[RADIOCARBON, VOL. 4, 1962, P. 1-12]

Radiocarbon

1962

RADIOCARBON DATING AT THE UNIVERSITY OF WASHINGTON I*

T. F. DORN,† A. W. FAIRHALL, W. R. SCHELL and Y. TAKASHIMA‡

Department of Chemistry, University of Washington, Seattle, Washington

INTRODUCTION

Beginning in 1955 a C^{14} dating apparatus was constructed at this University for the purpose of measuring the specific activity of tree rings selected from a specimen of Sequoia wood having 3000 growth rings (Dorn, 1958). The original purpose was to obtain a measure of the half life of C^{14} by essentially the inverse of C^{14} dating. For various reasons the project was not completed, and for about a year the apparatus stood idle for lack of financial support. This latter deficiency has now been rectified, at least temporarily, and research with the apparatus has been resumed. Fabrication of a second, 1 L counter is nearing completion.

In the meantime, others have investigated tree rings and other materials of known age and found interesting fluctuations in the C^{14} specific activity in past times. Our work on Sequoia tree rings has been resumed and results to date are reported in Part III of this paper.

In addition to the investigation of tree rings we have dated samples submitted to us by anthropologists, geologists, glaciologists, etc. These are reported in Part II of this paper.

Part IV consists of a short note concerning the mechanism of oxidation of radiogenic C^{14} in the atmosphere.

PART I: APPARATUS AND METHOD

The counter, having a volume of 10 L, consists of a copper cylinder 6 in. in diam and 24 in. long divided lengthwise into quadrants by means of horizontally and vertically-mounted 2.5 mil copper sheets. Electrolytic copper was used because of its cheapness and availability. Each quadrant has a 1 mil tungsten center wire and each has its own linear amplifier. All operate in anticoincidence, both with each other and with a surrounding ring of G. M. anticoincidence counters 30 in. long. The counter and guard ring are shielded by 8 in. of steel.

* Supported in part by grants from the National Science Foundation.

† Now at the Department of Chemistry, The University of the South, Sewanee, Tennessee.

‡ Permanent address: Department of Chemistry, Kyushu University, Fukuoka, Japan.

Samples are converted to methane by a simple, rapid method (Fairhall, Schell and Takashima, 1961). Sample pressures of up to ca. 150 cm Hg are measured with a mercury manometer. At this pressure, at room temperature, the counter contains ca. 11 g of carbon. Counting is satisfactory down to pressures of ca. 60 cm Hg.

Upper and lower discrimination is applied to signals from the amplifiers so that only signals originating in the counter of between 1.2 and 50 mv are accepted. A pulse generator is used to check the discriminator settings prior to every counting period. After passing the discriminators and the anticoincidence network the net anticoincidence signals from all four center wires are summed and recorded by a scaler. An elapsed-time printer records the time to collect 1000 net counts.

Our working standard for almost all measurements has been a specimen of 275-yr-old Sequoia wood, as determined by ring counting. The age-corrected activity of this specimen, corrected also for C^{13}/C^{12} differences, is 0.945 ± 0.016 of the activity of the NBS oxalic-acid standard. Therefore the dates reported in Part II would not change significantly if they had been computed on the basis of 0.95 of the activity of the NBS standard as the modern assay of C^{14}. The net counting rate of our Sequoia standard at a pressure of 148.9 cm Hg and 22°C is ca. 101 counts/min and has varied by $\pm$ 3% in a non-periodic way over the past two yr, presumably owing to slight changes in the parameters of the electronic system. The standard is measured periodically and is generally reproducible over the short term within 0.5%, i.e. 0.5 counts/min, which is ca. the reproducibility of the background counting rate.

The background counting rate of the counter has remained fairly constant over the past two yr at ca. 50 counts/min. The background rate is pressure-sensitive, the relation being

$$\text{Background} = 40 + 0.066\,p \text{ counts/min}$$

where p is the pressure in cm Hg. Since methane is more sensitive to fast neutrons than the more commonly-used CO_2 and no neutron shielding is employed, the pressure-dependent portion of the background may represent the neutron component. The remaining background may well be due to radioactive impurities in the counter and shield, since none of the material was of special purity. A background of 40 counts/min from such a source is not unreasonable in view of the large size of the counter. Background counts are taken once or twice a week as a check on the apparatus. Since the samples are ordinarily counted between 5:00 P.M. and 9:00 A.M. no diurnal variations in background have been looked for or observed in this time interval.

