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Carbon-14 Time Scale Extended: Comparison of Chronologies

Thermal diffusion isotopic enrichment of carbon-14 brings 75,000 years ago within dating range.

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Summary. Thermal diffusion isotopic enrichment of carbon-14 has extended the radiocarbon dating range to about 75,000 years ago. Twenty-eight samples obtained up to June 1976, mainly from northwest Europe, were dated. Consideration of the basic assumptions of carbon-14 dating and of the sources of contamination indicates that the ages are generally reliable. Together with the pollen analytic and stratigraphic evidence, the dates yield a more detailed radiocarbon time scale for climatic variations in northwest Europe, showing three early glacial interstades. The radiocarbon time scale agrees with the Camp Century chronology and with the thorium-230 ages of corals representing high sea level stands on New Guinea. There is a discrepancy between the radiocarbon time scale and the deep-sea chronology, which may be due to correlation errors. With a modified interpretation of the correlation, all four time scales agree within the estimated experimental uncertainties of the dating techniques used.

The range of the carbon-14 dating method, for most laboratories, is less than 50,000 years. The climatic fluctuations in the early part of the last glacial are beyond this range. Thermal diffusion isotopic enrichment of ^{14}C has been used to increase the sample activity relative to the counter background and thus to extend the range of β decay ^{14}C dating by about 20,000 years. The technical details of the enrichment have been described (*1, 2*). In this article I report a series of enrichment dates and propose a time scale for climatic fluctuations in the early part of the last glacial in northwest Europe. Because the major climatic fluctuations seem to occur globally, I compare the radiocarbon time scale for pollen-based temperature fluctuations with the age-calibrated Camp Century oxygen-18 record interpreted in terms of stades and interstades (*3*), with a deep-sea sediment chronology reflecting global ice volume (*4*), and with ages of high sea level stands recorded in coral terraces (*5*).

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Carbon-14 Dates

The area chosen for the study of the early part of the last glacial was the limited and relatively well-known part of northwest Europe between the Scandinavian and Alpine ice sheets. Samples were selected for enrichment when stratigraphic or pollen analytic evidence, or both, suggested that they belonged to the early part of the last glacial. Figure 1 shows the enrichment dates obtained up to June 1976 (*6*), together with stratigraphic information used for their interpretation. This information includes the position of the sample in the layer, the kind of material, and whether the beginning or the end of a period of peat growth was dated.

The ^{14}C activity of the enriched samples was measured in a proportional carbon dioxide counter. Its background counting rate was obtained from a least-squares fit of background data over several months. The ^{14}C enrichment was obtained from mass spectrometric measurements of the simultaneous ^{18}O enrichment by using an experimentally obtained relation. Sample activities were compared with 95 percent of the activity of a National Bureau of Standards oxalic acid sample, corrected to $\delta^{13}C = -19$ per mil (*7*). All sample activities were corrected for isotopic fractionation relative to $\delta^{13}C = -25$ per mil (the standard composition of organic material). The dates given are based on the conventional (Libby) ^{14}C half-life of 5568 years. The uncertainty given (1 standard deviation) is based only on Poisson counting statistics. Analysis of the background data showed that the Poisson statistics was the main cause of uncertainty. For samples with an activity less than 2 standard deviations, a minimum age is calculated. The ^{14}C activity of most samples has been corrected for the residual ^{14}C activity of the carbon dioxide sample used for background measurements. For samples indicated with an asterisk in Fig. 1, this activity is not accurately known; as far as this effect is concerned, these dates may be slightly too old.

Reliability of Old Sample Dates

The main problem is to establish whether the measured ^{14}C activity is from the original sample material or from some carbonaceous admixture. Because the residual ^{14}C activity is 1,000 to 10,000 times below that of modern carbon, old samples are very sensitive to recent additions. Admixture before sample pro-

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cessing is called sample contamination. Admixture during processing is called laboratory contamination.

