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Geochronometric Laboratory

Yale University

Technical Report to the Office of Naval Research

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The Natural C^{14} Contents of Materials

From Hard Water Lakes*

Edward S. Deevey, Jr., Marsha S. Gross, G. E. Hutchinson
and Henry L. Kraybill

In the ordinary procedure of radiocarbon dating, as developed by
Libby and his coworkers, it is assumed that the carbon, before entering
the material under investigation, had achieved isotopic exchange equili-
brium with the CO_2 of the air. It has been pointed out, notably by
Godwin,[1] that this assumption may well be false in the case of material
formed in hard waters, either by photosynthetic fixation of carbon in or-
ganic matter or by precipitation of $CaCO_3$. Ordinary hard waters contain
a considerable quantity of calcium bicarbonate, formed by the action on
limestone of rain or ground water containing free CO_2. The free CO_2
initially present in such waters may be regarded as in isotopic exchange
equilibrium with the CO_2 of the atmosphere; the limestone, however, is
usually very old compared with the half-life of C^{14}. The initial bicar-
bonate formed may therefore be expected to have about half the specific
activity of modern wood or other substances formed from atmospheric CO_2.
Exchange according to the scheme

$$HCO_3^- \rightleftharpoons H_2CO_3 \rightleftharpoons CO_2(aq.) \rightleftharpoons CO_2(gas.)$$
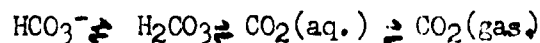
may then be expected and an approximately uniform distribution of C^{14} will
ultimately be reached. Since, however, at equilibrium an enrichment of C^{13}
of the order of 3 % occurs in the carbon of the HCO_3^- ion compared with the
CO_2 in the gaseous phase,[2] an enrichment of C^{14}, probably of the order of
6 %, is to be expected.[3]

It is known that some of the steps in the process outlined above are not instantaneous. Moreover, Ohle[4] has shown that in calcareous waters there is apt to be a considerable amount of colloidal $CaCO_3$ present. This colloidal carbonate is extremely stable in the absence of excess CO_2 even in the presence of the solid phase. It is probably formed as the result of the photosynthetic withdrawal of CO_2 from bicarbonate solutions. If this process occurred in the drainage basin, or at the surface of mud containing appreciable amounts of old carbonate, the colloidal $CaCO_3$ could provide a reservoir of carbon of low activity even in a water in which complete isotopic equilibrium existed between the components in ionic and true solution and in the gaseous phase.

In view of these theoretical possibilities and of the fact that Blau, Deevey and Gross[5] obtained evidence of spurious antiquity for a marl deposited in Pyramid Valley, North Canterbury, New Zealand, in what must once have been a shallow hard water lake, it has seemed desirable to examine the problem in greater detail.

Most of our samples are derived from Queechy Lake, New York, a small lake of area 60.8 ha., of maximum depth 13.6 m. and mean depth 6.9 m., lying on the Stockbridge marble, a metamorphosed palaeozoic limestone. The lake lacks inlets, and receives its water by seepage through the limestone and the overlying glacial drift which itself contains much of the country rock. A typical "marl girdle" is present in the shallow parts of the basin, and a considerable development of a benthic blue green algal mat has been noted. We have also studied two samples collected by Mr. R. J. Benoit in Lake Zoar, Connecticut, an artificial lake outside the region of outcrop of the limestone, but receiving its water from the Housatonic River, which drains the limestone north and west of New Milford, Conn. The bicarbonate alkalinity of both these

two lakes is given by Deevey[6] as 123 mg. HCO_3 $l.^{-1}$.

Several samples of the vegetation of soft-water lakes and bogs in Conn-ecticut have been used as controls in addition to the modern wood samples employed as standards. The results given in Table I are in counts per min-ute, corrected for carbon content. They refer to a layer of pure carbon of effective infinite thickness and area of $410 cm.^2$, in practice weighing about 10 grams. They are not otherwise corrected for the instrumental character-istics of our counters but comparison with the works of other investigators may be made by means of our value for modern wood. The error appended to each determination is the standard error due to counting statistics only. The error appended to each average value refers to the standard deviation of that mean value, as determined by the scatter of the individual results.

(TABLE I)

The dissolved, colloidal and suspended carbonate of the water of Lake Queechy was obtained by acidifying 650 liters of the lake water and collecting the evolved gas in ascarite. The carbon of the bicarbonate and carbonate in this water has the specific activity of a solution, formed by the action of atmos-pheric CO_2 on old limestone, that has proceeded half way to exchange equilibrium. The carbon of the modern lake water therefore has a spurious "age" of 2500 years. All the other carbon containing materials actually produced in the lake have low specific activities but none quite as low as the water. It is possi-ble that in the sample studied there was some CO_2 from colloidal or suspended $CaCO_3$ with a rather lower specific activity than that of the bicarbonate ion carbon present. The products of photosynthetic fixation and deposition of $CaCO_3$ are almost as low, however, which indicates that the carbon of the bicarbonate ion present in solution must have a considerably lower specific activity than that of the carbon of atmospheric CO_2.

