

Chapter 5

Isotopic Composition of Surface Continental Waters

5.1 Isotopic Balance of the Continental Waters

The isotopic composition of natural and artificial surface reservoirs is determined by several factors, the most important of which are (Gat et al. 1968; Merlivat 1970; Fontes 1976):

1. The isotopic composition and the amount of precipitation directly feeding the reservoir.
2. The isotopic composition of the surface and underground sources of water recharge as well as the rate of water inflow.
3. The isotopic composition of atmospheric vapor moisture and also the air humidity.
4. The rate of water outflow and also the process of evaporation.

The mass balance of reservoir during a period of time Δt may be given by the equation:

$$\Delta V = \left(\sum I - \sum Q - E \right) \Delta t + P, \quad (5.1)$$

where ΔV is the volume change of the reservoir; I is the component of the surface and subsurface water recharge; Q is the component of the surface and subsurface discharge; E is the mean rate of evaporation; P is the amount of precipitation during the time Δt .

The isotopic balance equation in this case is

$$R_L \Delta V + V \Delta R_L = \left(\sum R_I I - \sum R_Q Q - R_E E \right) \Delta t + R_P P, \quad (5.2)$$

where R is the value of mean isotopic ratio of the components of recharge and discharge.

The value R in Eq. (5.2) can be changed by value δ . Then, the equation acquires the form

$$\Delta(\delta_L V_L) \Delta t = \sum \delta_I I - \sum \delta_Q Q - \delta_E E + \delta_P P.$$

It is known (Craig and Gordon 1965; Merlivat 1970) that a liquid's evaporation rate in the atmosphere can be described by the equation

$$E = \kappa \frac{dC}{dz},$$

where E is the rate of evaporation (vapor flux from the unit of liquid surface); κ is the coefficient of turbulent diffusion; dC/dz is the vertical gradient of humidity.

For isotopic species of water ($H_2^{18}O$ or HDO), one has

$$E_i = \kappa_i \frac{dC_i}{dz}.$$

The values of the isotopic fractions in vapor R_E in this case can be given by

$$R_E = \frac{E_i}{E} = \frac{\kappa_i}{\kappa} \frac{dC_i/dz}{dC/dz}.$$

This equation in finite differences, after the coordinate dz is eliminated, obtains the form

$$R_E = \frac{\kappa_i}{\kappa} \frac{R_L/\alpha - hR_\alpha}{I - h}, \quad (5.3)$$

where h is the relative air humidity at altitude z above the water surface at a given temperature; R_L and R_α are isotopic ratios for liquid and atmospheric vapor, respectively; α is the equilibrium fractionation factor.

In the Eq. (5.3), it is accepted

$$\Delta C = 1 - h, \quad \Delta C_i = R_i/\alpha - hR_\alpha.$$

Designating $\kappa/\kappa_i = k$, Eq. (5.3) can be written as (Gat et al. 1968):

$$R_E = (R_L/\alpha - hR_\alpha)/k(1 - h). \quad (5.4)$$

Equations 5.3 and 5.4 give an idea about the parameters which determine the isotopic composition of the vapor flux. As Brezgunov (1978) has pointed out, these formulae are realistic in the physical sense only when both fluxes have the same sign that is when either evaporation or condensation of water and isotopic species occurs. If the fluxes have different signs, they should be considered separately while estimating the isotopic and mass balance of water in the reservoir.

An additional atmospheric resistance effect of fractionation of isotopes during the water evaporation in atmosphere, being defined by humidity and the parameters of the turbulent diffusion of vapor, Craig and Gordon (1965) is evaluated by

$$\Delta \varepsilon = (\kappa/\kappa_i - 1)(1 - h).$$

The isotopic composition of evaporating water expressed in δ values after such a transformation as described in Eq. 5.3 will be as follows:

$$\delta_E = \frac{\alpha^* \delta_L - h \delta_\alpha - \varepsilon^* - \Delta \varepsilon}{(1 - h) + \Delta \varepsilon}, \quad (5.5)$$

where $\alpha^* = 1/\alpha$, $\varepsilon^* = 1 - 1/\alpha$; δ_L , δ_α are the isotopic compositions of liquid and vapor.

