The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas

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Abstract—Fifty samples of rural air collected near the Pacific coast of North America have been analysed for carbon dioxide reporting, in addition to concentration in air, the isotopic abundances of C^{13} and O^{18}. A correlation observed for all samples between C^{13} isotope abundance and concentration in air can be explained by assuming an initial composition for atmospheric carbon dioxide of 0·031 volume per cent in air, C^{13}/C^{12} ratio −7·0 per mil., to which is added carbon dioxide of plant origin with a ratio of approximately −23 per mil. Minimum concentrations and associated carbon isotope ratios at different stations show very little variation (0·0307–0·0316 per cent, −6·7 to −7·4 per mil) and are believed to be representative of Pacific maritime air. Oxygen isotope abundances are approximately the same as for carbon dioxide in chemical equilibrium with average ocean water, but individual samples show variations which generally do not correlate with changes in concentration in air and are as yet unexplained.

INTRODUCTION

CARBON dioxide in the atmosphere has been studied for more than a hundred years. Nineteenth century measurements showed its concentration to vary, especially over continental areas. Causes for variation were not always understood, but the activity of plants explained the diurnal periodicity often observed for rural air, and the burning of fuel accounted for the high values of urban air reported (LUNDEGÅRDH, 1924, Chapter 1). New data in this century have confirmed these general features of continental air (HUTCHINSON, 1953), and more extensive measurements over the open ocean have established smaller but still significant variations for ocean air (BUCH, 1939, 1948). No accurate measurements have been reported for air far enough above the earth's surface to be completely removed from local influences. For this reason the often quoted figure of 0·03 per cent for the mean concentration of atmospheric carbon dioxide is only a rough approximation.

Several investigators have measured the abundance of the C^{13} isotope of atmospheric carbon dioxide and have shown that the carbon is appreciably lighter (lower C^{13}/C^{12} ratio) than that of the bicarbonate of natural waters or that of the carbonate of marine sediments. The first isotope measurements (MURPHY and NIER, 1941) are probably somewhat in error because of an isotopic effect attending the absorption of the carbon dioxide in hydroxide solution, but the recent measurements of CRAIG (1953) employing carbon dioxide condensed from air at liquid nitrogen temperature are believed to be correct. The present study was undertaken to determine what relationships might exist between variations in concentration and variations in the isotopic ratios of carbon dioxide in the atmosphere. To investigate the problem systematically, CRAIG's extraction method was modified to shorten the time required to process individual samples, oxygen isotope measurements were instituted, and a manometer was constructed to measure accurately the quantity of carbon dioxide for each sample.

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EXPERIMENTAL

Air samples were collected in evacuated five litre flasks under circumstances where local human influences were not likely to affect the air being sampled. Simultaneously with collection, the temperature and, where possible, humidity, wind, and barometric pressure, were recorded. The flasks were returned to the laboratory where the carbon dioxide was extracted and prepared for mass spectrometer analysis. Sample flasks were attached to a vacuum line, the sample pressure and temperature measured under laboratory conditions, and the sample pumped through a large spherical liquid nitrogen trap at reduced pressure. The condensate was freed from water-vapour by fractional distillation at dry ice temperature and the resulting gas, which could be verified by mass spectrometric analysis to be pure carbon dioxide, was condensed in a constant volume manometer constructed after a design of GERMANN (1914), where the quantity was measured. The purified gas was analysed in a modified double collector mass spectrometer as described by MCKINNEY et al. (1950)

Isotope measurements are expressed per mil by the function:

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) 10^3$$

where R is the absolute ratio of the abundance of two isotopes being compared. Differences in carbon-13 abundance between sample and standard are reported in terms of the relative carbon isotope ratio, δC^{13}, for which $R = C^{13}O^{16}O^{16}/C^{12}O^{16}O^{16}$, differences in oxygen-18 abundance in terms of δO^{18} for which $R = C^{12}O^{16}O^{18}/C^{12}O^{16}O^{16}$. The δ values were calculated from the experimental mass ratios 46/44 and 45/44 of sample and standard carbon dioxide gas by a method explained in detail by CRAIG (1957). The standard carbon dioxide gas to which analyses are referred is prepared from a particular sample of calcium carbonate obtained from a belemnite of the Pee Dee formation (Chicago standard "PDB-1") which has been previously employed as a primary standard by CRAIG (1953, 1957), EPSTEIN and MAYEDA (1953), and JEFFERY (1955).

Carbon dioxide concentrations are reported as parts per million (p.p.m.) of original air by volume (M_{CO_2}), water-vapour concentrations as volume per cent of original air (M_{H_2O}). Carbon dioxide concentrations in parts per million of dry air are also reported for samples for which humidity data are available.

Isotope ratios are considered to be accurate to $\pm 0.20\permil$ although analyses frequently agree within $\pm 0.05\permil$. Carbon dioxide concentrations are considered to be accurate to ± 1.0 p.p.m.

