Yale Natural Radiocarbon Measurements, I. Pyramid Valley, New Zealand and Its Problems

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HE GEOCHRONOMETRIC LABORA-TORY was established in 1951 under a grant to Yale University from The Rockefeller Foundation. Its program so far has been confined to radiocarbon measurements on the lines laid down by W. F. Libby (1-3) and followed in other laboratories (4-7). It is administered by an advisory board consisting of a chemist, a physicist, a geologist, two biologists, and two archaeologists. The Laboratory considers that methodologic investigations deserve first place, and although samples of unknown age are accepted for dating, preference is given to those materials whose analysis seems likely to throw light on the reliability of C¹⁴ dating in the widest variety of situations.

level of radioactive contamination that special precautions were essential if radiocarbon dating were to be possible in New Haven. Installation of a dust-free drybox (pressurized with filtered air) in which samples of purified carbon are mounted in the Libby-Kulp counter has produced satisfactory results, and no contaminated blanks were found between September, 1952, when three consecutive "zero" values were obtained on anthracite and Paleozoic limestone, and the beginning of the new series of tests in Nevada in March, 1953. A "zero" value is one in which the difference between sample and background counts is less than twice its own standard error, as shown in Table 1.

The atomic bomb tests at Eniwetok in November,

TABLE 1						
BLANK AND	Снеск	DETERMINATIONS	MADE	SINCE	SEPTEMBER,	1952

Sample	Description	Date prepared	Date counted	Counting rate, c/min
Y-127h	Paleozoic limestone	August	9/19	0.008 ± 0.06
	Anthracite	9/22	9/25	0.081 ± 0.06
	Anthracite	9/29	10/ 7	0.081 ± 0.06
Y-127x	Paleozoic limestone	11/12	11/15	0.028 ± 0.07
Y-127i	Paleozoic limestone	12/23	12/26	-0.100 ± 0.065
Y-141	Wood, Two Creeks Forest Bed, Manitowoc	, , (19)	11/10	1 005 - 0 000*
	Co., Wis., coll. F. T. Thwaites	6/12	11/19	$1.697 \pm 0.086^{\circ}$

* Corrected to 100% carbon.

Many individuals and organizations, too numerous to mention separately, have materially assisted the program in its first two years. Particular appreciation should be expressed to Hans Suess, who conducted operations through 1951, and to the U. S. Geological Survey, which made his services available.

Blank Determinations. After preliminary trials beginning in October, 1951, the first "blank" measurements (of C¹⁴ in anthracite) were made in December, 1951, and showed small but significant amounts of radioactive contamination, of the order of 0.6 ± 0.1 c/min. Some tests then indicated that this amount could be reduced to 0.2 c/min by rewashing the purified carbon in HCl and remounting, but it could not be eliminated. Numerous measurements in the first part of 1952 left no doubt that atomic explosions in the Pacific and in Nevada had so increased the local

¹ Supported in part by the Office of Naval Research, Project ONR-081-186, Contract Nonr 609 (05). urements of separate portions of the same samples, but an anthracite sample prepared shortly thereafter gave a satisfactory zero, and the next sample to be counted was wood from the Two Creeks Forest Bed, Manitowoe County, Wisconsin, submitted for checking purposes by F. T. Thwaites. The calculated age of 9929 ± 406 years was in agreement with the average of Libby's five analyses of Two Creeks material, 11,400 ± 350 years, indicating that it was at last possible to analyze ancient materials with normal accuracy.

1952, contaminated two samples, as shown by remeas-

Calibration Analyses of Modern Wood and Shell. Table 2 and Fig. 1 give the results of calibration assays made since the period of possible or probable contamination. All net counts have been corrected to 100 per cent carbon, for, as was first pointed out by Libby in an unpublished memorandum, if nitric acid instead of hydrochloric acid is used to dissolve un-

