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## RADIOCARBON AGE OF HOLOCENE CALCAREOUS SEDIMENTS IN EXPOSURE IN RUDAWA (CRACOW UPLAND)

**Summary.** Calcareous sediments occurring in natural outcrop in Rudawa consist of calcareous tufa and carbonate muds with intercalations of peat and peaty clay.  $^{14}\text{C}$  age determinations and  $\delta^{13}\text{C}$  measurements on carbonate samples with  $^{14}\text{C}$  dating of associated organic matter indicate deposition of calcareous series during the Atlantic phase, with the episode of erosion at its end.

### 1. INTRODUCTION

Holocene calcareous tufa occurring in valley of the Raclawka river and its affluent stream Szklarka are known for a long time (Zareczny, 1894) and in recent years were studied by several authors (Alexandrowicz, 1983; Szulc, 1986; Pazdur et al, 1987, in print). Recent field studies have also proved the occurrence of calcareous tufa in the lower course of Raclawka valley, on area of the Krzeszowice Through ca 2 km north of the church in Rudawa. Profile with calcareous tufa sediments is exposed in natural outcrop on eastern bank of river, in lower part of terrace 7 m high. Sediments of the studied profile indicate high variability of natural conditions of sedimentation in the past.

Carbonate sediments, and first of all calcareous tufa, occurring in investigated profile, belong to the class of sediments for which the  $^{14}\text{C}$  dating methodology is not completely elaborated till now. Inorganic carbon of calcareous tufa consists of old (inactive, i. e. free of  $^{14}\text{C}$ ) carbon from leaching of bedrock, and of biogenic carbon with the  $^{14}\text{C}$  activity at the moment deposition close to mean  $^{14}\text{C}$  activity of land vegetation. Relative amounts of inactive and active carbon in carbonate sediment is influenced by the type of bedrock and the whole cycle of processes which occur during leaching of bedrock limestones and marls by groundwater, and in consequence lead to isotopic fractionation. Moreover,

additional fractionation of carbon isotopes occurs during deposition of carbonate sediments. As was shown by numerous studies (see for example Usdowski et al, 1979; Szulc, 1984), sedimentation of calcareous tufa is caused by decrease of the amount of  $\text{CO}_2$  dissolved in water. This may be diffusional escape of  $\text{CO}_2$  and photosynthesis of hygrophytes. Mentioned processes of isotopic fractionation lead in final effect to serious difficulties in accurate determination of  $^{14}\text{C}$  concentration of carbonate sediments at the moment of deposition. In spite of this, in profiles incorporating both calcareous tufa and organic levels, radiocarbon age of tufa horizons may be determined though the errors associated with estimated  $^{14}\text{C}$  dates of tufa samples are, as rule, several times greater than typical laboratory errors of the radiocarbon dating method. The profile in Rudawa discussed in the present article belongs to this class.

## 2. DESCRIPTION OF THE PROFILE

Schematical cross-section of the sediments occurring in the outcrop is shown in Fig. 1. High variability of sediment types in whole profile, and particularly at depth from 1 m to 1.5 m, is characteristic feature. Basal part of profile, at the present level of the Raclawka river is built of limestone gravels mixed with silts and is overlain with 0.7 m thick series of ash-coloured muds with rusty streaks. In the next part of profile occurs a series of whitish-grey calcareous tufa which in top of series glide into muds with admixture of carbonate. Within this series there are three intercalations of thin organic horizons in form of peat or peaty clay layers 5 to 7 cm thick. Content of  $\text{CaCO}_3$  in calcareous tufa ranges from 90% (sample Rd4) to 79% (sample Rd5), while in overlying silts is equal to ca 5% (sample Rd 7). This series is overlain by dark-brown peaty silts (organic muds) of total thickness 1.2 m, with few pottery fragments in its middle part. At the top of profile occur 3.5 m thick yellowish-grey loessy silts (so called agricultural muds).