ANALYSIS OF DATA

The results of sampling at rural stations in Washington and California are presented in Table 1. Diurnal graphs of concentration and isotopic abundance for each station have been prepared to illustrate the data (Figs. 1–6). These data exhibit two salient features: minimum concentrations are nearly the same at all stations (Fig. 7); variations in the carbon isotope ratio are proportional to the reciprocal of molar concentration, i.e.

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

The smooth curves in Figs. 8 and 9 represent this relationship with coefficients $I(C^{13})$ and M calculated from the experimental data by the method of least-squares (WORTHING, 1943) separating the California and Washington data.

Values of $I(C^{13})$ and the average experimental deviation of δC^{13} from the least square relationship, separating the data of each station, are presented in Table 2, together with observed minimum concentrations and associated isotope ratios at each station. The average deviation of δC^{13} is nearly within experimental error

Table 1. Carbon dioxide composition and meteorological data for rural air*

California stations	Local time (hr min)	Air temp. (°C)	Wet bulb temp. (°C)	Rel. hum. (%)	μ_{H_2O} (vol.) (%)	Bar. press. (mm/Hg)	Wind (speed and direction) (knots)	Cloud (fraction and type)	μ_{CO_2} (moist) (p.p.m)	μ_{CO_2} (dry) (p.p.m)	δC^{13} (‰)	δO^{18} (‰)
Big Sur State Park Elevation 70 m (coastal redwood grove, 1 m above Big Sur River on footbridge, 18–19 May 1955)	12.15	24.7	15.3	34	1.05	754.0	2–4	clear	316.0	319.3	−7.41	+1.15
	18.15	18.3	14.4	66	1.38		calm	clear	321.0	325.5	−7.47	+1.16
	20.15	13.9	12.2	82	1.30		calm	clear	339.4	343.9	−8.36	+1.57
	22.00	12.8	11.7	88	1.30		calm	clear	366.0	370.8	−9.43	+1.60
	2.30	10.0	10.0	100	1.22		calm	clear	368.9	373.4	−9.80	+0.78
	5.30	8.3	8.3	100	1.09		calm	clear	388.6	392.9	−10.38	+1.14
	6.30	8.3	8.3	100	1.09		calm	clear	383.2	387.5	−10.18	+1.09
	8.30	15.6	13.3	78	1.38		calm	clear	344.7	349.5	−8.40	+1.47
	11.30	25.6	17.8	46	1.50		calm	clear	329.8	334.8	−7.80	+1.23
Yosemite National Park Tamarack Flats, elevation 1950 m (west slope of Sierra Nevada mountain range in mixed conifer forest, 1 m above Tamarack Creek on footbridge, 2–3 June 1955)	10.00	11.1	5.0	41	0.68	606.0	—	clear	321.4	323.6	−7.43	+0.04
	12.30	12.8	8.3	58	1.06		—	clear	312.9	316.2	−7.06	+1.31
	18.00	10.6	7.8	71	1.12		—	clear	333.8	337.6	−8.07	+1.37
	22.00	3.9	3.9	100	1.00		—	clear	356.1	359.7	−8.86	+2.86
	2.30	0.6	0.6	100	0.79		—	clear	356.0	358.8	−9.04	+1.95
	5.45	0.6	0.6	100	0.79		—	clear	363.3	366.2	−9.36	+1.68
	8.00	3.9	3.3	92	0.92		—	clear	360.8	364.2	−9.03	+1.34
Yosemite National Park Lake Tenaya, elevation 2500 m (50 m west of lake on open granite field, 3 June 1955)	10.00	10.6	3.9	33	0.63	567.0		clear	313.9	315.9	−7.04	+0.55
Yosemite National Park Tioga Pass, elevation 3000 m (100 m north of pass on snow field, 3 June 1955)	11.45	11.7	—	—	—	529.0	—	clear	318.3	319.8	−7.20	+0.35
Inyo Mountains Mt. Barcroft Station, elevation 3800 m (100 m west of building on snow field, 8 July 1955)	2.00	−2	—	—	—	482.8	SW 8	clear	311.5	—	−6.88	+0.07
	8.30	1	—	—	—	482.9	W 10	clear	313.3	—	−6.98	+0.07
	13.45	9	—	—	—	483.3	W 11	clear	313.5	—	−6.90	+0.32
Inyo Mountains Mountain Divide, elevation 4000 m (1 km north of Mt. Barcroft station on top of rock pile, 8–9 July 1955)	18.30	9	—	—	—	483.8	W 23	clear	313.7	—	−6.94	+0.63
	22.00	3	—	—	—	482.9	SW 10	clear	315.2	—	−7.09	+0.43
	2.00	1	—	—	—	482.1	SW 14	0.5 Ci	317.6	—	−7.15	+0.39
	6.00	2	—	—	—	—	SW 16	0.5 Ci	319.2	—	−7.01	+0.44
	11.30	6	—	—	—	480.9	S 6	0.5 Ci	316.4	—	−7.19	+0.27
	15.15	7	—	—	—	481.2	SW 7	0.5 Ci +Ac	314.5	—	−7.12	+0.33

