The Abundance of O^{18} in Atmospheric Water and Water Vapour

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(Manuscript received June 10, 1953)

Abstract

Investigations into the O^{18}-abundance in the precipitation from a warm front reveal a distinct process of fractionation explainable by the unequal pressures of the saturated vapours of H_2O^{16} and H_2O^{18}.

An explanation is given of the low O^{18}-abundance in glacial waters.

A method of experimental investigation into the mechanism of the process of precipitation is discussed.

Research upon the abundance in nature of the heavy oxygen isotope, O^{18}, has been carried on persistently for several years. Before World War II the most important method of measurement was by density tests made on water. Of late, however, excellent mass-spectrometers have become available, and these have made it possible through a relatively simple measuring technique to achieve an equally good reproducibility as by the density tests; and it is possible, moreover, by a suitable procedure to obviate the correction for the deuterium content in the water —a not inconsiderable correction, which is lacking in several of the density tests published in the relevant literature.

The O^{18} tests on water, recorded in this paper, were made with a mass-spectrometer of the Nier type (*1*). For technical reasons, e.g., owing to the vacuum, it is not possible to introduce the water directly into the apparatus. It is necessary, therefore, either to electrolyze the water and introduce the oxygen—a process which is not quite satisfactory, because of the undesirable action of the pure oxygen on the filament of the ionic source—or to shake the excess of water with carbon dioxide, as in the tests here under discussion. According to COHN and UREY (*2*), oxygen atoms are exchanged between CO_2 and H_2O, to the effect that equilibrium

$$CO_2^{16} + H_2O^{18} \rightleftharpoons CO^{16}O^{18} + H_2O^{16}$$

is achieved after the lapse of 3 hours. Next, the O^{18}-abundance in the carbon dioxide is measured and made equal to the O^{18}-abundance in the water multiplied by the coefficient of equilibrium of the process stated above, which at 25° C is equal to 1.080. From this the abundance of O^{18} in the water is computed. In similar manner the abundance of O^{17} may be found, though this is rarely of any significance. It is proved that the abundance of the three oxygen isotopes

$$O^{16} : O^{17} : O^{18} = 99.76 : 0.04 : 0.20\ \%,$$

depending to some extent on the origin of the water. Technically it is of importance that one never is faced with the need to measure these absolute values directly but only to determine differences, e.g., between O^{18}-abundances in two different samples of water. The absolute values can be found by determining the difference between the sample and a standard of known O^{18}-abundance. Difference tests on samples with O^{18}-abundance approximating the normal value of 0.20 % show a reproducibility of ± 0.0001 %.

DOLE, VROOMAN, a.o. (3, 4, 5) have determined the relative O^{18}-abundances in atmospheric air and water of various origins. The tests are set out in Table 1, where the O^{18}-abundance in the fresh water from Lake Ontario is made equal to 1.000.

Table 1

	O^{18}-abundance		Ref.
	relative	%	
Water:			
Fresh water, Lake Ontario	1.000	0.1972	(5)
Atmospheric water vapour from above Lake Ontario	0.991	0.1954	(5)
Glacier water, Lake Louise	0.977	0.1927	(5)
Dead Sea water	1.020	0.2011	(5)
Ocean water	1.009	0.1990	(4)
Air:			
Atmospheric oxygen.....	1.033	0.2033	(3)
Atmospheric carbon dioxide	1.040	0.2053	(5)

The variations in O^{18}-abundance, given expression in Table 1, are explainable principally through the fact that the ratio of the pressures of the saturated vapours of H_2O^{16} and H_2O^{18}, p_0^{16} and p_0^{18}, is more than 1. By experiment, RIESENFELD and CHANG (6) have determined p_0^{16}/p_0^{18} as:

$$\log_{10}(p_0^{16}/p_0^{18}) = 2.74/T - 0.0056 \qquad (1)$$

where T is the absolute temperature. In Fig. 1 (1) is plotted in a graph. At the temperature of 0° C $p_0^{16}/p_0^{18} = 1.01$. Conversely p_0^{18}/p_0^{16} is within the same temperatures approximately 0.99. This means that the O^{18}-abundance in vapour is obtainable ay multiplying with 0.99 the O^{18}-abundance in the water in equilibrium with the vapour. This directly explains,