Counting rates are computed from the record on the printer-timer. Individual time intervals for 1000 counts are always observed to fluctuate in the statistically expected manner except during the first two or three hours after the filling of the counter, when the counting rate is always observed to show a decrease to its equilibrium value. The source of this effect is unknown. Only the counting data following this "incubation" period are used in determining the average count.

A Consolidated Engineering Model 21-201 mass spectrometer is used to determine C^{13}/C^{12} ratios on the CO_2 prior to conversion to methane. CO_2 from

the Sequoia wood standard is used as a reference, and deviations are reported as dC^{13} to distinguish them from ordinary δC^{13} referred to carbonate standards. Isotope ratios are measured on all Sequoia wood samples and on artifacts submitted for dating where highest possible accuracy has been requested. Isotope ratios are not measured for very old samples.

Further details on the apparatus and method may be obtained by writing to the authors (AWF).

ACKNOWLEDGMENTS

Financial support for construction of the apparatus came from the departments of Physics and Chemistry in which one of the authors (AWF) holds a joint appointment. Such support is gratefully acknowledged, as are funds for support of current research activities from the National Science Foundation. We are indebted to Harold Fauska and Albert Wakefield for their assistance in construction of the electronic equipment, and to William Antonius for fabrication of the counter.

PART II: SAMPLE DESCRIPTIONS

All samples were pre-treated with warm 2% NaOH followed by treatment with 3 N HCl and distilled water. Each sample was counted overnight at least twice. During this interval more than 50,000 counts are recorded so that errors in the counting rate due to the number of atoms which decay is smaller than other sources of error, such as fluctuations in the background counting rate. The errors quoted are standard deviations based on replicate determinations of the net counting rate. Ages are calculated using 5568 yr for the half life of C^{14}. Where C^{13}/C^{12} isotope ratios were measured the dC^{13} relative to our Sequoia wood standard are given. As noted in Part I, the standard is indistinguishable in C^{14} activity from the NBS oxalic-standard.

I. GEOLOGIC SAMPLES

Pacific Northwest and Alaska

UW-1. Lake Cave, Skamania County, Washington **2170 ± 60**

A large fragment of partially charred root underlying a lava flow S of Mt. St. Helens (46° 05.8′ N Lat, 122° 12.7′ W Long). Beneath the flow are partly compacted sediments containing many charred root fragments. A stream has cut two small channels in these sediments exposing the root stump. Coll. 1960 and subm. by W. R. Halliday, Univ. of Washington, Seattle. $dC^{13} = -4.88$.

UW-2. Lava beds National Monument, California **780 ± 60**

Charcoal found in a pumice mine (41° 37.5′ N Lat, 121° 25.8′ W Long), under 4 ft of pumice, possibly from eruptions of Glass Mountain, covering a former lodgepole pine forest. Coll. prior to 1955 by C. Borman, Newell, California; subm. by R. G. Knox, Tule Lake, California. *Comment*: the time needed to reestablish present vegetation on the pumice has been estimated at ca. 500 yr; the date shows that this is reasonable. $dC^{13} = -2.81$.

UW-8. Seattle, Washington **12,300 ± 200**

Peat from within the pelvis of a fossil sloth, near the base of Miller Creek Bog (48° 28.3′ N Lat, 122° 18.3′ W Long). Formation of the bog probably followed shortly after the retreat of the last ice sheet from this vicinity. Discovered during excavation at the Sea-Tac Airport. Coll. and subm. by S. Mallory, Univ. of Washington, Seattle. $d\mathrm{C}^{13} = +0.09$.

UW-17. Cherry Point, Washington **24,200 ± 2100**

Wood in till beneath late or post-Vashon glacio-marine deposits, near base of seacliff N of Cherry Pt. on Georgia Strait at Aldergrove Rd. (48° 52.5′ N Lat, 122° 46.2′ W Long). Coll. 1961 and subm. by D. J. Easterbrook, Bellingham, Washington.

