

# Stable isotopes in precipitation

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## ABSTRACT

In chapter 2 the isotopic fractionation of water in some simple condensation-evaporation processes are considered quantitatively on the basis of the fractionation factors given in section 1.2. The condensation temperature is an important parameter, which has got some glaciological applications. The temperature effect (the  $\delta$ 's decreasing with temperature) together with varying evaporation and exchange appear in the "amount effect" as high  $\delta$ 's in sparse rain. The relative deuterium-oxygen-18 fractionation is not quite simple. If the relative deviations from the standard water (S.M.O.W.) are called  $\delta_D$  and  $\delta_{18}$ , the best linear approximation is  $\delta_D = 8 \delta_{18}$ .

Chapter 3 gives some qualitative considerations on non-equilibrium (fast) processes. Kinetic effects have heavy bearings upon the effective fractionation factors. Such effects have only been demonstrated clearly in evaporation processes, but may also influence condensation processes. The quantity  $d = \delta_D - 8 \delta_{18}$  is used as an index for non-equilibrium conditions.

The stable isotope data from the world wide I.A.E.A.-W.M.O. precipitation survey are discussed in chapter 4. The unweighted mean annual composition of rain at tropical island stations fits the line  $\delta_D = 4.6 \delta_{18}$  indicating a first stage equilibrium condensation from vapour evaporated in a non-equilibrium process. Regional characteristics appear in the weighted means.

The Northern hemisphere continental stations, except African and Near East, fit the line  $\delta_D = 8.0 \delta_{18} + 10$  as far as the weighted means are concerned ( $\delta_D = 8.1 \delta_{18} + 11$  for the unweighted) corresponding to an equilibrium Rayleigh condensation from vapour, evaporated in a non-equilibrium process from S.M.O.W. The departure from equilibrium vapour seems even higher in the rest of the investigated part of the world.

At most stations the  $\delta_D$  and varies linearly with  $\delta_{18}$  with a slope close to 8, only at two stations higher than 8, at several lower than 8 (mainly connected with relatively dry climates).

Considerable variations in the isotopic composition of monthly precipitation occur at most stations. At low latitudes the amount effect accounts for the variations, whereas seasonal variation at high latitudes is ascribed to the temperature effect. Tokyo is an example of a mid latitude station influenced by both effects.

Some possible hydrological applications are outlined in chapter 5.

## 1. Introduction

In the past decade an increasing number of investigators have treated the fractionation in nature of the most important isotopic components of water,  $\text{H}_2\text{O}^{16}$ ,  $\text{HDO}^{16}$  and  $\text{H}_2\text{O}^{18}$ . The main results may briefly be summarized in this way:

- (1) Fresh waters are poorer in heavy isotopes than sea water (GILFILLAN, 1934).
- (2) The great reservoir of water, the oceans, has a fairly uniform isotopic composition disregarding those parts, which are directly mixed with fresh water (EPSTEIN & MAYEDA, 1953).
- (3) The deuterium and oxygen 18 concentrations in sea water usually vary parallelly (FRIEDMAN, 1953).
- (4) The heavy isotope content in precipitation decreases with the condensation temperature, which is reflected by
  - (a) variation of the composition of precipitation from individual atmospheric cooling processes—in simple cases in accordance with the Rayleigh conditions (DANSGAARD, 1953),
  - (b) the heavy isotope concentrations in fresh water decreasing with increasing latitude and altitude (DANSGAARD, 1954), and

- (c) seasonal variation of the precipitation composition at high latitudes (EPSTEIN, 1956).
- (5) Kinetic effect in fast evaporation can disturb the above-mentioned parallelism between the deuterium and O<sup>18</sup> variations (CRAIG, BOATO & WHITE, 1956).
- (6) Exchange of isotopic molecules between vapour and liquid may play an important role (FRIEDMAN, MACHTA & SOLLER, 1962).

These are the most important steps in the endeavours for clarifying the laws, which govern the fractionation processes in nature. Such developments have not yet come to an end.

Parallely to these efforts much work has been done for utilizing the experiences in various fields, the glaciological applications being mainly represented by Epstein *et al.*, Confiantini, Picciotto, Dansgaard and Lorius, the hydrological applications by Friedman, Craig and others. Thousands of sea water samples and ten-thousands of fresh water samples have been analysed by mass spectrometry. However, relatively few of the data have been published in spite of many of them having more than local interest. This has for several years been a handicap for the investigation of the water turnover on a global scale as well as for the solution of such local problems, which are analogous to others already investigated elsewhere. A change of practice on this point would undoubtedly be useful for many investigators and may also lead to a higher degree of systematism and standardisation of the sampling technique, which is especially important for the interpretation of precipitation data.

Most of the present investigation is based on the world wide survey of hydrogen and oxygen isotopes in precipitation organized since 1961 by the International Atomic Energy Agency (I.A.E.A.) and the World Meteorological Organization (W.M.O.). The aims of this project can be broadly stated as (1) providing a knowledge of tritium input function in various parts of the world, a parameter necessary for the application of natural tritium to hydrological problems, and (2) obtaining data on the concentration of hydrogen and oxygen isotopes, from which it should be possible to deduce some characteristics of the circulation patterns and mechanisms of the global and local movements of water.

The stable isotope data from 1961 and 1962 will be given later in this journal. In section 4 some conspicuous regularities in the data are shown, and some possible explanations are pointed out in relation to the calculations on simple processes given in chapters 2 and 3. However, the interpretation is far from completion and several of the problems are still open for discussion. Even considering ERIKSSON's (1964) important approach much work still remains to be done for interpreting the comprehensive material on the basis of meteorological studies.

### 1.1. MEASURING TECHNIQUE

The average occurrences of the most important isotopic components of water, H<sub>2</sub>O<sup>18</sup>, HDO<sup>18</sup> and H<sub>2</sub>O<sup>16</sup>, are related as approximately

$$997680 : 320 : 2000 \text{ ppm (parts per million).}$$

Nowadays, precision measurements of deuterium and O<sup>18</sup> in natural waters are always made by a mass spectrometer. BOTTER & NIEF (1958) have been able to measure the absolute deuterium content in water, whereas no means are available for an accurate determination of the absolute O<sup>18</sup> content. It is much easier to measure relative or absolute differences between two samples. Fortunately, the greatest interest is attached to the variations in isotopic composition, the measurement of which is, consequently, a common feature of all techniques hitherto applied in this field.

In this work all data will be given as the relative deviation,  $\delta$ , of the heavy isotope content of a sample from that of a standard. If the absolute content is denoted by  $a$ ,  $\delta$  may be considered as

$$\delta = \frac{a_{\text{sample}} - a_{\text{standard}}}{a_{\text{standard}}} \cdot 10^3 \text{‰}.$$

The reference standard is SMOW (Standard Mean Ocean Water, CRAIG, 1961*b*). The measuring accuracy is  $\pm 2\text{‰}$  on  $\delta_D$  for deuterium and  $\pm 0.2\text{‰}$  on  $\delta_{18}$  for O<sup>18</sup>. For details of the measuring technique reference is made to DANSGAARD (1961).

If a sample composition is given by  $\delta'$  relative to a secondary standard, which deviates  $\delta_{st}\text{‰}$  from SMOW, the  $\delta$  for the sample relative to SMOW will be

$$\delta = \delta' + \delta_{st} + \delta'\delta_{st} \quad (1)$$

(BOATO, 1960). Thus, the  $\delta$  function is not additive in a simple sense.

### 1.2. ISOTOPE FRACTIONATION FACTORS

The isotopic composition of natural waters covers a large range, which amounts to more than 400‰ for  $\delta_D$  and 40‰ for  $\delta_{18}$ , i.e. at least 200 times the measuring accuracy used here, or 400 times the best accuracy obtainable.

Isotopic fractionation of water is caused by several processes in nature, e.g. biological activity and exchange with other materials; of greatest interest from meteorological, hydrological and glaciological points of view is the fact that the volatility of  $H_2O^{16}$  is higher than those of the heavy isotopic components. This causes fractionation in all condensation processes and also in the evaporation of well mixed liquid water.

The fractionation factors for such processes depend upon the temperature and the rate of reaction. If the process proceeds so slowly that the equilibrium conditions are practically realized at the boundary between the phases, the fractionation factor for evaporation of liquid water becomes simply the ratio between the vapour pressure of the light component ( $p$ ) and that of a heavy one ( $p' < p$ ):

$$\alpha = \frac{p}{p'}$$

At normal temperature the  $\alpha$ 's for HDO and  $H_2O^{18}$  are approx. 1.08 and 1.009, respectively. This means that vapour in equilibrium with water is depleted some 80‰ in deuterium and 9‰ in  $O^{18}$  relative to the water:

$$a_{\text{vapour}} = \frac{p'}{p} a_{\text{water}} = \frac{a_{\text{water}}}{\alpha}$$

or, when abbreviating the indices and assuming the water to be SMOW ( $\delta = 0$ ):

$$\delta_v = \frac{a_v - a_w}{a_w} = \frac{1}{\alpha} - 1. \quad (2)$$

Conversely, the first small amount of condensate from such vapour will have a composition, which is

TABLE 1

$t^\circ\text{C}$	$\alpha_D$	$\alpha_{18}$
100	1.029	1.0033 <sub>0</sub>
80	1.037	1.0045 <sub>0</sub>
60	1.046	1.0058 <sub>7</sub>
40	1.060	1.0074 <sub>0</sub>
20	1.079 <sub>1</sub>	1.0091 <sub>5</sub>
0	1.106 <sub>0</sub>	1.0111 <sub>0</sub>
-10	1.123 <sub>0</sub>	1.0123 <sub>0</sub>
-20	1.146 <sub>0</sub>	1.0135 <sub>0</sub>

$$a_c = \frac{p}{p'} a_v = \alpha \frac{a_w}{\alpha} = a_w, \quad (3)$$

i.e. the same as that of SMOW. Using  $\delta$  the corresponding calculation is the following: In analogy with (2) the condensate composition relative to the vapour is

$$\delta'_c = \alpha - 1. \quad (4)$$

Inserting (2) and (4) into (1) gives

$$\delta_c = \left(\frac{1}{\alpha} - 1\right) + (\alpha - 1) + \left(\frac{1}{\alpha} - 1\right)(\alpha - 1) = 0. \quad (5)$$

The  $\alpha_D$  and  $\alpha_{18}$  values used in this work for temperatures  $t > 0^\circ\text{C}$  are those measured by MERLIVAT *et al.* (1963) and ZHAVORONKOV *et al.* (1955), respectively. The  $\alpha$  values below the freezing point are difficult to measure but very important for condensation processes in nature, so we must use extrapolated values in the temperature range  $-20 < t < 0^\circ\text{C}$ . As to  $\alpha_{18}$ , the formula of Zhavoronkov *et al.*,

$$\alpha_{18} = 0.9822 \exp(15.788/RT),$$

has been used down to  $-20^\circ\text{C}$ , whereas the  $\alpha_D$  values have been chosen by a second order extrapolation from the curve found by Merlivat *et al.* (Table 1).

In section 2 a few equilibrium processes will be treated quantitatively.

If we turn to non-equilibrium processes, i.e. fast reactions, the situation becomes more complicated. The values given above cannot be applied in such cases, because of the existence of a kinetic effect on the fractionation during the change of phase. As pointed out by CRAIG, BOATO & WHITE (1956) the observations may

be understood qualitatively by assuming the rate of reaction,  $c$ , of the light component to be the fastest one:

$$c(\text{H}_2\text{O}^{16}) > c(\text{HDO}) > c(\text{H}_2\text{O}^{18}).$$

Considering an evaporation of water the relatively fast escape of  $\text{H}_2\text{O}^{16}$  corresponds to an increase of its vapour pressure and, thus, to effective fractionation factors,  $\alpha^k$ , higher than  $\alpha$ . DANSGAARD (1961) reported values of  $\alpha_{16}^k$  up to 1.019, corresponding to a 100‰ increase of  $\alpha_{16} - 1$ , which governs the simple evaporation-condensation processes (cf. eq. (2) and (4)).

The physical explanation for the kinetic effect is not known (not even the equilibrium case is fully explained), but we shall frequently, especially in section 3, touch upon some of its important consequences for the global movement of water.

Since any evaporation of water in nature takes place into environments, already containing some vapour, one must also consider the influence of exchange of isotopic molecules between the vapour and the evaporating water (DANSGAARD 1953; FRIEDMAN & MACHTA 1962; CRAIG *et al.*, 1963; ERIKSSON 1964). This influence, of course, depends upon the vapour content and its composition. The consequences for precipitation will be discussed in sections 3.3 and 4.2.3.

## 2. Equilibrium processes

In this chapter we shall treat the isotopic fractionation of water caused by some simple equilibrium processes, i.e. kinetic effects are neglected. The considerations are limited to two-phase systems with no supply of material from the environments, such systems not necessarily being identical with closed two-phase systems; e.g. Rayleigh processes are considered in sections 2.1.2 and 2.2. The results will later be compared with the actual findings.

### 2.1. CONDENSATION

Most important for the isotopic composition of precipitation is the condensation. As mentioned in section 1.2 the first small amount of water condensed from vapour in equilibrium with SMOW will have the same composition as SMOW (eq. (5)). By further condensation the vapour preferentially loses the heavy com-

ponents, i.e.  $\delta_v$  for the remaining vapour and, consequently,  $\delta_c$  for newly formed condensate both get more and more negative.

#### 2.1.1. Condensation in a closed two-phase system

If the condensation takes place in a closed two phase system with *equilibrium between the total liquid and vapour phases* at any stage, and if  $\delta_c$  for the first small amount of condensate is supposed to be zero,  $\delta_c^*$  for the total liquid phase can be shown to change by further condensation as

$$\delta_c^* = \frac{1}{\alpha_0} \cdot \frac{1}{\varepsilon F_v + 1} - 1, \quad \varepsilon = \frac{1}{\alpha} - 1,$$

$\alpha_0$  being the value of  $\alpha$  at the beginning of the processes, and  $F_v$  the remaining fraction of the vapour phase.

Similarly, for the composition of the vapour phase

$$\delta_v^* = \frac{1}{\alpha_0 \alpha} \cdot \frac{1}{\varepsilon F_v + 1} - 1.$$

For  $F_v \rightarrow 0$ :  $\delta_c^* \rightarrow \frac{1}{\alpha_0} - 1,$

which is equal to  $\delta_v^*$  for  $F_v = 1$ .

By *isothermal condensation*  $\alpha = \alpha_0$ , and  $\delta_v^* \rightarrow 1/\alpha_0^2 - 1$  for  $F_v \rightarrow 0$ . The two practically straight lines in Fig. 1 show  $\delta_c^*$  and  $\delta_v^*$  as functions of  $F_v$ .

If the condensation is caused by *cooling*,  $\alpha$  increases as the process proceeds. The compositions of the liquid and the vapour phases, denoted by  $\delta'_c$  and  $\delta'_v$ , are shown by the dashed curves in Fig. 1. The limit of  $\delta'_v$  for  $F_v \rightarrow 0$  cannot be stated, since  $\alpha$  is not known at very low temperatures.

When the temperature is low enough to allow *sublimation*, no exchange occurs between the solid and vapour phases. The composition of the newly formed solid material and that of the vapour will change as under Rayleigh conditions (curves  $\delta_c$  and  $\delta_v$  in Fig. 1, cf. p. 440), and the mean composition of the total solid phase will change as

$$\delta_s = \frac{1}{\alpha_0} \cdot \frac{1 - F_v^{\alpha_m}}{1 - F_v}$$

(cf. DANSGAARD, 1961, pp. 43-45),  $\alpha_m$  being the value of  $\alpha$  at the mean temperature.  $\delta_s$

corresponding to an isobaric cooling of saturated air from  $t_0 = 20^\circ\text{C}$  is shown by the thin, upper curve in Fig. 1.

2.1.2. Rayleigh processes

If the condensation of the vapour proceeds under Rayleigh conditions (i.e. a slow process with immediate removal of the condensate from the vapour after formation),  $\delta_c$  for the liquid or solid phase and  $\delta_v$  for the vapour phase will change as

$$\left. \begin{aligned} \delta_c &= \frac{\alpha}{\alpha_0} F_v^{\alpha_m - 1} - 1, \\ \delta_v &= \frac{1}{\alpha_0} F_v^{\alpha_m - 1} - 1, \end{aligned} \right\} \quad (6)$$

$\alpha$ ,  $\alpha_0$  and  $\alpha_m$  referring to the momentary condensation temperature  $t$ , to the initial temperature  $t_0$  and to  $(t + t_0)/2$ , respectively (cf. DANSGAARD, 1961, pp. 45-46). In case of isothermal condensation,  $\alpha = \alpha_0 = \alpha_m$ . In any case,  $\delta_c$  and  $\delta_v \rightarrow -\infty$  for  $F_v \rightarrow 0$  as indicated by the  $\delta_c$  and  $\delta_v$  curves in Fig. 1, which have been calculated by assuming an isobaric cooling of a saturated air mass from  $t_0 = 20^\circ\text{C}$ .

