

The geochemistry of the stable carbon isotopes*

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ABSTRACT

Several hundred samples of carbon from various geologic sources have been analyzed in a new survey of the variation of the ratio C^{13}/C^{12} in nature. Mass spectrometric determinations were made on the instruments developed by H. C. UREY and his co-workers utilizing two complete feed systems with magnetic switching to determine small differences in isotope ratios between samples and a standard gas. With this procedure variations of the ratio C^{13}/C^{12} can be determined with an accuracy of $\pm 0.01\%$ of the ratio.

The results confirm previous work with a few exceptions. The range of variation in the ratio is 4.5%. Terrestrial organic carbon and carbonate rocks constitute two well defined groups, the carbonates being richer in C^{13} by some 2%. Marine organic carbon lies in a range intermediate between these groups. Atmospheric CO_2 is richer in C^{13} than was formerly believed. Fossil wood, coal, and limestones show no correlation of C^{13}/C^{12} ratio with age. If petroleum is of marine organic origin a considerable change in isotopic composition has probably occurred. Such a change seems to have occurred in carbon from black shales and carbonaceous schists. Samples of graphites, diamonds, igneous rocks, and gases from Yellowstone Park have been analyzed. The origin of graphite cannot be determined from C^{13}/C^{12} ratios. The terrestrial distribution of carbon isotopes between igneous rocks and sediments is discussed with reference to the available meteoritic determinations. Isotopic fractionation between iron carbide and graphite in meteorites may indicate the mechanism by which early fractionation between deep seated and surface terrestrial carbon may have occurred.

I. INTRODUCTION

During the last decade a great amount of work has been done on the relative abundances of the isotopes of the lighter elements. In view of the known dependence of the thermodynamic properties of substances upon their mass, these lighter elements are the ones in which the slight mass differences caused by isotopic substitution can be expected to cause measurable isotopic fractionation in chemical and physical processes. This fractionation is generally a result of the difference in vapour pressure or of the deviation from unity of the exchange equilibrium constant between two molecules containing different isotopes of a constituent atom. Since many of these exchange equilibrium constants can be calculated or measured, knowledge of the variations in the relative abundance of the isotopes of an element may furnish a powerful tool for the evaluation of the various geochemical and biochemical cycles through which the element passes.

The element carbon is particularly satisfactory for this type of research because of its geochemical and biochemical importance and because of the relative ease of the laboratory technique required. RANKAMA [1], [2] has reviewed most of the work done on the relative abundances of the carbon isotopes in both cosmic and terrestrial material. The terrestrial abundance of C^{12} has been established as being about 90 times that of C^{13} , and variation in the C^{12}/C^{13} ratio of from 4 to 5% have been

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reported. Systematic differences in sets of data reported by different workers have been noted [1], [3], and too few samples have been measured to afford a sufficiently detailed picture of the isotopic geochemistry of carbon. The attainment of a precision in measurement of carbon ratios of better than ten times any previously reported has prompted an intensive survey of variations in the carbon isotope ratio in order to establish a definitive framework within which studies of detailed problems may be attempted.

II. EXPERIMENTAL PROCEDURE

The development of a mass spectrometer capable of extremely high precision in these measurements necessitated great care in the preparation of samples. Samples were converted to carbon dioxide by methods designed to give total yields free from any contamination either of sample or product gas. Such procedures as absorbing carbon dioxide in a basic solution were shown to cause measurable fractionation and hence were not used.

Carbon combustion apparatus

The conversion of carbon to carbon dioxide was carried out in a vacuum tight combustion system, the details of which are shown in Fig. 1. The combustion tube is quartz, half filled with copper oxide. The weighed sample in an alundum boat is placed in the combustion tube,

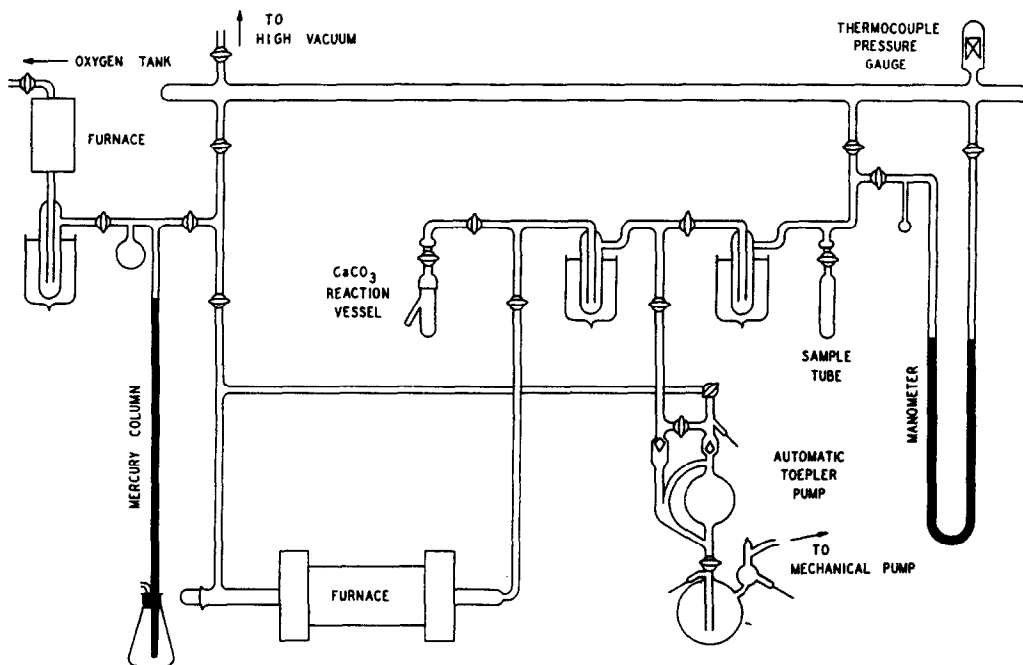


Fig. 1. Carbon combustion apparatus.

the ground glass joint replaced, and the system pumped down to high vacuum. Enough sample was generally used to provide 10–15 cc of carbon dioxide, though samples as small as 1 cc can be measured. Tank oxygen, purified by passing through a copper oxide filled combustion tube at 700° C and a trap cooled by liquid nitrogen, is then admitted to the system to a pressure of about 15 cm. The combustion system proper consists of the furnace, one trap, and an electrically operated Toepler pump which serves to recycle the gases through the copper oxide during the combustion which is carried out at 900–950° C. Carbon dioxide is condensed in the liquid nitrogen cooled trap during the combustion, and thus all carbon monoxide and other carbon

products are finally converted to carbon dioxide. The criteria used to establish the length of a run are the attainment of total yields for samples of known carbon content and the checking of results within the desired precision.

When the system has cooled down the carbon dioxide is purified by means of traps cooled by baths consisting of dry ice in a 1:1 mixture of chloroform and carbon tetrachloride, its volume is measured in the manometer, and the sample is then condensed into the sample tube for transfer to the mass spectrometer.

Liquids such as petroleum which might fractionate upon evacuation of the system are frozen down in the combustion boat with liquid nitrogen and remain frozen long enough for the system to be pumped out. Calcium carbonate samples can be converted to carbon dioxide in this apparatus by means of the reaction vessel in which 100% orthophosphoric acid was used. Preparation of the acid and details of the method have been described by McCREA [4] and UREY *et al.* [5]. Samples of carbonate which contained appreciable organic matter were first roasted in a stream of helium at 475° C, following the procedure described by EPSTEIN *et al.* [6]. Apiezon "N" stopcock grease was used as a lubricant throughout the system. An analyzed sample of carbon dioxide allowed to stand for one week in a tube containing this grease showed no change in isotopic composition.

Atmospheric carbon dioxide collection

Since experiments to be discussed in a following section showed that absorption of atmospheric carbon dioxide in basic solutions, *e.g.* barium hydroxide, could cause measurable isotopic fractionation, an apparatus was designed to condense out carbon dioxide from a measured volume of air. Details of this apparatus are shown in Fig. 2.

A ten litre flask with an outlet stop-cock connects through a ground glass joint to the vacuum line. Carbon dioxide is trapped out in a long spiral coil of copper tubing sealed into the line with copper to glass seals. (Copper rather than glass is used because of the high heat conductivity.) The coil is immersed in liquid nitrogen and as the air passes through both water and carbon dioxide

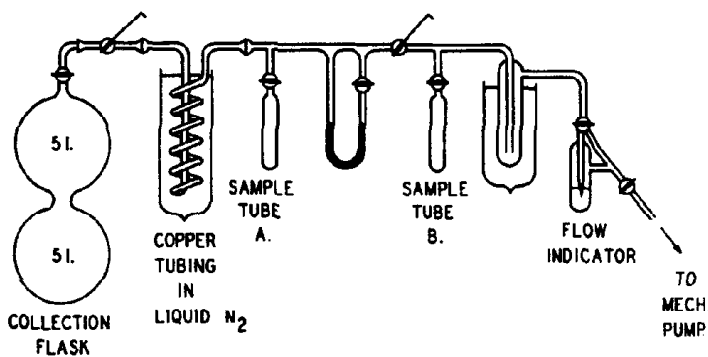


Fig. 2. Atmospheric carbon dioxide extraction.

condense out. The flow rate through the line is adjusted by means of two stopcocks with the plugs scratched for fine adjusting. With this modification the rate of flow could be throttled down to as low as 0.22 cc/sec, and the line pressure as shown by the manometer can be adjusted to as low as 2 mm of mercury. The duration of a run was generally about 13 hrs, after which the carbon dioxide was transferred to the sample tube for subsequent purification and mass spectrometric analysis. The average amount of carbon dioxide obtained was 3.5 cc for Chicago air.

The flow indicator on the line contains dibutyl phthalate, a liquid of very low vapour pressure. The glass trap on the line, immersed in liquid nitrogen, serves to prevent back diffusion of gases into the copper coil, and its contents when transferred to the adjacent sample tube serve to check whether any condensable gas is passing through the copper coil and being caught here. The maximum amount of gas present in this trap which was condensable in liquid nitrogen but not condensable in the dry ice bath (*i.e.* possibly carbon dioxide) was always less than 0.01 cc*.

* That these precautions were overly elaborate is shown by the fact that samples collected by running air from outside the laboratory through glass traps immersed in liquid nitrogen gave results falling right in the range of those collected in the manner described. Since the analyses varied by as much as 2.5‰, it seemed desirable to be sure the variation was due to natural causes by using the more elaborate procedure.

Collection of Yellowstone Park gases

Gases from the hot springs and geysers of Yellowstone National Park were collected in order to analyze the carbon present as carbon dioxide and methane. One litre flasks, opening through two diametrically opposed vacuum type stopcocks to which were sealed ground glass joints, were used as gas containers. Celvacene medium stopcock grease was used as a lubricant. From one joint on a flask a short piece of stout rubber tubing extended. From the other end a long piece of rubber tubing extended along a pole and was firmly attached to a large funnel which in turn was firmly attached to the pole. Close to the flask end and inserted in this piece of tubing was a glass T tube with a short piece of rubber tubing and a pinch clamp attached to the free end of the tube. The flasks and stopcocks were evacuated before leaving the laboratory.

At the edge of the hot spring the short piece of tubing and the funnel were dipped into the water. The flask was held so that the stopcocks were in a vertical line with the shorter piece of tubing below. The bottom stopcock was then opened and water rose into the flask, filling it. This served not only to fill the flask but to test the vacuum maintained by the flask. The upper stopcock was then opened, the pinch clamp on the T tube loosened, the free end of the T tube inserted in the mouth, and flask and tubing were then sucked full of water, expelling all air from the system. The pinch clamp was tightened, the funnel pushed out under water to the point in the spring where gas was bubbling up, and gas was allowed to bubble into the flask displacing the water which ran out the bottom tube still extending under the surface of the water. When the flask was full the stopcocks were closed and the flask replaced by another for a new collection. After the condensation of steam about four-fifths of an atmosphere of gases remained in the flask. Separation of the carbon dioxide from methane and other gases, and combustion of the methane were carried out in the combustion line previously described.

The mass spectrometer

The mass spectrometer used in this investigation is one of two such machines used by H. C. UREY and his co-workers in their work on oxygen isotopes and paleotemperatures. The basic details of this instrument have been described by NIER [7] and the changes made therein by MCKINNEY *et al.* [8]. The instrument is a double collecting sixty degree deflection mass spectrometer tube with the electronic and gas handling systems modified to measure small differences in the abundance of isotopes with extremely great sensitivity. These modifications permit the measurement of variations in the isotope ratio to an accuracy of $\pm 0.01\%$ of the abundance of these isotopes.

The recorded figures are the differences in the ratio of the mass 45 and mass 44 ion beams of the sample and the standard gas, expressed in permil of the ratio in the standard gas, *i.e.*,

$$\delta' = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) 1000$$

where R is the ratio of the abundances of the ions of mass 45 and mass 44. Since R is actually the ratio of $(\text{C}^{13}\text{O}^{16}\text{O}^{16} + \text{C}^{12}\text{O}^{16}\text{O}^{17})$ to $\text{C}^{12}\text{O}^{16}\text{O}^{16}$, a correction factor must be applied for the abundance of O^{17} . This correction factor to be subtracted from the number of ions of mass 45 is equal to twice the abundance ratio $\text{O}^{17}/\text{O}^{16}$, since the probability that one of the two oxygen atoms will be an O^{17} is twice the percent abundance of O^{17} in a mixture of O^{17} and O^{16} . NIER [9] has recently redetermined this value very accurately, and in the same paper has determined the absolute abundance ratio $\text{C}^{13}/\text{C}^{12}$ in a sample of the Solenhofen limestone as accurately as present day absolute abundances can be measured. He has very kindly furnished a sample of this specimen for a measurement of the difference between it and the standard used in this work. With this value and his value for the $\text{O}^{17}/\text{O}^{16}$ abundance ratio, a simple calculation gives the correction factor to be applied, namely that δ' in the above expression must be multiplied by 1.067. A detailed evaluation of this correction factor has been made and readers are referred to the original dissertation for this discussion.

A small correction must also be applied to δ' because of the slight amount of mixing of the sample and standard gases due to small imperfections in the ground glass ball joints in the inlet valve*. This factor is easily corrected for by noting the shift of the trace of the null point of the standard upon the recording potentiometer when the sample gas is pumped away.

* See Reference [8] for details of this valve.

During the period in which this work was done, the factor remained quite constant, the average value being 4.5% by which the recorded value δ' must be increased.