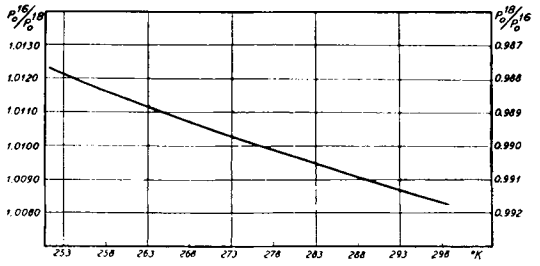

Fig. 1. The ratio of the pressures of the saturated vapours of H_2O^{16} and H_2O^{18}, p_0^{16}/p_0^{18}, plotted against the absolute temperature T.

first, why the O^{18}-abundance in the water vapour above the Lake Ontario is about 1 % less than in the water from the lake proper; second, that in fresh water, mainly a condensation of ocean water vapour, the O^{18}-abundance is about 1 less % than in ocean water; and third, that it is a fact, obviously, that the Dead Sea, where the affluent water is exclusively compensated by the high rate of evaporation, will attain a very high O^{18}-abundance. On the other hand, the low value for the Glacier water is not immediately explainable in a similar way.

Information on precipitation is sparse. HARADA and TITANI (7) have recorded that by observations on rains of long duration the density was higher in the beginning than at the end, and that snow-water is somewhat lighter than rainwater. RIESENFELD and CHANG (8) explain this phenomenon by equation (1), assuming that the O^{18}-abundance in the snow is equal to the O^{18}-abundance in the vapour, and that the latter value is dependent on the temperature of evaporation only. However, the variations mentioned in this paper with reference to the O^{18}-abundance in the precipitation exceed by several times the magnitudes that can be explained exclusively from the assumptions made by RIESENFELD and CHANG.

TEIS (9) found the following variations in the density of rain falling within the same period:

Time	cc	Δ d(γ/cc)
12^h00—13^h15	75	+ 0.4
13^h15—14^h30	150	− 2.3
14^h30—15^h45	75	− 2.3
15^h45—18^h15	60	− 2.3
18^h15—19^h15	40	− 0.3

Although it is not possible to distinguish between the H^2- and O^{18}-variations the results indicate a decrease in the O^{18}-abundance in the beginning and in contradistinction to the results obtained by Harada and Titani, and increase towards the end of the period.

A certain kind of precipitation frequently occurs at the so-called warm front. So far, no explanation in detail of the mechanism of this process can be given with any certainty. However, in principle, it so occurs that warm and humid air (Fig. 2) flows upwards over

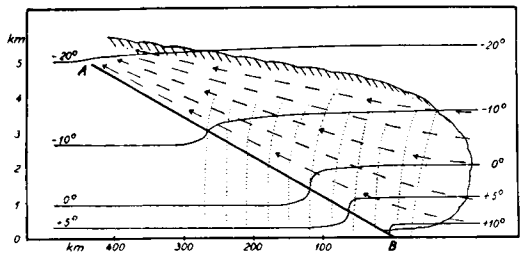

Fig. 2. Vertical section perpendicular to a warm front.

relatively cold air and is chilled so that some of its vapour is condensed. In the case of a cold front the cold air glides forward under the warm and humid air, which is carried aloft and chilled so that some of its vapour is condensed.

On June 22nd, 1952, a very strong warm front passed over the city of Copenhagen. In advance, some showers had fallen, and a cold front followed immediately upon the passage of the warm front. In the upper part of Fig. 3, plotted along the horizontal axis, are shown the atmospheric conditions prevailing at those times and in those places where the rainwater samples used in the present study were gathered. In the lower part of Fig. 3 the sections of the horizontal line indicate the time intervals within which precipitation occurred. The horizontal line-sections are set out above the time-axis at levels corresponding to the percentage excess of O^{18} in the precipitation in question compared with a certain standard. It will be seen that the rain showers which preceded the warm front show an excess of O^{18} of about 0.0023 ‰, whereas the rain from the upper part of the warm front is considerably lighter. Through the front (proceeding to the right in the figure) the O^{18}-abundance of the precipitation (hereinafter designated a_p) increases, and the rain falling at the point where the warm air commenced its upward motion is heavier even than the preceding showers of rain. On the arrival of the cold front a similar phenomenon occurs. However, because of the violent turbulence developed here, the conditions are so complicated that quantitative discussion is out of the question.

