VARIATIONS IN CONCENTRATION AND ISOTOPIC ABUNDANCES OF ATMOSPHERIC CARBON DIOXIDE

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The earth's atmosphere contains approximately 0.03% of carbon dioxide by volume; the oceans of the earth contain carbon dioxide as a dissolved gas in about the same concentration per unit volume. Although the abundance of carbon dioxide is thus quite small compared to the abundance of many other chemicals on or near the earth's surface, carbon dioxide, for several reasons, exerts a pronounced influence upon the biology, geology and meteorology of the earth, and therefore may be expected to affect climate.

The fact that life depends upon carbon dioxide as its primary source of carbon, the important role of carbon dioxide in the weathering of rocks by virtue of its acidic properties, and the effect of its strong infra-red absorption on the heat balance of the atmosphere are all regarded as contributing an influence on climate. The actual nature and the extent of this influence are uncertain, however, because the complex chemical setting of carbon dioxide makes it difficult to sort out the independent variables upon which the carbon dioxide-climate system depend.

It would be well, for example, to know what factors control the concentration of carbon dioxide in the atmosphere and oceans and to be able to predict how the concentration may be likely to change in the future. At the present time, however, there are insufficient geochemical data to establish these factors or to make reliable predictions. Several papers in this present conference will discuss the problems resulting from the uncertainty. One paper (by Plass) will also treat the possible effects of changes in the carbon dioxide chemical system on the heat balance of the atmosphere and climate. Taken together these papers should indicate the general state of knowledge of the connection between carbon dioxide and climate. The present paper will discuss certain limited aspects of the carbon dioxide system relating to the effect of terrestrial plants on atmospheric carbon dioxide. Although the viewpoint will necessarily be restricted by the lack of data which can be reliably applied to the general problem, the material may serve to illustrate some of the experimental methods associated with the problem, especially the use of isotopic measurements to deduce the behavior of atmospheric carbon in a local environment.

In the study now to be described, attention was directed to a study of air in virgin forests and in grassland where the air was likely to be affected by biological processes, and at desert and high mountain stations where local sources or acceptors of carbon dioxide being absent, the composition of the air should be essentially that of the free atmosphere.

Air samples were collected in evacuated five-liter flasks. The carbon dioxide was isolated by freezing in a liquid nitrogen trap and distilled at dry ice temperature to separate it from condensed water vapor. Gas concentrations were determined manometrically and the C^{13}/C^{12} ratio of the purified gas was measured with a mass spectrometer.

A diurnal variation in the gas concentration and carbon isotope ratio was observed at every station in forest or grassland, higher concentrations and smallest C^{13}/C^{12} ratios being in the early morning near sunrise, the opposite extremes being in the early afternoon. Although the magnitude of the variation differs greatly from place to place, the minimum concentration and associated carbon isotope ratios, occurring in the afternoon, tended toward the same values. These values agreed with the composition of air in non-vegetated rural areas and are probably characteristic of the free atmosphere. If so, the observed diurnal variation was due primarily to the addition of carbon dioxide at night by plant respiration rather than to the removal of carbon dioxide by assimilation during the day.

For the circumstance of adding to air carbon dioxide differing in C^{13}/C^{12} ratio by a constant amount from the carbon dioxide already present in the air, the C^{13}/C^{12} ratio of the carbon dioxide bringing about the change in gas concentration is given by:

$$(1) \qquad \delta C^{13} = I(C^{13}) + M(1/\mu_{CO_2})$$

Where M is an empirical constant determined from experimental values for δC^{13}, the deviation in per mil ($^{o}/oo$) of the C^{13}/C^{12} ratio from an arbitrary standard value* and from experimental values for the concentration of carbon dioxide, μ_{CO_2}, in parts-per-million of air. Values of $I(C^{13})$ in units of δC^{13} for some of the stations appear in Table 1 together with maximum and minimum concentration values. Values of $I(C^{13})$ are in the range of isotopic composition characteristic of terrestrial plant carbon,

*The carbonate standard from the University of Chicago (PDB-I) was used. $\delta C^{13} = \left[(R/R_{std})-1\right] \times 1000$, where R is the ratio C^{13}/C^{12}.

Consistent with an accumulation in the night air of carbon dioxide supplied directly by the plants or their decay products in the soil. The variations in isotope ratio at individual stations were nearly always proportional to the variations in concentration of carbon dioxide within the limits of mass spectrometer accuracy, consistent with a source of added carbon dioxide which was homogeneous in carbon isotopic composition.

Samples of air collected under circumstances where local plant activity would have no influence on the air were found to be of remarkably constant composition with respect to gas concentration and carbon isotope ratio (Table 2). Some small variability was observed in samples collected over a span of a few hours, but there was little evidence of seasonal trends or correlation with ordinary weather phenomena. The composition of air from the deserts of southwestern United States agreed closely with air from the high mountains of California. The data are consistent with concentration measurements of maritime polar air in the North Atlantic made by Buch and are believed to be characteristic of the maritime air mass semi-permanently associated with the Pacific coast of North America.

Two hypotheses have been advanced to explain why the C^{13}/C^{12} ratio of terrestrial plants is not constant. One hypothesis emphasizes the role of the local environment; the other, the role of the plants themselves. Wickman favored the former hypothesis after observing that the carbon isotope ratio of plants from the herbarium of the Riksmuseum in Stockholm showed a dependence on ecology, e.g. plants from windy locations showed a higher C^{13}/C^{12} ratio than plants which had grown where the air circulation was restricted. Craig from data on plants, many of which he collected himself, did not find any distinct ecological correlation but did observe that different parts of the same plant could have different isotope ratios, a result not easily attributed to ecological differences. Furthermore, he deduced from general considerations that under steady state conditions the reabsorption by the plants of carbon dioxide respired by the plants or released by the soil could not, as Wickman proposed, lead to an isotopic enrichment greater than that performed by the plants themselves.

