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UNIVERSITY OF KIEL RADIOCARBON MEASUREMENTS V

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Measurements reported in this paper were obtained with the 4.5 L and 3 L CO_2 counters, details of which were given earlier (Radiocarbon, v. 11, p. 423). The automatic data recording system built in 1968 (Hänsel, 1968) is now operating for both counting apparatus. For each one the counts of the guard counters ring (A counts), the total counts of the C^{14} counter (B counts), the coincidences of central and guard ring counter (AB counts), and the anticoincidences ($\overline{A}$B counts) are tape punched every 100th minute. By an ALGOL program, all counts are checked first for large disturbances. Secondly, equation $B = AB + \overline{A}B$ must hold (as an integral check for proper operation of logical circuitry and the data recording system) and finally statistical compatibility is examined before age and other data for the actual counting apparatus are computed. This detailed check of counting rates by computer has proved to be very efficient to yield reliable long-term measurements.

In 1969, a new technique for CO_2 gas purification was developed. In the former (Radiocarbon, v. 8, 1966, p. 235; Münnich, 1957a) CO_2 was absorbed in a NH_4OH–$CaCL_2$ solution and precipitated as $CaCO_3$. CO_2 was liberated again by sulfuric acid and dried. Gas quality, though generally good, in some cases showed great variations and purification had to be repeated. At the end of 1968, after 3 years of steady operation, ammonium carbamate contamination of glass tubes and bulbs prevented efficient gas purification. The use of active charcoal seems to be a reliable, straightforward purification technique.

CO_2 is prepared by combustion, using two quartz tubes as described by de Vries (1953). Oxidation is performed by hot Pt-Asbestos and CuO (600°C). A first purification step is accomplished by bubbling the gas through solutions of potassium permanganate, potassium bichromate, and a mixture of conc. sulfuric acid and diphenylamine (for binding nitrogen oxides). The gas is dried in a two-stage cold trap at −78°C and then frozen in two liquid air traps under vacuum pumping.

For secondary purification CO_2 slowly enters a stainless steel cold trap at liquid air temperature filled with 50 g of active charcoal. The trap outlet is vacuum pumped. When all the gas (ca. 5 L atm) is adsorbed, the inlet valve is shut and the trapped CO_2 is allowed to evaporate slowly, being trapped again in two succeeding vacuum pumped liquid air traps. Evaporation is completed by heating the charcoal to 100°C for about half an hour. CO_2, obtained in this way, does not require further purification or drying. Gas yield is better than 99.5%. Charcoal is regenerated by degassing at 750°C under vacuum. Up to January 1970, this process was applied to more than 90 gas samples; excellent counter gases have been obtained. Charcoal filling has not been replaced at this time. The second purification step is completed within two hours. Outgassing requires about the same length of time and often runs overnight.

Age calculations are based on 95% of NBS oxalic acid standard activity with modern value A.D. 1950. Results are calculated using Libby half-life and are given in the B.P. scale. Errors correspond to 1 σ variation of sample net counting rate including statistics of modern standard and background. Uncertainty in C^{14} half-life and in secular variations have not been taken into account. Unless otherwise stated dates are not corrected for isotopic fractionation.

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I. GEOLOGIC SAMPLES

Segeberger See series

Lake sediments of the Grosser Segeberger See (53° 56.6′ N Lat, 10° 19.4′ E Long), NW Germany. Coll. and subm. 1967 by F. R. Averdieck, Inst. f. Ur- und Frühgeschichte, Univ. Kiel, who also made pollen analysis. Basin of lake was formed by glaciers during last glaciation (Würm). In subsequent late glacial and post-glacial, detritus gyttja sediments up to 15 m thick were deposited. Samples were taken by a Livingstone corer (4 cms diam.). Except the basal meters of sediment, which consisted of pure clay, all layers contained enough organic material for C^{14} measurement within 6 to 12 cms. Carbonate was removed by chloric acid. Samples were taken ca. every 30 cm, and pollen were analyzed every 2.5 cm. Thus we have a complete pollen diagram of the whole post-glacial with a fairly close set of C^{14} dates. In this region, analogous measurements on bogs do not reach beyond 5000 or 6000 yr B.P.

