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CALIBRATED RADIOCARBON CHRONOLOGY OF ANNUALLY LAMINATED SEDIMENTS
FROM THE GOŚCIĄŻ LAKE

   Abstract. Annually laminated sediments in the Gościąż Lake cover
time interval of more than 12.500 yr. Radiocarbon age determinations
and $\delta^{13}C$ measurements were performed on both organic and carbo-
nate fraction collected at different depth of core G85. The core is
isotopically clearly bipartite: the value of apparent age in the
uppermost part is estimated to 1600 yr. while in the lowermost part
to ca 1400 yr. Corrected and calibrated radiocarbon dates of organic
fraction of samples from the core indicate strictly one-to-one
correspondence to the number of laminae.

1. INTRODUCTION

In recent years an increasing interest is observed in application of
isotopic methods to study of freshwater carbonate sediments. In particu-
lar lake marls. Investigations of changes of stable isotopes ^{13}C and ^{18}O
in lake marl profiles enable the reconstruction of geochemical. hydrolo-
gical and biological conditions of sedimentation and lead to the recon-
struction of paleoclimate. For any method of paleoclimatic reconstruction
an absolute and reliable time scale is needed. As the sedimentation of
lake marls in the region of the temperate zone is limited to the time
interval covering the last 15.000 years. the most suitable time scale is
provided by the radiocarbon method. This method has been applied to
dating lake marl sediments since many years (Stuiver. 1970: Geyh et al.
1971). but in recent years is used especially widely to dating either
bulk organic and /or carbonate fraction of sediment using conventional
counting methods (Pazdur. Pazdur. 1980; Turner et al. 1984; Srdoc et al.

1986; Pazdur et al. 1987) or selected macrofossils separated from the
ediment with the AMS techniques (Lister et al. 1984; Siegenthaler et al.
1984; Andree et al. 1986; Fowler et al. 1986).

Application of conventional ^{14}C dating method to dating of both carbo-
nate and organic fraction of lake sediment is difficult because initial
^{14}C activity (A_0) of sediment is as a rule unknown and may differ signi-
ficantly from the corresponding value of contemporary biosphere. There
are two main reasons of this difference: first, total dissolved inorganic
carbon (DIC) in lake water incorporates undetermined amounts of carbon
from different reservoirs with different concentration ^{14}C ranging from 0
to 100 pmc and different values of $\delta^{13}C$, ranging from ca $0^0/oo$ (ma-
rine mineral carbonate) to ca $-27^0/oo$ (dissolved CO_2 from plant respira-
tion and decay). Moreover, the sedimentation of lake marl is influenced
in different ways by the presence of water plancton and bacteria and
higher water plants. All these factors determine finally the fractiona-
tion of carbon isotopes, which is revealed by variable values of $\delta^{13}C$
and A_0 in both organic and carbonate fraction of lake sediment.

There are three main sources of organic carbon in lake sediments
(Pearson, Coplen, 1978); lacustrine plancton (with $\delta^{13}C=-30^0/oo$),
lacustrine plants ($\delta^{13}C=-21^0/oo$) and terrestrial plants ($\delta^{13}C=-24^0/oo$). In consequence, different values of A_0 are observed not only in
total carbonate and organic fraction, but also in specific components of
these fractions (marl and molluscs. humic and fulvic acids, lipids,
cellulose, aminoacids, etc; Turner et al. 1984; Fowler et al. 1986).

The most accurate chronostratigraphy of lake sediments may be ob-
tained on profiles of laminated sediments with annual lamination. Already
described profiles of annually laminated sediments from Europe cover
various time intervals of Late Glacial and Holocene. Numerous profiles of
laminated sediments are known from Sweden and Finland (Saarnisto, 1986)
with the longest sequence of ca 9500 laminae from Lake Valkiajärvi,
Finland (Saarnisto, 1985), but especially long sequences were found in
Lake Van, Turkey (ca 10,400 laminae; Kempe, Degens, 1979) and in Lake of
the Clouds in Minnesota, USA (ca 9 500 laminae; Anthony, 1977).

