

SMITHSONIAN MISCELLANEOUS COLLECTIONS  
VOLUME 81, NUMBER 11

## Hodgkins Fund

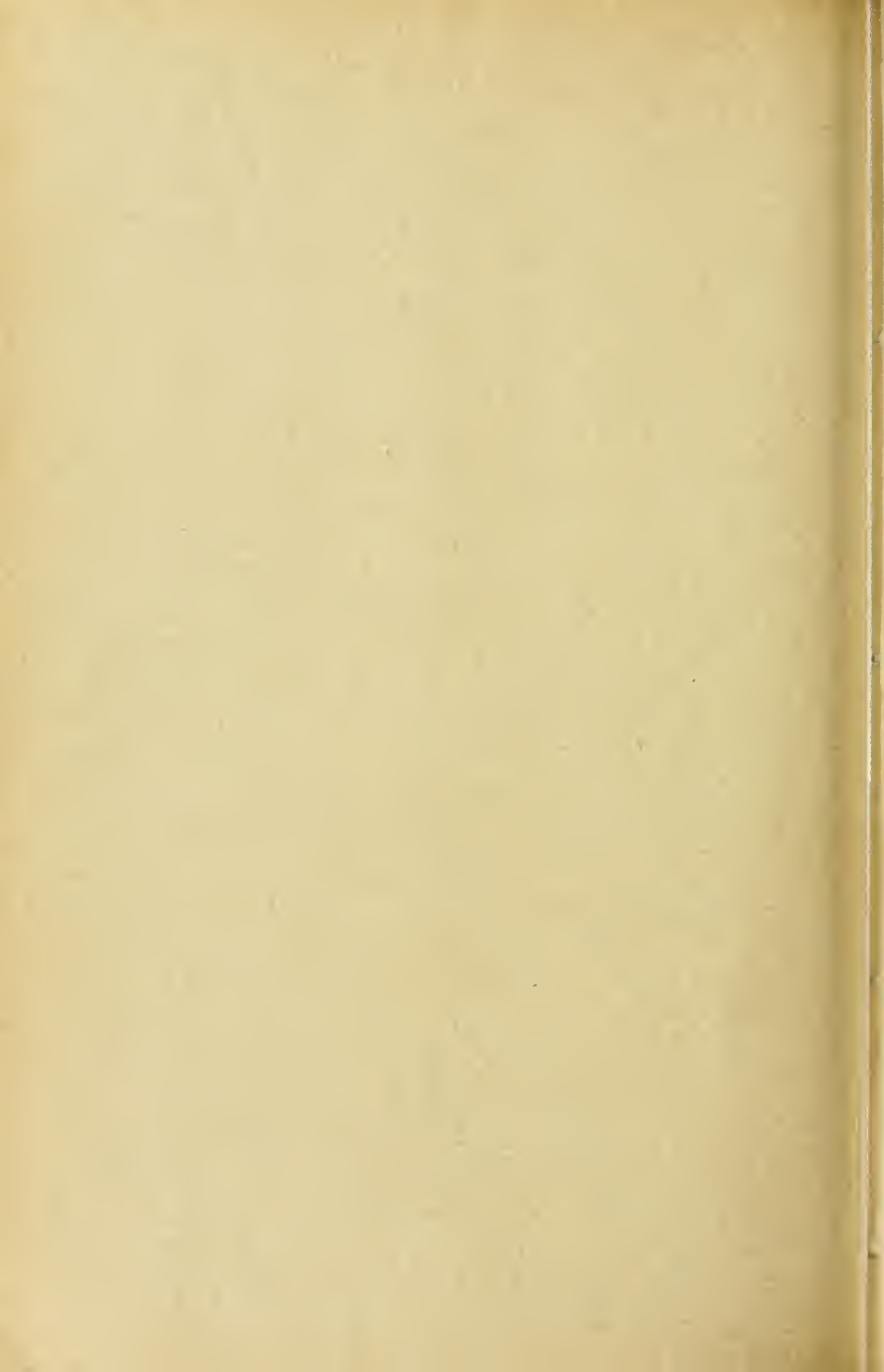
# ATMOSPHERIC OZONE: ITS RELATION TO SOME SOLAR AND TERRESTRIAL PHENOMENA

BY  
FREDERICK E. FOWLE



(PUBLICATION 3014)

CITY OF WASHINGTON  
PUBLISHED BY THE SMITHSONIAN INSTITUTION  
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### ATMOSPHERIC OZONE: ITS RELATION TO SOME SOLAR AND TERRESTRIAL PHENOMENA

BY FREDERICK E. FOWLE<sup>1</sup>

The reduction of the measurements of the output of radiation from the sun obtained at the Smithsonian station on Table Mountain, California (altitude 2,300 m.), encountered some difficulty which did not seem to be present at the station at Montezuma, Chile (altitude 2,900 m.), in the southern hemisphere. Preliminary reductions showed the presence of a direct relationship between the values obtained at Table Mountain for the radiation from the sun and the amount of ozone above that station. A yearly march present in the Table Mountain solar results, together with other irregularities, were eliminated when proper allowance was made for the amount of ozone above that station.

That ozone plays an important part in the interception of radiation coming to us from the sun, especially at the violet end of the spectrum, has been known for some time. It exerts absorption in the following places in the spectrum:<sup>2</sup>

(1) A very strong band in the ultra-violet, 0.2300 to 0.3100 $\mu$ , with its maximum at 0.2550 $\mu$  (the Hartley band).

(2) A complicated group, extending roughly from 0.3100 to 0.3500 $\mu$  (the Huggins band).

(3) A group in the yellow and red, 0.4500 to 0.6500 $\mu$  (the Chappuis band).

(4) A band in the infra-red between 9 and 11 $\mu$ .

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<sup>1</sup> A preliminary report of this research was read at the 9th annual meeting of the American Geophysical Union, April, 1928 (Ozone in the Northern and Southern Hemispheres, *Journ. Terr. Magn. and Atm. Electr.* **33**, 151, 1928).

<sup>2</sup> Adapted, with alterations in the wave-lengths of the infra-red band, from "The absorption of radiation in the upper atmosphere," C. Fabry, *Proc. Phys. Soc.* **39**, 1, 1926.

The longer wave-length portion of the Hartley band (1) has been used by Fabry and Buisson<sup>1</sup> and others to measure the amount of ozone in the atmosphere. On June 7, 1920, they found an equivalent layer of a little more than 3 mm. at normal temperature and pressure (ntp). They estimated that at  $0.2800\mu$  the ozone absorption would reduce the incident solar energy to  $10^{-16}$  of its entering value. Ozone, therefore, by its absorption in this band, limits the solar spectrum at its violet end as observable at the surface of the earth. Dr. Dobson<sup>2</sup> uses this band for measures both of the amount and the

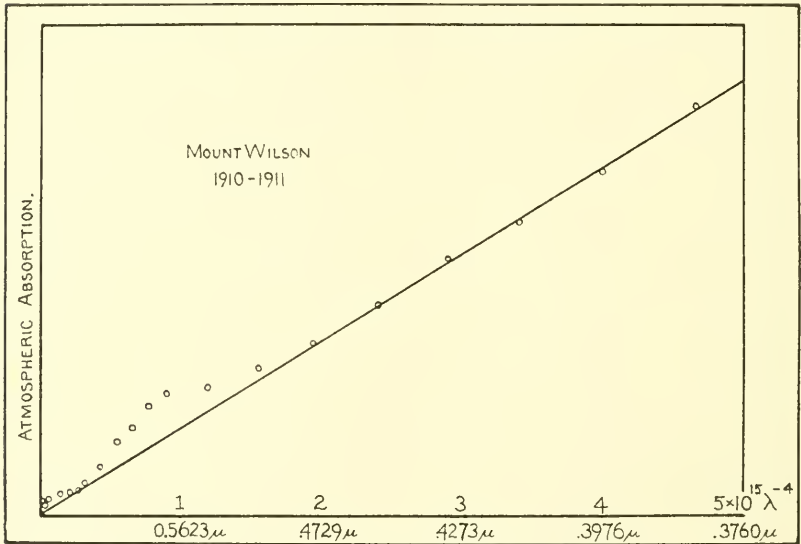


FIG. 1.—Atmospheric absorption coefficients showing ozone band (Fowle).

height of atmospheric ozone. He found a height of 30 to 40 km. above sea-level.

The Huggins band (2) was used by Cabannes and Dufay<sup>3</sup> for measures of the altitude of the ozone layer by light reflected from the zenith at the time of the setting sun. They found an altitude of 40 to 50 km. above the earth's surface.