The Rayleigh process thus leads to much higher fractionation than processes, in which the two phases are allowed to equilibrate by exchange. In nature, exchange will, more or less, smooth out the phenomenon. The curves  $\delta'_c$  and  $\delta_c$ , consequently, represent the two extremes to be expected.

In the following are given some calculations, based upon equation (6), on the variations of the deuterium and  $\text{O}^{18}$  components of the condensate in Rayleigh cooling processes.  $F_v$  has throughout been calculated as the mixing ratio (gram vapour per kg dry air) at the temperature  $t$  and the pressure  $p$ , divided by the initial mixing ratio at temperature  $t_0$  and pressure  $p_0$  (1000 mb). This procedure accounts for the variation of  $F_v$  due to changes in both temperature and pressure (or volume).

For the initial temperature  $t_0$  between  $0^\circ$  and  $80^\circ$  the cooling processes have been supposed to be isobaric, for  $t_0$  equal to  $100^\circ\text{C}$  isochoric (constant volume).

In the upper left part of Table 2, columns 2-7 give the remaining fractions  $F_v$  of the vapour as well as  $\delta_D$  and  $\delta_{18}$  for new condensate

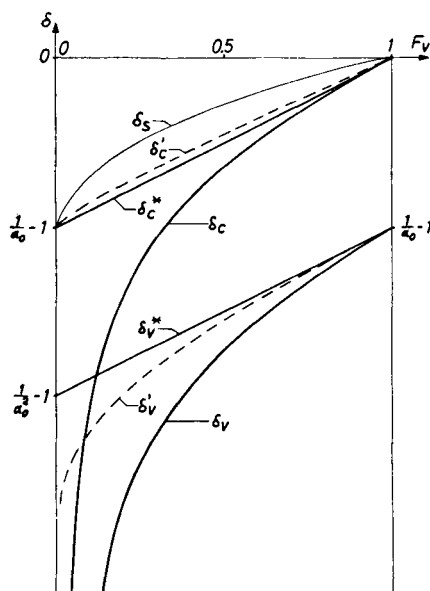


FIG. 1. Isotopic fractionation of the remaining vapour and of the condensate as a function of the remaining fraction,  $F_v$ , of vapour.

$\delta_v^*(\delta_c^*)$  equilibrium between the total liquid and vapour phases during isothermal condensation.

$\delta'_v(\delta'_c)$  same as above during condensation by cooling,  $\delta_v(\delta_s)$  sublimation by cooling.  $\delta_s$  is the mean composition of the solid phase.

$\delta_v(\delta_c)$  sublimation or condensation by cooling under Rayleigh conditions.  $\delta_c$  is the composition of newly formed condensate.

after  $20^\circ$  and after  $40^\circ$  isobaric cooling below  $t_0$ . Calculated data on moist-adiabatic cooling from  $t_0 = 0^\circ$  and  $t_0 = 20^\circ$  are given in the lower left part of Table 2. Due to the expansion, and the consequent less condensation, in such processes the  $\delta$ 's are numerically lower than the corresponding values in the isobaric case.

2.2. EVAPORATION

During their fall from the cloud to the ground the rain drops are subjected to evaporation and exchange with the environmental vapour. These processes are, thus, important for the final composition of liquid precipitation when it reaches the ground. The evaporation is relatively high in dry air, in which case the process probably proceeds under non-equilibrium conditions (EHHALT *et al.*, 1963). On the other hand,

TABLE 2

$t_0$ °C	Condensation by isobaric (for $t_0 = 100^\circ\text{C}$ isochoric) cooling						Evaporation (isothermal)			
	$t = (t_0 - 20)^\circ\text{C}$			$t = (t_0 - 40)^\circ\text{C}$			$F_w = 0.3$		$F_w = 0.1$	
	$F_v$ %	$\delta_D$ ‰	$\delta_{18}$ ‰	$F_v$ %	$\delta_D$ ‰	$\delta_{18}$ ‰	$\delta_D$ ‰	$\delta_{18}$ ‰	$\delta_D$ ‰	$\delta_{18}$ ‰
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0	20	-150	-17.1				122	13.4	247	25.8
20	26	-95	-11.7	5.2	-223	-28.2	92	11.1	184	21.5
40	30	-63	-8.2	7.7	-153	-19.8	71	8.9	140	17.1
60	32	-46	-6.0	9.6	-104	-14.0	54	7.1	107	13.6
80	27	-44	-5.4	8.7	-87	-11.4	44	5.4	86	10.0
100	49	-14	-1.6	2.1	-39	-4.3	34	4.0	67	7.6

Condensation by adiabatic cooling ( $p_0 = 1000$ mb)			
$t_0$ °C	$F_v$ %	$\delta_D$ ‰	$\delta_{18}$ ‰
0	29	-107	-12.9
20	43	-52	-6.6

in case of high humidity the exchange will possibly be the dominating factor (FRIEDMAN & MACHTA, 1962).

Thus, evaporation under Rayleigh conditions may very well be a process of negligible importance in nature. Nevertheless, for comparison this process has been treated quantitatively in the isothermal case using the usual formula

$$\delta_w = F_w^\epsilon - 1, \quad \epsilon = \frac{1}{\alpha} - 1, \quad (7)$$

in which  $\delta_w$  is the composition of the remaining fraction  $F_w$  of the water reservoir, if the initial composition is supposed to be  $\delta_w^0 = 0$ . In the right part of Table 2 are listed the calculated  $\delta_D$  and  $\delta_{18}$  for  $F_w = 0.3$  and  $0.1$  at various temperatures. All  $\delta$ 's are, of course, positive due to the preferential escape of  $\text{H}_2\text{O}^{16}$ .

2.3. TEMPERATURE EFFECT

Isothermal condensation never happens in the atmosphere. Any formation of precipitation is caused by some kind of cooling process. However, we cannot in general use the isotopic composition of a given amount of precipitation as an indication of the condensation temperature (not even in case of no kinetic, exchange or evaporation effects), because the observed composition of the individual rain is a function

of several parameters, e.g. the thermodynamic conditions during the cooling, the initial composition etc. The influence of the condensation temperature is the easiest to calculate, at least under simplified conditions. Cooling processes under Rayleigh conditions, have already been considered in section 2.1.2., and some of the results are listed in Table 2. Fig. 2 shows how  $\delta_{18}$  of the condensate decrease with temperature.

Logarithmic differentiation of eq. (6) gives

$$\log(\delta + 1) = \log \alpha - \log \alpha_0 + (\alpha_m - 1) \log F_v,$$

$$\frac{d\delta}{\delta + 1} = \frac{d\alpha}{\alpha} + (\alpha_m - 1) \frac{dF_v}{F_v} + \log F_v d\alpha_m,$$

$$\frac{d\delta}{dt} = \left( \left( \frac{1}{\alpha} + \frac{1}{2} \log F_v \right) \frac{d\alpha}{dt} + \frac{\alpha_m - 1}{F_v} \frac{dF_v}{dt} \right) (\delta + 1), \quad (8)$$

$d\alpha_m$  being put equal to  $\frac{1}{2} d\alpha$ .

Table 3 gives the isotopic change per degree cooling,  $d\delta/dt$ , for various initial dew points  $t_0$  and also the average values,  $(d\delta/dt)_a$ , in the temperature ranges  $t_0 \rightarrow (t_0 - 20)$  and  $(t_0 - 20) \rightarrow (t_0 - 40)$ . The figures in parenthesis refer to vapour-ice equilibrium. Apparently, one can easily measure a change corresponding to cooling  $1^\circ\text{C}$  at normal and low temperature.

Two attempts have been made to correlate the composition of precipitation with the temperature of formation. DANSGAARD (1953) measured rain from a warmfront, in which the air was moist-adiabatically cooled from  $t_0 = 12^\circ\text{C}$  to approx.  $-8^\circ\text{C}$ . The observed change in  $\text{O}^{18}$  content was 8‰, or 11‰ when applying an estimated correction for evaporation (and exchange) from the drops. The latter figure corresponds to 0.50‰ per centigrade in agreement with Table 3; linear interpolation to  $t_0 = 12^\circ\text{C}$  in column 13 gives, namely,

$$\left(\frac{d\delta_{18}}{dt}\right)_a = 0.45 \text{‰}/^\circ\text{C}.$$

In the low temperature range ( $-18$  to  $-30^\circ$ ) PICCIOTTO *et al.* (1960) found 8 and  $0.9 \text{‰}/^\circ\text{C}$  for  $D$  and  $\text{O}^{18}$  in Antarctic snow. These mean values are compared with  $d\delta/dt$  at  $-20^\circ\text{C}$  after an isobaric cooling from  $20^\circ\text{C}$  (vapour-ice equilibrium from  $0^\circ\text{C}$ ). Eq. (8) gives:

$$\frac{d\delta_D}{dt} = 7.7 \text{‰}/^\circ\text{C} \quad \text{and} \quad \frac{d\delta_{18}}{dt} = 0.95 \text{‰}/^\circ\text{C}.$$

In the following subsection Fig. 3 shows a linear correlation between the annual means of

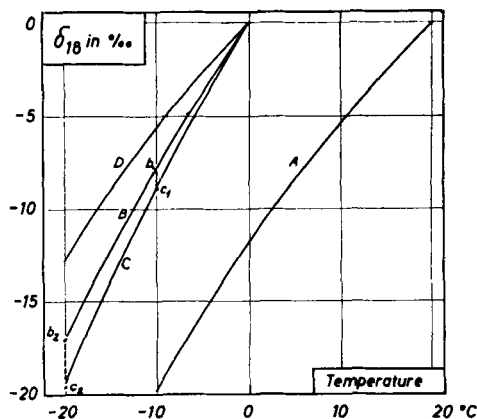


FIG. 2.  $\delta_{18}$  of newly formed condensate as a function of temperature in Rayleigh cooling processes. For the first stage condensate  $\delta_{18} = 0$ :

- A. Isobaric cooling. Vapour-water equilibrium.  $t_0 = 20^\circ\text{C}$ .
- B. Isobaric cooling. Vapour-water equilibrium.  $t_0 = 0^\circ\text{C}$ .
- C. Isobaric cooling. Vapour-ice equilibrium.  $t_0 = 0^\circ\text{C}$ .
- D. Moist-adiabatic cooling. Vapour-water equilibrium.  $t_0 = 0^\circ\text{C}$ .

The dashed lines reflect turnover from vapour-liquid (*b*) to vapour-ice equilibrium (*c*). Further sublimation by cooling will, practically speaking, follow the curve *C* (DANSGAARD, 1961).

TABLE 3. Variation (in ‰ per  $^\circ\text{C}$ ) of the isotopic composition of newly formed condensate in cooling processes.

Columns 2, 5, 9 and 12: slope of the  $\delta$ - $t$  curve at the initial temperature  $t_0$ . The figures in parenthesis refer to vapour-ice equilibrium. Columns 3, 6, 10 and 13: the average slope for the first 20 centigrades cooling. Columns 4, 7, 11 and 14: the average slope for the next 20 centigrades cooling.

Isobaric cooling

$t_0$ (1)	$d\delta_D/dt$ (2)	$(d\delta_D/dt)_a$		$d\delta_{18}/dt$ (5)	$(d\delta_{18}/dt)_a$	
		$t_0 \rightarrow t_0 - 20$ (3)	$t_0 - 20 \rightarrow t_0 - 40$ (4)		$t_0 \rightarrow t_0 - 20$ (6)	$t_0 - 20 \rightarrow t_0 - 40$ (7)
0	6.3 (6.9)	7.0 (7.7)		0.71 (0.82)	0.85 (0.97)	
20	4.0	4.8	6.4 (7.0)	0.48	0.58	0.78 (0.88)
40	2.7	3.2	4.5	0.35	0.41	0.58

Moist-adiabatic cooling

	(9)	(10)	(11)	(12)	(13)	(14)
0	4.3 (4.6)	5.6 (6.2)		0.51 (0.58)	0.64 (0.73)	
20	2.0	2.6	4.6 (5.3)	0.24	0.33	0.58 (0.67)
40	0.5	0.82	1.8	0.06	0.105	0.23

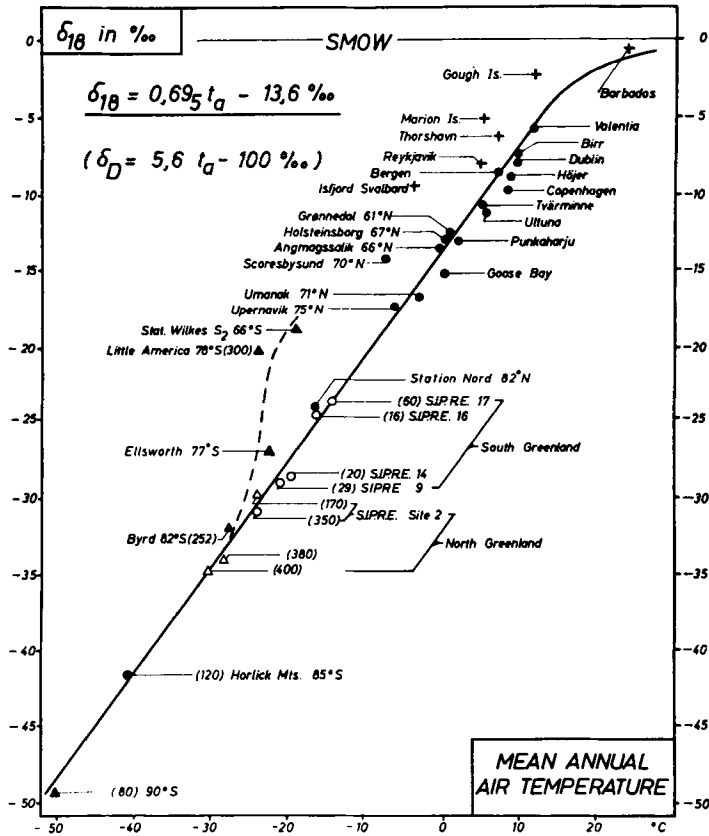


FIG. 3. The annual mean  $\delta_{18}$  of precipitation as a function of the annual mean air temperature at surface. The figures in parenthesis indicate the total thickness (in cm) of the investigated snow layers.

the  $O^{18}$  content in precipitation and the surface air temperature,  $t_a$ ,

$$\delta_{18m} = 0.695 t_a - 13.6 \text{ ‰} \quad (9)$$

over a very wide temperature range including North Atlantic coast stations and Greenland ice cap stations. If the mean surface temperature is supposed to vary parallel to the mean condensation temperature from one place to the other, equation (9) gives:

$$\left(\frac{d\delta_{18}}{dt}\right) \cong 0.70 \text{ ‰/°C.} \quad (10)$$

In the high temperature range ( $0 < t_a < 10^\circ\text{C}$ ) this figure should be compared to  $d\delta_{18}/dt = 0.66 \text{ ‰/°C}$ , calculated from equation (8) with  $t_0 = 20^\circ\text{C}$  and  $t = 5^\circ\text{C}$  after an isobaric cooling.

All the Greenland ice cap stations ( $-30 < t_a <$

$-10^\circ\text{C}$ ) are high altitude stations. The precipitating air masses are moist-adiabatically cooled, at least from  $t = 0^\circ\text{C}$ . Furthermore, they are always in vapour-ice equilibrium at the sites in question. Thus, we assume an isobaric cooling from  $t_0 = 20^\circ\text{C}$  to  $t = 0^\circ\text{C}$  followed by a moist-adiabatic cooling (vapour-ice) from  $t = 0^\circ$  to  $t = -20^\circ\text{C}$ . Equation (8) then gives  $d\delta_{18}/dt = 0.67 \text{ ‰/°C}$  at  $t = -20^\circ\text{C}$  (= the mid temperature in the interval considered) in fairly good agreement with (10).