Sample contamination. This type of contamination may vary greatly from sample to sample. However, careful choice of the sample and pretreatment to extract contaminants by mechanical means and by acid, alkali, and acid extractions give satisfactory results in most cases, even for samples 50,000 or more years old. The reliability of a ^{14}C date insofar as sample contamination is concerned has to be judged from two kinds of information.

1) Consistency of dates: (i) the age sequence of different samples from the same profile should be in accordance with the stratigraphic evidence, if a reliable stratigraphy has been established, and (ii) samples of different profiles, which are considered to be contemporaneous on the basis of pollen analytic, stratigraphic, or other evidence, should yield the same dates.

2) Activity of the material extracted in the chemical pretreatment. If the contaminant has been introduced into the sample by infiltrating groundwater (for instance, humic substances and carbonates) it may be expected to be somewhat more soluble than the bulk of the sample material, if peat, lignite, or wood samples are considered. In that case the contaminant will be found in the earlier extractions, but not in the last. Accordingly, the first extracts may show extra ^{14}C activity. The last extract should have an activity equal to that of the final pretreated sample or, in the case of enriched samples, no measurable activity.

The consistency of dates can be read from Fig. 1. Within the same profile the sample dates are in consecutive order. With the exception of Voglans, where one sample was probably contaminated, the stratigraphically older sample always yielded a greater age. Moreover, the age differences between the tops and bases of the peat beds yield peat growth rates that are quite reasonable. The contemporaneity of dates for related samples from different profiles is difficult to establish, because the pollen analytic and stratigraphic information is often insufficient to make an unambiguous correlation between the sample and a certain interstade. The uncertainty in the dates in this age range is also large when compared with the age differences between the various interstades.

Dissolved organic material was recovered from the first acidic and the alkaline extracts obtained in the chemical pretreatment. A rigorous acid-alkali-acid pretreatment was chosen since partial loss of sample material by dissolution is less serious than incomplete removal of contaminants. Generally, the ^{14}C activity of the material from the last alkali extractions was determined. With the exception of the Voorthuizen sample, none of these extracts showed statistically significant ^{14}C activity. Three of the first alkaline extracts showed ^{14}C activity (Voorthuizen, Samerberg, and Voglans), as did the acidic extract from the Amersfoort top sample. These results indicate that the contamination level of the samples was low. The more frequent occurrence of activity in the first extracts means that the pretreatment used was effective in removing contaminants. Therefore there is a good probability that the dates obtained for the samples were not seriously influenced by sample contamination.

A special case of sample contamination is the production of ^{14}C in the sample by cosmic radiation or natural radioactivity. This possibility was considered for the anthracite that was used to determine the background of the counter and for the Amersfoort and Beaverdam Creek samples. From the position of the sample and its uranium and nitrogen contents the activity due to in situ production of ^{14}C was estimated. In each case the result corresponded to the activity of a sample 100,000 or more years old, which showed that in situ production was negligible for these samples.

Laboratory contamination. This arises when contaminants are introduced into the sample during handling in the laboratory. Because the laboratory treatment is essentially the same for all samples, the possible degree of contamination can be detected by blank runs.

Laboratory contamination was evident from the activity of the first enriched anthracite sample (GrN-6533), which was 0.022 ± 0.010 percent of the modern carbon activity. During blank runs, the technical-grade combustion gases (nitrogen and oxygen) and even the sample combustion system yielded carbon dioxide whose quantity and activity were sufficient to explain the anthracite ^{14}C activity. Consequently, high-purity gases