The Chappuis band (3) is used in the present research. The band in the infra-red (4) is of importance because of its location at a wave-length where otherwise the atmosphere would be nearly trans-

<sup>1</sup> Journ. de Phys. **2**, 197, 1921.

<sup>2</sup> Proc. Roy. Soc. **110A**, 660, 1926; **120A**, 251, 1928.

<sup>3</sup> Journ. de Phys. et le Rad. **8**, 125, 1927.

parent to radiation out-going from the earth. It was observed in the laboratory by Ladenburg and Lehman,<sup>1</sup> and by the writer in the solar spectrum.<sup>2</sup>

A set of atmospheric transmission coefficients, freed as carefully as was possible from the effects of non-selective absorptions due to water vapor, dry dust, and particles associated with water vapor and called wet dust, was published by the writer in earlier papers.<sup>3</sup> The observations are shown in figure 1, redrawn from Fabry's article (*loc. cit.*). Cabannes and Dufay<sup>4</sup> used this data to show that the

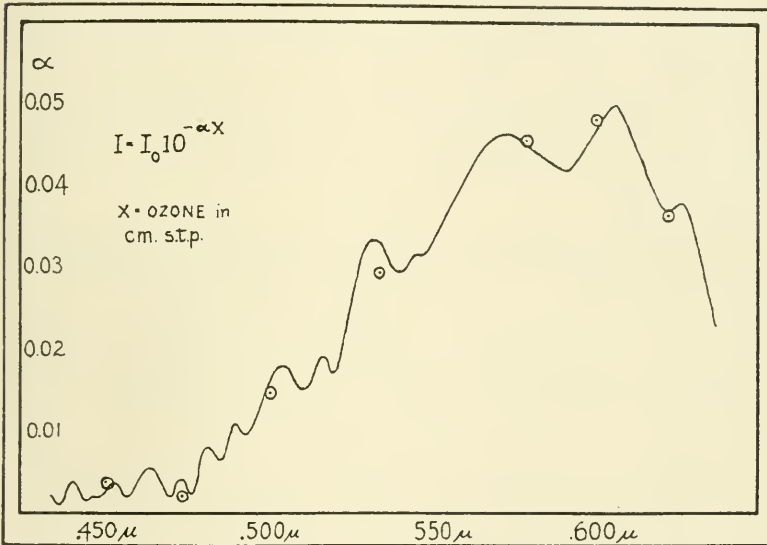


FIG. 2.—Atmospheric absorption in Chappuis yellow ozone band (Colange).

departures from the straight line of the points at wave-lengths greater than  $0.4729\mu$  were caused by ozone present in the atmosphere. Making the assumption that the atmospheric ozone amounts to 0.32 cm. ntp., they used the differences of ordinates between the observed points and the straight line, in the region of figure 1, just indicated, to calculate values of the absorption coefficients of ozone for a standard depth of 1 cm. ntp. Figure 2 shows the 7 resulting values plotted as circles and also a curve showing transmission coefficients

<sup>1</sup> Ann. d. Phys. **21**, 305, 1900.

<sup>2</sup> Smithsonian Misc. Coll. **68**, 1, 1917.

<sup>3</sup> Astrophys. Journ. **38**, 392, 1913; **40**, 435, 1914.

<sup>4</sup> Journ. de Phys. et le Rad. Sept. 1926.

for 1 cm. ozone as obtained in the laboratory by Colange.<sup>1</sup> The agreement is remarkable. The layer of ozone used by Colange was 18 cm. ntp., and from this the above curve was computed for 1 cm. ntp., by Bouguer's formula.

The same authors,<sup>2</sup> using a somewhat similar process, later utilized published observations, made by Smithsonian observers at their various stations, for further determinations of the ozone above these stations. These data had not been corrected for water vapor; also the values were taken from somewhat smoothed curves drawn through the plotted observed points. Further, because of gradually progressive changes in the transparency of the sky, comparatively few days furnish observations which are good enough for the above treatment. On these several accounts the investigation just cited is not fully satisfactory. In the following discussion only the original observations are used and they are treated by a method probably nearly independent of sky changes.

The results presently to be considered are to a considerable extent a by-product of spectro-bolometric observations originally made for the determination of the radiation emitted from the sun. Values from about 1,000 days have been utilized. In the ordinary reductions of this work, the ordinates of the solar energy curves (generally 6 curves per day) obtained with a 60° u. v. glass prism had already been read for about half of the days used. It has been the custom to read them on our plates at abscissae, among others, of 18, 20, 22, 24, 26, 28, and 30 cm. towards the violet from the infra-red band,  $\omega_1$ , at  $2\mu$ . These places correspond to wave-lengths of 0.764, 0.686, 0.624, 0.574, 0.535, 0.503, and 0.475 $\mu$ , respectively. This spectrum region includes the yellow Chappuis band due to ozone.

A preliminary futile attempt was made to use these ordinates to determine directly the depth of the ozone band. The band is masked by the numerous solar lines in that part of the spectrum. Indeed Fabry says: "The Chappuis bands have never been observed directly in the solar spectrum. I have often looked for them in the spectrum of the setting sun, but have never found them."

However, if the several observations of any day, made at each place in the spectrum at different zenith distances, are used to determine atmospheric transmission coefficients, and the resulting values are plotted against the corresponding deviations, the band is strongly

<sup>1</sup> Journ. de Phys. et le Rad. 8, 257, 1927.

<sup>2</sup> Journ. de Phys. et le Rad. 7, 257, 1926; 8, 353, 1927.



brought out as may be noted in figure 3. This figure shows results for days of great, medium, and negligible absorption in this band. The abscissae are prismatic deviations, the ordinates, atmospheric transmission coefficients for zenith sun. As the quantity of atmospheric ozone may be correlated to the amount of energy cut out by this band from the radiation coming to us from the sun, the area of

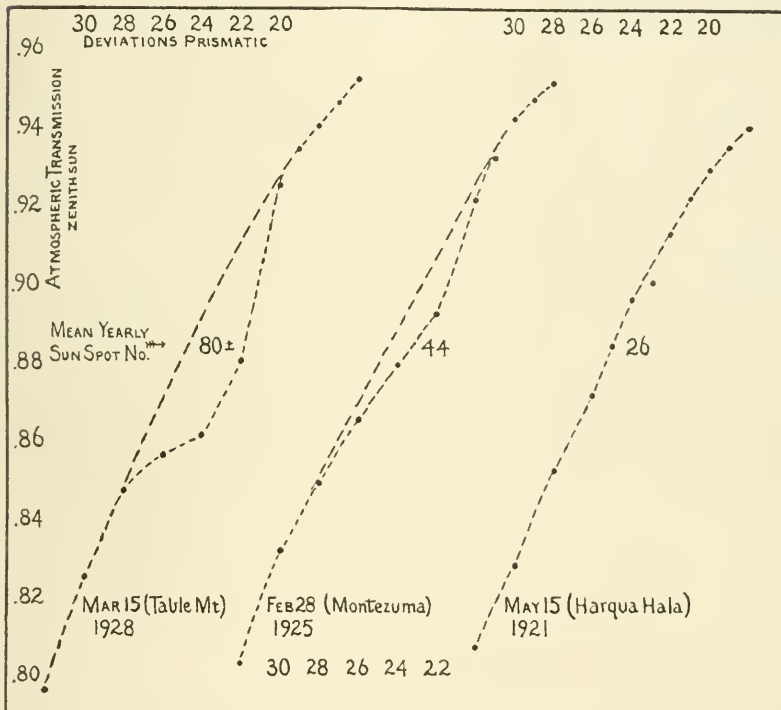


FIG. 3.—The Chappuis yellow ozone band.

this band, reduced to the proper energy units, has been utilized as a measure of the amount of ozone in the atmosphere.

A smooth curve is first drawn over the top of the band as indicated in figure 3. At any particular abscissa, let  $a_a$  represent the ordinate on the smooth curve drawn across the band, or, in other words, the transmission of the air for zenith sun with no ozone present;  $a_o$  is the corresponding transmission coefficient for ozone, and  $a$  the observed transmission. Then

$$a = a_o a_o \text{ or } a_o = a/a_a.$$

Calling  $e$  the corresponding energy at the selected place in the sun's spectrum, it may be assumed that approximately the amount of energy absorbed from the sun's rays by ozone is

$$\left(\frac{a}{a_a} \cdot e\right) \text{ summed for spectrum places 22, 24, and 26.}$$

The accuracy of these measurements, depending, at the greatest, on differences of the order of (0.890-0.860), cannot exceed 1 part in 30, assuming no accidental errors. Further, the measurements extend over times of from one to three hours. It is presumptuous to assume always a negligible change in the amount of ozone during such considerable times. Any change in the general transparency of the sky is probably negligible, since it would affect both the numerator and the denominator of the above expression. It takes only 30 seconds for the run through the part of the spectrum used, so that the time is short to produce differential errors within this band.