The mass spectrometric measurements are reproducible to $\pm 0.10\%$. In general the precision is even better than this, and in a series of checks made on thirty-four different combustions of seventeen different samples of easily combusted organic material the results were reproducible to $\pm 0.05\%$. Other samples do not check this well, but all errors fall within the 0.2% range. Gas samples from each series of runs were saved and run again during the next series of runs to check the standard gas for any slow changes with time, but the errors were purely random and showed no cumulative effect. It seems quite certain that errors larger than $\pm 0.1\%$ are due to some factor introduced during the combustion or preparation of the sample, or to an inherent inhomogeneity in the sample itself.

Presentation of data

The final values presented in this paper are then:

$$\delta \text{ in } \text{‰} = \left(\frac{C^{13}/C^{12} \text{ sample} - C^{13}/C^{12} \text{ standard}}{C^{13}/C^{12} \text{ standard}} \right) 1000.$$

Thus a negative value for δ indicates that the sample is "lighter", *i.e.* contains less C^{13} than the standard gas, and the values represent relative abundance variations only. The standard gas used throughout the investigation is carbon dioxide prepared from a Cretaceous belemnite, *Belemnitella americana*, from the Peedee formation of South Carolina. For comparison with absolute abundances in the literature [1], [2], [3], etc., one may note that NIER's sample of the Solenhofen limestone is -0.90% compared to this standard sample*. Dr. P. BAERTSCHI of the University of Basel has recently completed work on the C^{13}/C^{12} ratios in some one hundred and fifty carbonate rocks [59], and his data are presented in the same manner as those in this paper. These measurements may be compared directly by noting that BAERTSCHI's standard is $+2.34\%$ with reference to the one used here.

III. CARBON ISOTOPIC EXCHANGE EQUILIBRIA

At ordinary temperatures and above, and for all elements but hydrogen, the energy difference between two isotopic molecules is dependent only on the shift in the vibrational frequencies caused by the substitution of one isotope for another. Since the vibrational energy levels occupied by a molecule are temperature dependent, the isotopes of an element will distribute themselves between two compounds in thermodynamic equilibrium as a function of the temperature. Thus if the isotopic vibrational frequency shifts can be evaluated from spectroscopic data, the equilibrium constant for the isotope exchange reaction can be calculated as a function of temperature. It is then possible to discuss isotopic abundance data in terms of temperatures for equilibrium processes.

UREY [10] has presented a great many of these calculations in a general paper discussing the theory and applications of such calculations. The carbon compounds of geological interest for which calculations were made are carbonate ion, carbon dioxide, diamond, and carbon monoxide. The present author has calculated the partition function ratios for methane and combined these with those derived by UREY to furnish a complete table of exchange equilibrium constants for all carbon compounds of geological importance for which such calculations can be made. The method of calculation has been given in detail by UREY, and only the derived isotopic frequencies for methane will be presented here.

Using the four fundamental frequencies of methane as given by HERZBERG [11], and using the valence force assumption equations for methane [12], the force

* The C^{13}/C^{12} ratio of the standard gas is thus 88.89, based on NIER's determination. The C^{13}/C^{12} ratio of any sample in this paper is then $88.89/(1 + \delta/1000)$.

constants were solved for using the known frequencies. The frequencies of the $C^{13}H_4$ molecule were then derived from these equations by substituting mass 13 for mass 12. Since methane is a tetrahedral molecule with carbon at the centre, the ν_1 and ν_2 frequencies remain unchanged. The remaining frequencies were found to have the following values:

$$\nu_3^{(i)} = 3007.66 \text{ cm}^{-1}$$

$$\nu_4^{(i)} = 1298.90 \text{ cm}^{-1}.$$

The partition function ratios were then evaluated at the different temperatures and combined with those derived by UREY to give the exchange equilibrium constants between methane and the other compounds. Since the previous calculations were carried out only to temperatures of 600°K , it was not possible to derive values for higher temperatures.

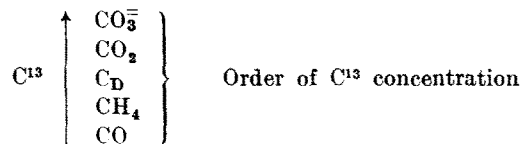
Table I presents the calculated equilibrium constants for exchange reactions between the various compounds. The body of the table contains the equilibrium constant at the temperature shown in the far right column between the molecules listed at the top of the column and at the left. If these constants are greater than

Table I. Carbon isotope exchange equilibria

	$\frac{C^{13}O_3}{C^{12}O_3}$	$\frac{C^{13}O_2}{C^{12}O_2}$	$\frac{C^{13}_D}{C^{12}_D}$	$\frac{C^{13}H_4}{C^{12}H_4}$	$\frac{C^{13}O}{C^{12}O}$	T, °K
$\frac{Q_2}{Q_1}$	1.2358	1.2169	1.2081	1.1369	1.1086	273.1
	1.2057	1.1909	1.1786	1.1220	1.0970	298.1
	1.1274	1.1233	1.1077	1.0821	1.0659	400
	1.0870	1.0877	1.0722	1.0599	1.0479	500
	1.0629	1.0656	1.0516	1.0458	1.0360	600
$\frac{C^{13}O_3}{C^{12}O_3}$	1.000	∞		∞	∞	0
		1.016	1.023	1.087	1.115	273.1
		1.012	1.023	1.075	1.099	298.1
		1.004	1.018	1.042	1.058	400
		0.999 ₄	1.014	1.026	1.037	500
	0.997 ₅	1.011	1.016	1.026	600	
$\frac{C^{13}O_2}{C^{12}O_2}$		1.000	0	∞	∞	0
			1.007	1.070	1.098	273.1
			1.010	1.061	1.086	298.1
			1.014	1.038	1.055	400
			1.014	1.026	1.038	500
		1.013	1.019	1.029	600	
$\frac{C^{13}_D}{C^{12}_D}$			1.000	∞	∞	0
				1.063	1.090	273.1
				1.050	1.074	298.1
				1.024	1.039	400
				1.012	1.023	500
			1.006	1.015	600	
$\frac{C^{13}H_4}{C^{12}H_4}$				1.000	∞	0
					1.026	273.1
					1.023	298.1
					1.015	400
					1.011	500
				1.009	600	

unity the heavier isotope will concentrate preferentially in the compound listed at the left. The figures in the first row are the ratios of the partition functions of the heavy and light molecules as defined by UREY [13].

These data show that in a general way the oxidized carbon compounds tend to concentrate C^{13} and the reduced compounds C^{12} , with the solid carbon, as represented by diamond, falling in between. This can be shown more simply by the following scale:



in which the compounds are arranged in the order of the magnitude of their partition function ratios. Each compound concentrates C^{13} over any compounds listed below it when an exchange mechanism is furnished by a suitable chemical reaction. It should be noted that at a temperature of about $500^\circ K$ the carbonate ion-carbon dioxide equilibrium constant becomes unity and above this temperature the equilibrium is reversed.

The tabulated values for carbonate ion are not calculated from spectroscopic data alone, but are fitted to a theoretical treatment which depends on measured natural abundance variations [10]. These values are shown in a later section to be in error, and thus too much reliance should not be placed on them. It is not possible to calculate values for graphite at the present time since there is no satisfactory theoretical treatment of the structure of this mineral. It is thus impossible to determine the origin of graphite from carbon isotopic measurements.

The relationship between the equilibrium constant for the exchange reaction and the actual measured values of the isotopic composition of the substances undergoing exchange is worthy of note. Using R for the corrected C^{13}/C^{12} ratio in a sample, we have for the measured δ in permil:

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) 1000.$$

For two substances, A and B, in isotopic equilibrium, the equilibrium constant $K = R_B/R_A$.

Since $\delta_A - \delta_B = \left(\frac{R_A - R_B}{R_{\text{standard}}} \right) 1000$, and since we can eliminate from this expression R_B by its relationship to K and R_A , and R_A/R_{standard} by its relationship to δ_A , we have:

$$\delta_A - \delta_B = (1 - K)(\delta_A + 1000).$$

The measured difference in permil between the two compounds differs from the deviation of the equilibrium constant from unity, expressed in permil, by only a small factor. This is a great convenience in comparing calculated and measured differences in isotopic composition, and is one of the reasons for presenting the experimental data as the permil deviations recorded, rather than as absolute ratios.

IV. THE SYSTEM: CARBONATE-AIR-ORGANIC CARBON

The general results of the investigation are presented in Fig. 3, in which the permil deviations from the standard are plotted by groups. The results agree generally with those of previous investigators, the main differences being the well marked

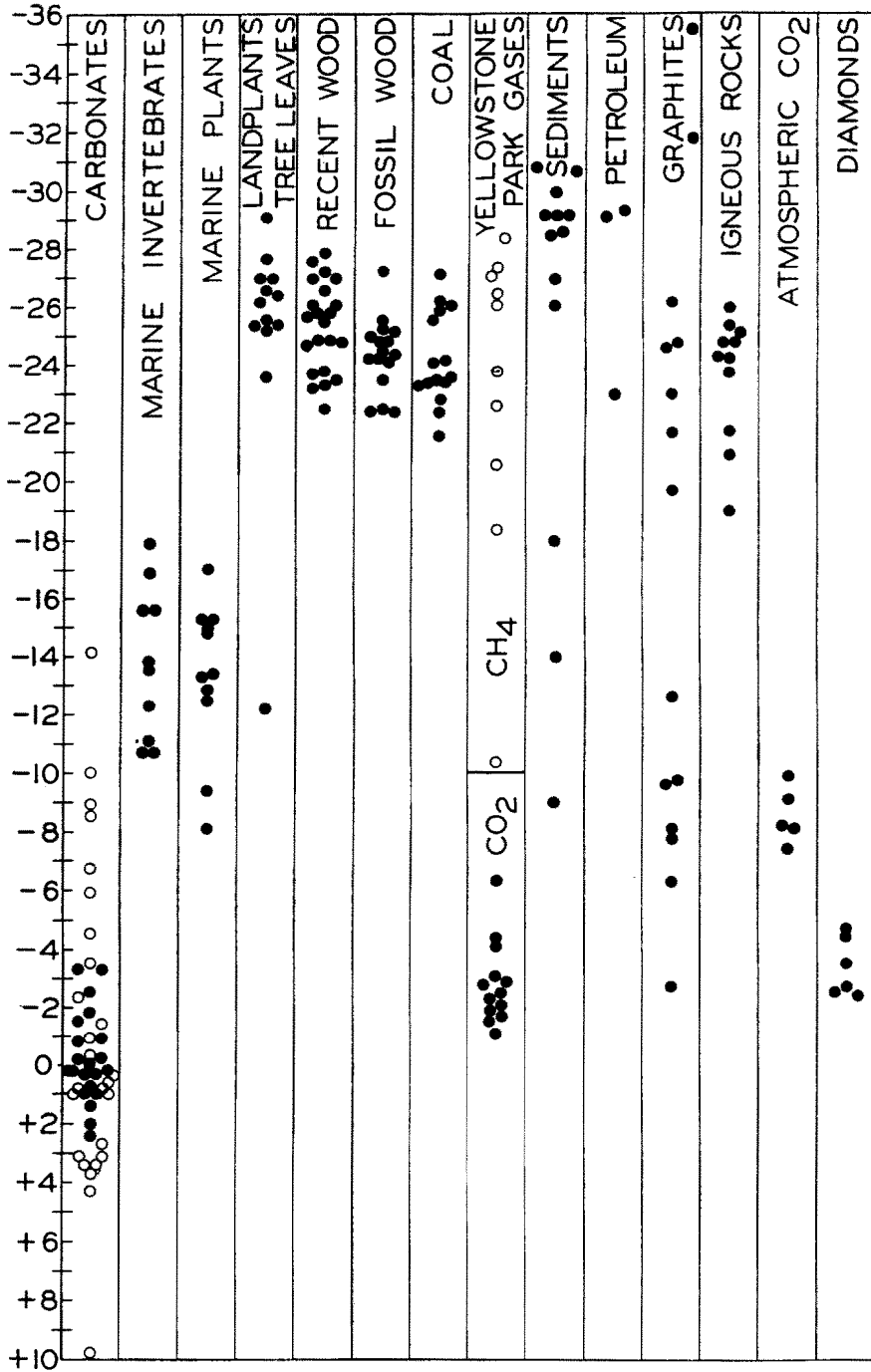


Fig. 3. $\delta^{13}C/^{12}C$ in ‰, of various carbonaceous samples.

division of organic carbon samples into marine and terrestrial groups, and the heavier results for atmospheric carbon dioxide.

Carbonates

The carbonates show a range of isotopic composition greater than that of any other group but the graphites, the range of δ being about 24‰. However the marine limestones, plotted as filled circles in Fig. 3, show a range of only 5.7‰. These values are presented in Table 2.

Table 2. *Isotopic composition of marine limestones*

No.	Sample	Location	δ ‰
19	Mississippian, Spergen (oolitic)	Bedford, Ind.	+ 2.4
12	Cretaceous Chalk	Dover Cliffs, England	- 2.0
13	Cretaceous Chalk, Selma	Oktibbeha Co., Miss.	- 1.4
8	U. Cretaceous, Niobrara	Bouider Co., Colo.	+ 1.0
15	Devonian, Onondaga	Onondaga Co., N.Y.	+ 1.0
3	Devonian, Jeffersonville	Jeffersonville, Ind.	+ 0.7
4	Silurian, Gasport	Lockport, N.Y.	+ 0.3
20	Ordovician, Holston	Knoxville, Tenn.	+ 0.3
22	Ordovician, Lowville	Lowville, N.Y.	+ 0.2
5	Ordovician, Trenton	Trenton Falls, N.Y.	- 0.2
21	Ordovician, Isle la Motte	Isle la Motte, Vt.	- 0.2
7	Silurian, Reynales	Rochester, N.Y.	0.0
11	Pleistocene, Anastasia	St. Augustine, Fla.	- 0.2
6	Silurian, Sodus	Rochester, N.Y.	- 0.3
16	Ordovician	Valcour Is., N.Y.	- 0.8
51	Jurassic, Solenhofen	Solenhofen, Bavaria	- 0.9
1	Pleistocene, Key Largo	Key Largo, Fla.	- 1.5
35	Pennsylvanian-Permian, Lykins	Boulder Co., Colo.	- 1.8
17	Ordovician, Pogonip	Ruth, Nev.	- 2.5
10	L. Cretaceous	Mt. Lebanon, Syria	3.3
29	Cambrian, Warrior (oolitic)	Tyrone, Penn.	- 3.3
Average			- 0.2

There is no sign of any age effect and if the mean isotopic composition of surface carbon has changed with time, one or more of the following possibilities has occurred: (1) the major portion of the change took place in the Pre-Cambrian, (2) local effects such as temperature and organic modification of carbon have been important enough to outweigh the age effect, or (3) the record has been destroyed by exchange.