Thus, the observed temperature effects are in agreement with those calculated under the assumption of the condensation part of the water cycle in nature being a simple Rayleigh process starting at  $20^\circ\text{C}$ . This is, of course, not the same as to state that all precipitation at high latitudes originates from those parts of the oceans, where the temperature is approx.



20°C. But as a simplified model the Rayleigh condensation is, apparently, sufficient for the interpretation of most observations (cp. p. 456).

### 2.3.1. Glaciological applications

As pointed out in the beginning of section 2.3., one cannot use the composition of the individual rain as a direct measure of the condensation temperature. Nevertheless, it has been possible to show a simple linear correlation between the annual mean values of the surface temperature and the  $O^{18}$  content in high latitude, non-continental precipitation (DANSGAARD, 1961). The main reason is that the scattering of the individual precipitation compositions, caused by the influence of numerous meteorological parameters, is smoothed out when comparing average compositions at various locations over a sufficiently long period of time (a whole number of years).

The somewhat revised and extended correlation is shown in Fig. 3. The mean annual  $\delta_{18}$  for the precipitation is plotted against the mean annual air temperature at surface,  $t_a$ , which varies approx. parallelly with the mean annual condensation temperature from one place to the other. The 38 considered stations are the following:

- (1) 17 continental stations from the North Atlantic region (filled circles) in the temperature range  $-17 < t_a < 11^\circ\text{C}$ .
- (2) 6 island stations with  $-4 < t_a < 25^\circ\text{C}$  (crosses).
- (3) Greenland ice cap stations and 1 Antarctica ice cap station (open circles) with  $-41 < t_a < -14^\circ\text{C}$  measured by the present author (the sample from Horlich Mtns. was collected by Dr. Bjørn Andersen, Norsk Polar-instituttt).
- (4) 4 Greenland and 5 Antarctica ice cap stations (triangles) with  $-50 < t_a < -19^\circ\text{C}$  measured by EPSTEIN & BENSON, (1959) and by EPSTEIN & SHARP (1962).

It is quite obvious that the curve should not exceed  $\delta_{18} = 0$  (SMOW), since positive  $\delta$ 's occur only as a result of special processes like accidental evaporation from liquid precipitation.

In the high temperature range ( $t_a > -5^\circ\text{C}$ ) a continental effect appears, the  $\delta_{18}$  decreasing for a given  $t_a$  when going inland. The reasons are probably (1) increasing participation of isotopically light re-evaporated fresh water, and

(2) increasing formation of convective rain; the difference between the surface temperature and the actual condensation temperature is, namely, greater in showers than in other types of precipitation processes.

For all Greenland stations (except Scoresby-sund) there is a very close correlation in the range  $-30 < t_a < 0^\circ\text{C}$ :

$$\delta_{18m} = 0.69_5 t_a - 13.6\text{‰}. \quad (9)$$

Owing to the smooth course of the mean annual isotherms on the Greenland ice cap the sites of formation of icebergs extruded from the West coast glaciers can be estimated using the  $\delta_{18}-t_a$  correlation. The equation used by DANSGAARD (1961) and SCHOLANDER *et al.* (1962) was not quite identical with (9), but the difference is small, and none of the conclusions drawn has to be changed.

The  $\delta_D-t_a$  correlation analogous to (9) may be derived by introducing the  $\delta_D-\delta_{18}$  relation (16) for continental stations (cf. subsection 4.1.2., p. 454):

$$\delta_D = 5.6 t_a - 100\text{‰}. \quad (11)$$

The glaciological application of the equations (9) and (11) mentioned above, and also the isotope-stratigraphic application of the seasonal change in composition (EPSTEIN & BENSON, 1959), are based upon the close correlation between the  $\delta$ 's and the condensation temperature. Other conditions for successful glaciological applications are, however, that (1) considerable accumulation occurs both in summer and winter; (2) the trajectories of precipitating air masses are roughly the same for the whole area considered and all the year round; (3) no considerable ablation takes place (by evaporation, melting or drift); and (4) the topography of the considered area is simple (cp. LORIUS, 1963).

If we look at the accumulation zone of the Greenland ice cap West of the ice shed, the above mentioned conditions are mainly fulfilled, e.g. precipitating air masses usually come from directions between South and West.

Antarctica, however, is surrounded by a relatively warm ocean, and a given location on the ice cap may receive precipitation from various directions and from air masses with essentially different pre-histories. Furthermore, in many parts of the continent the topography is not simple, and the precipitation is so sparse

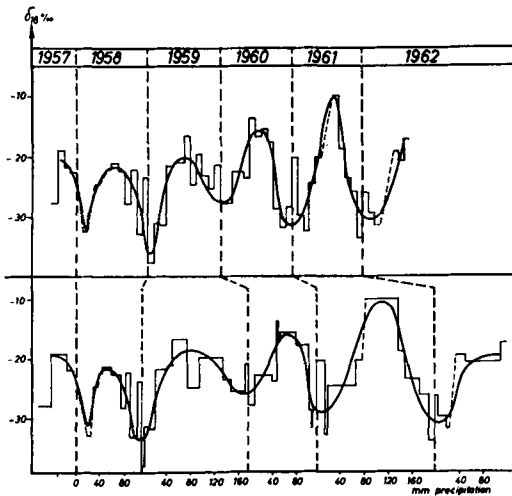


FIG. 4.  $\delta_{18}$  in monthly precipitation at station Nord ( $82^\circ$  N).

that ablation may disturb the stratigraphy. These may all be contributory reasons for the more complex correlation (if any) between  $\delta_{18}$  and  $t_a$  indicated by the 4 filled triangles (Fig. 3) for  $t_a > -25^\circ\text{C}$  in Antarctica.

Furthermore, the above may also explain why the isotope-stratigraphic method has met serious difficulties in Antarctica (EPSTEIN & SHARP, 1962), which never occurred in Greenland.

In this connection it may be useful to consider the  $\delta_{18}$  variation in precipitation at the Greenland station Nord ( $82^\circ$  N). The  $\delta_{18}$  record of monthly precipitation goes back to Sept. 1957 (Fig. 4). The mean annual air temperature is  $-17^\circ\text{C}$  and, consequently, the  $\delta_{18}$  is very low. The  $\delta_{18}$  curve shows approx. the same width of the minima and the maxima.

The method of determining annual accumulation on polar glaciers is based on the seasonal variation. Even though this variation broadly appears from Fig. 4, one can easily find  $\delta_{18}$  values, which are unusual for the season (cf. Sept. 57, Dec. 58 and Jan. 61).

In the lower section of Fig. 4 the horizontal lines are plotted proportional to the actual amount of precipitation. This curve could be the result of  $\text{O}^{18}$  analysis of samples collected on a nearby glacier, if no melting or drift had disturbed the stratigraphy. Such disturbances are sources of error in the glaciological method

just mentioned; evidently, on the hypothetical Station Nord glacier a snow drift of 25 mm water equivalent could erase the 1957-58 minimum. Unusual isotopic composition of a relatively large amount of precipitation constitutes another source of error; thus, it seems possible that the low Sept. 57 could be misinterpreted as a winter minimum.

#### 2.4. AMOUNT EFFECT I

In chapter 4, and especially section 4.2.3., a negative correlation will be demonstrated between  $\delta$  and the amount of monthly precipitation, i.e. low  $\delta$ 's in rainy months and high  $\delta$ 's in months with sparse rain. This "amount effect" is found all the year round at most tropical stations, and in the summer time at mid latitudes, but never at polar stations, where the temperature effect is the dominating factor.

When looking for reasons for the amount effect we are confronted with difficulties, mainly because of the extreme complexity of the isotopic turnover in the processes forming convective rain. The air moves in vertical direction, and the condensate formed at any stage falls down through all the foregoing ones. Thereby, it is mixed up with the droplets and takes up new vapour at the lower stages. On top of that, further complications are added by exchange in the cloud and, during the fall from the cloud to the ground, by exchange and evaporation in the non-saturated air (the situation is somewhat simpler in case of hail, cf. FACY *et al.* (1963)).

However, we may consider qualitatively several possible, and probably contributing, reasons for the amount effect: (1) Looking at a given mass of condensing vapour the  $\delta$  of newly formed condensate and, thereby,  $\delta_{\text{mean}}$  of the total amount of condensate,  $n$ , decrease as the cooling proceeds (cp. Fig. 1, p. 440). Since, furthermore,  $n$  increases with the degree of cooling, one may expect an amount effect with a negative correlation between  $\delta_{\text{mean}}$  and  $n$  in cases, where a given location is passed by storms of various degrees of development. (2) The fractionation by isotopic exchange between the falling drops and the environmental vapour (cf. section 3.3.) is most pronounced for light rain causing relatively high  $\delta$ 's in such rain, because the vapour below the cloud has not yet been

exposed to cooling processes (in heavy rain the vapour composition may, more or less, be determined by the liquid phase). (3) The same tendency would seem to appear due to evaporation from falling drops. Low humidity of the low altitude air causing a great relative loss of liquid material (i.e. small values of  $n$ ) and, thereby, considerable enrichment of the rain (i.e. high  $\delta$ 's).

Thus, both evaporation and exchange usually tend to enrich small amounts of rain in heavy isotopes. Low  $\delta$ 's in tropical rain must, therefore, be due to deep cooling of the air followed by only little enrichment by the other processes (e.g. in case of heavy and/or long lasting rain and high humidity), whereas high  $\delta$ 's could be due to either the rain being a first stage product and/or a later stage product enriched by exchange and evaporation (light rain and low humidity). Direct evidence of enrichment by evaporation from falling drops have been reported by DANSGAARD (1953, 1961, p. 71) and by EHHALT *et al.* (1963).

When going towards higher latitudes the amount effect becomes less pronounced, partly because of the lower degree of evaporation from falling drops. In the polar regions the isotopic composition is closely connected to the low altitude temperature, because most precipitation is formed at lower altitudes, and precipitating clouds consist usually of ice crystals, which are exposed to negligible isotopic fractionation by evaporation or exchange with environmental vapour (cf. section 3.3.).

One might expect that a parameter like the mean intensity of precipitation,  $i$ , would show some correlation with  $\delta$  in the tropics, because low intensity would seem to correspond to relatively (1) low degree of cooling and, at the same time, (2) high degree of evaporation and (3) exchange with low altitude vapour. However, such a correlation between  $i$  and  $\delta$  does not seem to be a general feature, at least not for continental stations.

Let us, as an example, consider Binza, Congo. For each period of precipitation the Congo Meteorological Service has observed the amount of precipitation ( $n$  mm) and the duration of the period ( $T$  hours). For 16 monthly samples the correlation coefficient between  $\delta_{18}$  and  $\sum n$  (=the total monthly amount of precipitation) is 0.82. However, the Binza data also enable us to calculate the weighted mean intensity of rain,

TABLE 4

Sample	$\sum n$ mm	$i$ mm/hour	$\delta_{18}$ ‰	Number of rain periods
Sept. 61	84	5.3	-1.75	7
Nov. 61	255	4.5	-8.48	34

$$i = \frac{\sum (n^2/T)}{\sum n} \text{ mm/hour}$$

for each month ( $i$  varied between 1.2 and 19.8 mm/hour,  $\delta_{18}$  between -0.35 and -8.48‰). The correlation coefficient between  $\delta_{18}$  and  $i$  is only 0.07. Thus,  $\delta$  has no correlation with  $i$ .

In Sep. and Nov. 1961 the rain fell with approx. the same mean intensity, but Nov. was dominated by frequent periods of rain, and the total amount was 3 times greater than in Sep. (Table 4). The very low  $\delta_{18}$  in Nov. is due to a combination of (1) deep cooling by high lifting and (2) generally high humidity and, consequently, relatively little enrichment by evaporation from falling drops.

These data point to the humidity (or rather the precipitative water, i.e. the total amount of water in a 1 cm<sup>2</sup> column) as being a very important factor, at least at continental stations. The same feature appears in the record on Copenhagen precipitation covering 8 years. In the relatively dry spring the  $\delta_{18}$ 's are generally almost 2‰ higher than in the autumn, in spite of the condensation temperature being generally lower in spring.

## 2.5. THE $\delta_D$ - $\delta_{18}$ RELATION

Whereas a  $F_v$ - $\delta$  diagram, e.g. Fig. 1, reflects only the fractionation of one heavy component relative to the light one (H<sub>2</sub>O<sup>16</sup>), the plotting of  $\delta_D$  against  $\delta_{18}$  opens up the possibility of following the important processes, in which the two heavy components behave in different ways, e.g. kinetic effects. However, it is worth noticing that even the simple equilibrium processes considered in this chapter lead to  $\delta_D$ - $\delta_{18}$  relations, which are not quite simple.

The condensation curves  $C_0$ ,  $C_{30}$  and  $C_{30}$  shown in Fig. 5 are obtained (partly from Table 2) by plotting the calculated  $\delta_D$  against the calculated  $\delta_{18}$  for the initial temperature  $t_0$  equal

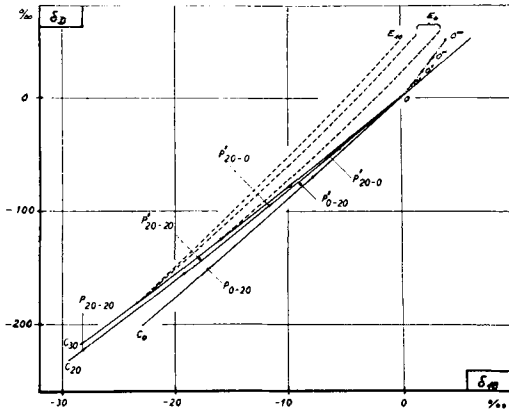


FIG. 5. Calculated  $\delta_D-\delta_{18}$  relations. The  $C$ -curves reflect the composition of newly formed condensate in isobaric condensation processes starting at  $0^\circ$ ,  $20^\circ$  and  $30^\circ\text{C}$ . The composition of the first stage product is supposed to be  $\delta_D=\delta_{18}=0$ . The  $E$ -curves reflect the composition of the remaining water in isothermal evaporation processes.

to  $0^\circ$ ,  $20^\circ$  and  $30^\circ\text{C}$ , respectively. Point  $O$  represents the composition of the first small amount of condensate released at  $t_0$ , i.e. SMOW. As the cooling proceeds, the composition of newly formed condensate changes so that its characteristic  $(\delta_D, \delta_{18})$  point moves down one of the curves depending on  $t_0$ . Temperature marks are given on the  $C_0$  and  $C_{30}$  curves for each 10 degrees cooling. E.g. the point  $P_{0-20}$  on  $C_0$  indicates the composition of new condensate released at  $t = -20^\circ$  in an isobaric process starting at  $t_0 = 0^\circ$ . Had the process been moist-adiabatic, the corresponding composition would have been that indicated by  $P'_{0-20}$ . Similarly, the "moist-adiabatic" points  $P'_{20-0}$  and  $P'_{20-20}$  correspond to the "isobaric" points  $P_{20-0}$  ( $t_0 = 20^\circ, t = 0^\circ$ ) and  $P_{20-20}$  ( $t_0 = 20^\circ, t = -20^\circ$ ) on  $C_{20}$ .

Already at this stage it is evident that, even under the very simplest assumptions, the position of a given rain in the  $\delta_D-\delta_{18}$  diagram is a function of several parameters, such as (1) the initial vapour composition, (2) the initial dew point  $t_0$ , (3) the degree of cooling,  $t_0-t$ , and (4) the way of cooling. Furthermore, it is clear that all rains cannot be expected to lie along one single curve in the  $\delta_D-\delta_{18}$  diagram; the way of cooling as well as  $t_0$  influence the slope of the curve, which reflects the preceding condensation from a given vapour reservoir.

Other, even more important factors, e.g. kinetic effects, will be mentioned in section 3.1.

The two dashed evaporation curves,  $E_0$  in Fig. 5, show the variation of a water reservoir evaporating at  $0^\circ$ , the initial compositions being given by two points on  $C_{30}$ . The curve  $E_{10}$  from the lower point reflects an evaporation at  $10^\circ$ .