<i>Wood</i> S-6 Hemlock, cut 1951, 0–10 yr rings 10/16/52 5.120 :	$\begin{array}{cccc} \pm .093 & 6.314 \pm .114 * \\ \pm .092 & 5.780 \pm .106 \\ \pm .093 & 6.080 \pm .110 \end{array}$
S-6 Hemlock, cut 1951, 0–10 yr rings 10/16/52 5.120	$\pm .093$ 6.314 $\pm .114^*$ $\pm .092$ 5.780 $\pm .106$ $\pm .093$ 6.080 $\pm .110$
	$\pm .092$ 5.780 $\pm .106$ + .093 6.080 + .110
171-1 Black oak, cut 1952, 10–20 yr rings 12/17/52 5.015	+.093 $6.080 + .110$
171-3 Same as 171-1 3/13/53 5.128 -	
172-1 Black oak, cut 1952, 10–20 yr rings 2/10/53 5.078 -	$\pm .093$ 5.796 $\pm .106$
172-2 Same as 172-1 2/13/53 4.801 :	$\pm .088 5.699 \pm .104$
Average of modern wood, exclu	ıding S-6 5.839 ± .053
Mollusks	
- Source uncertain, either Venus or Donax 10/14/52 5.058	$\pm .076 \qquad 6.143 \pm .092$
- Source uncertain, either Venus or Donax 10/20/52 5.580	$\pm .086 \qquad 6.618 \pm .102$
173 Venus mercenaria, from New Haven market, 1/5/53 6.002 - prob. L. I. Sound	$\pm .109 \qquad 6.844 \pm .124^{\dagger}$
174 Arca pexata, shells on beach at Pine Orchard, 2/11/53 4.897 - Conn. (L. I. Sound)	$\pm .095$ 5.824 $\pm .113$
175 Ostrea virginiana, from Rowe Oyster Co. 2/23/53 5.045 shuck heap (L. I. Sound)	$\pm .147$ 6.024 $\pm .175^{\dagger}$
176A Venus mercenaria (shell), from Tuckernuck 3/3/53 4.987 Shoal, Vineyard Sd., coll. alive; H. J. Turner	$\pm .094$ 5.761 $\pm .109$
177A Mytilus californianus (shell), San Mateo Co., 2/26/53 4.942 Calif., coll. alive; W. D. Hartman	$\pm .099$ 5.738 $\pm .115$
177B Flesh from Mytilus, 177 3/11/53 5.022	$\pm .091$ 5.836 $\pm .106$
200 Donax variabilis, Venice, Fla.; shells in 3/9/53 5.397 Peabody Museum, coll. 5-6 yr ago	$\pm .092$ 6.294 $\pm .107$
178 Dinocardium, recently cast on beach (hinge 3/4/53 4.944 digament still present), Port Aransas, Tex.; M. D. Burkenroad	$\pm .093$ 5.821 $\pm .110$
205 Pecten (shell), Apalachee Bay, Fla., coll. 3/16/53 4.464 - alive; Nelson Marshall	$\pm .080$ 5.365 $\pm .096^{\dagger}$
Average of modern shell All values Excluding two high values	$\begin{array}{c} 6.043 \pm .037 \\ 5.871 \pm .033 \end{array}$

TABLE 2 Assays of Modern Wood and Shell

* Carbon determination on samples exposed to air for 24 hr; correction probably too high.

† Poor counts; unusual internal inconsistency.

reacted magnesium after reduction of carbon dioxide, the purified carbon is of extremely small particle size and retains about 15 per cent of water even after drying *in vacuo*. Duplicate analyses of the carbon are routinely carried out immediately after completion of a count, by means of a combustion train in which an aliquot of the dry carbon is burned in oxygen and the carbon dioxide is collected in a weighed drying tube filled with ascarite.

From Table 2 it may be seen that while modern wood gives a consistent series of C^{14} values, modern marine shell provides some interesting contradictions. Of ten analyses, two are definitely higher than modern wood, agreeing with published results in suggesting a difference of the order of 10 per cent. Five of the other eight agree very closely with modern wood, and in the case of one sample (Y-177, Mytilus califor*nianus*), the flesh of the mollusks showed the same specific activity as the shells.

The published evidence for higher C^{14} content of marine shell consists of three analyses by Libby (8) and five by Kulp (4). Several of these were duplicate runs, and it appears that only four different sources of shell were used. The higher specific activity of shell observed in the past has doubtless proved acceptable because it seemed to be in line with the known difference, of about 3 per cent, between the C¹³ content of organic and inorganic carbonaceous sediments. Moreover, Craig (9) has found marine invertebrate carbonate to contain more C¹³ than organic carbon from marine plants and animals. If, as would be expected, the effect is still greater with the heavier isotope, there would be a difference of perhaps 6 per cent or more between the C¹⁴ content of shell and wood. This ex-



FIG. 1. Assays of modern wood and shell. The length of each line represents one standard deviation on either side of the mean.

pected difference is not borne out by our measurements.