Laminated sediments of Lake Gościąż, containing ca 12,500 couplets is
actually the longest known sequence, covering significant part of the
Late Glacial and whole Holocene, and offers therefore the unique opportu-
nity for detailed palaeoecological and palaeoclimatical reconstruction.
An outline of an interdisciplinary research project has been presented by
Ralska-Jasiewiczowa et al (1987). In addition to obvious significance of
this profile for Quaternary studies, which can hardly be overvalued, this
profile is of special interest for physical dating methods as it may be
used to study natural variations of ^{14}C concentration beyond the already
elaborated dendrochronological time scales. If precise correlation of the
number of couplets with astronomical time scale will be possible, the

measurements of ^{14}C concentration in macrofossils selected from indivi-
dual laminae would be used for calibration of the radiocarbon time scale.

This article is the second preliminary report on the chronology of
varved sediments from the Lake Gościąż. We present here the results of
^{14}C dating of 21 samples collected at various depths from core G85 taken
in 1985 by B. Wicik and K. Więckowski. In previous article (Pazdur et al,
1987) preliminary results with ^{14}C dates of 10 samples were reported.

2. LABORATORY METHODS AND RESULTS

Samples for dating were cut with knife from core G85 in form of 10
cm thick sections at various depths. First set of 10 samples was collec-
ted by M. F. Pazdur and K. Więckowski in December 1985. Those samples
were selected primarily from topmost and lowermost part of the core. This
set was next supplemented with two peat samples from basal parts of two
cores taken in April 1986 in eastern and western parts of Lake Gościąż.
Second set of samples was collected in December 1986 in order to supple-
ment the previous set, and especially to fill the gaps in the central
part of the core. Therefore, total set of dated samples consists of 21
sections of core G85, approximately uniformly distributed from depth 1.5
m to 15.5 m, and of two peat samples (G86W and G86E).

In laboratory partly crushed and homogenized samples were treated
with 8⁰/o HCl in a vacuum apparatus and CO_2 evolved from sample carbo-
nates was collected for ^{14}C dating. After completing of this step the
remaining insoluble residue was washed with distilled water, dried in an
electric oven and combusted in order to obtain CO_2 for dating total
organic matter. CO_2 obtained from both carbonate and organic fraction of
sample was purified in a standard way and then stored for at least four
weeks to achieve complete decay of ^{222}Rn. ^{14}C measurements were performed
using CO_2-filled proportional counters. Small aliquots of CO_2 were col-
lected for stable isotope determinations. Measurements of $\delta^{13}C$ were
performed on mass spectrometer MI1305 at the Mass Spectrometry Division
of the Institute of Physics, Maria Curie Skłodowska University in Lublin.

All results obtained till now are listed in Table 1. Radiocarbon
ages are presented as conventional ^{14}C dates, normalized to $\delta^{13}C=-$
25⁰/oo (Stuiver, Polach, 1977), using either measured or assumed values
of $\delta^{13}C$. Values of $\delta^{13}C$ of both carbonate and organic fractions
are quoted with respect to the PDB standard. Numbers of varves N corres-
ponding to dated samples were estimated from the graph prepared by K.
Więckowski (cf Ralska-Jasiewiczowa et al, 1987, Fig. 2). In several
samples the amount of CO_2 obtained after combustion of organic fraction
was very small. Those samples were dated on our small proportional coun-
ters (Pazdur, Walanus, 1986) after dilution with inactive CO_2 obtained
from combustion of pit coal. Resulting ^{14}C dates are therefore subjected

