

Chapter 4

Isotopic Composition of Atmospheric Moisture

4.1 Hydrogen and Oxygen Isotope Fractionation in the Hydrological Cycle

The main factor controlling the fractionation of isotopic species in surface waters is the difference in the saturated vapor between various water molecules: $P_{\text{H}_2^{16}\text{O}} > P_{\text{H}_2^{18}\text{O}} > P_{\text{HDO}}$. The fractionation factor in isotopic species of water molecules under equilibrium conditions is determined by the ratio of the saturated vapor pressure of light (p) and heavy (p') components (Eq. 2.49): $\alpha = p/p'$. The fractionation factor α at 20°C is 1.08 for HDO and 1.009 for H_2^{18}O . In this case, the vapor in equilibrium with water will be depleted in deuterium (D) by 80‰ and in oxygen-18 (^{18}O) by 9‰. The isotopic composition of the vapor is $R_v = R_w/\alpha$. If water is taken as a standard, then

$$\delta_v = \frac{(R_v - R_w)}{R_w} = \frac{1}{\alpha - 1}, \quad (4.1)$$

and the isotopic composition of the water relative to the vapor in equilibrium (vapor is taken as a standard) will be, by analogy, equal to

$$\delta_v = \alpha - 1. \quad (4.2)$$

The fractionation factors of D and ^{18}O increases with decrease in temperature (see Table 2.4). The dependence of the factor α on temperature in general is expressed by the Eq. 4.3

$$\alpha = a \exp\left(\frac{b}{RT}\right). \quad (4.3)$$

For oxygen, this dependence in the temperature range from -20 to $+100^\circ\text{C}$ can be described by Zhavoronkov's equation:

$$\alpha_{^{18}\text{O}} = 0.982 \exp\left(\frac{15.788}{RT}\right).$$

The most important process involved in the formation of the isotopic composition of atmospheric precipitation is the condensation of water vapor. In a closed system, a small amount of initial condensate obviously has the same isotopic composition as that of liquid in equilibrium with vapor. With the further condensation of moisture, the isotopic composition of the condensate changes in accordance with the Eq. 4.4 (Dansgaard 1964):

$$\delta_k = \left(\frac{1}{\alpha_0} \right) \left(\frac{1}{\varepsilon F_v + 1} \right) - 1, \quad (4.4)$$

where $\varepsilon = (1/\alpha) - 1$; α_0 is the fractionation factor at the beginning of fractionation; F_v is the remaining part of the vapor.

If the temperature remains constant, then $\alpha_0 = \alpha$. The isotopic composition of the remaining vapor phase δ_v can be described by the equation

$$\delta_v = \left(\frac{1}{\alpha_0 \alpha} \right) \left[\frac{1}{(\varepsilon F_v + 1)} - 1 \right]. \quad (4.5)$$

It follows from Eqs. 4.4 and 4.5 that with a decrease in temperature of the system the vapor, and therefore the liquid phase being formed, becomes depleted in heavy isotopes of hydrogen and oxygen to a greater extent.

Equations 4.4 and 4.5 describe the closed system in a state of equilibrium. If the condensate precipitates from the vapor phase directly into the solid one, the isotope exchange does not take place between the sublimate and the vapor. In this case, the isotopic composition of the condensate and the vapor phase can be given by the Rayleigh's equation (Dansgaard 1964).

$$\delta_c = \left(\frac{\alpha}{\alpha_0} \right) F_v^{\alpha-1} - 1, \quad (4.6)$$

$$\delta_v = \left(\frac{1}{\alpha_0} \right) F_v^{\alpha-1} - 1. \quad (4.7)$$

It is evident from Eqs. 4.6 and 4.7 that, in this case, the vapor phase becomes depleted in heavy isotopes to a greater extent during the cooling of the system. Figure 4.1 shows the dependence of isotopic fractionation of vapor and condensate as a function of the remaining amount of vapor F_v .

If Eq. 4.7 is expressed in logarithms and differentiated with respect to temperature t , the equation describing the dependence of the rate of isotopic fractionation $d\delta/dt$ on temperature changes is obtained. In other words one obtains a relationship describing the dependence of the isotopic composition of precipitation on temperature of condensation. The dependence is experimentally determined between the concentrations of ^{18}O and D isotopes in precipitation and the surface average temperature t_a of air (Dansgaard 1964). It is expressed for a broad range of temperatures by the equations

$$\delta^{18}\text{O} = 0.695t_a - 13.6\text{‰}, \quad (4.8)$$

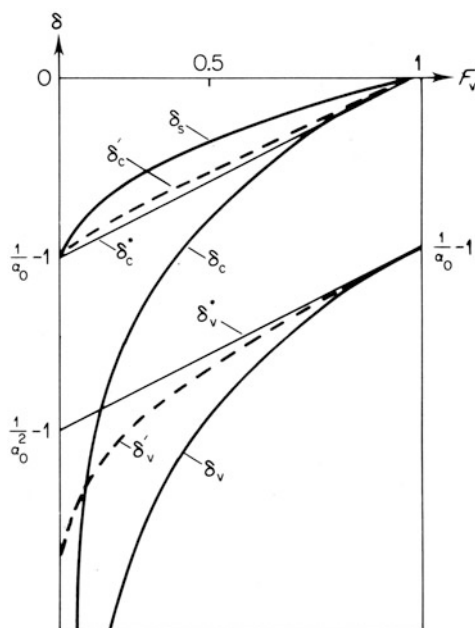


Fig. 4.1 Isotope separation in vapor–condensate system as a function of the vapor portion F_v remained: $\delta_v^*(\delta_c^*)$ is the equilibrium curve between the liquid and vapor phases for isothermal condensation; $\delta'_v(\delta'_c)$ is the same for condensation at cooling; $\delta_v^*(\delta_s)$ is the equilibrium curve for the sublimation process; δ_s is the averaged isotopic composition of the solid phase; $\delta_v(\delta_c)$ is the Rayleigh's curve for sublimation or condensation at cooling on the newly formed condensate. (After Dansgaard 1964)

$$\delta D = 5.6t_a - 100\text{‰}. \quad (4.9)$$

The dependence of isotopic composition on annual average temperature expressed by Eqs. 4.8 and 4.9 is only true for coastal regions with mild and cold climate. With the increase in distance from the sea, the continental effect appears. In this case, the calculated and experimental data do not often coincide. For example, for Vienna the annual average is $\delta^{18}\text{O} = -9\text{‰}$ whereas Eq. 4.9, using the annual average temperature (+9.5°C), produces $\delta^{18}\text{O} = -7\text{‰}$ (Drost et al. 1972). Mook (1970) has observed the continental effect even in the Netherlands.

The dependence of the oxygen and hydrogen isotopic composition upon the monthly average temperature t_m has been expressed in various ways. For example, for the Moscow region, the dependence is expressed by the following empirical equations (Polyakov and Kolesnikova 1978):

$$\delta^{18}\text{O} = (0.34 \pm 0.03)t_m - (12.6 \pm 0.3)\text{‰}, r = 0.82;$$

$$\delta D = (2.4 \pm 0.2)t_m - (101 \pm 2)\text{‰}, r = 0.89.$$

For Vienna, the corresponding equations are (Polyakov and Kolesnikova 1978; Hübner et al. 1979b):

$$\delta^{18}\text{O} = (0.40 \pm 0.04)t_m - (13.2 \pm 0.5)\text{‰}, r = 0.74;$$

$$\delta\text{D} = (2.8 \pm 0.3)t_m - (96 \pm 4)\text{‰}, r = 0.78;$$

$$\delta\text{D} = (2.94 \pm 0.19)t_m - (99.3 \pm 16.6)\text{‰}, r = 0.805.$$

For England, we have (Evans et al. 1979):

$$\delta^{18}\text{O} = 2.93t_m - 8.62\text{‰}, r = 0.77.$$

For the stations Thule, Groenedal, Nord, and Vienna, we have (Gat and Gonfiantini 1981; Yurtsever and Gat 1981):

$$\delta^{18}\text{O} = (0.521 \pm 0.014)t_m - (14.959 \pm 0.208)\text{‰}, r = 0.893, n = 363.$$

It is evident from Eqs. 4.8 and 4.9 that

$$\frac{d\delta^{18}\text{O}}{dt} \approx \frac{0.7\text{‰}}{1^\circ\text{C}}, \quad (4.10)$$

$$\frac{d\delta\text{D}}{dt} \approx \frac{5.6\text{‰}}{1^\circ\text{C}}, \quad (4.11)$$

The annual average value of $\delta^{18}\text{O}$ in precipitation from different regions is shown in Fig. 4.2 as a function of surface annual average temperature. (Dansgaard 1964)

The relationship between the content of D and ^{18}O in precipitation based on Eqs. 4.8 and 4.9 can be written in a general form as:

$$\delta\text{D} = a\delta^{18}\text{O} + b. \quad (4.12)$$

The value of the coefficient a can be determined from the relation

$$a = \frac{d\delta\text{D}}{d\delta^{18}\text{O}} = \frac{\frac{d\delta\text{D}}{dt}}{\frac{d\delta^{18}\text{O}}{dt}} = \frac{5.6}{0.69} \approx 8.0.$$

Dansgaard's theoretical calculations (Dansgaard 1964) and the experimental evidence of several researchers have shown that for such precipitation as rain and snow in most regions ranges from 8.0 ± 0.2 to 8.1 ± 0.4 . Some exceptions are the data obtained at island and ship stations located mainly in the tropical and subtropical zones. In this case, the slope of the line obtained for 15 stations is equal to 4.6 ± 0.4 . This fact has not yet been explained satisfactorily on theoretical grounds since the minimal theoretical value of the coefficient a in equilibrium during condensation (following Rayleigh's law in the range of temperatures $\pm 20^\circ\text{C}$) is equal to 7.5 (Dansgaard 1964).

