Radiocarbon Concentration in Pacific Ocean Water

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Abstract

Results of C^{14} determinations in surface water from the Pacific were in agreement with those reported by Rafter and Fergusson. However, abnormal C^{14} concentrations seem to exist locally, for which no oceanographic explanation can be given. It seems premature to draw conclusions from existing determinations as to the rate of increase of C^{14} in surface ocean water resulting from the uptake of C^{14} produced in the atmosphere by atomic bombs.

Samples from a constant depth of about 3,500 meters show a C^{14} content decreasing from south to north. This decrease may be attributed to radioactive decay of C^{14} during the time of migration. From this the northward component of the rate of water movement of about 0.06 cm/sec can be calculated. The C^{13} determinations, for the purpose of correcting the C^{14} values for isotope fractionation effects, were found to be remarkably consistent, although made on reburned acetylene.

Introduction

The C^{14} content of the bicarbonate of ocean water is of twofold interest: First, it offers a valuable method for the study of isotope exchange and transfer of carbon dioxide between the atmosphere and the ocean. Second, it can be used as a new tool in oceanography for the study of the movement of deep ocean water and the mixing of water masses. The rate of transfer of CO_2 from the atmosphere into the oceans was first discussed in the light of the C^{14} distribution by REVELLE and SUESS (1957), and independently by ARNOLD and ANDERSON (1957). An order of magnitude of about ten years was derived by these authors for the residence time of CO_2 in the atmosphere before it gets dissolved in the oceans. Subsequently several others, CRAIG (1957), FERGUSSON (1958), BOLIN and ERIKSSON (1959), attempted to establish a more precise figure for this residence time. All these considerations were based on the measurement of two empirical quantities: the apparent C^{14} age of ocean water, and the effect of industrial coal combustion on the specific activity of atmospheric CO_2. But the data up until now have been scarce, the observed effects o f small magnitude, and there has been uncertainty about such things as the size of the so-called geochemical carbon reservoirs (such as the terrestrial biosphere). However these data are treated, the calculated residence time can scarcely be very accurate. But the addition of artificial radiocarbon to the atmosphere by bomb explosions during the years from 1954 to 1958 will offer a much better opportunity to determine the accurate residence time and the geochemical pathway of CO_2 than the previous data afforded. A further discussion of this problem will therefore not be indulged in. Much more reliable answers will result from the combination of the data reported here with future observations during the coming decade. This paper will therefore be limited to the consideration of the use of radiocarbon as a means of following water movements.

Part of our data were obtained from samples collected during the International Geophysical
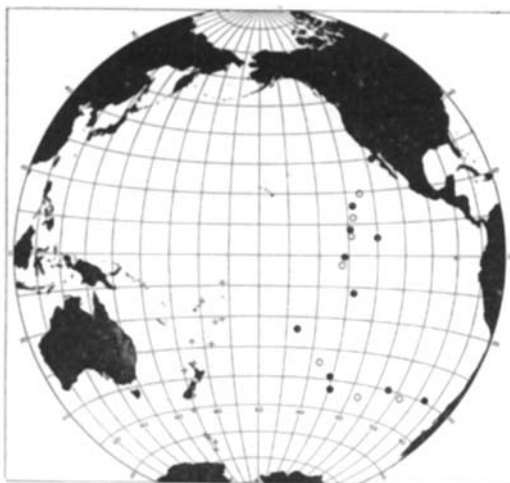
Fig. 1. Locations of sampling stations. Circles denote places where samples were taken by the Scripps Institution. Open circles indicate surface water; solid circles are deep water samples or profiles. Crosses show locations from which samples were analyzed by the New Zealand Institute for Nuclear Science.

Year for the study of secular variations (see Figure 1). During the next few years the C^{14} activity of surface water will undoubtedly increase continuously, as a result of bomb-produced C^{14} in the atmosphere. Measurements made at this laboratory and at the Institute for Nuclear Science in New Zealand will be a useful basis for future study of this problem in the Pacific Area.