The slopes of such curves have shown to be an important characteristic of natural fractionation processes. A mathematical expression for the slope,  $s_C$ , of the simple condensation processes is evaluated from equation (8), p. 441. Since this equation is valid for both the deuterium and the  $O^{18}$  component,  $s_C$  is calculated as

$$s_C = \frac{d\delta_D}{d\delta_{18}} = \frac{d\delta_D}{dt} \bigg/ \frac{d\delta_{18}}{dt}$$

Similarly, the slope  $s_E$  of the curves for isothermal evaporation is derived from (7):

$$d\delta_w = \epsilon F_w^{\epsilon-1} dF_w$$

valid for both components, i.e.

$$s_E = \frac{d\delta_D}{d\delta_{18}} = \frac{\epsilon_D}{\epsilon_{18}} F_w^{\epsilon_D - \epsilon_{18}} \tag{12}$$

Values of  $s_C$  and  $s_E$  are listed in Table 5 for all stages of the processes considered in Table 2. The columns 2 and 5 give  $s_C$  and  $s_E$  in the starting point  $(\delta_D = \delta_{18} = 0)$ . The figures in parenthesis denote mean values of the slopes from the beginning of the process to the stage in question.

Disregarding the initial value at  $t_0 = 100^\circ$ ,  $s_C$  is  $8.0 \pm 0.9$ , with a minimum at  $t_0 = 60^\circ$ . In the very important case  $C_{20}$  ( $t_0 = 20^\circ$ ), the mean value of  $s_C$  is  $8.0 \pm 0.2$ , over a range of 40 degrees cooling both under isobaric and moist adiabatic cooling. As stated by DANSGAARD (1961) a change from vapour-water to vapour-ice equilibrium will have no significant effect.

The value  $8.0 \pm 0.2$  is in accordance with earlier findings of  $8.1 \pm 0.4$  (sea water, FRIEDMAN, 1953),  $8.1 \pm 0.4$  (Greenland ice, DANSGAARD, NIEF & ROTH, 1960), and 8 (CRAIG, 1961). The latter author claims a slope of 5 to correspond to Rayleigh processes at liquid-vapour equilibrium at about  $100^\circ\text{C}$ . Such low slopes are certainly not found here, when using

TABLE 5. Slope of  $\delta_D - \delta_{18}$  curves.

$t_0$	$s_C$ . Condensation by isobaric cooling (for $t_0 = 100^\circ\text{C}$ isochoric)			$s_E$ . Isothermal evaporation		
	$t = t_0$	$t = t_0 - 20$	$t = t_0 - 40$	$F_w = 1$	$F_w = 0.3$	$F_w = 0.1$
(1)	(2)	(3)	(4)	(5)	(6)	(7)
0	8.9	8.5 (8.8)		8.6	9.6 (9.1)	10.5 (9.6)
20	8.2	7.9 (8.1)	7.5 (7.9)	8.1	8.7 (8.3)	9.4 (8.6)
40	7.8	7.6	7.2	7.7	8.2 (8.0)	8.6 (8.2)
60	7.7	7.5	7.2	7.5	7.9	8.2
80	8.3	7.6	7.2	8.0	8.3	8.6
100	11.6	8.5	7.9	8.6	8.8	9.1

$t_0$	$s_C$ . Condensation by adiabatic cooling ( $p_0 = 1000$ mb)		
	$t = t_0$	$t = t_0 - 20$	$t = t_0 - 40$
0	8.7	(8.3)	
20	8.0	(7.9)	(7.8)

the  $\alpha$ -values given in Table 1, which are the most reliable known to the present author.

It should be noted that whereas for isothermal evaporation

$$s_E \cong \epsilon_D / \epsilon_{18},$$

according to eq. (12), because the exponent  $\epsilon_D - \epsilon_{18}$  is small and constant, the slope of the condensation curves cannot be calculated approximately as

$$s_C = \frac{\alpha_D - 1}{\alpha_{18} - 1}, \tag{13}$$

mainly because the term containing  $d\alpha/dt$  in eq. 8 is not negligible; e.g. for  $t_0 = 20^\circ$  and  $t = -20^\circ$ , eq. (13) gives  $s_C = 10.9$ , whereas (8) gives 7.5 (Table 5).

A most interesting possibility has been pointed out by ERIKSSON (1964), namely, that  $\alpha - 1$  in the Rayleigh formula (6) should be replaced by  $\sqrt{\alpha} - 1$ , when considering average values, due to eddy diffusion processes in the atmosphere. This procedure gives the values of  $\delta_D$ ,  $\delta_{18}$  and  $s_C$  listed in Table 6 for the isobaric process from  $t_0 = 20^\circ$ , to  $t = -20^\circ$  i.e. only approx. 40 % of the fractionation calculated before, and an almost linear  $\delta_D - \delta_{18}$  curve with a slope close to 7.3.

### 3. Non-equilibrium processes

Any use of the  $\alpha$  factors (Table 1, p. 438) involves the assumption of equilibrium, which

is only true in practically infinitely slow processes. Many observations show that lack of equilibrium has important consequences for several *evaporation* processes in nature. However, up till now, only weak indications of kinetic isotope effect have been found in the investigated *condensation* processes. All reported examples (CRAIG, BOATO & WHITE, 1956; BOATO, 1960; CRAIG, 1961; EHHALT *et al.*, 1963; CRAIG, GORDON & HORIBE, 1963) have been concerned with local evaporation phenomena, whereas the process of highest importance for the global movement of water, namely the evaporation from the oceans, has never been the object of a systematic investigation.

#### 3.1. KINETIC EFFECT

The theory behind the non-equilibrium processes is very complicated (not even the  $\alpha$  values at equilibrium are fully explained). Qualitatively, however, many observed deviations from the

TABLE 6. Isobaric cooling from  $t_0 = 20^\circ\text{C}$ . Exponent  $\sqrt{\alpha_m} - 1$  in eq. (6).

$t^\circ\text{C}$	$\delta_D$ ‰	$\delta_{18}$ ‰	$s_C$
20	0	0	7.3
-20	-88	-12.1	7.5

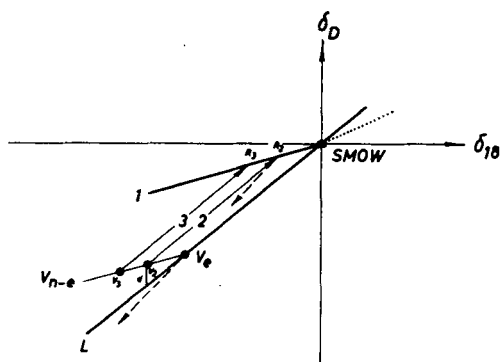


FIG. 6. The approximate  $\delta_D$ - $\delta_{18}$  relation in equilibrium processes (slope  $\cong 8$ ) and in non-equilibrium processes (slope  $< 8$  for evaporation, slope  $> 8$  for condensation). See text for details.

simple equilibrium processes can be interpreted as consequences of the various isotopic components having different rates of reaction,  $c$ :

$$c(\text{H}_2\text{O}^{18}) > c(\text{HDO}^{18}) > c(\text{H}_2\text{O}^{16}). \quad (14)$$

By extremely fast evaporation (into vacuum) one may, as a rough, approximation consider the flux of a given isotopic component from the water surface as being proportional, not only to the equilibrium vapour pressure of the component in question, but also to its rate of diffusion from the deeper layers. This would cause an effective fractionation factor of  $\alpha^K = \mu\alpha$  instead of  $\alpha$ ,  $\mu$  being the ratio between the diffusion rates of the light and heavy components, i.e.  $\alpha_D^K = \sqrt{19/18} \cdot 1.08 = 1.11$  for  $\text{HDO}^{18}$ , and  $\alpha_{18}^K = \sqrt{20/18} \cdot 1.009 = 1.063$  for  $\text{H}_2\text{O}^{18}$  in case of mono-molecular movement in the liquid phase. However, according to the cell-cluster model, the water molecules move in clusters, consisting of several molecules. If, for example, six molecules move together, the mass numbers of the isotopic components become 108, 109 and 110, the latter two clusters containing one deuterium and one  $\text{O}^{18}$  atom, respectively. Hence,  $\alpha_D^K = 1.09$ ,  $\alpha_{18}^K = 1.028$ . This is not far from the experimental results,  $\alpha_D^K = 1.075 - 1.090$ ,  $\alpha_{18}^K = 1.025$ , obtained by evaporation from a thin water jet into a fastly passing stream of dry air. However, in this case the presence of air highly reduced the rate of evaporation, so that the diffusion of the vapour into the air may be the critical point. Anyhow, the experiment shows

the deuterium component to be much less sensitive to kinetic effects than the  $\text{O}^{18}$  component, since  $\epsilon_D (= 1/\alpha_D - 1)$  deviated no more than 15 % from the equilibrium value, whereas  $\epsilon_{18}$  deviated 200 %.

According to eqt. (12) the slope of the first part of the curve for a fast evaporation at  $20^\circ\text{C}$  becomes 3.2, when using the above mentioned values of  $\alpha^K$ , instead of 8 in case of equilibrium. In Fig. 6 the line  $L$  is drawn with a slope of 8. By fast evaporation of a limited amount of SMOW, the composition of the remaining liquid would change along some line like the dotted one.

If vapour in equilibrium with SMOW is denoted by  $V_e$  on line  $L$  (slope = 8, Fig. 6), fastly evaporated vapour must have lower  $\delta_D$  and  $\delta_{18}$ , because  $\text{H}_2\text{O}^{18}$  is the fastest reacting component. The  $(\delta_D, \delta_{18})$  point,  $V_{n-e}$ , of such non-equilibrium vapour is laying above  $L$ , because  $c(\text{HDO}^{18}) > c(\text{H}_2\text{O}^{18})$ . The slope  $s_v (< 8)$  and length of  $V_e V_{n-e}$  depends upon factors like the humidity, the temperature and the wind speed component perpendicular to the water surface, the turbulence in the water etc.

The first stage of an equilibrium condensation from any vapour on the line  $V_e V_{n-e}$  will cause rain laying on line No. 1 ( $\delta_D = s_v \cdot \delta_{18}$ ) through SMOW, e.g. vapour  $V_2$  gives a first stage rain  $R_2$ ,  $V_3$  gives  $R_3$  etc. By further equilibrium condensation later stage rains will follow  $C$ -curves starting at  $R_2$ ,  $R_3$  or another point on line No. 1. According to Fig. 5 and Table 5 we do not commit any considerable error, at least not in the high  $\delta$  range, by approximating the  $C$ -curves to lines with slope 8. Consequently, in Fig. 6 the composition of later stage rains may be considered to move from the first stage point down along some line parallel to  $L$ , e.g. from SMOW along  $L$ , from  $R_2$  along line No. 2 etc. (at the same time the remaining vapour in question moves in the same direction from the  $V$  point).

The experiments show that evaporation from a limited water surface goes on under equilibrium conditions only by very slow removal of vapour. On the other hand, no distinct indication of non-equilibrium condensation has been reported till now, as far as the present author knows. Nevertheless, the relation (14) might also influence the condensation process in extreme cases, but in the opposite direction, because the relatively high rate of reaction of the light com-

ponent would counteract the preferential condensation of the less volatile heavy components, i.e. both of the  $\alpha^K$ 's would be lower than under equilibrium. If, in analogy with the evaporation,  $\alpha_D - 1$  is supposed to be less sensitive to kinetic effects than  $\alpha_{18} - 1$ , a hypothetical non-equilibrium condensation of vapour  $V_e$ , would give a first stage condensate deviating from SMOW along a line like No. 1. Let  $R_2$  be the composition of such first stage condensate. At later stages (continental rains?) the new condensate and the remaining vapour would follow a curve with a slope  $> 8$  (the line  $R_2V_e$  shown dashed in Fig. 6).

The above is only a rough, qualitative consideration which, nevertheless, may be useful, when trying to interpret the numerous data in chapter 4. In order to simplify the terminology we shall now introduce a new parameter:

The surplus of deuterium relative to  $L$  is in the following denoted by  $d$  (e.g. SMOW and  $V_e$  in Fig. 6 have  $d = 0$ , whereas  $V_2$  has a positive  $d$ ). This parameter can apparently be used for indicating non-equilibrium conditions.

*Equilibrium processes do not change the d-index for any of the phases*, e.g. SMOW ( $d = 0$ ) gives equilibrium vapour  $V_e$  ( $d = 0$ ). Furthermore, vapour  $V_2$  is condensed into  $R_2$  with the same  $d$  as  $V_2$ . By further equilibrium condensation both  $R_2$  and  $V_2$  move down line 2 parallel to  $L$ , i.e. their  $d$  remains unchanged.

*Non-equilibrium evaporation from a limited amount of water reduces the d-index of the water* as long as exchange is not a dominating factor, e.g. fast evaporation of a limited amount of SMOW would make the water moving upwards along a line with a slope  $< 8$  (dotted in Fig. 6), i.e. the  $d$ -index would get more and more negative. Similarly,  $n-e$  condensation from a limited amount of vapour would decrease the  $d$ -index of the vapour (cf. the dashed curve from  $V_e$  in Fig. 6), but this process does not seem to be common in nature.

*By Non-equilibrium evaporation from an infinitely large and well mixed reservoir, d of the water will, of course, remain constant and, disregarding exchange, the d-index of the vapour will be positive and it will increase with the rate of reaction* (cf.  $V_e \rightarrow V_{n-e}$  in Fig. 6; as usual, exchange between the phases will reduce the effect). In this very important case  $d$  is, thus, not only a non-equilibrium indicator, but even a "rate of evaporation" index. Furthermore,

TABLE 7. Mean  $\delta_{18}$  in ocean samples (EPSTEIN & MAYEDA, 1953).

Number of samples	Depth, m	Mean $\delta_{18}$ ‰
21	0- 25	+ 0.38
13	500-2000	- 0.19
8	4000-7500	- 0.41

supposing condensation to be an equilibrium process in nature, the averaged  $d$  of precipitation at a given locality reflects the rate of evaporation in the source area. This would seem to be a powerful tool in chemical meteorology.

### 3.2. THE COMPOSITION OF EVAPORATING OCEAN WATER

Unfortunately, relatively few measurements have been published on ocean water. The definition of SMOW (CRAIG, 1961 b) is based upon a NBS standard water and upon EPSTEIN & MAYEDA's (1953) data on 6 Atlantic, 11 Pacific and 2 Indian Ocean samples taken from 500 to 2000 m depth.

Owing to the evaporation from the surface layer of the oceans, which is not completely mixed with the rest, the upper layer has a composition with positive  $\delta$ 's relative to SMOW. This appears clearly from Epstein and Mayeda's data as seen in Table 7. Of these samples only one is from a latitude higher than  $45^\circ$ . In the first group 5 surface samples from the Atlantic subtropical high pressure region have a mean of  $+0.69\%$ , whereas the mean of 9 surface samples from the East Pacific is  $+0.15\%$ . Thus, the surface water shows measurable regional variations, but usually positive  $\delta_{18}$  because of the evaporation. If the evaporation takes place under non-equilibrium conditions, the evaporating surface water probably has a composition somewhere on the dotted line in Fig. 6, i.e. a negative  $d$ -index. The line  $L$  is, nevertheless, considered most rational to use as a reference, but it is worth noticing that SMOW represents evaporating ocean water only as far as first order effects are concerned.

### 3.3. EXCHANGE

A drop of water falling through saturated air of the same temperature will, practically speaking, be in quantitative equilibrium with

TABLE 8. Adjustment time ( $\tau_a$ ) and distance of fall ( $f_a$ ) for the HDO content in falling drops of radius  $r$ .

$r$ cm	$\tau_a$ sec	$f_a$ m
0.01	7.1	5.1
0.05	9.2	370
0.075	164	890
0.10	242	1600
0.15	360	2900

the vapour, i.e. per unit of time the number of water molecules leaving the drop is the same as that condensing on the surface of the drop. However, a further condition for isotopic equilibrium, i.e. for the above being true for each isotopic component, is that the heavy isotope content of the water phase,  $a_w$ , is  $\alpha$  times that of the vapour phase,  $a_v$ , or  $\delta'_w$  (relative to the vapour composition) being equal to  $\alpha - 1$  (cf. eq. (4)). Otherwise, the exchange of molecules between the phases will cause a successive change of  $a_w$  until it reaches the value  $\alpha a_v$  (or  $\delta'_w = \alpha - 1$ ).

The consequences of the process for the condensation in a cloud was discussed by DANS-GAARD (1953, p. 465), who assumed a fast equilibrium between the cloud droplets and the environmental vapour.

BOLIN (1958) has derived a formula for the adjustment time, i.e. the time it takes for a falling drop to reach to a composition, which deviates  $1/e$  of  $(\alpha a_v - a_w)$  from the equilibrium value,  $\alpha a_v$ . Bolin's formula was essentially verified experimentally by FRIEDMAN, MACHTA and SOLLER (1962). Some of their results for the HDO component are listed in Table 8.