Because the results presently to be given differ so considerably in magnitude and range from the values of Dr. Dobson and those associated with him, it has been thought advisable to devote considerable time and study to the indications of the Chappuis band.

Is the discrepancy due to the presence of other atmospheric lines within the Chappuis ozone band? A count of the number of atmospheric lines, designated as such in St. John's recent revision of Rowland's Solar Spectrum Table,<sup>1</sup> leads to the following table:

Spectrum range	Wave-length range	Number of lines		
		atm <sup>c</sup>	H <sub>2</sub> O	O <sub>2</sub>
27-29	0.490-.520 $\mu$	0	0	0
25-27	0.520-.555	16	1	0
23-25	0.555-.600	311	244	43
21-23	0.600-.653	81	104	42

In figure 4 the area of that part of the ozone band under trial corresponding to the region of the first three lines of the above table is plotted against the corresponding precipitable water vapor in the atmosphere; in figure 5, is similarly plotted that corresponding to the lower line. No connection with water vapor can be certainly inferred from these two plots. What little dependence there seems to be is in the wrong direction; that is, the greater the water vapor, the smaller, on the average, seems to be the area of the band. This apparently inverse effect probably results because the season of greatest water

<sup>1</sup> Carnegie Institution Publications, 306, 1928.

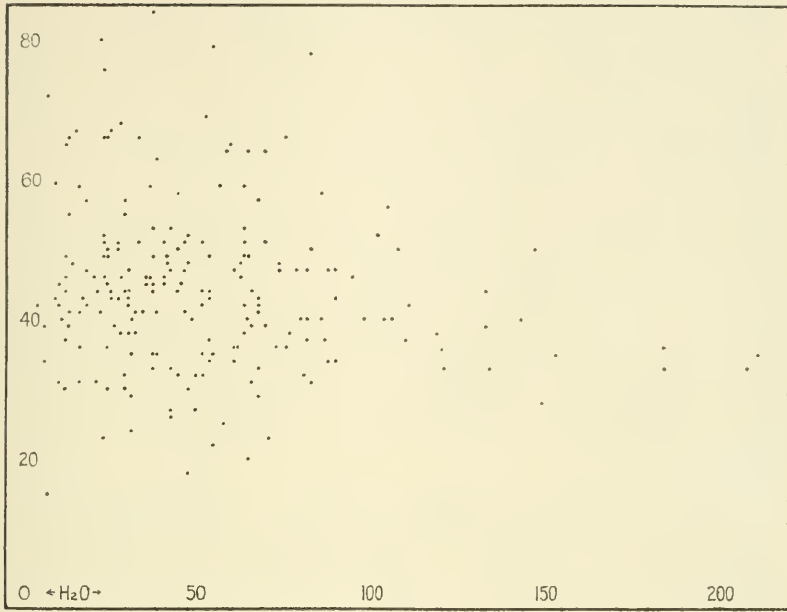


FIG. 4.—Abscissae, ppt. H<sub>2</sub>O; ordinates O<sub>3</sub>; 0.47 to 0.60 $\mu$ .

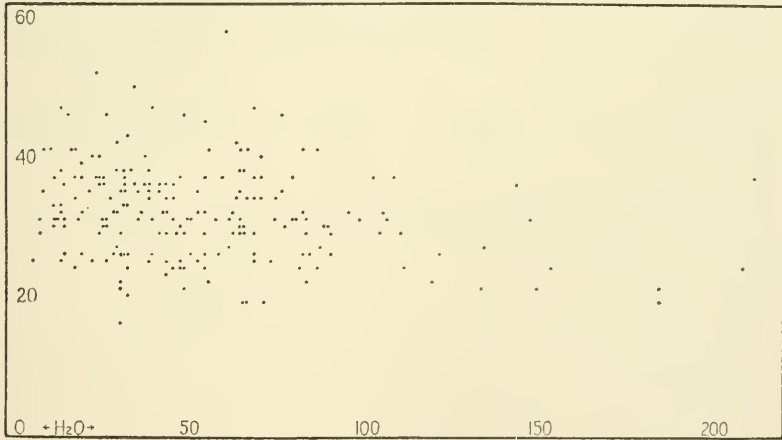


FIG. 5.—Abscissae, ppt. H<sub>2</sub>O; ordinates O<sub>3</sub>; 0.60 to 0.66 $\mu$ .

vapor comes considerably later in the year than that for the area-maximum of the band, yet before the time for its maximum.

A far more detailed study of the transmission coefficients in the region of this band has been made than was possible with the somewhat separated measurements in the spectrum made for the solar-radiation work. Plates for two days were reread and coefficients determined for each maximum and each minimum of the solar lines visible in the observed energy curves (fig. 6, curve *a*). Unfortunately, between deviations 20 and 22, and 27 and 28, such a process was impossible because of instrumental contingencies. The resulting coefficients determined independently for the two days of observations are plotted in curves *b* and *c*. This is a useful transformation, resulting, as it does, in a spectrum, *b* or *c*, showing only atmospheric lines, from an energy curve like *a* where the solar lines are dominant practically to the exclusion of any indication of atmospheric absorptions.

Assuming for the time being the validity of Bouguer's formula, a further step was taken. Entering figure 2 for the corresponding wavelength with the transmission coefficient determined at place 24 from the curve *c* of figure 6, the amount of ozone was determined. With this amount of ozone, and the transmission coefficients at all the maxima and minima of the curve in figure 2, an ozone band was computed, using the line across the top of the band in curve *c* of figure 6 as the basis. The result is plotted in curve *d* of figure 6. The agreement between *c* and *d* is better than could be expected and is indeed remarkable. Apparently because the writer is using a purer spectrum than Colange, the deflections in curves *b* and *c* are more marked than in curve *d*, but the agreement in position is satisfactory. Between deviations 26 and 30, the coefficients are too small to expect any accuracy. It seems therefore highly probable that practically all of this band as observed is due to ozone.

The writer, as already stated, prefers to express the results which follow in terms of a quantity fairly directly coming from the observations, namely, the amount of energy cut out from the incoming solar energy by this yellow Chappuis band. These results may be approximately reduced to amounts of ozone (ntp.) by using Bouguer's formula with the constant determined by Colange (*loc. cit.*) as indicated by the following table:

Band area .....	30	40	50	60	70	80	90	100	cal. $\times 10^{-4}$
Ozone .....	0.90	.160	.200	.230	.260	.290	.320	.350	cm. ntp.

