North American Glacial History Extended to 75,000 Years Ago

The range of carbon-14 dating is extended through isotope enrichment techniques.

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Summary. By concentrating carbon-14 through thermal diffusion, it is possible to extend the range of carbon-14 dating to 75,000 years ago. Samples with very low contamination levels have been encountered, and a reliable chronology appears possible. A Pacific Northwest climatic curve has been derived from palynological studies. The Pacific Northwest curve and the Great Lakes glacial history are age-calibrated by radiocarbon dating. The climatic patterns in the Pacific Northwest and Northwest Europe are similar in the early part of the last glaciation, with interstades near 60,000, 65,000, and 70,000 years ago. An age of 74,700 years for the St. Pierre interstade indicates a possible correlation with the previous interglacial.

The carbon-14 technique is a fairly routine method for dating organic materials with ages up to 40,000 years. This is reflected in our knowledge of the chronology of the Wisconsin glaciation. The ages of late Wisconsin events are much better known than those of earlier stages. Recently, the ^{14}C detection limit has been improved at the Quaternary Isotope Laboratory to 0.1 per mil of modern activity. This makes it possible to date samples back to 75,000 years ago, provided sample contamination is much less than 0.1 per mil. With this new capability we have dated samples of early Wisconsin age from two North American regions. In this article technical aspects of dating older samples are first discussed. A time scale for the glacial history of the Great Lakes region and the Pacific Northwest is then given, together with palynological information for the Pacific Northwest.

Technical Aspects

The scarcity of dates for older materials is related to the technical difficulties in measuring small sample activities. Whereas organic materials grown in equilibrium with atmospheric ^{14}C levels of the last century have specific disintegration rates of 13.6 counts per minute per gram of carbon, a sample with an age of ten half-lives (about 56,000 radiocarbon years) has only $1/2^{10}$ of this activity left, or 0.013 count/min per gram of carbon. For a small sample containing 1 g of carbon, one has to wait an average of more than 1 hour for a single β decay. This small activity has to be measured in counters that also register radiation from other sources, such as cosmic radiation that escapes detection by the guard ring that surrounds the sample counter, or natural radioactive traces left in the construction material of the counter.

To reduce the background count (the radiation detected by the counter for a filling completely lacking ^{14}C), utmost care in the selection of counter materials such as quartz or copper is needed. The contribution of cosmic radiation, or cosmic ray–produced secondary radiation in the shield, to the background can be reduced by placing the counters underground. At the Quaternary Isotope Laboratory, a shield consisting of 10 meters of earth and 30 centimeters of lead reduces the cosmic ray–related contribution to the background appreciably (*1*).

For determining the age of old materials a large sample size is preferable because the measured activity is proportional to the amount of sample. A larger sample requires a larger counter, which of course also has a higher background count rate (B), but the maximum age limit is determined by the ratio $S_0/B^{1/2}$ (where S_0 is the counting rate for an age of zero), so that generally larger samples are required to determine greater ages. There are physical limitations to the counter size, however, and also to the filling pressure because the counting gas properties of most gases deteriorate with increasing pressure. In our laboratory the largest counter has a counting volume of 4.2 liters, with a carbon dioxide filling pressure of 3.1 atmospheres. The background counting rate is 1.6 count/min and the counting rate of the National Bureau of Standards oxalic acid standard is 96 count/min. Nearly 7 g of carbon has to be combusted to carbon dioxide to fill the counter. With 4 days of counting, the maximum age range for this sample size is 60,000 years; for smaller samples it is less (for instance, 47,000 years for a 1-g carbon sample). A more detailed discussion of the technical aspects of the counters is given elsewhere (*1*).

A sample 60,000 years old has a ^{14}C activity equal to 0.6 per mil of its original (zero age) activity. This detection limit can be further reduced by concentrating the ^{14}C of the sample before placing it in the counter. With a thermal diffusion isotope enrichment system ^{14}C activities are routinely increased by a factor of 6 to 7 in our laboratory. This reduces the detection limit to about 0.1 per mil and increases the age limit by 15,000 years to 75,000 years.

Sample sizes of about 60 to 120 g of carbon are needed for the enrichment process. The carbon dioxide derived from sample combustion is reduced to carbon monoxide and enriched in Clusius-type (hot wire) thermal diffusion columns. The enrichment process is time-consuming; it takes about 5 weeks for a sixfold enrichment. The columns essentially transport the heavier ^{14}CO from a 120-liter top volume to an 8-liter bottom volume. For a sixfold enrichment in the bottom volume the top volume is depleted of one-third of its original ^{14}CO content. The ^{14}C enrichment is calculated from the ^{18}O enrichment, which is determined by using a mass spectrometer (*2*).