Water from the depths of the ocean contains carbon that may be several thousand years old, and Kulp *et al.* (5) have suggested that coastal upwelling of deep water may account for the high apparent age (low C¹⁴ activity) of marine shell samples from Peru, Japan, California, and the Aleutians. It seems unlikely to us that most of the marine shells we measured incorporated old carbon from upwelled water, since they came from places as different as Vineyard Sound, Long Island Sound, Venice (Florida), Port Aransas (Texas), and San Mateo County (California). It is still more unlikely that they could all have picked up just the correct amount of old carbonate to bring their counting rate to that of modern wood.

If the published C¹³ and C¹⁴ analyses are correct. how can we rationalize our determinations showing agreement between assays of shell and wood with the measurements (including two of our own) showing shell to be enriched in heavy isotopes? Although it is certainly too early to give a detailed picture, we would like to attempt a preliminary sketch. With carbon dioxide in air as a starting point, photosynthesis by plants reduces the specific activity by discriminating against the heavier isotope. Solution of CO₂ into sea water may be accompanied by a slight enrichment in the heavier isotopes because of the difference in solubility equilibria. Marine plants, photosynthesizing dissolved CO₂, discriminate against the heavier isotope just as land plants do, bringing the specific activity of their carbon down to that of wood (or perhaps to a slightly higher value because of the solubility equilibria). If marine animals deposit metabolic carbonate in their shells, the isotope ratio reflects that of their food source and will be close to that of wood. If, on the other hand, they deposit ocean carbonate directly, or if (as seems more probable) the calcium carbonate laid down at the edge of the mantle exists for some time in a form that can exchange with ocean carbonate, the shell will have a higher specific activity than

wood. These various possibilities in combination will lead to variation in the C^{14} content of shell, perhaps around two favored modes, one close to that of wood and the other significantly higher. We realize that this is a complex and rather special hypothesis, but it is the only one we can suggest to reconcile the available data.

Upwelling of deep ocean water containing old carbon would, of course, result in decreased specific activity of shell from the area. This situation is only likely on the west coasts of continents in subtropical latitudes, in the equatorial countercurrent region, or a few other more special localities. In fresh water lakes a far more important source of old carbon is likely to exist, wherever ground water is dissolving old limestone. It is quite probable that such water entering lakes and swamps would meet photosynthesizing plants before equilibrium with atmospheric CO. was established, giving spurious ages to photosynthetically precipitated marl or fossil plant remains, as Godwin (10) and others have pointed out. It may be significant in this connection that Baertschi (11) found less C13 in fresh water carbonates than in marine carbonates, relative to their O¹⁸ contents. We are presently engaged in the determination of the specific activities of various types of material from a hardwater lake. In addition, the Pyramid Valley series discussed below seems to provide a case in point.

Even in the absence of fossil carbon near the lake, there is always the possibility of the establishment of local geochemical epicycles in more or less closed habitats which produce a greater enrichment or depletion than occurs in the main cycle in the biosphere. Wickman (12) shows this clearly for C^{13} , and it may reasonably be expected to complicate C^{14} contents of swamps or richly vegetated lakes.

The problem presented by modern shell analyses illustrates the fact that the biogeochemistry of carbon is too little understood to permit the uncritical application of radiocarbon dating to all carbonaceous materials regardless of their origin. While awaiting the results of studies of marine carbon in the Lamont Laboratory and of lacustrine carbon at Yale it seems best to use the standard wood value in discussing dates obtained from calcareous matter. It must always be borne in mind that such dates are far more likely to be spurious than those obtained from organic samples. We certainly feel that the practice of using a shell value 6 or 10 per cent higher than wood is in need of modification.

Errors. Error terms are customarily attached to radiocarbon dates on the basis of the standard deviation of the counting statistics alone. In spite of a clear discussion by Arnold (13), this practice has confused and misled the majority of people who are most interested in the dates. We propose to abandon it.