There is clearly no difference between the activity of the organic carbon in the submerged water-plants of the lake and of the carbon of the carbonate deposit associated with these plants. Both Chara and Potamogeton doubtless use bicarbonate ions as a carbon source, and the fact that both the organic and carbonate carbon are derived from the same material presumably underlies the identity in C^{14} content.

The two emergent plants growing rooted in the shallow waters of the lake, namely Scirpus and Carex, clearly obtained their carbon directly from the atmosphere.

The Lake Zoar samples, though somewhat richer in C^{14} than those from Queechy Lake, are still deficient in C^{14} when compared with modern wood. Evidently isotopic exchange equilibrium is not fully achieved in a relatively shallow river over a course of 15 miles.

The first runs on Y-56 and Y-29 appear to be abnormally high compared to the two later runs. This could be caused by slight contamination; however, no independent evidence of contamination was recorded at the time. The mean for all the soft-water plants is $6.15c./min.^{-1}$ including, or 6.04, excluding these samples. Such values are comparable with that from the modern wood of Black Birch studied during the present investigation but are slightly higher than some of our earlier wood samples. The significance of this slight difference is under investigation.

It is apparent that if marl, shell or water-plants that developed in an ancient lake geochemically comparable to Queechy were used in radio-carbon dating, spurious ages, up to 2,000 years in excess of the true values, would be obtained. The rejection of the Pyramid Valley dates based on lake marl, as suggested by Blau, Deevey and Gross, is obviously justified. Great care must clearly be exercised in the future when material from highly calcareous

regions is being examined. It seems probable that in alkaline lakes in closed basins in semi-arid regions not underlain by limestones, all the carbon in the carbonate and bicarbonate in the water is of atmospheric origin. Samples from such lakes are likely to be free from the error here discussed.

Acknowledgments.

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1. Godwin, H., Amer. J. Sci., 249: 301-307 (1951).

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3. Anderson, E. C., and W. F. Libby, Phys. Rev., 81: 64-69 (1951).

4. Ohle, W., Arch. f. Hydrobiol., 46: 153-285 (1952).

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February 19, 1954.

TABLE I

Blanks			
	Anthracite		-0.00 ± 0.08
	"		-0.09 ± 0.08
	Palaeozoic limestone		-0.10 ± 0.09
	"	"	-0.06 ± 0.11

Modern Wood

Y-239	Black Birch (<u>Betula</u> <u>lenta</u>) 10-20 years old, Ansonia, Conn.	5.96 ± 0.11
Y-171	Black Oak (<u>Quercus</u> <u>velutina</u>) Ansonia, Conn.	$5.78 \pm 0.11a$
"	" "	$6.08 \pm 0.11a$
Y-172	Black Oak (<u>Quercus</u> <u>velutina</u>) Ansonia, Conn.	$5.80 \pm 0.11a$
"	" "	$5.70 \pm 0.10a$
	Average of Modern Woods	$5.86 \pm .08$

Soft-water localities in Connecticut, emergent vegetation

Y-29	<u>Chamaedaphne</u> <u>calyculata</u>, Old Man MacMullen's Pond, Canaan	6.33 ± 0.10
"	" "	5.99 ± 0.12
Y-30	<u>Vaccinium</u> sp. "	6.20 ± 0.08

Soft-water Localities in Connecticut, submerged vegetation

Y-63	Sphagnum spp., Bethany Bog	6.03 ± 0.10
Y-56	Mixed submerged phanerogams, Lake Quassapaug	6.44 ± 0.10
"	" " "	5.93 ± 0.12
	Average of soft-water plants	6.15 ± 0.08

TABLE I (cont.)

Queechy Lake

Y-145-6	CO_2 from bicarbonate and carbonate in water	4.6 ± 0.1
Y-145-3	Chara sp. organic carbon	5.07 ± 0.07
"	" inorganic calcareous material	5.02 ± 0.10
Y-145-4	Potamogeton sp. organic carbon	4.99 ± 0.11
"	" " "	5.18 ± 0.16
Y-145-5	" inorganic calcareous incrustation	5.02 ± 0.11
"	" " "	5.09 ± 0.11
Y-145-2	Elliptio (E.) complanatus	
	soft parts	4.83 ± 0.11
	" " "	4.82 ± 0.08
Y-145-1	shell	5.20 ± 0.14
"	" "	4.87 ± 0.07
Y-224	Deep water mud	4.68 ± 0.09
"	" " "	4.97 ± 0.15
Y-21	Scirpus sp., emergent	6.00 ± 0.10
Y-22	Carex cf. lasiocarpa, emergent, from shallow water	6.11 ± 0.08

Lake Zoar

Y-20	Hydrodictyon reticulatum	5.44 ± 0.11
Y-27	Elodea sp.	5.35 ± 0.09

a. Previously reported in Blau, Deevey and Gross (5).

b. Determined by Dr. Hans E. Suess and expressed as 77 ± 2 % of the value for modern wood. The mean value for modern wood is taken here as the mean of all modern woods and soft water samples, namely 6.02.

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