulchella*, *Cochlicopa lubrica* and *Carychium tridentatum*.

The succession of molluscan assemblages from Sieradowice illustrates the evolution of fauna during the Late Vistulian, Lower and Middle Holocene. In the whole described sequence the content of forest snails is considerably low and changes in assemblages are expressed in changing relations between meadow snails, mesophile snails, hygrophile species and water molluscs. The same pattern was observed in other regions of the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Vertigo substriata
Vertigo moulinsiana
Truncatellina cylindrica
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Fig. 1

Małopolska Upland (Alexandrowicz, 1984). In consequence three groups of molluscan fauna can be distinguished: a fauna with the predominance of ecotypes B and C, a fauna with a considerable number of hygrophile snails (ecotype D_1) and a fauna with a high content of water molluscs (ecotype D_2). They correspond to open, moderately humid environment, open humid habitats and episodes of overflooding of the valley floor.

The first stage of sedimentation took place in a woodless, moderately humid environment with meadows and bushes, developed in the cold climate of the Late Vistulian. The first fossil soil is connected with meadows and marches spread in the valley. This episode is dated as the Preboreal phase: 9600 - 9700 years BP. During the Boreal phase and at the beginning of the Atlantic phase the environment was more dry and the area surrounding the valley was partly covered with forest. In the lower part of the Atlantic phase the floor of the valley was overflooded and a permanent water basin was formed for a short time. Between 7 and 8 thousand years BP the basin was drained and replaced with meadows and marches, but during the next two thousand years it was overflooded again. The beginning of the Subboreal phase is marked by the development of the upper soil. The pedogenesis was connected with a moderately humid, open area with meadows and marches. The soil represents a final stage of sedimentation of calcareous sediments. Muds covering the mentioned soil represent deluvial deposits, accumulated in habitats partly overflooded and partly drained.

Fig. 1. Succession of molluscan assemblages from the Late Glacial and Holocene sediments in Sieradowice. L - lithostratigraphy: S - calcareous silts and muds, LS - lower soil, Tt - tufa and travertines, US - upper soil, D - muds, O - intercalations of organic material, R - stratigraphical range of selected species of snails. M - malacological diagram (based on the number of specimens): A - forest snails, B - species typical for open environment, C - mesophile snails, D_1- hygrophile snails, D_2- water molluscs, N - molluscan assemblages described in the text.

Rys. 1. Następstwo zespołów malakologicznych w późnoglacjalnych i holoceńskich osadach w Sieradowicach. L - litostratygrafia: S - mułki i iły węglanowe, LS - dolna gleba kopalna, Tt - martwice i trawertyny, US - górna gleba kopalna, D - mady, O - wkładki substancji organicznej, R - zasięgi stratygraficzne wybranych gatunków mięczaków. M - diagram malakologiczny (oparty na liczbie osobników): A - mięczaki leśne, B - gatunki typowe dla środowisk otwartych, C - mięczaki mezofilne, D_1 - mięczaki higrofilne, D_2 - mięczaki wodne, N - zespoły mięczaków opisane w tekście

4. RADIOCARBON CHRONOLOGY OF CALCAREOUS SEDIMENTS IN THE SIERADOWICE SITE

4.1. General problems of ^{14}C dating of calcareous sediments

Radiocarbon dating of organic remnants is based on two well known assumptions, i.e., i) the ^{14}C concentration in all living organisms was the same in the past, being equal to the normalized extrapolated ^{14}C activity of recent wood, and ii) the dated samples behaves as a closed system with respect to the carbon cycle in nature. It is well established now that these assumption are fulfilled for terrestial vegetation, so, as a rule, radiocarbon dating of wood, charcoal, peat, plant detritus, and so on, does not present serious technical and interpretational problems. On other hand, there is a large class of sediments which are of unquestionable importance for studies of the Quaternary period, but their ^{14}C dating is unreliable because of violation of either the first assumption or both of them.

The most important source of uncertainity of ^{14}C dates of continental freshwater carbonate sediments is connected with the difficulty of estimation of true initial ^{14}C activity of the sediment. Geochemical studies on deposition of recent and fossil tufa and travertine sediments indicate that in many cases presumption of the value of a_0 equal to 85 pmc (pmc=percent of modern carbon; mean ^{14}C activity of land vegetation is defined as 100 pmc), i.e. the same value as is used in ^{14}C dating of speleothems, leads to approximately correct ages (Srdoc et al, 1980, 1982, 1983). However, large scatter of the value of a_0 is observed, from ca 50 pmc to ca 95 pmc (Thorpe et al, 1980, 1981; Pazdur, Pazdur, 1986).