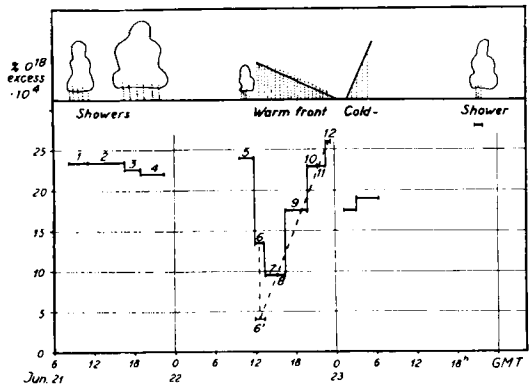

Fig. 3. The upper part shows weather conditions and structure of the atmosphere at the place and time of collections of rainwater for analysis. The horizontal line-sections in lower part of the figure indicate the time intervals during which precipitation occured. These sections are placed above the time-axis at distances which correspond to the percentage excess of O^{18} in the corresponding rainwater sample as compared with a certain standard.

Following the movement of the air upwards through the front, the drop in a_p (to the left in the figure) can be qualitatively explained through equation (1): The first rain, precipitated after the upward motion of the air had begun, according to (1), has a higher O^{18}-abundance than the vapour from which it was condensed. Hence, the remaining vapour has become lighter and the rain condensed therefrom is consequently lighter again than the first rain, and so on. There is, however, a slight increase in a_p in the rain originating from the topmost layers of the warm front. This might possibly be attributed to the fact that this rain had been subject to vigorous evaporation during the relatively long fall through the cold air.

This fact also goes to explain qualitatively the low figure for O^{18}-abundance in the glacier water, Table 1, as it may be assumed that this water exclusively came from high altitudes above the ocean surface, thus corresponding to the topmost part of the warm front.

This interpretation seems to be more likely than an earlier statement made in the literature where the low O^{18}-abundance is ascribed to an isotopic fractionation assumed to take place in the melting of the ice during which "the O^{16}-rich molecules, being the most energetic of the possible isotopic combinations, would be prevalent in the early fractions of the liquid phase" (SILVERMAN (*10*)). Regardless of the fractionation that may occur during the first part of the melting the water, for a

considerable period of time, must average an O^{18}-abundance equal to or higher than that of the precipitation, since accumulation of H_2O^{18} can not take place. The only reason possible for any difference between these two values must be ascribable to evaporation which would cause the O^{18}-abundance in the melting water to rise above that of the ice and the precipitation.

The explanation put forward in this paper find support in measurements of the O^{18}-abundance in six chunks of ice from Greenland glaciers. These chunks of ice, picked up from the sea, originated from the inland ice-cap, where the precipitation presumably falls at temperatures down to $-50°$C. The O^{18}-abundances relative to that of fresh water from lake Ontario were found be in the vicinity of 0.977 to 0.984 in good agreement with the value of glacial water given in Table 1. The ice investigated was taken from the central part of the chunks, which should preclude any possibility of exchange with sea water. Such exchange, otherwise, would contribute to an increase in O^{18}-abundance, which would also take place in the event of evaporation. Hence, the cause of the extremely low values must be looked for, exclusively, in the very great loss of moisture occurring in the air previous to the formation of the precipitation involved.

Before attempting a quantitative explanation of these conditions, it is necessary to consider more closely the mechanism of the warm front process: In the process of condensation primarily cloud droplets of diameter 10 μ are formed. From these droplets and/or from the vapour, rain drops of diameter 1 mm are formed. Observations indicate that at least in our latitudes precipitation is not likely to occur until the clouds have reached an altitude where the topmost part is at a temperature below $-10°$ C. Consequently, BERGERON (*11*) has assumed that at this temperature some ice-crystals are formed which, on account of the supersaturation of the surrounding vapour, would rapidly increase in size at the expense of the water droplets and in consequence drop down. There are, however, rain-clouds which do not extend above the 0°-isotherm, showing that rain drops can be formed in other ways than from ice-crystal-nuclei. FINDEISEN (*12*) and LANGMUIR (*13*) have investigated the possibility of producing rain drops through collisions of cloud droplets. If the droplets are not of equal size they are likely to collide in falling because of their differing velocities. It is probable, however, that a certain minimum size is required for a collision to result in the merging of two drops.