## 3. LABORATORY METHODS

Radiocarbon age determinations were performed on peat or peaty silt samples, as well as on organic and carbonate fractions of calcareous tufa samples. Sampling places and sample codes are indicated in Fig. 1. In all samples except Rd5 there was enough amount of organic matter for  $^{14}\text{C}$  age determination. All radiocarbon dates, normalized to  $\delta^{13}\text{C} = -25\text{‰}$  according to recommendations of Stuiver and Polach (1977), with corresponding measured values of  $\delta^{13}\text{C}$ , are listed in Table 1. Measurements of  $\delta^{13}\text{C}$  were performed on mass spectrometer MI1305 at the Institute of Physics, Maria Curie Skłodowska University in Lublin. Values of  $\delta^{13}\text{C}$  of organic samples were not measured and were all assumed as equal to  $-25\text{‰}$ . In the last column of Table 1 are given values of true age  $T_{\text{pr}}$  of dated samples. For tufa samples containing organic matter the correspon-

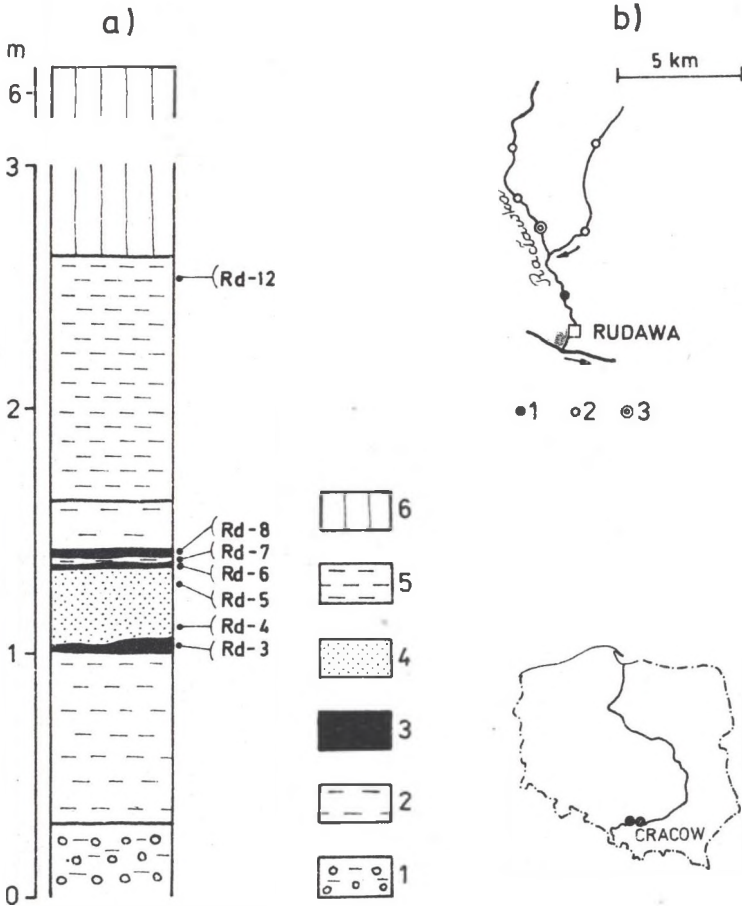


Fig.1. Schematic profile of sediments in the studied outcrop in Rudawa. 1 - gravels, 2 - silts, 3 - peat and peaty clays, 4 - calcareous tufa, 5 - peaty silts (organic mud), 6 - loessy silts (arable mud). B - investigated localities: 1 - described profile, 2 - profiles studied by S. W. Alexandrowicz (1983), 3 - main outcrop in Raciawka valley