Depletion of the initial ^{14}C activity of the carbonate sediment with respect to that of land vegetation is known as a "reservoir effect" and leads to an artificial ageing of ^{14}C dates of carbonate samples by the value $T_{app} = 8033 \ln a_0$, called the apparent age. The value $a_0 = 85$ pmc is equivalent to $T_{app} = 1300$ years, the above quoted values of a_0 correspond to values of apparent age equal to 5600 and 850 years, respectively. Accurate determination of the true value of apparent age (or the corresponding value of a_0) in the investigated profile of carbonate sediment is therefore necesary for correct dating of selected layers or levels which mark essential episodes of development of the sediment. For accurate ^{14}C dating it is also important to check if the apparent age may be regarded constant in the whole profile.

The value of the apparent age may be estimated by dating of one or several carbonate samples which contain enough amount of organic matter. Assuming that both carbonate and organic fractions of dated sample are of same age we obtain

$$T_{app} = T_C - T_{org} \quad (1)$$

where T_C and T_{org} denote ^{14}C dates obtained on carbonate and organic fractions, respectively. At the same time it is assumed that the true age T of this sample is determined by the ^{14}C date of the organic fraction, $T = T_{org}$. For carbonate samples, or those which do not contain enough amount of organic matter, the corresponding value of true age is therefore determined from obvious relation

$$T = T_C - T_{app}. \quad (2)$$

Presumed constancy of the apparent age in the profile may be judged either directly from comparison of corresponding values of T_C and T_{org} of several samples selected from different parts of the profile, or indirectly from measured values of $\delta^{13}C$ of dated carbonate samples. The values of $\delta^{13}C$ resemble isotopic composition of dissolved inorganic carbon (DIC) in a stream water, but are modified by numerous processes involved in the course of precipitation of $CaCO_3$ (biogenic or abogenic sedimentation, type of the bedrock, hydrological regime, etc; Szulc, 1983). Especially important are the measurements of of $\delta^{13}C$ in ^{14}C dating of groundaters. Geochemical models describing the changes of isotopic composition of DIC in water (Mook, 1976, 1980; Eichinger, 1983) make it possible, under certain geochemical and hydrogeological conditions, to determine initial ^{14}C activity of HCO_3^- ions from measured values of $\delta^{13}C$. However, till now no theoretical models exist which would allow to determine in a similar way the initial ^{14}C activity of freshwater carbonates. Moreover, attempts of applications of the models mentioned above, and also the models described by other authors, lead to unsatisfactory results (Krajcar et al, 1985).

4.2. Laboratory methods

Tufa samples of mass ca 50 g were treated with 80% HCl and CO_2 evolved was quantitatively collected and then purified in a standard way and stored during at least four weaks prior to ^{14}C measurements. After HCl treatment of samples of the S3 series, which were collected from levels rich in organic matter, the remaining insoluble residue was washed, dried and combusted to obtain CO_2 for independent ^{14}C age determination. All ^{14}C age measurements were performed at the Radiocarbon Laboratory of the Institute of Physics, Silesian Technical University in Gliwice using proportional counters filled with pure carbon dioxide. Measurements of $\delta^{13}C$ and $\delta^{18}O$ were made at the Laboratory of Mass Spectrometry of the Institute of Physics of the Maria Curie Skłodowska University in Lublin.

4.3. Results

Radiocarbon dates obtained on tufa samples and associated organic matter with the corresponding values of $\delta^{13}C$ and $\delta^{18}O$ are listed in Table 1 together with the ^{14}C dates of samples from organic horizons under- and overlying the series of tufas and calcareous muds. The values of T_C and T_{org} denote conventional ^{14}C dates in the BP scale (i.e. in years before AD 1950) of carbonate and organic fraction, respectively, calculated from well known formula

$$T = 8033 \ln S_O/S_N, \qquad (3)$$

where S_N is measured ^{14}C concentration in dated sample, normalized for isotopic fractionation according to commonly accepted convention (Stuiver, Polach, 1977)

$$S_N = S\,[1 - 2(25 + \delta^{13}C)/1000] \qquad (4)$$

while S_O denotes the ^{14}C activity of modern biosphere, defined as 0.95 times the normalized activity of the NBS Oxalic Acid Standard. The values of $\delta^{13}C$ and $\delta^{18}O$ are quoted versus the PDB standard.