Equation 5.5 can be conveniently used to obtain an equation describing the isotopic balance of reservoirs. To obtain a precise value of δ_E , it is necessary to measure the parameters δ_L , δ_α and h directly and know the values of ε^* and $\Delta\varepsilon$. The value ε^* can be calculated easily with the help of equilibrium factor at given temperatures. The $\Delta\varepsilon$ value has been estimated in a number of experimental and theoretical works which were estimated in detail in Brezgunov's review paper (1978). According to experimental data, $\Delta\varepsilon_{18O}$ is dependent on humidity:

$$\Delta\varepsilon_{18O} = (1 - h)16\text{‰}.$$

At constant humidity, the ratio $\Delta\varepsilon_D/\Delta\varepsilon_{18O}$, as shown by the experimental and theoretical estimations of Craig and Gordon (1965) and Merlivat (1970) ranges from 0.5 to 0.85, but in a number of experiments (Craig and Gordon 1965; Gat 1970) $\Delta\varepsilon_D$ exceeds $\Delta\varepsilon_{18O}$ by 2–4 times. Such deviations between experimental and theoretical values were explained by Craig and Gordon in terms of extra isotopic effects at the boundary of the liquid–vapor system, which might be provided by differences in the condensation (vaporization) coefficients for isotopic species of the molecules. The values of the parameter $k = \kappa/\kappa_i$ in Eq. 5.4 have been found, experimentally, to range between 1.016 and 1.020 for oxygen-18 (^{18}O) and 1.009 and 1.0136 for deuterium (D) (Merlivat 1970). Gat et al. (1968) have considered particular values on the basis of work by Craig and Gordon (1965) calculated to be $k_D = 1.009$ and $k_{18O} = 1.016$. However, such an assumption, as was noted above, is based on the fact that the condensation coefficient for isotopic molecules does not undergo visible variations.

It follows from Eq. 5.3 that the isotopic composition of water vapor above the reservoir is determined both by the isotopic composition of evaporated water and by the isotopic content of atmospheric moisture. If under natural conditions the evaporation occur in accordance with the Rayleigh's distillation law, then water and vapor should be in isotopic equilibrium at any moment. In this case, the isotopic composition of vapor over the reservoir is equal to $R_E = R_L/a$ (R_L is the isotopic composition of the reservoir water at time t) and the isotopic composition of water during evaporation would be given by the Rayleigh's formula (Brodsky 1957)

$$R_L = R_0(V_0/V)^{(\alpha-1)/\alpha} = R_0(V/V_0)^{(\alpha-1)/\alpha}, \quad (5.6)$$

where R_0 and R_L are the ratios of the isotopic species of water initially and at time t ; V_0 and V are the initial and final volumes of water.

Taking logarithms of Eq. 5.6, we obtain

$$\ln R_L = \ln R_0 + \varepsilon \ln F,$$

where $\varepsilon = 1/\alpha - 1$; $F = V/V_0$.

Substituting δ values for R and taking into account that $\ln(1 + \kappa) \approx \kappa$ at $\kappa \ll 1$, one obtains

$$\delta_L - \delta_0 = \varepsilon \ln F.$$

In other words, during the Rayleigh's evaporation, the expression for $(\delta_L - \delta_0)$ becomes a linear function of $\ln F$. This is convenient for analyzing experimental data while studying the change in a liquid's isotopic composition during evaporation (Figs. 5.2 and 5.5).

If under conditions of Rayleigh's evaporation, the volume of the reservoir V_0 remains unchanged due to recharge, then the isotopic composition of the water at any time may be found from the equation (Brodsky 1957).

$$\alpha \ln [(\alpha - 1)/(\alpha - R_L/R_0)] = V/V_0. \quad (5.7)$$

The maximum enrichment, which might be attained in this case at $V \rightarrow \infty$, is $R_0\alpha$. Under real conditions, the changes in the isotopic composition of water in the drying reservoir do not follow the Rayleigh's law because the thermodynamic and isotopic equilibrium between water and vapor does not occur here.