With regard to the first mentioned theory HOUGHTON (*14*) has calculated that the time required for an ice-crystal of diameter 20 μ tc grow by sublimation to a diameter of only 200 μ would be 5 to 10 minutes in the most favourable circumstances, and that it would require several hours for its growth to the size of a rain drop (diameter 1 mm). However, the same investigator (*15*) has also calculated the time required for a droplet of diameter 30 μ to grow exclusively by collision in air containing 20 μ-droplets of the order of 1 g/m^3. The result shows that 105 min. are required for the droplet to grow frow 30 μ to 20 μ,0 and only 18 min. to grow from 200 μ t theo diameter of 1 mm. From these facts Houghton concludes that it is most likely that the process of sublimation predominates in the beginning, and that the process of collision gradually assumes a greater role as the droplet or the crystal increases in growth. Since the volume increases directly with the third power of the diameter it may be concluded, further, that the greater part of the volume of water which reaches the ground as rain is formed by the process of collision.

On this basis, a picture of the formation of precipitation of the warm front, in best agreement with our present knowledge, may be drawn. Thus, AB in Fig. 2 represents the boundary between the warm air and the cold air, the warm air crossing from the right side upwards to the left side. When the cloud is chilled to slightly below the dew point (the humidity being about 102 %), the formation of cloud droplets begins. Apart from a very slow settling velocity due to gravity the cloud droplets will follow the course of the air. During the following upwards glide an increase in the number of cloud droplets occurs as a result of the continued cooling of the vapour, while a decrease in number occurs because some of the droplets either evaporate on to, or collide with, the heavier particles falling from above (ice-crystals, or else water drops). Most of the

precipitating particles develop near the −10° isotherm. At that level ice-crystals are formed which during the downward drop increase in size; to begin with mainly owing to diffusion and sublimation of the vapour which is highly super-saturated relative to ice. Later, when the particles have grown considerably, their further increase is mainly due to collisions with the surrounding cloud droplets. When the cloud is dense a rain drop may grow to such an extent that it becomes unstable and splits up into two or more drops. If the air below the boundary is relatively dry, a considerable evaporation of the rain drops will take place after their departure from the cloud.

On factor of importance to the O^{18}-abundance (a_p) in the rain is the relationship between the cloud droplets and the surrounding water vapour. On the surface of the droplet evaporation and condensation are constantly going on. These two processes mutually maintain equilibrium, if the size of the droplet remains constant. At all events, however, they will cause an exchange of water molecules between the vapour and the droplet. If this exchange is extremely rapid, the O^{18}-abundance in the droplet must correspond to that in the surrounding vapour. Whereas if the exchange is extremely slow the O^{18}-abundance in the droplet will correspond with that of the vapour at the place where the droplet was formed, i.e., because of the oblique movement of the droplet, at a considerably lower level of the front. In reality the exchange goes on at a final, probably not very high, rate and consequently a precipitating particle while falling will accumulate cloud drops with an O^{18}-abundance corresponding to that of the vapour which is still at a lower level than the precipitating particle. Fig. 4 shows hypothetical tracks of particles falling through a cloud. Owing to the fact that the tracks are diverted by the wind, especially while the precipitant particle is small, the lines drawn are not vertical. The curve *d* represent the course to be taken by certain precipitating particle in order to acquire the same O^{18}-abundance as that of an actual particle, supposing the exchange between the cloud droplets and the vapour to be complete and immediate. Thus the rain collected at *C* has followed the track of *c*, while its O^{18}-abundance is representative of the H_2O^{18}-value of the cloud along the track of *d*.