4.4. Apparent age of tufas in the Sieradowice profile

The apparent age of tufa samples was determined on the basis of comparison of the results of ^{14}C age measurements of carbonate and organic fraction in five samples collected from levels enriched in organic matter (samples of the S3 series). Dated samples cover whole time interval of tufa deposition, i.e. from ca. 10 000 BP to ca 5000 BP. The values of T_{app} calculated according to eq. (1) are listed in the next to the least column in Table 1 together with their errors obtained by square combination of errors of T_C and T_{org}. As may be seen, the values of T_{app} fall within rather wide interval from ca 500 to 1200 years. However, no clear systematic dependence of T_{app} upon age of sample or depth in the profile was found. Since the scatter of values of T_{app} of individual samples significantly exceeds the quoted values of errors, the problem of constancy of the apparent age in the profile calls for additional independent legitimation. As was mentioned before, valuable information on possible variations of the apparent age in the profile of carbonate sediments can be obtained from analysis of $\delta^{13}C$.

The dependence of $\delta^{13}C$ upon the age of carbonate fraction T_C (for samples of series S3 and S7) and upon the age of organic fraction T_{org} (S3 series only) is shown in Fig. 2. In linear approximation by the least squares method we obtain

$$\delta^{13}C = (-4.73 \pm 0.62) - (0.45 \pm 0.07)T_C \qquad (5)$$

$$\delta^{13}C = (-4.10 \pm 0.25) - (0.55 \pm 0.03)T_{org} \qquad (6)$$

Despite high negative correlation between $\delta^{13}C$ and T_C (r=-0.62) and also between $\delta^{13}C$ and T_{org} (r=-0.99), practically identical equation of straight lines (5) and (6) indicate that the value of T_{app} could be regarded constant in the whole profile. This conclusion is confirmed also by lack of any correlation between T_{app} and $\delta^{13}C$ (r=-0.02). We can therefore state that the apparent age is constant and estimate its value as the mean of individual values determined on five samples of the S3 series

$$\langle T_{app} \rangle = 910 \pm 120 \text{ yr.}$$

Table 1

Results of radiocarbon age determinations and ^{13}C and ^{18}O measurements in tufa samples

Sample	T[a]	C/O[b]	Lab. no.	Age yr BP	$\delta^{13}C$ ‰	$\delta^{18}O$ ‰	Tapp yr	Tcca yr
S3T	H	O	Gd-1572	4870±70	-	-		
S3/68	G	C	Gd-1715	6030±70	-7.03	-10.08	930	5120±140
S3/68	G	O	Gd-1718	5100±80	-28.40	-		
S3/158	G	C	Gd-3042	8150±60	-7.90	-9.55	1040	7240±130
S3/158	G	O	Gd-2199	7110±160	-28.30	-		
S3/310	G	C	Gd-2197	8560±120	-8.50	-9.67	480	7650±170
S3/310	G	O	Gd-3045	8080±80	-28.70	-		
S3/457	C	C	Gd-1716	9890±80	-8.98	-9.22	1220	8980±140
S3/457	C	O	Gd-2200	8670±110	-28.10	-		
S3/550	G	C	Gd-3043	10,480±70	-9.40	-11.42	880	9570±140
S3/550	G	O	Gd-1722	9600±80	-28.6	-		
S3B	H	O	Gd-2056	9630±100	-	-		
S3A	W	O	Gd-1574	9680±60	-	-		
S1A	W	O	Gd-2057	11,360±220	-	-		
S7/115	G	C	Gd-3238	6550±40	-8.12	-8.93		5640±130
S7/130	G	C	Gd-3239	6750±50	-8.00	-8.71		5840±130
S7/170	G	C	Gd-1959	7110±90	-7.97	-10.39		6200±150
S7/260	C	C	Gd-3240	8160±80	-9.00	-11.15		7250±150
S7/330	G	C			-9.16	-10.38		
S7/410	C	C	Gd-1962	9510±90	-8.70	-10.24		8600±150
S7/525	G	C	Gd-2485	10,020±130	-9.35	-10.39		9110±180
S7/605	G	C	Gd-3246	10,230±90	-9.82	-10.85		9320±150