As shown in the previous chapter, in case of thermodynamic disequilibrium in a system the rate of transition of molecules HDO and H_2^{18}O from the liquid into the gaseous phase will be determined by difference in the diffusion coefficient of the molecules H_2O , HDO, and H_2^{18}O . In contrast to the processes of equilibrium fractionation when the fractionation factors in the water–vapor system are 1.08 for H_2O –HDO and 1.009 for H_2O – H_2^{18}O , the difference in the coefficients in the case of diffuse separation is not so great. For the above-mentioned pairs of molecules, the coefficients are 1.009 and 1.016, respectively.

The observed relationship between D and ^{18}O content in precipitation, expressed by the equation $\delta\text{D} = 8\delta^{18}\text{O} + 10\text{‰}$, is evidence that the moisture condensation occurs under conditions which are sufficiently close to those at equilibrium. Under these conditions, the D and ^{18}O fractionation factors might be assumed to be equal to those for systems in equilibrium such as 1.08 for D and 1.009 for ^{18}O at 20°C .

During evaporation, under nonequilibrium conditions, the difference between the D and ^{18}O content is limited not only by the value of the fractionation factors but also by the ratio of the diffusion rates of the molecules such as the coefficient $k = \kappa_i/\kappa$ in Eq. 5.3. This leads to a more gentle sloping curve of δD against $\delta^{18}\text{O}$ for water in open reservoirs.

As Dansgaard (1964) has pointed out, in this case the fractionation factor can be given by the expression $\alpha^k = \alpha k$. Hence,

$$\alpha_{\text{D}}^k = 1.08 \times 1.009 = 1.09; \quad \alpha_{^{18}\text{O}}^k = 1.009 \times 1.016 = 1.025.$$

The value of the ratio $d\delta\text{D}/d\delta^{18}\text{O}$ can be obtained by differentiating Eqs. 4.6 and 4.7, which are similar to the relationship described by Eq. 5.6, since $V/V_0 = F$, and $\delta = R_L - 1$ since $R_0 = 1$:

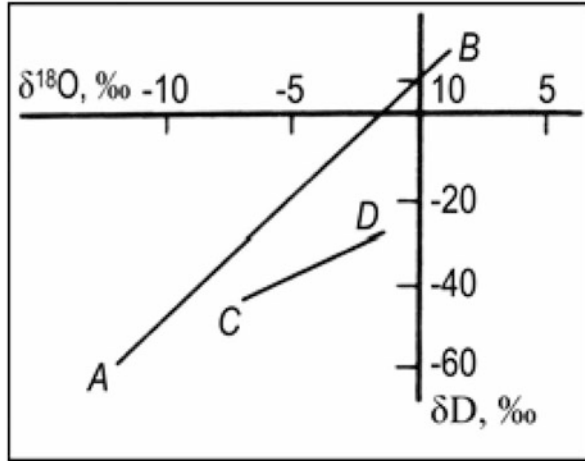
$$d\delta\text{D}/d\delta^{18}\text{O} = (\varepsilon_{\text{D}}/\varepsilon_{^{18}\text{O}})F^{\varepsilon_{\text{D}} - \varepsilon_{^{18}\text{O}}}, \quad (5.8)$$

where $\varepsilon = (1 - \alpha)/\alpha$.

Equation 5.8 can be approximated by ^{18}O

$$d\delta\text{D}/d\delta^{18}\text{O} \approx \varepsilon_{\text{D}}/\varepsilon_{^{18}\text{O}}, \quad (5.9)$$

Fig. 5.1 Schematic relationship between δD and $\delta^{18}O$ values for precipitation (AB) and for closed continental basins (CD)



since the index $\epsilon_D - \epsilon_{18O}$ differs only slightly from zero and at a given temperature is a constant.

The slope of the line describing changes in D and ^{18}O concentrations in a solution during Rayleigh's evaporation (at $t = 20^\circ C$ $\alpha_D = 1.08$ and $\alpha_{18O}^k = 1.009$) will be

$$d\delta D/d\delta^{18}O \approx (\alpha_D - 1)\alpha_{18O}/(\alpha_{18O} - 1)\alpha_D \approx 8. \tag{5.10}$$

Under nonequilibrium conditions of evaporation, when kinetic factors are important (at $20^\circ C$ $\alpha_D^k = 1.09$; $\alpha_{18O}^k = 1.025$), one has

$$d\delta D/d\delta^{18}O \approx (\alpha_D^k - 1)\alpha_{18O}^k/(\alpha_{18O}^k - 1)\alpha_D^k < 8. \tag{5.11}$$

It follows from Eqs. 5.10 and 5.11 that for nonequilibrium water vaporization from closed reservoir the values of δD and $\delta^{18}O$ lie below Craig's line plotted for atmospheric precipitation on a line with a smaller gradient (Fig. 5.1).