After oxidation of the carbon monoxide to carbon dioxide, the enriched gas is used to fill the counters. An 8-liter filling

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goes into the smaller, 2.3-liter counter, which has an age limit for direct counting of about 58,000 years. Two batches totaling 120 g of carbon have to be prepared for the 4-liter counter. The enrichment system is a modified version of the apparatus described by Grootes and co-workers (*3*, *4*).

Sample Contamination

The arrangement described above makes it technically feasible to detect ^{14}C activities equal to 0.1 per mil of the original activity. However, the measured age of a sample with such low activity is very much dependent on sample contamination. Through decay, the sample activity is reduced by a factor of 2 for each 5600 radiocarbon years elapsed. When modern material is added to the extent of only 0.1 per mil, the measured activity of the 75,000-year-old sample with its own activity of 0.1 per mil doubles to 0.2 per mil, and the measured sample age will be 5600 years younger. To double the sample activity of a 56,000-year-old sample one has to add 1 per mil contamination; a similar doubling is achieved for a 37,000-year-old sample by adding a full 1 percent contamination. In both instances the measured sample age will be 5600 years younger.

These examples show that identical absolute age anomalies are caused by a 0.1 per mil addition of young material to a 75,000-year-old sample, by a 1 per mil addition to a 56,000-year-old sample, and by a 1 percent addition to a 37,000-year-old sample. For each 19,000-year increase in the age of a sample, contamination by young material causes a ten times larger absolute age error.

We have measured the ages of samples with activities equivalent to 0.1 per mil of the original ^{14}C activity, and we have also measured samples yielding "infinite" ages, whose present ^{14}C activity is less than 0.1 per mil. Thus samples do exist for which the sum of their own activity, added field contamination, and added laboratory contamination is less than 0.1 per mil of the original ^{14}C activity. Whereas a 0.1 per mil contamination still appreciably influences the measured age of a 75,000-year-old sample, it changes the age of a 60,000-year-old sample by only 1300 years. Evidently samples exist in nature that are sufficiently clean to give reliable radiocarbon ages in the 60,000-year range.

Proof of lack of contamination is more difficult for samples with ages in the 70,000-year range. Indications of the absence of contamination are obtained from sample measurement, as described above. Agreement between ages of samples from different localities but from the same geological event is a strong indication of age reliability. Although absolute proof is lacking, we feel it is unlikely that our measured sample ages in the 70,000-year range differ by more than a few thousand years from the conventional radiocarbon age.

Sample pretreatment. Wood is treated with a hot alkali solution to remove humic acids and other components that may have been added after deposition of the wood. Peat is subjected to a shorter treatment with more dilute alkali. The leached fraction from these treatments can be dated and the age compared with the age of the cleaned material. When the leached fraction is appreciably younger than the cleaned material, sample contamination is indicated. Grootes (*4*) used this technique for approximately 20 samples and found only one with a clear indication of contamination. When strict sample collection criteria (such as a till cover several meters thick, fresh exposure without evidence of weathering, and no visible sign of rootlets) are used, the age of the leached fraction seldom proves contamination. Therefore no attempt was made to date the leached fractions of the samples for which ages are reported here.

The old sample ages have been obtained for both wood and peat samples. Shell material, a favorite for dating postglacial events, exchanges with atmospheric ^{14}C and is less suitable for dating the early and late Wisconsin.

Glacial History

The samples for which ages are reported here are associated with the history of the Laurentide ice sheet in the Great Lakes region and with the glacial history of the U.S. Pacific Northwest. The ^{14}C determinations make it possible to compare the chronological sequence of climate events in both areas.

For fluctuations of the ice sheet during the last 50,000 years, we used the compilations of Dreimanis and Goldthwait (*5*). For earlier events our most important date (sample QL-198) is $74{,}700^{+2700}_{-2000}$ radiocarbon years ago for wood from the St. Pierre interstade. It places this interstade very early in the Wisconsin and calibrates the Great Lakes chronology beyond 50,000 years, as shown in Fig. 1. The age of approximately 65,000 years obtained previously at the University of Groningen (*6*) for the St. Pierre interstade appears too young. The younger age can be explained by laboratory contamination of enriched samples dated before 1967 at Groningen (*4*).