[a]Type of deposit: G - gyttja, C - calcareous mud, H - humus, W - wood

[b]O - organic fraction, C - carbonate fraction

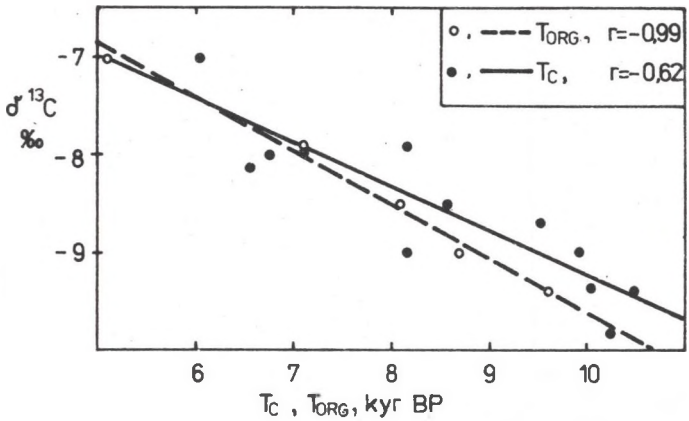

Fig. 2. Values of $\delta^{13}C$(PDB) of calcareous tufa samples in function of T_{org} and T_C

Rys. 2. Wartości $\delta^{13}C$(PDB) w próbkach martwic w funkcji T_{org} i T_C

Such value of the apparent age is equivalent to initial ^{14}C activity equal to a_0 = 89 pmc. The values of true ages of carbonate samples quoted in the last column of Table 1 were obtained from eq. (1) assuming same value of T_{app} for all carbonate samples.

5. STABLE ISOTOPES ^{13}C AND ^{18}O

Isotopic composition of oxygen in freshwater carbonates is commonly regarded as a sensitive indicator of temperature of sedomentation. In the case of speleothems it is possible to determine absolute values of temperature from measured values of $\delta^{18}O$ in calcite and $\delta^{18}O$ in inclusive water. In studies of lake sediments relative changes of the temperature of lake water can be estimated from measured $\delta^{18}O$ values. The relation between temperature and $\delta^{18}O$ in tufa carbonates is not explained in details till now. Very few published papers dealing with recent tufa sediments (Usdowski et al, 1979; Thorpe et al, 1980; Friedman, 1970) indicate strong violation of isotopic equilibrium in the process of sedimentation and the influence of kinetic effects in the reaction of $CaCO_3$ precipitation on $\delta^{18}O$. Attempts undertaken by Friedman (1970) and Usdowski et al (1979) to estimate temperature of sedimentation of recent tufas using the procedures developed for speleothems do not lead to satisfactory results.

Values of $\delta^{18}O$ in tufa carbonate, shown in Fig. 3, reveal significant change with the age ^{14}C, described by correlation coefficient