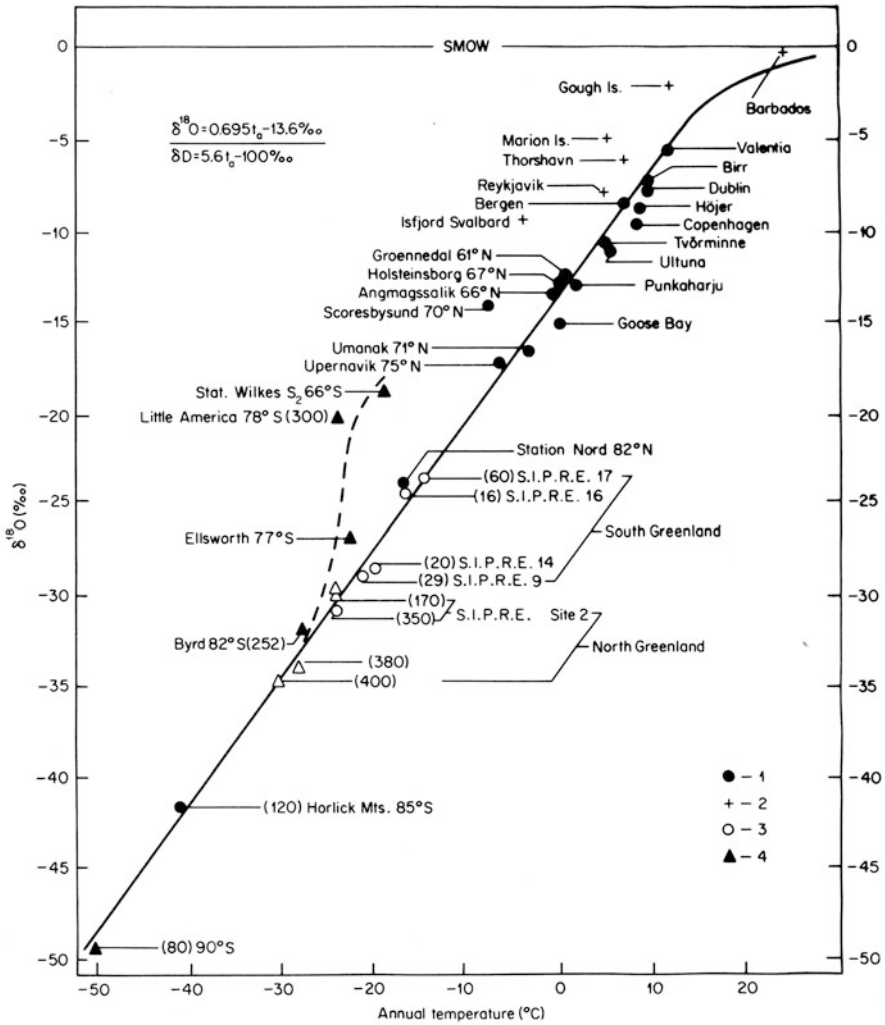


Fig. 4.2 Annual mean values of $\delta^{18}\text{O}$ in precipitation as a function of air temperature of the Earth's surface. (1) Continental stations of the North Atlantic; (2) Island stations; (3 and 4) Greenland and Antarctic stations. Figures in the brackets mean the snow layer thicknesses investigated. (After Dansgaard 1964)

Constant b in Eq. 4.12 characterizes the degree of disequilibrium in the system caused by the evaporation of initial masses of the ocean water, that is the rate of its evaporation. If the evaporation of the ocean water occurs under equilibrium conditions, b will be equal to zero; however, due to kinetic effects provided by the evaporation of water under non-equilibrium conditions the vapor formed becomes depleted in ^{18}O to a slightly greater extent. Therefore $b \neq 0$; for most stations on the

Earth, where experimental determination of D and ^{18}O in precipitation were carried out, $b = 10\%$. The values of b obtained on some island and ship stations are lower and sometimes below zero. Parameter b in Eq. 4.12 was defined by Dansgaard (1964) as $d = \delta\text{D} - \delta^{18}\text{O}$ (where d is the 'excess parameter' determining the D excess in the atmospheric precipitation relative to its amount in the equilibrium process, when $d = 0$).

For some regions, the value d is $>10\%$. For example, on the East Mediterranean coast $d = 22\%$ (Gat and Carmi 1970), for Japanese islands $d = 17.5\%$ (Sakai and Matsubaya 1977), for Alexandria $d = 15.9$, for Karizimir $d = 23.35\%$, and for Invercargill $d = -0.3\%$ (Yurtsever and Gat 1981). The parameter d is affected by the process of condensation of the precipitation and its value is decreased with distance from the region of vapor formation and the place of precipitation (continental effect). For Valentia $d \approx 10$, for Vienna $d \approx 5\%$, for Moscow $d \approx 0$.

As per Yurtsever and Gat (1981), in general case the mean weighted value of $\overline{\delta\text{D}}$ and $\overline{\delta^{18}\text{O}}$ is described by many-parametric dependence of form

$$\delta^{18}\text{O} = a_0 + a_1T + a_2P + a_3L + a_4A,$$

where T is the mean monthly temperature in $^{\circ}\text{C}$; P is the mean monthly amount of precipitation in mm; L is the geographic latitude in grad.; A is the altitude over the sea level in m ; a_0, a_1, a_2, a_3, a_4 are the regressive coefficients.

Calculation by the least square method for the 91 IAEA network stations has given the following values of the coefficients: $a_1 = 0.815$; $a_2 = 0.303$; $a_3 = 0.722$; $a_4 = 0.007$.

The relationship between δD and $\delta^{18}\text{O}$ for precipitation, plotted from experimental data, is given in Fig. 4.3. This dependence was first reported by Craig (1961a) based on a great number of experiments. Therefore, the regression line

$$\delta\text{D} = 8\delta^{18}\text{O} + 10\% \quad (4.13)$$

is often called the Craig line.

Correlation dependence between the mean weighted (annual) values of $\overline{\delta\text{D}}$ and $\overline{\delta^{18}\text{O}}$ for many stations ($n = 74$) calculated by Yurtsever and Gat (1981) have the form

$$\overline{\delta\text{D}} = (8.17 \pm 0.08)\overline{\delta^{18}\text{O}} + (6.03 \pm 3.08), \%, r = 0.997.$$

The equation is close to the Craig's dependence. For stations of the North American continent, the dependence obtained by Yurtsever and Gat is

$$\overline{\delta\text{D}} = (7.95 \pm 0.22)\overline{\delta^{18}\text{O}} + (10.56 \pm 0.64), \%, r = 0.997.$$

It should be noted that Eq. 4.13 is only true for the annual average hydrogen and oxygen isotopic data with respect to different regions of the Earth and needs to be corrected for the analysis in the other time ranges (Gat and Dansgaard 1972).

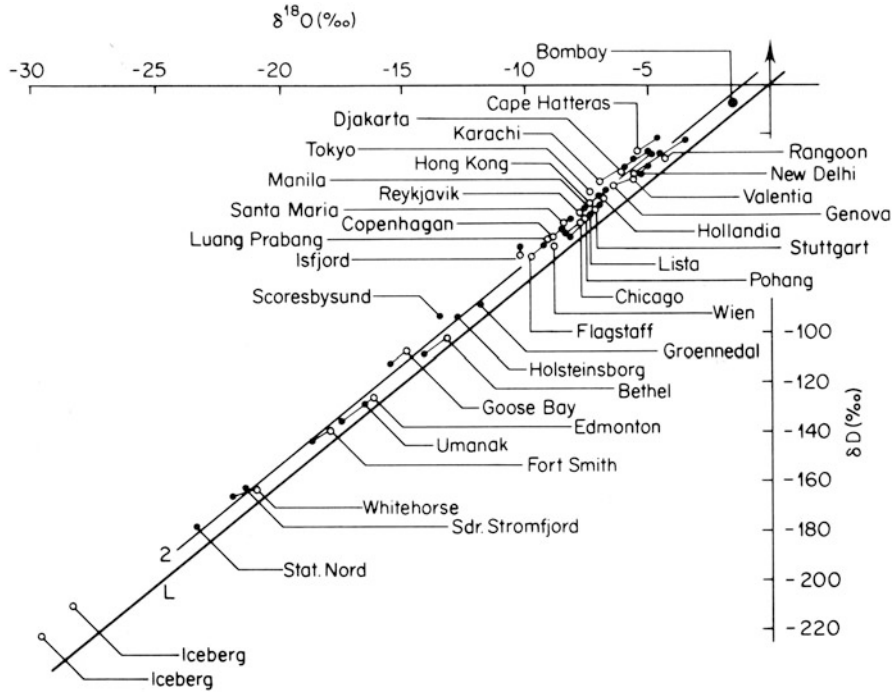


Fig. 4.3 D and ¹⁸O relationship in precipitation and continental meteoric water based on the global network data of the Northern hemisphere and expressed by $\delta D = 8\delta^{18}O + 10\text{‰}$. (After Dansgaard 1964)

Regression analysis of many years’ observations of D and ¹⁸O concentrations in precipitation at individual stations on monthly average basis have shown that for the equation $\delta D = a\delta^{18}O + b$, the regional coefficients given in Table 4.1 should be taken into account.