Puget Sound series

The following eight samples of peat identify and correlate a series of non-glacial sediments underlying drift of the most extensive glacial advance, called Vashon, and overlying Salmon Springs (Crandell, Mullineaux and Walden, 1958) drift.

UW-7. Johnson Point **27,900 ± 800**

Peat layer interbedded in a sequence of silt and clay layers, overlain by Vashon till (47° 10.6′ N Lat, 122° 49.1′ W Long), exposed in wave-cut cliff ca. 500 ft S of and on the E side of Johnson Point alt 35 ft above high tide. Coll. 1961 by J. Noble, Olympia, Washington; subm. by J. H. Mackin, Univ. of Washington, Seattle.

UW-10. Powder Wharf **34,700 ± 1100**

Peat layer 2 ft above the base of a 65 ft-thick Kitsap clay formation, Sceva (1950) overlying Salmon Springs rusty sand and gravel. Coll. ca. 100 ft NW of Powder Wharf at ca. 8 ft above the base of the bluff (47° 6.9′ N Lat, 122° 45.3′ W Long). Coll. 1961 by J. Noble; subm. by J. H. Mackin. *Comment*: this layer should date the beginning of the Kitsap clay formation in this region.

UW-11. Powder Wharf **31,300 ± 900**

Peat layer from the center of the Kitsap clay formation. Coll. ca. 200 ft S of Powder Wharf at ca. 40 ft above the road cut (47° 6.8′ N Lat, 122° 45.3′ W Long). Coll. 1961 by J. Noble; subm. by J. H. Mackin.

UW-12. Tahlequah **27,900 ± 1200**

Peat layer, 5 in. thick, supposedly interbedded within Salmon Springs formation, 3 ft above the base of the bluff 1 mi NW of Tahlequah ferry dock, Vashon Island (47° 20.8′ N Lat, 122° 31.7′ W Long). Coll. 1961 by D. Molenaar, Olympia, Washington; subm. by J. H. Mackin. *Comment*: date, and relations of UW-10 and 13, indicate that assignment of peat to Salmon Springs formation is probably incorrect.

UW-13. Port Ochard **31,400 ± 1600**

Peat layer, 4 in. thick, located at road level ca. 1 mi W of Port Orchard

Salmon Springs formation. Coll. 1961 by D. Molenaar; subm. by J. H. Mackin. (47° 32.2′ N Lat, 122° 39.8′ W Long). At or near the base of Sceva's Kitsap clay member below thick pre-Vashon sand unit, and lying above Crandell's Salmon Springs formation. Coll. 1961 by D. Molenaar; subm. by J. H. Mackin.

UW-19. Cormorant Passage **33,000 ± 1000**

Peat from a discontinuous peat bed at the top of 50 ft of interbedded sand and gravel derived from sources to the E and SE; on a bluff at 60 ft alt on the S side of Cormorant Passage (47° 08.3′ N Lat, 122° 37.8′ W Long). Peat is overlain by gravel and sand of a northern provenance. Coll. 1961 and subm. by G. Kimmel, Tacoma Washington.

UW-20. Tacoma Narrows **34,500 ± 1000**

Peat from a bluff below Tacoma along the Narrows (47° 17.8′ N Lat, 122° 31.8′ W Long). From sand, clay and gravel unit which was similar in provenance to that of UW-19. Coll. 1961 and subm. by G. Kimmel.

UW-25. Maplewood **32,700 ± 1000**

Peat in a bluff at ca. 125 ft above sealevel in the vicinity of Maplewood, Kitsap County (47° 24′ N Lat, 122° 33′ W Long). Coll. 1961 and subm. by G. Kimmel.

UW-9. Wanapum Dam, Columbia River **31,600 ± 900**

Fragment of peat in glacial outwash gravel underlying normal Columbia River alluvial gravel near Vantage, Washington (46° 52.8′ N Lat, 119° 58.3′ W Long). Near W end of powerhouse block in excavation at Wanapum dam site. Coll. 1961 by R. Fryxell, Vantage, Washington; subm. by J. H. Mackin. *Comment*: the age of the peat sets an upper limit on the age of the glacial outwash.