It would be difficult to ascribe any systematic difference between Pre-Cambrian and later limestones to an age effect, since the Pre-Cambrian limestones have generally been dolomitized and/or converted to marble, and such processes could have resulted in a changed isotopic abundance. Conversely, a real age effect could have been obliterated by these processes. With reference to a general destruction of the total record, UREY *et al.* [5] have discussed the probability of alteration of the isotopic composition of calcium carbonate during geologic time by dolomitization and solid state diffusion. Crystal size has an important effect on alteration by diffusion and we should expect the fossil fragments to preserve the record better than finer grained material. Thus the relatively large difference between the two Pleistocene samples from Florida in Table 2, sample No. 1 being a coral limestone and sample number 11 a coquina composed of coarse shell debris, indicates that the organism effect may be of major importance in determining the carbon isotopic composition of

a clastic limestone. This is further shown by Table 3 which gives the isotopic composition of calcium carbonate from several modern marine invertebrates from two locations in Florida. These samples are widely divergent, showing that different animals in the same environment can fractionate carbon quite differently in laying down their shells. In the paper mentioned above, UREY and his co-workers showed that the carbon and oxygen isotopic record in a Jurassic belemnite from the Isle of Skye was almost certainly preserved since seasonal variations in the O^{18} concentration and large irregular variations in the C^{13} concentration were found. The erratic C^{13} variations were attributed to possible fractionation by marine plants. They further showed that brachiopods, oysters, and belemnites from the Upper Cretaceous of England show marked differences in C^{13} concentration, and also differ from the chalk matrix. These results indicate that original differences due to some sort of vital effect of the organism have been preserved, as subsequent exchange of carbon should have obliterated these differences.

Table 3. Isotopic composition of marine invertebrates

No.	Sample	Location	δ ‰ Organic carbon	δ ‰ CaCO ₃
81	Echinoderm, <i>Arbacia</i>	Miami, Fla.	-17.9	-3.5
82	Tunicate	Miami, Fla.	-16.9	—
83	Shrimp	Miami, Fla.	-15.6	—
84	Shrimp	Miami, Fla.	-15.6	—
85	Echinoderm, Starfish	Miami, Fla.	-13.8	-5.9
86	Gastropod, <i>Leucozonia cingulifera</i>	Miami, Fla.	-13.5	-0.3
87	Coral, <i>Porites porites</i>	Long Key, Fla.	-12.3	-1.4
88	Toad Crab, <i>Hyas</i>	Long Key, Fla.	-11.1	—
89	Hermit Crab, <i>Pagurus</i>	Long Key, Fla.	-10.7	—
90	Gastropod, <i>Fasciolaria tulipa</i>	Long Key, Fla.	-10.7	+0.4

It is interesting to note that the heaviest and lightest samples analyzed are both oolitic limestones. Oolites are generally believed to represent deposition in shallow, strongly agitated waters, as they are usually associated with well worn quartz grains and clear carbonate cement rather than mud, and many oolitic limestones are cross bedded. Although the presence of oolites would seem to indicate rather similar formations, examination of thin sections of these formations under the petrographic microscope shows important differences. The Cambrian Warrior limestone (No. 29) is a dark, well sorted, calcarenite composed of oolites and about 5% of quartz fragments in a matrix of anhedral calcite and dolomite. There are no fossil fragments. The Mississippian Spergen (or Salem) is a well sorted microcoquina consisting of fragments of fossil debris, especially Foraminifera, with a typical disarticulated detrital appearance. Quartz is a very minor constituent. The rock is still fairly porous though there is some incipient lithification. Oolites form only a small percentage of the rock and are nowhere near as abundant as in the Warrior formation; moreover they are much smaller in size. In a later section it will be mentioned that dolomitization, if it causes any change at all, seems to enrich carbonate in C^{13} , and since the Warrior formation is lighter than the Spergen this cannot be the cause of the difference. Thus it would seem that the presence of fossil remains

in the one formation constitutes the main difference. Without this factor, one might tend to attribute the difference to a possible change in the C^{13}/C^{12} ratio of surface carbon, since evidence discussed below shows that rate of precipitation of carbonate can affect the isotopic composition, and the oolitic character of these formations would indicate that both represent rapid precipitation. However, the fossiliferous character of the one formation appears to be a quite reasonable explanation of the isotopic difference.

Table 2 shows that the next heaviest formations after the Mississippian Spergen are the English Cretaceous chalk and the Selma and Niobrara Cretaceous chalks of the United States which are deposits analogous to the English chalk. These chalks consist of fine white calcareous mud in which are found *Globigerina* specimens and remains of planktonic algae known as rhabdoliths and coccoliths [14]. These are calcite plates derived from the Coccolithophoridae group of the yellow-green algae [15] which are of great importance in contributing to calcareous bottom sediments*. The origin of the fine friable carbonate mud which makes up the body of the chalk is not certainly known, but the abundance of pelagic micro-organisms and the noteworthy absence of most other fossils may indicate that the planktonic algae play an important part in causing the precipitation of calcium carbonate by changing the pH of the water during photosynthesis.

Table 4 gives results of analyses of carbonate from five modern marine algae. Since algae remove carbon dioxide from the water it is not surprising that the results deviate not only from the range of the marine limestones but from the carbonate

Table 4. Isotopic composition of marine plants

No.	Sample	Location	δ ‰ Organic carbon	δ ‰ CaCO ₃
70	<i>Corallina</i> sp.	Mt. Desert, Me.	-17.0	-4.5
72	<i>Halimeda</i> sp.	Miami, Fla.	-15.3	+4.3
71	<i>Laurencia</i> sp.	Miami, Fla.	-15.3	-
73	<i>Halimeda</i> sp.	Palau Is., S.W. Pacific	-15.0	+3.4
74	<i>Nematium</i> sp.	Miami, Fla.	-14.8	-
75	Kelp, Laminariales	La Jolla, Calif.	-13.4	-
76	<i>Penicillus</i> sp.	Long Key, Fla.	-13.3	+3.7
77	Phytoplankton**	Gulf Stream, Atlantic	-12.9	-
78	<i>Thalassia</i> sp.	Long Key, Fla.	-12.5	-
80	<i>Acetabularia</i> sp.	Miami, Fla.	-9.4	+3.1
79	Angiosperm	Long Key, Fla.	-8.1	-

** Mixture of *Scugilla thiebautii* and *S. erythraeum*, collected by Dr. HILARY MOORE.

of invertebrates from the same location by a wide margin. All but one of these samples are relatively enriched in C^{13} . Sample 70, *Corallina*, is light, but the table shows that organic carbon from this sample is also lighter than the others, and some other effect may be important here. These analyses, though far too few for confident discussion, permit the postulate that the enrichment in C^{13} of the chalk deposits

* Another group sometimes classed in the yellow-green algae is that of the Dinoflagellata, many of which carry on photosynthesis and flourish to an extent exceeded only by the diatoms. This latter group generally leaves no remains as they are armoured only by cellulose plates which are easily destroyed.

over other limestones may be due to the presence of algae carrying on photosynthesis during the carbonate deposition, which deposition may in large part have been due to photosynthesis.

At the opposite end of Table 2 there are certain similarities which might be noted in passing, namely the occurrence of two red bed formations. The Lykins formation (No. 35) is a buff and red limestone of the Colorado red bed sequence. The Lower Cretaceous limestone from Mt. Lebanon, Syria (No. 10) occurs in a sequence that has been interpreted as representing a transition from terrestrial to marine deposition [16]. Red beds make up the beginning of the sequence and at the base of the succeeding Aptian where marine deposition reportedly begins, the strata are coarsely pisolitic. Above these strata are various limestone, sandstone, and shale layers, generally rich in iron, oolitic hematite, and hematite concretions. The exact location of the sample analyzed in this sequence is not known, but it contains large numbers of *Nerinea* and is almost certainly derived from the *Nerinean* rich zone near the centre of the lower Aptian. Though the origin of red beds is still unsolved, the concentration of ferric iron shows deposition under oxidizing conditions characterized by more nearly complete oxidation of carbonaceous matter than generally occurs. In fact, many red beds contain spots of non-red colour attributed to a small particle of organic carbon which escaped oxidation and later reduced and decolorized the iron oxide [14]. Since organic carbon is much lighter in isotopic composition than carbonates (Fig. 3), the relative deficiency of C^{13} in these formations might be attributed to equilibration with carbon dioxide produced from organic carbon during deposition. Such a mechanism requires the presence of a good deal of organic matter and seems to be a doubtful hypothesis. The Pogonip limestone (No. 17), also relatively light, is a nonred bed formation, but the sequence in which it occurs is highly fossiliferous and again the organism effect may be of major importance.

MCCREA [4] has presented calculations for the fractionation of O^{18} and C^{13} between carbonate ion in calcite lattice and in aqueous solution. He calculated that C^{13} should be enriched in solid calcite by $4.20/100$ at $0^\circ C$, and $3.80/100$ at $25^\circ C$ over carbonate ion in solution. MCCREA actually succeeded in precipitating calcium carbonate that showed this deviation, and found that calcium carbonate first precipitates with the same isotopic abundance of C^{13} and O^{18} as the aqueous ions, and that with very slow precipitation the solid comes to isotopic equilibrium as each layer is added. With rapid precipitation there is no difference between the isotopic ratio in solid and in aqueous ion. The oolitic Cambrian Warrior formation undoubtedly represents relatively rapid precipitation and it may be that the relative enrichment of C^{12} in this and the other light formations is due in large part to precipitation so rapid that isotopic equilibrium was not attained. The chalks were deposited under quiet water conditions much more favourable for attainment of equilibrium and this factor may have contributed to the enrichment of C^{13} observed in these formations. Many more analyses of these various types of limestones are needed before any certain conclusions can be drawn as to the factors affecting the isotopic composition of these rocks.

In summary, the variations in C^{13}/C^{12} ratio in limestones may be attributed to the following factors: (1) variations in the calcium carbonate parts of organic debris incorporated in the rock, probably due in part to a vital effect of the organism,

(2) variations in precipitated carbonate due to photosynthesis of marine plants, (3) possible equilibration with organically derived carbon dioxide, and (4) degree of attainment of isotopic equilibrium during precipitation. The relative importance of these factors with regard to specific formations can only be established after a great many analyses have been made on a large number of limestones, limestone constituents, and marine algae and invertebrates. In this respect it should be pointed out that since there is some sixty times as much inorganic carbon in the ocean as in the atmosphere, the effect of temperature variation will be a much greater change in the isotopic composition of atmospheric carbon than in the calcium carbonate of the ocean. If there has been any trend with time in the mean C^{13}/C^{12} ratio of surface carbon, it either reached an equilibrium or near-equilibrium value before the end of the Pre-Cambrian, or was of such slight magnitude that it has been obscured by the variations mentioned above.

Table 5. *Isotopic composition of dolomites*

No.	Sample	Location	δ ‰
36	Dolomitic limestone Silurian, Lockport	Rochester, New York	+ 2.7
37	Dolomitic limestone Ordovician, Knox	Knoxville, Tennessee	- 2.3
52	Randville dolomite without algal structures	Lake Antoine quarry, Dickinson Co., Mich.	+ 1.2
53	Randville dolomite without algal structures	Quinnesec exposure, Dickinson Co., Mich.	+ 1.1
54	Randville dolomite with algal structures	Lake Antoine quarry, Dickinson Co., Mich.	+ 1.1
55	Randville dolomite with algal structures	Quinnesec exposure, Dickinson Co., Mich.	+ 1.2

Table 5 gives the isotopic composition of the few dolomites investigated. The four samples of the Randville dolomite were analyzed in order to determine whether the so-called algal structures occurring so extensively in this formation possessed an isotopic composition different from the parts of the formation where the structures are lacking*. The samples are from two locations about two miles apart, and all four samples give the same analysis within the precision of measurement. This rather striking result might seem to indicate that dolomitization can smooth out isotopic differences over large areas, though the possibility that the samples were originally identical cannot of course be ruled out. The Randville is a calcarenite [14] and much of the detrital debris may have been derived from contemporaneous algal reefs. All the dolomites analyzed fit well with the general range of marine limestones. Other writers have presented evidence that dolomites tend to fall in the heavier portion of the range found in limestones [17], though there are too few analyses extant to be conclusive and the proposed mechanism for such a phenomenon rests on a rather superficial treatment of solution kinetics. To the writer it appears dubious that carbon isotope analyses will be of much value in studying

* These samples were furnished by Dr. N. GREENMAN, who will report his work on this formation at a later date.

dolomitization though a series of analyses of a partially dolomitized limestone made in conjunction with a study of the structural petrology of the rock might prove interesting.

Table 6 presents five analyses of marbles, two of which are dolomitic and do not differ significantly from the others. The Grenville limestone is somewhat heavy but the other samples all fall within the limestone range and metamorphism of these rocks does not seem to have produced any striking isotopic change.

Table 6. *Isotopic composition of marbles*

No.	Sample	Location	δ ‰
41	Ordovician, West Rutland	West Rutland, Vt.	+ 0.9
42	Cambrian, Murphy	Tate, Ga.	+ 1.0
47	Pre-Cambrian, Grenville	Gouverneur, N. Y.	+ 3.1
43	Dolomitic marble Pre-Cambrian, Inwood	Thornwood, N.Y.	+ 0.8
44	Dolomitic marble Cambro-Ordovician, Stockbridge	Lee, Mass.	+ 0.6

Table 7 shows the results of analyses of some non-marine carbonates covering a range of about 24‰. Sample number 27 from Tivoli, Italy, is by far the heaviest sample analyzed in this work. The recorded value is the average of two samples which differed by only 0.02‰. One can only guess as to the reason for this striking enrichment in C¹³. The travertine is deposited by the Tivola River near Rome and

Table 7. *Isotopic composition of fresh water carbonates*

No.	Sample	Location	δ ‰
27	Travertine	Tivoli, Italy	+ 9.8
56	"Hot Water Ice"	Angel Terrace Yellowstone Nat. Park	+ 3.6
57	"Globular Shells"	Angel Terrace Yellowstone Nat. Park	+ 3.4
58	Travertine	Silver Gate Yellowstone Nat. Park	+ 5.9
25	Post-Cretaceous Travertine	Suisun, Calif.	- 6.7
28	Pleistocene Calcareous Tufa	Mumford, N.Y.	- 8.5
59	Stalactite	Blue Mounds Cave, Wis.	- 8.9
26	Travertine	Great Salt Lake, Utah	- 10.1
60	Pre-Cambrian Dunite	Jackson Co., N. Car.	- 14.1

it may be that volcanic phenomena, in conjunction with the previously mentioned reversal of isotopic equilibrium between carbonate ion and carbon dioxide at higher temperatures, have produced such an effect. TWENHOFEL [18] attributes the precipitation of this limestone to the agitation of the carbonate bearing water by falls and rapids which causes a loss of carbon dioxide from the water, and it appears that this precipitation has been so rapid that isotopic equilibration with the atmosphere has not taken place.