For the United Kingdom, the following relationship has been obtained on a monthly average basis (Bath et al. 1979; Evans et al. 1979):

$$\delta D = 6.6\delta^{18}O + 1.3\text{‰}; r = 0.83;$$

$$\delta D = 6.6\delta^{18}O + 1.4\text{‰}; r = 0.85;$$

For the Europe, as a whole (Evans et al. 1979):

$$\delta D = 6.9\delta^{18}O - 0.3\text{‰}; r = 0.95.$$

For the northeast of Brazil, this dependence has the form (Salati et al. 1980):

$$\delta D = 6.4\delta^{18}O + 5.5.$$

Table 4.1 Calculated numerical factors ($\delta D - \delta^{18}O$ relationship) for monthly average precipitation data of some observational stations. (From Polyakov and Kolesnikova 1978)

Type of Station	Station	Annual Average Data		Number of Month's Observations	Monthly Average Factors		Correlation Factors r
		Precipitation (mm)	Vapour Pressure (mb)		a	b	
Island	Hawaii	3470	21.3	92	4.0 ± 0.5	3.0 ± 1.1	0.66
-	Azores	1200	15.4	48	5.5 ± 0.6	4.0 ± 1.0	0.92
-	Valentia	1400	10.7	72	6.1 ± 0.6	-3.7 ± 0.5	0.80
-	Adak	1400	6.0	66	6.1 ± 0.6	-8.9 ± 5.4	0.80
-	Isford	350	3.7	42	6.1 ± 0.4	-8.5 ± 3.7	0.93
-	Nord	150	1.1	78	7.2 ± 0.2	-8.2 ± 3.4	0.99
Coastal	Gibraltar	815	15.4	48	5.6 ± 0.4	-0.6 ± 1.4	0.91
-	Bethel	490	4.3	48	5.9 ± 0.2	-39.7 ± 2.8	0.97
-	Barrow	110	1.7	66	5.5 ± 0.5	-39.7 ± 9.5	0.84
Continental	Vienna	660	8.5	108	6.1 ± 0.3	-11.5 ± 3.5	0.92
-	Moscow	575	6.5	60	6.0 ± 0.5	-26.2 ± 6.7	0.89

As Table 4.1 shows, the coefficient a for all stations appeared to be less than 8. There is tendency of the coefficient b to decrease with a decrease in the annual decreases to approximately -8.3 and remains constant within the wide range of temperature from 5 to 18°C . The dependence of the coefficient b upon the annual average temperature t ($^\circ\text{C}$) can be approximated by:

$$b = -(24 \pm 5) + 1, 2\bar{t}.$$

As the atmospheric moisture travels further from the Atlantic across the Eurasian continent, b decreases by approximately 0.7‰ per 100 km and the decrease of the relative values of D and ^{18}O concentrations is $2.5 \pm 0.5\text{‰}$ and $0.35 \pm 0.05\text{‰}$ per 100 km, respectively. Similar relationship for Europe and Africa has been reported by Sonntag et al. (1979).

The dependence of b upon temperature is probably the result of the processes involved during the non-equilibrium condensation of the precipitation and during the partial evaporation of the liquid-droplet part of the moisture cloud whilst the primary source of moisture vapor is continental.

As pointed out by Polyakov and Kolesnikova (1978), for all regions with an annual average temperature $\bar{t} < 20^\circ\text{C}$, the relationship between δD and $\delta^{18}\text{O}$ in the total annual precipitation follows the empirical relationship

$$\delta\text{D} = 8\delta^{18}\text{O} + 10 - 0.7l^2\text{‰},$$

where l is the distance from the ocean (the source of water vapor) in thousands of kilometers. For the coastal and island stations, $l = 0$.

Therefore, Craig's equation (Eq. 4.13) branches out on sets of parallel lines with varying slopes which are dependent on distance from the ocean.

The relationship between the isotopic composition of the monthly average precipitation for the stations with annual temperature in the range of $-15^\circ\text{C} < t < 20^\circ\text{C}$ can be approximated by the empirical equation

$$\delta\text{D} = 6\delta^{18}\text{O} - 0.7l^2 + 0.7\bar{t} - 7\text{‰}.$$

The relationship between δD and $\delta^{18}\text{O}$ for different regions is often used for the interpretation of data for hydrogeological reconstructions. Craig's equation, which determines the global relationship between the D content and the ^{18}O on an annual average basis is often employed. As seen from Table 4.1, the regional effects are not taken into account, which might lead to appreciable errors.

The description of the formation processes of isotopic composition of precipitation based on equilibrium, the Rayleigh fractionation is the approximate natural model of moisture condensation and precipitation. Nevertheless, in a series of cases, the use of Rayleigh's formula for natural processes coincides satisfactorily with the experimental data. Thus, Eriksson (1965b), suggested that atmospheric moisture be considered as the uniform vapor phase in which the liquid phase forms under isothermal conditions in accordance with the Rayleigh mechanism. With such an assumption, the average isotopic composition of atmospheric precipitation R_p is a function of the

atmospheric moisture W and the water content in the vertical atmospheric column, that is

$$\frac{dR_p}{R_p} = (\alpha - 1) \left(\frac{dW}{W} \right). \quad (4.14)$$

Under isothermal conditions, $\alpha = \text{const.}$ Integrating Eq. 4.14 and substituting $\ln R_p = \ln(1 + \delta_p) \approx \delta_p$, one obtains

$$\delta_p = 2.3(\alpha - 1)lgW + B. \quad (4.15)$$

Equation (4.15) describes the process of advective transition of moisture in the atmosphere. For turbulent process, Eriksson (1965b) suggests the substitution of $\sqrt{\alpha - 1}$ for $\alpha - 1$; then

$$\delta_p = 2.3\sqrt{\alpha - 1}lgW + R. \quad (4.16)$$

The experimental justification of Eqs. 4.15 and 4.16 carried out by Eriksson by comparing the annual average isotopic composition of atmospheric precipitation for a series of island stations showed that, despite the considerable scattering of the experimental evidence, the points in the diagram $\delta^{18}\text{O}-lgW$ are predicted by the above equations for $\delta^{18}\text{O} = 1.009$.

Brezgunov (1978), on the basis of the analysis of a large amount of experimental data, obtained empirical relationship between δD and lgW for regions of meridional water vapor transition above the ocean and inland transition above Europe and North America. For winter, this relationship in the case of the sea profile is

$$\delta D = 106lg p - 138\text{‰}, \quad (4.17)$$

and for the inland profile, it is

$$\delta D = 193lg p - 215\text{‰}. \quad (4.18)$$

For summer, in the case of sea profile, the relationship is

$$\delta D = 174lg p - 219\text{‰}, \quad (4.19)$$

and for the North American continent, it is

$$\delta D = 313lg p - 456\text{‰}. \quad (4.20)$$

Brezgunov noted that the greater rate of δD decrease in summer precipitation with the decrease of $lg p$ ($d\delta D/dlg p$), for the stations of the ocean and North American inland profiles, in comparison with winter precipitation, may be explained by the additional isotopic fractionation provided by raindrop evaporation below the level of the clouds.

The dependence of the content of heavy hydrogen and oxygen isotopes on the vapor condensation temperature leads to seasonal deviations of D and ^{18}O in precipitation reaching a maximum in summer and minimum in winter. For the same

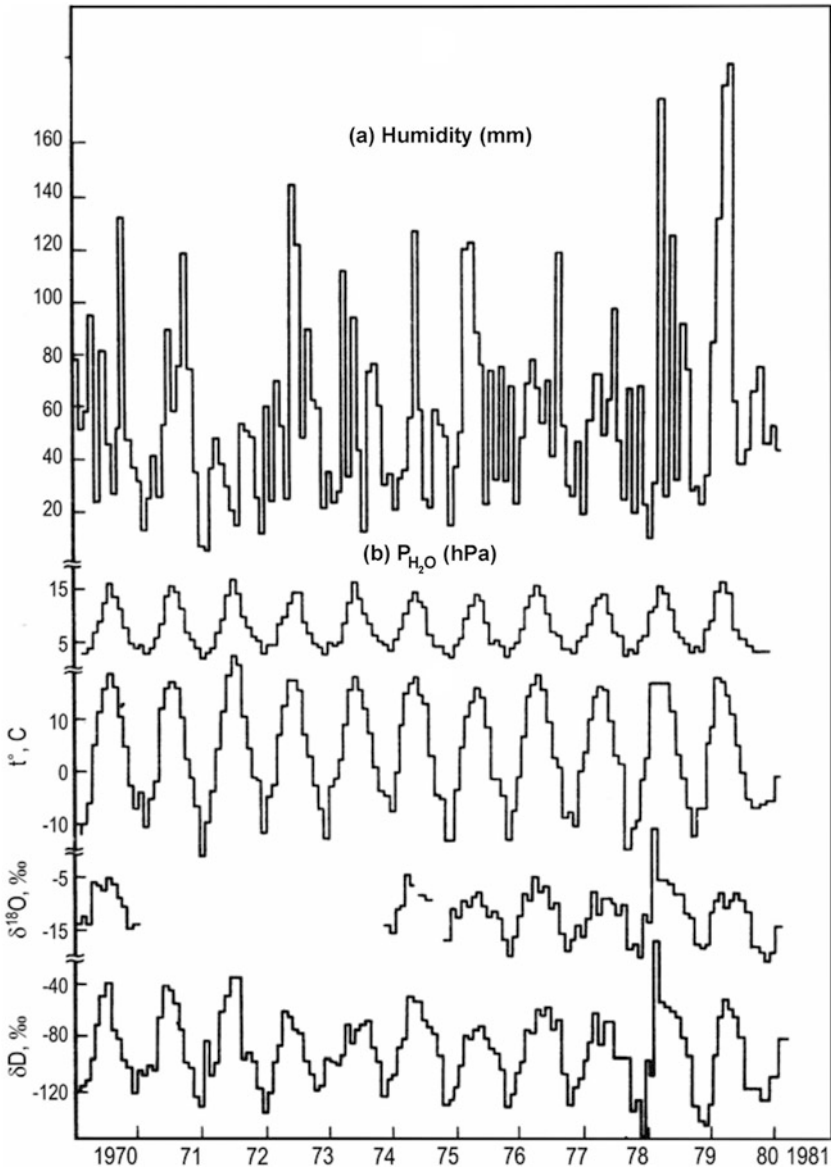


Fig. 4.4 Seasonal variation of δD and $\delta^{18}O$ in precipitation, its amount, vapor pressure and temperature for Moscow station in 1970–1980

reason, the oxygen and D concentrations in meteoric waters decrease in higher latitudes and altitudes. Figure 4.4 demonstrates seasonal variation in contents of the heavy isotopes of hydrogen and oxygen for Moscow station (Zeleny settlement).