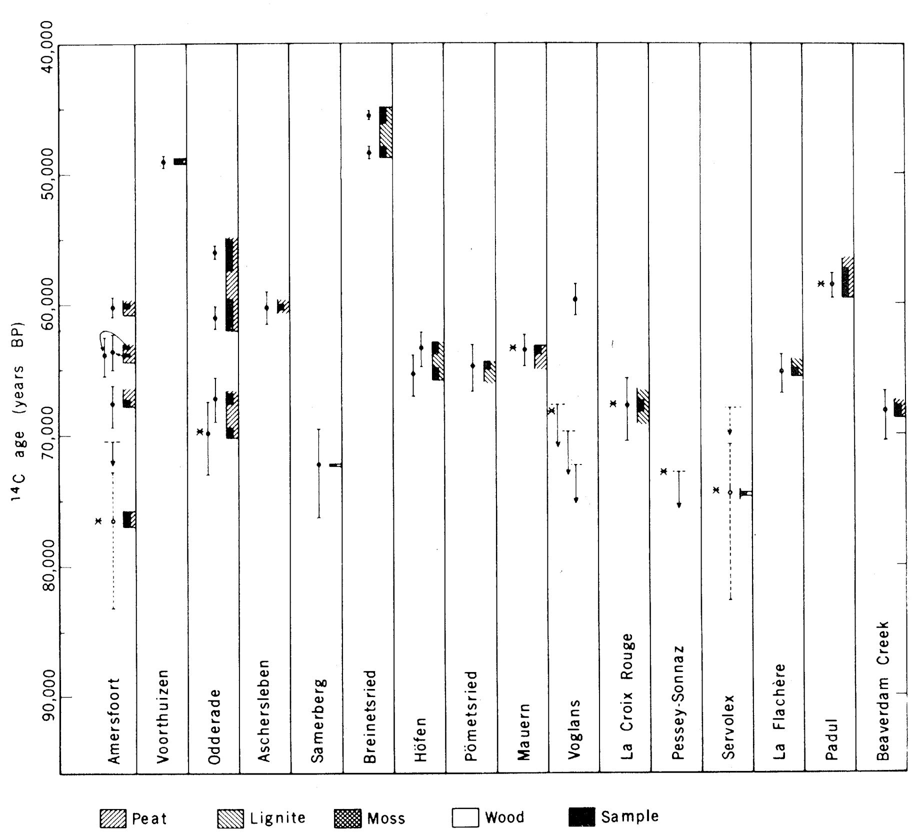

Fig. 1. Dates for the enriched ^{14}C samples. With the exception of the deepest sample at Amersfoort (a stadial peat) all samples consist of organic material of interstadial or interglacial origin. The climate during deposition at Voorthuizen and Breinetsried was very cool; the Amersfoort samples date the transition of stadial to interstadial conditions and also represent cool climatic conditions. In each block the black portion shows the position of the sample. If the beginning or the end of a period of peat growth was dated, that part of the block is closed; otherwise it is left open. Points with solid error bars show the conventional ^{14}C age plotted on the ordinate. Points with dashed error bars represent samples whose activity was between 1 and 2 standard deviations and indicate apparent ages. Arrows are used where the activity was too low for statistical significance. An asterisk indicates that the date was not corrected for residual activity of the background carbon dioxide sample.

were chosen for the combustion, and the combustion line was cleaned thoroughly before each use. Furthermore, because the high blank values for the combustion line were due to a memory effect (volatile compounds of the sample condense during combustion in cooler parts of the combustion line), only old samples were processed in this combustion system. Also, since the zinc-asbestos mixture used for the reduction of carbon dioxide to carbon monoxide seemed suspect, the zinc and the asbestos were specially cleaned. These precautions reduced laboratory contamination to below our detection limit (apparent anthracite age > 76,400 years).

The ^{14}C age is calculated from the measured activity of the sample. The difference between this age and the sample age in calendar years is determined by the degree to which the basic assumptions of radiocarbon dating are fulfilled. In particular, as the age range increases a slow drift of the original atmospheric ^{14}C concentration may become serious. Indications are, however, that the ^{14}C concentration over the last 100,000 years was at least within a factor of 2 of its standard value (*8*). For samples 50,000 or more years old this means a difference between the ^{14}C and the terrestrial time scale of 10 percent or less.

So far, it is concluded that contaminants can be eliminated to a sufficient degree to permit the measurement of the true activities of properly selected samples and that the ^{14}C activity can be converted to a radiocarbon age for the extended range. The dates obtained so far seem generally consistent and reliable.