General Comment: by linear extrapolation of Libby values of the upper layers, we get an apparent age of 940 yr B.P. for contemporary sediment. Also some pollen analytic boundaries show about the same age difference when compared with corresponding layers in bogs. C^{13} values show no severe isotopic fractionation between atmospheric CO_2 and sediments; the discrepancy may be explained by the assumption (cf. Münnich, 1957b), that in the lake part of dead carbon is recycled according to

$$CO_3^{--} + CO_2 + H_2O \rightarrow HCO_3^{-}.$$

We assumed a constant fraction of dead carbon in the organic part of lake sediments and tested different values for this fraction to get the correct age of 0 yr B.P. for contemporary sediments. With 10% dead carbon, the measured Libby age (Table 1, col. 4) is 800 yr older than the real Libby age (col. 5). These values were corrected dendrochronologically until 6000 B.P. according to pub. tree-ring data (Willkomm, 1968). The straight line representing the least squares fit to these "astro-

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TABLE 1
C^{14} dates of Segeberger See sediments
Age calculations were made without δC^{13} corrections.

C^{14} – Labor Kiel		Grosser Segeberger See			KI – 235	
1	2	3	4		5	6	
Lab. no.	Depth within sediment m	C^{13} ‰	Libby age measured, ± 1σ B.P.		Libby age "real" B.P.	Range of dendrochronol. corr. age (from 5) A.D./B.P.	
235.01	13.90		12690 ±	130	11890		
02	13.67	–25	11890	95	11090		
03	13.34		12290	340	11490		
04	12.94		11320	120	10520		
05	12.63		10750	280	9950		
06	12.27		10770	280	9970		
08	11.64		10180	390	9380		
09	11.36		10670	170	9870		
10	11.14		9950	130	9150		
11	10.85		9560	75	8760		
12	10.56		9250	100	8450		
13	10.22		8760	55	7960		
14	9.94		8020	50	7220		
16	9.33		6880	85	6080		
17	9.10	–24	7270	85	6470		
19	8.35		6730	90	5930		
20	8.06		6240	60	5440		
21	7.81		6030	85	5230		
43	7.41	–25	6060	95	5260		
23	7.27		5820	45	5020	–3910 to	–3730
44	6.77		5250	95	4450	–3390	–3000
25	6.54		5610	90	4810	–3720	–3420
26	6.30		4960	40	4160	–2900	–2600
27	6.07		5040	80	4240	–3150	–2630
28	5.80		4930	45	4130	–2850	–2570
29	5.44		4660	95	3860	–2500	–2140
30	5.10		4550	75	3750	–2450	–2080
31	4.65	–31	4110	45	3310	–1750	–1530
33	4.09		4150	55	3350	–1930	–1570
34	3.64		3630	70	2830	–1200	– 980
35	3.32	–27	3650	110	2850	–1210	– 960
36	3.11		3120	55	2320	– 570	– 300
37	2.68		2730	75	1930	– 130	+ 210
38	2.42		2580	65	1780	110	300
39	2.18		2390	50	1590	280	470
40	1.66		2070	60	1270	630	820
41	1.36		1930	60	1130	730	950
42	1.11	–31	1890	60	1090	780	980