It was found that the values of δD and $\delta^{18}O$ depend on the amount of precipitation. This phenomenon is called 'amount effect' (Dansgaard 1964). The calculations done by Yurtsever and Gat (1981) for tropical stations with close mean annual temperatures give the following relationship between mean annual values of $\sqrt{\delta^{18}O}$ and precipitation P :

$$\sqrt{\delta^{18}O} = (-0.015 \pm 0.0024)P - (0.047 \pm 0.419); r = 0.874.$$

It is seen from this equation that precipitation is decreased in ^{18}O by about 1.5‰ in each 100 mm. The average mean monthly values for two stations (Apia and Madang) gives mean correlated relationship between the mean monthly values of $\delta^{18}O$ and P (Yurtsever and Gat 1981):

$$\text{for Apia } \delta^{18}O = (-0.010 \pm 0.003)P - (1.56 \pm 0.42);$$

$$n = 52$$

$$r = 0.67$$

$$\text{for Madang } \delta^{18}O = (-0.011 \pm 0.002)P - (3.95 \pm 0.69);$$

$$n = 48$$

$$r = 0.60$$

For both these stations, the average decrease of precipitation in ^{18}O is equal to about 1‰ in 100 mm.

It is evident from Fig. 4.1 and from Eqs. 4.4 and 4.6 that development of the amount effect seems to relate to the degree of condensation of the initial vapor cloud at the formation of precipitation. Levin et al. (1980) observed depletion in ^{18}O of the subsequent portion of precipitation in the mountain region Negev, Israel. The last portions of precipitation (on 1 mm) were collected automatically by special hermetic device. The results obtained were as follows:

Precipitation (mm)	$\delta^{18}O$
1 st	-3.27‰
2 nd	-4.79‰
3 rd	-5.56‰
4 th	-7.27‰
Mean value	-5.22‰

The $\delta^{18}O$ value of precipitation in total sample taken by standard sampler was -5.45‰.

Because of dependence of isotopic composition of precipitation on temperature, D and ^{18}O concentrations in meteoric waters decrease at increase of latitude and absolute mark of the land. The highness effect is developer different in regions with different climatic conditions. The gradient values $\Delta\delta D/\Delta h$ and $\Delta\delta^{18}O/\Delta h$, as a rule, are varying in ranges of 1.5-4‰ (per 100 m for δD) and 0.15-0.5‰ (per 100 m for $\delta^{18}O$) (Yurtsever and Gat 1981).

4.2 Isotopic Balance in the Global Hydrologic Cycle at Evaporation and Condensation of Water

The unity of natural waters on the Earth consists of their genetic relationship which has continued during the whole history of the hydrosphere. The principal reservoir of the hydrosphere—the ocean—contains about 97% of the total amount of water, taking no account the water being bonded in rocks. The other 3% is represented by the polar and continental glaciers, which have accumulated about 2.2% of water in the solid phase, the underground waters (0.7%), and the surface continental waters, which make up less than 0.05% of the total amount of water. The water vapor in the atmosphere represents a small part of the water (about 0.0015%) but is the most dynamic element of the hydrosphere, responsible for the genetic relationship between the ocean and the continental surface and groundwaters. While the total mass of the atmosphere is about 5.2×10^{21} g the mass of water vapor equals to about 1.3×10^{19} g, which amounts to about 0.25%. The mean synoptic rate of motion of the air in the atmosphere is 10^3 cm/s and the time of the average water cycle is equal to 11 days. Thus the process of hydrosphere mixing proceeds rather intensively. In the previous section, it was pointed out that out of $\sim 4 \times 10^{20}$ g of annual average precipitation a quarter falls over the continents and three-quarters over the oceans. At the same time evaporation from the ocean surface exceeds that from the continents, being 85% and 15%, respectively. The difference between precipitation and evaporation over the continents is equal to 10% or $\sim 3.7 \times 10^{19}$ g, which corresponds to that mass of water which is being annually exchanged between the ocean and continents through the atmosphere. The continents return to the ocean the same amount of water in the form of surface and groundwater run-off.

The most important problem in hydrology is the determination of natural principles governing the process of the water cycle on the Earth and the variation of the ratio of its elements with time. The existence of the evaporation-condensation-atmospheric precipitation process is absolutely indisputable from the moment when water appeared on the Earth. However, now the volume of the hydrosphere and the water balance within it has changed with time, and it is not yet understood if its origin is a result of the continuous degassing of water from the Earth's interior. If the bulk of the Earth's ocean has not changed during the greater part of its history, then the question arises as to the timing and mechanism of its appearance. The temperature history of the Earth has played a decisive role in the origin and evolution of the hydrosphere and also in the evolution of water cycle elements. The geological and paleontological facts give evidence on secular variations of temperature in the range of 6–8°C or more on the Earth's surface. The causes of these variations remain unknown. In the meantime, they play an important role in the evolution of the surface 'shells' of the Earth since the atmosphere, the hydrosphere, and the biosphere are very sensitive to these small temperature variations. In extreme times of temperature variation, the catastrophic phenomena have taken place. Temperature variations in the surface shells of the Earth were observed up to Archean times, that is approximately 2.7×10^9 year ago. The age of the most ancient rocks discovered

on the Earth is about 4×10^9 years. Any other evidence of temperature processes which took place earlier have not been observed as they happened in the times of high-temperature evolution of the Earth.

The study of oxygen and hydrogen isotopic ratios in water and other objects (rocks, gases, organic and mineral remains of buried organisms, etc.), which have interacted with water in the past, throws light upon the origin and evolution of the hydrosphere. In the present section, we consider some principal facts concerning the formation of the isotopic composition of water which is constantly being removed from the ocean into the atmosphere, transferred in the form of water vapor and precipitation, and finally rained out over the ocean and the continents. This will help us to better understand the mechanism of water movement in nature and, on the basis of data of isotopic composition of water molecules observed in natural conditions, to produce more reliable accounts of the global and regional water balance. Besides, the understanding of the principles of the distribution of stable isotopes of water during its circulation broaches the question of the hydrosphere's evolution and origin.

The problem is to find out what values of isotopic ratios are characteristic for water vapor coming from the ocean surface into the atmosphere and how the isotopic composition of various forms of vapor, from which precipitation is formed, is distributed when falling over continents and oceans. Finally, the problem is reduced to the composition of water balance on genetic basis.

The isotopic composition of hydrogen and oxygen in precipitation in global scale was studied for last 50 years, on the stations of the International Atomic Energy Agency/World Meteorological Organization (IAEA/MWO) Isotopes-in-Precipitation Network which are located in different climatic zones. This international project started working in 1961 and included more than 100 stations (see Fig. 4.5). The network covered continental, coastal, island, and ship stations. About half of the samples and the meteorological data from all network stations were sent to the IAEA Laboratory in Vienna for analysis. The remainder samples were forwarded to cooperating laboratories in the member states. The IAEA has acted as the collection agency for data on the distribution of the stable isotopes and tritium in hydrological cycle. All the information is available in special report series publications and on Internet site of the IAEA.

The picture of the ^{18}O global distribution in atmospheric precipitation prepared by Yurtsever and Gat (1981) and complemented by the authors with the data of the former USSR area is presented on Fig. 4.6. It gives general view about distribution of ^{18}O concentration in precipitation before 1981 and does not take into account possible regional changes because of climatic variations.