Table 1

Results of ^{14}C and ^{13}C measurements

Sample	Depth m	F a)	Lab. No.	Age yr BP	$\delta^{13}C$ o/oo(PDB)	N	T_{cal}
1	2	3	4	5	6	7	7
G85/10	1.5-1.6	C	Gd-2583	2100±90	-0.99		
		O	Gd-4066	1730±100	-30.24	150	130
G85/9	2.65-2.75	C	Gd-3230	2200±40	+1.20		
		O	Gd-2649	2340±80	-29.30	700	680
G85/8	3.05-3.15	C	Gd-5008	3660±50	(0±1) b)		
		O	Gd-2571	2730±120	-30.36	900	1050
G85/11	3.9-4.0	C	Gd-5082	3880±70	+1.26		
		O	Gd-2620	3050±80	-28.55	1500	1340
G85/12	4.9-5.0	C	Gd-2618	4680±120	+1.61		
		O	Gd-2621	3800±90	-30.17	2100	2250
G85/7	6.1-6.2	C	Gd-3277	5350±50	-1.20		
		O	Gd-2527	4230±120	-31.52	2900	2750
G85/13	6.9-7.0	C	Gd-5086	5690±80	+0.49		
		O	Gd-2623	5040±110	-30.67	3900	3700
G85/14	7.9-8.0	C	Gd-5094	6280±80	+0.35		
		O	Gd-2626	5530±100	-30.63	4800	4410
G85/15	8.9-9.0	C	Gd-5088	7390±70	-0.04		
		O	Gd-4100	6320±120	-31.37	5400	5460
G85/6	9.60-9.65	C	Gd-1992	7930±70	-1.05		
		O	Gd-2564	6840±390	(-32) b)	6000	5960
G85/16	10.0-10.1	C	Gd-5091	8190±100	-0.49		
		O	Gd-2624	7630±120	-31.23	6500	6860
G85/17	10.45-10.55	C	Gd-5095	8420±90	-2.16		
		O	Gd-4105	7880±150	-31.59	7000	7200
G85/18	11.0-11.1	C	Gd-5096	8800±70	-1.80		
		O	-	-	-	7600	-
G85/5	11.45-11.50	C	Gd-3231	9160±50	-4.54		
		O	Gd-2476	8960±120	(-32) b)	8200	-
G85/19	12.0-12.1	C	Gd-5098	10230±90	-6.05		
		O	-	-	-32.78	8900	-
G85/20	12.5-12.6	C	Gd-2627	10710±150	-6.38		
		O	Gd-4103	10240±250	-34.08	9400	9800
G85/21	13.0-13.1	C	Gd-5099	10830±80	-6.58		
		O	Gd-4104	10790±220	-34.34	9900	10300
G85/4	13.5-13.55	C	Gd-3225	10640±60	-8.29		

Table 1 (contd)

1	2	3	4	5	6	7	7
		O	Gd-2464	10640±100	-35.44	10400	10300
G85/3	14.45-14.50	C	Gd-3223	12100±90	-6.96		
		O	Gd-4067	11270±350	-34.23	11400	10900
G85/2	15.00-15.05	C	Gd-4007	12570±130	-7.82		
		O	Gd-4013	11980±430	(-33)[b]	11800	11700
G85/1	15.40-15.50	C	Gd-5048	13480±120	-8.02		
		O	Gd-2584	12650±140	-33.19	12400	12400
G86W		O	Gd-5059	12120±110	-		
G86E		O	Gd-3305	11960±80	-30.24		

[a]dated fraction: C-carbonate, O-organic; [b]estimated value

to relatively large errors, exceeding ±200 yr (samples G85/6R, G85/20R, G85/21R, G85/3R and G85/2R). The amount of CO_2 obtained from sample G85/19R was too small to be counted, so only $\delta^{13}C$ measurement was made on this gas. CO_2 from sample G85/18R was lost because of accidental damage of glass reservoir. Some samples were not subjected to $\delta^{13}C$ measurements, the values quoted in parentheses are estimated by approximated interpolation of observed trends.

3. DISCUSSION

All ^{14}C dates of organic and carbonate fractions are shown in Fig. 1 in function of depth. Error bars denote ±1σ standard deviations. There are several characteristic features of this plot, which should be noted: 1) very smooth and approximately linear dependence of organic fraction dates upon sampling depth; 2) approximately constant difference of ^{14}C dates of organic and carbonate fractions, equal to ca 1000 yr in significant part of core (at depths from 3 to 10 m); 3) slight but significant age inversion of both organic and carbonate fraction dates of sample G86/4 with respect to overlying sample G85/21; 4) clearly outlying value of carbonate fraction age of sample G85/9 (the only sample for which $T_C < T_{org}$).