Samples 56 and 57 were freshly deposited when collected at Yellowstone Park. They represent two modes of travertine precipitation described by ALLEN and

DAY [19]. Sample number 56 is "hot water ice" which collects as a thin transparent crust on the surface of still pools, gradually breaking up and sinking. Sample 57 consisted of hollow globular shells a few mm in diameter formed on ripple edges around gas bubbles. A thin film of carbonate forms around the outer surface of the bubble and gradually thickens into a hollow sphere. The analyses show no difference in the isotopic composition of the two types. ALLEN [20] cited a great deal of evidence including actual experiments with wooden blocks to show that travertine deposition at Mammoth Hot Springs was not dependent on the activity of the algae present in the springs and was primarily due to escape of carbon dioxide from the hot water, precipitating carbonate dissolved by the action of ascending carbon dioxide and water on limestones. It is possible to ask if the observed isotopic data can be correlated with a simple temperature equilibrium independent of the action of algae. ALLEN and DAY [19] reported a temperature of about 340° K for Angel Terrace. Assuming that this is the present temperature and that the previously mentioned data of McCREA can be extrapolated linearly, aqueous carbonate ion in equilibrium with the Angel Terrace carbonate would be about +0.4‰. A later table shows that ascending carbon dioxide at Yellowstone Park averages -2.8‰. Thus the difference is 3.2‰. A later section of this paper will show that the equilibrium constants between carbonate ion and carbon dioxide listed in Table 1 are in error, and as a rough first approximation should be decreased by a factor of two. With this correction, Table 1 shows that a 3.2‰ difference corresponds to a temperature of 370° K, to be compared with the assumed measured value of 340° K. These calculations are admittedly extremely rough, but it appears reasonable that the observed isotopic composition of the travertine can be explained by simple exchange equilibrium.

The remaining samples form a group of extremely light carbonates whose deficiency in C¹³ may, in lieu of a better explanation, be tentatively ascribed to possible equilibration with organically derived carbon dioxide. The carbonate bearing waters may flow through rock containing organic debris either as an original constituent or deposited therein by ground water. In this connection it should be noted that the Great Salt Lake travertine has been interpreted as being deposited by streams which flow into the lake and deposit carbonate about their mouths because of the high salinity of the lake [18].

Marine organic carbon

Organic carbon from marine plants and invertebrates was analyzed in order to determine the isotopic composition of living marine organisms. Carbonate was removed from these samples by soaking in dilute HCl. Since some bleaching of plants results from this process there was a possibility that the treatment might affect the isotopic composition. However, tests made on non-calcareous plants such as fresh water algae showed no significant change in analyses resulting from this procedure. The Florida plants and invertebrates were autoclaved when collected. The other samples represent dried specimens.

Table 4 lists the results for organic carbon in marine plants, all but numbers 78 and 79 being algae. Though not a large selection, the samples include specimens from quite distant areas which are concordant with the Florida samples. Carbonate was analyzed from five of these samples as noted in the table. The three Florida

samples for which analyses of both carbonate and organic carbon were made show an interesting relationship in that the C^{13} content increases in the carbonate as it decreases in the organic carbon, and it would seem that a further investigation of this point might be worthwhile.

Table 3 shows the analyses of organic carbon and carbonate in ten invertebrates from the two Florida areas. Here a trend shows up quite remarkably, in that the specimens from one area are all lighter than those from the second area. Table 4 shows the same trend for the Florida plants with the exception of No. 80. This geographical correlation may perhaps be due to the production of light carbon dioxide by combustion of coal and oil in Miami, or to different amounts of decaying organic matter in the waters. The marine invertebrates show about the same range as the algae which is to be expected since the algae are the ultimate food source of all marine animals. The perfect agreement between the two shrimps (of the same species, unfortunately not determined) is surprising and may indicate that they prefer a specific type of food. There is no indication of a relationship between organic carbon and carbonate in the invertebrates.

The terrestrial plants

The first step in the study of terrestrial plant carbon was to make a survey of the trees in order to see if any variation due to altitude or geography could be observed. For this purpose tree wood from all over the world including samples of the same species from different locations and of different species in the same location was analyzed. Table 8 presents the results for twenty-two modern trees.

The results on wood samples show no apparent major geographical correlation. Samples from Wyoming alone cover almost the entire range of the data. The average value for the American samples is -25.3‰ , with a range from -22.5 to -27.9‰ ; the average value for non-American woods is -25.4‰ ranging from -23.3 to -27.6‰ . The Wyoming trees do show a slight local correlation, with the samples from N.W. Wyoming (Yellowstone Park) all falling in a group lighter than the group of S. Wyoming samples though the range of each group is rather large.

There seems to be no important species effect. Firwood, *Abies lasiocarpa*, from two Wyoming areas differs by 4‰ , and sagebrush from the two locations differs by almost 3‰ . Ash samples from Switzerland and Sweden differ by more than 1‰ . It appears that local environmental effects obscure any tendency of trees of the same species to remain constant. However, other work by the author shows that wood varies throughout one individual tree, and thus we should not expect to find individuals of the same species remaining constant.

Table 8. Isotopic composition of present day wood, tree leaves, and land plants

No.	Sample	Location	$\delta \text{‰}$ Wood	$\delta \text{‰}$ Leaves and plants
91	Fir, <i>Abies lasiocarpa</i>	N.W. Wyoming	-27.9	-29.1
92	<i>Mimusops ditandriifolium</i>	Liberia	-27.6	---
93	Iron wood, <i>Rhamnidium ferreum</i>	Marshall Islands	-27.3	---
94	<i>Pinus contorta</i>	N.W. Wyoming	-27.1	-27.0

The geochemistry of the stable carbon isotopes

Table 8. (Continued)

No.	Sample	Location	δ ‰ Wood	δ ‰ Leaves and plants
95	Maple, <i>Acer saccharinum</i>	Illinois	-27.0	-27.7
96	Sagebrush, <i>Artemesia tridentata</i>	N.W. Wyoming	-26.6	—
97	<i>Sterculia excelsa</i>	Bolivia	-26.1	—
98	<i>Nothofagus messzeisii</i>	New Zealand	-26.1	—
99	Balsa, <i>Ochroma</i>	Peru	-25.9	—
100	Pencil cedar, <i>Cryptocarya</i>	N.S.W. Australia	-25.8	—
101	<i>Dacrydium cupressinum</i>	New Zealand	-25.7	—
102	<i>Chlorophora excelsa</i>	Liberia	-25.6	—
103	Willow, <i>Salix bebbiana</i>	S. Wyoming	-25.0	-26.4
104	Black locust, <i>Robinia pseudoacacia</i>	S.W. Kansas	-25.0	-25.4
105	Ash, <i>Fraxinus excelsior</i>	Sweden	-24.9	—
106	Osage orange, <i>Machua</i>	Illinois	-24.7	-26.6
107	Fir, <i>Abies lasiocarpa</i>	S. Wyoming	-23.8	-25.2
108	Sagebrush, <i>Artemesia tridentata</i>	S. Wyoming	-23.7	—
109	Ash, <i>Fraxinus excelsior</i>	Switzerland	-23.5	—
110	<i>Pistacia terebinthos</i>	Palestine	-23.3	—
111	Cedar, <i>Chamaecyparis obtusa</i>	Japan	-23.3	—
112	Pine	New Mexico	-22.5	—
116	Blue grass	Illinois	—	-27.0
119	<i>Vaccinium</i>	S. Wyoming	—	-26.2
120	Clover	S. Wyoming	—	-25.6
121	Purple asters	S. Wyoming	—	-25.4
124	Grass	N.W. Wyoming	—	-23.6
125	Grass	S.W. Kansas	—	-12.2
Average			-25.4	-26.3*

* Excluding No. 125.

Samples of wood from high altitudes are as follows:

Fir (91)	7400'
Pine (94)	7200'
Sagebrush (96)	7200'
<i>Sterculia</i> sp. (97)	9000'
Willow (103)	7000'
Fir (107)	9900'
Sagebrush (108)	7300'
Pine (112)	12000'

There is absolutely no correlation with altitude. The wood samples represent specimens collected during the period from 1892 to 1950, and there is no correlation between the date of collection and the isotopic composition. Thus if there has been any regular change in the isotopic composition of atmospheric carbon dioxide the effect has been masked by other factors acting randomly. All the Wyoming samples were collected in 1950, and they cover almost the total range of isotopic composition.

Table 8 also lists analyses made of leaves of seven of the trees and of six green terrestrial plants. Although leaf carbon does not differ markedly from wood carbon, the leaves of an individual tree are all lighter than the wood of the tree by amounts

ranging from about 0.5 to 2‰ except in the case of the pine. In the pine they are equal. In all these measurements wood and leaves were taken from a single branch of the tree. It is interesting to note that both sets of fir samples representing two different locations show an almost identical difference between wood and needles, the difference being 1.2‰ for sample 91 and 1.4‰ for sample 107*. These samples show about the same location correlation as the corresponding trees in the case of the Wyoming samples, with the S. Wyoming samples generally a trifle heavier. The Illinois samples match better. Indications are that slight effects due to local differences in the isotopic composition of atmospheric carbon dioxide are present.

A further check on the altitude effect was possible because of two groups of samples having been collected from the same location with the exception that one group was collected on the continental divide in the mountains while the other was collected in the valley below. The location was the Sierra Madre Mountains in southern Wyoming with the Platte Valley below. Samples 103, 108, and 120 were collected in the valley bottom at 7000 ft while samples 107, 119, and 121 were collected on the continental divide at 9900 ft altitude. These two sets cover exactly the same range and the asters and the clover analyze the same.

Sample number 125 poses another problem. This is a sample of grass from southwestern Kansas and the analysis is far heavier than all the others. The area is in the Red Hills district, an arid region mantled by the Permian red beds which are salt and gypsum bearing. The soil is pedocalcic, concentrating calcium carbonate in the upper horizons, and in fact the water in this area is about the hardest water in the country. Water bearing calcium carbonate is drawn to the surface by capillary action where it evaporates depositing the carbonate in the soil. Wood and leaves from this area fell in the normal range, but it is clear that grass would be far more likely to pick up carbonate which would then increase the C¹³ content in the sample. However, this sample was treated with HCl to remove all carbonate and rerun, whereupon it gave an identical result. This shows that the sample has either utilized bicarbonate or carbonate ion directly in its photosynthesis, or that it has used carbon dioxide derived from the bicarbonate ion. The latter alternative is probably the case since evaporation of water at the surface would liberate CO₂ derived from carbonate which could easily be absorbed by grass. Mixing with air would cause the trees to show no effect. The other grass samples were also treated with HCl to make sure no carbonate was present. These all fall in the range of the other samples.

To shed more light on the carbon source of plants in contact with a calcium carbonate containing medium, it was decided to analyze some fresh water plants. Many of these plants deposit calcium carbonate around themselves because of the pH change when carbon dioxide is removed from the water during photosynthesis. Three fresh water plants showing varying amounts of calcium carbonate present were selected from the University Botany Department tanks and analyzed. One

* These samples also show almost identical differences in the percentage of carbon in the air dry sample as determined by combustion, the difference in carbon percentage between wood and needles being 3.7% for the former set and 3.5% for the latter, the needles being higher in each case. Further, the pine wood and needles (94) showing identical isotope ratios also show identical percentages of carbon. No other correlation with carbon percentage has been discovered though it has been looked for in all groups of samples analyzed.

sample was carbonate free, another had only a small amount, and the third had a great deal of carbonate. The analyses were as follows:

126. <i>Rhizoclonium</i> sp.	—22.7 ⁰ / ₀₀
127. <i>Anacharis</i> sp. (<i>Elodea</i>)	—20.1 ⁰ / ₀₀
128. <i>Cladophora</i> sp.	—13.5 ⁰ / ₀₀

All these samples were treated with HCl so that the analyses represent the organic carbon present. *Rhizoclonium*, a green algae, showed no reaction with HCl, and a check analysis made without HCl treatment gave the same analysis so that the amount of carbonate that could have been present was very small. *Anacharis*, an angiosperm, possessed a small amount of carbonate. *Cladophora*, a green algae, possessed a great deal of carbonate and reacted vigorously with HCl. It is seen that *Rhizoclonium* falls in the range of the land plants, while the other two are heavier by progressive amounts.

Atmospheric carbon dioxide

NIER and GULBRANSEN [21] reported atmospheric carbon dioxide as being from 12 to 20⁰/₀₀ lighter than their carbonate samples, and MURPHEY and NIER [22] reported a value for air which would be about —23⁰/₀₀ on the scale used here. These values have been discussed by several authors [22], [10], [1], who felt that the values were too high and probably represented contamination with carbon dioxide derived from the combustion of coal in cities. It is not possible to calculate the equilibrium isotopic difference between carbonate ion and air directly, since the partition function ratio of carbonate ion cannot be calculated with any certainty. The reason for this is that the equations for the vibrational frequencies require five constants for the determination of four frequencies if a quadratic expression for the potential energy is used, and the valence force and central force approximations give complex force constants [10]. UREY and GREIFF [23] made a calculation for the exchange of carbon using estimated frequencies and obtained results close to those listed in Table 1. The values actually listed in Table 1 for exchange between carbon dioxide and carbonate ion were calculated by UREY [10] using the average of the values reported in the literature for the difference in C¹³ content between limestones and the atmosphere. Thus if the reported values for carbon were incorrect, the calculated equilibrium constants are also incorrect.