The global estimation of the average isotopic ratios of hydrogen and oxygen for ocean vapor may be given from the condition of mass balance of the evaporating and precipitating water. From the material balance of evaporation–precipitation ($E = P$) it follows that $\delta E = \delta P$, that is when the water comes back into the ocean its isotopic composition should be restored. When considering the isotopic balance of the ocean during the evaporation–precipitation cycle, the continents play an insignificant role since they obtain, in the form of precipitation, only 10% of the water evaporated from the oceanic surface. Thus, Craig and Gordon (1965) proposed to consider the ocean

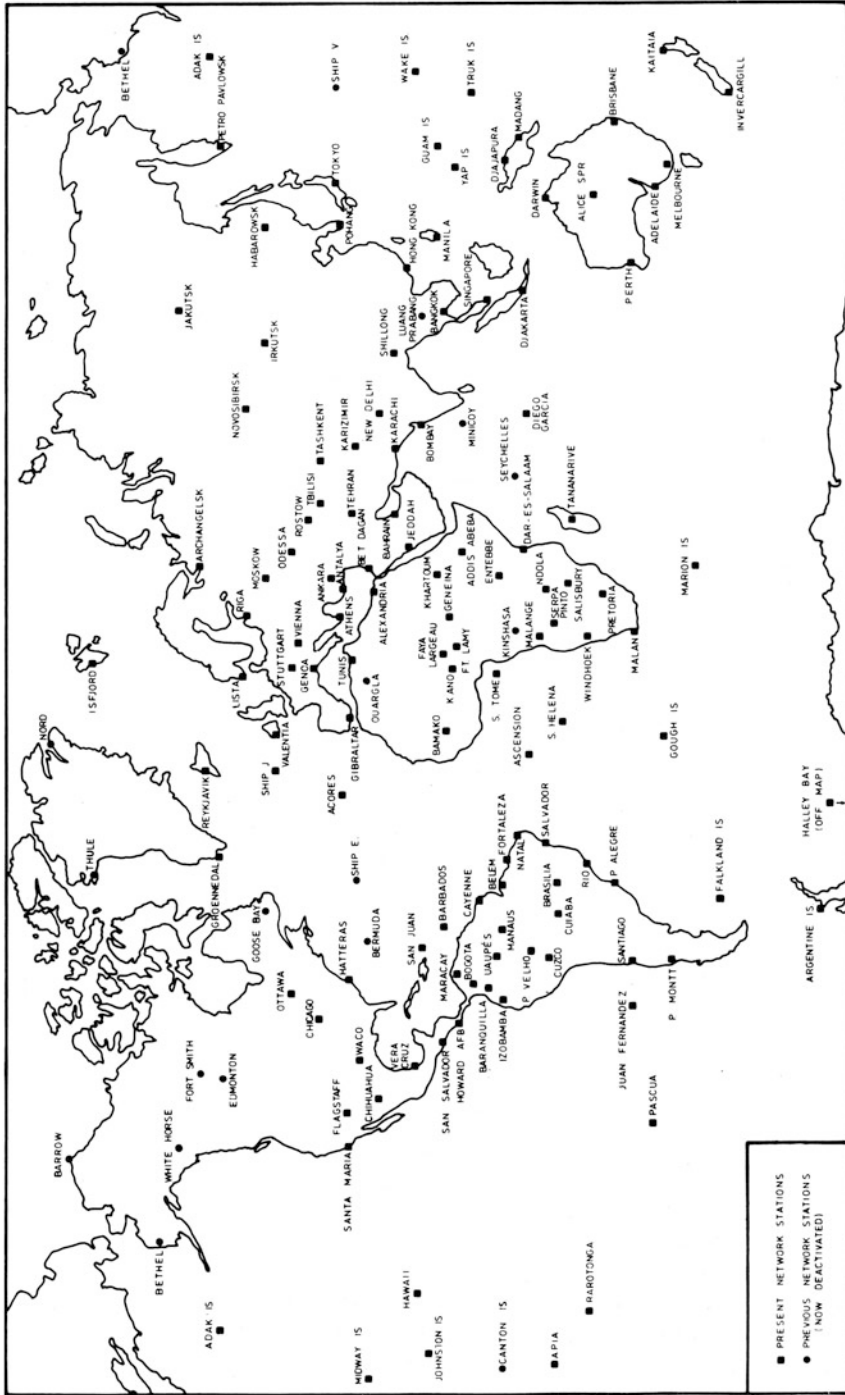


Fig. 4.5 Schematic map of the IAEA/MWO Isotopes-in-Precipitation Network Stations at 1975

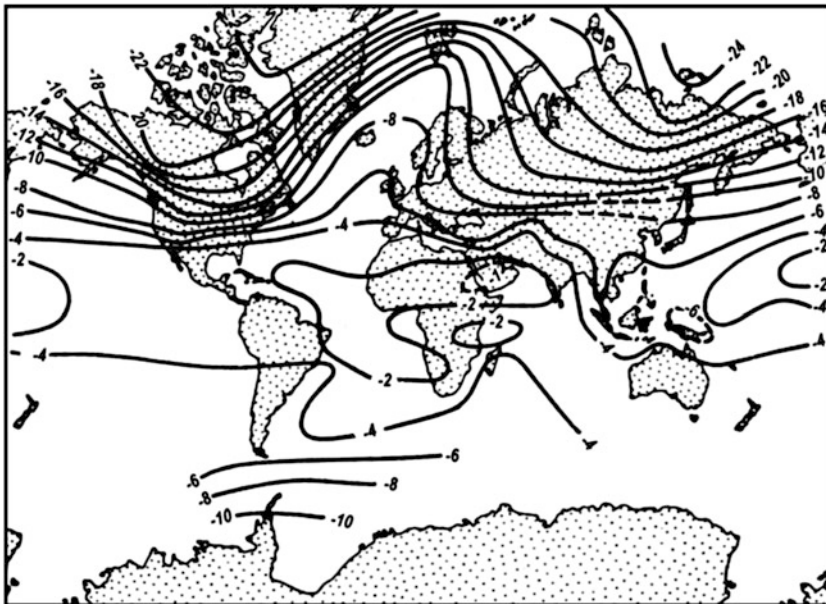


Fig. 4.6 Global distribution of $\delta^{18}\text{O}$ in atmospheric precipitation based on data having at least two series of observation. (From Yurtsever and Gat 1981; Ferronsky and Polyakov 1983)

as a closed system. It is logical that for separate regional oceanic conditions, the influence of continental run-off and contribution of melt-water from polar glaciers should be considered.

On the basis of experimental data on precipitation distribution, the amounts of which are in accordance with latitudinal belts, we can expect the following approximate values of latitudinal ^{18}O abundances:

Latitudes	Ratio of Precipitation	$\delta^{18}\text{O}$ (‰) (mean value)
0°—20°	0.5	-2
20°—40°	0.4	-5
40°—90°	0.1	-15

Using these data, Craig has derived the following theoretical values of isotopic ratios for oceanic vapor and precipitation, which are equal to $\delta^{18}\text{O} = -4\text{‰}$ and $\delta\text{D} = -22\text{‰}$. These magnitudes are close to the average ones in continental precipitation, in contrast to high latitudes where the above-mentioned values are significantly lower, but the amount of precipitation for these regions of the isotopic balance for the North American continent (Craig and Gordon 1965) the mean values are $\delta^{18}\text{O} = -5\text{‰}$ and $\delta\text{D} = -30\text{‰}$, which agree with the accepted data above.

In the case of equilibrium evaporation from the ocean surface without the influence of atmospheric moisture and kinetic effects, the mean values of isotopic ratios are $\delta^{18}\text{O} = -9\text{‰}$ and $\delta\text{D} = -70\text{‰}$, as reported by Epstein and Mayeda (1953) and Dansgaard (1964). The experimentally observed data on the isotopic composition of vapor over the ocean (see Fig. 4.3) is evidence in favor of the isotopic ratios being considerably lower than those suggested by the material balance and even lower than the values corresponding to equilibrium conditions ($\delta^{18}\text{O}$ is varying from -11 to -14‰). According to Craig and Gordon (1965), the given facts can be explained by the character of steady global circulations of atmospheric air and also those of condensation of atmospheric precipitation. This process can be outlined as follows. Dry atmospheric air descends to the ocean surface in the trade wind regions where it picks up the water vapor and moves it to the equatorial belt, where the majority of the vapor rises to high atmospheric layers and precipitates its moisture by cooling and condensation. The remaining vapor moves away from the trade winds to the high latitudes where it undergoes an analogous process. This general study system of atmospheric circulation, in which the isotopic variations and the humidity of air are reflected in transport and mixing conditions, is restricted by the local vertical convective flows, rich in water vapor, which form areas of cumulus clouds saturated with moisture. Therefore, we never observe in nature the full saturation of any atmospheric layer with moisture but only local domains of condensation in a general flow of circulating masses of air and water vapor. In these conditions, the vapor above the sea will never be in equilibrium with water even if there is no kinetic effect.

The isotopic variations in vapor and precipitation are explained by Craig and Gordon with the help of a simplified single-stage precipitation model. They assumed that there is a homogeneous layer of atmospheric moisture and in the precipitation region, there is a large ascending flux of moisture being evaporated from the ocean surface. Thus, compared with this flux, insignificant amount of moisture precipitates. In such case, the isotopic composition of precipitation will be formed by a single-stage equilibrium fractionation between the condensing moisture and atmospheric vapor. From the isotopic balance equation, one obtains the following values of δD and $\delta^{18}\text{O}$, characteristic for elements of the considered system. The slope of the straight line precipitation ($\delta^{18}\text{O} = -4\text{‰}$, $\delta\text{D} = -22\text{‰}$)—atmospheric vapor ($\delta^{18}\text{O} = -13\text{‰}$, $\delta\text{D} = -94\text{‰}$) is equal to 6 and for the line atmospheric vapor-equilibrium vapor ($\delta^{18}\text{O} = -8\text{‰}$, $\delta\text{D} = -67\text{‰}$) the slope is equal to 5.5. The slope of the line atmospheric vapor-surface sea water ($\delta^{18}\text{O} = +1\text{‰}$, $\delta\text{D} = +5\text{‰}$) is about 6.5. For the isotopic ratios in the equilibrium vapor–evaporating vapor system, ascending from the ocean surface, both kinetic effects and atmospheric humidity are important. If kinetic effect is low enough and humidity is large enough, the relationship can be reversed. At normal conditions for the observed parameters in the ocean–atmosphere system, the equilibrium vapor will be lighter than the ascending flux of evaporating moisture. In nature, the reverse may occur only in high latitudes.