At a steady state, when no significant changes in the volume of the reservoir occur, the isotopic composition of well-mixed water tends toward a constant value

$$R_L = \frac{(1 - h)R_I s + hR_a/k}{1/\alpha k + (1 - h)(1 - s)}, \tag{5.12}$$

where s is ratio of the mean rates of recharge and evaporation.

Equation 5.12 is only true if short time variations of the parameters α , R_I , R_a , h permit one to consider their mean values to be constant in time.

Assuming that water loss from the reservoir takes place only due to evaporation that is $s = I/E = 1$, then Eq. 5.12 becomes

$$R_L = \alpha k[(1 - h)R_I + h(R_a/k)]. \tag{5.13}$$

Equation 5.13 gives the value of maximum isotopic enrichment of reservoirs with constant volume. It is obvious that at $h = 0$ (for evaporation when air humidity equals

zero) $R_L = \alpha_k R_I$. This expression corresponds to the maximum isotopic enrichment for evaporation of a liquid at constant level during Rayleigh's distillation where α is substituted by $\alpha k = \alpha^k$.

If the level of the reservoir is reduced only by evaporation and recharge does not occur ($I=0$), then the integration of Eqs. 5.1 and 5.2 under these conditions yields the following expressions for the isotopic composition of the reservoir as a function of V/V_0 :

$$R_L = \frac{[R_0(1/\alpha k - 1 + h) - hR_\alpha/k](V/V_0)^{(1/\alpha k - 1 + h)/1 - h} + hR_\alpha/k}{1/\alpha k - 1 + h}. \quad (5.14)$$

The Eq. 5.14 is similar to the formula for Rayleigh's distillation (Eq. 5.6), but in this case the kinetic factors, the isotopic composition of the atmospheric vapor, and the air humidity should be taken into account.

In drying reservoirs, that is when $(V/V_0) \rightarrow 0$, the final isotopic composition of water can be found from the expression

$$R_L = \frac{hR_\alpha/k}{1/\alpha k - 1 + h}. \quad (5.15)$$

It follows from the analysis of Eqs. 5.14 and 5.15 that under natural conditions of an existing reservoir, the isotopic composition of its water does not increase to infinity—as the Rayleigh's equation (Eq. 5.6) suggests—but tends toward some stationary condition determined by parameters α , k , h and R_α (see Figs. 5.5 and 5.7).

For $h=1$, when the reservoir is in thermodynamic equilibrium with the vapor, the isotopic composition R_α which is independent of the isotopic composition of the reservoir, one has

$$R_L = R_\alpha \alpha. \quad (5.16)$$

Under such conditions, the water in the reservoir attains isotopic equilibrium with the atmospheric moisture. It follows from Eq. 5.12 that the isotopic composition of water is governed both by evaporation and by recharge of water having an isotopic composition R_I . Therefore, for seas where rivers play an important role in the formation of water bodies, D and ^{18}O content is lower than that in the ocean, so for the Black Sea $\delta\text{D}_{\text{SMOW}} = -18.8\text{‰}$ and $\delta^{18}\text{O} = -3.15\text{‰}$; for the Caspian Sea, the values are even lower.

As it was earlier noted, by experimental results and natural observations, it was found that the isotopic composition δ_L of an evaporated reservoir in natural conditions tends to have some stationary state δ_L^S (in the δ -values). It was shown in the works of Craig and Gordon (1965), Gonfiantini (1965), Fontes et al. (1979) that the value δ_L^S for a basin with stationary level is determined by equation

$$\delta_L^S = \frac{[(E/I)h\delta_\alpha + (\alpha = h)\delta_I(\varepsilon_V + 1)] + (E/I)\alpha\varepsilon_V}{(\alpha - h)(I - E/I)(1 + \varepsilon_V) + \alpha(E/I)}.$$

For the drying lakes, one has

$$\delta_L^S = \frac{\alpha\varepsilon_V + h\delta\alpha(1 + \varepsilon_V)}{h(1 + \varepsilon_V) - \alpha\varepsilon_V},$$

where $\varepsilon_V = \varepsilon^* + \Delta\varepsilon$ is the total effect of enrichment of the evaporated water and a is activity of water in the solution.