The second date of importance for the Laurentide ice sheet history (QL-963) is 45,800 ± 700 years ago for wood from

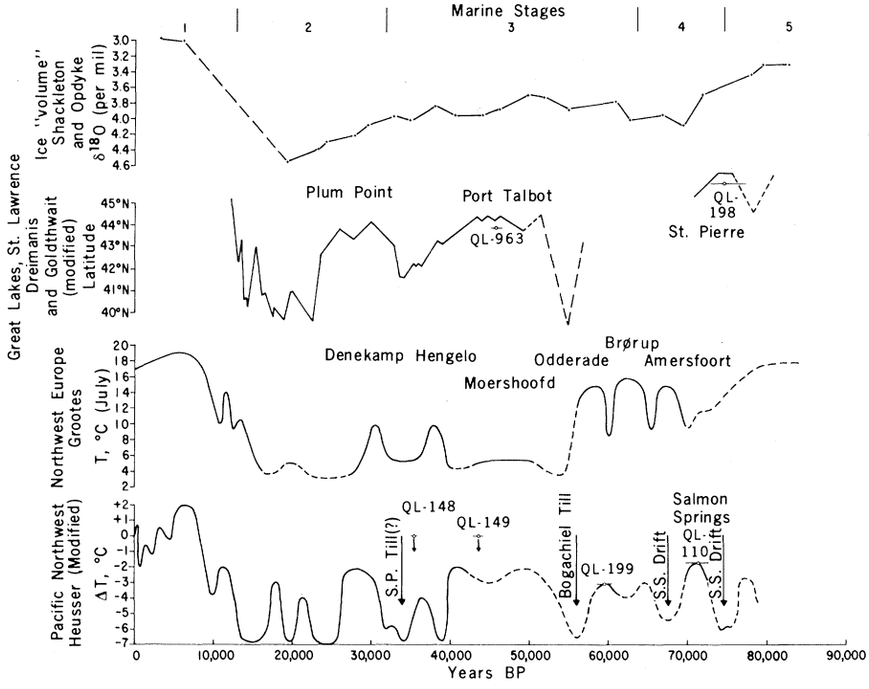

Fig. 1. Carbon-14 chronology of climate changes in the Pacific Northwest (*7*), Northwest Europe (*4*), and the Great Lakes region (*5*). The time scale of the $\delta^{18}O$ curve (*12*) is based on the assumption of a constant sedimentation rate.

the Pine River organic horizon in Manistee County, Michigan. The date establishes this locality as the most northerly (^{14}C dated) extent of the Port Talbot interstade beds and brings the retreat of the Laurentide ice sheet to 44°12′N at that time (Fig. 1).

The curve for the Pacific Northwest in Fig. 1 is based on a reconstruction of temperature changes from pollen assemblages of the Hoh-Kalaloch pollen stratigraphy (*7*) (see Fig. 2). These assemblages are directly radiocarbon-dated to about 43,000 years ago. The further age calibration given in Fig. 1 was achieved by correlation with other geologic sections. One of these is near Salmon Springs, Washington, where a sequence of two drifts is separated by a peat layer from which the Salmon Springs nonglacial interval has been inferred (*8*). These two drifts are representative of the Salmon Springs glaciation (*S.S. Drift* in Fig. 1). The Salmon Springs nonglacial at the type locality can be correlated palynologically with the first interstade after the Puyallup interglaciation in the Hoh-Kalaloch sequence. The age of the peat collected at the Salmon Springs type locality is $71{,}500^{+1700}_{-1400}$ years (QL-110) and anchors Heusser's climatic reconstruction near 70,000 years ago (Fig. 1).

A second age calibration point for the Pacific Northwest is derived from the Bogachiel River site, south of Forks, Olympic Peninsula, where till overlies peat that has an age of 59,600 ± 700 years (QL-199). Actually two different samples were dated; one sample was directly counted without enrichment and dated at $57{,}000^{+2400}_{-1900}$ years ago, whereas the independently combusted and enriched sample yielded the age quoted above. Glacial conditions near 59,000 years ago fit the Pacific Northwest climatic curve only in the manner shown in Fig. 1. The pollen data, to be discussed later, agree with this interpretation.

A further possible indirect calibration of the Pacific Northwest climatic curve is provided by samples from the Strawberry Point site on Whidbey Island. The interpretation of the geologic sequence and its age has been complex (*9–11*). Two organic horizons, Strawberry III and Strawberry II, were dated in our laboratory. The thickness of the lowermost organic (peat) horizon is about 30 cm (Strawberry II). A sample from the top 10 cm of this horizon (QL-149) gave an age of $43{,}900^{+1000}_{-900}$ years, whereas the bottom 10 cm (QL-151) was dated at $43{,}600^{+1000}_{-900}$ years ago. The new dates confirm, within the larger statistical error, the Groningen date of $47{,}600^{+3300}_{-1800}$ radiocarbon years ago (GrN-5257) reported previously for Strawberry II (*6*).