324

Station	Time	Air temp (°C)		Humidity (%)		Pressure	Wind vector	Cloud	Conc.	Conc.	δ	δ
Inyo Mountains												
White Mountain Summit, elevation 4300 m (on top of rock pile, 9 July 1955)	13·00	6	—	—	—	—	—	0·5 Ci	313·6	—	−6·97	+0·30
	14·00	6	—	—	—	—	—	0·5 Ci	313·5	—	−7·04	+0·32
Washington stations												
Hart's Pass												
Elevation 1900 m (crest of Cascade Mountains, in middle of gravel road, 31 August–1 September 1955)	13·00	20·0	—	—	—	—	W 5–10	clear	313·7	—	−7·41	−0·45
	18·30	12·2	—	—	—	—	0–1	clear	311·7	—	−6·98	−0·21
	23·00	6·7	—	—	—	—	calm	clear	321·4	—	−7·38	−0·30
	5·45	5·6	—	—	—	—	calm	clear	319·7	—	−7·51	−0·27
	14·00	18·9	—	—	—	—	W 2–5	clear	307·4	—	−6·84	+0·08
Olympic National Park												
Beach Trail no. 6, elevation sea level, (Pacific coast, on sand beach, 6–7 September 1955)	9·45	12·2	—	100	—	—	S 5–10	clear	309·6	314·1	−6·88	+0·29
	Next day 15·15	14·4	—	100	—	—	SW 10–15	1·0 St	308·7	313·8	−6·85	−0·21
Olympic National Park												
Hoh River Ranger Station, elevation 170 m (500 m northwest of ranger office, in dense rain forest, 1 m above Taft Creek on footbridge, 6–7 September 1955)	13·00	18·9	—	68	1·77	765·0	calm	1·0 Sc rain at 14·00	346·2	352·5	−8·45	+0·20
	17·30	17·2	—	75	1·70	748·0	calm	0·4 Sc	343·0	348·9	−8·07	+0·49
	21·30	12·8	—	94	1·50	760·5	calm	clear	332·3	337·4	−7·97	−0·16
	1·45	13·1	—	100	1·50	759·7	calm	1·0 Sc	404·1	410·2	−10·79	−1·93
	6·15	12·5	—	100	1·46	759·2	calm	1·0 Sc	392·3	398·2	−10·54	−1·79
	9·15	13·1	—	100	1·50	759·5	calm	0·7 Sc	382·0	387·9	−9·77	−1·69
	13·00	15·8	—	69	1·33	759·2	S 1–2	1·0 Sc	308·5	312·6	−6·66	−0·43
Rock Lake												
Elevation 600 m (2 km from north end of 1 x 30 km lake on west sloping hill above lake, in very dry grassland with scattered pine trees in lake basin area. Air collected 0·3 m above roof of low shack, 10–11 September 1955)	14·45	29·4	—	—	—	—	SW 5–10	clear	312·3	—	−6·99	+0·17
	18·00	29·2	—	—	—	—	calm	clear	311·9	—	−7·01	+0·13
	22·30	14·7	—	—	—	—	E 0–1	clear	328·4	—	−7·93	−0·49
	2·30	11·1	—	—	—	—	E 0–1	clear	336·3	—	−8·23	−0·63
	6·00	11·1	—	—	—	—	E 2–4	clear	319·4	—	−7·49	−0·03
	9·30	15·6	—	—	—	—	SW 5–15	clear	311·0	—	−6·85	+0·19
	12·30	21·9	—	—	—	—	SW 5–15	clear	309·4	—	−6·83	+0·36