The question of normalization presents a serious problem in the comparison of data from different laboratories. The oxalic acid standard distributed by the National Bureau of Standards is now used widely. In order to correct for isotope fractionation effects, results are normalized to a δC^{13} of -25 per mil relative to the Chicago PDB standard (CRAIG, 1957 a). The Lamont normalization, which we have adopted, uses this correction as well as a factor of 0.95 times the δC^{14} of the oxalic acid standard (BROECKER and WALTON, BROECKER and OLSON, 1959).[1]

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[1] It should be pointed out that the reference C^{14} in the oxalic acid standard is *not* corrected for any deviation of its δC^{13} from the chosen standard value of -25 per mil. The δC^{13} of the oxalic acid standard is actually -18.65 ± 0.13 per mil relative to the PDB standard (Private communication of Toshiko K. Mayeda to J. R. Arnold). In case of deviation from this value, due to isotope fractionation in the laboratory, the δC^{14} measured for the standard should be corrected accordingly.

Sampling and measurements

On the Downwind Expedition of the International Geophysical Year, six surface samples and ten samples from deep water were collected and the carbon dioxide extracted and processed directly on shipboard. The samples for the profiles were collected with the same sampling equipment but stored in 50-gallon steel drums and processed on shore shortly after the return of the ships. The Atlantic samples, obtained from Dr. John Lyman, were in the form of barium carbonate and were collected and processed in a different manner.

The water samples were taken in a sampler of approximately 50-gallon capacity constructed in the Special Developments Shop of the Scripps Institution of Oceanography under the direction of Mr. J. D. Frautschy. The sampler consisted of a stainless steel barrel about five and one-half feet long and fifteen inches in diameter, closed at each end by stainless steel flanges sealed with soft plastic gasket material. When closed, the end flanges were held together in place by a strong steel spring in the axis of the barrel. The flanges could be opened by a detachable "cocking" lever and held open about five inches from the ends of the barrel by a tripping mechanism which would be released by a messenger. When lifted inboard, the water sample was transferred as quickly as possible through a rubber hose into a "process tank" on deck built from a 50-gallon glass-lined hot water heater, and filled with nitrogen gas before the transfer to avoid contact with the carbon dioxide of the air. The tank was fitted with a tightly bolted top plate with lead-in tubes for the addition of acid and the inflow and exit of nitrogen gas to flush out the liberated carbon dioxide. Two liters of concentrated HCl was added to each charge of the tank, and nitrogen was passed in through a coarse diffusion head at a rate of from one to four liters per minute, and finally led into an absorption bottle through a sintered-glass diffuser. The process tank was warmed with heating coils to a temperature of 40 to 50° C, under which conditions it was ascertained that all the CO_2 in the water was liberated and absorbed in a minimum of four hours. Twice this time or more was used in routine runs.

The carbon dioxide in the nitrogen stream

was absorbed in one liter of concentrated ammonia solution saturated with barium chloride. We believe that absorption in ammonium hydroxide solution is much faster than in alkali hydroxide, and that the use of ammonium hydroxide represents a real improvement over techniques used elsewhere. The one-liter bottle, containing the remaining solution and the precipitated barium carbonate, was tightly stoppered and returned to the laboratory. This method proved very satisfactory, in spite of the fact that the precipitation of solid $BaCO_3$ on the diffuser head generally made its replacement necessary at least once during a run. Completion of the absorption could always be verified, however, by replacing the absorption bottle with a fresh one and observing whether precipitation of barium carbonate continued or not. In the absorption of the CO_2 from some of the later samples, strontium chloride was substituted for barium chloride. In any case, the strontium or barium carbonate was reduced with magnesium metal to the carbide, which was then hydrolyzed to acetylene.

Hydrochloric rather than sulfuric acid was used for acidification with the thought that it would interfere less with the subsequent determination of radium. In five liters of each sample, after the removal of carbon dioxide, barium sulfate was precipitated by the addition of barium chloride. This precipitate, carrying with it the radium, was washed and separated by decantation and returned for the determination of radium.

The deep samples for the C^{14} measurements were all taken from depths of about 3,500 meters. In each case a Nansen bottle was suspended about five meters below the sampler in such a way that the bottle, with its protected and unprotected thermometers, was tripped when the large sampler closed. From these thermometer readings the depth was accurately determined in the standard manner.