Both peat and wood chips were collected from the 10-cm-thick Strawberry III layer. The ages of the wood (QL-148b) and peat (QL-148a) are, respectively, 35,600 ± 300 and 35,400 ± 200 radiocarbon years, in agreement with the previously reported age (I-1880) of $34{,}900^{+3000}_{-2000}$ years.

Strawberry III is overlain by a diamicton (*9*). This whole sequence agrees with the climatic curve of the Pacific Northwest given in Fig. 1. The section, however, is not critical for the age calibration of the Pacific Northwest because samples from the Hoh-Kalaloch section were also dated directly in this age range. The internal agreement between the peat ages of Strawberry II and the agreement between the wood and peat ages of Strawberry III confirm the reliability of the ^{14}C dates for these materials.

One of the previously dated samples of the Salmon Springs interstade (GrN-4116c) was evidently contaminated, as indicated by the reported finite age of 50,100 ± 400 years. The Salmon Springs glaciation has sometimes been extended to include a time interval up to nearly 25,000 years ago. From the new date and the climatic reconstruction (Fig. 1), the drift sheets preceding and following the Salmon Springs appear to have been deposited in a period of about 10,000 years between 65,000 and 75,000 years ago. Strict adherence to the type-locality nomenclature would exclude the extension of the Salmon Springs glaciation terminology to episodes occurring more recently than about 65,000 radiocarbon years ago.

For comparison, two other climatic chronologies are shown in Fig. 1. The Northwest European chronology has been calibrated by ^{14}C dating by Grootes (*4*). The ice volume curve, derived from oxygen isotopic measurements (*12*), is age "calibrated" by (i) assigning the age of 126,000 years to the warmest part of stage 5e (the temperature maximum of the previous interglaciation) in the marine oxygen isotopic record, and (ii) assuming constant sedimentation rates in the core for the last 126,000 years. The age of 126,000 years for stage 5e is obtained by correlating the oxygen isotopic record with ages of ^{230}Th-dated corals from beaches formed during the high sea-level stand in stage 5e (*13–15*).

Climatic curves of the last glaciation have often been compared with each oth-

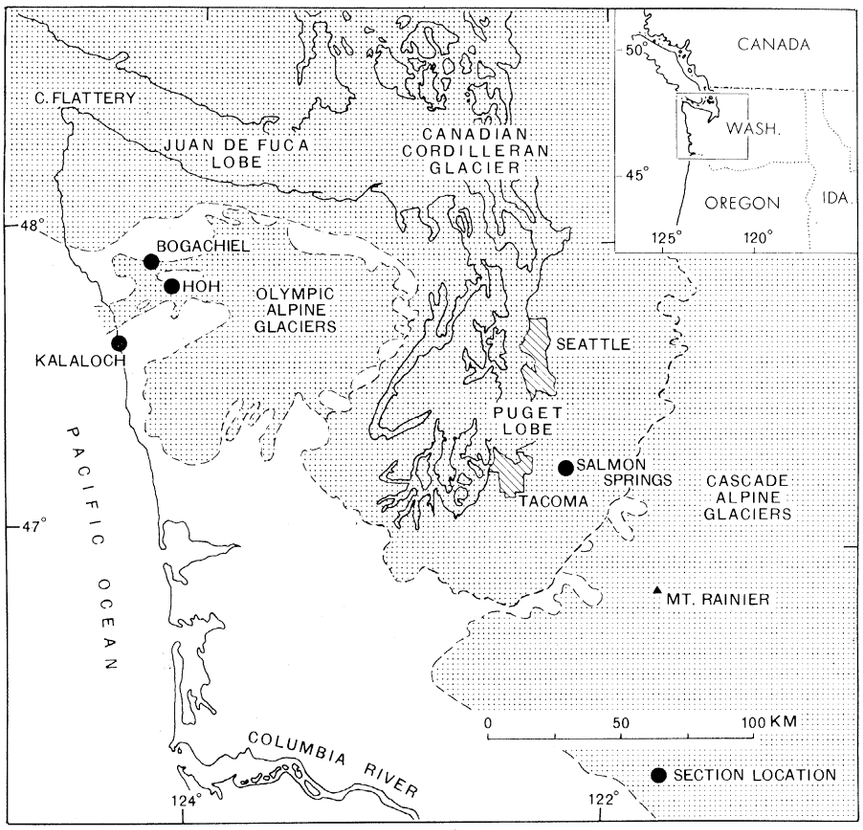

Fig. 2. The Pacific region of Washington. Section sites are shown in relation to the extent of the Puget and Juan de Fuca lobes of the Fraser glaciation, the Olympic alpine glaciers during the Salmon Springs glaciation, and the Cascade alpine glaciers at various time during the Pleistocene (*17*).