The most important point for any further discussion of obtained ^{14}C dates includes estimation of the magnitude of ageying of ^{14}C dates caused by fractionation of carbon isotopes and resulting depletion of initial ^{14}C activity A_0 of sediment ($A_0 < 100$ pmc). This ageying is commonly described by the apparent age of sediment

$$T_{app} = -8033 \ln (A_0/100). \tag{1}$$

$$T_c \cdot T_{org} \quad (kyr\ BP)$$

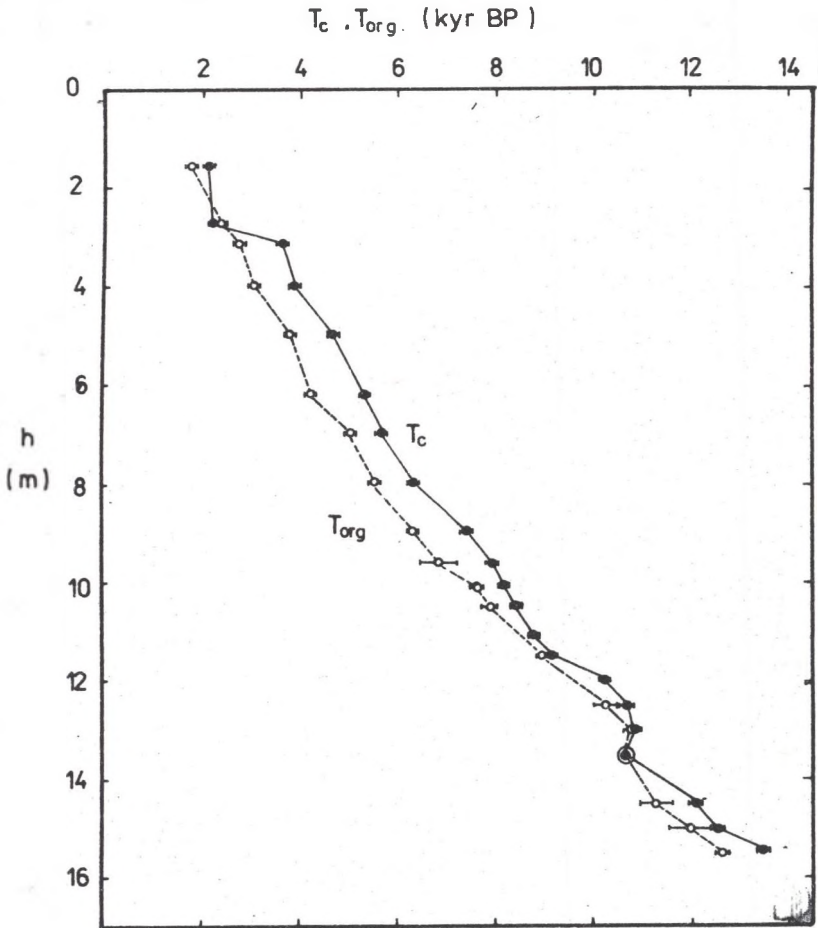Fig. 1. Conventional ^{14}C dates of organic and carbonate fraction in function of depth.

Rys. 1. Konwencjonalne daty radiowęglowe frakcji organicznej i węglanowej w funkcji głębokości.

Fig. 2. Conventional and calibrated [14] dates (a) and measured values of $\delta^{13}C$ in carbonate (b) and organic (c) fraction of lake sediments in function of the number of couplets N.