Kinetic term $\Delta\varepsilon$ depends on the air relative humidity and the water activity and $\delta^{18}\text{O}$ is described by the following dependency (Fontes et al. 1979a): $\Delta\varepsilon = [14.4 \times (a - h)/a] \times 10^{-3}$. The δ -value, substituted into above formula, is expressed in parts of the unit ($\delta = \delta_{\text{measured}} \times 10^{-3}$).

If the lake discharges water Q , then in stationary state for full mixing lakes $\delta_Q = \delta_L^S$. In this case, the total water recharge and the evaporating flux have the following relationship: $I = E(\delta_L^S - \delta_E) / (\delta_L^S - \delta_I)$ (Zimmermann 1979).

If the lake volume and also the hydrological and climatic parameters can be accepted constant, then isotopic composition of the lake water in time comes to the stationary state in accordance with the equation (Zimmermann 1979)

$$\ln(\delta_L^S - \delta_L) = -(1/\tau)t + \ln(\delta_L^S - \delta_Q),$$

where τ is the mean value of the residence time of water in the lake which is determined by relation V/I ; V is the reservoir volume; I is the total water recharge which includes the surface and ground inflow and atmospheric precipitation over the lake surface.

For the reservoir which has not reached steady state in isotopic content, the value τ can be determined by the time dependence relation $\ln(\delta_L^S - \delta_L) = -(1/\tau)t + \ln(\delta_L^S - \delta_Q)$ (Zimmermann 1979).

If one plots dependence $\ln(\delta_L^S - \delta_L)$ with reference to time, then the point should be put on the straight line with the slope $1/\tau$.

The combination of water (Eq. 5.1) and isotope (Eq. 5.2) balance assuming that $\delta_I = \delta_P$, gives the following relationship between the rate of the water evaporation E and the total discharge from the lake (Hübner et al. 1979a):

$$E = Q(\delta_L - \delta_Q) / (\delta_E - \delta_I).$$

This equation makes it possible to calculate the values E and Q by one known parameter and experimental values δ_L and δ_Q . In this case, the value δ_E can be calculated by Eq. 5.5. The isotope methods have wide application in study of the lake water balance. The methods are used for indirect assessment of the underground recharge and discharge of lake. As a rule, determination of these parameters by traditional hydrological means have difficulties. The examples of such a solution can be found in the IAEA proceedings on Isotopes in Lake Studies (IAEA 1979).

5.2 Isotopic Composition of the River and Lake Water

Let us now consider some peculiarities of the formation of isotopic composition of surface continental waters. The most complete regional survey of characteristic D contents in surface continental waters is given by Friedman et al. (1964) and for Canada by Brown (1970). The isotopic composition of water in rivers, lakes, and other reservoirs is dependent on the isotopic composition of atmospheric precipitation