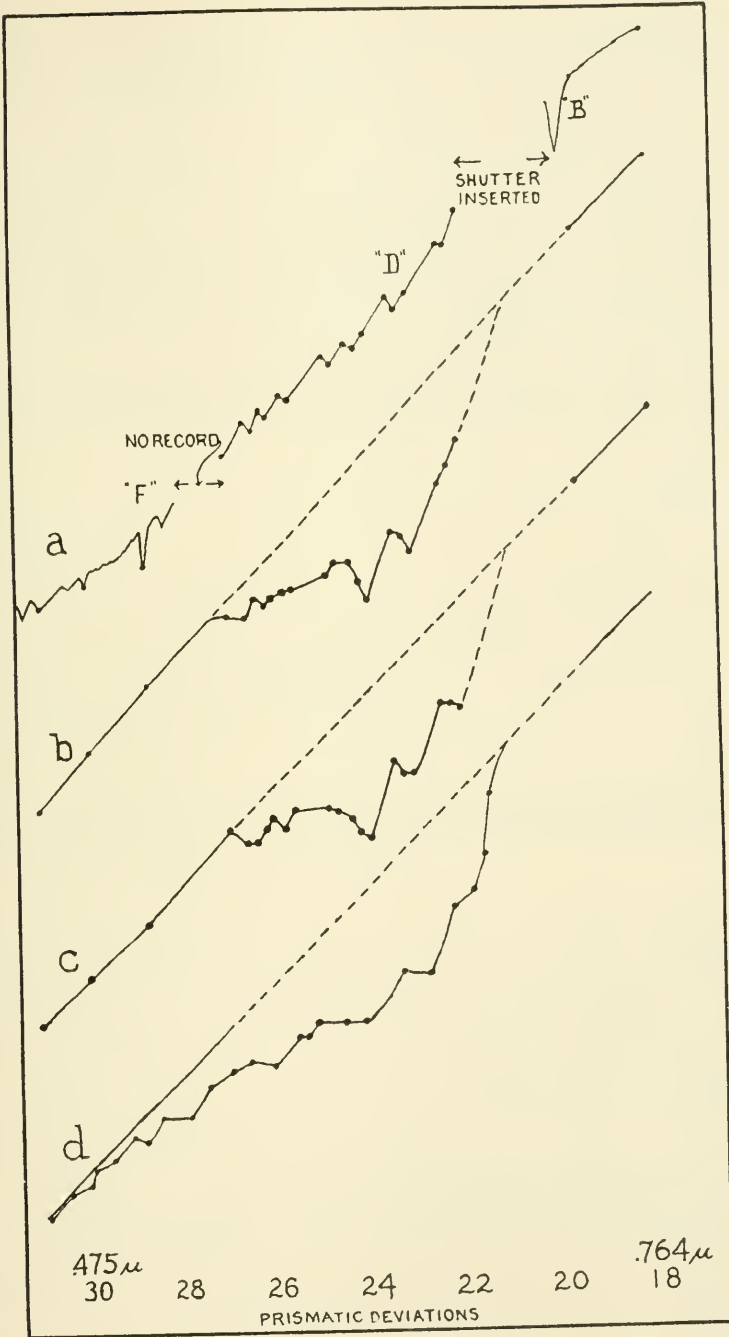


FIG. 6.

The use of Bouguer's formula is unsafe for banded absorptions, except possibly for a very pure spectrum, and as an interpolation formula. Langley<sup>1</sup> long ago showed its inapplicability in a region where quite different coefficients of absorption occur, and his logic is even more applicable in the present case where these occur in close juxtaposition, and in banded spectra where the resolving power is comparatively poor. Safer substitutes for Bouguer's formula may be employed. For instance, in estimating atmospheric precipitable water the writer always uses an absorption curve calibrated as far as possible in the laboratory. A curve approximately of the shape

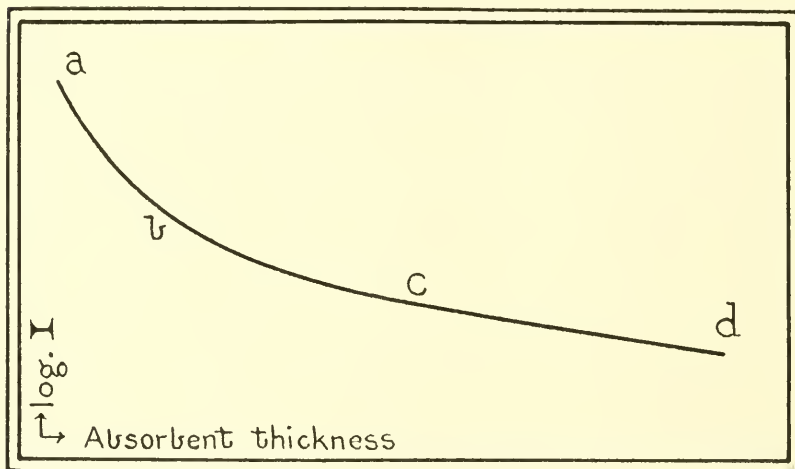


FIG. 7.

indicated in figure 7 would be expected. Where lines of strong absorption occur alternately with those of high transmission, the curve of figure 7 does not tend to approach a zero value of  $I$  with increasing absorbent, but to become horizontal for a finite value of  $I$ . Assuming Bouguer's formula to hold we should have a straight line, tangent to some portion of this curve. In view of the state of affairs indicated in figure 7, we should hesitate to use Bouguer's formula for computing the amounts of ozone, unless for data requiring very little extrapolation from the amounts of ozone used in the laboratory to determine the constant of the formula. It may be that these considerations explain certain discrepancies between Dr. Dobson's results

<sup>1</sup> Ann. Astrophys. Observ. Smithsonian Inst. 2, 16, 1908.

and mine at the same stations. He is working at a spectrum place where the coefficient  $a$  in the formula,

$$I = I_0 10^{-ax}$$

is very large, ranging from about 1 to 4. He is therefore probably working far down on the nearly horizontal portion of a curve such as is indicated in figure 7 where a large change in ozone makes a comparatively small change in the observed spectrum intensity values. On the other hand, in the Chappuis band used by the writer, the coefficient  $a$  is so small, about 0.04, that the band is very difficult to observe visually. Therefore we may assume that the writer is measuring in a band where a small change in ozone produces a great change in the observed quantity. In other words, for the amount of ozone present in the atmosphere, the Chappuis band is a more sensitive indicator of changes in atmospheric ozone than that employed by Dr. Dobson.

With these preliminary remarks, attention may be drawn to figure 8, in which recent observations made at Table Mountain with Dobson's apparatus, and reduced by him to cm. ozone ntp. are compared with the writer's results as expressed in areas of the Chappuis band. The average amount of ozone for this interval of time as computed by the preceding table from the writer's results is about 0.23 cm. ntp., while Dobson finds about 0.22 cm. The range of the variation found by the writer much exceeds that found by Dobson, but nevertheless a marked correlation exists between the two series.

The writer cannot leave Dr. Dobson's work without one further remark about his method. He states,<sup>1</sup> "It has been shown that there is a close connection between the amount of ozone in the upper atmosphere and the pressure conditions in the upper part of the troposphere and the lower part of the atmosphere," and states that, "it is remarkable that the ozone situated at so great a height" (40 to 50 km., as indicated by the results of Cabannes and Dufay, 30 to 40 km. by Dobson himself) should be so closely connected with variations of pressure much lower down."

Dr. Dobson<sup>2</sup> uses two methods in his evaluation of the amount of atmospheric ozone. In the first he takes as the general atmospheric transmission coefficient

<sup>1</sup> Proc. Roy. Soc. **120A**, 251, 1928.

<sup>2</sup> *Mo. Not. R. A. S.* **86**, 259, 1926. Proc. Roy. Soc. **110A**, 660, 1926.

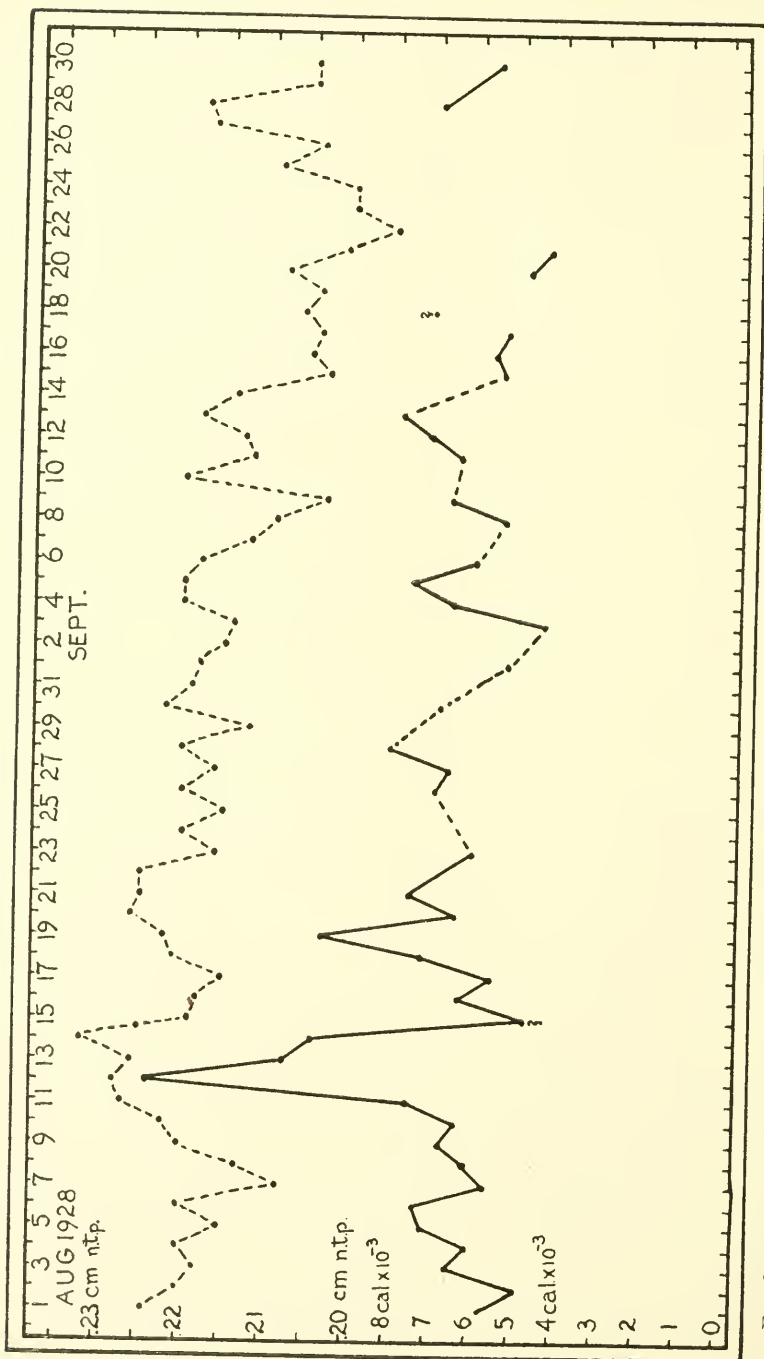


FIG. 8.—Upper dotted curve, Dr. Dobson's values for Table Mountain. Lower curve, the writer's values for Table Mountain.