Rys. 2. Konwencjonalne i kalibrowane daty radiowęglowe (a) oraz zmierzone wartości $\delta^{13}C$ frakcji węglanowej (b) i organicznej (c) w funkcji liczby lamin.
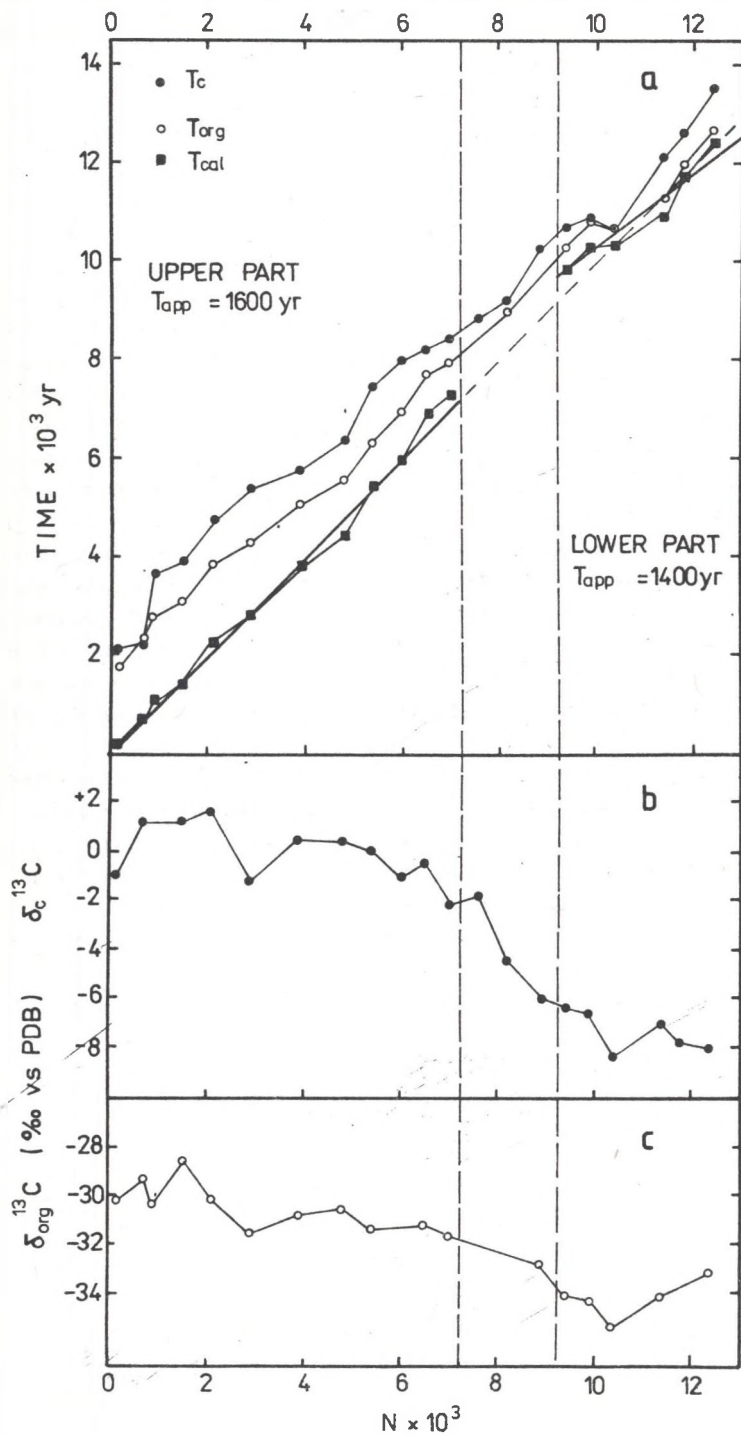
The magnitude of fractionation of carbon isotopes is indicated by the value of $\delta^{13}C$. As was shown in studies of calcareous tufa sediments (Pazdur, 1987), constant value of $\delta^{13}C$ in the profile indicates constant value of the apparent age. It seems reasonable to apply this statement also to calcareous lake sediments. ^{14}C dates and $\delta^{13}C$ values of both organic and carbonate fractions are shown in Fig. 2 in function of the number of couplets N. The values of $\delta_c^{13}C$ and $\delta_{org}^{13}C$ show characteristic changes in the profile, similar to those observed in other profiles of lake sediments (Mörner, Wallin, 1977). Observed variations of $\delta^{13}C$ in profile of lake sediments are controlled by a number of correlated factors, namely by changes in temperature and the rate od supply of molecular CO_2 in the lake water, changes of terrestial vegetation in the vicinity of lake, changes in organic productivity and hardeness of lake water, changes in relative production of submersed macrophytes and plancton, and, finally, by fermentation of lake mud (Hakansson, 1985).

