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Natural Radiocarbon from Cosmic Radiation

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C^{14} produced by the $N^{14}(n, p)$ reaction of cosmic-ray neutrons has been detected and identified. The C^{14} concentration of biological methane was enriched by factors of up to 260-fold by thermal diffusion to raise the activity to convenient levels for counting. The pure methane was used as the filling gas in large Geiger-Müller counters.

The activity in biological methane was found to be 10.5 disintegrations per minute per gram C, or 0.95×10^{-12} gram C^{14} per gram C. This is in reasonable agreement with the value predicted from the estimated values of the cosmic-ray neutron flux and the amount of carbon in exchange equilibrium with the atmosphere. No significant activity was detected in petroleum methane.

A discussion of the thermal diffusion enrichment factor is given.

1. INTRODUCTION

It is well established[1–7] that neutron secondaries are produced in the atmosphere by the cosmic radiation. Less well established is the total number, Q, of neutrons produced per cm^2 of the earth's surface per second. The recent paper of Korff and Hammermesh[7] allows a rough estimate of Q to be made. Integration of their curve for neutron production rate per gram *vs.* depth from the top of the atmosphere gives Q as 0.8 neutrons/cm^2/sec.

The neutrons probably are produced with several Mev energy[3] and collide with air molecules until they are captured. From the known large, slow neutron-capture cross section for $N^{14}(n, p)C^{14}$ it is quite clear that the main part of Q must result in the formation of C^{14} atoms in the atmosphere. Korff[8] has given this conclusion previously.

As suggested earlier[9a] this radiocarbon should be detectable in living matter, and the present article reports evidence for its existence in about the expected amount. The existence of such "cosmic radioelements" has been anticipated by one of us[9b] shortly after the discovery of artificial radioactivity.

The amount to be expected can be estimated by realizing that a state of radioactive equilibrium must have been established if the flux of incoming neutrons, Q, has remained essentially unchanged over the last ten to fifteen thousand years (two to three C^{14} half-lives); i.e., the number of C^{14} atoms disappearing per second by emission of beta-particles must just equal the number being formed per second. The latter number will be $5.1 \cdot 10^{18}\, Q$, where $5.1 \cdot 10^{18}$ is the earth's surface area in cm^2. This means that there must be just enough C^{14} on earth to emit $5.1 \cdot 10^{18}\, Q$ beta-particles per second, and taking the half-life to be about 5000 years[10a, b] we find this to be equivalent to some 22 metric tons, or 110-million curies of radiocarbon. Thus the total amount will be known to the same accuracy that Q is known.

Since it is known that most of the neutrons are formed and captured again in the upper half or two-thirds of the atmosphere, we must assume

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[1] C. G. and D. D. Montgomery, Phys. Rev. **56**, 10 (1939).
[2] S. A. Korff, Rev. Mod. Phys. **11**, 211 (1939).
[3] H. A. Bethe, S. A. Korff, and G. Placzek, Phys. Rev. **57**, 573 (1940).
[4] E. T. Clarke and S. A. Korff, J. Frank. Inst. **232**, 217 (1941).
[5] S. A. Korff and E. T. Clarke, Phys. Rev. **61**, 422 (1942).
[6] S. A. Korff and M. Kupferberg, Phys. Rev. **65**, 253 (A) (1944).
[7] S. A. Korff and B. Hammermesh, Phys. Rev. **69**, 155 (1946).
[8] S. A. Korff, Terr. Mag. **45**, 133 (1940).
[9a] W. F. Libby, Phys. Rev. **69**, 671 (1946).
[9b] A. V. Grosse, J. Am. Chem. Soc. **56**, 1922 (1934).
[10a] A. F. Reid, J. R. Dunning, S. Weinhouse, and A. V. Grosse, Phys. Rev. **70**, 431 (1946).
[10b] W. D. Norris and M. G. Inghram, Phys. Rev. **70**, 772 (1946).

TABLE I.