The method of obtaining the carbon dioxide for the analyses in the literature was that of pumping air through barium hydroxide solutions to precipitate barium carbonate. Unless all the carbon dioxide is retained by the solution in this method, there is a possibility of fractionating the isotopes because of the difference in mean molecular velocity between the two isotopic molecules. This fractionation was tested for by running air slowly through a glass trap cooled in liquid nitrogen and at the same time pumping air through barium hydroxide solution with a bicycle pump. The mass spectroscopic analyses were respectively —9.1⁰/₀₀ and —23.1⁰/₀₀, or a difference of 14⁰/₀₀. The bicycle pump was calibrated for volume and it was found that only a 10% yield of carbon dioxide was obtained. Running air very slowly through a Ba(OH)₂ trap on a vacuum line gave an analysis of —15.3⁰/₀₀. Jars of Ba(OH)₂ set out in the open collected CO₂ which analyzed —25.4⁰/₀₀, and another bicycle pump collection gave —24.5⁰/₀₀.

At this point the line shown in Fig. 2 was set up to be sure of getting all the carbon dioxide out of air. However, the analyses fell in the same range as those of samples obtained with glass traps cooled in liquid nitrogen. Five analyses have been made of Chicago air with the following results:

Wednesday/12 April 1950	-8.1 ⁰ / ₀₀
Wednesday/19 April 1950	-9.1 ⁰ / ₀₀
Sunday/21 May 1951	-7.4 ⁰ / ₀₀
Thursday/24 May 1951	-9.9 ⁰ / ₀₀
Sunday/17 June 1951	-8.2 ⁰ / ₀₀

Yields were measured on the last three runs as they were made on the line shown in Fig. 2. They gave respectively 0.034%, 0.037%, and 0.034% CO₂ in air. The Sunday values represent a minimum of contamination by industrial combustion and show a smaller yield and more C¹³ as would be expected since the organic fuels are around -25⁰/₀₀. The observed variations are probably due to the factors of wind direction and amount of industrially derived CO₂ in the air. Since it is not known how much of a correction should be made for the addition to the atmosphere of these combustion products, it would seem reasonable to take -7⁰/₀₀ as a tentative value for atmospheric carbon dioxide until data for air over the oceans can be obtained. If this value then represents roughly (say $\pm 2^0/_{00}$) the equilibrium constant between carbonate and carbon dioxide, the values in Table 1 are too high and as a first approximation we might decrease them by a factor of two. It is not worthwhile to recalculate the constants by UREY'S method until better data can be obtained for ocean air and carbonate.

Distribution of the carbon isotopes within the system

Since the terrestrial plants are found to be lighter than atmospheric carbon dioxide by some 18⁰/₀₀, we see that they carry on a separation of isotopes by some mechanism. We may ask if the observed separation can be explained by a physical or kinetic process, or if it is necessary to postulate some near-equilibrium biochemical mechanism operating during photosynthesis.

The passage of carbon dioxide from the atmosphere into a leaf has been discussed in detail by RABINOWITCH [24], [25]. Diffusion rates through the stomata are extremely rapid due to the fact that diffusion through small pores becomes proportional to the diameter rather than the area of the pore. Since leaves absorb carbon dioxide in excess of normal solubility of the gas there must be a conversion of carbon dioxide to bicarbonate, which is accomplished by solid carbonates and a water soluble buffer, believed to be phosphate, which combine with water and carbon dioxide to form bicarbonate ions.

The fractionation of the carbon isotopes when carbon dioxide is absorbed by barium hydroxide is not the equilibrium thermodynamic distribution between the gas and aqueous phase, but is due to the greater velocity of diffusion of the lighter molecules through air together with the absence of a C¹³ enriched gas phase above the liquid because of mass transport and mixing by air currents. It is assumed that the ocean carbonate and atmospheric carbon dioxide are in isotopic equilibrium, and in fact such a fractionation should not occur in this system because there is no greater reservoir supplying the atmosphere. Carbon dioxide passes into a leaf by diffusion through the stomata into the substomatal cavities along a concentration

gradient. The diameters of the stomata are of the order of 10^{-3} cm, while the mean free path of carbon dioxide is approximately 5×10^{-6} cm, and thus separation due to diffusion through a porous barrier cannot take place. Nevertheless, diffusion through the air in the pores may cause some separation.

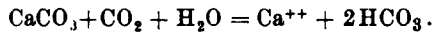
Since carbon dioxide collected by absorption in barium hydroxide falls just into the range of composition of terrestrial plants, the question arises as to whether the mechanisms of fractionation are essentially the same. The ratio of the number of molecules of two isotopic masses which will strike a unit area of a free surface is inversely proportional to the square roots of the molecular weights, and thus for pure carbon dioxide above a barium hydroxide solution the lighter isotope should be concentrated in the solution by a factor of $11^{0/00}$ if no enriched gas phase is allowed to form. However, for diffusion through air the separation is dependent upon the ratio of the diffusion coefficients, which is given by the expression [31]

$$\frac{D_1}{D_2} = \frac{C_2 + C'}{C_1 + C'} \sqrt{\frac{M_1 + M'}{M_1 M'} \frac{M_2 M'}{M_2 + M'}}$$

where the subscripts 1 and 2 refer to the concentrations and molecular weights of the isotopic molecules, and the primed terms refer to air. This gives $D_{44}/D_{45} = 1.0041$ or $4.1^{0/00}$ enrichment of the lighter isotope, whereas the measured value was $14^{0/00}$ for carbon dioxide pumped through barium hydroxide solution. It appears that other factors such as the effects of surface films or differences in activation energies for passage through the surface layers may be important, and since we cannot adequately explain the fractionation performed by a barium hydroxide solution, we are not in a position to compare this fractionation directly with that performed by terrestrial plants. Time was not available for further study of this problem and it seems likely that no simple hypothesis will explain all the facts. The extent to which fractionation during photosynthesis and growth may occur is not known at all. Information discussed in a later section of this paper indicates that different plant compounds show a different isotopic composition, but we do not know what the effect of this will be on the total isotopic composition of a plant.

Fig. 3 shows that the marine plants also concentrate C^{12} with respect to atmospheric carbon dioxide, though to a smaller extent. This concentration of the lighter isotope indicates that the same fractionation mechanism is probably operative, since any effect caused by the presence of carbonate should result in an enrichment of C^{13} . This effect may be produced by (1) actual use of bicarbonate ion in photosynthesis, or (2) use of heavy carbon dioxide produced by the buffering action of the bicarbonate ions. RABINOWITCH [24], [25] has given a detailed discussion of the evidence for utilization of bicarbonate ion in photosynthesis. The great majority of evidence favours the view that if the ions are used at all it is only in small proportion to the amount of carbon dioxide used. Although recent work has again brought this question up [26], [27], RABINOWITCH concludes, "Pending further analysis concerning the role of carbonate ions . . . we will proceed on the old assumption that the rate of photosynthesis is primarily a function of the concentration of the molecular species CO_2 in the immediate surroundings of the cells, and that the main effect of the presence of HCO_3^- ions is to prevent this concentration from depletion during photo-synthesis".

The mechanism of the buffering action of bicarbonate ions is illustrated by the equation:



Upon exhaustion of carbon dioxide by photosynthesis, the equilibrium shifts to the left and half the carbon in the bicarbonate ions which reassociate will replenish the CO_2 supply while the other half will be precipitated as CaCO_3 . This is the mechanism by which an aquatic plant deposits calcium carbonate as it carries on photosynthesis. The slow diffusion rate of carbon dioxide in aqueous solution and subsequent exhaustion of carbon dioxide in the solution has long been recognized by plant experimentalists who make certain that the solution is well buffered by increasing the concentration of bicarbonate ion. This buffering action appears to be a logical cause for the enrichment in C^{13} of marine plants as compared to terrestrial plants. Upon removal of carbon dioxide from the surrounding water, the bicarbonate ions will release CO_2 which is heavy with respect to atmospheric carbon dioxide. The mean isotopic composition of this sub-system is that of the bicarbonate ions, and with approach to isotopic equilibrium the carbon dioxide will tend to be light and the precipitated calcium carbonate heavy with respect to this mean. Since the bicarbonate carbon is split equally between CaCO_3 and CO_2 , the precipitated carbonate will be appreciably enriched in C^{13} over average carbonate which is equilibrated against the relatively much smaller amount of carbon dioxide in the atmosphere. Thus the plants absorb carbon dioxide enriched in C^{13} with respect to the atmosphere and precipitate carbonate enriched in C^{13} with respect to average carbonate, as indicated by the data in Table 4. The isotopic composition of organic carbon in marine plants will then be the result of a mixture of carbon from dissolved carbon dioxide and from bicarbonate ions and will fall in a range between the carbonates and the terrestrial plants. This mechanism explains the enrichment in C^{13} of the grass from S.W. Kansas (Table 8) and also the fact that the analyses of the fresh water plants showed that the more calcium carbonate a plant deposited around itself, the more enriched in C^{13} was the organic carbon of the plant. Variations in isotopic composition may be expected to occur depending upon how nearly isotopic equilibrium is approached between carbonate, bicarbonate ion, and carbon dioxide. This problem involves rate factors both of isotopic and chemical equilibration, and may have an important effect on the isotopic composition of carbon in the various compounds. These rate factors have been investigated by UREY and several co-workers [28], [29], [30], who have shown that the isotopic exchange of carbon proceeds by different reactions according to the pH of the solution. However, it is not known how these results apply to sea water where conditions are much different because of the many substances in solution. These exchange reactions are slow, but can be catalyzed by various substances such as the enzyme carbonic anhydrase which occurs in red blood cells. This enzyme has been reported to be present in marine algae, but it does not appear that the evidence is certain [25], [26].

V. FOSSIL WOOD AND COAL

Having surveyed present day organic carbon, we now turn to the fossil terrestrial carbon. The first group of specimens represents ancient trees ranging from about 2000 years ago back to the last glacial period and before. Table 9 lists the specimens,

The geochemistry of the stable carbon isotopes

Table 9. Isotopic composition of fossil wood

No.	Sample and Location	Age in years	δ ‰
129	Spruce, Alaska (505)	2300	-24.3
130	Wood, Illinois (364)	3500	-27.3
131	Cypress, Egypt (12)	4800	-22.4
132	Wood, Minnesota (497)	11300	-24.4
133	Spruce, Wisconsin (308)	11400	-25.6
134	Spruce, Wisconsin (536)	11400	-24.9
135	Wood, Missouri (385)	12100	-25.1
136	Wood, Alaska (301)	12600	-22.5
137	Cypress, S. Carolina (363)	> 17000	-24.5
138	Wood, Illinois (466)	> 17000	-25.2
139	White spruce, Minnesota (496)	> 19000	-24.3
140	Wood, Ohio (508)	> 17000	-22.5
141	Wood, Alaska (299)	> 20000	-23.5
142	Wood, Illinois (510)	> 20000	-24.9
143	Wood, Illinois (533)	> 25000	-24.1
144	Wood, Illinois	—	-25.3
Average			-24.4

their ages, and the isotopic composition. All but one of the samples were furnished by Dr. W. F. LIBBY, and the ages listed are those determined by him by radioactive C^{14} dating. The numbers in parentheses following the samples are LIBBY's sample numbers, and descriptions of the individual samples can be found listed by these numbers in the publications by ARNOLD and LIBBY [32] and LIBBY [33]. Sample 144 is a sample of wood from the Farmdale glacial stage, furnished by L. HORBERG. Its age, by analogy, is comparable to that of No. 142 and 143. Several samples of this group showed carbonate contamination and were treated with dilute HCl prior to combustion.

The average of the sixteen samples is just 1‰ heavier than the average of modern wood samples. With the exception of No. 130, wood from a Lake Chicago deposit, the range extends from -22.4 ‰ to -25.6 ‰ which is just about the lower half of the range of modern wood samples. It appears that there is no correlation of isotopic composition with age of the sample.

It should be noted that the restricted range of the samples, if significant, cannot be accounted for by a difference in temperature, since the isotopic composition of atmospheric carbon dioxide should become lighter with a cooler mean temperature (Table 1). Most of these samples are undoubtedly representative of colder climatic conditions than prevail today. In particular, No. 139 is from the Peorian interglacial period which has been well documented geologically as having had a cool, moist, subarctic climate. The two Wisconsin samples are from the Two Creeks forest bed and grew during the interval between the Cary and Mankato substages of the Wisconsin glaciation when conditions were probably closely akin to those now prevailing in northern Minnesota. Yet sample No. 131 from Egypt, the heaviest specimen found, probably grew during the so-called Climatic Optimum when the climate reached a maximum of warmth and dryness.

Table 10 gives the analyses of fifteen coal samples ranging in age from Pennsylvanian to Pleistocene, and the average value weighted by including the average

Table 10. *Isotopic composition of coal*

No.	Sample	Age	Location	δ ‰
191	Peat	Pleistocene	Ontario	-27.2
192	Lignite	Tertiary	Germany	-26.3
193	Cannel Coal	Pennsylvanian	Kentucky	-26.1
194	Lignite	Tertiary	Iceland	-25.9
195	Anthracite	Cretaceous	Colorado	-25.6
196	Anthracite	Pennsylvanian	Pennsylvania	-24.2
197	Bituminous	Pennsylvanian	Pennsylvania	-24.1
198	Lignite	Paleocene	N. Dakota	-23.6
199	Lignite	Paleocene	N. Dakota	-23.4
200	Lignite	Paleocene	N. Dakota	-23.4
201	Bituminous	Pennsylvanian	Virginia	-23.5
202	Wealden Coal	L. Cretaceous	Sweden	-23.3
304	Boghead Coal	Pennsylvanian	Illinois	-22.9
203	Graphitic Anthracite	Pennsylvanian	Rhode Island	-22.4
204	Lignite	Tertiary	Saxony	-21.6
Weighted average				-24.2

of the three N. Dakota samples as one sample. These three samples are from the Tongue River member of the Fort Union formation and are from three different counties. Samples 198 and 200 were taken from mines about 125 miles apart. Within the precision of measurement there is no difference in isotopic composition, a rather surprising example of uniformity. Evidently the source material of the coal and the environmental conditions of deposition were extremely uniform over large areas.