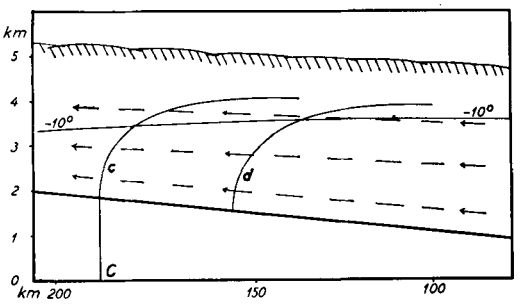

Fig. 4. Imaginary tracks of precipitant particles falling through a cloud.

In this connection it may be worth while to mention a method which, at any rate in principle, might permit us to determine what proportion of the precipitation is due to condensation and what proportion is due to collisions with cloud drops. At a certain locality in the cloud the O^{18}-abundance of the cloud droplets, the vapour and the rain drops are designated a_c, a_v, and a_p, respectively. Then a_c, according to the above, will be bigger than $1.010 \cdot a_v$ at 0° C. If the precipitation is formed exclusively through collisions, a_p will be equal to a_c. If a_p is less than a_c, the fraction, x, due to the condensation of vapour along the track, can be determined by the equation:

$$\left.\begin{aligned} & a_p = x \cdot 1.010 \cdot a_v + (1-x)a_c, \\ \text{or} \quad & x = \frac{a_p - a_c}{1.010 \cdot a_v - a_c} \end{aligned}\right\} \qquad (2)$$

Hitherto, technical difficulties by collecting separately water from cloud droplets, vapour and precipitant perticles have impeded an experimental determination of x.

Since, inter alia, x in equation (2) is unknown, a quantitative determination expressive of a_p is not possible. It is possible to solve the problem only by assuming that the distance between the tracks of *c* and *d* (Fig. 4) is 0. If so, the expression for a_p will be a function, first, of the O^{18}-abundance in the vapour before the upward glide starts ($a_p°$); second, of the average temperature

$$T_0 = \frac{1}{Q}\int t \cdot dq$$

along the track of the first released precipitating particle (t being the temperature of the small element of water and water vapour, dq, taken up by the particle in an infinitesimal section of its track, and Q being the total volume absorbed); and, third, of the corresponding temperature, T, along the track of the observed precipitation. Leaving out of consideration the assumption of the distance between c and d being 0, an expression for a_p may be deduced to give correct values for variations in the a_p along the front, if

1. in each of the tracks of precipitation in the cloud the air in rising from d to c is chilled in equal degree;
2. no evaporation takes place from the drop during its fall from the cloud to the ground.

1. presumably is satisfied in sufficiently close approximation, while 2. rarely or never is realized. Since the evaporation increases with the distance from cloud to ground, the observed difference will be less than the computed value. Hence the expression renders the maximum value for variations in a_p.

With the partial pressures of H_2O^{18} and H_2O^{16} termed p^{18} and p^{16}, Raoult's Law of equilibrium between vapour and cloud droplets makes

$$\left.\begin{aligned} p^{18} &= \frac{a_c}{100}\cdot p_0^{18} \\ \text{and} \qquad p^{16} &= \frac{100-a_c}{100}\cdot p_0^{16} \end{aligned}\right\} \qquad (3)$$

where p_0^{18} and p_0^{16} represent the vapour pressures of pure H_2O^{18} and pure H_2O^{16} respectively, and where the index, c, may be changed into p on the supposition that the part played by the process of collision is considerably greater than the part played by the condensation process.

Hence the O^{18}-abundance in vapour is

$$a_v = \frac{p^{18}}{p^{16}+p^{18}}\cdot 100$$

and after inserting (3)

$$\left.\begin{aligned} a_v &= \frac{a_p\cdot p_0^{18}}{(100-a_p)p_0^{16}+a_p p_0^{18}}\cdot 100 = \\ &= \frac{100}{\left(\frac{100}{a_p}-1\right)\frac{p_0^{16}}{p_0^{18}}+1} \end{aligned}\right\} \qquad (4)$$

whence

$$\frac{100}{a_v}-1 = \left(\frac{100}{a_p}-1\right)\frac{p_0^{16}}{p_0^{18}}$$

and

$$a_p = \frac{100}{\left(\frac{100}{a_v}-1\right)\frac{p_0^{18}}{p_0^{16}}+1}\ \% \qquad (5)$$