UW-27. Mt. Hood, Oregon **1680 ± 70**

Part of a log from the Stadter Buried Forest, kept in the office of the Mazamas, a mountaineering club in Portland, Oregon. Tentatively identified as *Libocedrus decurrens* by H. E. Erickson, Forest Products Lab., Univ. of Washington. Coll. sometime between 1926 and 1931 from the S side of a spur separating Reid and Zig-Zag glaciers, called Illumination Spur, at alt 6200 ft (45° 22.0′ N Lat, 121° 42.1′ W Long). Subm. by A. E. Harrison, Univ. of Washington, Seattle. *Comment*: the age of the sample could correspond to that of a mudflow on Mt. Hood dated 1670 ± 200 (M-898, Michigan V) or it might be related to a period of glacial expansion ca. 1800 yr ago (Heusser, 1953; L-106C, Lamont I; Y-304, Yale III). The site must be revisited to determine whether the logs are buried in mudflow material or in a lateral moraine.

Glacier Bay series, Alaska

The following five samples were collected in 1961 and submitted by K. Bengtson, Univ. of Washington, Seattle, as part of a continuing effort to resolve the Late Wisconsin and recent chronology of the Glacier Bay area of southeastern Alaska (cf. Yale II; Yale III).

UW-14. Brady Glacier, E Margin **685 ± 40**

Wood from the outside of a 2-ft diam stump having 300 growth rings. Much other wood was nearby. The stump, transported by the Brady glacier from an unknown but probably nearby location at somewhat lower alt, was partially imbedded in upended position ca. 20 ft below top of a lateral moraine adjoining the Brady glacier at alt 1750 ft (58° 33.4′ N Lat, 136° 42.9′ W Long). $d\mathrm{C}^{13} = -3.25$.

UW-15. Brady Glacier, E Margin **260 ± 50**

Wood from the outside of a log ca. 2.8 ft in diam, transported to NE by a distributary tongue of the Brady glacier from an unknown, but probably nearby point of growth at somewhat lower alt. Specimen was found on ice surface near end of distributary tongue, 300 ft SW of a small unnamed lake at alt 1658 ft (58° 34.9′ N Lat, 136° 39.8′ W Long). $d\mathrm{C}^{13} = -4.27$.

UW-16. Wood Lake, W side **1380 ± 100**

Wood from the outside of an ice-sheared stump at alt 250 ft in the valley of Wood Creek (58° 33.8′ N Lat, 136° 30.3′ W Long). This tree appears to have been partially buried in gravel by ice-marginal streams accompanying invading ice from Geikie Inlet to the N. Subsequently the tree was sheared by ice, and outwash gravel and overlying till protected it until recent exposure by stream action. Base of tree was not visible but the specimen, one of several, was upright, and probably rooted in place. $d\mathrm{C}^{13} = -3.81$.

UW-18. Glacier Bay, Alaska **3700 ± 1000**

Peat from the bottom of a small tarn located ca. 300 ft S of the SE corner of an unnamed lake just E of De Langh Mountain at alt 75 ft (58° 25.2′ N Lat, 136° 51.9′ W Long). The bottom of the tarn was sampled with a borer which struck sand and clay 2 ft below the surface. The sample is a basal section of the peat layer. *Comment*: sample was ca. 1/15 the size needed to fill the counter to its minimum operative pressure. It was diluted with methane prepared from coal and counted at a total pressure of 70 cm Hg. More "dead" methane was added to a total pressure of 106 cm Hg and the sample was counted again. The net rates were 1.8 and 2.0 counts/min respectively.

UW-21. Brady Glacier, W Margin **433 ± 80**

Wood from one of a group of upright stumps, probably rooted in place, whose bases are buried in sand ca. 6 ft below grade in a large marginal stream draining the W side of the Brady glacier (58° 25.5′ N Lat, 136° 51.8′ W Long). This tree was probably killed at the time a major advance of the Brady glacier diverted ice-marginal drainage from Taylor Bay directly into the Pacific via the valley in which the tree was growing.