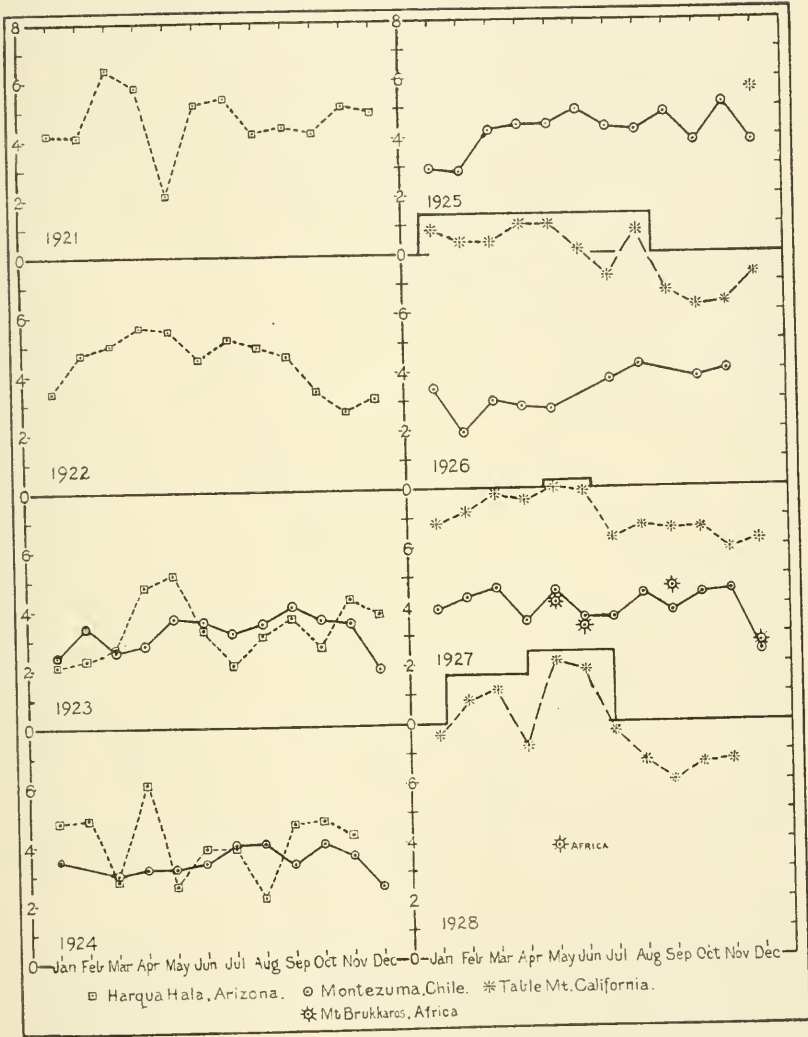


FIG. 9.

where

$$K = \beta + \delta + ax$$

$\beta$  is the absorption coefficient due to small particles,  
 $\delta$  is the absorption coefficient due to large particles,  
 $a$  is the absorption coefficient due to 1 cm. ozone ntp.,  
 $x$  is the thickness of ozone atmospheric in cm. ntp.

Now it seems to the writer that the very variations with atmospheric pressure which Dr. Dobson throws into  $x$ , belong fully as

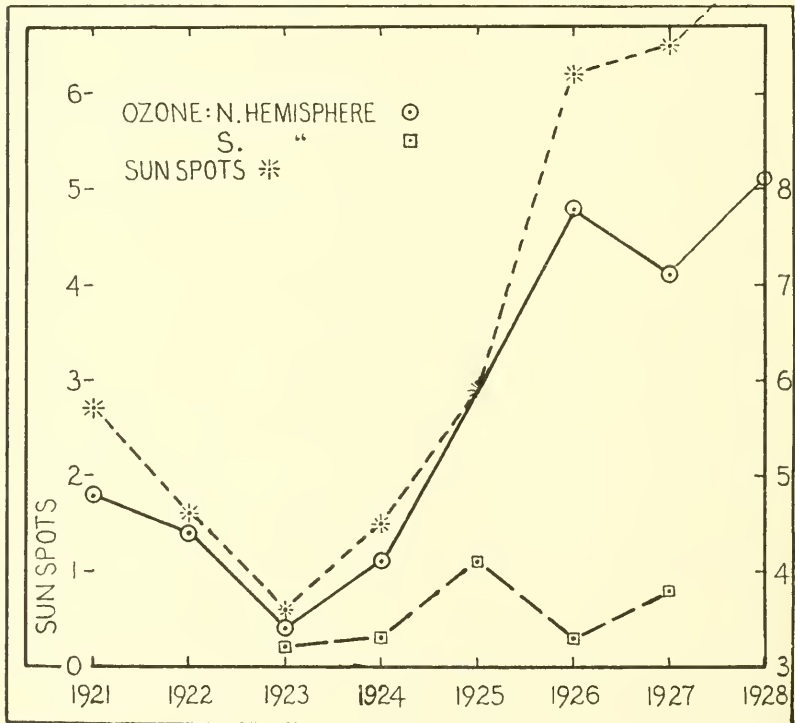


FIG. 10.

legitimately, and very probably, to both  $\beta$  and  $\delta$ . All this relates to what Dr. Dobson calls his "long method," dependent upon several observations during the day. In his second or "short method" he uses the expression

$$x = \frac{(\log I_o - \log I'_o) - (\log I - \log I') - (\beta - \beta') \sec z}{(a - a') \sec z}$$

In the determinations by this "short method" he assumes that  $\delta$  does not vary with  $\lambda$  and uses a value for  $\beta$  obtained from the formula

of Rayleigh. Although both these assumptions may be allowable up to a certain accuracy it seems likely that from either of them a variation dependent upon the atmospheric pressure or water vapor may have been introduced.

Let us now turn to the results of observations made at Harqua Hala (altitude 1,770 m.) and Table Mountain (2,300 m.) in the United States of America, Montezuma (2,900 m.) in Chile, and Mt. Brukkaros (1,600 m.) in Africa, embodied in the following table and figures 9, 10, and 11. The table gives only the monthly and

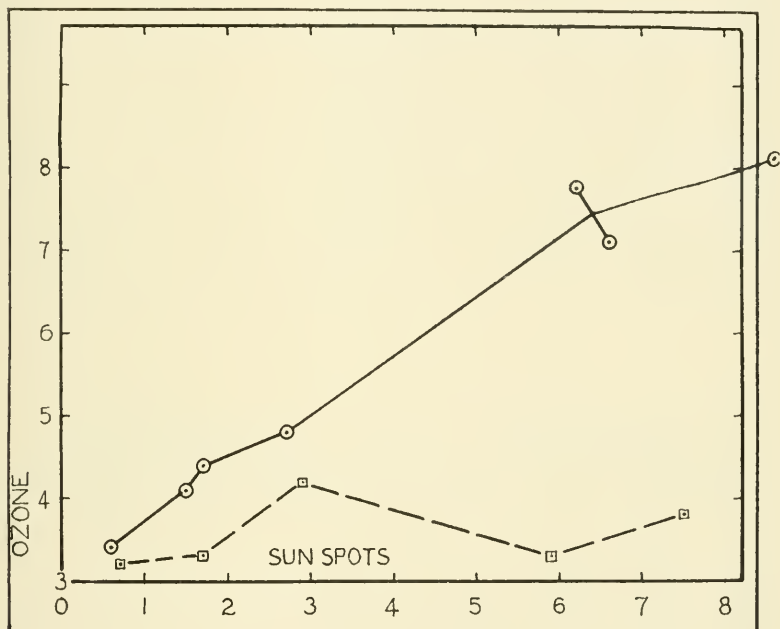


FIG. 11.

yearly means; hence the plotted points, especially in the plots of yearly means, figures 10 and 11, depend upon a considerable number of day's observations but not always every successive day. The Wolfer spot numbers and the magnetic character values here given are computed employing only the days of radiation observations. In my preliminary paper, already referred to, the plots related to daily values, and even with the few values there utilized from the 1926 and 1927 observations at Table Mountain, showed a distinct correlation between the ozone, the spot numbers, the magnetic character and the flocculi for the corresponding days.