Within the interval $258 < T < 293$ equation (1) may be approximated by the straight line

$$\frac{p_0^{16}}{p_0^{18}} = 1.03139 - 7.80\cdot 10^{-5}\cdot T \qquad (6)$$

Next re-calculating (5) we get

$$a_p = \frac{100}{\left(\frac{100}{a_v}-1+\frac{p_0^{16}}{p_0^{18}}\right)\cdot\frac{p_0^{18}}{p_0^{16}}} =$$

$$= \frac{100}{100+\left(\frac{p_0^{16}}{p_0^{18}}-1\right)a_v}\cdot a_v\frac{p_0^{16}}{p_0^{18}}$$

$$a_p \cong \frac{100}{100.002}\cdot a_v\frac{p_0^{16}}{p_0^{18}} = 0.99998\cdot a_v\frac{p_0^{16}}{p_0^{18}}$$

whence

$$a_p = (1.03137 - 7.80\cdot 10^{-5}T)a_v \qquad (7)$$

With A representing the total volume of H_2O^{18} in the M g of water vapour contained in one m³ of saturated air, we have

$$A = \frac{20}{18}\cdot\frac{Ma_v}{100}\ \text{g}$$

and

$$dA = \frac{20}{1800}(M\cdot da_v + a_v\cdot dM) \qquad (8)$$

However, dA being equal also to the condensed quantity of H_2O^{18}, we get

$$\left.\begin{aligned} dA &= \frac{20}{1800}a_p dM = \frac{20}{1800}\cdot \\ &\cdot(1.03137 - 7.80\cdot 10^{-5}T)a_v dM \end{aligned}\right\} \qquad (9)$$

From (8) and (9) we get

$$Mda_v + a_v dM = (1.03137 - 7.80\cdot 10^{-5}T)a_v dM,$$

whence

$$Mda_v = (0.03137 - 7.80\cdot 10^{-5}T)a_v dM =$$
$$= (c_1 - c_2 T)\,a_v\,dM,$$

and

$$\frac{da_v}{a_v} = (c_1 - c_2 T)\frac{dM}{M} \qquad (10)$$

Since M is equal to 100^3 times the density of saturated vapour or

$$M = 100^3 \frac{18}{29} 0.001293 \frac{273}{T} \frac{E}{760} = 288 \frac{E}{T} \qquad (11)$$

where E represents the pressure of saturated vapour in mm Hg at $T°$ K, we get

$$dM = 288\left(\frac{dE}{T} - \frac{E}{T^2}dT\right) = \frac{288}{T^2}(TdE - EdT) \qquad (12)$$

By Clapeyron's formula

$$dE = \frac{LdT}{T(v_1 - v_2)} \qquad (13)$$

where v_1 and v_2 respectively represent the volume of 1 g water in the vapour phase and in the liquid phase, while L represents the heat of vaporisation. Since $v_2 \ll v_1$ and

$$v_1 = \frac{1}{18}\frac{RT}{E}$$

(13) may be written

$$dE = \frac{18L}{RT^2} EdT$$

which inserted in (12) gives

$$dM = \frac{288}{T^2}\left(\frac{18L}{RT} - 1\right)EdT \qquad (14)$$

and from (10) together with (11) and (14) we get

$$\frac{da_v}{a_v} = (c_1 - c_2 T)\left(\frac{18L}{RT^2} - \frac{1}{T}\right)dT \qquad (15)$$

L however is dependent on T. In the interval $258 < T < 293$ we may with good approximation put

$$L = 745.7 - 0.550\ T = (c_3 - c_4 T)\ \text{cal/g}.$$

Thereby (15) is transformed into

$$\frac{da_v}{a_v} = (c_1 - c_2 T)\left[\frac{18c_3}{RT^2} - \left(\frac{18c_4}{R} + 1\right)\frac{1}{T}\right]dT$$

or

$$\frac{da_v}{a_v} = \left\{c_1 c_2 \frac{18}{R}\frac{1}{T_2} - \left(\frac{18}{R}(c_1 c_4 + c_2 c_3) + c_1\right)\frac{1}{T} + \left(\frac{18c_4}{R} + 1\right)c_2\right\}dT = \left(C_1\frac{1}{T^2} - C_2\frac{1}{T} + C_3\right)dT$$