er. Beyond 40,000 years these curves normally lack age calibration, and the resulting comparisons are not very convincing. Three of the four climatic histories in Fig. 1 are calibrated by ^{14}C dating and should not shift beyond the errors of the age measurements.

There is excellent agreement between the European and Pacific Northwest curves for part of the climatic history. The ages of three interstades in the Pacific Northwest—approximately 60,000, 65,000 (based on interpolation), and 71,000 radiocarbon years—agree with the ages that mark the beginnings of the Odderade, Brørup, and Amersfoort interstades, 60,500 ± 600, 64,400 ± 800, and 68,200 ± 1100 years, respectively (*4*). The age difference of 3300^{+2000}_{-1900} years between the Salmon Springs interstade date of $71,500^{+1700}_{-1400}$ years ago (QL-110) and the date for the beginning of the Amersfoort interstade, 68,200 ± 1100 years ago, is small and statistically not very significant. The three interstades are followed in both regions by a pronounced cold interval around 55,000 years ago.

Detailed agreement between the European and Pacific Northwest climatic histories is lacking for the interval from 30,000 to 55,000 years ago. There appears to be a correlation between Strawberry II and the Moershoofd climatic amelioration. Although the age differences are small, the Denekamp and Hengelo warming trends are not reflected in the Pacific Northwest curve at the same time. Of course, not all local climatic trends are of a global nature; some events may have been caused by the regional recession or advance of nearby ice sheets.

In the Great Lakes region, the Port Talbot interstade appears to be contemporaneous with the less pronounced European Moershoofd interstade and the Pacific Northwest interstade [pollen zone 5 of Heusser (*7*)] between 40,000 and 50,000 radiocarbon years ago.

As discussed above, the age of the Amersfoort interstade is not significantly different from the age of Salmon Springs interstade and they may well be contemporaneous. However, the age difference between Amersfoort and St. Pierre is 6500 years, with a standard error in the difference of about 2300 years. This age difference is nearly 3 standard deviations. The technical problems of measuring the ages of such old samples in different laboratories (contamination, background counts, and so on) are not included in the age errors, which are calculated mainly from the statistical variability in counting rates, and at present we do not believe that the dates prove conclusively that the Amersfoort and St. Pierre interstades are not contemporaneous. Of course it is possible that the St. Pierre date is a minimum age. If so, St. Pierre could be the latest stage of the previous interglacial.

Shackleton and Opdyke's oxygen isotopic curve (*12*) reflects the changes in oceanic isotopic composition caused by the removal of isotopically light water to Pleistocene ice sheets. The change in oceanic isotopic composition is an indirect measure of ice volume. Ice removed at high latitudes in the earlier stages of ice sheet formation has lower isotopic ratios than ice removed later on, when ice margins have progressed to the maximum limit. Thus the earlier ice additions change oceanic isotopic ratios more than the later ones do. The ice volume curve is therefore less sensitive for changes in ice margins in the Great Lakes region than for changes near Hudson Bay. Yet it is a global measure of ice volume change, and as such is given for comparison with the more regional ice margin fluctuations in the Great Lakes area.

The marine oxygen isotopic stages for Pacific core V28-238 are given at the top in Fig. 1. Stage 4, as computed on the basis of a constant sedimentation rate, lasted from 75,000 to 64,000 years ago (*12*). This stage represents the onset of climatic deterioration after the previous interglacial and may be correlative with (i) the oldest of the Salmon Springs drifts, and (ii) the cold episode preceding Amersfoort. If so, the end of stage 4 would be the onset of the warming trend that resulted in the stage 3 Amersfoort and Salmon Springs interstades. Thus the age of the end of stage 4 in the marine sequence would actually be about 70,000 conventional radiocarbon years (72,000 years when the more precise ^{14}C half-life of 5730 years is used instead of the conventional 5568 years). Another correlation has been given by Grootes (*4*), but our preference is for an age of 70,000 radiocarbon years at the boundary of stages 3 and 4.