Sample No. 304 represents a type of boghead coal occurring in the Tradewater group of the Pennsylvanian of Fulton County, Illinois. It is not a true boghead coal as it contains a large proportion of anthraxylon. The coal has recently been described by KOSANKE [34] who discovered the bed and kindly furnished a sample for analysis. It contains the algal remains, typical of boghead coal, derived from algal colonies growing on the top of the peat bog under fresh water conditions. The isotopic composition of the sample falls within the ranges of coal and modern terrestrial plants.

These samples were tested as usual for carbonate contamination which was removed by HCl. It is apparent from the results that alteration to coal has little effect on the isotopic composition of wood. The samples range up to the Pleistocene where the fossil wood samples begin, and thus it appears quite reasonable to assume they were derived from wood of essentially the same range of isotopic composition as present day wood. The average of the samples is just 1‰ heavier than the average of modern wood specimens and is the same as the average of the fossil wood samples, while the ranges of the three groups are practically the same. There is no correlation with age, another indication that the isotopic composition of surface carbon has not changed appreciably since the Paleozoic. There seems to be no correlation between isotopic composition and degree of coalification, since bituminous coal and anthracite from Pennsylvania show no difference. In this respect it would be interesting to analyze specimens grading into the graphitic anthracite from lower ranking coals. It appears, however, that variations in coal samples are mainly due to variations in source material.

VI. SEDIMENTARY ORGANIC CARBON

Fig. 3 shows that the carbon found in sedimentary rocks is in general extremely light, and that petroleum, generally believed to be derived from marine organisms, is also very light. It is evident that these rocks contain carbon greatly enriched in C^{12} over present living marine organisms, and though in some cases this may be the result of contamination with terrestrially derived carbon, many of the samples are even lighter than the land plants. The lack of a trend of isotopic composition with age in limestones, fossil wood, and coal, is strong indication that the isotope ratio of surface terrestrial carbon has not changed much since the beginning of the Paleozoic. Thus we have good reason to believe that the marine plants and animals of the ancient seas had an isotopic composition similar to those of the present, and it therefore appears that there is some difference in the processes leading to the formation of coal and oil such that coal retains the isotopic composition of its source material virtually unaltered while petroleum ends up with a greatly changed isotope ratio. Further, it appears that the carbon in black shales may undergo alteration in a manner similar to petroleum. Table 11 presents the results of the analyses of the various sediments and of three petroleum samples. All carbonate bearing specimens were treated with HCl before combustion.

Table 11. Isotopic composition of sedimentary carbon

No.	Sample	Age	Location	$\delta^{0/100}$
205	<i>Cyrtograptus</i> shale	Silurian	Missouri	-30.8
206	Upper shale	Huronian	Canada	-30.7
207	Green River shale	Eocene	Colorado	-30.0
208	Middle shale	Huronian	Canada	-29.2
209	Oil shale	Unknown	Tasmania	-29.2
210	Bituminous shale	Devonian	New York	-29.2
211	Alunskifer	L. Cambrian	Norway	-28.9
212	Alunskifer	L. Cambrian	Norway	-28.3
213	Michigamme slate	Huronian	Michigan	-28.5
214	Black shale	Pennsylvanian	Illinois	-27.0
215	Black shale	Pennsylvanian	Illinois	-26.1
216	Carbonaceous shale	Pennsylvanian	Pennsylvania	-18.0
217-28	Organic mud	Recent	Florida	-14.0*
229	Metamorphic chalk	Cretaceous	Palestine	9.0
230	Crude oil		Pennsylvania	29.4
231	Residual tar		Illinois	29.2
232	Crude oil		California	23.0

* Average value.

In an attempt to trace this alteration a series of samples of recent organic mud deposited around Lignum Vitae Island in the Florida Keys was analyzed. These samples were collected by Dr. C. EMILIANI who will published a discussion of the samples at a future date. Twelve samples were taken around the island in water ranging from several inches to several feet in depth and over both rocky and muddy bottom areas. It was thought if alteration of isotopic composition was occurring, such a change might be correlated with a change in the percentage of carbon in the organic fraction of the mud as the material decayed. Accordingly the isotopic composition of

organic carbon was plotted against the percentage of carbon in the fraction remaining after removal of carbonate by HCl treatment. Since a non-combustible residue was always present which consisted for the most part of quartz but may also have contained some metallic compounds derived from the organisms, the analyses were plotted against the carbon percentage of the acid treatment residue calculated both including and excluding this non-combustible residue. The results gave in both cases a complete scatter diagram and no correlation was possible. Eight of the samples fell in the narrow range from -10.8‰ to -12.7‰ which fits nicely with the range determined for plants and animals from Long Key, Florida. Four samples gave analyses of -14.3‰ , -16.6‰ , -21.9‰ , and -22.6‰ . These samples were entirely uncorrelated with differences in carbon percentage, and it seems quite probable that these variations are due to contamination by debris from terrestrial plants which grow on the island. The percentage of carbon in the organic fraction including the non-combustible residue ranged from 25.5 to 49.6 with an average of 36.1; excluding the non-combustible residue the range was 46.0 to 53.1 with an average of 49.2%.

These samples do not tell us the effect on the carbon of extreme reducing conditions such as are believed to be present during the formation of black shales. They represent perhaps the average incorporation of organic material into a limestone or shale accumulating in shallow water. In this connection we have two other similar samples. No. 229 is a sample from the Upper Cretaceous Maestrichian chalk of the Eastern Nazareth Mountains, Palestine, furnished by H. LOWENSTAM and described by him (personal communication) as having been contact metamorphosed by a small basalt plug. The sample is black with carbon fixed in the rock from the organic material present. This sample falls in the lower range for marine carbon indicating that its isotopic composition has not been altered much. Sample 216, from Green Co., Pennsylvania, is also fairly heavy, though it falls at the upper limit of the marine organic carbon range. This shale is probably non-marine and is seen in the hand specimen to contain fragments of terrestrial plants. The analysis of the sample probably reflects a mixture of carbon derived from terrestrial plants and fresh-water carbonate precipitating algae.

The remaining samples are all very light and represent a group of black shales and schists, oil shales, and bituminous and graptolitic shales. The two Pennsylvanian black shales (No. 214 and 215) are samples of the black shale overlying coal No. 5, from Springfield, Illinois, and Logan County, Illinois, respectively, and are both of marine origin as shown by the fossils they contain*. They are both heavier than the rest of the group, perhaps because they contain some coaly material. Sample No. 205 is from the Moccasin Springs formation at Cape Girardeau, Missouri. Samples 206 and 208, of Huronian age, are respectively the Upper shale lying above, and the Middle shale lying below, the Iron Formation of the Knob Lake area, Quebec-Labrador, Canada. Samples 211 and 212 are from the carbonaceous schist formation at Oslo, Norway. Number 211 contained no carbonate, while No. 212 had a considerable amount of carbonate. No. 213 is a sample of the Michigamme slate from the Crystal Falls area in upper Michigan. There is a striking similarity between the isotopic composition of black shales, oil shales, and petroleum itself, which may represent the result of similar depositional conditions.

* J. M. WELLER, personal communication.

It should be noted that it is inherently possible for the physical processes of migration and fractional distillation to be a contributing factor to the difference in isotopic composition of petroleum from its source material if different fractions of petroleum tend to concentrate the isotopes differentially. Accordingly three quite different samples of petroleum were analyzed. No. 230 is a crude oil occurring in the Devonian rocks of Titusville, Pennsylvania, and is an extremely light oil typical of the Pennsylvania oils. No. 231 is a sample of a heavy black tarry residue of the petroleum which once filled a coral reef at Thornton Quarry in Chicago (H. LOWENSTAM, personal communication; sample furnished by him). This tar was left behind as the oil escaped and we should expect that if petroleum is light because of the above mentioned physical effects, this sample should be heavy. However, it is identical in isotopic composition with the Pennsylvania oil.

WEST [35] determined the C^{12}/C^{13} ratio in both the propane and n-butane fractions of thirty-four samples of petroleum from two Kansas oil fields. These fractions were separated by fractional distillation, and the averages of the two groups were identical. Thus, the available evidence indicates that such effects do not play a part in the enrichment of C^{12} in petroleum and that some aspect of the environment of formation is important. Sample No. 232 is a heavy black oil from the Upper Pliocene Tulare horizon of the South Belridge Field in the San Joaquin Valley, California, one of the youngest producing horizons known. The analysis is distinctly heavier than the other two, indicating perhaps that there is a time effect in the process enriching the lighter isotope in the oils.

Indications are, then, that environmental conditions during and after the accumulation of organic material are responsible for the different courses taken by the coals on one hand and the black shales and oil shales on the other hand. This is possible if specific organic compounds concentrate the isotopes differentially and then are differentially attacked during decomposition. The actual processes by which coal and oil have been formed are the subject of a vast literature in which there is much disagreement and there is no intention of going into the subject here. Complete discussion can be found in the texts by PETTIJOHN [14], TWENHOFEL [18], and RAN-KAMA and SAHAMA [36]. However, the following facts are generally agreed on: (1) that coal, oil, and the black shales are all accumulated under reducing conditions which in the case of coal inhibit the action of microorganisms because of the presence of organic acids, (2) that waxes, resins, fats, and oils are much less easily decomposed than other organic compounds, (3) coals have undergone much less total decomposition than petroleum, (4) aquatic plankton, algae, crustacea, etc., contain more fats, oils, and waxes than terrestrial plants and therefore the resulting decomposition products become enriched in fatty substances [36]. It is clear that if fats, oils, and waxes can be shown to enrich C^{12} over the more easily decomposed substances we have a mechanism for explaining the observed isotopic distribution. Such evidence actually exists, as shown by the work of R. O. BELKENGREN (cited by MURPHEY [37]) who found that fats reject C^{13} more than any other substance encountered and that plant fats were about 1% lower in C^{13} content than cellulose. Moreover, waxy material tends to concentrate in the leaves of terrestrial plants, which we have seen are generally somewhat enriched in C^{12} with respect to their associated wood. It may be, then, that the enrichment of petroleum in C^{12} is due to the concentration of compounds containing carbon derived to a great extent from the fats and oils

present in the source material, such a concentration not taking place in the formation of coal.

According to this hypothesis we should expect that methane derived from decomposition of marine organisms under reducing conditions should be just a little enriched in C^{13} with respect to the isotopic composition of the organisms. Two samples of carbon derived from atmospheric methane collected during commercial liquefaction of air were furnished by Dr. W. F. LIBBY for analysis. Since 80 to 90% of living matter is in the ocean [25] the bulk of this methane is probably derived from marine organic matter. The analyses of the two samples are as follows:

233. U.S. Methane *	-10.7‰
234. British Methane **	-41.3‰

The large difference between the samples is surprising and check combustions and analyses were made on each with identical results. However, Dr. LIBBY informed the writer that the British sample was believed by the company which furnished the sample to have been contaminated with petroleum products during the process of extraction. LIBBY found that while the U.S. sample showed a C^{14} activity entirely characteristic of living biological material, the British sample did indeed show an apparent contamination with a "dead" substance such as petroleum. Since the C^{13}/C^{12} ratio of this sample is so light it appears quite probable that this is the case. The U.S. sample lies in the range of marine organic carbon, and is slightly heavier than the mean. Though this analysis is quite reasonable, it should be noted that some fractionation may have been introduced during the various steps of obtaining carbon from the methane.

VII. IGNEOUS ROCKS, GRAPHITE, AND DIAMONDS

Igneous rocks

Table 12 presents the results obtained from the analysis of a group of igneous rocks. These samples were crushed in a stainless steel mortar to which a thick chrome plating was applied in order to reduce mortar contamination. A blank of *Pyrex* glass crushed and powdered with much grinding yielded a maximum percentage

Table 12. *Isotopic composition of carbon in igneous rocks*

No.	Sample	Location	% C	δ ‰
235	Olivine Basalt [38]	Hawaiian Islands	0.014	-24.8
236	Olivine Basalt [39]	Hawaiian Islands	0.008	-25.4
237	Andesite [40]	Hawaiian Islands	0.030	-24.8
238	Basaltic Andesite [41]	Hawaiian Islands	0.016	-25.2
239	Melilite-nepheline basalt [42]	Hawaiian Islands	—	-26.0
240	Trachyte [43]	Hawaiian Islands	—	-19.0
241	Kimberlite	Transvaal, S. Africa	—	-23.8
242	Columbia River Basalt	Picture Gorge, Ore.	0.073	-24.3 †
252	Native Iron	Disco Island, Greenland	1.93	-24.3 †
255	Native Iron	Kaersut, Greenland	0.13	-20.9 †
257	Basalt	Kaersut, Greenland	—	-21.8 †

† Average of series.

* *Linde Co., Tonawanda, N. Y.*

** *British Oxygen Co., London.*

of carbon of $6 \times 10^{-4}\%$ upon combustion. Samples were powdered and tested with HCl for carbonate, and those found to contain carbonate were treated with the acid and washed in the centrifuge until neutral. Samples of the dried powders averaging around 5–7 g were then combusted for times ranging from 2–18 hrs at temperatures of 900–950° C.

A series of six analyses of Columbia River Basalt samples gave results ranging from -23.4 to -25.1 ‰. These samples were from different outcrops and thus the variation may be real. Recombustion of previously combusted samples yielded no further carbon dioxide, and a check combustion in which the sample was mixed with ignited lead chromate showed no increase in yield; thus it appears that total yields were obtained. However, it was found that HCl treatment reduced the yield of carbon to one-third, with no change in analysis. This decreased yield is probably not due to carbonate removal but to loss of carbon in the centrifuge, as is observed with graphite samples. The carbon percentage listed for Columbia River Basalt is the determination made on one untreated sample. In all cases of rocks in which carbonate was present, no carbon percentage is listed.

Only two of the Hawaiian samples contained carbonate. One of these, No. 240, was run both with and without acid treatment, and the analysis after acid treatment was 2‰ lighter showing that in this case carbonate enriched in C^{13} was removed from the sample. The figures in brackets in the sample column refer to the references in which chemical analyses and descriptions of these Hawaiian Island samples are to be found. These analyses show a most surprising apparent correlation between FeO content and isotopic composition. The analyses and the corresponding FeO percentage in the rock are as follows:

240.	-19.0 ‰	2.40 %
237.	-24.8 ‰	5.48 %
235.	-24.8 ‰	6.58 %
238.	-25.2 ‰	7.16 %
236.	-25.4 ‰	9.02 %
239.	-26.0 ‰	10.66 %

No. 240 is the trachyte sample, the most siliceous rock occurring in the islands, and certainly an anomalous phase. Excepting it, the isotopic differences are small, and thus many more analyses are necessary to establish this relationship.