Rys. 1. Schematyczny profil osadów w odsłonięciu w Rudawie: 1 - żwiry, 2 - mulki, 3 - torfy i muly torfiaste, 4 - martwice wapienne, 5 - mulki torfiaste (mady organiczne), 6 - mulki lessopodobne (mady rolnicze). B: Badane stanowiska osadów czwartorzędowych: 1 - profil opisany w niniejszej pracy, 2 - profile badane przez S. W. Alexandrowicza, 3 - główna odkrywka w dolinie Raciawki

ding value of  $^{14}\text{C}$  age of organic fraction  $T_{\text{org}}$  is accepted as true age  $T_{\text{pr}}$ . For sample Rd5, collected from topmost level of tufa series, direct determination of  $T_{\text{pr}}$  was not possible because of minute amount of organic matter. However, the knowledge of the true age of this sample is of primary importance for correct interpretation of other  $^{14}\text{C}$  dates from this profile because of age inversion of  $^{14}\text{C}$  dates of samples Rd4, Rd6 and Rd7. Differences between  $^{14}\text{C}$  dates of samples Rd6 and Rd7 and the  $^{14}\text{C}$  date of sample Rd4 significantly exceed quoted errors of age measurements, so we must conclude that observed inversion of  $^{14}\text{C}$  ages is caused by redeposition of levels containing samples Rd6 and Rd7. In consequence,

Table 1

Results of measurements of  $^{14}\text{C}$  age of sediments  
from the studied profile

Sample	Lab.no.	F	Type	Age yr BP	$\delta^{13}\text{C}$	$T_{\text{app}}$ yr	$T_{\text{pr}}$
Rd 12	Gd-4062	O	PS	2930 $\pm$ 150			2930 $\pm$ 150
Rd 8	Gd-2447	O	PT	5260 $\pm$ 110			5260 $\pm$ 110
Rd 7	Gd-4061	O	ST	7440 $\pm$ 150			7440 $\pm$ 150
	Gd-3226	C		8880 $\pm$ 80	-8.87	1440 $\pm$ 160	7440 $\pm$ 150
Rd 6	Gd-2446	O	PT	7250 $\pm$ 140			7250 $\pm$ 140
Rd 5	Gd-3227	C	CT	10720 $\pm$ 70	-8.29	(5580 $\pm$ 460)	5140 $\pm$ 470
Rd 4	Gd-2461	O	CT	6140 $\pm$ 100			6140 $\pm$ 100
	Gd-3216	C		10970 $\pm$ 70	-9.20	4830 $\pm$ 120	6140 $\pm$ 100
Rd 3	Gd-3166	O	PT	7630 $\pm$ 70			7630 $\pm$ 70

F = dated fraction; O - organic fraction of sample, C - carbonate fraction of sample; Sample types: PS - peaty silts, PT - peat and peaty clays, ST - silts, CT - calcareous tufa.

the knowledge of true age of sample Rd5 should help to decide if redeposition is limited exclusively to samples Rd6 and Rd7 or the layer of calcareous tufa, represented by samples Rd4 and Rd5, was also reworked.

#### 4. DISCUSSION

True age of tufa sample Rd5 may be determined by comparison with results obtained during studies on  $^{14}\text{C}$  dating of calcareous tufa sediments, in a similar way as other profiles of tufa sediments (Pazdur, 1987a). Radiocarbon dating of calcareous tufa leads to serious difficulties (Pazdur, Pazdur, 1986b; Thorpe et al, 1981) caused mainly by unknown value of initial  $^{14}\text{C}$  activity of carbonate at the moment of its deposition. This value, determined by the course of sedimentation and dependent also on the type of tufa (Pazdur, 1987a) is reflected in observed value