Source	Sample number	Calculated C^{14} enrichment	C^{13} concentration from mass spectrometer, %	% CH_4 in gas before final purification	Date taken	Total count rate including background (counts per minute)
Petro methane	I	1	1.04	99.6	10/16/46	340.6±1.0
	II	1	1.04	99.6	10/16/46	342.6±1.0
	III	25	6.55	97.2	1/ 6/47	345.8±1.3
Bio-methane	III	1	1.04	99.4	12/ 5/46	342.9±2.0
	I	10	7.36	93.6	10/17/46	348.7±1.3
	VII	32	11.02	99.9	12/ 2/46	364.0±1.5
	VIII	260	63.5	97.2	2/10/47	562.0±2.9

that the radiocarbon will enter the life cycle by conversion to CO_2 by reaction with atmospheric oxygen, and thus will be distributed throughout all living matter and all inorganic substances containing carbon which are in exchange with atmospheric CO_2 on a 5000-year scale (principally dissolved carbonates in sea water). By estimating from geochemical data the amount of carbon existant on earth in living matter, atmospheric CO_2, and ocean carbonate, we then can predict the specific radioactivity to be expected. We shall take in this estimate the biosphere[11] to contain $5\cdot10^{13}$ metric tons, the ocean carbonate[12] $3\cdot10^{13}$ tons, and the atmospheric[11] CO_2 $6\cdot10^{11}$ tons, for a total of $8.1\cdot10^{13}$ tons, or 1.3 moles of carbon per cm^2, on earth. Assuming further that due to the 5000-year half-life ample time has been available for the establishment of a nearly uniform world-wide distribution throughout all living matter, we calculate that $0.3\cdot10^{-12}$ grams of radiocarbon should be found per gram of living carbon or that the specific activity of living carbon should be 3 beta-particles per minute per gram. The accuracy of the estimate depends on the accuracies with which the neutron production rate, Q, and the amount of living and exchangeable matter are known. The error in Q may be as much as a factor of two or three, and the amount of living and exchangeable carbon may not be known to better than a factor of two, principally due to uncertainty about the biosphere value, so we expected the specific activity to lie between outside limits of 1 and 10 disintegrations per minute per gram. The value reported here is 10.5, in reasonably good agreement.

2. METHOD

The difficulty of detecting the expected specific activity of about 10^{-12} curies per gram of living carbon made isotopic concentration before measurement extremely desirable. Since the thermal diffusion columns at the Houdry Process Corporation operate normally on methane for the production of C^{13} enriched material, it was hoped that methane derived immediately from living material could be obtained. This proved to be possible through the kindness of the city of Baltimore. The Patapsco Sewage Disposal Plant of that city produces an illuminating gas, derived directly from sewage, containing about 60 percent methane, the rest being CO_2 with only traces of N_2. After absorption of CO_2 by soda-lime a very pure methane remains. Particularly important is the fact that no ethane, propane or higher hydrocarbons can be detected in it by modern methods; thus it is an ideal gas for carbon isotope separation in thermal diffusion columns. (The one-half percent of hydrocarbon impurities in the purest petroleum methane (99.5 percent) concentrate in the thermal diffusion columns together with $C^{13}H_4$ and thus greatly pollute the concentrate.) Six hundred liters of this biomethane were used and concen-

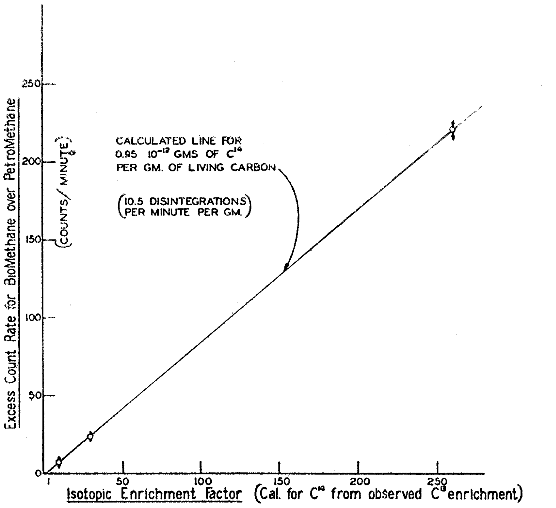

FIG. 1. Radioactivity of biomethane samples *vs.* isotopic enrichment. (6.5-mm Hg pressure in 1900-cc counter at room temperature.)