The difficulties have arisen from the instability of evaporation and moisture exchange for different oceanic regions as one tries to develop the model, describing formation of isotopic composition of moisture transferred in the atmosphere. The most important oceanic region from the viewpoint of moisture exchange is the trade

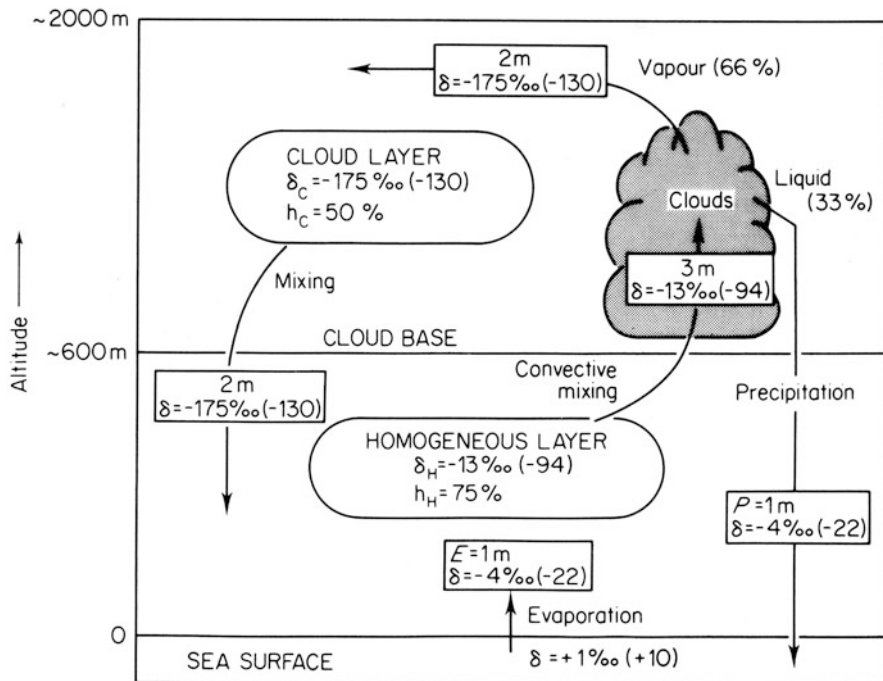


Fig. 4.7 Two-layer model for vapor and precipitation isotopic composition formation and their motion in the ocean–atmosphere–ocean system for trade winds regions. (After Craig and Gordon 1965)

wind region between 30°N and 30°S, which incorporates about 50% of the total area of the Earth and receives three-quarters of annual amount of precipitation and evaporation. The structure of the atmosphere in this region, derived from numerous experimental investigations, and the characteristic average values of isotopic ratios of individual atmospheric elements, according to Craig and Gordon (1965), are shown in Fig. 4.7.

The model consists of two atmospheric layers. Up to 600 m above sea level, a lower homogeneous layer can be distinguished which is well mixed by turbulent stirring. The specific humidity of this layer changes sharply in the first 10–20 m above the sea and then remains almost constant up to 600 m with humidity equal to 75%. The second, cloud layer is characterized by the active process of convective mixing with large-scale descent of dry air and local jets of rising air rich in water vapor around which cumulus clouds are formed. The thickness of the second layer is restricted by the extent of the moist, preferentially convective mixed layer of the outer trades. About this layer is the trade-wind inversion section, separating the second layer from the dry upper troposphere above. The location of the inversion section varies from an altitude of 2 km in the outer trade wind belt to 4 km near the equator. The two principal layers are separated by an intermediate layer with a thickness of about

100–300 m, which is characterized by a specific humidity which, approximately, decreases linearly towards the cloud layer. The cloud layer displays a mostly uniform humidity of about 50%. If the problem of the isotope balance of the exchanging moisture is considered from the principal viewpoint of a system in a steady state, then this model may, to some extent, represent the relationship between the ocean and the atmosphere as a whole. Thus, both the material and isotopic balances in the system during evaporation–precipitation process should be taken into account. The loss of moisture evaporated from the ocean surface (10%) and precipitating over the continents is not considered. Assuming the lower homogeneous and upper cloud layers have common values of humidity equal to 75% and 50%, respectively, evaporation–precipitation amounts to about 1 m per year, and the isotopic ratios, according to the observed data, equal $\delta^{18}\text{O} = -13\text{‰}$ and $\delta\text{D} = -94\text{‰}$ for the vapor in the homogeneous layer, and $\delta^{18}\text{O} = +1\text{‰}$ and $\delta\text{D} = +10\text{‰}$ for the surface ocean water, the model may be described by the following equations.

The first equation is just the mass balance equation of moisture in the system

$$P = I(h_1 - h_2), \quad (4.21)$$

where P is the amount of precipitation; h_1 and h_2 are humidity of the upper and lower cloud layers; I is the exchange constant between the upper and lower layers, equal to the flux of moisture between them when the air is saturated.

As shown in Fig. 4.7, the flux of moisture characterized by Eq. 4.21 is equal to a water layer 3 m thick being transported from the lower layer to the upper one and a layer 2 m thick from the upper layer to the lower one.

The second equation relates the isotopic composition and humidity of these layers:

$$h_1(\delta_p - \delta_1) = (\delta_p - \delta_2), \quad (4.22)$$

where δ_p is the isotopic ratio for precipitation; δ_1 and δ_2 are isotopic ratios of water vapor in the upper and lower layers.

From the last equation for the upper cloud layer, other parameters being known, we obtain $\delta_2^{18}\text{O} = -17.5\text{‰}$ and $\delta_2\text{D} = 130\text{‰}$.

The third equation, relating the isotopic composition in precipitation and water vapor, can be written on the basis of the model chosen for the formation of precipitation. One may assume that condensation of precipitation takes place in the upper layer from the water vapor ascending from the lower layer for certain values of the parameters describing the cloud layer, but in this case the isotopic composition of vapor of the cloud layer can be described by Eq. 4.22. To obtain the fixed isotopic ratios for precipitation δ_p and vapor of the cloud layer δ_2 , at known vapor pressures, the fractionation factors of ^{18}O and D (1.0135 and 1.124) are required. The initial precipitation temperature corresponding to these values must range between the limits from -10°C to -20°C , which is significantly lower than the observed temperature in nature. The isotopic data show independently that precipitation is formed from the ascending flux of moisture flowing from the lower layer, being a component of the exchange process between the two layers. At the same time the observed temperature criteria lead to a conclusion that condensation of vapor rising from the lower layer

is not just a process of equilibrium formation of precipitation but is governed by the more complicated mechanism of inversion distillation similar to those observed in a rectification column.

The atmospheric model, made up of two layers, which has been proposed by Craig and Gordon, principally for estimating the isotopic balance of moisture resulting from the interaction between ocean and atmosphere, can be considered as a basis for the development of more detailed models of water movement through the atmosphere based on isotopic investigations both in oceanic regions and in the ocean—continent system, but in contrast to the oceanic conditions in the evaporation–precipitation cycle, where a 10% loss of evaporating moisture (being precipitated over the continents) may be neglected, a gain of 10% of ocean water represents 40% of the continental moisture as a whole. The other 60% is secondary evaporating moisture from the continental surface, which was previously precipitated. Thus, assuming the previous considerations (see Fig. 4.7), about 40% of water vapor in a continental region would be contributed by lower and upper atmospheric layers with fixed isotopic composition, depending upon proportions of the vapor mixing. The isotopic ratios of moisture evaporating from the continental surface will have lower values compared with the moisture evaporating from the ocean surface. At the same time the net water run-off from continents into the ocean will be enriched in D and ^{18}O compared with their content in precipitation and will correspond (in accordance with the isotopic balance) to the isotopic ratios of water vapor moving from the ocean surface to the continents.

4.3 Isotopic Composition of Atmospheric Water in the Past

While considering conditions of formation of isotopic composition of precipitation, it is interesting to give data on the evolution of isotopic ratios with time, using as an example the Antarctic ice sheet. Epstein et al. (1970) studied ice samples from a borehole drilled in 1968 at the Antarctic Byrd Station ($80^{\circ}01'\text{S}$, $119^{\circ}31'\text{W}$), located on 1,530 m above sea level. Isotopic studies of the ice were carried out for depths ranging from 99 to 2,162 m. The total depth of the borehole was 2,164 m. The geomorphologic surface conditions in this region are such that the danger of any catastrophic contribution of ice from other regions is improbable. In addition, there is no evidence that it has been found more than 600 m below sea level.

In Fig. 4.8, the results mentioned above are given, each point representing the mean value of a water sample obtained from the ice core ranging in size from 30 to 151 cm. The exceptions are the last points representing samples taken from the borehole bottom. The relationship between δD and $\delta^{18}\text{O}$ for the investigated profile follows the equation $\delta\text{D} = 7.9 \delta^{18}\text{O}$. The variation in the age of the ice with depth was calculated from the rate of snow deposition using recent values of accumulation of snow equal to 12 g/cm^2 of water per year. On the left side of the figure the vertical scales of the borehole depth and age are not linear, since the age scale increases disproportionately with the depth scale. On the right-hand side of the figure pictured