One of our programs involves dating a series of samples related to early Chilean glacial advances. One of these samples, QL-61, was dated previously at $56,000^{+2000}_{-1700}$ years (*16*). We now have an enrichment date for this sample of $62,600^{+1300}_{-1100}$ years. This first tentative result shows that this event also falls in the triple interstadial sequence discussed for Europe and the Pacific Northwest.

Samples related to the last interglacial fall outside our dating limit. Two samples of interglacial age were measured, mainly as a check on possible laboratory contamination. A peat sample (QL-197) from the Missinaibi Interglacial Formation in northern Canada yielded an infinite age of more than 72,500 years, and a wood sample (QL-114) from the Kalaloch site was dated as older than 74,000 years.

Pacific Northwest Interstade

Environments

The Pacific Northwest climatic curve in Fig. 1 is from the Hoh-Kalaloch area, whereas the older ^{14}C dates are from the Bogachiel and Salmon Springs sites (Fig. 2). We will show in this section that the climatic events at Bogachiel and Salmon Springs can be tied to the Kalaloch-Hoh sequence through palynological correlations.

Salmon Springs is the older of the two Washington interstades. Located at 47°13′10″N, 122°13′13″W, approximately 13 kilometers east of Tacoma at an elevation of 75 m in the Puyallup-Duwamish valley of the Puget Lowland (Fig. 2), the type section consists principally of peat and underlying volcanic ash interbedded between drifts of two Salmon Springs glaciations (*8*). The drifts are part of two sheets laid down by readvances of the Puget Lobe of the Canadian Cordilleran glacier (*17*). Pollen stratigraphy of the peat and volcanic ash (Fig. 3) is divided into two pollen assemblage zones (*18*). Gramineae, Cyperaceae, and Compositae (grasses, sedges, and composites) in the lower zone are the major nonarboreal types, which later give way to arboreal *Pinus* (pine) and *Picea* (spruce). The upper zone consists of an assemblage of *Abies* (fir), *Tsuga heterophylla* (Western hemlock), and *Pinus*.

The vegetation at the beginning of the record is interpreted as having been tundra and park tundra, which was gradually invaded by *Pinus* and *Picea*. Forest dominated by *Abies* developed next, but an advanced state of succession was never completely reached. Disturbance of the communities—possibly by fire, as indicated by significant percentages of *Pinus*—continued throughout the time of arboreal pollen deposition. The forest is believed to have its closest analog in the montane forest of today. This view is supported by the poor representation of subalpine *Tsuga mertensiana* and by the absence of Douglas fir (*Pseudotsuga menziesii*) in the Puget Lowland during much of the Holocene. But the interpretation is not unequivocal, because the species of *Abies* pollen in the section could not be determined. Four species,

A. grandis, *A. procera*, *A. amabilis*, and *A. lasiocarpa*, at present occupy the Pacific slope of Washington between sea level and timberline. A park tundra species, *A. lasiocarpa*, is believed to be ruled out as a possible contributor to the assemblage, whereas any or all of the others that reach montane elevations are likely to have contributed to the pollen rain preserved during the Salmon Springs interstade.

Correlation of the Salmon Springs pollen stratigraphy with zones 7 and 8 in the Kalaloch sequence is based on the succession at Kalaloch of predominantly nonarboreal Gramineae, Cyperaceae, and Compositae to arboreal *T. heterophylla*, *Picea*, and *Alnus* (alder). Moreover, zone 7 is the warmest interstade at Kalaloch and is dated at more than 47,000 years ago (Y-2322 and Y-2323). The differences between the assemblages in the two sections are probably due to climatic differences between the coastal environment at Kalaloch and the more continental setting at Salmon Springs. Forest at Salmon Springs appears to have been montane in character, while at Kalaloch it was of a lowland type. The average July temperature, estimated from present-day temperature and vegetation patterns and modern pollen rain relationships (*7*), was approximately 6°C below the present temperature during the time represented by zone 8 and only 2°C lower during zone 7 time.

The younger interstadial Bogachiel section is at 47°53′00″N, 124°20′00″W, at an elevation of 120 m on the western Olympic Peninsula about 65 km southeast of Cape Flattery (Fig. 2). At this locality, compact, deeply weathered till overlies peat, which rests on a diamicton consisting of pebbly sand containing peaty clasts. The till was deposited by an alpine glacier that orginated in the Olympic Mountains and flowed down the Bogachiel valley. Pollen stratigraphy of the peat (Fig. 3) shows chiefly Gramineae, Cyperaceae, and Compositae, except in the lower portion, where a predominance of *Pinus* is followed by an assemblage consisting of *T. mertensiana* (mountain hemlock) and *Picea*. The record begins with a park tundra in which *Pinus* pioneered under a warming climate. Subalpine forest followed, achieving stability for a time in the prevailing environment. Finally, tundra and park tundra redeveloped. The sequence indicates an interval of falling temperature during which the Bogachiel glacier advanced and ultimately passed over the section site.