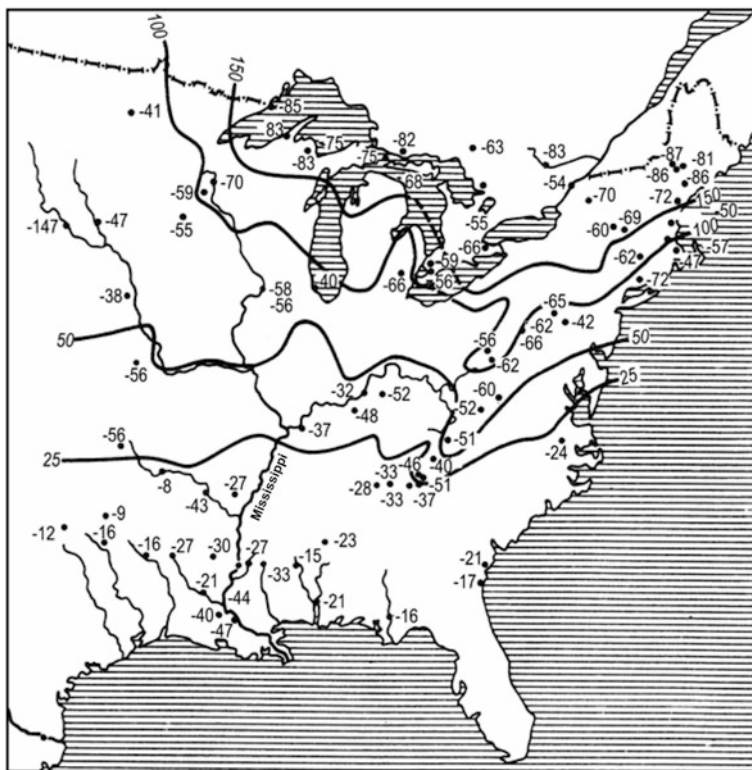


Fig. 5.2 Map of δD values for the Missouri–Mississippi river basin and East Atlantic coast of the United States plotted on the data of 1956–1959. Contours show thickness of snow cover in centimeter. (After Friedman et al. 1964)

feeding these reservoirs. The surface continental waters are less subject to isotopic variations with time compared with atmospheric precipitation, and the springs and wells which do not dry up are the most reliable sources of water for determination of isotopic ratios characteristic of a given region.

Figure 5.2 shows the regional characteristic of D concentrations in Mississippi river water and the East Atlantic coast of the United States (Friedman et al. 1964). The basin of the Mississippi river covers a considerable area of the eastern region of USA, characterized by a comparatively low height above the sea level and wide ranges of temperature, which determine the initial isotopic composition of atmospheric precipitation. Figure 5.2 shows the isolines of annual snow cover well correlated with relative D content in the surface water. As expected, an even closer correlation is observed between the relative D content and the ratio of the amounts of snow and rain falling down as atmospheric precipitation. In this case, an increase in the proportion of snowfall results in a decrease of the D content and vice versa.

Figure 5.2 may serve as an example of regional D distribution. Equation 4.13 can be used as a first approximation in obtaining a picture of oxygen isotope distribution.

Table 5.1 Estimates of the apparent hydrogen isotopic ratio of vapor pressures and water from the saline lakes and their recharge. (Friedman et al. 1964)

Lakes	$\delta D, ‰$		Estimated ratio of vapor pressure	Origin of source water
	Lake water	Source water		
Piranid Lake	-30	-87	0.942	Truckee river
Mono Lake	-62	-130	0.927	Sierra Nevada near crest
Soda Lake	-51	-130	0.918	
Owens Lake	-97	-135	0.958	Los Angeles aqueduct
Salton Sea	-41	-136	0.901	Colorado and Alamo rivers
Great Salt Lake	-89	-130	0.934	Yellowstone plateau
Harney Lake	-40	-114	0.923	Silvies river
Mean value			0.923	
Corresponding temperature			18°C	

Evaporation from the basin as well as from the surface of its catchment area is an important factor governing the formation of the isotopic composition of surface waters. As a result of this process, water becomes enriched in heavy isotopes compared with the local precipitation. In this case, the final effect on basins from the regional point of view depends upon the ratio of precipitation to evaporation and conditions of supply. In arid regions, where evaporation exceeds precipitation, the total isotopic balance shows a deficit of the light isotopes. For the humid regions, where precipitation exceeds evaporation, a deficit of heavy isotopes should be observed. Finally, for regions having a balanced amount of evaporation and precipitation, the isotopic balance should also be held. On the continents, the role of balancing the isotopic composition is played by large rivers, the basins of which lie in different climatic areas from humid to arid.

The influence of evaporation on the isotopic composition of basins may be demonstrated by investigating closed and particularly saline lakes (see Table 5.1). According to theoretical data obtained for this group of lakes, the fractionation should occur at 18°C but as the authors themselves pointed out, their estimations are imprecise since the initial data on the isotopic composition of the inflow water from tributaries are not accurate enough, the water losses due to underground discharge have not been taken into account, and the water in the lakes does not attain complete mixing.