The carbon in these igneous rocks lies generally in the range of terrestrial organic carbon, and may represent contamination of the lavas by organic material derived from coal or soil, or deposition of humic material by ground water. Nevertheless, the possibility of primary carbon cannot be ruled out. CHAMBERLIN [44] analyzed quantitatively the gases obtained by heating a great many rocks in vacuum, and found that CO_2 , CO, CH_4 , H_2 , H_2S , and N_2 were present in varying percentages. The proportions of the water gases will of course vary with the degree of equilibrium established during the extraction and with the FeO content, and thus the analyses yield no information as to the state of the carbon in the rocks. CHAMBERLIN did show that the gases were not present in cavities, as they could not be liberated by crushing alone. It is interesting to note that the percentages of carbon obtained by CHAMBERLIN are quite similar to those found in this work. He gives the volume of gas produced per unit volume of rock, and assuming a density of 3 for basalt,

his analyses recalculate to 0.10 % carbon in Disco Island Basalt, and 0.014 % carbon in basalt from Kilauea, Hawaii.

The samples of native iron in Table 12 are from the Disco Island Basalt of Greenland in which masses of iron up to twenty tons in weight are found. This iron also occurs disseminated through the rock and is thus undoubtedly of terrestrial origin. SMITH [45] made a great many chemical analyses of the iron in its different occurrences and found that the percentage of nickel in the iron varied from 1–2.6 % in most specimens, but rose to 6.5 % in some extremely malleable specimens. The iron samples exhibit Widmannstätten figures when etched. Other authors have confirmed that the nickel content averages around 2.5 % [46], [47]. This is a great enrichment over the amount of nickel in average igneous rocks. The ratio of iron to nickel calculated from SMITH's figures ranges from 14 to 45. Using the figures of GOLDSCHMIDT for the average amount of nickel in gabbros and those of DALY for the iron (both cited by RANKAMA and SAHAMA [36]), we get a ratio of 560.

The Disco Island samples here analyzed are from a large piece of iron occurring in the basalt on Disco Island, Ovipak, Greenland. The Kaersut iron is from Kaersut on the neighboring peninsula of Nugsuaks, and consists of small irregular globules of iron, several mm in diameter, disseminated through basalt*. As shown in Table 12, the percentage of carbon in this iron is much less than in Disco Island iron. Chemical analyses of two combusted samples made here by A. UCHIYAMA show nickel percentages of 3.50 and 3.41 in the pure iron. Specific gravity determinations on pieces of this specimen averaged 3.50, and the specimen is thus calculated to be 24 % iron by weight.

The iron in the basalt is generally assumed to have resulted from reduction by lignites through which it has passed [48], though the high nickel content is difficult to explain on this basis. The carbon from these samples falls into the range of coal and wood, and thus appears to have been derived from surface organic matter. Nevertheless we cannot use this as evidence for the reduction theory, since the other igneous rocks analyzed contain carbon of like composition and the source of this carbon is not known. Further, if the Disco Island iron has ascended from the depths as such, it would have picked up surface carbon from the lignites anyway, and given the same analysis.

The analyses of carbon in native iron were found to vary with the length of the combustion run, and in Disco Island iron the analyses ranged from $-25.7^{0}/_{00}$ to $-22.8^{0}/_{00}$, as the combustion time was varied from 1.5 to 17.5 hrs. Two samples of Kaersut iron combusted 5 hrs and 12 hrs agreed, but a sample combusted 18 hrs was heavier by $0.6^{0}/_{00}$. However, samples of the basalt separated from the Kaersut iron, and combusted 4 and 11 hrs, agreed perfectly. The iron samples were fairly coarse to prevent contamination from drilling and sawing, and it appears likely that the variation may be due to the presence of different phases of carbon with different isotopic composition, which do not combust with equal facility. Such phases may be iron carbide, carbon in solid solution, and graphite**. This problem reflects directly on the determination of the carbon isotope ratio in meteorites, since iron meteorites contain these phases.

* National Museum specimen number 53479; their gift.

** CHAMBERLIN [44] states that iron carbide occurs in Disco Island iron.

Accordingly samples of graphite and iron carbide from the Canyon Diablo meteorite were analyzed to see if a difference could be observed. The results were as follows:

259. Graphite — 6.3‰
 260. Cohenite — 17.9‰.

The graphite was taken from a troilite nodule as a one gram lump, and three analyses checked. The iron carbide sample, obtained from C. PATTERSON and H. BROWN, was taken from a residue obtained by dissolving a slab of iron in dilute HCl, and contained some iron phosphide. Three analyses were made which checked to 0.4‰ with the combustion time ranging from three to twelve hours. The carbon yields showed a range of 1%, and both yield and isotopic analysis varied regularly with time, the analysis becoming heavier with time as in the Disco iron.

Thus it appears that fractionation of carbon between various phases in iron can be observed, and analyses of carbon in meteorites will not be significant until this factor is taken into account. There is an intriguing possibility of perhaps determining relative meteoritic temperatures by this method. Time and equipment were not available to pursue this problem further; it is hoped to return to it in the future.

Graphites

The analyses of graphites cover almost the entire range of observed variations in the carbon isotope ratio. The interpretation of these results suffers from the serious handicap imposed by the inability to calculate the exchange equilibrium constant between graphite and other compounds, as previously noted. Table 13 lists the

Table 13. Isotopic composition of graphites

No.	Occurrence	Location	δ ‰
261	Schist	Laramie Range, Wyo.	-35.5
262	Schist	Laramie Range, Wyo.	-31.8
263	Schist	Laramie Range, Wyo.	-26.2
264	Schist	Laramie Range, Wyo.	-24.8
265	Schist	Trelen, Senja, Norway	-24.6
266	Schist	Jennestad, Troms, Norway	-23.0
267	Schist	Skaland, Senja, Norway	-21.8
268	Gneiss	Vegardshei, Risor, Norway	-19.7
269	Pegmatite	Lewiston, Maine	-12.6
270	Schist	Laramie Range, Wyo.	-9.8
271	Pegmatite	Bleiklia, Bamle, Norway	-9.7
272	Gneiss	Ceylon	-8.1
273	Pegmatite	Montana	-7.8
274	Gneiss veins	Montana	-6.3
275	Marble	Montana	-2.7

results obtained on fifteen samples, together with the type of occurrence and general location. No difficulty was experienced in obtaining checks within the desired precision, and all carbonate bearing samples were treated with HCl prior to combustion.

Samples 261-264, and 270, are from various graphitic schists occurring in the Laramie Range in eastern Wyoming, collected by W. H. NEWHOUSE and G. DE VORE (detailed locations given in original dissertation). They are all of Pre-Cambrian age.

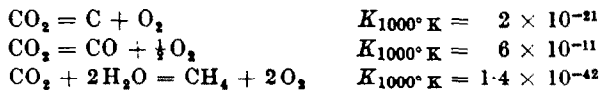
Samples 265–268, and 271, are a series of Norwegian samples furnished by H. RAMBERG. The Senja and Troms samples are Late Silurian, while the Risør and Bamle samples are Pre-Cambrian. The Ceylon graphite, No. 272, represents extremely extensive graphite development, the mineral occurring in large masses and veins of almost pure graphite, in pegmatite veins, and in disseminated scales, in the acid crystalline rocks of Ceylon which are regarded as an extremely metamorphosed series of Archean sediments. These occurrences have been well described by WADIA [49]. The Montana samples, furnished by F. C. ARMSTRONG, are from the Pre-Cambrian Cherry Creek formation, taken from Crystal Graphite Mine in Beaverhead County. No. 273 is graphite from a quartz-feldspar pegmatite in the gneiss about 25 ft underground. No. 274 is coarsely crystalline vein graphite from an epithermal vein about 100 ft underground. Dr. ARMSTRONG states that no contemporaneous calcite is known to be associated with these vein deposits. No. 275 is graphite in marble from the surface, and is not extensive in occurrence.

There is a distinct tendency for the graphitic schists to be light with respect to graphites in gneisses, pegmatites, and veins, and it is indeed tempting to conclude that the one type represents organically derived carbon while the heavier graphites have been formed from limestones. Thus RANKAMA [1] presented a set of analyses of graphitic and carbonaceous schists, all but one of which fell in a range including, but somewhat heavier than, the range of organic material. He discussed the geologic setting of the samples and concluded that the final proof of organic origin could not be deduced from geologic evidence, but that the similarity of the isotopic composition of the rock samples and the organic carbon settled the question and showed that they were of organic origin. He thus concluded that certain carbonaceous accumulations were established as genuine Archean fossils: *Corycium enigmaticum* Sederholm. WICKMAN and VON UBISCH [50] also stated that the isotopic composition of graphite derived from carbonate carbon should be close to that of the carbonate, and greatly different from graphite derived from organic matter. Therefore they were able to conclude that graphite from the Arenville series of New York was not of organic origin.

Nevertheless, we should be hesitant in accepting such conclusions. While they may be perfectly valid, the chemical evidence is not sufficient to justify them. Two points should be noted. First, many light graphite samples lie above the range of present day marine organic carbon and some are even lighter than terrestrial organic carbon. Thus, unless the mean isotopic composition of surface carbon has changed with time, the graphite carbon, if organically derived, is not representative of its source but has been altered in the same way that black shale and petroleum carbon appear to have been changed. Secondly, and more important, it has been tacitly assumed that it is not possible to derive light graphite from heavy carbonate, nor heavy graphite from light organic carbon. Without a knowledge of the fractionation factors between these various compounds at the temperatures postulated for graphite formation, it is impossible to make such an assumption. We have seen that it has proved impossible to date to calculate these factors. Moreover, even if such calculations (or measurements) can be made, we have no assurance that such processes took place under equilibrium conditions; in fact, we do not even know what compounds were involved in the formation of graphite. It is clear that it is quite unsafe to postulate the source of a graphite deposit on the basis of its isotopic

composition, and in fact quite the opposite should be done: namely, we should attempt to gain knowledge of the isotopic fractionation from the available geologic evidence.

Unfortunately, the geologic evidence is not decisive. Many large graphite deposits have been assumed to be of organic origin on the basis of the association with recrystallized sediments, the size of the deposits, and the apparent lack of any other large scale mechanism. However, many other theories have been suggested. WADIA [49] noted that the large vein deposits of Ceylon graphite are generally associated with limestone masses, and concluded that they were derived from the conversion of limestone to calcium and magnesium silicates during intense metamorphism and magmatic intrusion. He suggested that CO_2 was either dissociated or reduced by hydrogen, a mechanism that has been postulated in many cases of graphite-limestone association. The difficulty with this theory is the decomposition of CO_2 , which must go to C, CO, or CH_4 . Equilibrium constants for the equations representing the possibilities are [51]:



with all equilibrium constants decreasing below this temperature. Thus CO_2 is stable over the whole range of metamorphism unless some reducing element is present. Both hydrogen and free iron will reduce CO_2 , but the sediments do not contain free iron and if hydrogen is postulated to come from organic matter, then the carbon can also be derived from organic matter. It is of course possible that in some cases juvenile hydrogen rising from the depths may have reduced the carbon.

It seems likely that most graphite deposits are derived from both carbonate and organic matter. Organic carbon will react with both water and carbon dioxide at metamorphic temperatures, and reactions involving C, CO, CO_2 , CH_4 , H_2O , and H_2 will take place. The isotopic composition of the resultant graphite will be dependent upon the temperature, the degree to which the various equilibria obtain, and on the relative amounts of carbon derived from organic matter and calcium carbonate. Wide variations in isotopic composition, such as are observed, are certainly to be expected. In some instances the carbon may be almost entirely derived from organic carbon and may never have been volatilized; in other cases a great deal of exchange with and addition of carbonate may have taken place. But whatever the mechanism, it appears very doubtful that isotopic abundance data will cast much light on the formation of graphites. We should rather hope that increasing geologic knowledge of the processes involved will help to interpret the isotopic data.

Diamonds

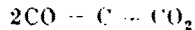
Six small octahedral diamonds from the Kimberley mines in South Africa were analyzed with the following results:

276.	-2.4‰
277.	-2.5‰
278.	-2.7‰
279.	-3.5‰
280.	-4.4‰
281.	-4.7‰

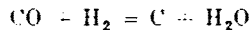
No information is available as to geographical and other relations between the specimens. One hundred per cent yields were obtained in each combustion and it appears that the variation is real.

Diamonds have often been assumed to be of deep seated igneous origin because of the high pressures at which diamond becomes the stable form of carbon: 18000 atm at 400° K and 36000 atm at 1000° K [51]. The South Africa diamonds are found in kimberlite, a serpentinized peridotite consisting of fragments of many types of rocks embedded in a ground mass of serpentine and serpentinized olivine. These rocks occur in steep funnel shaped pipes which break through and include fragments of shales, quartzites, granites, and other rocks. WILLIAMS [52] has given a complete summary of the vast amount of data and the many arguments over the method of emplacement of the rock and the actual source of the diamonds. He believed that the kimberlite ascended as an olivine-phlogopite magma, carrying "transported" masses of pyroxene, olivine, and garnet, and derived from an underlying peridotite magma in which the diamonds had originally crystallized. Since then both field relations and experimental evidence (BOWEN and TUTTLE [53]) have shown that peridotite or serpentine magmas cannot exist as such in the upper levels of the crust, and that such olivine rich bodies have been intruded at temperatures of around 500° C, perhaps as crystalline masses lubricated by some interstitial liquid.

Theories opposed to the igneous origin of diamonds have generally held that they were formed during the process of intrusion under high shearing stress from carbon present in sediments such as the highly carbonaceous Karroo black shales which surround many of the S. African deposits. We may ask if the isotopic data can be used as evidence for or against such theories. Clearly the diamonds are markedly divergent from the range of organic carbon. However, it is possible that such reactions as



or



may have been involved; both these equilibria favor the dissociation of CO over the range of temperature in which the kimberlites were probably intruded. If we can assume that the carbon was deposited as diamond rather than graphite then we can use the fractionation factors listed in Table 1. The difference between the isotopic composition of diamonds and black shales is about 24‰, which would indicate a temperature, assuming equilibrium, of about 500° K. Since we do not know how good the calculations actually are, the agreement with the estimated temperature is at least good enough so that the isotopic data do not throw any weight against the mechanism. The interaction of calcium carbonate and organic carbon discussed in connection with the graphites would apply here also.