*Big Sur and Yosemite stations: air temperature and wet bulb by sling psychrometer to +0·5°F (+0·3°C); mean barometric pressure for station estimated from altitude by an approximate barometric formula, value used in determining relative humidity. Inyo Mountain stations: air temperature by mercury thermometer to ±0·5°C; barometric pressure by mercury barometer to ±0·1 mm/Hg; wind vector by recording cup anemometer and wind vane. Hart's Pass, Olympic and Rock Lake stations: air temperature by mercury thermometer to ±0·3°C. Olympic stations: humidity based on dry and wet bulb readings measured at Hoh River Ranger Station, humidity assumed at Beach Trail no. 6, barometric pressure by aneroid barometer to approximately ±0·01 in/Hg (±0·3 mm/Hg). At all stations except Inyo Mountains, wind vector estimated visually. Cloud estimated visually at all stations. Ci = cirrus, Ac = altocumulus, Sc = stratocumulus, St = stratus, m = meter, km = kilometre.
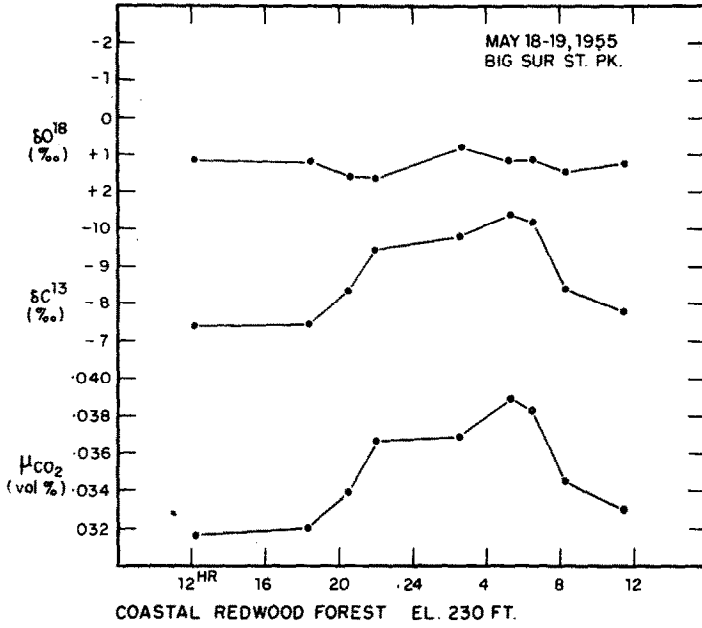
Fig. 1. Diurnal variation in the concentration and isotope ratios of atmospheric carbon dioxide in a coastal redwood forest of California.
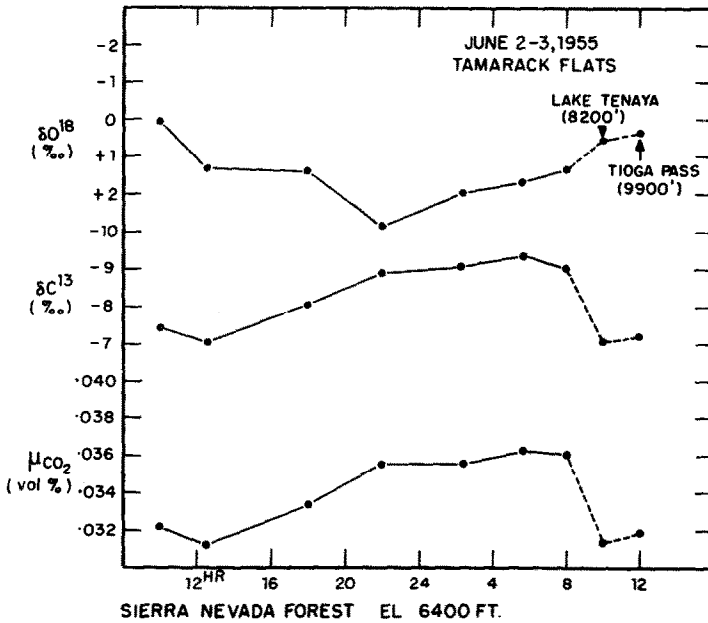

Fig. 2. Diurnal variation in the concentration and isotope ratios of atmospheric carbon dioxide in a forest of the Sierra Nevada.
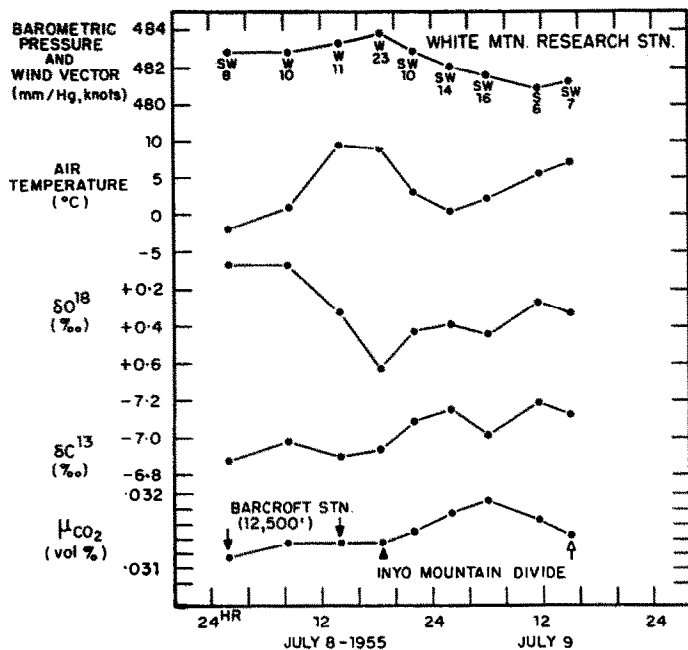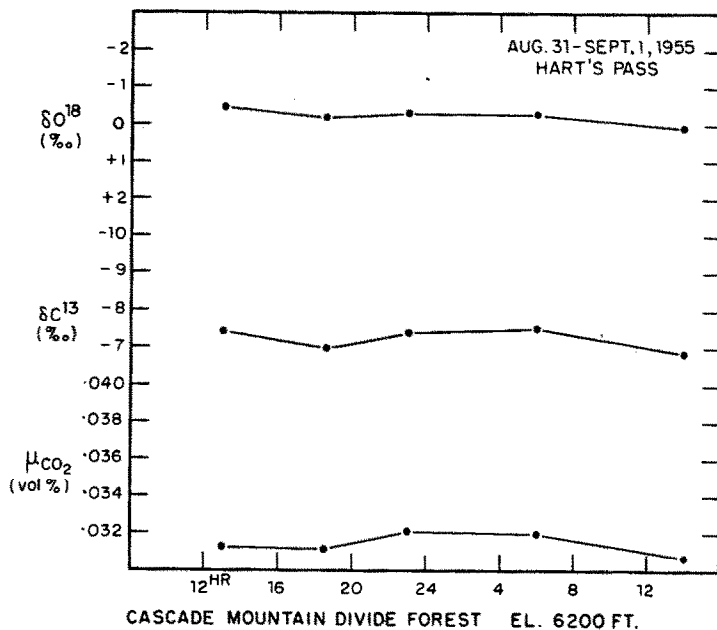
326