With one exception, the surface samples were obtained through the ship's salt-water pumping system, which operates without diffusing air into the water. One water sample was obtained from mid-depth, 400 meters.

The La Jolla Radiocarbon Laboratory uses the method developed at the U.S. Geological Survey in Washington (SUESS, 1954) in which acetylene serves as the counting gas. The C^{14}

counting was done in a special low-level counter developed by HOUTERMANS and OESCHGER (1958) and manufactured in the instrument shop of the Physikalisches Institut, University of Bern, Switzerland. This counter showed a background of less than two counts per minute at one atmosphere and a sensitive volume of about 1.7 liters. Total counting time for each sample was several days.

Discussion of results

The results of the measurements are given in Table 1, 2 and 3, and shown in Figure 2. They contain two remarkable features: (1) the occurrence of abnormal surface water concentrations of C^{14}; and (2) a distinct, regular increase in the apparent age of deep water from south to north.

Surface water samples. Careful measurements in the laboratory of the Institute for Nuclear Science, New Zealand (RAFTER and FERGUSSON, 1957; FERGUSSON, 1958) have shown that the activity of the surface water in the South Pacific decreases from lower toward higher latitudes along with decreasing stability of the thermocline. Values more than 150 per mil below the equilibrium value are found beyond the Antarctic convergence. Considering the uncertainty in the calibration and the experimental errors of about one per cent, our results agree very satisfactorily with the New Zealand findings. In comparing results we have assumed a difference between the New Zealand and Lamont normalizations of − 61 per mil. In a few cases, however, there is considerable deviation from the general trends. One abnormal sample was found by Rafter and Fergusson (BURLING and GARNER, 1959) with an activity of more than three per cent below the expected, and the investigators attribute this deviation to chemical effects from storage in a steel drum. We believe that in our case such an explanation of the deviations is highly improbable. Along the La Jolla coast and in offshore areas varying ΔC^{14} values ranging from − 50 to about − 80 per mil have been obtained. These variations can be explained by upwelling water along the California coast. It is well known that such upwelling results in great differences in the local properties of surface water at different times and locations. The vertical circulation and mixing of surface
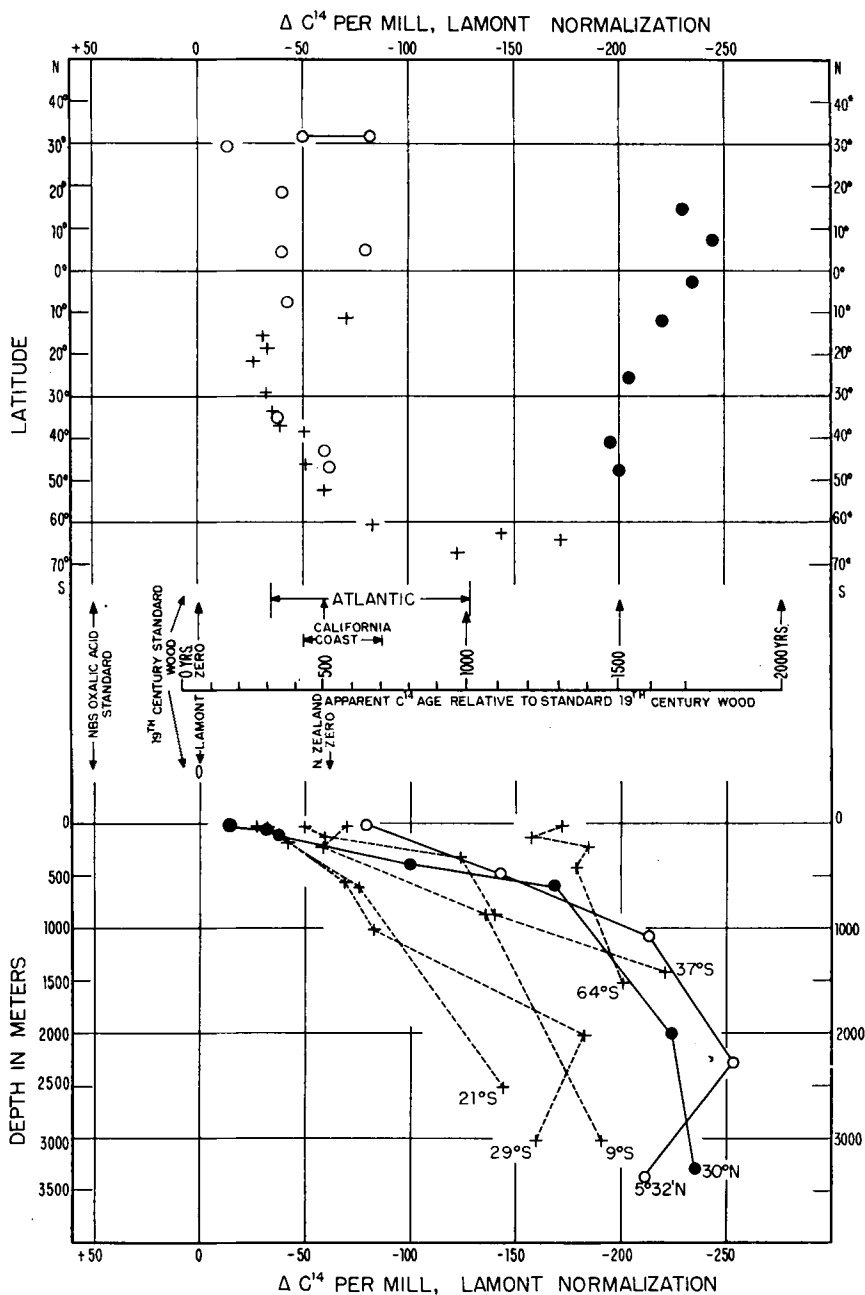
Fig. 2. Upper part: ΔC^{14} plotted as a function of latitude for surface water samples (open circles indicate La Jolla measurements, crosses New Zealand measurements), and for samples from approximately 3,500 m. depth (solid circles).