There are several reasons for this change. There is a widespread tendency to accept the error term, expressed in years, as being an outside limit; instead it is just the value that gives a 2:1 chance that the



FIG. 2. Stratigraphic section through the deposits at Pyramid Valley, New Zealand, with radiocarbon dates and suggested correlations with late-Pleistocene sequences in Europe and elsewhere in New Zealand.

error is no greater than the given one. Apart from this, and contrary to the expressed opinion of other investigators, we feel that the dating process is susceptible to errors which in their cumulative effect may very well exceed those to be expected from counting statistics. Among these are the possibility of chance contamination, erratic changes in cosmic ray background, slight changes in counter efficiency, counting of spurious pulses from carbon dust or other sources, and no doubt a good many other undiagnosed difficulties in laboratory operation. Finally, there are nonlaboratory errors to be considered, and these are the ones most difficult to evaluate. These include the questions of calibration discussed above and the nature of the material to be dated, especially its mode of deposition and the circumstances of its preservation during thousands of years. These problems are being investigated, but they are amorphous and no quick solutions are in sight.

For these reasons we prefer to express our radiocarbon dates as "most probable ages" with the observation that an error of 10 per cent is not unlikely, and the warning that errors of 25 per cent are not impossible.

Pyramid Valley, New Zealand. A series of samples collected by R. S. Duff and R. C. Murphy from the

famous moa deposit at Pyramid Valley, North Canterbury, in the South Island of New Zealand, combines methodologic and stratigraphic interest to an unusual degree. Figure 2 shows the stratigraphy of this deposit, which is discussed in great detail elsewhere (14). The correlation of the section with the postglacial pollen sequence in New Zealand (15) is based on incomplete pollen studies by W. F. Harris. The upper lake, in whose deposits the moa remains are embedded, appears to be of Sub-Atlantic age (beginning ca. 2500 years ago, according to the chronology widely accepted in western Europe [16]). The underlying sedge peat presumably dates from the Sub-Boreal, roughly 4000 to 2500 years ago. The moas were intrusive into the lake deposit, evidently having fallen through the crust provided by the uppermost forest humus while feeding on podocarp trees, and the humus itself presumably records a relatively dry phase, to be correlated with one of the climatic cycles that produced "recurrence surfaces" in European bogs. Points of greatest stratigraphic interest include (1) the use of radiocarbon dates to confirm interhemisphere correlation of late-Pleistocene climatic sequences, amplifying what can be tentatively inferred from scanty pollen data, and (2) the age of the moas. There is no good evidence that the Maori, who reached the North Island in force about A.D. 1350, ever knew the moas, and the moa that was hunted by the basically Polynesian but non-Maori people known as Moa-hunters (17), whose sites are chiefly found on the South Island, was a small species, *Euryapteryx*. For the other moas, especially the largest type, *Dinornis*, mystery surrounds both the cause of extinction and its date. Pyramid Valley contains no archaeologic remains, but it is one of several places where *Euryapteryx* and *Dinornis* occur together.

The methodologic interest of the series consists in the possibility of comparison of radiocarbon analyses based on carbonates and organic carbon at the same stratigraphic horizon. Not many marine shells had been tested at the time the study was undertaken, and no difficulty was anticipated from using such comparisons to explore the carbon cycle of hard freshwater lakes. The Pyramid Valley swamp is surrounded by Tertiary limestone, and this rich source of fossil carbon might be expected to contribute old carbon to the lake by way of bicarbonate in ground water. If carbon exchange between the lake or ground water and the atmosphere is slow, a departure from equilibrium would result, and the water, the organisms, and particularly the sediments of the lake would give spuriously high radiocarbon ages. This expectation seems to be confirmed, although the uncertainty in the modern C¹⁴ content of carbonate carbon makes the demonstration less striking than it appeared at first.

Table 3 gives the results, duplicate determinations having been made wherever possible; ages of calcareous samples are calculated according to two assumptions, that the C¹⁴ contents of shell and wood are identical and that modern shell contains 10 per cent more C¹⁴ than modern wood. The former assumption, of course, reduces the ages of calcareous samples, but it may be seen that on this assumption the oldest marl (sample Y-144-3) appears older, and on the latter assumption all three marl samples appear as old or older than the peat (sample Y-144-4) that underlies the marl.

The age of the moa is presumably correctly given by the age of the organic fraction of its crop contents. 670 years (sample Y-129-A). The discrepancy between this figure and that of 1800 ± 150 years obtained on a portion of the same specimen by Kulp et al. ([5], sample L-129) may arise from the fact that the carbon correction was not applied to the Lamont analysis. The revised date points even more definitely to the probability that Dinornis, like Europatery, was contemporary with primitive men and was exterminated by them. The inorganic fraction of the same sample. Y-129-B, is the only one of the series in which duplicate determinations are far enough apart to suggest inhomogeneity. This fraction was presumed to be the matrix of the crop contents, but R. C. Murphy, who collected it, admits the possibility that the marl came from a higher level in the excavation and was mixed with the organic remains during packing. The inhomogeneity could be accounted for by the fact that the

TABLE 3

DATES FROM PYRAMID VALLEY, WAIKARI, NORTH CANTERBURY, NEW ZEALAND

Dates based on calcareous material are calculated on the assumption that wood and shell have identical C¹⁴ contents; values in parentheses assume that modern shell contains 10% more C¹⁴ than modern wood.