By integration of this expression from a_v^0 to a_v, respectively from T_0 to T, we get

$$\ln\frac{a_v}{a_v^0} = C_1\left(\frac{1}{T_0} - \frac{1}{T}\right) + C_2 \ln\frac{T_0}{T} + C_3(T - T_0)$$

or

$$\frac{a_v}{a_v^0} = e^{\frac{C_1}{T_0}} \cdot T_0^{C_2} \cdot e^{-C_3 T_0} \cdot e^{-\frac{C_1}{T}} \cdot T^{-C_2} \cdot e^{C_3 T}$$

whence

$$a_v = K \cdot e^{-\frac{C_1}{T}} \cdot T^{-C_2} \cdot e^{C_3 T} \qquad (16)$$

Finally from (7) and (16) we get

$$\log a_p = \log(1 + c_1 - c_2 T) + \log K - C_2 \log T + \left(C_3 T - \frac{C_1}{T}\right)0.43429 \qquad (17)$$

From this formula (17) a_p can be determined as a function of T when once the constants have been calculated from the meteorological facts of the problem under consideration.

Based upon the Nier value, 0.2039 % for the O^{18}-abundance in atmospheric oxygen (*16*), we obtain the values shown in the third column of Table 1; thus from column 2 $0.2039\frac{1.009}{1,033} = 0.1990$ % for ocean water, and for vapour from ocean water, $0.1990 \cdot 0.991 = 0.1972$ %. However, because of the variation with temperature of p_0^{16}/p_0^{18}, the latter quantity to some extent depends on this variable factor. In equation (3) substituting 0 for c and regarding a_0 as the O^{18}-abundance in ocean water, equation (3) becomes valid for the partial pressures respectively of H_2O^{18} and H_2O^{16}; and substituting 0 for p in (4) this equation becomes valid for vapour from ocean water. Upon the insertion of $a_0 = 0.1990$ % and the elimination of less significant terms, we get

$$a_v = 0.1990\frac{p_0^{18}}{p_0^{16}}\ \% \qquad (18)$$

Table 2 shows a_v at various vaporisation temperatures:

Table 2

t °C.	T °K	a_v %
0	273	0.1970_1
6	279	0.1970_9
13	286	0.1971_9
19	292	0.1972_7
25	298	0.1973_5
		mean 0.1972

It will be seen that a_v varies only slightly with the temperature of the sea, and if we assume the evaporation from the oceans to be $a_v = 0.1972$ %, no great error is committed.

For the warm front earlier discussed we insert in equation (17) $T_0 = 285°$ K, $a_v^0 = 0.1972$ %, corresponding to the conditions existing in the warm air at the beginning of the upward motion taken together with the values introduced in the computation, viz:

$$c_1 = 0.03137$$
$$c_2 = 7.80 \cdot 10^{-5} \text{ grad}^{-1}$$
$$c_3 = 745.7 \text{ cal/gram.}$$
$$c_4 = 0.550 \text{ cal/gram.grad.}$$
$$R = 1.9864 \text{ cal/grad.mol.}$$

and further the values derived therefrom: K, C_1, C_2 and C_3, and we get

$$\log a_p = \log (1.03137 - 7.80 \cdot 10^{-5} T) + 1.44555 - \\ - 0.76066 \log T + (4.92 \cdot 10^{-4} T - 225.89/T) \cdot \\ \cdot 0.43429 \qquad (19)$$

The variation of a_p with T is shown graphically in Fig. 5.