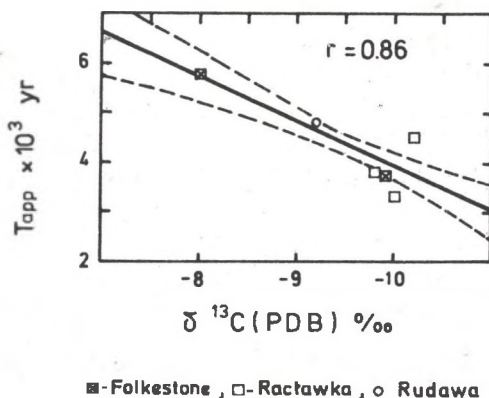


Fig. 2. Dependence of apparent age  $T_{app}$  upon  $\delta^{13}\text{C}$ . Experimental data include values from tufa profiles in Folkstone (Thorpe et al, 1981), Raclawka valley (Pazdur et al, 1987) and single value obtained on sample Rd 4 from studied profile in Rudawa (see Fig. 1). Solid line - least squares line, dashed line indicate 10% error limits for  $T_{app}$ . Single distinctly outlying result from the Folkstone profile ( $T_{app}=580 \text{ yr}$ ,  $\delta^{13}\text{C}=-11.30\text{‰}$ ) is not shown in this Figure and does not enter into calculations

Rys. 2. Zależność wieku pozornego  $T_{app}$  od  $\delta^{13}\text{C}$ . Dane eksperymentalne zawierają wartości z profilu murtwic w Folkstone (Thorpe et al, 1981), z Doliny Raclawki (Pazdur et al, 1987) oraz pojedynczą wartość dla próbki Rd4 z badanego profilu. Linia ciągłą oznaczono prostą najmniejszych kwadratów, linie przerywane oznaczają przedziały błędów (10%) wartości  $T_{app}$ . Wyraźnie odstająca wartość otrzymana w profilu Folkstone ( $T_{app}=580 \text{ yr}$ ,  $\delta^{13}\text{C}=-11.30\text{‰}$ ) nie została pokazana na rysunku i nie została uwzględniona w obliczeniach

of the apparent age  $T_{app}$  of carbonate fraction of tufa samples (Pazdur et al, 1987; Pazdur, 1987a). Apparent age  $T_{app}$  is defined as difference of  $^{14}\text{C}$  ages of carbonate fraction ( $T_c$ ) and organic fraction ( $T_{org}$ ) of sample, i. e.

$$T_{app} = T_c - T_{org}$$

This definition is valid under assumption that the value  $T_{org}$  determines strictly the moment of sedimentation.

For correct estimation of the true age of calcareous tufa sample we should know first if the value of apparent age in the studied profile can

be regarded constant or not (Pazdur, 1987a). The constancy of  $T_{app}$  in the profile is indicated by values of  $\delta^{13}C$  of individual samples from the profile.

For sample Rd4 collected from basal layer of tufa series the value of apparent age is equal to  $4830 \pm 120$  yr, while  $\delta^{13}C = -9.20\text{‰}$ . This relatively high value is similar to the values of  $T_{app}$  estimated for calcareous tufa in the well-known classical outcrop in the Racławka valley (Szulc, 1986; Pazdur et al, 1987). Tufa sediments occurring in this profile consist mostly of deposits of highly energetic turbulent water flow. Similar high values of  $T_{app}$  were observed by Thorpe et al (1981) in profile of tufa sediments in Folkestone (southern England). The values of  $T_{app}$  from these two sites (i.e. Folkestone and Racławka) are shown in Fig. 2 in function of corresponding values of  $\delta^{13}C$  together with above mentioned value for sample Rd4. Resulting dependence of  $T_{app}$  upon  $\delta^{13}C$  is described by least squares line

$$T_{app} = (13.70 \pm 2.79) \pm (0.98 \pm 0.29) \delta^{13}C.$$

Correlation coefficient of  $T_{app}$  and  $\delta^{13}C$  is equal 0.86. Measured value of  $\delta^{13}C$  of Rd5 is equal to  $-8.29\text{‰}$ , and the value of apparent age of this sample, estimated from above equation, is equal to  $5580 \pm 160$  yr. True age of sample Rd5 is therefore equal to  $5140 \pm 770$  BP, and in fact coincides with measured age of sample Rd8, equal to  $5260 \pm 110$  BP.