Radiocarbon Time Scale

From the dates given in Fig. 1 a time scale has been derived for the climatic fluctuations in the early part of the last glacial in northwest Europe. The time scale is based on the distribution of the finite ages obtained and on the detailed stratigraphy and pollen analysis at Amersfoort (*9*).

For the distribution of enrichment dates 19 samples dated between 56,000 and 73,000 years ago were considered. To provide an objective criterion for sample contemporaneity, the chi-square value for various combinations of dates was calculated. It was assumed that deposition under interstadial conditions started synchronously at different places, which is reasonable because differences due to the migration of plant species are generally small compared with the measurement uncertainty. Chi-square values having reasonable probabilities (.50, .92, and .82, respectively) were obtained when the dates were divided into three groups (55,000 to 61,000, 61,000 to 66,000, and 66,000 to 73,000 years ago) and the date for the top of the upper peat bed at Odderade ($55,900^{+600}_{-500}$, GrN-7054) was left out. For this bed the age difference between top and bottom of the layer is much larger than 1 standard deviation. When the pollen analytic and stratigraphic evidence was taken into account, slightly different groups were obtained, but the chi-square values still had good probabilities (.20, .15, and .66, respectively). Thus the simplest explanation for the observed distribution of dates is that there was a close succession of three early glacial interstades between 73,000 and 56,000 years ago. The stratigraphy and pollen analysis of the Amersfoort profile agree with the existence of three early glacial interstades. The conclusion is derived from the following information.

1) The difference in radiocarbon ages of the three interstades exceeds twice their standard deviation; thus the observed age differences are statistically significant.

2) The influence of contamination is small or absent, based on the low ^{14}C activity measured for the material extracted during chemical pretreatment. A low degree of contamination was expected because the samples were taken from a fresh exposure where no signs of infiltration from higher levels could be observed.

3) The pollen analysis indicates a cold stadial character for the lowermost sample. This peat was situated immediately above a peat layer of clearly interglacial (Eemian) character. In the basal layers of each of the two higher dated peat beds evidence of cold stadial conditions was observed. Higher in each peat bed the pollen analytic data indicate warmer climatic conditions. The upper peat bed has a thin bed of eolian sand intercalated in its upper part. Above this the pollen diagram again has a stadial character, with an indication of the beginning of an amelioration of climate at the top. Together with the dates obtained, this suggests that the higher bed consists of the remnants of two peat layers deposited during different interstades. The main part of the interstadial deposits must have been lost by erosion.

The early glacial character of the peat layers at Amersfoort is also indicated by the presence of a higher, cryoturbatic peat bed above 1.5 to 2 meters of loamy cover sands. This peat has provided pollen spectra showing an extremely high occurrence of herb pollen characteristic of the Middle Weichselian. Radiocarbon ages of $51,700^{+3700}_{-2400}$ (GrN-5375) and > 51,000 (GrN-5404) years (*10*) confirm the early glacial character of the underlying peat beds. There is also supporting evidence for the existence of three early glacial interstades from other localities in northern Germany (Odderade, Oerel, and Aschersleben) (*11*).

From the dates and the pollen analytic investigations the climatic curve for the last glacial in The Netherlands (*12*) can be more precisely extended beyond 50,000 years ago (Fig. 2A). The concurrence of many ^{14}C dates shows that the major climatic trends for The Netherlands are valid for the whole of northwest Europe. It should be noted, however, that the temperature scale gives the estimated July temperature for The Netherlands only. For other areas systematic differences in temperature may be encountered and the relative amplitude of the fluctuations may be different. The interstades in Fig. 2A are designated by names established for the Weichselian glacial sequence of The Netherlands, northern Germany, and Denmark. Until the position of stratigraphic units on an absolute time scale has been unambiguously established, only local names should be used for other areas.

Comparison of Chronologies

Changes in climate have been indicated in such diverse features as the distribution of pollen preserved in sediments, continental loess deposits, the oxygen isotopic composition of glacier ice, variations in faunal assemblages and oxygen isotopic compositions of carbonate skeletons in deep-sea sediments, and coral terraces. The patterns of climatic fluctuations obtained by different techniques and from largely different localities are generally strikingly similar.