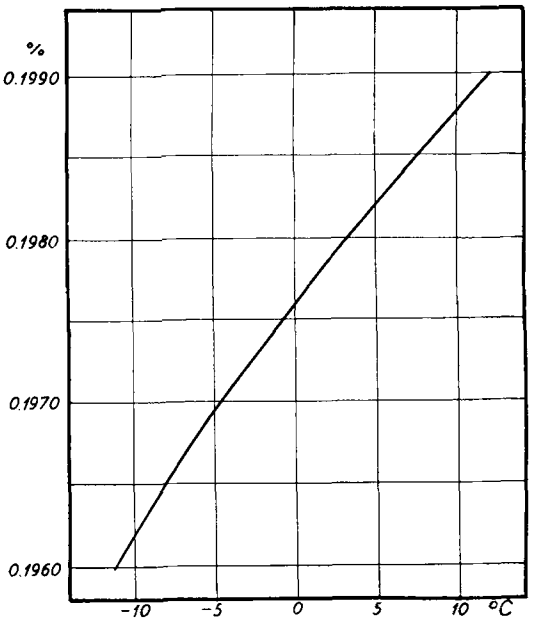

Fig. 5. The calculated variation of the O^{18}-abundance of precipitation plotted against the temperature of condensation.

The altitude of the warm front, whereby is understood the distance from the ground to the topmost level of the boundary from which precipitation reaches the ground, most likely was 3.5 to 4 km in the instance mentioned. At that altitude the temperature must have been in the vicinity of -7 to $-11°$ C, assuming a saturation adiabatic rate extending upward (along the front) from an elevation of 200 m and a temperature of $+12°$ C at that level. According to Fig. 5, a fall in temperature from $+12°$ C to -7 or $-11°$ C should cause a maximum change in a_p from 0.1990 % to 0.1966 or 0.1960 %; hence, between 0.0024 or 0.0030 %; which is in satisfactory agreement with the measured value in Fig. 3: 0.0016_5 %, especially considering the fact that in the calculation the evaporation from the rain drops in falling from the cloud to the ground was not included. Drawing a straight line in Fig. 3, through the levels of collections of rain, Nos 12 to 7, we get, by a line intersecting No. 6 vertically, the value for the O^{18} excess at No. 6, $+0.0004$ %, to some extent corrected for evaporation. Thus, the measured a_p change is corrected to 0.0022 %, per cent which is in good agreement with the calculated value for the maximum change in a_p, viz: 0.0024 to 0.0030 %.

However, the measured absolute values of a_p differ considerably from the values calculated here. In the warm front here discussed the a_p was found to vary between 0.1976 and 0.1959_5 %; whereas the a_p according to the calculations should have changed from 0.1990 to about 0.1963 %.

A reason for this is that the circulatory process of the water in nature is far from being so ideal as assumed in the above. Thus a_v^0 is not solely dependent on T_0 but also on the pre-history of the air. For example, the air may have absorbed some of its water vapour over solid ground, i.e., from fresh water of an O^{18}-abundance about 0.0018 % lower than in ocean water. In air of this description a_v will be less than supposed in the case discussed in the above. However, if maritime air only is considered deviations of this nature should be of slight importance.

More important is the fact that air rarely is chilled so much that the absolute humidity practically becomes to. This means that the general circulatory process, which consists of the following three processes:

1. Saturated air at T_0 (with a_v^0 as stated in Table 2) will liberate rain by cooling to $T°$;
2. The air is again heated to $T_0°$;
3. The air is saturated with water vapour at $T_0°$;

will alter the a_v considerably, bacause the a_v remaining in the air after process 1. will be less than a_0^0. When the air in process 3. has absorbed a certain quantity of water vapour of O^{18}-abundance a_v^0, the a_v for the total quantity of vapour must also be less than a_v^0.

Such a fall in a_v naturally cannot proceed indefinitely. Since the air continually passes through circulatory processes, an equilibrium has been established where the final a_v on an average is just so much below the values stated in Table 2 that the decrease in a_v during process 1. is balanced by the increase in a_v during process 3. The final mean value of a_v is dependent on the climatic and geographic conditions.

A third reason for the disagreement in the absolute values is, no doubt, the fact that the warm air in question had given off moisture before starting the upward movement at Copenhagen.

However, the significant part of this investigation is that these considerations have no effect on the agreement between the computed and the measured, corrected *changes* in a_p. Actually, the insertion in (17) of a value for a_v^0 differing 0.0014 %, from the value earlier used makes no essential difference in the calculated a_p changes.

Further investigations into these problems will be discussed in a later paper.

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