## 5. CONCLUSIONS

Deposition of series of calcareous tufa and peats in the studied profile was lasted during whole Atlantic phase, from  $7630 \pm 70$  till  $5260 \pm 110$  BP, i.e. shorter than in the classical profile in the upper part of the Racławka valley, where calcareous tufa were deposited since  $7280 \pm 350$  till  $1970 \pm 350$  BP (Pazdur et al, 1987). The beginning of calcareous tufa sedimentation coincides with the Holocene climatic optimum (as determined by  $^{14}C$  date of sample Rd4 ( $6140 \pm 100$  BP), while the end of tufa deposition coincides with the end of Atlantic phase ( $5140 \pm 170$  BP). Coincidence of  $^{14}C$  dates, marking the end of tufa deposition (sample Rd5;  $5140 \pm 170$  BP) and beginning of deposition of peaty silts (sample Rd8;  $5260 \pm 110$  BP) seems to support the authenticity of series of calcareous tufa. The presence of deposits dated to older part of the Atlantic phase in the upper part of profile (dates:  $7250 \pm 140$  BP,  $7440 \pm 150$  BP) leads to conclusion that there was an episode of erosion at the end of the Atlantic phase, resulting in deposition of reworked peaty and limy silts. Deposition of peaty silts has lasted till the end of the Subboreal phase, as indicated by  $^{14}C$  date of sample Rd12 ( $2930 \pm 150$  BP) from top of organic series. Similar feature was noted in the Sancygniówka valley, where the end of organic series deposition is dated to ca 3090 BP (Snieszko, 1985).



Not earlier than at the end of the Subboreal phase the upper part of the Racławka river drainage basin was deforested in result of extensive human agricultural activity. This deforestation caused rapid erosion of loessy cover and deposition of loessy agricultural mud. This process is well known in the vicinity of Cracow and in the Nida Basin. In the Sancygniówka valley the beginning of sedimentation of loessy muds is estimated to ca 2700 BP (Snieszko, 1986), i.e. similarly as in the investigated site. In Ojcow locality in the Prądnik valley the formation of typical loessy muds has began not earlier than ca 1510 BP (Alexandrowicz, in print), though silts deposited in this locality since 2280 BP show certain similarity to loessy muds.

#### ACKNOWLEDGEMENTS

The authors are indebted to Dr Romuald Awiuk for his help in stable isotope measurements. This study was supported in part by grant from the Central Research Project CPBP O3.13 to the Radiocarbon Laboratory. Radiocarbon dates were sponsored by the Geological Enterprise in Cracow.

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Wpłynęło do Redakcji 7 marca 1987 r

## WIEK RADIOWĘGLOWY HOLOCENSKICH OSADÓW WĘGLANOWYCH Z ODSŁONIĘCIA W RUDAWE

### Streszczenie

Osady węglanowe występujące w naturalnym odsłonięciu w Rudawie zawierają serię martwic wapiennych i mulków węglanowych z wkładkami torfu i mułków torfiastych. Pomiar  $^{14}\text{C}$  i  $\delta^{13}\text{C}$  w osadach węglanowych oraz oznaczenia wieku metodą  $^{14}\text{C}$  stowarzyszonej z węglanami materii organicznej wskazują, że tworzenie tej serii osadów trwało przez prawie cały okres atlantycki, przy czym pod koniec tego okresu wystąpił proces erozji.

## РАДИОУГЛЕРОДНЫЙ ВОЗРАСТ ГОЛОЦЕНОВЫХ ИЗВЕСТНЯКОВЫХ ТУФОВ ИЗ С. РУДАВА

### Резюме

Карбонатные осадки выступающие в натуральном открытии вблизи села Рудава содержат серию карбонатных илов и известняковых туфов. Определения концентрации радиоуглерода и стабильного изотопа  $^{13}\text{C}$ , проведены для образцов карбоната, сравнены с результатами определения возраста органического вещества. Получены результаты указывают что процесс осадконакопления карбонатной серии имел место через почти целый атлантический период. Около конца этого периода выступила фаза эрозии.