The plot of $\delta_c^{13}C$ in function of the number of varves N (Fig. 2b) shows distinct secular trend, but three intervals of quite different behaviour may be distinguished. Similar features, though slightly supressed, may be also seen in plot of $\delta_{org}^{13}C$ (Fig. 2c). In the first interval (N<7000) the values of $\delta^{13}C$ show slight systematical changes with N with superposed distinct variations. In spite of this, values of both $\delta_c^{13}C$ and $\delta_{org}^{13}C$ in this time interval may be regarded as approximately constant. The second interval (7200<N<9400) is characterized by an abrupt change of $\delta_c^{13}C$, amounting to ca 5⁰/oo. Corresponding change of $\delta_{org}^{13}C$ is significantly lower and is equal to ca 2.5⁰/oo. In the third interval (N>9400) variations of $\delta^{13}C$ are similar as in the first one, and, consequently, the values of both $\delta_c^{13}C$ and $\delta_{org}^{13}C$ may be regarded as being approximately constant. Corresponding mean values of $\delta^{13}C$ of both organic and carbonate fraction in the first and third interval are quoted in Table 2. There is distinct correlation between $\delta_c^{13}C$ and $\delta_{org}^{13}C$, shown in Fig. 3. This correlation can be described by the least squares line

$$\delta_{org}^{13}C = (-30.51 \pm 0.23) + (0.500 \pm 0.052)\delta_c^{13}C \qquad (2)$$

with correlation coefficient r=0.932.

In our previous preliminary report (Pazdur et al, 1987) we have estimated the value of apparent age in the upper part of core G85 to 1600 yr. Corrected organic fraction dates obtained by substracting this value

$$T_{corr} = T_{org} - T_{app} = T_{org} - 1600 \qquad (3)$$

were then calibrated using recently published calibration tables (Pearson, Stuiver, 1986; Stuiver, Pearson, 1986; Pearson et al, 1986). Resulting calibrated dates are listed in the last column of Table 1 and are
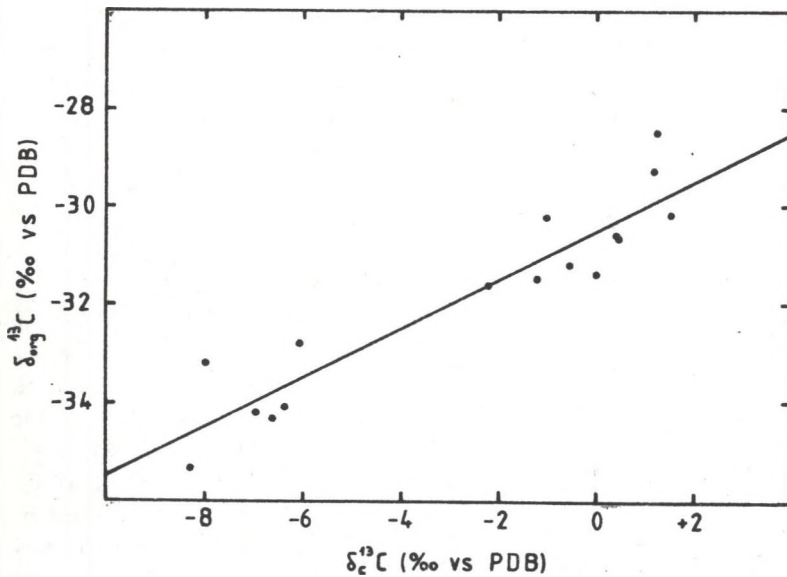
Fig. 3. Correlation between values of $\delta^{13}C$ in carbonate and organic fraction.

Rys. 3. Korelacja między wartościami $\delta^{13}C$ we frakcji węglanowej i organicznej.