II. ARCHAEOLOGIC SAMPLES

Peter Cave series, Sherwood, Tennessee

Charcoal associated with material judged to be Late Woodland culture from Peter Cave (35° 07.0′ N Lat, 85° 54.8′ W Long). Coll. 1961 and subm.

by P. C. Hartney, Univ. of the South, Sewanee, Tennessee. *Comment*: another sample from the same level as UW-26 was measured at the same time as samples UW-4 and 5. This sample gave an age ca. twice as old as the present measurement, and it also gave an inordinately high weight of ash, suggesting that the acid leach of the charcoal prior to combustion had failed to remove deposited $CaCO_3$ derived from the limestone of the cave. The somewhat older age of UW-5 relative to UW-6 may reflect a similar but smaller amount of contamination by carbonate.

UW-4. 18 in. below the surface **1340 ± 100**

UW-5. 24 in. below the surface **1686 ± 60**

UW-26. 30 in. below the surface **1540 ± 70**

UW-3. Priest Rapids Dam, Washington **1690 ± 80**

Bone from 45-YK-5, an Indian midden site on an alluvial fan at the mouth of Sourdough Creek 3.5 mi upstream from Priest Rapids Dam, Columbia River (46° 41′ N Lat, 119° 57′ W Long). The sample consists of a set of horn cores, probably of mountain sheep, recovered from the lower stratum of the upper midden at a depth of 159 cm below the surface in Cut W-11. These cores were in association with medium sized points of varieties mainly found below the small notched points predominant in the later horizons. Coll. 1958 and subm. by R. E. Greengo, Univ. of Washington. *Comment*: the date is several hundred years later than expected.

UW-22. Vantage, Washington **1715 ± 60**

Charcoal from 45-GR-77, an Indian midden and housepit site on the E bank of the Columbia River, ca. 14.5 mi upstream from the Vantage Bridge and near "Simmons Graveyard," a large burial site (46° 41′ N Lat, 119° 57′ W Long). Sample was taken from a hearth or burned structure near the original center of a large housepit. These remains lay at the base of dark midden soil and near the base of the cultural deposit, ca. 150 cm below the surface of the ground. Projectile points of a type believed diagnostic of Late Middle Columbia River culture were found in close association. Coll. 1960 and subm. by R. E. Greengo, Univ. of Washington. $d\mathrm{C}^{13} = -6.95$.

UW-24. Fossil Bay, Washington **1514 ± 40**

Indian Shell midden on Fox Cove, N of Fossil Bay, Sucia Island (48° 45′ N Lat, 122° 54′ W Long). The sample consists of charcoal from several areas within the apparently homogeneous upper midden of Locality B. This midden is characterized by a predominance of bone artifacts similar to those of Carlson's San Juan Phase (Carlson, 1960). Another portion of the site, Locality A, ca. 100 m to the N, is notable for a relatively greater number of chipped- and ground stone-artifacts, with a few of bone. Coll. 1960 and subm. by R. E. Greengo. $d\mathrm{C}^{13} = -5.65$.

PART III. MEASUREMENTS ON SEQUOIA TREE RINGS

Samples of tree rings have been selected from three specimens of sequoia wood. The first specimen is a radial cut from a log which was once part of the

tree identified as D-22 (Douglass, 1920) and having 3000 growth rings. The second specimen, called TL-1 (for the University of Arizona's Tree Ring Laboratory) was cut from a large Sequoia stump, not previously studied by Douglass, thought from its size and growth-ring pattern to be at least 2000 yr old. The third specimen was a wedge-shaped block from a medium-sized tree felled in 1950. The growth rings from the bark layer back ca. 275 yr to the tip of the wedge were very wide and this specimen was chosen as the working standard of pre-industrial wood. In the two older specimens the outermost rings are very close together and the sapwood has undergone considerable decomposition. For his assistance in the collection of these specimens, in the summer of 1955, and for the painstaking counting of the rings, we are indebted to Terah L. Smiley of the Geochronology Lab., Univ. of Arizona.