The arboreal episode characterized by *T. mertensiana* is correlated with a comparable episode in pollen assemblage zone 6 at Kalaloch, where the Gramineae, Cyperaceae, and Compositae are otherwise also the major constituents. Apparent differences in pollen stratigraphy at the two sites are explained by local factors affecting the nearby vegetation. The Bogachiel site, for example, was close to glacier termini, whereas Kalaloch was relatively distant from fluctuating ice fronts and was never glaciated. The mean July temperature during the interstade was on the order of 5° to 6°C below the present temperature, excluding the interval when subalpine forest (*T. mertensiana* and *Picea*) succeeded, when it was 3° to 4°C lower. On the whole, the Bogachiel interstade was

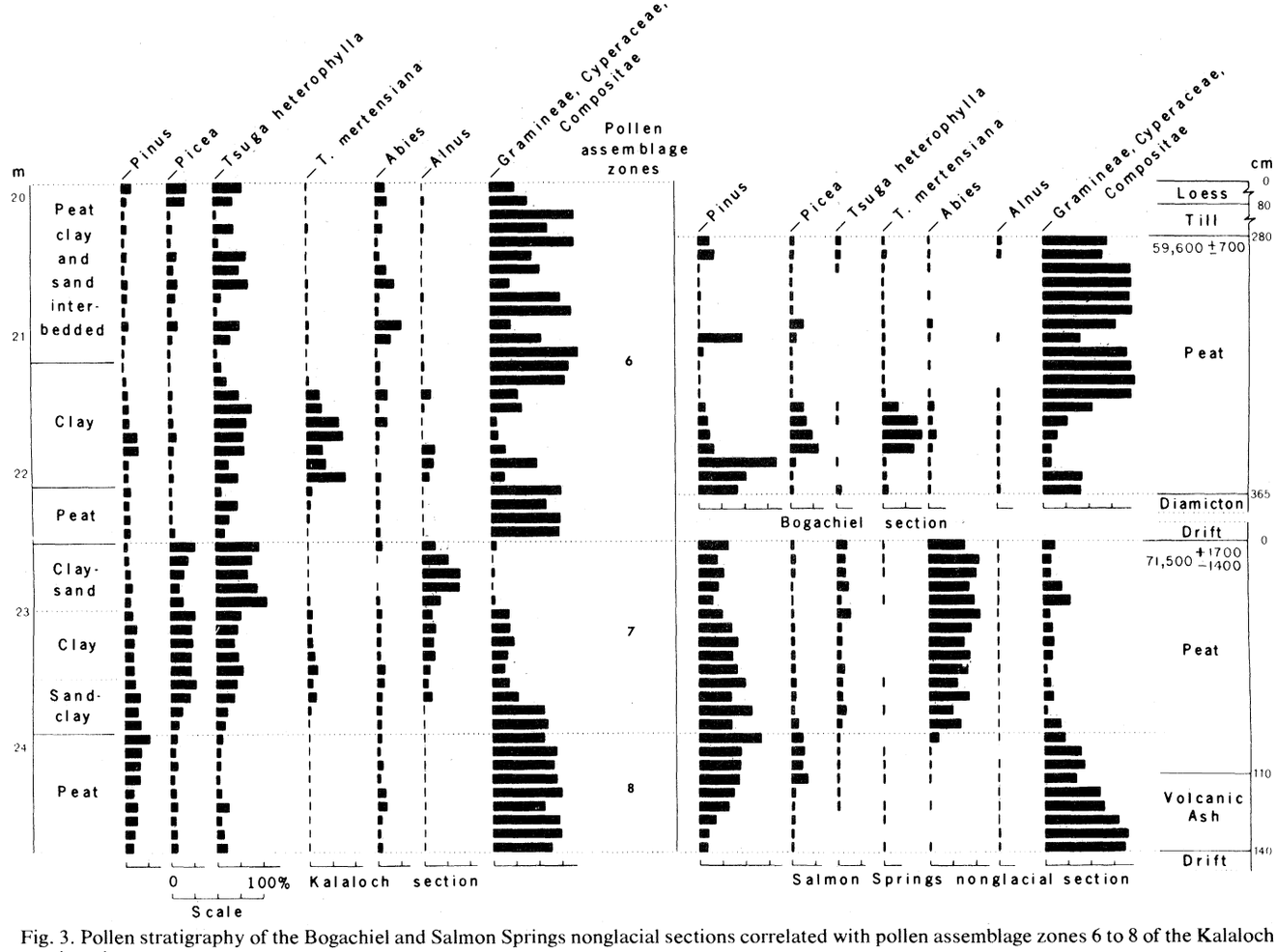

Fig. 3. Pollen stratigraphy of the Bogachiel and Salmon Springs nonglacial sections correlated with pollen assemblage zones 6 to 8 of the Kalaloch stratigraphy.