Fig. 3. Diurnal variation in the concentration and isotope ratios of atmospheric carbon dioxide and variations in barometric pressure, wind vector, and air temperature over barren ground near White Mountain Research Station in the Inyo Mountains of California.

Fig. 4. Diurnal variation in the concentration and isotope ratios of atmospheric carbon dioxide in a forest at the crest of the Cascade Mountain range of Washington.

327
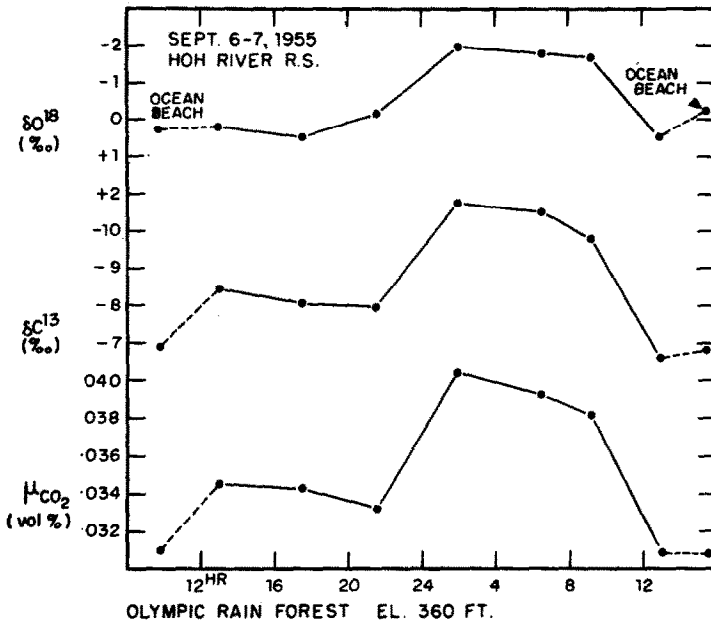
Fig. 5. Diurnal variation in the concentration and isotope ratios of atmospheric carbon