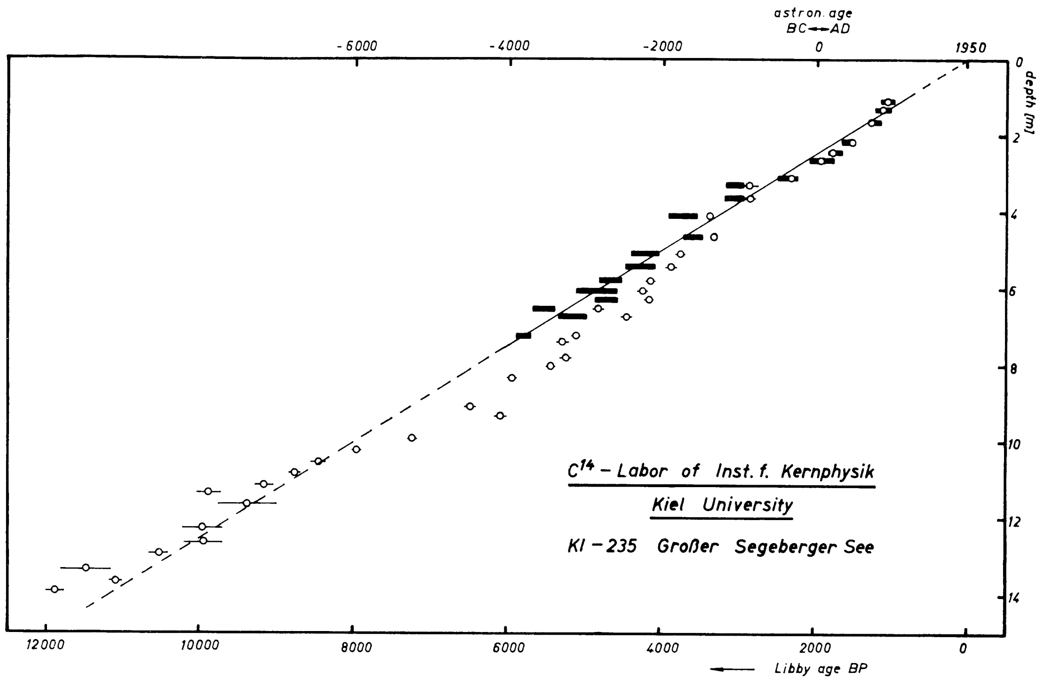

Fig. 1. C^{14} dates of Segeberger See sediments. Circles: "real" Libby age = Libby age −800 yr (Table 1, col. 5) in B.P. scale; bars: range of dendrochronol. corr. age (Table 1, col. 6) in A.D./B.C. scale.

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nomical" dates yields the required value of 0 B.P. for surface sediments (Fig. 1).

According to these values, mean sedimentation rate was fairly constant during the last 6 millennia except for short variations. Fig. 1 assumes similar rates of sedimentation and chemical behavior of the lake during period investigated. If these assumptions are valid, then differences between the "real" Libby age and the extended straight line may be interpreted as variations in the recent value of the C^{14} content. It follows from Fig. 1 that deviation of recent activity has a maximum of $\Delta C^{14} = 110‰$ corresponding to 900 yr between 6000 B.P. and 7500 B.P. (astronomic age) and decreases to 0‰ at 8500 B.P. Beyond 8500 B.P., Libby age and astronomic age do not show statistically significant difference. These determinations support the results of Stuiver concerning sedimentation in 3 lakes (Stuiver, 1967; 1969, p. 550) and calibration by varve chronology (Tauber, 1970).

KI-315. Soholm, Profile 4 **104.5 ± 1.2%**

Rootlets, 165 cm below surface, taken from soil sec. near Soholm (54° 41.9′ N Lat, 9° 4.6′ E Long), Schleswig-Holstein, Germany. Coll. and subm. 1969 by G. Jatho, Geog. Inst., Univ. Kiel. Surface vegetation: *Calluna, Pinus, Picea.* Below several differently strong leached sandy layers a meadow ore layer extended ca. 60 cm to 160 cm depth, overlying sample. *Comment*: sandy meadow ore layer was formed in Middle age when large areas were deforested for production of charcoal needed for smelting of numerous local bog-iron ore deposits. Rootlets should date beginning of meadow ore layer formation, because younger vegetation was not expected to penetrate stone-like layer. Result disproves assumption.

KI-317. Soholm, Profile 1 **12,250 ± 170**
10,300 B.C.

Well-preserved wooden branches, 280 cm below surface, from soil sec. (54° 43.5 N Lat, 9° 1.9′ E Long) near Soholm, Schleswig-Holstein, Germany. Coll. and subm. 1969 by G. Jatho. Overlying sample were several layers of alternating humus and bleached sands. Deepest layer that was to be dated by branches was formed by air blown sands.

II. ARCHAEOLOGIC SAMPLES

Möllenknob series

Excavations near Archsum (54° 52.7′ N Lat, 8° 22.5′ E Long) on Sylt I., Germany (Radiocarbon 1968, v. 10, p. 331; 1969, v. 11, p. 428). Coll. 1967 by R. Kenk; subm. 1967 by G. Kossack and F. R. Averdieck, Inst. f. Ur- und Frühgeschichte, Univ. Kiel.

Möllenknob 245(2)

Cereals, weeds, and small pieces of charcoal from small ditches. Younger Bronze age or older pre-Roman Iron age.

KI-243. Fraction A **2970 ± 60**
1020 B.C.

Coarse fraction consisting of cereals only.