Apparently,  $\tau_a$  and, consequently, the corresponding distance of fall,  $f_a$ , increase rapidly with  $r$ . Thus, cloud droplets equilibrate almost instantly. Even large drops may undergo considerable change in composition. However, the composition of the liquid phase must be expected to be the dominating one in cases of heavy and long lasting rainfall, especially if the drops travel through relatively stagnant air.

Evidently, attempts to interpret the isotopic composition of rain should involve the consideration of the vapour composition, but, unfortunately, this is not technically feasible in a world wide project like that described in chapter 4.

If the humidity is less than 100 %, a net evaporation will diminish the drop, and a kinetic effect will complicate the situation. Unlike the case treated by CRAIG *et al.* (1963) the isotopic composition of the drop does not reach to a constant value before the drop disappears, because the diminishing mass of the drop will cause a decreasing velocity of fall and, thereby, a decreasing rate of evaporation.

Exchange between snow and vapour can only affect the outer layers of molecules appreciably and is, therefore, considered negligible.

#### 4. The I.A.E.A.-W.M.O. precipitation survey

As mentioned in the introduction a world wide precipitation survey has been organized by I.A.E.A. and W.M.O. since 1961. Samples of monthly precipitation have been collected for isotope analysis at an increasing number of stations (at present over one hundred) spread over all continents (Fig. 7).

The stable isotope data on samples from 1961 and 1962 will be given later in this journal.

##### 4.1. THE MEAN ANNUAL ISOTOPIC COMPOSITION

Up till now, a complete record of stable isotope measurements covering at least one year has been obtained from some 70 stations. The data indicated on the five following figures are mean values,  $\delta_m$ , of samples of monthly precipitation.

Whenever possible,  $\delta_m$  has been calculated over all months of a whole number of years. Due to changing weather conditions from one year to the other, the  $\delta_m$  can, of course, vary as well, especially at dry stations, where it may be determined by a few rain storms. Nevertheless, with this remark in mind, the  $\delta_m$ 's have been interpreted tentatively as normals in the following, but if the composition at a single station is in contradistinction to that of otherwise apparently similar stations, one should probably wait a couple of years to decide whether this is accidental or not.

The simple mean value, e.g. over 12 months,

$$\delta_m = \frac{1}{12} \sum_{i=1}^{12} \delta_i$$

reflects the gross climatic conditions the year round, whereas the weighted mean value



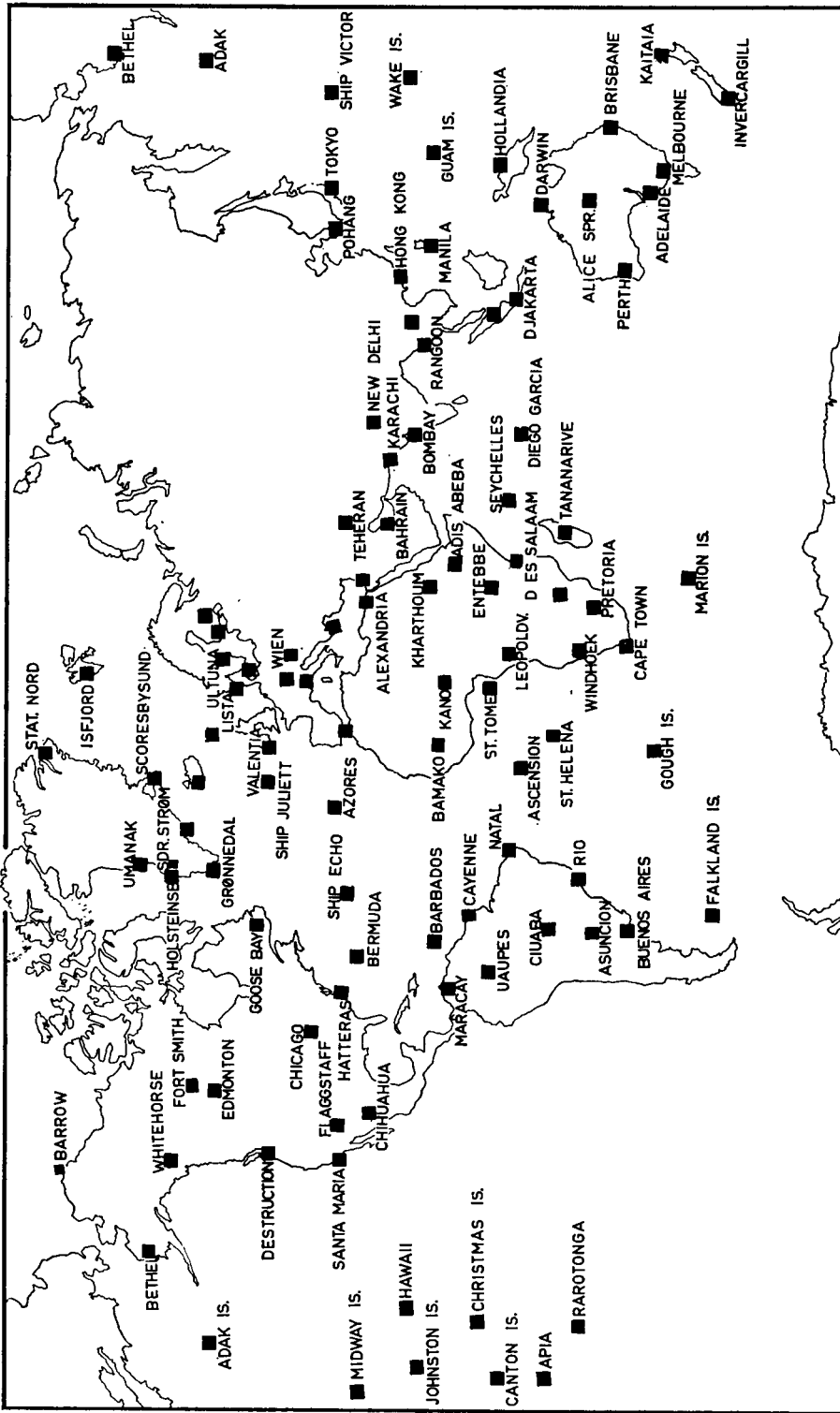


Fig. 7. The I.A.E.A.-W.M.O. precipitation network.

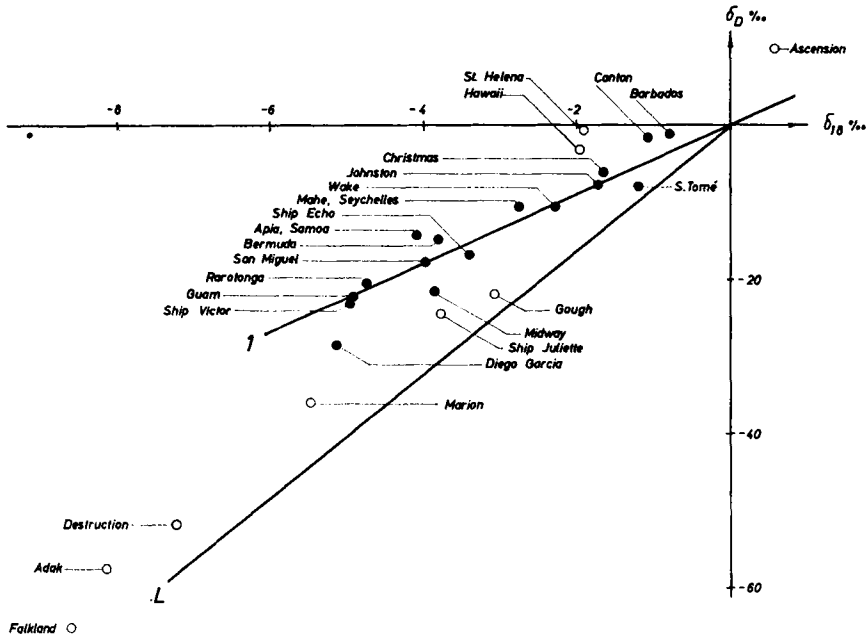


FIG. 8. Unweighted means for island stations.

$$\delta_m^w = \frac{1}{P} \sum_{i=1}^{12} (p_i \cdot \delta_i)$$

$p_i$  and  $P$  being the monthly and annual amount of precipitation, is rather determined by the conditions in the rainy periods.

In some cases with occasionally very sparse precipitation the unweighted mean,  $\delta_m$ , may be heavily influenced by a few months, in which the more or less accidental evaporation from falling drops causes  $\delta$ 's extremely deviating from normal. In regions with dry seasons, the weighted  $\delta_m^w$  is, therefore, preferred as a basis for comparison.

4.1.1. Island stations

In Fig. 8 the dots indicate the unweighted mean composition ( $\delta_{Dm}$ ,  $\delta_{18m}$ ), for tropical and subtropical islands (filled circles) and for other islands (open circles). Let us, for a moment, look apart from Ascension, Hawaii and St. Helena for reasons given below, and from Canton, because at this latter station the rainfall was rather unusual in the period considered; thus, 4 out of 12 months had less than 10 % the normal precipitation; with the amount effect in mind the unweighted Canton composition may, therefore, be interpreted at being unusually high.

The ( $\delta_{Dm}$ ,  $\delta_{18m}$ ) points for the other 15 tropical islands and ships fit reasonably well to the heavy line No. 1 through SMOW:

$$\delta_D = (4.6 \pm 0.4) \delta_{18} + (0.1 \pm 1.6) \quad (15)$$

calculated by the method of the least squares. The correlation coefficient is  $0.95 \pm 0.09$ .

The heavy isotope content is not connected with the surface temperature. However, there seems to be some correlation with the mean monthly amount of precipitation, which is below 100 mm at each of the stations Barbados, Canton, S. Tome, Johnston, Christmas and Wake, but from 120 to 245 mm at the lower 10 stations. This effect of low  $\delta$ 's in abundant rain was discussed in section 2.4. and will be shown more clearly later (section 4.2.3.).

The slope of 4.6 indicates that the simple Rayleigh condensation process under equilibrium conditions cannot account for the isotopic fractionation, since the calculation on such processes gives 7.5 as the lowest slope in the temperature range  $20 > t > -20^\circ\text{C}$ . Neither can a kinetic effect in the condensation be responsible for the phenomenon, because this effect would be reflected by a slope higher than 8 (cf. section 3.1., p. 449).

It is more profitable to consider the rain at

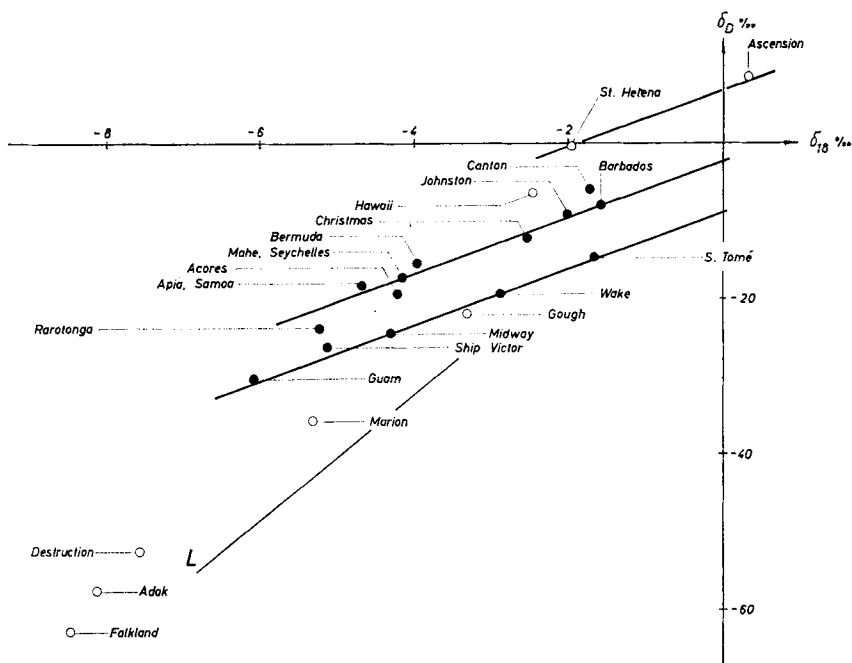


FIG. 9. Weighted means for island stations.

the tropical island stations as being representative for the first stage of the condensation of ocean vapour. A tropical cloud over the ocean has an influx of air containing vapour formed by fast evaporation of sea water. If the vapour composition deviates (along the line  $V_e - V_{n-e}$ , Fig. 6) from the equilibrium composition ( $V_e$ ) to a degree, which increases with the cloud activity, the first stage of equilibrium condensation should produce rains along a line through SMOW and with a slope  $< 8$ , as described in section 3.1., p. 449. This model apparently fits the observations quite well (cf. lines No. 1 in Figs. 6 and 8).

St. Helena, Hawaii and Ascension seem to deviate significantly from the rest. As to Hawaii the precipitation in 1962 was only half the normal, so the normal composition is probably closer to line No. 1. This is supported by the fact that the unweighted mean composition for the more normal year 1963 was  $\delta_{Dm} = -6.9\%$ ,  $\delta_{18m} = -2.51$ . A possible explanation for the odd composition at St. Helena, (Hawaii?) and Ascension is this: They are all three located on the equatorward side of a subtropical high pressure. The prevailing winds have an equatorward component and come from regions with cool sea currents. The air masses are unstable,

and they have not reached to build up the high amount of precipitable water (total amount of water vapour in a column of air), which is typical for the low latitude islands in the Western parts of the oceans. Therefore, the first stage condensation temperature,  $t_0$ , is considerably lower than the evaporation temperature,  $t_e$  (though the precipitation may still represent a first stage condensation). If the corresponding  $\alpha$ -values are denoted by  $\alpha_0$  and  $\alpha_e$ , the equations (2), (4) and (5) on p. 438 give for the first condensate from equilibrium vapour:

$$\delta_c^0 = \frac{1}{\alpha_e} - 1 + \alpha_0 - 1 + \left( \frac{1}{\alpha_e} - 1 \right) (\alpha_0 - 1) = \frac{\alpha_0}{\alpha_e} - 1.$$

Since  $\alpha_0 > \alpha_e$ , the first stage condensate will be enriched relative to SMOW, corresponding to the points  $O'$ ,  $O''$  etc. (Fig. 5, p. 447) for  $t_e - t_0 = 10^\circ$ ,  $20^\circ$  etc. Furthermore, a kinetic effect in the evaporation will cause first stage condensate along a line with slope  $< 8$  through one of the displaced  $O$ -point, i.e. a pattern into which St. Helena, Hawaii and Ascension fit (cf. Fig. 8).

Of the 6 remaining island stations, Marion, Ship Juliette and Gough are lying close to the polar fronts, and Reykjavik, Adak and Falkland on higher latitudes. They all fit—more or less—

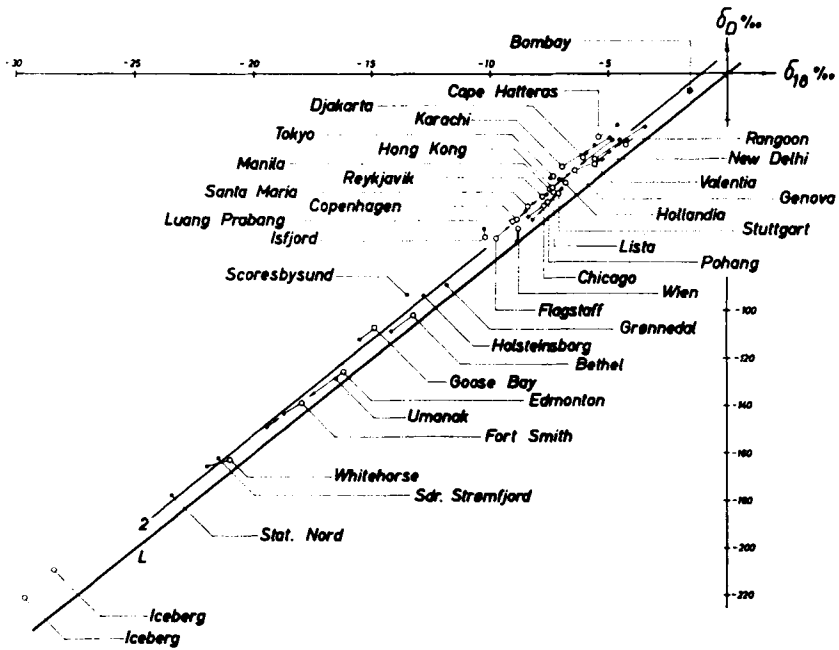


FIG. 10. Weighted (open circles) and unweighted (dots) means for Northern Hemisphere continental stations, disregarding Africa and the Near East.