dioxide in a rain forest of the Olympic Peninsula of Washington.
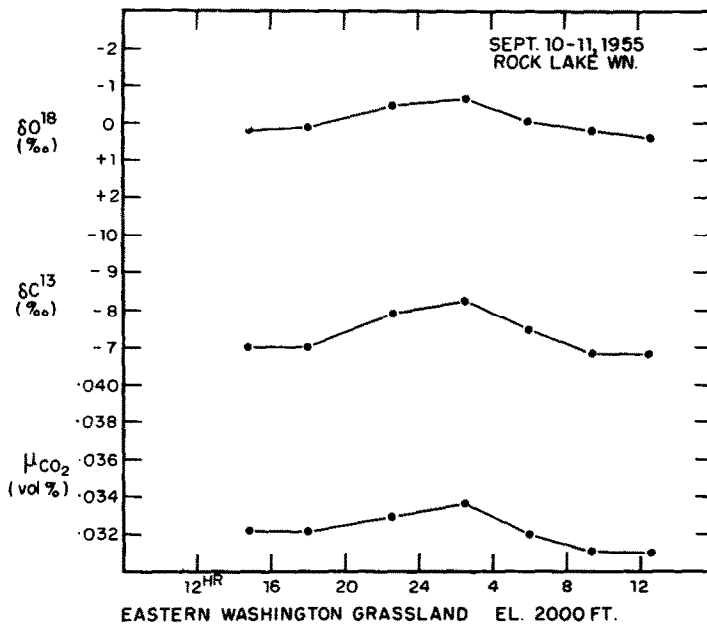
Fig. 6. Diurnal variation in the concentration and isotope ratios of atmospheric carbon
dioxide in grassland of eastern Washington.
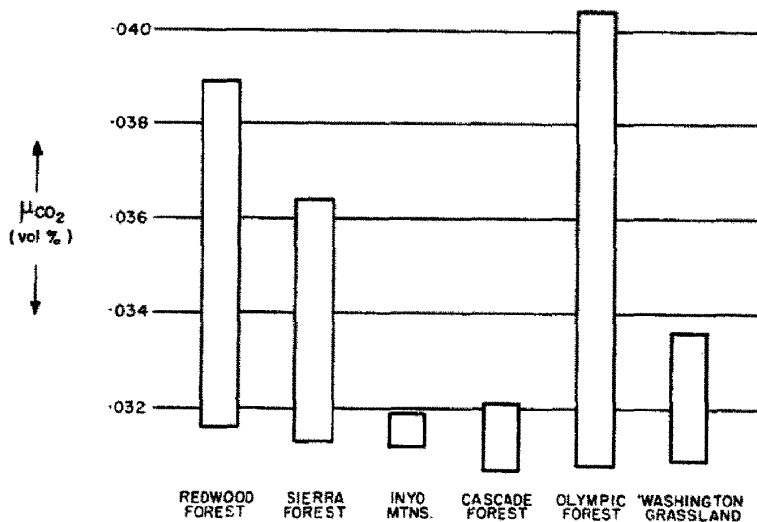
Fig. 7. Range in concentration of atmospheric carbon dioxide at various stations in Washington and California.
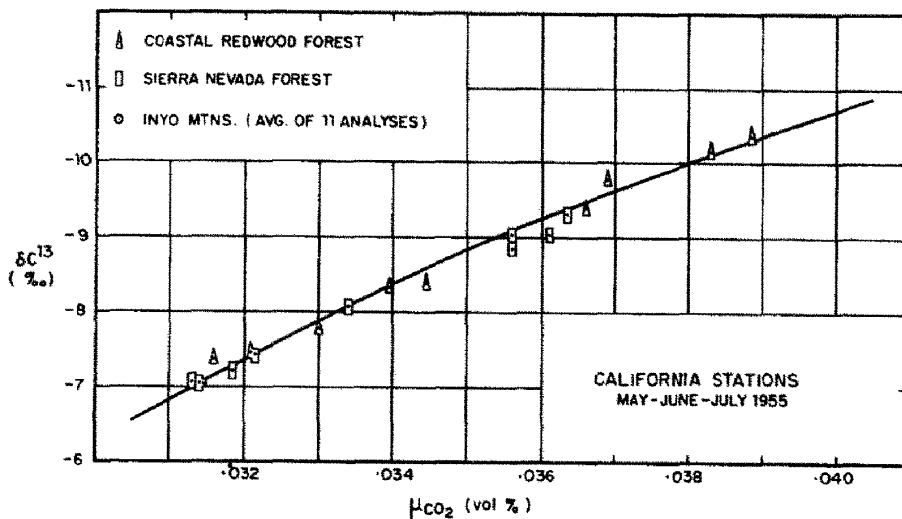
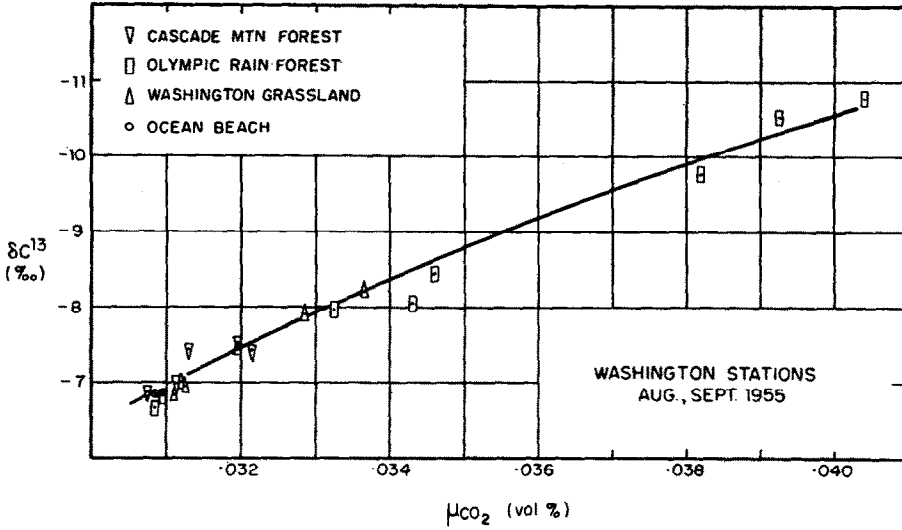Fig. 8. Relation between carbon isotope ratio and concentration of atmospheric carbon dioxide for California stations.