Most of the samples taken for measurement included ca. 10 growth rings, and none included more than 20 rings. In order to avoid complications arising from the deposition of younger, more soluble components in the fiber of the wood as the sapwood changed to heartwood (which in these very old trees appears to take 100 yr or more) the wood was pulped to extract the cellulose. This was accomplished by first leaching the puverized sample with 1% NaOH followed by a treatment with 8% $NaClO_2$. This treatment removed ca. half the wood and left a nearly white residue. This was burned in a stream of oxygen and the CO_2 from the combustion was condensed with a bath of liquid oxygen. During the transfer of the CO_2 to the CH_4-conversion apparatus a sample was taken for C^{13}/C^{12} isotope ratio measurement. Since all counting data are normalized to the Sequoia sample of A.D. 1687, isotope ratios are likewise referred to this sample as standard, giving the quantity which we call dC^{13}, defined as

$$dC^{13} = \frac{R_{\text{sample}} - R_{\text{tree std.}}}{R_{\text{tree std.}}} \times 1000$$

where $R = C^{13}/C^{12}$.

All net counting rates are normalized to a counter pressure of 148.9 cm Hg. We have established that the net counting rate of a sample is proportional to pressure and slight differences in the sample pressures can be corrected in this way. The limits of error on the measured net rates are standard deviations based on replicate measurements. The quantity dC^{14} is calculated from the net counting rates and the C^{13}/C^{12} isotope ratios in the following manner:

$$dC^{14} = \frac{A^*_{\text{sample}} - A_{\text{tree std.}}}{A_{\text{tree std.}}} \times 1000$$

where $A^*_{\text{sample}} = A_{\text{sample}} \cdot e^{\lambda(t-275)} \left(1 - 2\frac{dC^{13}}{1000}\right)$.

Here (t – 275) is the tree ring age of the sample relative to the 275-yr old standard, and 5568 has been used for the C^{14} half life.

The experimental results are tabulated in Table 1, and the values of dC^{14} are plotted against the calendar date of the ring samples in Fig. 1. Examination of these data leads us to the following conclusions: the C^{14} content of the atmosphere has remained substantially constant over the past 3000 yr but there may be fluctuations of a few percent within a time interval of a few hundred

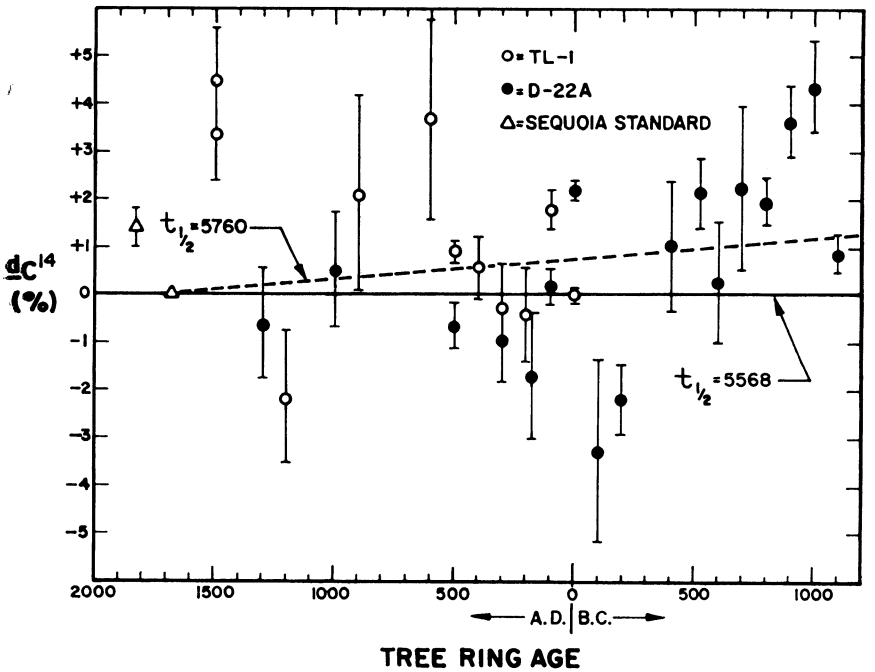

Fig. 1. C^{14} content of Sequoia wood of various ages relative to Sequoia wood grown in A.D. 1687. Age corrections are computed on the basis of 5568 yr for the half life of C^{14}. The dashed line gives the locus of dC^{14} for age corrections based on 5760 yr for the half life of C^{14}.