Middle part: Normalization and the conversion of ΔC^{14} to apparent ages is indicated. All values, except that for the NBS oxalic acid standard, are normalized to a δC^{13} of $-25°/oo$ relative to the Chicago PDB standard.

Lower part: ΔC^{14} as a function of depth. Crosses indicate New Zealand measurements. Open circles show results on samples collected by J. A. Knauss, and solid circles by J. E. Reid.

Table 1. IGY downwind expedition[1]

Collector: N. W. Rakestraw

Dates of Collection: October through December 1958

C^{13} measurements: P. Eberhardt in laboratory of H. C. Urey

LJ No.	Field No.	Latitude	Longitude	Depth meters	Salinity ‰	O_2 (l/l)	T °C	δC^{13} per mil PDB Standard ($\pm$ 0.2 ‰)	ΔC^{14} in per mil ($\pm$ 8 ‰) Lamont Normalization
58	2	19° 35′ N	125° W	0	34.69	4.82	24.4	—0.5	—40
62	6	5° N	130° W	0	34.40	4.65	28.0	—0.1	—40
66	8	7° ′ S	132° W	0	34.68	4.88	26.7	—1.0	—42
68	11	34° 50′ S	135° 53′ W	0	35.05	5.64	17.7	—0.4	—38
90	14	46° 30′ S	116° W	0		6.78	9.2	—0.7	—60
93	16	42° 43′ S	96° W	0		6.64	11.5	—0.6	—62
60	4	11° N	128° 31′ W	400	34.65	0.13	10.9	—1.5	—103
59	3	14° 58′ N	127° 31′ W	2987	34.69	2.73	1.66	—1.2	—230
61	5	7° 08′ N	129° 16′ W	3508	34.69	3.43	1.48	—1.4	—243
63	7	2° 08′ S	131° 27′ W	3473	34.69	3.48	1.52	—1.3	—235
57	9	14° 29′ S	135° 30′ W	3449	34.69	3.73	1.58	—1.8	—220
67	10	25° S	145° W	3560	34.65	4.05	1.54	.—2.9	—204
69	12	40° 35′ S	132° 10′ W	3500	34.67	4.00	1.50	—1.2	—195
88	13	46° 46′ S	123° 53′ W	3550	34.69	4.03	1.62	—2.0	—200
91	15	40° 37′ S	103° 20′ W	3500	34.67	4.10	1.85	—2.5	—180
94	17	39° 33′ S	84° 10′ W	3500		4.15	1.46	—1.9	—196