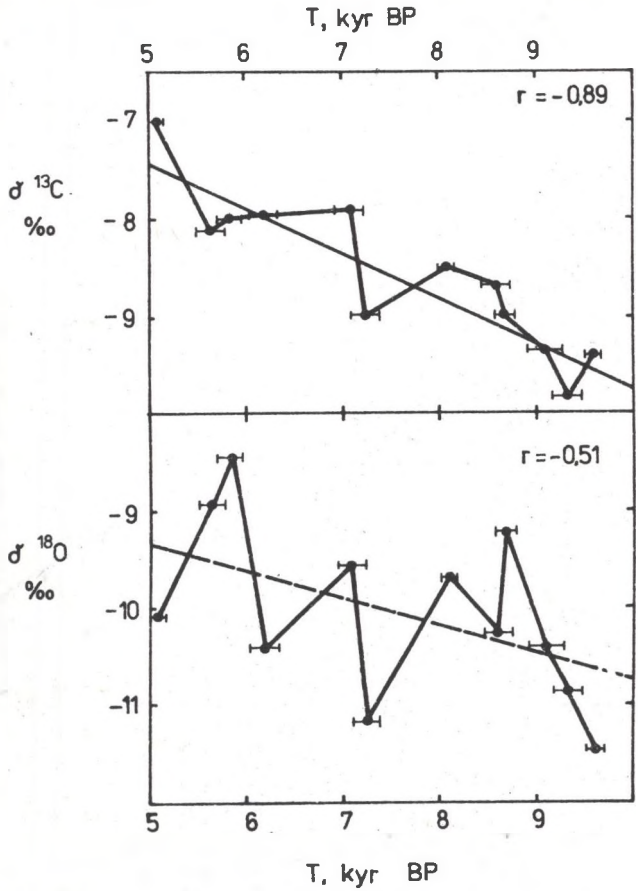

Fig. 3. Secular changes of $\delta^{13}C$(PDB) and $\delta^{18}O$(PDB) in calcareous tufa profile

Rys. 3. Wiekowe zmiany $\delta^{13}C$(PDB) i $\delta^{18}O$(PDB) w profilu martwic

r=0.51. Therefore, the existence of positive trend of temperature changes in the time interval from ca 9000 BP to ca 5000 BP can be undoubtly concluded. Assuming linear dependence between $\delta^{18}O$ and the ^{14}C age of carbonate sediment the mean rate of $\delta^{18}O$ change is equal to

$$\Delta\delta^{18}O/\Delta T = (0.28\pm0.15)\,‰/1000 \text{ year}.$$

Because of isotopic inequilibrium in the process of $CaCO_3$ precipitation a transition from the $\delta^{18}O$ changes observed in the profile to the temperature changes needs an assumptions that apart of evaporation processes the temperature gradients of $\delta^{18}O$ in carbonate and in water are the same. Taking for calculation the value of the temperature gra-

dient of $\delta^{18}O$ in recent meteoric water estimated by Różański (1984) for the territory of southern Poland, equal to 0.37‰/°C, we obtain that during the time of deposition of calcareous tufa sediments in Sieradowice profile, i.e. from ca 9000 BP to ca 5000 BP the mean rate of increase of the temperature was equal to ca 0.8°C per 1000 years.

The values of $\delta^{13}C$ shown in Fig. 3 in function of age reveal systematic increase with the mean rate

$$\Delta\delta^{13}C/\Delta T = (0.46 \pm 0.07)‰/1000 \text{ years}.$$

Such positive trend of secular changes of $\delta^{13}C$ is characteristic for lacustrine sediments (Geyh, 1983) due to decreasing ratio o volume to surface of the lake. Marked positive correlation between $\delta^{13}C$ and $\delta^{18}O$ in Fig. 4 (r=0.53) lead us to the presumption that the short-term distinct deviations of $\delta^{13}C$ values from the secular trend which is shown by the solid line in Fig. 3, resemble periods with increased contribution of photosynthesis caused by rise of temperature. Similar short-term deviations are observed also in other sites of tufa sediments in the southern Poland (Pazdur et al, ms in prep.) and may be therefore regarded as typical for calcareous tufa sedimentation.

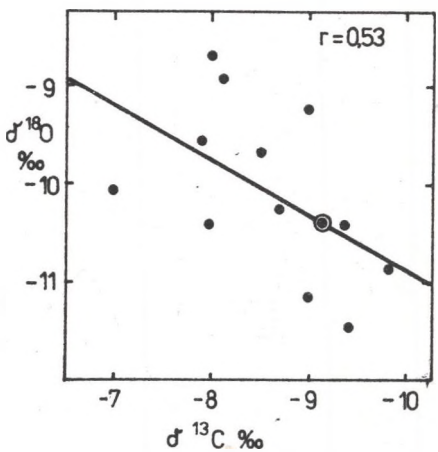

Fig. 4. Correlation between values of $\delta^{18}O$(PDB) and $\delta^{13}C$(PDB) in tufa samples

Rys. 4. Zależność między wartościami $\delta^{18}O$(PDB) i $\delta^{13}C$(PDB) w próbkach martwic

6. CONCLUSIONS

Investigated sediments in the Sieradowice site were deposited from the Late Glacial till end of the Atlantic phase. Calcareous tufa represent the most important series of sediments in the investigated profiles. Tufa sedimentation was favored by warm and wet climate during the Atlantic phase. Reliable dating of individual layers of calcareous tufa was possible because of presence of several layers enriched with organic matter which have lead to accurate determination of the value of apparent age. Precise radiocarbon dating of the whole sequence of sediments enables to set results of geologic and malacological studies in absolute time

scale and to formulate the following conclusions:

1. Before the Allerød the valleys in the described region were dissected due to an episode of vertical erosion.
2. The mentioned episode caused slope processes, expressed by the accumulation of deluvial sediments - calcareous silts and muds.
3. At the beginning of Holocene the mechanical denudation was gradually replaced by the chemical denudation, producing material for the development of calcareous sediments (tufa and travertines).
4. In the early stage of the Subboreal phase of Holocene, in the second phase of the vertical erosion the valley floor covered with a thick sequence of tufa and travertines was dissected and drained.
5. The succesion of molluscan assemblages indicate that during the Late Glacial, Lower Holocene and Middle Holocene the valley floor was periodically overflooded and drained, covered with meadows, marches and even water basins.
6. Isotopic composition of carbon in samples of calcareous tufa indicates that sedimentation of calcareous tufa took place in semilimnic conditions.
7. Changes of isotopic composition of oxygen indicate relatively high increase of temperature ca 9500 BP and warm period between 9500 BP to 5000 BP.

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HOLOCEŃSKIE MARTWICE WAPIENNE W SIERADOWICACH - GEOLOGIA, MALAKOLOGIA, RADIOCHRONOLOGIA I IZOTOPY STABILNE

Streszczenie

W obrębie badanego stanowiska wyróżniono trzy typy sekwencji litostratygraficznych osadów węglanowych. Badania terenowe doprowadziły do wyróżnienia epizodu erozji wgłębnej, po którym nastąpiło uruchomienie procesów stokowych. W następnej fazie dominujące znaczenie miała denudacja mechaniczna, stopniowo przechodząca w chemiczną. W okresie subboreal-nym nastąpił drugi epizod erozji wgłębnej. Dokładne pomiary wieku metodą ^{14}C próbek martwic i stowarzyszonej materii organicznej wykazują stałą wartość wieku pozornego, wynoszącą 910±120 lat. Sedymentacja serii martwic zachodziła od początku holocenu do końca okresu atlantyckiego. Wyniki badań malakologicznych wskazują, że począwszy od późnego glacjału aż do początku neoholocenu dno doliny było okresowo zatapiane i osuszane. Mierzone wartości $\delta^{13}C$ w próbkach martwic wykazują systematyczne zmiany z wiekiem osadu, co dowodzi, że sedymentacja martwic zachodziła w warunkach semilimnicznych. Wyniki pomiarów $\delta^{18}O$ wskazują na gwałtowne ocieplenie ok. 9500 BP i utrzymywanie się stosunkowo wysokiej temperatury aż do ok. 5000 BP.

ГОЛОЦЕНОВЫЕ ИЗВЕСТНЯКОВЫЕ ТУФЫ ИЗ С. СЕРАДОВИЦЕ - ГЕОЛОГИЯ, МАЛАКОЛОГИЯ, РАДИОХРОНОЛОГИЯ И СТАБИЛЬНЫЕ ИЗОТОПЫ

Резюме

В исследованном разрезе обнаружили три типы литостратиграфических последовательностей известняковых осадков. Геологические разведки привели к выделению эпизода эрозии и следующих скоточных процессов. В следующей фазе истинное значение имели процессы механической и химической денудации. В суббореальном периоде выступил второй эпизод эрозии. Точные определения возраста радиоуглеродным методом, проведены на образцах известняковых туфов и сопутствующего органического вещества привели к определению величины кажущего возраста известняковых осадков, равной 910±120

лет. Процесс осадконакопления известняковых туфов продолжался с начала голоцена до конца атлантического периода. Результаты малакологических исследований показывают, что в рассматриваемом интервале времени дно долины было периодически заливано водой и осушано. Измеренные значения $\delta^{13}C$ в образцах известняковых туфов проявляют систематическую изменчивост доказывая, что накопление известняковых осадков происходило в почти озерных условиах. Результаты измерений $\delta^{18}O$ доказывают существование резкого потепления климата проблизительно 9500 лето тому назад и сохранение релятивно высокой температуры до почти 5000 лет тому назад.