It is interesting to note that sample No. 241 in Table 12, a kimberlite from the Transvaal, gave an analysis entirely similar to the other igneous rocks. This sample contained no diamonds. Whether the carbon in this and the other igneous rocks represents true igneous carbon or merely contamination with surface organic matter we are not in a position to say.

Nevertheless, it is possible to ask if either the C¹³ enriched diamonds or the C¹² enriched igneous rocks can represent a reasonable value for the mean carbon isotope ratio of the earth. WICKMAN [54] calculated the ratio of oxidized to reduced carbon

in the sediments using a corrected value for the isotopic composition of diamond obtained by NIER and GULBRANSEN [21] as the value for the mean carbon ratio of the earth. KAMEN [55] made such a calculation using as a mean the average of the values obtained by NIER and GULBRANSEN for Ceylon graphite, a meteorite, and a diamond. From the geological viewpoint it is clear that there is no justification for the use of these values. We have an entire lack of evidence that diamonds or graphites should have been formed from primeval terrestrial carbon at all, let alone with no fractionation of the isotopes during their formation. A similar statement applies to the calcites labeled as igneous by RANKAMA [1] citing MURPHEY'S work. HUTCHINSON [56] has correctly reversed the procedure and used the estimates of the amounts of carbon in the various sediments to calculate this mean value. From the data of MURPHEY [37] and RANKAMA [1], he was able to show that the meteoritic mean could not apply to the original material of the accessible lithosphere and of the biosphere. However, as noted below, he erred in the conclusion he drew from his calculations.

This calculation is based on the fact that the amount of reduced carbon which has been incorporated into the shales and the amount of oxidized carbon in the limestones must be in the inverse ratio of the deviation of the isotopic ratio of the reduced carbon from the terrestrial surface mean to the deviation of the isotopic ratio of the oxidized carbon from the terrestrial surface mean*. (The rest of the carbon on the earth is negligible compared to these vast reservoirs.) These amounts of carbon have been calculated in various ways from both geochemical data and stratigraphic measurements, and it is clear that we can place more reliance on them than on any arbitrarily chosen mean. Following HUTCHINSON then, we use the two sets of estimates of KUENEN [57] and CLARKE [48] for the proportions of the sediments comprised by shales and limestones, and the figures of CLARKE [48] for the percentages of carbon therein, and use values from this work of $-0.20/_{\infty}$ for the isotopic composition of the average limestone and $-29.20/_{\infty}$ (rough weighted average) for that of the average shale.

We then obtain for KUENEN'S estimate of 15 % limestones and 65 % shales, a mean of $-7.0/_{\infty}$ on our scale. For CLARKE'S estimate of 5 % limestones and 80 % shales, we obtain a mean of $-15.6/_{\infty}$. KUENEN'S limestone percentage represents an extreme estimate, and HUTCHINSON feels that the more usual figure given by CLARKE may be a little low. The true value should lie between these figures, perhaps around $-12.0/_{\infty}$.

* The exact general relationship is:

$$R_M = \frac{N_A \left(\frac{R_A}{R_A + 1} \right) + N_B \left(\frac{R_B}{R_B + 1} \right)}{\frac{N_A}{R_A + 1} + \frac{N_B}{R_B + 1}}$$

where R_M is the mean isotopic ratio of the element in the system considered, R_A and R_B are the isotopic ratios of the element in compounds A and B , and N_A and N_B are the number of atoms of the element in compounds A and B respectively. From this one derives the relationship expressed in the text by substituting $R_B = R_A + \delta$ and expanding in terms of δ . Neglecting second order terms in δ , one finally obtains:

$$\frac{N_A}{N_B} = - \frac{(R_B - R_M)}{(R_A - R_M)}$$

which is valid for small differences in isotopic composition. Thus for hydrogen one should use the exact expression.

The isotopic composition of S. African diamonds appears to be clearly divergent from the terrestrial surface mean and is enriched in C^{13} with respect to it. Moreover, the igneous rock carbon is also divergent and enriched in C^{12} with respect to the mean. Thus it appears that we are unable to point to any carbon deposits as representing the original isotopic composition of surface terrestrial carbon. If the diamonds are actually representative of the original terrestrial mean, then the carbon in the deep interior of the earth must be enriched in C^{13} with respect to the diamonds by an amount depending on the relative proportions of carbon in the interior and on the surface. On the other hand, if the diamonds are representative of deep seated carbon, then the original terrestrial mean lies somewhere between the diamonds and the surface mean, its exact value depending on the amounts of carbon in the two habitats. In either case the surface would have been enriched in C^{12} with respect to the interior at some early time.

The Canyon Diablo meteorite graphite is heavier than our surface mean while the iron carbide is lighter. The Canyon Diablo value reported by MURPHEY [37] would be about -7‰ on the scale used here (from comparisons of Solenhofen limestone) while the graphite value reported here was -6.3‰ ; a fairly good check. MURPHEY'S average value for meteorites is then -22‰ on this scale. The average value found by TROFIMOV [58] for thirty-nine meteorites (26 stones, 10 irons, and 3 pallasites) would be about -15.5‰ though here we have no comparison standard. These data indicate that the meteorites are probably enriched in C^{12} with respect to the surface mean. HUTCHINSON [56] also reached this conclusion, but then stated that if the meteoritic mean applies to the whole earth there must have been an impoverishment in C^{13} in the superficial layers of the lithosphere at an early stage. Actually the opposite is true, for if the terrestrial mean is lighter than the carbon in the sediments, the carbon in the interior must be lighter yet than the surface mean. Thus the surface must have been enriched in C^{13} at this early stage, while the interior was enriched in C^{12} .

There is some justification for preferring the latter alternative rather than the conclusion based on the diamond as representative of either the terrestrial mean or of deep seated carbon. If the carbon in the igneous rocks analyzed in this work represents true deep seated carbon, the mean terrestrial value should lie between the values for the igneous rocks and the surface mean. MURPHEY'S average meteorite value of -22‰ is a few per mil heavier than most of the igneous rocks, and TROFIMOV'S value estimated at -15.5‰ on our scale is heavier than the igneous rocks and just at the light end of the upper limit for the surface mean. (TROFIMOV'S non-meteoritic analyses are somewhat heavier than MURPHEY'S values for the same types of samples, indicating that there may be some analytical effect). The analyses of the Canyon Diablo meteorite indicated that iron carbide tends to concentrate C^{12} with respect to the graphite phase, and thus the enrichment of surface carbon in C^{13} could have taken place by an early separation of iron carbide and graphite, the iron carbide sinking to the depths while the graphite remained behind perhaps due to its solubility in magmas or to reaction with hydrogen to give methane. Thus a rather consistent picture can be postulated to be associated with the alternative that the meteoritic mean may indeed be close to that of the earth as a whole, though it is evident that a much more detailed study of carbon in meteorites and igneous rocks must be made before the hypothesis can be established as valid.

VIII. ISOTOPIC COMPOSITION OF HOT SPRING GASES

Gases from fourteen hot springs and geysers of Yellowstone National Park were collected, and the methane and carbon dioxide analyzed, according to the methods outlined in Section II. In five cases the amount of methane present was too small to analyze. In one case (No. 288) the volume of carbon dioxide was too small to analyze as only a small amount of gas was collected from this spring. ALLEN and DAY [19] have made volumetric analyses of the gases from many Yellowstone hot springs and all these samples except numbers 289, 298, and 300-1 were taken from springs or geysers which they have analyzed. Detailed geographical locations for all samples are given in the original dissertation from which this paper is taken. In general the relative volumes of the CO₂ and CH₄ agreed roughly with those of ALLEN and DAY, CO₂ averaging around 85% and CH₄ around 0.8% of the total gas excluding water. The small amount of CO₂ in No. 288 agreed with the finding of ALLEN and DAY that the gas from this geyser contained only 0.90% CO₂. The gases found by ALLEN and DAY in these springs were CO₂, CH₄, H₂, O₂, N₂, A, and H₂S. No CO was found. The occurrence of oxygen with hydrogen and other reduced gases is clearly anomalous and probably represents atmospheric oxygen carried down by descending water, and thus ALLEN and DAY have averaged their samples lowest in nitrogen and corrected this by removing the oxygen and the corresponding atmospheric proportion of nitrogen. The average composition of the uncontaminated permanent gases is then: CO₂—98.26, H₂—0.11, CH₄—0.11, N₂ + A—0.86, H₂S—0.66.

It is possible to ask if the observed isotopic ratios can be a consequence of thermodynamic equilibrium between the gases coupled with a temperature defined isotopic exchange reaction. The isotopic exchange equilibrium constants between CO₂ and CH₄ given in Table 1 were calculated and plotted against temperature. The measured δ values of CO₂ and CH₄ were then inserted in the equation previously presented for the relation between δ values and exchange equilibrium constants, which in this case can be written

$$K = \frac{1000 + \delta \text{ CO}_2}{1000 + \delta \text{ CH}_4}$$

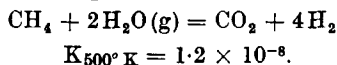
and with the resulting K values the equilibrium temperatures were interpolated from the plotted curve. These gas samples were collected in August 1950, and no surface water temperature measurements were made at that time, but on September 12, 1951, Chief Park Naturalist D. CONDON very kindly measured these surface temperatures. The calculated isotopic equilibrium temperatures and the surface water temperatures are given in Table 14 together with the isotopic analyses of the carbon dioxide and methane.

The average equilibrium temperature is found to be about 300° C. The calculated temperature range appears to be reasonable though there is only the slightest indication that the higher temperatures may be correlated with somewhat warmer surface waters. Sample 284-5 which is markedly different from the others in both temperatures was found to yield CH₄ much enriched in C¹³ with respect to the others, and it appears that there is some anomalous factor about this spring which cannot be explained. These calculated equilibrium temperatures would represent a "freezing in" of both the thermodynamic and isotopic equilibrium, since the one is the

Table 14. Isotopic composition of Yellowstone gases

No.	Hot spring	δ ‰		Calc. eqib. temp. °K	Surface temp. °C
		CO ₂	CH ₄		
282-3	Daisy Geyser	-1.1	-28.4	481	90
284-5	Diamond Spring	-1.5	-10.4	820	82
286-7	Iron Spring	-1.7	-27.4	500	92
288	Artemesia Geyser	—	-27.1	—	—
289	Bank of Iron Creek	-1.9	—	—	—
290-1	Black Sand Basin	-2.1	-26.5	513	89
292	Chinaman Spring	-2.3	—	—	—
293-4	Punch Bowl Spring	-2.5	-22.6	571	96
295-6	Kaleidoscope Group	-2.8	-23.8	562	94
297	Hurricane Vent Spring	-2.9	—	—	—
298	Porcelain Basin	-3.1	—	—	—
299	Teakettle Spring	-4.1	—	—	—
300-1	Firehole Lake	-4.4	-26.1	539	92
302-3	Ojo Caliente	-6.4	-20.6	678	95
Average		-2.8	-23.6		

mechanism for the other. The equilibrium between the gases is represented by



The observed proportions of gas require a large amount of water. It seems probable that the gases would have been equilibrated in the presence of liquid water at all the calculated temperatures, thus removing any possibility of calculating the proportion of juvenile water ascending with the gases. We simply do not know the depth to which meteoritic water can penetrate.

The above discussion is based on the assumption that the gases reacted and approached thermodynamic and isotopic equilibrium. It is of course possible that such is not the case; for example if methane derived from decaying surface plants were mixed with ascending carbonate derived carbon dioxide just below the surface, the same analyses might be obtained. Nevertheless, the general tendency for the C¹³ content to increase in the methane as it decreases in the carbon dioxide would seem to indicate that isotopic exchange has taken place. Such a relationship would not be exact if the mean isotopic composition of the source fluctuated from area to area. Since the carbon dioxide proportion of the gas is so large with respect to the methane, the mean isotopic composition of carbon from each spring is practically identical with that of the carbon dioxide. Thus the relatively large range of the carbon dioxide analyses indicates that such fluctuations of the mean carbon isotopic composition may have occurred. Further, indications are that the relative proportions of the gases may be altered after the quenching of the equilibrium; for example the isotopic composition of methane from Artemesia Geyser and Iron Spring, which are only a few yards apart geographically, is practically identical, while the CO₂/CH₄ ratios in the two differ by a factor of 1000. A further indication that isotopic exchange has taken place is the fact that several samples deviate from the range of terrestrial organic matter, and also that the variation in the methane analyses is so great. Methane yields from samples 289 and 292, not large enough to analyze

individually, were combined with a resultant analysis of -18.4‰ which also deviates from the terrestrial range.

It appears likely that these gases may have been derived from sediments underlying the present rhyolite plateau, which have been intruded by rhyolite magma. Limestones react with silica to give CO_2 , and decompose on heating, and at the same time organic matter in the sediments produces a small amount of methane. The hot ascending gases react and approach thermodynamic and isotopic equilibrium until at a certain stage the equilibrium becomes quenched in. The small difference in isotopic composition between the mean carbon and average limestones indicates that much the greater part of the carbon is derived from the limestones, the observed fluctuations in the mean being due to varying proportions of carbon derived from limestones and sedimentary organic matter.

CONCLUSION

Isotopic analyses of a large number of carbon samples have served to outline more fully the variations encountered in nature and to construct a more precise picture of the range of variations encountered in the various geological occurrences of carbon. Increased precision of analysis permits the study of small variations within the various classes of samples and thus extends the application of the isotopic chemistry of carbon to a finer geological scale. Previous studies of carbon isotope ratios have been chiefly concerned with the origins of graphite and dolomite, and with various attempts to calculate the carbon balance of the earth. In this paper it is shown that deductions of the inorganic or organic origin of graphites are based on the tacit assumption that the various isotopic exchange equilibria between graphite and other compounds cannot produce "light" graphites from "heavy" carbon and vice-versa. Until the compounds involved in graphite formation, and the isotopic exchange equilibria between these compounds, are known such assumptions are untenable, and studies of graphite formation should be based only on the data of geology and chemical thermodynamics. Data on the dolomite problem are insufficient but application of carbon isotope studies to the subject does not appear to be promising. There are as yet no analyses of material which geologists would agree on as representing true primordial terrestrial carbon or truly igneous carbon, though carbon in the igneous rocks here analyzed may ultimately prove to be of igneous origin. The general results of this study indicate that future work on carbon in limestones, shales, petroleum, volcanic gases, meteorites, and igneous rocks should provide valuable geochemical information when combined with geological studies.

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