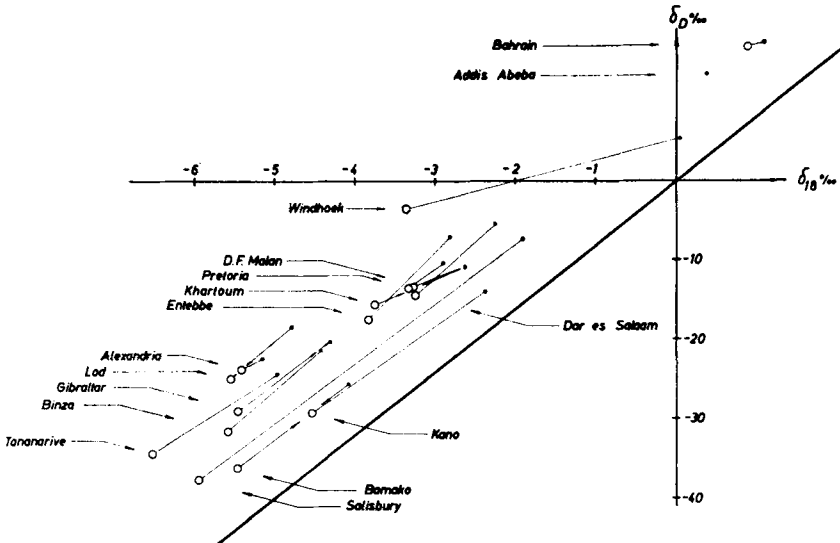


FIG. 11. Weighted (open circles) and unweighted (dots) means for African and Near East stations.

the line for continental stations. Precipitation occurs mainly in connection with cyclonic activity and frontal lifting.

If we consider the weighted means ( $\delta_{18m}^w, \delta_{Dm}^w$ ) shown as large circles in Fig. 9 (filled for tropical and subtropical stations, otherwise open), it seems as the low latitude stations split up into three groups along three (heavy) lines, all with a slope close to 3.5:

$$\delta_D = 3.5 \delta_{18} + d_0.$$

- (1)  $d_0 = +6.5\%$ : Ascension, and St. Helena. Their common climatic features are outlined above.
- (2)  $d_0 = -2.5\%$ : Canton, Christmas, Johnston, Apia, Barbados, Seychelles, Ship E., Bermuda. The 4 former stations are all located in the mid Pacific.
- (3)  $d_0 = -9.0\%$ : S. Tome, Wake, Midway, Ship V. and Guam. The 4 latter stations are all located in the Western part of the Pacific. They have all more than 1000 mm of annual precipitation.

The slope (3.5) being lower than that of line No. 1 for the unweighted means (4.6) may indicate that the intense rain, which dominates the weighted means, originates from vapour released from sea water in a very fast evaporation.

Furthermore, the low value of  $d_0$  in group (3) could be due to the mean condensation temperature for the heaviest rain being relatively low (very high clouds), i.e. such rain does not correspond to a first stage condensate.

Practically all  $\delta_m^w$ 's are lower than the corresponding  $\delta_m$ 's. This is, of course, a result of the amount effect. At Hawaii, no amount effect is observed, because the precipitation is uniformly distributed over all months.

#### 4.1.2. Northern hemisphere continental stations, except Africa and the Near East

The unweighted means for 34 stations shown as dots in Fig. 10 and 1 Antarctic station, which falls outside the frames of the figure, determine a line (No. 2) with the equation

$$\delta_{Dm} = (8.04 \pm 0.14) \delta_{18m} + (9.5 \pm 1.5), \quad (16)$$

the correlation coefficient being  $0.995 \pm 0.018$ . For clearness, only fractions of this line are shown in Fig. 10.

The equation for the weighted means is

$$\delta_{Dm}^w = (8.1 \pm 0.1) \delta_{18m}^w + (11 \pm 1). \quad (17)$$

Both of the equations (16) and (17) are in essential agreement with that given by CRAIG (1961 a).

The position of a given station in the diagram is first and foremost determined by the condensation temperature: all tropical stations lie along the upper end of the line, all polar stations along the mid and lower end. However, Fig. 10 also demonstrates the importance of loss of moisture from an air mass during its passage of extensive territories (cf. the continental effect, Fig. 3 and p. 444) and, especially, high mountains; cf. Bombay → New Delhi, Valentia → Stuttgart → Vienna, Holsteinsborg (West coast of Greenland) → Sdr. Strømsfjord (on the other side of high mountains, at the same altitude and with the same mean air temperature as Holsteinsborg).

Line No. 2 in Fig. 10 (eq. 16) fits very well in with a  $C_{20}$  curve displaced  $+9.5\%$  in deuterium. A comparison with line No. 2 in Fig. 6 and the explanation on p. 449 leads to the conclusion that most continental precipitation on the Northern hemisphere is formed on later stages of an equilibrium condensation from ocean vapour, which has been evaporated in a non-equilibrium process fast enough to give a surplus of deuterium,  $d = +10\%$ .

Another (weaker) indication of the evaporation from the ocean being a non-equilibrium process is deduced from the odd position of Bombay in Fig. 10 with considerably higher  $\delta$ 's than the other stations: In the rainy season the prevailing monsoon winds reach only 700–1000 m above the ground level, and the enormous amounts of rain (550 mm per month from June through Aug.) cannot originate exclusively from this layer. Most of the rain is rather released by convective activity above the monsoon air. On the way down through this air, the isotopic composition of the drops is more or less adjusted by exchange to that of the water in equilibrium with the monsoon vapour. If we assume the exchange to be complete, and that we are dealing with the first stage of the condensation, the composition of Bombay rain reflects that of the monsoon vapour and the

deviation of the rain from SMOW is equal to the deviation of the monsoon vapour from vapour in equilibrium with SMOW. The former deviation is  $-7\text{‰}$  and  $-1.4\text{‰}$  for HDO and  $\text{H}_2\text{O}^{18}$  with a ratio of 5.0.

4.1.3. Other continental stations

The African stations (plus Teheran, Lod and Bahrain) are plotted in Fig. 11, the unweighted means as dots, the weighted means as open circles with lower  $\delta$ 's than the former due to the amount effect. A low slope of the line connecting a dot with its corresponding circle (e.g. Windhoek) indicates non-equilibrium evaporation from falling rain of low intensity. The stations Kano (Nigeria) and Bamako (Mali) both have a monsoon climate like that of New Delhi, and their positions in the diagram are, accordingly, close to line No. 2 in Fig. 10 ( $d = 6\text{‰}$ ). The other African and Near East stations, however, have generally a higher  $d$  than the European, North American and Asian stations (cf. Table 9).

If we turn to *South America*, the Northeastern part of the continent is steadily dominated by moist trade winds from the Atlantic Ocean. Fig. 12 shows that both the weighted and the unweighted means at the coast stations Cayenne, Natal, Rio de Janeiro and Buenos Aires are close to the line No. 1 for tropical island stations. A continental effect is responsible for the low  $\delta$ 's at the inland station Ciuaba. The apparent lack of amount effect at Asuncion is due to the mean values being calculated from only 4 samples collected in rainy months.

Of the 8 investigated *Australian and New Zealand* stations only the tropical Darwin has a  $d < 10\text{‰}$  (Fig. 13).

From *Antarctica* we have only one representative sample collected at Horlick Mountains ( $85^\circ\text{S}$ ) by Dr. Bjørn Andersen. The heavy isotope content is very low ( $\delta_D = -338.3\text{‰}$ ,  $\delta_{18} = -41.94\text{‰}$ ) and corresponds to the very low

TABLE 9.  $d$  for weighted means.

Stations	$d\text{‰}$	$d$ mean
Northern hemisphere	+ 9.4	+ 9.4
Africa and Near East	+ 14.8	+ 14.4
South America	+ 12.6	
Australia	+ 14.1	

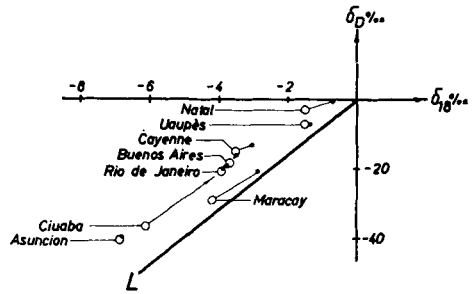


Fig. 12. Weighted (open circles) and unweighted (dots) means for South American stations.

mean air temperature (cf. Fig. 3, p. 443). Of the more than hundred investigated stations, this is the only one with a negative  $d$  ( $-2.8\text{‰}$ ), which may indicate that at least part of the precipitation originates from considerably colder regions of the ocean than in other parts of the world, including the Greenland ice cap (cf. the positive  $d$ 's for the two icebergs). Referring to Fig. 5, a condensation starting at  $t_0 = 0^\circ\text{C}$  would proceed along  $C_0$  with a slope  $> 8$  and, thus, lead to negative  $d$ 's at very low temperatures, even if the initial vapour had a minor positive  $d$ . (cf. FRIEDMAN *et al.*, 1964, p. 197).

In conclusion, a region consisting of (1) Africa and the Near East, (2) South America and (3) Australia except the moist, tropical regions, has precipitation with  $d \approx 14\text{‰}$  (approx. 5‰ higher than Northern Hemisphere continental stations, cf. Table 9). On the lines of the conclusion in the foregoing subsection this is taken as an indication of such precipitation originating from maritime vapour ( $V_3$  in Fig. 6) formed under conditions, which are farther from equilibrium than in other parts of the world. The

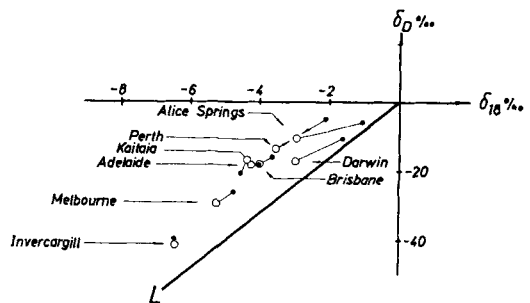


Fig. 13. Weighted (open circles) and unweighted (dots) means for Australian and New Zealand stations.

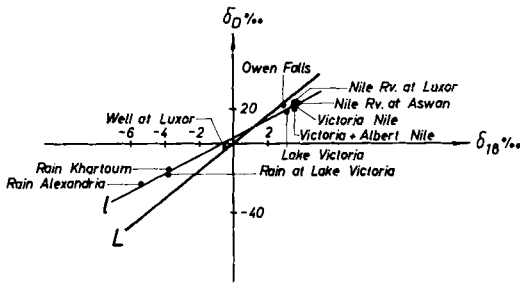


FIG. 14. Weighted means for precipitation at East African stations and February composition of the Nile River.

existence of dry climates prevailing in extensive areas of the above mentioned region supports this suggestion, as such climatic conditions would seem to lead to an increase in the isotopic departure of the vapour from the equilibrium vapour.

#### 4.1.4. Isotopic fractionation along the Nile River

A number of river and ground water samples were collected from North and East Africa along the Nile River in Feb. 1964. Although the following considerations are made on a slender basis, they give some indication of the isotopic turnover in this interesting region.

In Fig. 14 the weighted mean composition of rain at Entebbe has been plotted as representative for the supply of water to Lake Victoria. The Lake Victoria water (sampled at Entebbe) and also the Owen Falls (20 km from the lake) both deviate along the line 1 with a slope of approx. 5 indicating fast evaporation from the lake. In addition to the weighted mean composition of rain at Entebbe Fig. 14 shows those at Khartoum and Alexandria, which also fit line 1 through the February composition of the Nile.

Shortly after having passed Lake Albert, the (Albert) Nile water has a composition (with negative  $d$ ), which is essentially the same as the composition two weeks later at Aswan and Luxor, some 3000 km further North. Thus, if the sparse winter supply of water (and exchanged vapour) to the Nile from the winter dry regions North of  $5^{\circ}$  N can be neglected, the evaporation from the river cannot be considerable in winter (cp. FRIEDMAN *et al.*, 1964).

Whereas the drainage of Lake Victoria is roughly unchanged during the year, the addi-

tional water from the tributary rivers is considerable in the summer time. The composition of the Nile during high water must, consequently, be much closer to that of Khartoum rain. This is supported by the sample collected from a deep well at Luxor (Fig. 14), approx. 3 km from the Nile, because the ground water at this location probably represents a weighted mean of the Nile river.

Thus, it is reasonable to assume both the tributary water and the Nile water far North to be somewhere along line 1 and, since possible seeping does not cause any fractionation, this is also true for the evaporated material. Consequently, the evaporation from the Nile takes place under non-equilibrium conditions corresponding to a slope of 5, as would also be expected considering the dry climate in question.

#### 4.2. THE MEAN MONTHLY ISOTOPIC COMPOSITION

The hitherto considered annual mean values are most suitable for the investigation of the global movement of water. If we want to look at the local isotope effects, we must, of course, consider the monthly samples. They give some more detailed informations and enable us to investigate possible correlations between the isotopic composition and parameters like the condensation temperature, the origin of the vapour and the amount of precipitation.

A  $\delta_D - \delta_{18}$  plot of the monthly samples from the individual station is one useful mean for studying the local isotope turnover and its fitting into a large pattern on a global scale. Unfortunately, it is not feasible to present a  $\delta_D - \delta_{18}$  diagram for each of the many stations. Neither is it the purpose of this paper to look into local details, such as water balance problems, though complete stable isotope records as those given in the appendix must constitute a good basis for such studies (cf. section 4.1.4.).

Instead, some of the most conspicuous features have been listed in Table 10 for those stations from which a reasonably representative number of data are available up till now. Furthermore, in section 4.2.2. six groups of typical  $\delta_D - \delta_{18}$  correlations will be defined.

Table 10 shows in Column 1: name and country of the station, alphabetic order.

Column 2: number of samples considered (from 1961-62, a few from 1963).

TABLE 10

s = summer, w = winter, a = autumn. *Column 2:*  $n$  = number of monthly samples. *Column 5:*  $d$  = surplus of deuterium relative to line  $L$ , cf. Fig. 6. *Column 6:* Temperature effect, cf. section 4.2.4. *Column 7:* Amount effect in ‰ change of  $\delta_{18}$  per 100 mm precipitation. Scattering in ‰, cf. section 4.2.3.