Table 2

Mean values of $\delta_c^{13}C$ and $\delta_{org}^{13}C$ in the upper and lower part of core G85

Part of core	n_c	$\delta_c^{13}C$	n_o	$\delta_{org}^{13}C$
upper	12	-0.24 ± 1.24	11	-30.51 ± 0.95
lower	6	-7.34 ± 0.80	5	-34.25 ± 0.79

shown as black squares in Fig. 2a. These values may be now directly compared with the corresponding numbers of couplets. The least squares line which describes the dependence of T_{cal} upon N is equal to

$$T_{cal} = (-70\pm110) + (1.02\pm0.03)N \qquad (4)$$

and is shown as solid straight line in the left-hand part of Fig. 2a. The correlation coefficient is equal to 0.9967; mean scatter of experimental points with respect to the least squares line is equal to s=210 yr. Taking into account quoted values of errors of estimated coefficients

of the least squares line we can conclude that there is strictly one-to-
one correspondence between the number of couplets N and calibrated radio-
carbon dates in the upper part of core. This statement means that the
couplets represent really annual laminations in the time interval from ca
100 to ca 7000 calendric years before present.

     The value of apparent age in the lower part of the core G85 was in
our previous report estimated to ca 600 yr basing on comparison of orga-
nic fraction dates of sample G85/1 from the lowermost part of the core
with two ^{14}C dates of peat samples from basal parts of supplementary
cores G86E and G86W. With only four ^{14}C dates in this part of core and no
calibration curve available in the time interval from 9000 to 12,000 yr
BP we were not able to draw any further conclusions from these data. At
present the set of ^{14}C dates in this interval was supplemented by dating
two additional samples (G85/20 and G85/21; see Table 1). Much more impor-
tant fact is, however, in that with the publication of the Calibration
Issue of "Radiocarbon" (1986, vol. 28, No. 2B) a calibration curve of ^{14}C
dates in this time interval was made available (Stuiver et al, 1986).
This curve should be regarded as tentative one, especially if used as an
extension of the two "official" curves of G. W. Pearson and M. Stuiver.
Having in view tentative value of this curve we have used it to calibrate
corresponding corrected organic fraction dates T_{org} of samples from the
lower part of core G85. In the first attempt the corrected values of T_{org}
were calculated using formerly estimated value of T_{app} equal to 600 yr.
Resulting values of corrected and calibrated dates are compared with the
number of couplets N in Table 3. As is indicated by differences T_{cal}-N
listed in the last column of Table 3 such values can hardly be accepted;
calibrated ^{14}C dates are systematically shifted by ca 700 yr with respect
to the number of couplets N. Though several explanations of this discre-
pancy are possible (1-error in counting of the number of couplets, 2-
break in deposition, 3-systematic error of calibration curve), the most
probable source of this shift is in erroneous value of T_{app} used to
correct values of T_{org}. Therefore several trials were made to compare
values of T_{cal} obtained under assumption of the values of T_{app} ranging
from 1200 to 1600 yr. The best correlation between T_{cal} and N has been
obtained for T_{app}=1400 yr. Resulting values are quoted in Table 4; the
least squares line which approximates this relation has the form

$$T_{cal} = (2080 \pm 920) + (0.81 \pm 0.11)N, \qquad (5)$$

the coefficient of correlation r=0.964; residual dispersion of expe-
rimental points with respect to the least squares line (5) is equal to
s=290 yr. The obtained equation (5) seems not to confirm the existence of
strictly one-to-one correspondence between the calibrated ^{14}C dates and
the number of couplets N (which was found in the upper part of core). It
should be pointed, however, that the considered interval of time is

Table 3

Comparison of corrected and calibrated ^{14}C dates in the lower
part of core for T_{app}=600 yr with the number of couplets

Sample	N	T_{org}-600	T_{cal}	T_{cal-N}
G85/20	9,400	9,640	10,700	+1300
G85/21	9,900	10,190	11,300	+400
G85/4	10,400	10,040	11,100	+700
G85/3	11,400	10,670	11,800	+400
G85/2	11,800	11,380	12,600	+800
G85/1	12,400	12,050	13,000	+600