Although many different curves have been related to climate, the time scales for the last interglacial-glacial cycle have been derived by only two independent radioactive dating methods—radiocarbon dating and thorium or protactinium dating—and by two more indirect dating methods involving ice flow calculations corrected by assuming a constant periodicity of climatic oscillations (*3*) and a constant deep-sea sedimentation rate (*13*). The radiocarbon time scale presented here is compared with three other standard chronologies in Fig. 2.

Camp Century (Fig. 2B). The time

scale is based on the assumption of a constant periodicity of $\delta^{18}O$ fluctuations in the ice. If the interpretation by Dansgaard *et al.* (*3*) of the $\delta^{18}O$ fluctuations in the Camp Century ice core in terms of stadial and interstadial periods is correct, the age of the climatic oscillations in the early part of the last glacial is approximately 8 percent lower on the ^{14}C than on the Camp Century time scale. Three percent of this can be attributed to the use of the conventional ^{14}C half-life of 5568 years instead of the more accurate value of 5730 years. The remaining discrepancy of 5 percent is well within the estimated uncertainty of the time scales (about 10 percent).

Deep-sea (Fig. 2C). The time scale is based on ^{14}C dates back to about 30,000 years ago. Beyond that it is based on interpolation between the present and 126,000 years ago, assuming a constant sedimentation rate (*13*), or on thorium-protactinium dates of the sediment (*14*). Furthermore, the three $\delta^{18}O$ minima of stage 5 have been correlated with three dated coral terraces representing high sea-level stands on Barbados at about 80,000, 104,000, and 125,000 years ago (*15*). For stage 5 of the deep-sea chronology there are two time scales because in the construction of the generalized deep-sea paleotemperature time scale for the last 700,000 years the exact position of the last interglacial remained undecided (*4*).

Assuming that the pronounced positive $\delta^{18}O$ peak indicating maximum global ice volume (stage 4, Fig. 2C) corresponds to the maximum cold at the beginning of the Pleniglacial in The Netherlands around 55,000 years ago (Fig. 2A), the difference between the time scales for this event is about 15,000 years ($\sim$ 25 percent). Even if the ^{14}C age is increased by 3 percent (half-life correction) this discrepancy is significantly larger than can be expected from the accuracy of the two time scales. The deep-sea record lacks the detail required for further comparison in the younger stage 3 and the older stage 5. Because the youngest part of the deep-sea time scale is also based on ^{14}C, the discrepancy will decrease for younger ages and, probably, increase for the older part of the time scales.

New Guinea (Fig. 2D). The time scale is based on ^{14}C dates (terraces I and II) and on ^{230}Th dates of aragonitic corals (*5*). The coral terraces date from periods of relatively high sea-level stands, related to a reduced ice volume and a relatively warmer climate (either interglacial or interstadial). They do not provide information on climate development or on the intermediate cool stadial periods. The agreement between the ages of terraces I to IV and those of the northwest European interstades on the ^{14}C time scale (Fig. 2A) is excellent. Because the three early glacial interstades were separated by only short cold intervals, it seems probable that they gave rise to only one complex terrace. It should be noted that the ages of terraces V to VIIb agree with the ages corresponding to the negative $\delta^{18}O$ peaks of stage 5 in the deep-sea chronology of Shackleton and Opdyke (*13*) (Fig. 2C).