[1] The values for ΔC^{14} given here differ slightly from those previously reported (Rakestraw, Oeschger and Suess (1959) Preprints, International Oceanographic Congress, p. 440). They are calculated with a revised calibration.

Table 2. Samples from La Jolla beach or offshore

LJ No.	Material	δC^{13} ‰ PDB	ΔC^{14} ‰ $\pm$ 10	Date of Collection
86	Shells, collected alive (mytilus Californianus), La Jolla Shores	—8.3	—85	1953
48	Vellela velella, SW of Farallon Islands	—23	—82	15 April 1957
70	Kelp (Macrocystis pyrifern)	—16	—70	8 July 1957
65	Red Tide (Gonyaulax)	—18	—60	18 August 1958
97	Shells, collected alive (mytilus Californianus), La Jolla Shores	+ 0.6	—37	February 1959
127	Carbonate from Pier Water	— 2.3	—88	4 August 1959

water with that from lower depths results in variations in the C^{14} activity of surface water as well as in other characteristics, such as temperature. One measurement (LJ 149) gave an abnormally high value for which we have no explanation.

As FERGUSSON's results show (1959) one must be cautious in interpreting increases in the C^{14} activity of surface water as a conse-

quence of uptake of bomb C^{14} from the atmosphere. Many measurements will be necessary to determine the rate of this uptake.

Deep water samples. The C^{14} concentration of a particular deep water sample may be influenced by the following factors:

1) The degree of equilibration between the CO_2 in the water and that in the atmosphere, provided the water mass can be regarded as a

Table 3. Profiles

Collector	Dates of Coll.	C¹³ done by	LJ No.	Field No.	Latitude	Longitude	Depth Meters	Salinity ‰	O₂ (ml/liter)	T °C	δC¹³ (PDB) ‰	ΔC¹⁴ Lamont Normalization
John A. Knauss	July, 27, 28, 1959	R. Bowen (H.C. Urey Laboratory)	146	1	5° 32′ N	120° 05′ W	10	33.50	4.45	27.5	—1.22	—79
			140	2	»	»	485	34.67	0.25	7.88	—2.51	—143
			147	3	»	»	1080	34.63	0.94	4.12	—1.81	—213
			139	4	8° 29′ N	120° 09′ W	2280	34.70	2.34	1.97	—1.66	—253
			137	5	»	»	3370	34.70	3.25	1.58	—0.74	—211
Joseph Reid	October 14, 1959	S. Epstein, Cal Tech	149	1	30° 04′ N	118° 02′ W	10	33.48	5.13	19.30	+1.9	—13
			150	2	»	»	75	33.44	5.70	15.85	+1.0	—32
			151	3	»	»	120	33.48	5.12	13.40	+0.2	—38
			152	4	»	»	390	33.16	0.90	6.60	—1.9	—100
			153	5	»	»	600	34.35	0.32	5.21	—6.0	—169
			154	6	»	»	2000	34.66	—	2.00	—1.6	—238
			158	7	»	»	3300	34.67	2.30	1.60	+0.3	—235
Atlantic samples submitted by John Lyman	July 8, 9, 1957	P. Eberhardt (H.C. Urey Laboratory)	123	878	27° 34′ N	59° 38′ W	25	36.42	4.94	25.72	—0.2	—33
			124	879	»	»	3163	34.87	6.21	2.75	—2.0	—115
			125	880	»	»	5944	34.85	—	2.13	—1.9	—140

closed system. If not, then the water mass must be considered as a sum of components, each with a different history.

2) The time since such equilibration occurred, during which radioactive decay has taken place.