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[11] W. J. Vernadsky, *Geochemie in Ausgewählten Kapiteln* (Akademische Verlagsgesellschaft, Leipzig, 1930).

[12] V. M. Goldschmidt, *Geochemische Verteilungsgesetze der Elemente* (Norwegian Academy, Oslo, 1938), Vol. 9.

trated in the two thermal diffusion plants at Marcus Hook, Pennsylvania. The concentrates were purified from substantial percentages of nitrogen by appropriate condensations and distillations in a usual vacuum train at liquid to solid nitrogen temperatures. The purity of the final samples, submitted for radioactivity measurements, were determined by the Consolidated Engineering mass spectrometer and are given in column 4 of Table I.

The degree of enrichment of any C^{14} present was determined by measurement of the C^{13} enrichment and calculation of the corresponding enrichment factor for C^{14} as described in Section 5. The calculated factors were submitted together with the samples by the Houdry Process Corporation group before they were measured at Chicago. It would have been possible, of course, to calibrate the columns empirically with synthetic C^{14} but fear of contamination would preclude such a hazardous step. Such a procedure should, however, increase the accuracy of the determination in the future.

The measurement of the radioactivity was accomplished by utilizing the principles that living carbonaceous material will differ from chemically identical material which has been buried for times long with respect to the 5000-year half-life of radiocarbon by containing radiocarbon, and that isotopically enriching living material will increase its radiocarbon content. The material used in all cases was pure methane gas. The counters of about two-liter volumes were filled alternately with "biomethane" from the Baltimore sewage and with the same pressure of "petromethane" from oil wells. Careful measurements were made of the count rates with the two fillings. The main part of the rate, in general, except for the richest biomethane sample, was due to cosmic radiation and general laboratory background. It was expected that this would be identical for both types of gas and that any difference in these rates would be due to inherent radioactivity of the gas itself. The proof that the activity was due to C^{14} was that burning of the methane to CO_2 and precipitating $CaCO_3$ carried the activity and that the absorption curve in aluminum of the $CaCO_3$ radiation was identical within the experimental error with that for synthetic C^{14}. In addition, the proportionality of the activity of the gaseous methane to the C^{14} enrichment factor proved further that the radioactivity was due to a carbon atom of mass 14.

TABLE II. Bio VIII sample in standardized counter.

Sample (6.5-cm Hg press.)	Total count rate (counts/min.) including background
Petro II	312.5±1.4
Bio VIII	429.2±2.4
Difference	116.7±2.8
Difference, corrected for end loss	125±3
Moles CH_4 in counter	$3.82 \cdot 10^{-3}$
Unenriched specific activity of living carbon	2.1±0.3 counts/sec./mole
Unenriched specific activity of living carbon	10.5±1 counts/min./g
Abundance of C^{14} in living carbon (gms/gm)	$0.95 \cdot 10^{-12}$

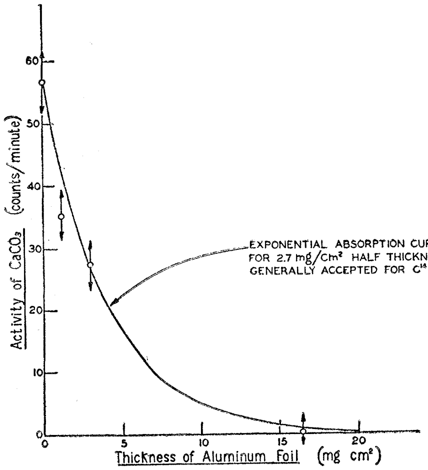

FIG. 2. Absorption of $CaCO_3$ radiation in aluminum and aluminum-absorption curve for synthetic radiocarbon (C^{14}).

