Variations in the Relative Abundance of the Carbon Isotopes

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Although several isolated attempts have been made to determine the relative abundances of the carbon isotopes, there is no record of any systematic study undertaken to determine whether or not variations are present in naturally occurring sources of carbon. The C^{12}/C^{13} ratio has been measured by the spectroscope and the mass spectrograph. Using the spectroscopic method Jenkins and Ornstein[2] found the value 106, while Brosi and Harkins[3] obtained the value 92.2 ± 3.7. With the mass spectrographic method, Vaughan, Williams and Tate[4] found the value 91.6 ± 2.2, whereas Aston[5] has given 140 ± 14 for this ratio.

In the present work the carbon was studied in the form of carbon dioxide with the high intensity, high resolving power mass spectrometer already described.[6] The C^{12}/C^{13} ratio was assumed to be proportional to the relative heights of the mass 44 and mass 45 peaks in the apparatus, due allowance being made for the $C^{12}O^{16}O^{17}$ contribution to the 45 peak. The O^{16}/O^{17} ratio[7] was assumed to be 2500 in making the correction. In the present work this value was checked within 10% by determining the ratio of heights of the 32 and 33 peaks when oxygen was admitted to the apparatus. Possible variations in the abundance of O^{17} would not affect the conclusions of this experiment appreciably as the presence of this isotope accounts for only about 10% of the 45 peak.

The samples used fall into four classes according to their mode of formation: (1) igneous carbons, (2) limestones, (3) plant forms, and (4) unclassified. The diamond and graphite samples were included in the igneous group for most evidence appears to verify this classification. The present work gives additional evidence. Within each group samples of different ages were selected where possible in order to determine whether or not the age of the sample affects the C^{12}/C^{13} ratio.

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(2) Jenkins and Ornstein, *Proc. Acad. Sci.*, **35**, 1212 (1932).

(3) A. R. Brosi and W. D. Harkins, *Phys. Rev.*, **52**, 472 (1937).

(4) A. L. Vaughan, J. H. Williams and J. T. Tate, *ibid.*, **46**, 327 (1934).

(5) F. W. Aston, *Proc. Roy. Soc.* (London), **A149**, 400 (1935).

(6) A. O. Nier, *Phys. Rev.*, **52**, 1041 (1937).

(7) Mecke and Childs, *Z. Physik*, **68**, 362 (1933).

To prevent any fractionation process which might affect the ratio, an excess of all chemical reagents was used in preparing the carbon dioxide samples. Where necessary the samples were burned in a combustion furnace in the usual manner, and the purified gas was collected in an excess of barium hydroxide solution. The barium carbonate formed was washed, dried and treated with concentrated sulfuric acid in an evacuated system. In case of the limestones the original sample was pulverized and treated with the acid. The carbon dioxide was then dried and collected in a sample bottle. Before making the measurements it was frozen out with liquid air and gaseous impurities were pumped off. The sample of carbon dioxide in air was collected by pumping air through barium hydroxide solution and treating as above.

The grouping of the data in the table shows that the abundance ratio apparently depends upon the source of carbon. Although the absolute values may be as much in error as 2%, due to systematic discriminations in the mass spectrometer, the difference in the ratios should be significant, as all samples were studied under nearly identical conditions. As shown in the table, determinations were made at three different times, and it can be seen that the results are reproducible with only a few exceptions within 0.5%.

TABLE I
C^{12}/C^{13} RATIO FOR VARIOUS SOURCES OF CARBON

Sample	Source	Age, 10^6 yrs.	Series 1	2	3
	1. Igneous C				
Graphite	Ceylon	500+	89.7	89.9	
Meteorite	Cosby's Creek, Tennessee	900 ±	89.6	89.1	
Diamond	Kimberley Mines, Africa	60?		89.0	
	2. Limestones, $CaCO_3$				
Grenville	New York	1200	87.2	88.3	88.2
Ordovician	Vermont	380	88.6	88.5	
Clam shell	Boston	Present	88.7	88.6	
	3. Plant Sources				
Anthracite coal	Tennessee	250	92.1	91.7	91.5
Wood	Mass. pine	Present	91.8	91.2	
	4. Unclassified				
Dry Ice	Virginia coal	230+	91.6	90.8	
Oil	West Texas	200+		91.2	
Air[a]	Mass. 3/14/38	Present	92.5		
Air[b]	Mass. 3/22/38	Present		89.8	89.9
Na_2CO_3	Michigan limestone	300+	88.3	88.3	
Clam flesh	Boston	Present		90.1	

In general the process of formation of the limestones leads to a slight fractionation of the isotopes, favoring the heavier isotope, if one asumes that the igneous carbons represent the original carbon ratio and that equilibrium was attained between the carbon dioxide in air and the $CO_3^=$ ion in the water. Urey and Greiff[8] have calculated the equilibrium constant of the reaction between CO_2 and $CO_3^=$. This may be only one of the fractionation factors but it indicates the tendency to favor the heavier isotope in the formation of limestones. An age effect appears to be present in the limestones in Series 1. However, the paucity of data seems to make any definite conclusion impossible.

The formation process of plant material and subsequent changes into coal tend to concentrate the light isotope, if air is assumed to have the ratio 89.9. The value 92.5 in Series 1 is inexplainable.

The unclassified data fit in well with the above conclusions if the mode of formation is learned from other sources. As an example, the sodium carbonate sample, with a ratio of 88.3, would lead one to assume that the sample was prepared from a limestone. This was found to be true upon investigation of its source.

In conclusion, one can say that the carbon isotopic abundance ratio apparently varies slightly in nature. Such variations may be related to the mode of formation. It is obvious that more data are needed to substantiate these effects which may lead to a new method for determining the origin of carbon compounds in nature.

If one assumes for the sake of calculation that

the C^{12}/C^{13} ratio is 90 and uses the isotopic weights[9] 12.0041 and 13.0079 for carbon, together with a conversion factor 1.000275 in going from the physical to the chemical scale, an atomic weight of 12.012 is computed for carbon. This is to be compared with the chemically determined value 12.010 found by Baxter and Hale[10] and Scott and Hurley.[11] It is interesting to note that a 2% change in the carbon abundance ratio will affect the chemical weight by only 2 parts in the fourth decimal place.

The authors are indebted to the geological museums of Tufts College and Harvard University for some of the samples and to Professor A. C. Lane, Chairman of the National Research Council Committee on the Measurement of Geologic Time, for checking the age data of the various samples.

Summary

A mass spectrometer of high sensitivity and high resolving power has been applied to determine the variations in the relative abundances of the carbon isotopes in naturally occurring forms. The compounds studied fall naturally in four groups: (1) igneous carbon, (2) limestones, (3) plant forms, and (4) unclassified. The C^{12}/C^{13} ratio appears to depend upon the classification of the compound. In general, the heavy isotope seems to be preferred in limestones and the light isotope in plant forms. The maximum variations in the C^{12}/C^{13} ratio are about 5%. The atomic weight of C is calculated to be 12.012 based on a value of 90 ± 2 for the ratio in air.

(8) Harold C. Urey and Lotti J. Greiff, This Journal, **57**, 321 (1935).

(9) Bainbridge and Jordan, *Phys. Rev.*, **51**, 384 (1937).

(10) Baxter and Hale, This Journal, **59**, 506 (1937).

(11) Scott and Hurley, *ibid.*, **59**, 1905 (1937).