3) Oxidation of particulate or dissolved organic matter. Settling of particulate organic matter from the ocean surface and subsequent oxidation will add younger carbon and decrease the apparent radiocarbon age. Evidence of such a process may possibly be obtained from the O_2 distribution in the water.

4) Redissolving of carbonaceous sediments from the ocean bottom. Geological evidence indicates that such processes are in general too slow to affect C^{14} concentrations.

The Pacific deep water obtained its C^{14} through exchange with the atmosphere south of the Antarctic convergence below 60° S. latitude, or through admixture of surface water from lower latitudes. New Zealand measurements show that exchange is incomplete and the water masses sink with a ΔC^{14} of about — 150 or less (apparent C^{14} age of 1,200 to 1,500 years). Our measurements show a further increase in apparent age of 200 to 300 years as the water moves toward the equator. This age difference may well indicate the true travel time of the water mass. At the same time a decrease in O_2 occurs that can be attributed to oxidation of organic matter. Assuming that this organic matter reached the deep water by sedimentation from the surface and is correspondingly high in C^{14}, this addition of younger carbon to the dissolved bicarbonate will make the radiocarbon age of the water appear too young. Sea water con-

tains about 2.3 millimol per liter of carbon in the form of bicarbonate. On its way from $40° S$ to $15° N$ the water loses about 1.3 milliliters or 0.055 millimol of oxygen, equivalent to about 4.2 % of the carbon present. The carbon added by oxidation of organic matter may be about 20 per cent higher in C^{14} and therefore may increase the C^{14} concentration of the water mass by $0.042 \times 20 \%$ $= 0.84 \%$. This corresponds to a decrease in the apparent age of about 100 years. Figure 2 shows that the difference in the apparent C^{14} age for the samples from around 3,500 meters depth between $40° S$ and $15° N$ was found to be between 200 and 300 years. If the oxygen in this water mass was consumed by organic carbon from the surface, then the true travel time of the water would be about 100 years longer. Assuming that effects from other processes, such as the dissolving of particulate inorganic carbonate, are unimportant, then we can estimate the travel time for $55°$ of latitude (6,100 km) as 300 ± 100 years. This corresponds to an average northward component of the velocity of the water of 0.06 ± 0.02 cm/sec.

Our evidence leads us to expect that radiocarbon studies will be more valuable in explaining water movements in the Pacific than in the Atlantic, where conditions are apparently more complicated.

Profiles. The variation of the C^{14} concentration as a function of depth in the Pacific was investigated at two stations. The samples from one station were collected by Dr. John Knauss on the Doldrums Expedition of the Scripps Institution of Oceanography; those of the other station by Mr. Joseph Reid on another cruise. In both cases the seawater samples were brought ashore in 55-gallon drums and processed at La Jolla. The results obtained show a more regular depth dependence than those obtained by the New Zealand laboratory. The C^{14} concentration was found to decrease almost linearly with depth down to about 1,000 meters and from there downwards to remain almost constant (Figure 2). One profile showed evidence for a C^{14} minimum at a depth of about 2,000 meters. Until the occurrence of this at other stations is verified, speculation as to its significance is scarcely profitable.

C^{13} *results.* The mass spectroscopic C^{13} determinations carried out by Dr. Samuel Epstein and Mrs. Iren Vidzuinas at the California Institute of Technology, and in Dr. Urey's laboratory at La Jolla by Dr. Peter Eberhardt and Dr. Robert Bowen, are remarkably consistent. They show a relatively small spread, much smaller than that found at the Lamont laboratory (BROECKER, TUCEK, and OLSON, 1959) in samples from the Atlantic. Also, their variations follow qualitatively the expectation that the C^{13} should show lower values at depths where oxidation of organic matter may have taken place, than at the surface where photosynthesis predominates. The lowest C^{13} value observed (LJ 153) is in a sample which comes from a depth near that of the oxygen minimum. However, it should be noted that the C^{13} determinations were made on reburned acetylene, and that small isotope fractionations in the laboratory during extraction of CO_2 and preparation of acetylene cannot be excluded.

Acknowledgments

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