Fig. 9. Relation between carbon isotope ratio and concentration of atmospheric carbon dioxide for Washington stations.

at all stations. Minimum concentrations and carbon isotope ratios fall in a narrow range (307 to 316 p.p.m., -6.7 to $-7.4\%_{00}$), oxygen isotope ratios in a somewhat wider range ($+1.2$ to $-0.2\%_{00}$). Average minimum concentrations and associated carbon isotope ratios for forest and grassland stations (311 p.p.m., $-6.96\%_{00}$) agree closely with values for stations over barren ground (312 p.p.m., $-6.92\%_{00}$), oxygen isotope ratios agree less closely ($+0.67$ and $+0.14\%_{00}$, resp.).

At Washington stations, variations in the oxygen isotope ratio appear to be nearly proportional to concentration (Fig. 10) although values scatter more than
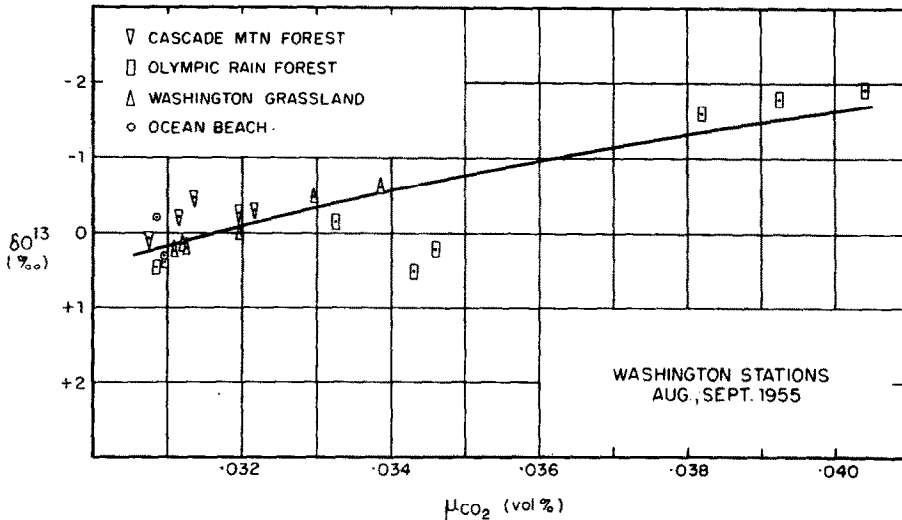

Fig. 10. Relation between oxygen isotope ratio and concentration of atmospheric carbon dioxide for Washington stations.

330

Table 2. Characteristic composition of atmospheric carbon dioxide

Station	Month of 1955	Minimum μ_{CO_2} (p.p.m.)	δC^{13} at minimum μ_{CO_2} (‰)	δO^{18} at minimum μ_{CO_2} (‰)	$I(C^{13})$ (‰)	$I(O^{18})$ (‰)	Av. dev. in δC^{13} (‰)	Av. dev. in δO^{18} (‰)	No. of analyses
Forest or Grassland									
Big Sur State Park	May	316	−7·41	+1·15	−24·1	—	0·098	—	9
Yosemite National Park	June	313	−7·06	+1·31	−23·1	—	0·076	—	7
Hart's Pass	August	307	−6·84	+0·08	−21·0	−6·4	0·120	0·116	5
Olympic National Park	September	309	−6·66	+0·43	−24·2	−10·9	0·134	0·39	7
Rock Lake	September	309	−6·83	+0·36	−25·0	−11·7	0·046	0·047	7
Barren Ground									
Yosemite National Park	June	314	−7·04	+0·55	—[a]	—	—[b]	—	2
Inyo mountains	July	312	−6·88	+0·07	—[a]	—	0·063	—	11
Olympic National Park	September	309	−6·85	−0·21	—[a]	—	—[b]	—	2

[a] Concentration variation too small to establish value.   [b] Insufficient data to establish value.

331

for carbon. Values of $I(O^{18})$ based on a relationship for oxygen analogous to equation (1) have been calculated for these stations by the method of least squares and appear in Table 2. The average experimental deviation of δO^{18} is nearly the same as for δC^{13} at two stations but is considerably greater at the other (Olympic rain forest). For California stations no proportionality with concentration is apparent at all, but for the Inyo mountain station a correlation may exist between the oxygen isotope ratio and barometric pressure (Fig. 3).