Station (1)	$n$ (2)	$\delta_{18}$ max min (3)		Slope (4)	$d$ max min (5)		Temp. effect (6)	Amount effect (7)
Acores (see San Miguel)								
Adelaide, Australia	12	-1	-5	$8 \pm 1.5$	15	-	-	
		exc. Jan.	-8					
Addis Ababa, Ethiopia	4	+3	-3	(10)	20	11	-	-
Adak, N. Pacific	12	-5	-11	$8 \pm 1$	8	-	-	-
Alexandria, Egypt	7	-4	-6	-	18	-	-	+
Alice Springs, Austr.	10	+5	-4	$5 \pm 1$	18	-10	-	+?
		exc. Jan.	-8	exc. Jan.				
Apia, Samoa, S. Pac.	10	-2	-7	-	19	-	-	+
Ascension Isl., S. Atl.	13	+2	-1	-	5	-	-	+?
Athens, Greece	13	-2	-8	$8 \pm 1.5$	19	-	-	+
Bahrain	8	+6	-2	$3 \pm 1$	23	-12	-	-
Barbados Isl., N. Atl.	22	+2	-4	$8 \pm 1.5$	5	-	-	-1.2 2
Bermuda Isl., N. Atl.	12	-2	-6	-	16	-	-	-
Bethel, Alaska	12	-9	-21	$7.5 \pm 1$	5	+	+	-
Binza, Congo	16	0	-9	$8 \pm 1$	14	-	-	-2.2 4
Bombay, India	10	0	-3	$8 \pm 1.5$	5	-	-	-
Brisbane, Australia	12	-2	-4	$8 \pm 2$	14	-	-	+
		exc. Jul.	-11					
Buenos Aires, Argentine	18	-2	-8	$8 \pm 1$	13	-	-	-
Canton, S. Pac.	23	+2	-3	-	7	-	-	-1.5 2
		exc.						
		Dec. 62:	-10					
Cape Hatteras, U.S.A.	12	-3	-7	$4.5 \pm 1.5$	22	4	-	+
				exc. Jan.				
Cape Town (see D. F. Malan)								
Cayenne, Fr. Guiana	8	-2	-5	-	11	-	-	+?
Chicago, U.S.A.	12	-2	-19	$7 \pm 1$ (w)	22	-15	0.35	+ (s)
				$5 \pm 1$ (s)				
Chihuahua, Mexico	7	-4	-9	-	12	-	-	-
Christmas Isl., N. Pac.	13	0	-3	-	7	-	-	-1.3 2.5
Cuiaba, Brazil	13	+3	-10	$8.0 \pm 0.5$	11	-	-	-3.6 6
Dar es Salaam, Tangan.	20	0	-7	$8 \pm 2$	13	-	-	-1.2 4
Darwin, Australia	7	+2	-4	$3.5 \pm 1$	16	-9	-	-
		exc. Jan.	-9	exc. Jan.				
Destruction Isl., E. Pac.	9	-6	-9	$4 \pm 2$	21	7	-	-
D. F. Malan, S. Africa	17	-1	-7	$6 \pm 1.5$	24	-2	+	-
Diego Garcia, Ind. Oc.	8	-3	-6	$6 \pm 2$	13	-	-	-
Djakarta, Indonesia	12	-3	-9	$8.0 \pm 0.5$	15	-	-	+
Edmonton, Canada	17	-11	-26	$8.0 \pm 0.5$	7	0.4	-	-
Entebbe, Uganda	12	0	-8	$10 \pm 1$	11	-28	-	-2.2 3
Falkland (see Stanley)								
Flagstaff, Arizona	13	0	-16	$8 \pm 1$	10	+	+	- exc.
								for $p < 15$
Fort Smith, Canada	9	-13	-26	$8 \pm 1.5$	3	+	+	-
				exc. Aug.				
				& May				
Genoa, Italy	13	-3	-9	$8 \pm 1$ (w)	16	-25	-	-
		exc. Jul.	+2	$4.3 \pm 1$ (s)				
Gibraltar (see North Front)								
Goose Bay, Canada	20	-10	-28	$8.0 \pm 0.3$	12	+	+	-
Gough Isl., S. Atl.	21	-1	-5	-	3	+	+	-



Table 10 (continued)

Station (1)	n (2)	$\delta_{18}$		Slope (4)	d		Temp. effect (6)	Amount effect (7)	
		max (3)	min		max	min			
Guam Isl., Pac.	13	-1	-8	$8 \pm 1.5$	17	-	-2.0	1.6 exc. Sep. $p = 550$	
Hawaii (Hilo), N. Pac.	23	-1	-4	-	12	-	-	-	
Hollandia, New Guinea	22	-3	-9	$8 \pm 1.5$	11	-	-	+	
Hong Kong (Kings Park)	20	0	-12	$7 \pm 1$	8	-	-1.4	5	
Isfjord, Svalbard	15	-6	-15	$7.5 \pm 1$	14	-	-	-	
Johnston Isl., N. Pac.	12	0	-3	$5 \pm 2$	6	-	-1.5	2	
Kano, Nigeria	11	+10	-8	$5.2 \pm 0.5$	19	-20	-	-2.2	5
				8 in rainy season					
Karachi, Pakistan	7	+1	-13	$8 \pm 1$	12	?	-	+	
Lista, Norway	20	-4	-9	$8 \pm 1$	7	+	-	+(s)	
Lod (Beth Dagon), Israel	13	0	-8	$5.5 \pm 1.5$	31	4	-?	+	
Luang Prabang, Laos	13	0	-13	$8.0 \pm 0.5$	12	-	-	+	
Mahe, Ind. Ocean	15	+4	-8	$5.5 \pm 1$	20	-8	-	-1.8	5 exc. Feb.
				exc. Sep. ( $p = 350$ )					
Manila, Philippines	19	0	-10	$8.0 \pm 0.5$	14	-	-1.4	5 for $p < 200$	
Maracay, Venezuela	12	+1	-7	$8 \pm 1.5$	2	-	-3.5	?	
Marion Isl., S. Atl.	21	-3	-6	-	8	-	-	-	
Melbourne, Australia	12	-1	-9	$7.0 \pm 0.3$	16	6	+	+(s and a)	
Midway, N. Pac.	13	-1	-6	$8 \pm 1$	9	-	-	+	
								Feb.-Aug.	
Natal, Brazil	9	+1	-3	-	5	-	-	?	
New Delhi, India	15	+3	-11	$8 \pm 1$	5	-	-	(+)	
North Front, Gibraltar	13	-4	-7	-	23	-4	-	+	
				exc. Jun. & Sep.					
Nord, Greenland	17	-9	-33	$7.4 \pm 0.5$	10	+	-	-	
Perth, Australia	12	0	-5	$4 \pm 1$	17	-13	+	+	
				exc. Jan. (+6, $p = 2$ )					
Pohang, Korea	21	-4	-9	-	7	(+)	-	(+)	
Pretoria, S. Africa	17	0	-5	$5 \pm 1.5$	20	-6	-	-2.0	3
Rangoon, Burma	12	-2	-8	$7 \pm 1.5$	11	-	-	-	
Rarotonga, S. Pac.	6	-2	-6	-	18	-	-	+	
Reykjavik, Iceland	14	-5	-11	$8 \pm 1$	10	+	+	+	
Rio de Jan., Brazil	13	-2	-6	$8 \pm 1.5$	12	-	-	+	
Salisbury, S. Africa	22	+8	-10	$8 \pm 0.5$	8	-	-	+	
				$6.5 \pm 1$ (for pos. $\delta_{18}$ )					
San Miguel Isl., N. Atl.	11	-2	-6	$8 \pm 1.5$	14	-	-	+	
Santa Maria, Cal., U.S.A.	6	+1	-10	?	6	-	-	+	
S. Tomé Isl., S. Atlantic	9	0	-4	-	2	-	-	+	
				exc. May				+14	
St. Helena, S. Atl.	8	-1	-2	-	15	-	-	-	
Seychelles, (see Mahe)									
Stanley, S. Atl.	14	-6	-12	$8 \pm 1$	4	?	-	?	
Stuttgart, Germany	23	-4	-16	$8 \pm 1$	4	+	-	-	
				$6.5 \pm 1$ (s)					
Tananarive, Madagascar	11	-2	-10	$8 \pm 1$	15	-	-	(+)	
Teheran, Iran	14	+4	-7	$5 \pm 1.5$	22	-11	(+)	(+)	
				exc. Sep.					
Tokyo, Japan	22	-4	-12	$4.7 \pm 1$	21	0	+	+	
								(exc. w)	
Uaupès, Brazil	7	+4	-5	-	4	-	-	-	

Table 10 (continued)

Station (1)	n (2)	$\delta_{18}$		Slope (4)	d		Temp. effect (6)	Amount effect (7)	
		max	min		max	min			
Waco, Texas, U.S.A.	11	-2	-6	?	11	-	+		
Wake Isl., Pac.	12	0	-5	8 ± 1	8	-	-1.6	2	
Valentia, Eire	12	-2	-7	8 ± 1	7	+	?		
Weather Ship E, N. Atl.	12	0	-6	3 ± 1.5	22	-5	-	?	
Weather Ship J, N. Atl.	13	-1	-7	8 ± 1.5	6	+	?		
Veracruz, Mexico	9	-4	-12	8 ± 1	10	-	-		
Whitehorse, Canada	24	-16	-28	5.5 ± 1	22	-18	+	-	
Vienna, Austria	19	-1	-16	exc. Apr. (w)8 ± 1.5 (s)6 ± 1	17	-10	+	+	(s)
Windhoek, S. Africa	14	+9	-8	8 ± 1.5 3.5 ± 1.5 for pos. $\delta_{18}$	28	-28	-	+	

Column 3: range of  $\delta_{18}$ .

Column 4: the slope (with uncertainty) of the line representing the best approximation to the apparent  $\delta_D - \delta_{18}$  correlation.

Column 5: the *d*-index of this line (cf. p. 450) if it has a slope close to 8; otherwise the maximum and minimum of *d* for the individual samples. In case of no  $\delta_D - \delta_{18}$  correlation the mean *d* for the individual samples is given.

Column 6: distinct temperature effect (in ‰  $\delta_{18}$  per °C) usually indicated by a +; lack of distinct temperature effect is denoted by -.

Column 7: distinct amount effect denoted by + or, in some cases by the slope (in ‰ change of  $\delta_{18}$  per 100 mm precipitation) and the width of the band obtained by plotting the individual monthly  $\delta_{18}$  as a function of the monthly precipitation (cf. section 4.2.3.).

4.2.1. The range of  $\delta_{18}$

Referring to the sections 2.3. and 2.4. the  $\delta_{18}$  values at a given station vary due to the influence of many factors. Three of the most important reasons are (1) varying condensation temperature (most pronounced at high latitudes, especially under continental conditions), (2) varying degree of evaporation from falling drops (most pronounced in regions with alternating rainy and dry seasons, especially in hot climates), and (3) seasonal shift of source area of the precipitating vapour.

Table 10, column 3, gives some impression of the  $\delta_{18}$  range for the individual station. To

facilitate a general survey mean values have been calculated for stations with common climatic features. If some station is missing in this connection, and if no special remark is made, the reason is incomplete knowledge to one or more of the parameters in question.

In Table 11 the ocean islands and weather ships (column 2) have simply been arranged according to their latitude (column 1). Furthermore, in

Column 3:  $t_a$  = the mean annual air temperature at surface.

Column 4:  $\Delta t_m$  = the mean difference between the highest and lowest monthly mean air temperature at surface.

Column 5 and 6:  $p_{max}(p_{min})$  = the average amount of precipitation fallen in the rainiest (dry-est) month, from which samples have been analysed.

Column 7:  $\delta_{18m}$  = the average of the mean annual  $\delta_{18}$ .

Column 8:  $\Delta\delta_{18m}$  = the mean difference between the highest and lowest  $\delta_{18}$  measured for the individual station.

$\Delta\delta_{18m}$  is practically the same for the 3 groups of stations. However, the reason for the variation reflected by  $\Delta\delta_{18m}$  is not the same. At the low latitude stations  $\Delta t_m$  is only 2°C, whereas the low  $p_{min}$  indicates the occurrence of periods with sparse precipitation; consequently, the  $\Delta\delta_{18m}$  should be ascribed to the amount effect (section 2.4). Conversely, at the mid and high

TABLE 11. Ocean islands and weather ships.

Latitude (1)	Stations (2)	$t_a$ °C (3)	$\Delta t_m$ °C (4)	$p_{max}$ mm (5)	$p_{min}$ mm (6)	$\delta_{18m}$ ‰ (7)	$\Delta\delta_{18m}$ ‰ (8)
0°-23°	{ Apia, Ascension, Barbados, Canton, Christmas, Gaum, Hawaii, Johnston, S. Tome, Wake }	26.2	2.1	237	16	-1.6	4.0
23°-45°	{ Acores, Bermuda, Gough, Midway, Ship E. }	18.9	8.1	361	96	-3.4	4.4
45°-90°	{ Adak, Falkland, Marion, Ship J. }	6.8	7.8	261	52	-6.6	5.2

latitude stations the relatively high  $p_{min}$  indicates a more uniform distribution of the precipitation the year round; the high  $\Delta t_m$  ( $=8^\circ\text{C}$ ) points to a simple seasonal temperature variation as being responsible for the  $\delta_{18}$  variation.

The temperature effect is also reflected by  $\delta_{18m}$  decreasing with  $t_a$ . However, the  $\delta_{18m}$  and  $t_a$  values are hardly relevant for calculating the temperature effect, if only for the reason that the altitude of the formation of precipitation is higher at low latitudes than at high latitudes. What should be compared is the mean condensation temperature and  $\delta_{18m}$ .

4.2.2. Slope of  $\delta_D = f(\delta_{18})$  Table 10, Column 4

A  $\delta_D - \delta_{18}$  plot of the individual monthly samples from a given station shows the charac-

teristics of the relative  $\delta_D - \delta_{18}$  fractionation. Only a few typical examples of such plots will be given below. However, a study of all diagrams shows distinct common features for many stations.

In the following are shown six types and degrees of correlation. Practically all stations fit into one of these six groups:

I. All samples relatively close together. No distinct correlation between  $\delta_D$  and  $\delta_{18}$  (Fig. 15). To this group belong:

- |             |               |
|-------------|---------------|
| Acores      | Hawaii        |
| Apia        | Johnston (IV) |
| Ascension   | Marion        |
| Bermuda     | Natal         |
| Canton      | San Tome      |
| Destruction | Ship E. (IV)  |
| Gough       | Ship J.       |

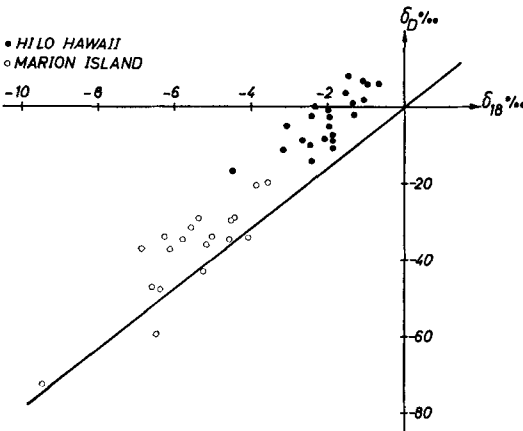


FIG. 15. Monthly precipitation at Hilo, Hawaii, and Marion Island.

i.e. disregarding Natal (cf. p. 456), only island stations and ships with no dry season and little seasonal temperature variation. Ship E. and Johnston may also be incorporated into group IV.

A few stations are very much like the above, except for a few samples with either (a) considerably lower  $\delta$ 's than the rest and displaced from these by a slope  $\sim 8$  (due to heavy rain; e.g. point  $P_1$  in Fig. 15; this is true for Dar es Salaam, Brisbane and Adelaide) or (b) considerably higher  $\delta$ 's than the rest and displaced from these by a slope  $< 8$  (due to fast evaporation from falling drops; this is true for the periodically dry Perth).

II. Wider  $\delta$ -range than group I. Distinct linear correlation with slope  $\cong 8$  as shown in Fig. 16 ( $\delta_D = 8\delta_{18} + d$ ). To this group belong:

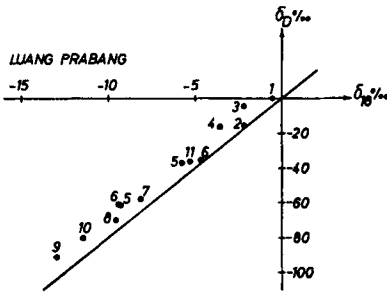


FIG. 16. Monthly precipitation at Luang Prabang, Laos, Slope = 8. The figures indicate the number of the month.

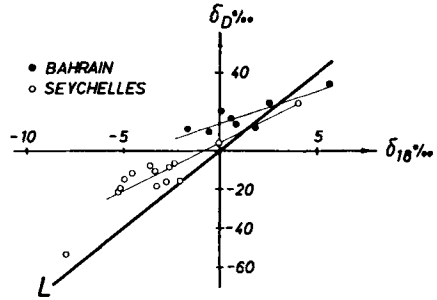


FIG. 18. Monthly precipitation at Bahrain and Mahe, Seychelles Islands. Slope < 8.

- |                |               |
|----------------|---------------|
| Adak Island*   | Karachi       |
| Barbados Isl.  | Leopoldville  |
| Bethel*        | Lista*        |
| Bombay         | Luang Prabang |
| Buenos Aires   | Manila        |
| Djakarta       | Maracay       |
| Edmonton*      | Midway        |
| Falkland Isl.* | New Delhi     |
| Flagstaff      | Rangoon       |
| Goose Bay*     | Reykjavik*    |
| Guam Isl.      | Rio de Jan.   |
| Hollandia      | Valentia*     |
| Isfjord*       | Wake Isl.     |

- |            |            |
|------------|------------|
| Chicago    | Stuttgart  |
| Fort Smith | Tananarive |
| Genoa      | Windhoek   |
| Kano       | Vienna     |
| Salisbury  |            |

The wide  $\delta$ -range is caused by either (1) considerable amount effect or (2) considerable seasonal temperature variation (denoted by \*).

It is interesting that all South and East Asian stations under the influence of the monsoon are included in this group.

All stations but Flagstaff, New Delhi and Edmonton are situated close to an ocean.