colder than the Salmon Springs one; the maximum temperature probably averaged 1° to 2°C lower.

Before now, finite ages of the climatic changes interpreted from the Hoh-Kalaloch stratigraphic sequence were not established earlier than pollen assemblage zone 5. The chronology, controlled by 29 ^{14}C ages, was finite only to about 43,000 years ago. Extension of the chronology to zones 6 and 7—back to approximately 75,000 years ago—now provides additional time planes not only for continental and intercontinental correlation but also for correlation with the marine pollen stratigraphy, which in the Northeast Pacific is tied in with the oxygen isotopic stages (*19*). The continental and marine pollen zonation has been correlated with the oxygen isotopic stratigraphy through stage 6 (*20*).

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21. The palynological work was supported by NSF grant DEB 76-12561, and the ^{14}C research by NSF grant EAR 76-81598. The wood sample from the Missinaibi Formation was collected by R. G. Skinner in 1970 at 50°22′N, 82°43′W on the right bank of the Soweska River, Ontario. The wood sample from the St. Pierre beds was collected in 1972 by R. G. Skinner and W. Blake, Jr., at 46°03′N, 72°47′W on the east bank of the St. François River, 2.5 km southeast of the town of Pierreville, Quebec. The peat sample from the Salmon Springs type locality was collected in 1974 by C. J. Heusser and D. J. Easterbrook. The Bogachiel peat was also collected in 1974, by C. J. Heusser and L. E. Heusser. W. R. Farrand submitted the wood sample of Port Talbot age, which was collected from the northern bank of the Pine River, Manistee County, Michigan (44°12′N, 85°51′W). Comments by P. M. Grootes and R. L. Burk substantially improved this article. All ^{14}C dates in this article are in radiocarbon years BP.

The Glycosylation of Hemoglobin: Relevance to Diabetes Mellitus

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cells is covalently linked to glucose, resulting in the formation of a chromatographically distinct minor component designated by Allen *et al.* (*5*) as hemoglobin A_{Ic} (Hb A_{Ic}) (see Fig. 1). Interest in Hb A_{Ic} was considerably enhanced by the discovery that there is a two- to threefold increase in this glycoprotein in patients with diabetes mellitus (*6*). In this article we review the structure and the biosynthesis of glycosylated hemoglobin and then consider its relevance to the pathogenesis, diagnosis, and management of diabetes.

The extraordinary diversity among proteins is considerably enhanced by posttranslational modifications (*1*). A wide variety of proteins owe many of their functional properties to the covalent attachment of carbohydrates at certain residues in the polypeptide chain. Such modifications often provide enhanced stability or solubility, or both. Protein glycosylation is particularly important in maintenance of the integrity of plasma membranes and in facilitating the secretion of proteins into the extracellular space. These specific modifications are generally under precise enzymatic control. In contrast, certain proteins may undergo nonenzymatic glycosylation. This phenomenon depends on the presence of a high concentration of the free sugar and often requires nonphysiologic incubation conditions. For example, the "browning" reaction is well recognized in the dairy industry. When milk is heated for prolonged periods, carbonyl groups on sugars combine with amino groups on proteins such as casein to form Schiff base adducts, resulting in the formation of a heterogeneous, poorly soluble brown product (*2*). This type of reaction can also modify small proteins such as insulin (*3*) and oligopeptides (*4*).

Recently, attention has been focused on the nonenzymatic glycosylation of human hemoglobin. Unlike the browning reaction, the glycosylation of hemoglobin takes place under physiologic conditions, at a specific site on the protein. Normally, about 5 percent of hemoglobin in a population of normal human red

Minor Components of Human Hemoglobin

Human hemoglobin is less heterogeneous than that of most other mammals. In adults and children above the age of 6 months, about 90 percent of their hemoglobin is Hb A ($\alpha_2\beta_2$), a tetramer composed of two pairs of unlike polypeptide chains, each attached to the prosthetic heme group. The α and β

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