yr. There are indications of C^{14} maxima at ca. A.D. 1500, A.D. 500, and 1000 B.C. and of C^{14} minima ca. A.D. 1200 and 100 B.C. These results are substantially in agreement with similar studies in other laboratories (Munnich, Ostlund and de Vries, 1958; Ralph and Struckenrath, 1960; Suess, 1961; Willis, Tauber and Munnich, 1960). If this conclusion is correct it will be of interest to uncover the reason for the fluctuations. Moreover, there is no reason to doubt that similar fluctuations may have occurred in the more remote past; possibly they were even larger if the cause is climatic. This possibility may limit the ultimate usefulness of the C^{14}-dating method for obtaining absolute ages; for comparison of relative ages the method will remain extremely useful. A second conclusion from the data is that they do not afford a critical test of the half life of C^{14}. The dashed line on the figure represents the locus of $dC^{14} = 0$ for age corrections based on a half life of C^{14} of 5760 yr (Mann, Marlow and Hughes, 1961; Watt, Ramsden and Wilson, 1961). A longer half life tends to reduce the magnitude of the deviations of dC^{14}, particularly for the oldest samples. The suggestion of fluctuations in the C^{14} content of the atmosphere remains, however.

Some of the data reported here, particularly those with larger experimental error, were obtained near the beginning of the period when the counting apparatus was being put back into operation and its operating char-

https://doi.org/10.1017/S0033822200036456 Published online by Cambridge University Press

acteristics were unfamiliar. Many of these samples are being remeasured, and additional samples will be measured in a continuing study of tree rings.

TABLE 1

C^{14} content of Sequoia tree rings relative to A.D. 1687 Sequoia wood

Tree ring sample	Counts/min	dC^{13}(‰)	dC^{14}(‰)
1300 A.D. (D-22)	96.0 ± 1.20	–2.33	–6.7 ± 12.4
1000 A.D.	93.9 0.68	–2.77	+4.8 12.3
500 A.D.	87.5 0.56	+1.32	–6.7 4.8
300 A.D.	84.3 0.80	–3.66	–9.5 8.6
170 A.D.	83.8 1.10	+4.03	–17.1 13.3
100 A.D.	83.9 0.30	+0.95	+1.9 3.8
0 A.D.	84.6 0.10	+1.10	+21.8 1.9
100 B.C.	79.0 1.63	+0.92	–32.6 19.6
200 B.C.	79.2 0.60	+2.87	–21.8 7.6
400 B.C.	79.3 1.13	0.00	+10.4 13.3
500 B.C.	79.4 0.57	+0.59	+21.8 6.6
600 B.C.	76.6 0.88	–1.42	+2.8 12.4
700 B.C.	77.7 1.20	+1.47	+22.8 17.0
800 B.C.	76.6 0.32	+2.42	+19.9 4.7
900 B.C.	76.5 0.39	+0.94	+36.1 7.5
1000 B.C.	75.8 0.84	–0.94	+43.6 9.5
1100 B.C.	72.0 0.30	–4.52	+8.5 3.8
0 A.D. (TL-1)	82.6 ± 0.10	+0.47	0.0 ± 1.0
100 A.D.	85.3 0.30	+1.19	+18.0 3.8
200 A.D.	84.9 0.80	+4.00	–3.8 9.5
300 A.D.	85.0 0.76	–3.21	–2.8 9.4
400 A.D.	87.9 0.52	+3.66	+5.7 6.6
500 A.D.	88.2 0.10	+2.35	+9.5 1.9
600 A.D.	92.7 1.80	+2.02	+37.0 20.9
900 A.D.	94.7 1.85	+2.10	+20.8 20.8
1200 A.D.	93.5 1.22	–2.27	–21.8 14.2
1500 A.D.	103.7 1.10	–1.55	+44.6 11.3
1500 A.D.	102.6 1.00	–1.51	+33.2 10.4
1830 A.D. (Wedge)	105.5 ± 0.30	+0.98	+14.2 ± 3.8