Another example of elucidating the relationship between lake water, sources feeding them, and atmospheric vapor is the investigation of hydrogen and oxygen isotope distribution in the basin of the Issyk-Kul Lake (Brezgunov et al. 1979, 1981). The Issyk-Kul Lake is located in a high mountain valley in Tien Shan at an altitude of 1,600 m above sea level. Its total area is 6,200 km² with an average depth of 280 m. More than 50 rivers flow into the lake from the slopes of the surrounding mountains and are fed mainly by ice-melt waters. The annual run-off of the rivers is about 4 km³ and the mean annual amount of precipitation is about 250 mm (~1,5 km³). The temperature of the lake's surface water in July–August is equal to 18–19°C and in January–February never drops below +2°C.

Due to natural conditions of its location, the Issyk-Kul basin, with a total area of about 22,000 km², a surface which never freezes, and being a source of intensive

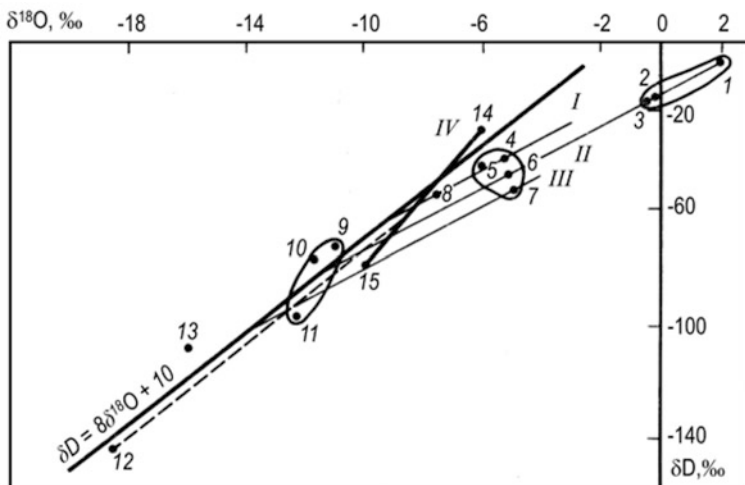


Fig. 5.3 Plot of δD versus $\delta^{18}O$ for natural waters sampled in June 1975 in the Issyk-Kul Valley. Kara Kel Lake water; 2–3 Issyk-Kul Lake water; 4 precipitation from Cholpon-Ata Station; 5 precipitation from Pokrovka Station; 6 precipitation from Przhevalsk Station; 7 precipitation from Rybachye Station; 8 precipitation from Bolshaya Kyzyl-Su Station; 9–10 Chon Kyzyl-Su river water; 11 Dzhergalan River water; 12 precipitation from Bolshaya Kyzyl-Su Station in December 1975; 13 calculated values of ‘lake’ vapor isotopic composition; I, II, III evaporation lines with slope of 5; IV condensate ‘mixture’ line reflecting the ‘lake’ and ‘regional’ vapor mixture degree. (After Brezgunov et al. 1979)

evaporation (condensation of atmospheric moisture is localized on the slopes of the mountain ridges surrounding the lake), can be considered as unique natural model of the global circulation of waters.

The authors (Brezgunov et al. 1979) carried out systematic investigations of the isotopic content in the lake and river waters, sources of groundwaters, atmospheric precipitation, glaciers, and water vapor in the valley from 1974.

The relationship of natural waters of the Issyk-Kul basin is given in Fig. 5.3, plotted in δD – $\delta^{18}O$ coordinates, drawn the data of June 1975. Here the experimental points may be subdivided into three groups. The first group (points 1, 2, 3) corresponds to lake water, characterized by the greatest values of δD and $\delta^{18}O$ and the minimum value of parameter b in Eq. 4.12. Close to the line for meteoric waters lie points 9, 10, 11, which correspond to the isotopic composition of water from rivers. Points 4, 5, 6, 7 belong to the third group and lie between those of the first two groups; they correspond to the isotopic composition in precipitation, measured at the coastal stations, and form a sufficiently independent set. Far from this set of points lies the point 8, which corresponds to the isotopic content in precipitation at high mountain station of Bolshaya Kyzyl-Su. Point 12, corresponding to the isotopic composition in atmospheric precipitation obtained in December 1975 for the same station, makes it possible to compare the range of seasonal variations of hydrogen and oxygen isotopic content for the same region. Note that the mean δD and $\delta^{18}O$

values calculated for samples obtained in June and December for Bolshaya Kyzyl-Su station lie in the domain corresponding to the river water in $\delta\text{D}-\delta^{18}\text{O}$ diagram.