## THE OBSERVATIONS

Harqua Hala, 1921					Harqua Hala, 1922				
Month	No. obs.	Ozone area	Wolfer spots	Magn. ch.	Month	No. obs.	Ozone area	Wolfer spots	Magn. ch.
Jan.	9	42	27	0.6	Jan.	8	34	11	0.7
Feb.	14	41	31	.4	Feb.	5	47	23	1.0
Mar.	11	64	51	.8	Mar.	5	50	81	.9
Apr.	7	58	16	1.0	Apr.	5	56	15	1.0
May	3	34	45	1.1	May	7	55	8	.7
June	7	52	27	.4	June	7	45	4	.7
July	1	54	100	.5	July	4	52	18	.4
Aug.	4	42	20	.9	Aug.	2	49	11	.2
Sept.	13	44	18	.3	Sept.	3	46	6	.8
Oct.	11	42	17	.7	Oct.	4	34	4	.8
Nov.	5	51	18	.6	Nov.	3	27	4	.1
Dec.	4	49	14	.3	Dec.	4	31	10	.2
Year	89	48	27	0.6	Year	57	44	17	0.7

Harqua Hala, 1923					Montezuma, 1923				
Month	No. obs.	Ozone area	Wolfer spots	Magn. ch.	Month	No. obs.	Ozone area	Wolfer spots	Magn. ch.
Jan.	6	21	5	0.4	Jan.	2	24	10	0.9
Feb.	3	23	2	.3	Feb.	4	34	2	.6
Mar.	4	27	8	.7	Mar.	10	26	3	.4
Apr.	4	48	7	.6	Apr.	12	28	7	.4
May	5	52	2	.5	May	7	37	3	.5
June	3	33	10	.8	June	14	36	13	.4
July	1	21	0	1.4	July	6	32	2	.4
Aug.	3	31	3	.5	Aug.	4	35	2	.4
Sept.	2	37	10	.8	Sept.	5	41	10	.4
Oct.	3	27	12	.4	Oct.	4	36	8	.5
Nov.	1	43	7	.7	Nov.	3	35	9	.8
Dec.	2	38	0	.1	Dec.	2	19	0	.6
Year	37	34	6	0.5	Year	73	32	7	0.6

Harqua Hala, 1924					Montezuma, 1924				
Month	No. obs.	Ozone area	Wolfer spots	Magn. ch.	Month	No. obs.	Ozone area	Wolfer spots	Magn. ch.
Jan.	4	48	2	0.9	Jan.	4	35	0	0.5
Feb.	3	49	7	.2	Feb.	..	..	..	..
Mar.	2	28	0	.5	Mar.	4	30	0	.8
Apr.	1	61	0	.2	Apr.	4	32	10	.3
May	3	26	14	.8	May	4	32	22	.7
June	7	39	18	.7	June	4	34	22	.4
July	4	39	9	.8	July	4	40	25	.6
Aug.	1	22	11	.1	Aug.	5	40	11	.1
Sept.	3	47	19	.6	Sept.	4	33	22	.5
Oct.	5	48	25	.6	Oct.	4	40	26	.6
Nov.	3	33	31	.7	Nov.	5	26	22	.6
Dec.	..	..	..	..	Dec.	14	25	21	.4
Year	36	41	15	0.6	Year	56	33	17	0.5

Montezuma, 1925					Table Mountain, 1926				
Month	No. obs.	Ozone area	Wolfer spots	Magn. ch.	Month	No. obs.	Ozone area	Wolfer spots	Magn. ch.
Jan.	10	29	6	0.5	Jan.	16	88	69	0.9
Feb.	3	28	15	.5	Feb.	11	84	68	.6
Mar.	17	42	22	.4	Mar.	15	84	50	.8
Apr.	13	44	29	.5	Apr.	14	90	38	.8
May	13	44	38	.4	May	24	90	68	.6
June	14	49	24	.8	June	18	81	74	.5
July	7	43	37	.3	July	23	72	57	.5
Aug.	2	42	19	.8	Aug.	22	88	62	.5
Sept.	4	48	63	.9	Sept.	28	67	62	.7
Oct.	3	38	43	.7	Oct.	24	62	66	.6
Nov.	2	51	54	.8	Nov.	9	63	50	.5
Dec.	2	38	76	.4	Dec.	7	73	80	.4
Year	90	42	29	0.5	Year	211	78	62	0.7

Montezuma, 1926					Table Mountain, 1927				
Month	No. obs.	Ozone area	Wolfer spots	Magn. ch.	Month	No. obs.	Ozone area	Magn. ch.	Wolfer spots
Jan.	1	34	84	0.7	Jan.	2	68	72	0.4
Feb.	1	19	162	1.2	Feb.	4	72	80	.8
Mar.	2	30	38	.9	Mar.	4	78	87	.5
Apr.	4	28	43	.9	Apr.	5	76	87	.8
May	2	27	38	.6	May	5	80	79	.4
June	..	..	..	..	June	4	79	65	.3
July	3	37	34	.6	July	3	63	40	.1
Aug.	2	42	61	.4	Aug.	12	67	51	.8
Sept.	..	..	..	..	Sept.	6	66	60	.8
Oct.	3	37	82	1.2	Oct.	5	66	60	.7
Nov.	2	40	73	.5	Nov.	6	59	66	.4
Dec.	..	..	..	..	Dec.	2	62	36	1.0
Year	20	33	59	0.8	Year	58	69	65	0.6

Montezuma, 1927					Table Mountain, 1928				
Month	No. obs.	Ozone area	Wolfer spots	Magn. ch.	Month	No. obs.	Ozone area	Wolfer spots	Magn. ch.
Jan.	1	39	77	1.5	Jan.	16	76	70	..
Feb.	1	43	82	1.0	Feb.	11	87	79	..
Mar.	1	46	131	.2	Mar.	19	92	93	..
Apr.	4	35	86	1.2	Apr.	12	72	83	..
May	3	45	93	.2	May	20	101	73	..
June	3	36	86	.1	June	25	98	93	..
July	3	36	52	.3	July	20	77	102	..
Aug.	3	44	44	.8	Aug.	31	67	83	..
Sept.	2	38	90	.6	Sept.	18	60	79	..
Oct.	2	44	68	2.0	Oct.	18	66	..	..
Nov.	3	45	61	.1	Nov.	14	67	..	..
Dec.	2	24	65	.7	Dec.	..	..	..	..
Year	28	38	75	0.7	Year	204	81	85	..

From the data of the preceding table and the corresponding figures several phenomena are notable :

(1) There is a very decided yearly march, as has been noted by other observers.

(a) In the northern hemisphere we may take the maximum and minimum of this march as follows :

Maximum	Minimum
1921 March <sup>1</sup>	Sept.
1922 March	Nov.
1923 April-May	Aug. ?
1924 April	Aug. ?
1925 (April, Dobson)	(Oct., Dobson)
1926 April-May	Oct.
1927 April-May (April, Buisson)	Nov. (Nov., Buisson) <sup>2</sup>
1928 May	Sept.

(b) and in the southern hemisphere as follows :

Maximum	Minimum
1923 Sept.	March
1924 Aug.-Sept.	March
1925 ?	Feb.
1926 Aug.	April ?
1927 not definite	not definite.

whence :

(2) In the yearly march the maxima and minima occur at nearly the same seasons of the year in the northern and southern hemispheres, though of course not in months of the same name. The maxima occur between April and May, the minima between August and November in the northern hemisphere and vice versa approximately in the southern.

(3) A marked correlation exists between the ozone and the Wolfer sun-spot numbers for the observations of the northern-hemisphere stations, as indicated in figures 10 and 11. The range of the yearly means for the area of the yellow band is from 20 to 100 (see fig. 9).