In conclusion, the new ^{14}C time scale for the sequence of interstadial and stadial periods recorded by pollen in northwest Europe agrees over its entire range with the Camp Century time scale for $\delta^{18}O$ fluctuations in the Greenland ice and with the ^{230}Th-dated high sea levels on the coast of New Guinea. For the older part of the last glacial there is a discrepancy between the ^{14}C time scale and the common interpretation of both versions (*13, 14*) of the deep-sea time scale. The observed discrepancy may be due to one or more of the following: (i) incorrect (too young) ^{14}C dates, especially because of contamination; (ii) incorrect deep-sea time scale because the assumption of constant sedimentation rate is only approximately valid; and (iii) incorrect correlation between the deep-sea

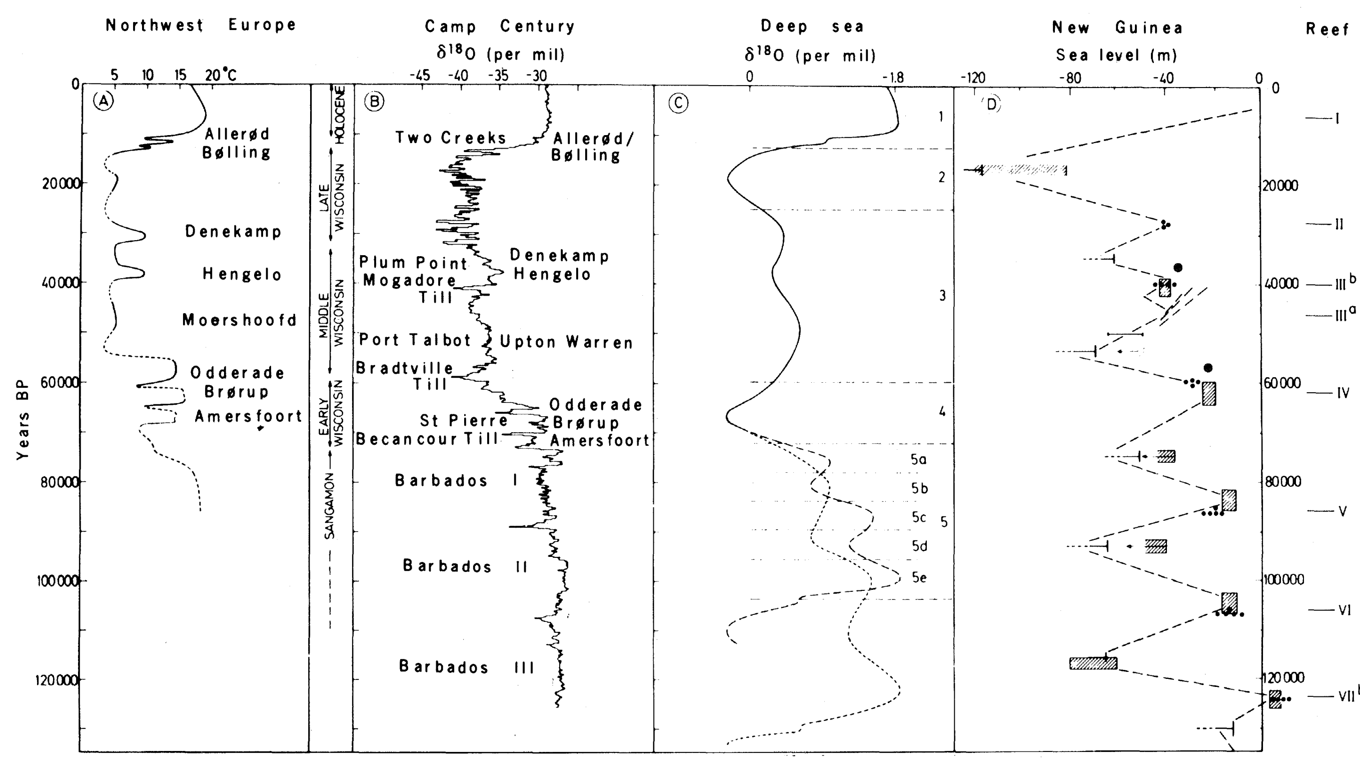

Fig. 2. Comparison of climatic chronologies for the last interglacial-glacial cycle. (A) Pollen record in northwest Europe dated with ^{14}C; dashed lines are used for periods where no organic deposits are preserved. (B) The $\delta^{18}O$ record of the Camp Century ice core (Greenland); the time scale is based on the constant periodicity of $\delta^{18}O$ variations (*3*). (C) Generalized $\delta^{18}O$ deep-sea record; the time scale is based on ^{230}Th-^{231}Pa dates and interpolation between the present and 126,000 years ago, using a constant sedimentation rate. (Dashed line) Emiliani and co-workers (*14*); (dotted line) Shackleton and Opdyke (*13*). (D) Coral terraces associated with high sea level stands on the coast of New Guinea, dated with ^{230}Th (and ^{14}C) (*15*).

record and the coral terraces or the continental pollen record.