The present data tend to support a local environment hypothesis. Because of the method of sampling, these data yield only average values for the isotopic composition of the carbon dioxide respired by the plants and the soil. These average values given by the term $I(C^{13})$ of equation (1) should be characteristic of the isotopic fractionation between the organic phases and the local air supply uninfluenced by any isotopic effects which may

Table 1. Composition of Forest and Grassland Air

Station, Elevation and Date	μCO_2 Minimum (ppm)	μCO_2 Maximum (ppm)	$I(C^{13})$ (o/oo)
Coastal Redwood Canyon, Calif. 150 m., June 6-7, 1956	335	384	-26
Olympic Rain Forest, Wash. 170 m., Sept. 6-7, 1955	308	404	-24
Coastal Redwood Valley, Calif. 70 m., May 18-19, 1955	316	389	-24
ditto, June 5-6, 1956	314	374	-25
Sierra Nevada Pine and Fir Forest, Calif. 1950 m., June 2-3, 1955	313	364	-23
ditto, June 10-11, 1956	314	357	-24
Mogollan Rim Pine Forest, Ariz. 2100 m., May 16-17, 1956	316	326	-21
Cascade Mtn. Divide Forest 1900 m., Aug. 31-Sept. 1, 1955	307	321	-21

Table 2. Average Composition of Desert, Ocean and High Mountain Air

Date	Station & Elevation	μmin.	μ max.	δC^{13} average	No. of analyses
June 3, 1955	Sierra Nevada, Calif. 2500-3000 m.	314	318	-7.1	2
June 22, 1955	Southern Calif. beach, O m.	313	315	-7.4	2
July 8-9, 1955	Inyo Mountains, Calif. 3800-4300 m.	312	319	-7.0	11
Sept. 6-7, 1955	Wash. beach O m.	309	310	-6.9	2
Nov. 27, 1955	Southern Calif. Bay 400-900 m. (fr. aircraft)	315	315	-7.0	3
Jan 31-Feb. 2, 1956	Borrego Desert, Calif. 340 m.	311	318	-7.2	11
Mar. 9-14, 1956	Inyo Mts., Calif. 3800	315	318	-7.1	29
Apr. 21-22, 1956	Sonora Desert, Ariz. 550 m.	314	320	-7.4	11

occur within the plants themselves. For this reason the data might be expected to correlate with environmental factors affecting the isotopic enrichment process, if such exist.

In Table I stations are arranged in order of decreasing locally respired carbon dioxide. As predicted by Wickman's hypothesis the values of $I(C^{13})$ are more positive (less enrichment) the smaller the amount of respired carbon dioxide. Wickman's values for plants grown in "notoriously windy places"* (converted to per mil) lie between -20.8 and -21.1°/oo, in close agreement with the values of $I(C^{13})$ at Mogollan Rim and Cascade Mountain divide where, as indicated by the low maximum gas concentration values (μCO_2), locally respired carbon dioxide was nearly absent. On theoretical grounds it can be shown that an enrichment greater than that performed by the plants themselves is permitted under steady state conditions provided that the concentration of carbon dioxide in the atmosphere near the plants rises above the average atmospheric value periodically, e.g. diurnally, a possibility not previously considered, but suggested by the present data. Calculation indicates that the enrichment observed for the various stations in this study is, in each case, very nearly the maximum predicted for steady state conditions on the assumption that the observed carbon dioxide concentration values are representative of the entire growing season.

If the environmental hypothesis proves to be correct, carbon isotope measurements of plants may offer a clue to climate. It is known from studies by Lundegardh that the amount of locally respired carbon dioxide in a plant environment depends upon such factors as temperature and rainfall. It might indeed be possible to deduce information about past climates from carbon isotope studies of fossil plants. On the other hand, the possibility that plant isotope ratios may be affected by local environments should indicate that the use of such ratios as an index of regional or world-wide changes in the carbon isotope ratios may be invalid unless special evidence is available that the plants sampled had grown in places where no local environment developed.

Measurements of the concentration of atmospheric carbon dioxide extend over a period of more than a hundred years. It is characteristic of all the published data that the concentration is not

*Not to be confused with Wickman's desert plants, some of which showed still more positive values. Wickman suggested that cyclic enrichment might be smallest either in deserts or at constantly windy places, but if his data are representative, it is difficult to allow both possibilities. His theory accords with the present data only if the low-valued desert plants are in some way anomalous as referred to by Craig (1954 paper, page 116) and hinted at in Wickman's paper (page 253) where he excluded them from what he calls the "main series of terrestrial plants."

constant even for locations well removed from local sources or acceptors of carbon dioxide. Recent extensive measurements over Scandinavia, reported currently in Tellus, emphasize this variability: observations vary from 280 to 380 parts per million of air. These measurements are in sharp contrast to those obtained in the present study. The total variation at desert and mountain stations near the Pacific coast of North America, 309 to 320 parts per million is nearly an order of magnitude less than for the Scandinavian data. The author is inclined to believe that this small variation is characteristic of a large portion of the earth's atmosphere, since it is relatively easier to explain the large variations in the Scandinavian data as being a result of local or regional factors than to explain in that way the uniformity over more than a thousand miles of latitude and a span of nearly a year, which has been observed near the Pacific coast. The geochemical task of assigning a reliable value to the average concentration of atmospheric carbon dioxide will prove easier if this hypothesis is correct.