<sup>1</sup> The writer is inclined to discount the appearance of the low value in May, 1921, as abnormal, possibly due to erroneous observing, and to consider the general march of the curve as indicating the minimum in September. Somewhat similar judgments occur later in the table.

<sup>2</sup> C. R. 186, 1229, 1918.

(4) In the southern hemisphere no such strong correlation is apparent between the spot numbers and the ozone. The corresponding range is only from 20 to 30. However the errors of the readings of the area when this is small are comparatively great; indeed the observations do hint a slight relationship.

The writer suggests that the following considerations point to a fifth deduction from the observations.

The ozone present in the upper air has been generally considered as formed from the oxygen there present by the action of ultra-violet light from the sun. Radiation of very short wave-length (less than  $0.1850\mu$ ) acts upon oxygen, transforming it into ozone. It is not improbable that radiation of this wave-length reaches the earth from the sun. If so, it must produce ozone in the earth's atmosphere, but only in the *highest* levels, because it cannot reach the lower strata. Radiation of wave-length  $0.1850\mu$  is completely absorbed by 10 m. of air at ntp., and could scarcely penetrate lower than a stratum 40 km. above the earth. On the other hand, radiation lying between  $0.2000$  and  $0.3000\mu$  decomposes ozone, and between these two opposite actions a state of equilibrium would be established. Since the ozone-destroying wave lengths penetrate deeper into the atmosphere, this naturally limits the ozone layer to a high altitude.

It is possible though that another agency than ultra-violet light works to produce ozone. The investigations of Milne<sup>1</sup> and Pike<sup>2</sup> indicate the great probability that electrified particles gain such velocities on the sun that they are projected outwards into space from that body. Mme. Curie<sup>3</sup> has shown that the  $\alpha$ -particles emitted from radium salts ozonize oxygen. Electrons with a velocity of  $1.80 \times 10^8$  cm./sec.<sup>4</sup> are capable of producing ozone from oxygen. It is also produced by the silent electrical discharge.

Suppose then that there are two causes at work producing the ozone of the earth's atmosphere: One portion may then be due to the ultra-violet light from the sun, and present over both hemispheres; the other, caused by particles emitted from the sun of such a polarity that, when they reach the earth's field, they drift towards the northern hemisphere, above which alone would the ozone due to this last cause be abundantly present. The particles would then necessarily have a positive charge, *e. g.*,  $\alpha$ -particles.

<sup>1</sup> Mo. Not. R. A. S. **86**, 259, 1926.

<sup>2</sup> Mo. Not. R. A. S. **88**, 3, 1927.

<sup>3</sup> C. R. **183**.

<sup>4</sup> Franck and Hertz, Verh. Deutsch. Phys. Ges. **15**, 34, 1913.



With the assumption of these two sources for the origin of the atmospheric ozone, several of the phenomena shown by the observations of this paper fall in line, and our fifth conclusion will be:

- (5) (a) Due to the ultra-violet light from the sun, there is a layer of ozone, varying apparently very little with the sun-spot period, and situated over both the northern and southern hemispheres and showing an annual march having its maximum in the spring of both hemispheres and its corresponding minimum in the autumn.
- (b) There is another layer formed under the bombardment of electrical particles (probably positive ions) emitted from the sun and showing strongly a dependence upon solar activity as indicated by Wolfer's sun-spot numbers. At the only minimum of spots observed this layer appeared practically absent, the measurements indicating the presence of the (a) layer alone.

Though the corresponding marches during the year of the ozone (which the writer proposes to attribute to the first of the above causes) occur in different months in the two hemispheres, the seasons of maximum and minimum are the same, namely, spring and autumn. One might be led to suppose that these variations are due to some dependence upon the annual and reciprocal marches in the two hemispheres of the air-masses through which the sun's rays could penetrate for the formation of ozone. Further at the tropical station at Montezuma the sun is more nearly overhead and the air-mass change smaller, which might perhaps account for the smaller annual range there. However the maxima and minima do not occur at times when the sun is farthest from or nearest to the zenith, when there would be the greatest and least air-masses.

Another circumstance might lead to an explanation of the annual march and its reciprocal effect in the two hemispheres so far as concerns the times of occurrence of the maxima and minima. Annually, as viewed from the earth, the sun's equator reaches its greatest southern displacement ( $7.25^\circ$ ) about March 7, and its greatest northern displacement about September 8. The aspect of the sun's disk as seen from the earth at these epochs is shown in figure 12. Since the earth subtends only about  $30'$ , as seen from the sun, under either circumstance, the sun would have practically the same aspect as viewed by ultra-violet light from either the northern or southern hemispheres of the earth. However, the ultra-violet light would probably be strongly scattered by the particles of the solar corona, and this annual shift of the far more extensive and considerably

more oblate corona might have a differential effect on the intensity of the ultra-violet light reaching the separate hemispheres.

Returning again to Dr. Dobson's results, he finds much the same values in both hemispheres. He now has an observer in New Zealand (1928).<sup>1</sup> He states<sup>2</sup> that he finds very little connection of his observations with the sun-spot cycle, and that little apparently in a reverse sense from that *clearly* indicated by the writer's results. He obtains an altitude for his ozone layer from the Hartley band at 30 to 40 km., whereas Cabannes and Dufay get an altitude from the

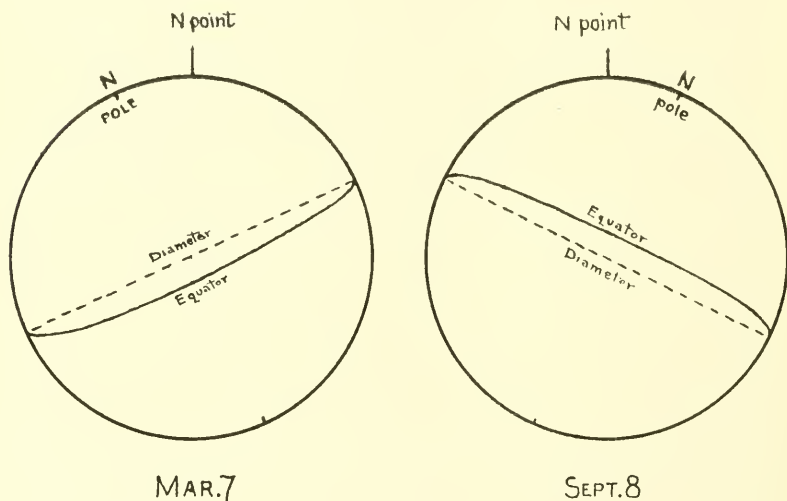


FIG. 12.

Huggin's band of 40 to 50 km. One might hazard the suggestion that it is not beyond possibility that the band used by Dr. Dobson corresponds to such a state of the molecule that only ozone formed by ultra-violet light is in the proper molecular state to effect absorption; whereas the band in the yellow is due to a molecular state which measures absorption due to ozone formed by either process. It will presently be seen how such supposition as to two layers of ozone is in line with the conclusions drawn from magnetic data relating to two separate strata, the lower of which is assumed to be due to ultra-violet light.

<sup>1</sup> Observatory, 51, 381, 1928.

<sup>2</sup> Proc. Roy. Soc. 114A, 532, 1927.

Turning to the literature of Terrestrial Magnetism, the writer was both surprised and pleased to find decided support lent by the phenomena of terrestrial magnetism to this hypothesis of two quantities of ozone formed by two separate agencies. Furthermore, these two layers were not only ascribed to the same two agencies as already stated, but assumed to be probably separate layers.

If we consider magnetically quiet days, we find a similar yearly march in the magnetic elements, the maxima and minima, however, occurring somewhat later, namely, in June and December at Greenwich; and further a regular march with the sun-spot period. This march is so regular as to lead to the inference that it is due to a general change in the whole solar disk accompanying the sun-spot period. Further there occur disturbed days which seem to be connected with specially disturbed conditions localized on the sun's disk, for they show a definite tendency to recur at successive rotations of the sun's disk.<sup>1</sup>

"There are few facts of greater significance," writes Dr. Chapman, "with respect to the relation between magnetic changes and the sun, than the tendency shown by the earth's magnetic activity to return to its condition at any particular time, after the lapse of one or more periods of synodic rotation of the sun."