3. MEASUREMENT OF RADIOACTIVITY

The gaseous methane was introduced into a brass cylinder counter with glass heads cemented in place with de Khotinsky cement. The volume between the heads was 1900 cc, the diameter being 3 inches, and the length 18 inches. Alternate readings were taken with 6.5-cm Hg pressure of petro- and biomethane samples in the counter. A standard external sample of U_3O_8 was used to check that the counter sensitivity was the same for all fillings. The counter was completely surrounded by a 1.5-inch thick lead shield to reduce the background.

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TABLE III. Data on chemical and physical identity of the radioactivity.

A. *Activity of $CaCO_3$ obtained by combustion of the CH_4*

Weight of $CaCO_3$ counted	1.2 g
Average thickness of layer of $CaCO_3$	5 mg/cm^2
Total activity in $CaCO_3$ if all in CH_4 was carbon	386 counts/min.
Expected[13] count from smooth solid $CaCO_3$ of this total activity and thickness	111 counts/min.
Observed count	56.6±5 counts/min.

B. *Aluminum absorption data*

Absorber thickness	Expected for C^{14}	Observed
0 mg/cm^2	(56.6)	56.6±5
1.14	42.5	35.0±3.5
2.94	27.1	27.3±4
16.40	1.0	0 ±3

smaller counter was used with plane heads machined out of Lucite. This counter, 2×24 inches in dimensions, was calibrated for loss at the ends by counting a gas sample containing synthetic radiocarbon at comfortable intensity in two counters of the same diameter, but different lengths. Taking the difference in rates at a given pressure of gas then gave the true rate for a counter with no end losses and of length equal to the difference in lengths. The end loss correction for the counter used on the methane samples was 7 percent.

The most concentrated biomethane sample (Bio VIII) was burned and $CaCO_3$ precipitated to establish that the radioactivity was chemically carbon rather than hydrogen (possibility of tritium existed). This was measured in a screen wall counter[14a, b] with the chamber wall maintained at a negative potential of about 135 volts with respect to the screen so the maximum sensitivity to the $CaCO_3$ radiation was obtained. The expected radioactivity was found and the absorption curve in aluminum was obtained by mounting foils over the sample and remeasuring in the same counter.

4. DATA

Tables I and II give the enrichment data and the corresponding count rates for the large glass head counter.

Figure 1 presents the difference between bio- and petromethane count rates plotted against enrichment factor. The fact that the three points fall on a single straight line demonstrates the internal consistency both of the enrichment factors and the counting data.

Table II gives the counting data for the 260-fold enriched biomethane sample (Bio VIII) in the standardized Lucite head counter.

The data on the identity of the radiation are given in Table III.

The absorption data are given in Table III and plotted in Fig. 2, together with the generally accepted curve for synthetic radiocarbon radiation.

5. C^{14} ENRICHMENT CALCULATION

In a two-component gas, the general equation[15] giving the transport τ, of one species in a diffusion column is

$$\tau = H(1-c)c - K(dc/dz) \qquad (1)$$

where c is the mole fraction of the species, z is the coordinate along the column, and H and K are net transport coefficients. It is necessary to determine H and K experimentally because of ignorance of the force law involved and limitation in determining the functional effect of conditions in an operating column.

The extension of the treatment[16] to the separation of three isotopic species simultaneously can be made so that if the mole fraction of one can be experimentally determined, the concentration of the other two can be calculated. The general case is quite complicated and difficult of solution, but solutions can be made for cases with limiting conditions. Specifically, in the separation of $C^{12}H_4$, $C^{13}H_4$, and a very small concentration of $C^{14}H_4$, the fundamental transport equations become:

$$\tau_1 = H(1-c_1)c_1 - K\frac{dc_1}{dz}, \qquad (2)$$

$$\tau_2 = \frac{33(2-c_1)}{34+c_1}Hc_2 - K\frac{dc_2}{dz}, \qquad (3)$$

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[13] W. F. Libby, Ind. Eng. Chem., Anal. Ed. **19**, 2 (1947).