KI-244. Fraction B **3060 ± 65**
1110 B.C.

Second fraction of sample. *Comment*: no significant difference between the two fractions.

KI-237. Möllenknob 288(11) **2070 ± 45**
120 B.C.

Carbonized cereals and Gramineae, 100 to 120 cm below surface. Some rootlets of recent origin had to be removed. Expected age: ca. A.D. ± 0.

KI-249. Münchsteinach PfA-Reg 11/1 (1966-1970) **295 ± 50**
A.D. 1655

Human skull, from Münchsteinach (49° 34.4′ N Lat, 10° 37.1′ E Long), Germany. Coll. 1966 by H. Metzeler, Evang. Luth. Pfarramt, Münchsteinach/Neustadt a.d. Aisch; subm. 1968 by H. Helmuth, Anthropol. Inst., Univ. Kiel. Skull was found when renovating the former Benediktinerabtei Münchsteinach, 30 cm below floor flaps. Considering C^{14} variations (Willkomm, 1968) skull may date from A.D. 1450 until 1640.

KI-316. Eggstedt **2190 ± 50**
240 B.C.

Peat, enclosing a human skull, found near Eggstedt and Schafstedt (54° 4′ N Lat, 9° 15′ E Long), Schleswig-Holstein, Germany. Coll. 1969 by J. Peters, Eggstedt; subm. 1969 by H. Helmuth and F. R. Averdieck. Probably originating from pre-Christian Iron age, 500 B.C. to ± 0 B.C. *Comment* (F.R.A.): belongs to Pollen Zone X (Overbeck, 1950, p. 106). Low but significant values of *Fagus* and *Carpinus*. Cereals below 1%, but *Secale* and *Linum usitatissimum* are found.

Belau series

Samples of Belau (54° 6.7′ N Lat, 10° 29.5′ E Long), NW Germany. KI-90 and KI-230 coll. and subm. 1966 by F. Tidelski, who also made pollen analysis (unpub.). KI-283 coll. 1967 by E. Erich and subm. 1968 by F. R. Averdieck. *Comment* (E.E. and F.T.): samples coll. near to Schmalensee lake for proving the name *stagnum colse* (= lake of charcoal) appropriate. Other authors attribute name to the Stocksee (6 kms E) and thus obtain unnecessary extension of *limes Saxoniae,* wall of frontier built by Charlemagne (Ostertun, 1967).

KI-90. **4270 ± 60**
2320 B.C.

Wood (*Quercus*) 170 cm below surface. Forest was necessary for charcoal production of greater extent.

KI-230. **4800 ± 75**
2850 B.C.

Peat of about same stratigraphic layer as KI-90.

KI-283. **2530 ± 40**
580 B.C.

Charcoal.

III. DENDROCHRONOLOGIC SAMPLES

Wienhausen series

Dendrochronologically dated wood from monastery of Wienhausen/Celle (52° 34.5′ N Lat, 10° 12′ E Long). Coll. and subm. by D. Eckstein and J. Bauch, Lehrstuhl f. Holzwirtschaft, Univ. Hamburg, Reinbek. Dated by D. Eckstein and J. Bauch.

KI-238. Wienhausen 1 $\Delta = (-4.6 \pm 4.1)‰$ **690 ± 35**
A.D. 1260

A.D. 1275 to 1285

KI-239. Wienhausen 2 $\Delta = (-8.3 \pm 3.5)‰$ **730 ± 30**
A.D. 1220

A.D. 1265 to 1275

KI-240. Wienhausen 3 $\Delta = (-17.5 \pm 4.0)‰$ **970 ± 35**
A.D. 980

A.D. 1095 to 1105

General Comment: A.D. values under sample are determined by tree-ring counting. Δ values are calculated according to:

$$\Delta = 1000 \frac{A_m \cdot e^{\lambda T} - A_o}{A_o}$$

where A_m = measured activity (not corrected for δC^{13}, because trees never have a serious deviation to $\delta C^{13} = -25‰$); T = dendrochron. age B.P.; $\lambda = \frac{1}{8270}$ = best value available for decay constant; $A_m \cdot e^{\lambda T}$ is activity reduced for A.D. 1950; and A_o = standard recent activity (= 95% of oxalic acid).

Correction

In Kiel IV, v. 11, p. 425, 3rd line of Keitum series should be omitted.

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