DISCUSSION

Rural air samples were all collected from the layer of air close to the ground, and, except for Inyo Mountain and ocean beach samples, were collected under circumstances where the metabolic activity of plants might be expected to influence the carbon dioxide composition of the air. This is so because plants exchange carbon dioxide with the atmosphere by means of respiration and assimilation and also because carbon dioxide is evolved from the ground through decay of organic material in the soil and respiration of plant roots. Air was sampled at least three metres from any living plants to be out of range of extremely local carbon dioxide gradients. In three cases (coastal redwoods, Sierra Nevada forest, Olympic rain forest) a bridge over a small stream afforded a good location, conveniently removed from low lying plants but at the same elevation as ground level air in the vicinity of the stream. In another instance (Washington grassland) the roof of a low shed beside a railroad track was used; at Hart's Pass (Cascade mountain crest) the middle of a dry gravel road. At all these five stations the data suggested minimum carbon dioxide concentrations in the afternoon and maximum concentrations in the late evening or early morning hours. Similar alternations have almost always been noted in the carbon dioxide content of air over land. Numerous observations going back to the early nineteenth century indicate the generality of this effect (LUNDEGÅRDH, 1924), and with little doubt, it may be attributed to the metabolic activity of terrestrial plants and the respiration of the soil.

The pronounced regularity with which the carbon isotope ratio follows changes in carbon dioxide concentration suggests a simple cause for mutual variation in these quantities. When to air is added carbon dioxide differing in carbon isotopic abundance by a constant amount from the carbon dioxide initially present in the air, changes in the carbon isotope ratio of the total atmospheric carbon dioxide will be proportional to the reciprocal of molar concentration. If equation (1) is used to describe this relationship, the carbon isotope ratio of the carbon dioxide which brings about the change in concentration will be equal to the term, $I(C^{13})$. Computed values of this term vary, for different stations, from -21 to $-25\%_0$, a range in isotope ratio which agrees well with the range found generally for the carbon of terrestrial plants (WICKMAN, 1952; CRAIG, 1953). Thus the relationship between carbon isotope ratio and molar concentration observed for the carbon dioxide of rural air is explained if carbon dioxide is added to or subtracted from the atmosphere by plants or their decay products.

On the other hand, the uniform concentration and carbon isotope ratio of afternoon air samples cannot be primarily a result of biological activity. In a

restricted air supply but under average conditions of light, temperature and mineral fertilization, plants are able to reduce the concentration of carbon dioxide to significantly lower values than have ever been observed under natural conditions (EGLE and SCHENK, 1952), and until the minimum concentration is reached where plant assimilation and respiration of carbon dioxide just balance, there is no known biological regulatory process which will predict the same concentration of carbon dioxide for such widely varied plant environments as are represented in the present data. The observed uniformity must therefore be a result of some rather general meteorological circumstance which operated at the times when these samples were collected. Such a recurring characteristic composition strongly implies that all local influences of vegetation have been wiped out at these times by mixing of ground level air with air from above or beyond the zone of vegetation influence, and that this mixed air over these rather widely separated stations during several months of the year, at least, was conspicuously constant in carbon dioxide composition. At several locations samples were deliberately taken under circumstances where vegetation would have no influence on the air even near the ground. The data for the Olympic beach station represents air blowing briskly off the Pacific Ocean. In the Inyo Mountains and Sierra Nevada (Lake Tenaya and Tioga Pass) air was collected above almost completely barren ground and always in a good wind. The concentrations and carbon isotope ratios at these stations agree very closely with those of forest and grassland stations at times of minimum concentration (Table 2). The concentrations are consistent with those of maritime polar air collected north of Iceland with a range ˙309–317 p.p.m. (BUCH, 1948) and, quite probably, the data represent a carbon dioxide composition characteristic of the maritime polar air which is nearly always present over the Pacific coast of North America (PETTERSEN, 1940, p. 165).

Oxygen isotope ratios agree approximately with carbon dioxide in equilibrium with mean ocean water at 25°C, for which $\delta O^{18} = -0.1\%_0$) (EPSTEIN and MAYEDA, 1953, as corrected by CRAIG, 1957). Samples associated with minimum concentrations range from $+1.3$ to $-0.2\%_0$, forest and grassland samples from $+2.9$ to $-1.9\%_0$.

Most of the individual values do not appear to correlate with any measured meteorological or chemical quantity, but an interesting relationship is suggested by the data for the Inyo Mountains. During the period before the passage of a pressure wave, indicated by maximum barometric pressure near 18·00 on 8 July, the oxygen isotope ratio changed noticeably, reflecting the change in barometric pressure, while the carbon isotope ratio and carbon dioxide concentration were constant within the precision of measurement. The slight rise in concentration after the maximum pressure was reached was reflected in the carbon isotope ratio but appeared to have only a small influence on the oxygen isotope ratio which continued to follow the barometric pressure. The effect, if real, must be explained by a process which affects only the oxygen isotope ratio. The isotopic equilibrium of the oxygen of carbon dioxide with the oxygen of ocean water is such a process. Since the equilibrium fractionation between phases is temperature dependent with a coefficient of approximately -0.2 per thousand per degree centigrade (UREY, 1947), a correlation with barometric pressure could be the result of partial

mixing of air from different air masses which were equilibrated with water of differing oxygen isotopic composition or at different temperatures.

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