Table 4

Comparison of corrected and calibrated ^{14}C dates in the lower
part of core G85 for T_{app}=1400 yr with the number of couplets N

Sample	N	T_{org}-600	T_{cal}	T_{cal-N}
G85/20	9,400	8,840	9,800	+400
G85/21	9,900	9,340	10,300	+400
G85/4	10,400	9,240	10,300	-100
G85/3	11,400	9,870	10,900	-500
G85/2	11,800	10,580	11,700	-100
G85/1	12,400	11,250	12,400	0

relatively, short (ca 3000 yr), and, moreover the obtained least square
line is seriously influenced by the obvious anomaly of ^{14}C dates of
samples G85/4 and G85/21 (inversion of ^{14}C dates; see Fig. 1).

It appears, however, that the calibrated ^{14}C dates in the lower part
of the core fit strictly the dashed line obtained by extrapolation of the
least squares line from the upper part of core. Therefore the new least
squares line may be calculated using all data from both upper and lower
part of core. The equation of this line has the form

$$T_{cal} = (-8\pm110) + (1.00\pm0.02)N. \qquad (6)$$

Correlation coefficient r=1.00; standard dispersion of experimental

points with respect to line (6) is equal to 260 yr, i. e. slightly exceeds mean standard error of ^{14}C age determination of single sample. The plot this line cannot be distinguished from that corresponding to the upper part of core (shown in Fig. 2a).

4.   CONCLUSIONS

Presented results of ^{14}C and ^{13}C measurements in 21 samples from core G85 and their analysis lead to the following conclusions:
1. lamination of sediments in the investigated core is really annual, as is indicated by strictly one-to-one correspondence between calibrated radiocarbon dates and the number of couplets in the whole core covering time interval from ca 12,400 to about 150 yr BP.
2. Core is isotopically bipartite, as is shown by the measured values of $\delta^{13}C$ and estimated values of the apparent age.
3. The values of calibrated ^{14}C dates of two peat samples (G85E and G85W), exceeding 13,000 yr BP may indicate that the sedimentation of organic deposits in the lake basin had started ca 500 yr earlier, i. e. at the Bolling phase.

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CHRONOLOGIA RADIOWĘGLOWA ROCZNIE LAMINOWANYCH OSADÓW Z JEZIORA GOSCIĄŻ W SWIETLE KALIBRACJI RADIOWĘGLOWEJ SKALI CZASU

Streszczenie

Rytmicznie warstwowane osady z Jeziora Gościąż obejmują przedział czasu ponad 12,500 lat. Oznaczenia wieku metodą [14]C i pomiary $\delta^{13}C$ wykonano na frakcji organicznej i węglanowej 21 próbek pobranych z różnych głębokości rdzenia G85. Wyniki badań izotopowych wskazują na wyraźną dwudzielność rdzenia; wartość wieku pozornego w górnej części rdzenia wynosi 1600 lat, zaś w części dolnej 140 lat. Skorygowane i kalibrowane daty radioweglowe wykazują ściśle jednoznaczną korelację z liczbą lamin rocznych.

РАДИОУГЛЕРОДНАЯ ХРОНОЛОГИЯ ГОДИЧНО РАССЛОЕННЫХ ОСАДКОВ ИЗ ОЗЕРА ГОСЦИОНЖ (С УЧЕТОМ КАЛИБРАЦИИ РАДИОУГЛЕРОДНОГО ВОЗРАСТА)

Резюме

Ритмически расслоенные осадки из озера Госционж охватывают интервал времени более 12000 лет. В докладе представлены результаты определений возраста и измерений $\delta^{13}C$. Измерения проводили на общем органическом веществе и карбонатах из 21 образцов отобранных на разных глубинах колон-

ки G85. Полученные результаты изотопных исследований свидетельствуют,
что секвенциа осадков состоит из двух частей. Величина кажущего возраста
в верхней части колонки равна 1600 лет, в нижней части 1400 лет. Доказа-
но, что результаты определения радиоуглеродного возраста, при учтении
кажущего вазраста и калибровки радиоуглеродной шкалы, проявляют взаимно
однозначное ответствие с числом слоев.