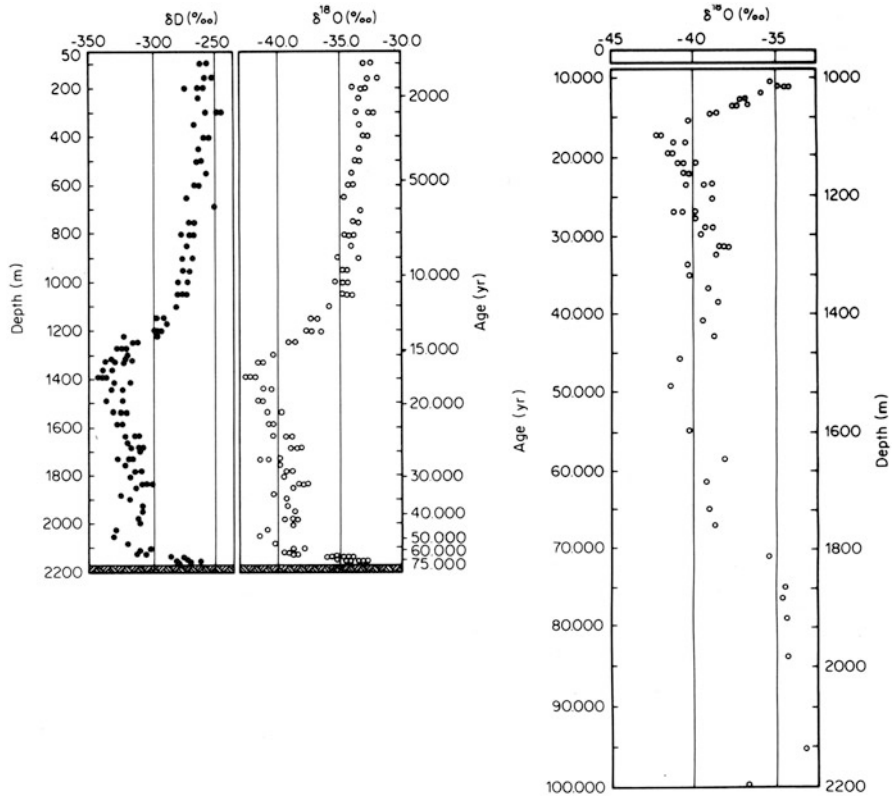


Fig. 4.8 Relationship between D and ¹⁸O content in the ice sheet profile for the Antarctic Byrd Station. (After Epstein et al. 1970)

for δ¹⁸O, the age of the layers and their thickness, starting from 1,000 m, are given in a linear scale.

From the analysis of the magnitudes and character of isotopic variations in the ice sheet with time, the authors of the study provided the following interpretation. If the observed isotopic variations in the upper 300 m during the last 2,500 years could be related to some random factors resulting in temperatures 2–3°C lower than the modern ones, then, in the range of depths from 1,050 to 2,160 m, they certainly show considerable climatic variations in the past. The corresponding time interval 11,000–75,000 years ago is commonly related to the last period of cooling on the Earth during Pleistocene. Using the variations of isotopic ratios with time, it is possible to obtain the colder periods, corresponding to 17,000, 27,000, 34,000, and 40,000 years ago and warmer ones, corresponding to 25,000, 31,000, and 39,000 years ago. It is rather interesting that the last phase of maximum cooling (being 17,000–11,000 years ago) corresponds with the end of the Wisconsin period of cooling for the northern hemisphere. An analogous coincidence in the two hemispheres is also observed for

the other cold and warm phases during the entire time period. The data characterizing the bottom part of the ice sheet then modern ones for the Byrd station. This warmer period should ended 75,000 years ago. Emiliani's data (Emiliani 1970, 1978), based on oxygen isotope studies of fossil pelagic foraminifera, and the data provided by study of the Greenland ice sheet estimated for the time period of Wisconsin glaciation, are close to those given above. The temperature varies by 7–8°C between glacial and non-glacial periods (see Fig. 4.8).

Similar results were obtained by Dansgaard et al. (1969) for 1,300 m ice column from a borehole at Camp Century Station in Greenland and also by Gordienko and Kotlyakov (1976) while studying an ice column 1,000 m in height obtained at the Antarctic Vostok Station, but according to Gordienko and Kotlyakov, the temperature variations between the Holocene and Pleistocene glaciation in the Antarctic have only been of the order of 5°C. Thus, it is possible that Epstein et al. (1970) did not take into account the decrease of heavy hydrogen isotopic composition resulting from difference in altitude marks in the ice sheet provided by the ice melting, which could be 500 m for the Byrd station.

According to Emiliani and other authors the temperatures varied in these periods by ~5–6°C for the equatorial region of the Atlantic ocean, ~7–8°C for the Caribbean basin and ~3–4°C for the equatorial part of the Pacific Ocean. As for variations of isotopic composition in glacial-nonglacial times, according to Epstein et al. (1970) and Dansgaard et al. (1971), the Greenland and Antarctic ice sheets were depleted in oxygen by average of 10‰ and the ocean waters were enriched in oxygen by an average of 0.5‰ during glacial periods.

Isotopic composition change in atmospheric precipitation in the past because of climate change on the basis of continental ice sheets study was also considered by Vasilchuk and Kotlyakov (2000). During the period of 1970–1998 at the Russian Vostok Station in Antarctica, a borehole up to 3,623 m in depth was done and covered the time interval from 0 to 420,000 years. The age of several thousand years for the upper part of ice sheet was studied by the annual layer counting. The deeper accumulations determined by modeling of the ice flowing. The acceleration mass spectrometry techniques based on the cosmogenic radioactive isotopes ^{14}C , ^{10}Be , ^{36}Cl , ^{26}Al was also used.

Hydrogen isotopic composition of the ice core from Vostok Station varies in the range from –420 to –480‰. Its higher values (from –420 to –460‰) reflect relatively short periods of interglacial warming and more lower values (from –460 to –480‰) characterize long periods of the glacial cooling. Until now, this is the only borehole covering the last glacial–interglacial cycles: the Würm glacial epoch (10,000–120,000 years); Riß–Würm interglacial (120,000–140,000 years); Riß glacial (140,000–220,000 years); Great interglacial (220,000–320,000 years); and Mindel glacial (320,000–420,000 years). It was found that the last glacial epoch is characterized by three temperature minimums which happened 20,000, 60,000, and 110,000 years ago. The interglacial peak came 130,000 years ago. 1.5–2.0°C. The warmer were XII, XVI and XX centuries, and cooler were XII–XV and XVII–XIX centuries. The last interval is called as small glacial period. The paleoclimatic studies of the Earth were carried out on the basis of analysis of ice cores from Camp

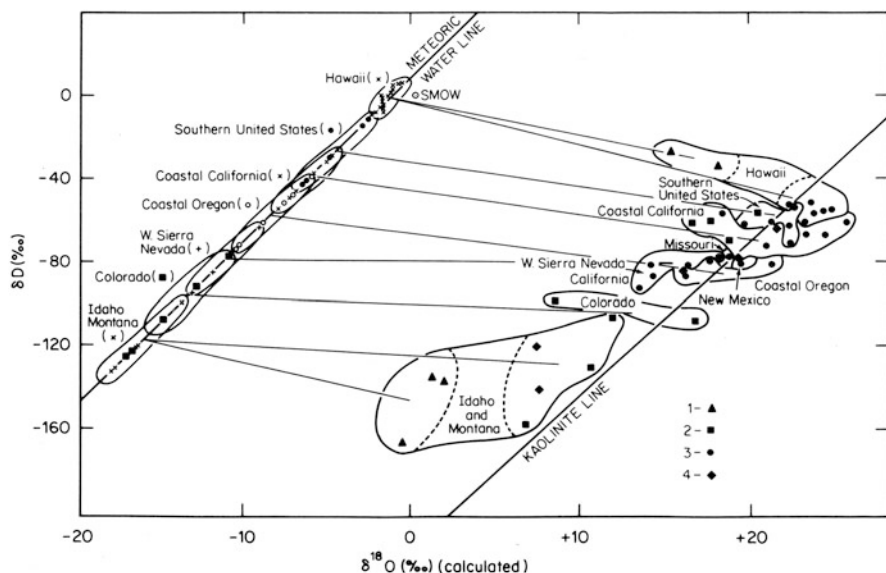


Fig. 4.9 Relationship between δD and $\delta^{18}O$ values of clay minerals and hydroxides from modern soils formed on igneous parent rocks in the United States. (1) gibbsite and amorphous Al-Si-Fe hydroxides; (2) montmorillonite; (3) kaolinite; (4) mixed kaolinite and montmorillonite. Also shown is the kaolinite line of Savin and Epstein (1970a) and isotopic composition of typical meteoric waters from various US regions. (After Lawrence and Taylor 1971)

In Fig. 4.10, the map of North America is shown with isolines δD values for Tertiary meteoric waters calculated by Sheppard et al. (1969) and Taylor (1974) based on the isotopic studies of various Tertiary meteoric–hydrothermal systems and also upper zone clay and weathering deposits of Tertiary age. Comparing this map with recent δD values for meteoric waters of the North American continent, which are shown in Fig. 4.11 and based on data collected by Dansgaard (1964), Friedman et al. (1964), and Hitchon and Krouse (1972), one finds that for the Tertiary isolines of δD there is a tendency towards enrichment about 1–2‰. As Taylor (1974) has pointed out, these data are in accord with the theory that the climate was warmer in the Tertiary age not only in the North America but also in the other regions of the Earth and particularly in former USSR (Petrov 1975).