[14] (a) W. F. Libby, Phys. Rev. **46**, 196 (1934). (b) D. D. Lee and W. F. Libby, *ibid.* **55**, 245 (1939).

[15] R. C. Jones and W. H. Furry, Rev. Mod. Phys. **18**, 151 (1946). This very excellent review, entitled "The separation of isotopes by thermal diffusion," gives a comprehensive picture of the fundamentals involved in general gaseous thermal diffusion. Because of the diverse origin and development of the concepts, this article is used for general reference.

[16] The development of the relationships used and their application is to be described separately by A. F. Reid and D. Tanguy.

where subscripts 1 and 2 refer to $C^{13}H_4$ and $C^{14}H_4$, respectively, and H and K are the $C^{13}H_4$ transport coefficients.

Upon application of the equations to the separation system used, calculation of the relative concentrations of $C^{14}H_4$ could be made for simultaneous enrichments of $C^{13}H_4$. The measured concentration change with time of the $C^{13}H_4$ followed the theoretical values faithfully, indicating a uniformity of column operation, which permitted some simplification. However, a small amount of nitrogen was present which concentrated in the same direction as the heavy methane; some uncertainty as to its distribution is reflected in the limit of the $C^{14}H_4$ enrichment calculations.

Figure 3 is a plot of the characteristic ratios of bottom to top isotope ratios for the system used when it is originally filled with an atmosphere of normal methane. Because of the nitrogen present and early withdrawals made to purge a large portion of it, calculation of the C^{14} enrichment required individual modifications for each case.

6. DISCUSSION AND CONCLUSIONS

In earlier brief reports[17a, b] the observations were given and certain deductions made in abbreviated form. A more complete discussion seems in order.

The enrichment factor count-rate correlation (Fig. 1) indicates that the activity is carried in a molecule with the thermal diffusion characteristics of methane of mass 18 present in low concentration in the original biomethane. The fact that the activity follows the chemistry of carbon rather than hydrogen indicates that the activity is due to a carbon isotope of mass 14. Finally, the agreement of the absorption data with those for synthetic C^{14} further confirms the identification of the activity with C^{14}.

One might worry about the disagreement in Table IIIA between the expected count from the solid $CaCO_3$ (111 c/m) and the observed (56.6 c/m). We believe this is not serious, however, since the precipitate certainly was not smooth, as had to be assumed to make the calculation of the expected figure of 111. The $CaCO_3$ was purposely allowed to crystallize in large crystals to reduce the chance of loss due to exchange with atmospheric CO_2 during the necessary exposure to air while the sample and the foils were being mounted. It was also true that the mounting, by moistening with ethanol and allowing to dry, resulted in a sample visibly rough with ridges and thick spots.

The possibility that the C^{14} found in Baltimore sewage had an origin other than the cosmic radiation is very remote. Our sample was taken on September 2, 1946, at which time no radiocarbon from the Atomic Energy Commission had been sent to anyone in Baltimore, according to Dr. P. C. Aebersold of the Isotopes Research Branch in Oak Ridge. The possibility that the atomic bombs or the piles may have been the origin seems very remote also when one realizes that our result corresponds to the existence of some 10^8 curies or about 20 metric tons of radiocarbon in nature—an amount far larger than any synthetic source could have produced to date. Of course, it will be desirable to examine other samples of living carbon to establish the uniformity of the distribution, and efforts in this direction are intended. In this connection it is hoped that all plants concentrating C^{13} will use "live" feed and arrange to measure their products for radioactivity to collect further data on the natural abundance.