III. Fig. 17: Slope  $\cong 8$  for low  $\delta$ 's (variations due to amount effect and/or temperature effect). Slope < 8 for high  $\delta$ 's in relatively dry and/or warm season (fast evaporation from falling drops). To this group belong:

All these stations have a continental climate. For Chicago, Fort Smith, Stuttgart and Vienna the low slope part of the relation is a pronounced summer phenomenon with intense evaporation under relatively dry and warm (hot) conditions. For Salisbury and Windhoek the low slope occurs in the Southern hemisphere winter, which is the relatively dry season in South Africa.

For Kano and Tananarive some samples are situated along the prolongation of the low slope line. The whole low slope line represents the precipitation at the beginning and at the end of the rainy season, whereas the samples from the rainy season are along the line with slope  $\cong 8$ .

IV. Fig. 18: Slope < 8 (found in South African rains by EHHALT *et al.*, 1963).

To this group belong:

- |               |                 |
|---------------|-----------------|
| Alice Springs | Melbourne       |
| Bahrain       | Nord            |
| Darwin        | Pretoria        |
| Gibraltar     | Seychelles Isl. |
| Lod           | Whitehorse      |

and possibly

- |                        |           |
|------------------------|-----------|
| Cape Town (D.F. Malan) | Hong Kong |
| Diego Garcia Isl.      | Johnston  |

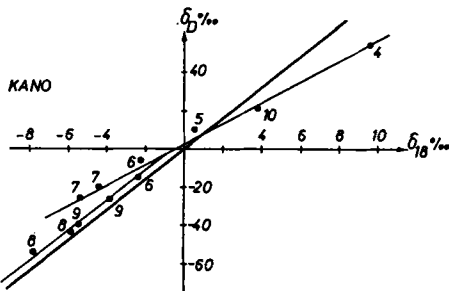


FIG. 17. Monthly precipitation at Kano, Nigeria. The figures indicate the number of the month.

Of the island stations Mahe, Seychelles, is located in the Western part of the Indian Ocean, i.e. in one of the source areas of the monsoon vapour. The net evaporation is extremely high, and the vapour cannot be expected to be in equilibrium with the ocean water. This

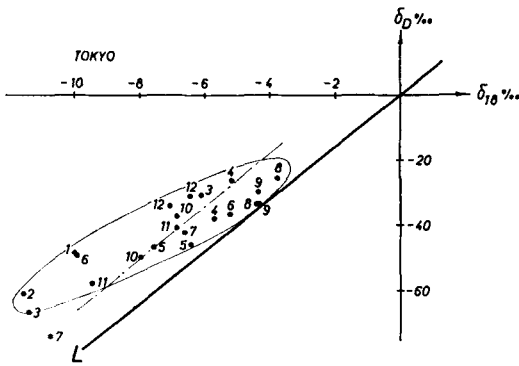


FIG. 19. Monthly precipitation at Tokyo. Seasonal variation of  $d$ : All winter months are above the thin, dashed line, which corresponds to  $d = +14\%$ .

may be the reason why 10 out of 11 monthly samples are close to the line (Fig. 18)

$$\delta_D = (4.8 \pm 1) \delta_{18} + (4 \pm 8),$$

which is practically identical with eq. (15); cf. also the suggested explanations for line No. 1 in Figs. 6 and 8 (p. 449 and p. 453).

Several of the above-mentioned stations at low latitudes have a generally dry climate (Alice Springs and Bahrain) or a periodically dry climate (Darwin, Gibraltar, Lod and Pretoria). The amount effect accounts for the  $\delta$  variations and non-equilibrium evaporation from falling drops probably accounts for the low slope.

At the two high latitude stations Nord and Whitehorse the precipitation is sparse. The

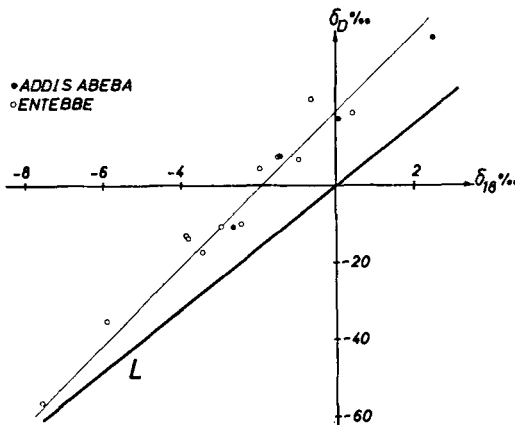


FIG. 20. Monthly precipitation at Entebbe, Uganda, and Addis Abeba, Ethiopia. Slope  $> 8$ .

temperature effect is responsible for the  $\delta$  variations. The summer (rain) samples have generally higher  $\delta$ 's but lower  $d$ 's than the winter (snow) samples, and non-equilibrium evaporation from the liquid precipitation probably accounts for the low slope.

V. Fig. 19: Seasonal variation of  $d$ , high in winter, low in summer. To this group belong Pohang and Tokyo.

As to Tokyo the  $\delta$ 's are dominated by the temperature effect in the winter and by the amount effect the rest of the year (cf. section 4.2.3., p. 464). In winter the prevailing wind direction is Northwest (i.e. from the Asian continent). The dry continental winds collect moisture from the Sea of Japan in a fast evaporation (high  $d$ ). Much of this moisture is precipitated on the Northeastern slope of the Island. The rest is possibly mixed up with Pacific vapour causing precipitation in Tokyo with not too low  $\delta$ 's, but relatively high  $d$ . In the summer time the prevailing Southeasterly winds produce occasionally heavy rainfall of the monsoon type with low  $d$ .

VI. Fig. 20: Slope higher than 8.

In spite of the limited number of samples this seems to be the case for Entebbe and Adis Abeba. If so, the reason might be that light rains (with high  $\delta$ 's in accordance with the amount effect) exchange with fastly evaporated fresh water (with high  $d$  in accordance with the kinetic effect) to a higher degree than heavy rain.

#### 4.2.3. Amount effect II

The amount effect has been discussed in section 2.4. and demonstrated in sections 4.1.1. (pp. 452 and 454, cf. also Fig. 9), 4.1.2. (cf. the low latitude stations in Fig. 10), 4.2.1. (p. 461) and 4.2.4. (p. 465).

However, the clearest indication of the  $\delta$ 's and the amount of rain varying in antiphase at low latitude stations appears by considering the individual monthly samples, or rather the unweighted means for two neighbouring months. Such means of  $\delta_{18}$  are shown as dots in the upper parts of Figs. 21, 22 and 23 for Wake, Binza (Leopoldville) and Tokyo respectively. The open circles indicate  $\delta_{18}$  in a single month. The dashed curve shows the corresponding variation of  $\delta_D$ . Under the  $\delta$ -diagrams is plotted the average precipitation,  $\bar{p}$ , of two neighbour-months.

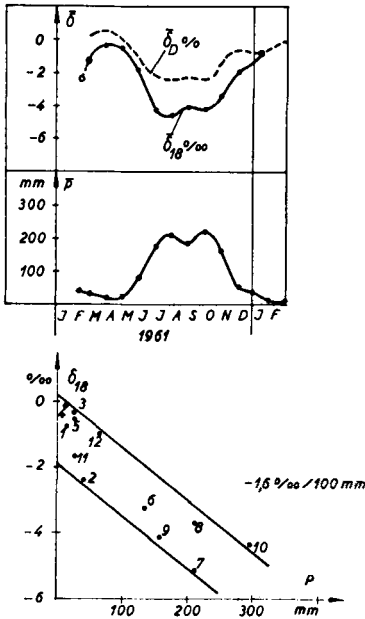


FIG. 21. Amount effect at Wake Island. Upper section:  $\bar{\delta}$  = mean  $\delta$  of two neighbouring months. Mid section:  $\bar{p}$  = the corresponding amount of precipitation. Lower section:  $\delta_{18}$  plotted against  $p$  for the individual month.

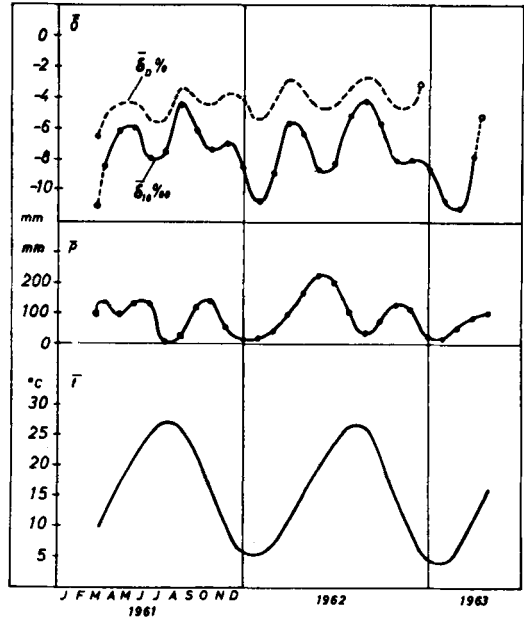


FIG. 23. Combined temperature effect and amount effect at Tokyo. Upper section:  $\bar{\delta}$  = mean  $\delta$  of two neighbouring months. Mid section:  $\bar{p}$  = the corresponding amount of precipitation. Lower section: The corresponding mean air temperature at surface.

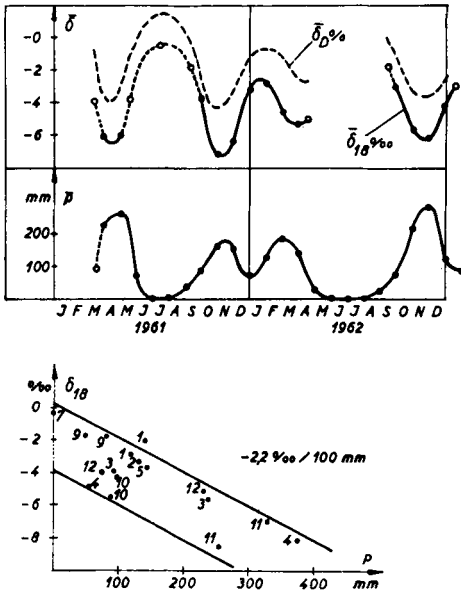


FIG. 22. Amount effect at Binza (Leopoldville), Congo. See legend to Fig. 21.

For the tropical Wake and Binza  $\bar{\delta}$  and  $\bar{p}$  are, obviously, varying with a negative correlation factor. This is also true for Tokyo (Fig. 23) except in the winter time, when the monthly mean temperature is only 5°C, i.e. when the climate of the Japanese Islands is more like that of high latitude regions, in which the temperature effect dominates the isotopic variation. The  $\delta_{18}$  curve for Tokyo reflects a seasonal variation due to strongly varying temperature (the  $\delta_{18}$  has an absolute maximum in summer and an absolute minimum in winter) superimposed by a short periodic variation in anti-phase with  $\bar{p}$  (except in mid winter).

In the lower parts of Figs. 21 and 22  $\delta_{18}$  for the individual months have been plotted against  $p$ . The amount effect may be characterised by the slope and width of the band covering most of the points, for Wake:  $-1.6\text{‰}$  per 100 mm, width  $2\text{‰}$ , for Binza:  $-2.2\text{‰}$  per 100 mm, width  $4\text{‰}$ . These figures are listed in Table 10, column 7, together with the corresponding ones for other low latitude stations. However, in many cases, e.g. Tokyo, a correlation clearly

TABLE 12

Group	Station	$\delta_s - \delta_w$ ‰
A	Apia, Samoa	-2.1
	Guam	-2.4
	Seychelles	-2.5
	Wake	-2.2
B	Bamako	-4.3
	Binza	-2.2
	Ciaba	-5.4
	Hong Kong	-5.1
	Manila	-3.5
	Maracay	-3.6
	New Delhi	-2.4
	Rio de Janeiro	-2.3
	Salisbury	-6.5
Windhoek	-2.6	
C	Genova	+3.0
	Gibraltar	+4.0
	Perth	+3.0
D	Chicago	+8.6
	Copenhagen	+2.8
	Edmonton	+7.6
	Flagstaff	+5.6
	Fort Smith	+4.0
	Goose Bay	+5.6
	Nord	+9.7
	Sdr. Strømfjord	+7.9
	Stuttgart	+5.5
	Whitehorse	+3.1
	Vienna	+5.2
E	Cape Hatteras	-3.3
	Isfjord	-2.7

appears in a  $\bar{\delta} - \bar{p}$  plot (upper parts of Figs. 21-23), but not in a  $\delta_{18} - p$  plot (lower parts of Figs. 21 and 22). In such cases presence of a  $\bar{\delta} - \bar{p}$  correlation is indicated by a + in Table 10, column 7.

The amount effect is distinct for practically all low latitude stations with varying  $p$ . For the 6 tropical islands: Canton, Christmas, Guam, Johnston, Seychelles and Wake it averages in  $\delta_{18}$  to  $-1.6\%$  per 100 mm (width 2.5%) and for the 8 partly continental stations: Binza, Ciaba, Dar es Salaam, Entebbe, Hong Kong, Kano, Manila and Pretoria the average is  $-2.0\%$  per 100 mm (width 4.5%), i.e. a little higher than for the islands.

At many mid latitude stations the amount effect is found in the summer time, e.g. Chicago, Copenhagen and Melbourne, whereas the lower part of Fig. 4, p. 445, shows no amount effect

at the high latitude station Nord, probably because of negligible convective activity and little evaporation from liquid precipitation.

#### 4.2.4. Seasonal variation

In this section  $\delta_s$  and  $\delta_w$  denote the un-weighted means of the summer and winter months, respectively. On the Northern hemisphere this means May-Oct. and Nov.-Apr., and vice versa on the Southern hemisphere. All the stations for which  $|\delta_s - \delta_w| > 2$  are listed in Table 12.

The islands in group A and the more or less continental stations in group B are all located at low latitudes. They have all rainy summers and relatively dry winters. The negative values of  $\delta_s - \delta_w$  reflect the amount effect.

The mid latitude stations in group C have all relatively dry summers. Both the amount effect and the temperature effect contribute to the positive values of  $\delta_s - \delta_w$ .

Most of the stations in group D are high latitude continental stations. The seasonal variation of the temperature at surface is more than  $16^\circ\text{C}$  (more than  $25^\circ\text{C}$ , if we disregard the 3 European stations). None of these stations has a dry season. The generally high values of  $\delta_s - \delta_w$  are mainly due to the temperature effect.

The two stations in group E are both lying in the Gulf Stream and they should be compared with the high latitude island stations, none of which shows distinct seasonal variation. The negative  $\delta_s - \delta_w$  at Isfjord, Svalbard, is interesting, the more so as (1) the monthly mean temperature varies from  $+5^\circ\text{C}$  in July to  $-12^\circ\text{C}$  in March, (2) the highest  $\delta_s - \delta_w$  ( $+10\%$ ) is found at Station Nord only 800 km West of Isfjord. The reason may be that the climate at Isfjord is dominated by moist air masses from mid latitudes, whereas that of Station Nord is frequently influenced by air masses from the Arctic Ocean.

## 5. Hydrological applications

The well known glaciological applications of isotope variations are based upon the consequences of the temperature effect, which appear as

- (1) seasonal variation,
- (2) variation with the altitude.

The latter variation has also been demonstrated in rather dry and warm climates (e.g. in Greece;

PAYNE, personal communication, 1963), and it may, under favourable conditions, be used as a hydrological tool, e.g. for investigating local sources of ground water.

A third consequence of the temperature effect (often combined with the evaporation effect) is

(3) the variation with the amount of rain in the Tropics and the Subtropics, which has been demonstrated in the above. This variation may also involve some hydrological scopes, especially in nonmountainous zones of the Tropics, where (1) and (2) are negligible. Thus, one might think of using the low  $\delta$ 's of abundant rain for clarifying parts of the water turnover at a given locality, e.g. the contributions of such rain to the ground water and to the run-off water.

Finally, it should be mentioned that the fractionation connected to the evaporation

(4) increase of  $\delta$  with the degree of evaporation (cf. 2.2.),

(5) variation of  $d\delta_D/d\delta_{18}$  with the rate of evaporation (cf. 3.1.),

involve the possibility of elucidating the sides of a local hydrological pattern, especially in dry areas, in which evaporation from surface water is an important factor.

In principle, any natural tracing of water can be used for hydrological studies. This tracing is weak (usually less than 100 times the meas-

uring accuracy) relative to artificial tracing of minor amounts of water. On the other hand, the natural labelling of water occurs in a much larger scale than in any hydrological experiment with artificially induced tracers, e.g. a heavy thunderstorm may release enormous amounts of isotopically light water over a large area, which counteracts the weak labelling of the water.

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