PART IV: A NOTE CONCERNING THE MECHANISM OF OXIDATION OF RADIOGENIC C^{14} IN THE ATMOSPHERE

A problem of considerable interest to the C^{14} dating method is the mechanism by which nascent C^{14} becomes oxidized to CO_2 so that it may enter the biosphere. It has often been tacitly assumed that the C^{14} produced in the atmosphere by the $N^{14}(n,p)C^{14}$ reaction is oxidized to CO_2 in a short period of time (cf. Libby, 1955; Anderson, 1953). However, in a very interesting experiment (Pandow, MacKay and Wolfgang, 1960) in which N_2-O_2 mixtures were irradiated with neutrons in a reactor, it was shown that the C^{14} was produced as CO and not as CO_2. By inference, atmospheric C^{14} would likewise be produced as CO.

Pandow *et al.* considered a number of possible mechanisms by which atmospheric CO might be oxidized to CO_2 and concluded that there was no mechanism by which this oxidation could be accomplished in the atmosphere. They proposed the interesting hypothesis that the oxidation was accomplished

in the soil by the microorganism *B. oligocarbophilus*. This would make this organism the naturally "hottest," in terms of C^{14} specific activity, of any species on earth. By inference, other organisms feeding on this one would likewise have an abnormally high specific activity, etc. While it would seem unlikely that any specimens which are dated by C^{14} derive any significant fraction of their carbon directly or indirectly from *B. oligocarbophilus*, one would feel more satisfied if a mechanism could be found by which exchange of nascent C^{14} with atmospheric CO_2 was accomplished in the atmosphere.

There is a possible mechanism for the oxidation of CO which Pandow *et al.* did not consider and which we have begun to investigate experimentally. The proposed mechanism involves activation of CO_2 by ultraviolet light from the sun with subsequent collision of the activated molecule with a $C^{14}O$ molecule, during which the exchange reaction

$$CO_2 + C^{14}O \rightarrow C^{14}O_2 + CO$$

might take place. Reaction between unactivated CO and CO_2 does not take place at ordinary temperatures although a number of investigators have shown that exchange does take place under α, β and γ-ray irradiation of the gaseous mixture (Lind and Bardwell, 1925; Hogan, 1954; Harteck and Dondes, 1955; Stranks, 1958). CO_2 absorbs strongly in the ultraviolet region, an energy region which exceeds the activation energy of the exchange reaction.

The experiments to test this hypothesis consist of mixing ca. equal volumes of CO_2 and CO, of which one or the other species is labeled with C^{14}. After exposing the mixture to ultraviolet light from a deuterium source the initially non-labeled species is separated by condensing the CO_2 with liquid nitrogen. After further purification, the radioactivity of the desired component is measured. In order to demonstrate that a trace of the other, radioactive, component is not responsible for the observed radioactivity, it suffices to show that the apparent exchange increases linearly with total irradiation. This is indeed found to be the case. Thus, after irradiation of identical mixtures of labeled CO_2 and CO each for a different length of time the initially non-labeled CO was separated and purified. An aliquot was counted in a small thin-window gas cell inserted beneath a thin-window GM counter. The observed net counting rates of the sample for 0, 1, 2, and 4 hr of irradiation were 0 ± 0.5, 4.2 ± 0.5, 9.2 ± 0.6 and 17.1 ± 0.9 counts/min, respectively. When CO was the initially-labeled component, aliquots of CO_2 separated from the mixture showed 0 ± 0.5, 2.7 ± 0.5, 6.2 ± 0.7 and 10.5 ± 0.6 counts/min above background for the same irradiation times. Since the specific activities of the labeled species were ca. the same in the two sets of experiments, the higher counting rates for corresponding irradiation times when CO_2 was the initially-labeled species probably imply that photochemical decomposition of the CO_2 component into CO + O had occurred as well.

Before it can be established that the principal mechanism by which atmospheric $C^{14}O$ is oxidized by CO_2 is the one which we have proposed, it will be necessary to study this reaction under a variety of conditions, e.g. at a variety of pressures, in the presence of much larger amounts of N_2 and O_2, etc. Such studies are in progress and will be reported elsewhere at a later date.

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