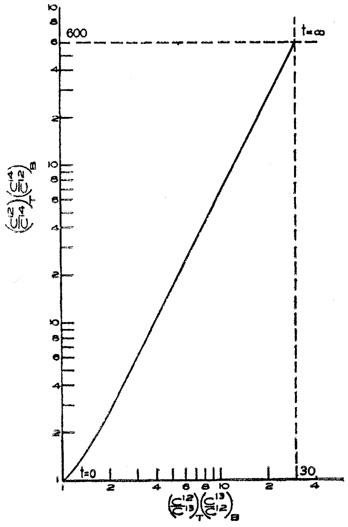

FIG. 3. Characteristic concentration curve of the Marcus Hook thermal diffusion unit.

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[17] (a) E. C. Anderson, W. F. Libby, S. Weinhouse, A. F. Reid, A. D. Kirshenbaum, and A. V. Grosse, Science **105**, 576 (1947).
(b) A. V. Grosse and W. F. Libby, *ibid.* **106**, 88 (1947).

In a strict sense our data show only that our particular sample of Baltimore sewage methane contained radiocarbon to the extent of 10.5 disintegrations per minute per gram of carbon, and that our sample of petroleum methane contained considerably less than this. These results fit so well with the theory of cosmic-ray production of radiocarbon, and are so difficult to explain at present on any other basis, that we believe the theory to have been confirmed. We plan further tests, particularly on the assumption of uniformity of distribution, and have at hand at the moment samples of living matter from Antarctica, killed in Antarctica, through the kindness of the Navy Department and Operation Highjump. It is anticipated that improvements in our counting technique will make the assay less difficult. In fact, we anticipate that isotopic enrichment may not be necessary for material at the present living level.

Since the radiocarbon originates in the top layers of the atmosphere, thereby entering the life cycle and all living matter, and since the neutron intensity at sea level is negligible, we are led to the prediction that the intake of radiocarbon by living bodies will cease when they die, and that the period of time elapsed since death will be measurable by direct comparison of the specific activity of the specimen with that of living matter in general. In other words, if we can assume that the specific activity of living matter has remained constant over the time interval being measured, a specimen 5000 years buried will have 5.3 counts per minute per gram of carbon rather than the original 10.5. By invoking isotopic enrichment it should be possible to measure samples as old as 40,000 years. Of course, the limit could be extended by further enrichment, though the effort required would probably be prohibitive in most cases. It is planned to measure certain dated samples as a check on these conclusions.

It is clear from the nature of our postulates that the specific activity of living matter gives the ratio of the number of cosmic-ray neutrons per cm^2 and per unit time to the amount of living and exchangeable carbon per cm^2. It is hoped that the result will be useful to both the cosmic-ray physicists and geochemists in establishing these two quantities. The present result seems to indicate that either the number of neutrons is about three times as large as the data of Korff and Hammermesh[7] indicate, or that the amount of exchangeable carbon is about one-third the figures postulated in the references cited above. It is impossible at the moment to say which of these is more likely, or whether some intermediate situation obtains.

A search for other cosmic radio elements has been started.

7. ACKNOWLEDGMENTS

We are grateful to Messrs. George E. Finck and R. J. Trautman of the Department of Public Works of the city of Baltimore, to Dr. H. G. Swope, Secretary of the A.C.S. Committee on Water, Sewage and Sanitation and to Dr. Abel Wolman of Johns Hopkins University for their cooperation, to the Sun Oil Company for the use of their thermal diffusion columns, to Mr. W. H. Johnston for assistance in the counting measurements, to Mr. D. Tanguy for assistance in calculations, and to Mr. J. T. Dooley for technical assistance.

Note added in proof: Since submitting this article a second sample of Baltimore sewage methane obtained from a different disposal plant a few miles away has been isotopically enriched 60-fold for C^{14} (22.2 percent C^{13}) and counted. The result was 10 ± 1 counts per minute per gram, in agreement with the earlier measurements.