There are discordances between the succession of events with the ozone phenomena and those that are magnetic, so that the events may be confused with complications not due to the same cause, but the following discussion by Dr. Chapman (*loc. cit.*) seemed of special interest:

"These conclusions regarding the 'disturbance' solar agent have a direct bearing on the 'general' solar agent which affects the regular diurnal magnetic variations over the sunlit hemisphere. If the former consists of electrical corpuscles, the latter cannot do so—no mere difference of mass or sign of charge would account for the complete difference of distribution of the two agents reaching the earth. On the other hand, the apparently sole alternative among possible ionizing agents, viz., ultra-violet light, seems to accord with all the properties which the 'general' solar agent has been shown to possess: for the latter affects the sun-lit hemisphere almost exclusively, it arises from the sun's surface as a whole, and its intensity varies only gradually, from time to time, in correspondence with the general activity of the sun."

<sup>1</sup> Dr. Chapman, Trans. Cambridge Phil. Soc. 22, 341, 1919.

And he later continues, "The facts hitherto reviewed may next be considered in their bearing upon atmospheric questions. One such question is, Are the layers affected by the two kinds of solar emissions the same or different, and if different, what is their relative situation?"

"Even, *a priori*, it would be expected that two such different emissions as corpuscles and ether waves will have different powers of penetration into the atmosphere, though it would not be possible, on such grounds alone, to decide whether the 'absorbing' layers were wholly distinct or not. The magnetic phenomena, however, give a fairly clear indication that they are practically distinct without overlapping \* \* \*," and he reaches the conclusion "that the magnetic disturbance layer is situated at a higher level than the diurnal variation layer." He infers from this that the magnetic disturbance layer (due to ions from the sun) is situated between 90 and 120 km. and the diurnal variation layer (due to ultra-violet light), between 10 and 90 km.

Dr. Chapman has added a note dated July, 1919: "In a paper read (on May 22, 1919) before the Institution of Electrical Engineers, and shortly to be published, I have suggested that the ultra-violet radiation \* \* \* may be some type of gamma-radiation, and that the corpuscles are (as Vegard has urged) alpha-particles. If both these processes originate from radio-active processes on the sun, the gamma-rays would be expected to penetrate more deeply into our atmosphere than the alpha-particles." All of which falls in with the observations and suggestions of the present paper.

Lord Rayleigh<sup>1</sup> has recently published observations which relate to a phenomenon possibly allied to that of ozone. These observations are measurements of the intensity of the auroral green line in the light of the night sky together with similar measurements of the intensity in the spectrum of the night sky on each side of this line. McLennan<sup>2</sup> has shown that this green line owes its existence to a metastable state of the oxygen atom. Whereas the green line is always present in the light of the night sky, the negative bands of nitrogen

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<sup>1</sup> Proc. Roy. Soc. **119A**, 11, 1928.

<sup>2</sup> Nature, **122**, 38, 1928.

which are an important feature of the auroral spectrum, are not usually present.

Rayleigh's observations (fig. 13) apparently indicate an annual march in the intensity of this green line with two maxima—the smaller maximum occurring nearly contemporaneously with the single maximum in the ozone march, the larger with the ozone minimum. In the southern hemisphere, as with ozone, the months of the occurrence of these maxima are reversed but, of course, not the season.

Omitting observations made at Claremont which Rayleigh considers faulty, together with those for some stations with only few observa-

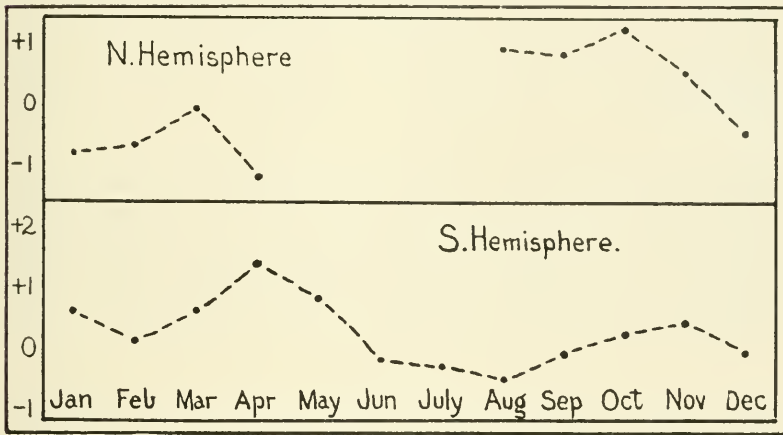


FIG. 13.—Lord Rayleigh's observation on Aurora green line. The gap in the northern hemisphere results is due to the impossibility of observations during these months in England because of twilight.

tions the following table was formed. The values given relate to a comparison of night sky observations with a standard source of light. For details the reader is referred to Lord Rayleigh's article. The scale units are such that in passing up one unit the intensity is multiplied by the anti-logarithm of 0.1 or 1.259; three steps on the scale are equivalent to a factor  $(1.259)^3$  or approximately a doubled intensity. The presentation is different from that of Rayleigh so as to separate the stations of the northern and southern hemispheres. It indicates that the auroral line averages of greater intensity in the northern hemisphere while the parts of the spectrum on either side show no such difference.

Place, latitude longitude	No. obs.	Time range	Mean intensity			
			Red	Auroral green	Blue	
Lerwick	+60° 1° W	86	Sept. '25-Apr. '27	-2.8	+0.6	+5.7
England	52 1 E	81	Nov. '25-Oct. '26	-2.5	+0.5	+6.4
Kingston	44 77 W	6	Apr. '26-May '26	+0.1	+2.3	+9.5
Victoria	40 123 W	108	Sept. '25-Mar. '27	-3.2	+0.8	+6.3
Mt. Wilson	34 117 W	83	Sept. '25-Feb. '27	-2.9	+1.1	+6.8
Hawaii	19 150 W	116	Oct. '25-Nov. '26	-3.2	+0.3	+6.5
Kodaikanal	10 77 E	54	Oct. '25-Jan. '27	-2.8	-0.1	+6.2
Gilgil	0 37 E	5	Sept. '25	-2.7	+1.5	+6.6
Northern mean				-2.5	+0.9	+6.7
Cape	-34° 18° E	199	Nov. '25-Nov. '26	-2.7	+0.7	+7.1
Arequipa	16 71 W	31	Apr. '26-Nov. '26	-3.1	-0.3	+6.5
Canberra	35 149 E	149	Mar. '25-Oct. '26	-3.2	+0.4	+6.5
Christ Church	44 73 E	56	Feb. '26-Feb. '27	-1.0	+0.4	+7.0
Southern mean				-2.5	+0.3	+6.8

Before summarizing the results of this paper, the writer wishes to express his appreciation of the criticisms of Dr. Abbot, and the aid furnished by Miss Margaret Marsden and Mr. Hugh Freeman in the many computations, as well as his indebtedness to the workers in the field whose observations made possible this discussion.

#### SUMMARY

The amount of energy absorbed from the incoming solar radiation by the yellow ozone band has been used to measure the variations in the amount of atmospheric ozone during the years from 1921 to 1928. These observations have been made in both the northern and the southern hemispheres.

The resulting values show a distinct yearly march in both hemispheres. In the northern hemisphere the maxima of this march occur between April and May, the minima between August and November; in the southern hemisphere the maxima occur between August and September, the minima between April and May. In other words in both hemispheres the maxima occur in the spring, the minima in the autumn.

In the northern hemisphere a marked relationship exists between the ozone and the Wolfersun-spot numbers. The range in the monthly mean values for the ozone numbers is great and between  $20 \times 10^{-4}$  and  $100 \times 10^{-4}$  calories absorbed per  $\text{cm}^2$  per minute from the incoming solar energy.

In the southern hemisphere no such marked relationship is noted, although one may be masked by the small range and corresponding inaccuracy in the values. The range is only from  $20 \times 10^{-4}$  to  $50 \times 10^{-4}$  calories.

It is suggested—and such a suggestion is strengthened by magnetic data—that we are dealing with two layers of ozone. The first is due to ultra-violet light coming from the sun and hence existing over all the stations. The second is assumed to be due to positively electrified particles emitted from definitely disturbed areas of the sun. This second effect reasonably shows a strong correlation with the Wolfer sun-spot numbers. Probably because these positive particles are deflected towards the earth's north pole this layer of ozone is found over the northern hemisphere stations only. At sun-spot minimum it is negligible so far as the present measurements indicate.

All the results of the present paper are based on monthly and yearly means. A consideration of the daily values would be another story. The plot published in the preliminary paper was based on daily values for only two years at Table Mountain. The short study then made of the daily values would indicate that what may be said of the connection between many magnetic values and solar disturbances may be said of ozone; that although with monthly and yearly averages, solar spottedness, for example, goes hand in hand with the amount of ozone, yet a day of many spots may pass with no increase of ozone and vice versa.