It should be noted that, although the conclusions of Taylor (1974) on the milder climate in the Tertiary (between the Paleogene and Neogene, i.e., about 26 million years ago) have been confirmed by several geological arguments, the differences in the δD values between the recent meteoric waters and atmospheric precipitation during Tertiary, are not likely to be as great as depicted in Figs. 4.10 and 4.11. Yapp and Epstein (1977), citing a private communications with Friedman, considered that all the δD values in Fig. 4.11 should be divided by factor of 1.04, correcting laboratory error. Besides, the question concerning the period during which the information is covered and enclosed in the hydrogen isotopic composition of hydroxide groups of

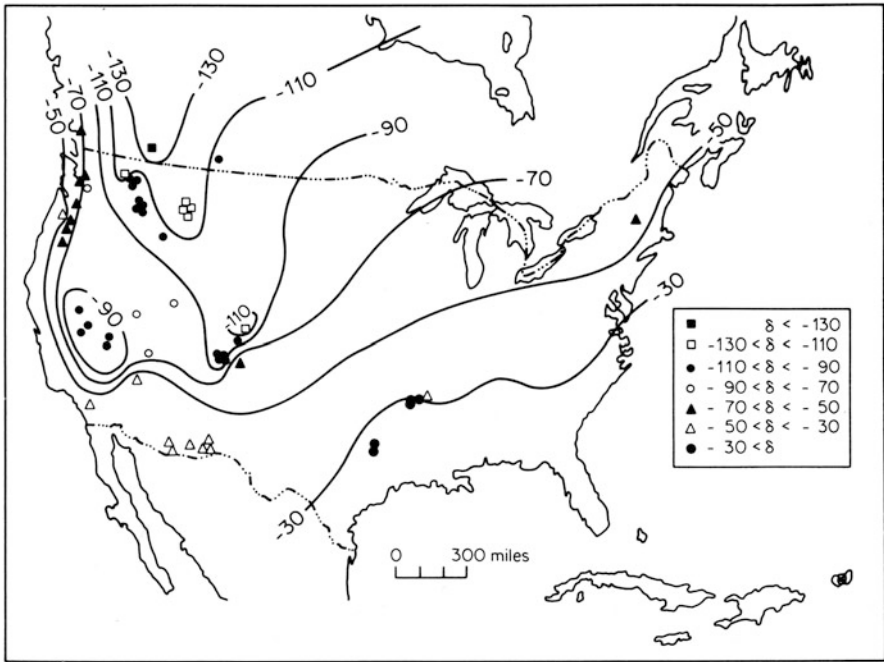


Fig. 4.10 Schematic map of the North American continent showing calculated δD values of Tertiary meteoric waters. (After Taylor 1974. © IAEA, reproduced with permission of IAEA)

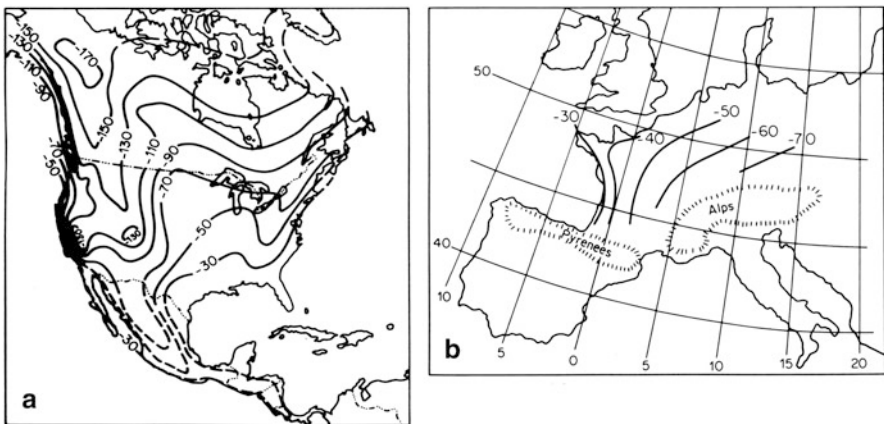


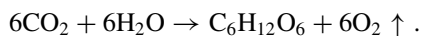
Fig. 4.11 Map of contours of the average δD values of recent meteoric surface waters; (a) for North America (from Taylor 1974); (b) for Western Europe. (From Sonntag et al. 1979. © IAEA, reproduced with permission of IAEA)

Fig. 4.12 Map of δD values of recent meteoric waters obtained for various locations of the United States by means of hydrogen isotopes in plant cellulose (points) and by direct measurements. (From Yapp and Epstein 1977. © IAEA, reproduced with permission of IAEA)



clay minerals has not yet been solved. There is evidence (James and Baker 1976) to suggest that isotopic exchange between the hydroxide groups and interlayer water takes place at room temperatures. Therefore, caution is needed when making the paleotemperature reconstruction of individual geological periods using hydrogen isotope analysis of hydroxide groups of clay minerals.

In recent years, Epstein et al. (1976), Epstein and Yapp (1976), and Yapp and Epstein (1977) have developed techniques of paleotemperature studies based on hydrogen isotopic content in the cellulose of wood plants. Cellulose is a polysaccharide of the form $(C_6H_{10}O_5)_n$, formed in plants from monosaccharides, for example glucose $C_6H_{12}O_6$, which is formed in turn by photosynthesis involving water and carbon dioxide



It is obvious that, during photosynthesis the hydrogen of glucose and cellulose—being formed it—is in isotopic equilibrium with meteoric waters of the region of the plants' growth. Experiments show that cellulose extracted from plants by nitration and extraction with alcohol–benzol mixture is depleted by about 20‰ in D compared with water (Epstein et al. 1976). Therefore, the corresponding average isotopic composition of atmospheric precipitation can be reconstructed on the hydrogen isotopes content in plant's cellulose. Yapp and Epstein (1977), taking modern plants as an example, found a good relationship between δD values obtained indirectly from the hydrogen isotopic content in the cellulose of plants and direct measurements of δD in precipitation for various regions of the United States (Fig. 4.12). They showed experimentally that hydrogen isotopic exchange in C-H groups is extremely

limited. These circumstance makes it possible to use variations in the hydrogen isotopic content in the fossil cellulose of plants for paleotemperature reconstructions. In particular, the climatic change on the North American continent during the last Pleistocene (Wisconsin) glaciation between 9,500 and 22,000 years before present has been estimated. The age of fossil plants was determined to be 22,000 years ago and the relative D content in atmospheric precipitation was 19‰ higher than the recent one. Yapp and Epstein explained this in terms of a gentle temperature gradient between the ocean and inland surface; cooling of the oceans; higher δD values for the surface oceanic waters; variation of the ratio of summer and winter precipitation; and a positive shift in the δD value in the oceanic vapor provided by the depleted influence of kinetic factors during evaporation of water at lower temperatures.

The reconstruction of the isotopic composition of glacial lakes—Whittlesey and Aquassiz—had made it possible to estimate the average hydrogen isotopic content (and the average oxygen isotopic content calculated by Craig's equation) of the North American ice sheet. It has been found that δD values for Whittlesey Lake vary from -89 to -113 ‰ and $\delta^{18}O$ values vary from -12 to -15 ‰. From data obtained while studying the woods grew on the shore of Lake Aquassiz, the average hydrogen and oxygen isotopic content for this lake was found to be (δD from -103 to -129 ‰, $\delta^{18}O$ from -14 to -17 ‰). The average $\delta^{18}O$ value of -15 ‰ for the North American ice sheet during the Wisconsin glaciation was estimated by Yapp and Epstein.

The application of hydrogen isotopic composition in the C-H group of cellulose as a paleothermometer needs to be carefully tested under natural and laboratory conditions despite the coincidence of independent geological estimations presented by Epstein and Yapp (1976, 1977). In particular, as pointed out by Ferhi et al. (1977) and Long and Lerman (1978), the formation of isotopic composition of hydrogen, oxygen, and carbon in cellulose is influenced not only by the isotopic composition of atmospheric precipitation but also by the temperature at the time of cellulose formation, the type of plant, and the environmental humidity. At low air humidity (Gonfiantini 1965), an intensive evaporation of water from the leaves of plants results in considerable enrichment of the leaves' moisture and, therefore, in the heavy isotopes of hydrogen and oxygen which are the products of photosynthesis.

Epstein and Yapp (1976) were criticized by Wilson and Grinsted (1975), who had previously proposed a biochemical thermometer based on the temperature dependence of the hydrogen fractionation factor between water and plant cellulose of the form C-3 with photosynthesis in the same way as described by Kalvin. They determined the temperature coefficient for a biochemical thermometer to be equal to $-5\% / ^\circ C$ (Wilson and Grinsted 1975). This effective dependence of the hydrogen isotope composition of cellulose of plants upon temperature disagrees with the data obtained by Epstein and Yapp (1976). The latter found that, for 25 tests on the cellulose of various plant types, growing in different climatic conditions with δD values in atmospheric precipitation varying over the range of 180‰, the δD values in the C-H group of cellulose differ from those in atmospheric precipitation by -22 ‰ with an average standard deviation of ± 11 ‰ (1σ).

Answering the critical remarks of Wilson and Grinsted, Epstein (1978) explained the marked deviations of the experimental data by the presence of OH-groups which

readily exchanged isotopes of hydrogen during Wilson and Grinsted's isotopic analyses of cellulose. As an example of δD determination, Epstein made 19 cuts across the three annual rings of a New Zealand pine *Pinus Radiata*, which had grown between May 1915 and April 1917, and produced a satisfactory qualitative coincidence of the δD values in plant cellulose with seasonal variation of δD in modern atmospheric precipitation (1963–1967) for the northern region of New Zealand. Epstein (1978) made the following conclusions:

1. Variations of δD in C-H groups of the plant's cellulose reflect hydrogen isotopic variations in atmospheric precipitation.
2. Wilson and Grinsted's statement that a biological thermometer with a temperature coefficient $-5\%/^{\circ}C$ permits estimation of variations of limiting temperatures with an error better than $0.1^{\circ}C$ is not supported by the available experimental data.
3. The method of analysis of hydrogen isotopic composition of cellulose, suggested by Wilson and Grinsted (1975, 1977), requires further verification.
4. Despite the fact that hydrogen isotopic content in plant cellulose gives agreeable qualitative coincidence with variations in atmospheric precipitation, a number of factors which are related to the kind of plants and the intensity of evapotranspiration may influence the hydrogen isotopic fractionation, depending on the climatic conditions of the region where the plant is growing.

All these circumstances require further experimental studies which should account for the influence of the above-mentioned factors upon the isotopic composition of the plant's cellulose.