Sample	Description	Probable age, years		
Y-129-A	Crop contents of a large Dinornis, "about 5 ft" in marl of upper lake	610 720		
	deposit, collected in 1947 by R. C. Murphy, Ameri- can Museum of Natural History. A portion of this sample was L-129, dated 1800 ± 150 years by Kulp <i>et al.</i> (1952)	Av. 670		
Ү-129-В	Marl matrix from Y-129-A. Two runs, one of large lumps, other of calcareous	330 (1100) 780 (1550)		
	remainder, suggest in- homogeneity	Av. 560 (1330)		
Y-144-1	Upper marl, 3 ft., collected in 1952 by R. S. Duff, Contentum: Museum	$2600 (3400) \\ 2900 (3700)$		
	Canterbury Museum	Av. 2750 (3550)		
Y-144-2	Lower marl, 4 ft. 3 in.; collected by R. S. Duff	3300 (4100) 3500 (4200)		
		Av. 3400 (4150)		
Y-144-3	Clayey marl from lowest part of upper lake de- posit, 5 ft. 3 in.; col- lected by R. S. Duff	4300 (5100)		
Y-144-4	Peat underlying upper lake	39 00		
	deposit, 6 ft. 3 in.; col- lected by R. S. Duff	3400		
	···· •	Av. 3650		
Y-144-5	Wood, embedded in marl	3300		
	samples, 3 ft. 11 in.:	3900		
	collected by R. S. Duff	Av. 3600		

largest lumps of marl were picked out separately, while hydrochloric acid was then used to make a chemical separation of the calcareous and organic carbon of the remainder. Whether the calcareous and organic fractions differ in age or not depends on the assumptions, and cannot be decided.

The anomalously great age of the wood, sample Y-144-5, could be accounted for if the wood originally grew in the swamp that produced the peat, but found a false stratigraphic position later. It might have been kicked into such a position by a moa, not necessarily from directly below, but from the margin of the lake basin, where the marly deposit is thinner and the peat therefore lies closer to the surface. There is evidence that the moa remains drifted through the mud after the birds were trapped (18), and it would seem that wood could have done so too. Assuming that the wood was in fact contemporary with the peat (sample

Y-144-4), we have evidence that the date of the peat is correct; the aquatic plants of the peat might have incorporated some fossil carbon from the water, but the wood must have obtained its carbon from the air. The confirmation of the age of the peat, suggested to be Sub-Boreal on the basis of the pollen sequence, is the most important result of the study from the strati-

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graphic point of view. However, lack of knowledge of isotope equilibria in lakes and in the sea presents a more challenging problem to C14 dating at present than does late-Pleistocene stratigraphy, and since the modern value to which ancient carbonate carbon should be referred is no longer obvious, we intend to continue the methodologic attack.

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Copenhagen Natural Radiocarbon Measurements, I.¹

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ONSTRUCTION of a C¹⁴ dating apparatus in Copenhagen began in the fall of 1951, and the first unknown samples were dated in the summer of 1952. The technique used is largely that developed by Anderson, Arnold, and Libby (1) and later modified by Kulp (2). The only significant deviation from the classical set up is the use of a double screen wall counter as described by Anderson and Levi (3). This instrument (Fig. 1) consists of two independent detector units in a com-

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mon envelope and a triple sample cylinder. The sample is mounted on the middle section of the cylinder, while the two outer sections provide the areas for the background countings. As in the conventional screen wall, the positions of the sample cylinder can



be alternated between two extremes. In one position, the sample on the middle section is exposed to detector A and a background area to detector B (cf. Fig. 1); in the other position, the sample is exposed to B and the other background to A. This arrangement has two advantages. First, the counting time necessary to arrive at a given statistical accuracy is reduced by $\frac{1}{2}$, and second, background and sample counts are registered simultaneously, whereby the effect on the net count of possible temporal fluctuations in the background is eliminated. The overall length of the screen