Both the ^{14}C dates used for the northwest European time scale and the thorium and protactinium dates on aragonitic corals used in support of the deep-sea time scale were obtained and checked carefully. Their accuracy does not warrant the observed discrepancy. It is therefore suggested that the dates obtained by both radioactive dating methods are correct and that the discrepancy is caused by correlation errors or variations in the sedimentation rate, or both.

A New Correlation

Stage 5 of the generalized deep-sea $\delta^{18}O$ curve (Fig. 2C) has been correlated with three coral terraces dated on Barbados. The increase in $\delta^{18}O$ in stage 4 indicating increased global ice volume follows the youngest terrace, dated at about 80,000 years ago, and is thus assigned an age of 65,000 to 70,000 years. On New Guinea, however, several more terraces have been dated (Fig. 2D), and on Barbados a 60,000-year-old terrace has been found (*16*). If this terrace can still be correlated with stage 5, then stage 4 will be younger, with an age of about 55,000 years, in excellent agreement with the age of the maximum northwest European cooling on the ^{14}C time scale.

Having four terraces in stage 5 would seem to contradict the generalized $\delta^{18}O$ curve, which shows only three warmer periods in this stage. This need not be serious, however, because the original $\delta^{18}O$ curves for individual cores V28-238 (*13*) and P6304-9 (*17*) showed a fine structure much more complex than the generalized curve. These individual curves would easily fit four warm intervals in stage 5 [a more detailed discussion has been given elsewhere (*2*)]. If it is assumed (i) that the large increase in global ice volume recorded in stage 4 followed the formation of the 60,000-year-old terrace and (ii) that maximum global ice volume is correlated with maximum cold in the northwest European pollen record, then all four time scales discussed agree within the estimated experimental uncertainties of the dating techniques. A global pattern of climatic variation with time can then be obtained from the combined information.

As a consequence of the new correlation, stage 5 would comprise both the last interglacial and the three early glacial interstades as defined in the northwest European pollen record. This is supported by the pollen record and by the $\delta^{18}O$ record of Camp Century, which indicate only slightly cooler conditions during the early glacial interstades than during the preceding interglacial period (but distinctly warmer than during the following pleniglacial interstades). Stage 5a might have to be divided into a younger phase, $5a_1$ (60,000 years ago, high sea level, early glacial interstades), and an older phase, $5a_3$ (85,000 years ago, high sea level).

For the climatic curves that are now available, the correlation proposed above seems the most plausible one. It yields good agreement of the time scales, confirming the reliability of the dates used. Further investigations are necessary to prove or disprove the proposed correlation. A detailed analysis of the interglacial pollen record might reveal cold phases corresponding to stages 5b and 5d of Emiliani and co-workers (*14*). At the same time, a study of deep-sea cores reflecting high sedimentation rates should be undertaken to obtain a more detailed deep-sea chronology, which is essential for a close correlation with the continental record. In particular, a combined study of pollen and $\delta^{18}O$ in marine sediments may prove valuable (*18*). Since the volume of the Laurentide ice sheet was much larger than that of the Scandinavian ice sheet, the deep-sea $\delta^{18}O$ fluctuations will mainly follow the changes of the former. Maximum cold in northwest Europe and maximum global ice volume can only be correlated if the temperature pattern obtained from pollen analysis in northwest Europe is synchronous with North American ice volume changes. A detailed and complete pollen diagram and ice volume record of the North American continent covering the last interglacial and the subsequent early part of the last glacial will be important.

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