The data given in Fig. 5.2 visibly reflect the process of hydrogen and oxygen isotopic fractionation. Here, the relative values of D and ^{18}O content in waters of the Issyk-Kul lake are considerably greater than the rivers which are the major sources of lake water. This is due to the evaporation. The straight line in the diagram, connecting data for the river and lake waters, has slope of about 5, which is characteristic for the line of evaporating water. Maximum values of δD and $\delta^{18}\text{O}$ (point 1) are found for the Kara Kel Lake water. The closed lake is small (area is equal to 0.5 km^2) and shallow (depth is $\sim 10\text{ m}$), and it is situated 500 m from the southern shore of the Issyk-Kul Lake. The excess of D and ^{18}O in the water of this small lake reflects its high rate of water exchange.

On the right of the meteoric water line in the diagram there are points which characterize the isotopic composition of precipitation in the coastal region, and for which the parameter b (Eq. 4.12) is negative. Brezgunov et al. (1979) have explained this phenomenon in terms of the evaporation of raindrops in the atmosphere below the cloud layer, resulting in the enrichment in heavy isotopes of atmospheric precipitation taken near the surface. The reduction of the parameter b to negative values in the summer precipitation is a feature of most high latitude stations, which was noted first by Dansgaard (1964). It was found that, other things being equal, the lower the relative humidity of air below the cloud layer, the more is the rainwater enriched in heavy isotopes and the value of parameter b becomes lower.

Using the experimental data on the isotopic composition of water in lakes and rivers and those of atmospheric vapor from the five stations situated around the Issyk-Kul Lake, Brezgunov et al. (1979) evaluated hydrogen and oxygen isotopic content in atmospheric moisture about the lake. In order to carry out the calculations, they used the model of isotopic fractionation by interaction of the reservoir with the atmosphere and the corresponding expressions (Eq. 5.5).

Expression (Eq. 5.5), representing the ratio of heavy isotope flux to the flux of moisture, can be written in terms of δ values as follows:

$$\delta_E = \frac{(\delta_L/\alpha) - \delta_A h - \varepsilon - \Delta\varepsilon}{1 - h + \Delta\varepsilon},$$

where δ_E , δ_L , and δ_A correspond to the isotopic composition in the evaporating flux of moisture, reservoir water, and atmospheric moisture; ε and $\Delta\varepsilon$ are values, expressed in δ units, related to equilibrium and kinetic fractionation factors.

For the stationary evaporation process and the model of the reservoir with constant level $\delta_E = \delta_I$ (where δ_I is the heavy isotopic content in the inflow sources).

For a reservoir with a constant level, such as the lakes in question, for known δ_L , δ_I values and air humidity above the reservoir and known values of the equilibrium kinetic fractionation factors from the previous expression, we found that:

$$\delta_A = \frac{\delta_L - \delta_I(1 - h) - \varepsilon - \Delta\varepsilon}{h}.$$

According to this expression, in which the values of ε and $\Delta\varepsilon$ were derived from Dansgaard (1964) and Merlivat (1970), the values $\delta\text{D} = -108\text{‰}$ and $\delta^{18}\text{O} = -16\text{‰}$

were found to be close to the corresponding values of the water vapor determined experimentally.

In addition, by analyzing the data on the isotopic composition of precipitation in the investigated valley and water vapor above the lakes, the atmospheric vapor mixing proportions were estimated. The position of the intersection points of the evaporating lines *I*, *II*, and *III* in Fig. 5.3, which has a slope equal and close to 5 and which passes through the points with isotopic content of precipitation with mixing line *IV*, made it possible to estimate the proportion of these two components in the atmospheric vapor (the regional component and that component removed from the lake) in the precipitation which fell in the June 1975 in different locations of the Issyk-Kul valley. It was found that in the western part of the valley (Rybachye station) the precipitation was almost completely formed of water vapor from outside the region. Precipitation in the eastern part of the valley (Przhevalsky station) was composed from 20% of the lake vapor and 80% of the regional vapor. The maximum contribution of lake vapor (up to 40%) was found in the central part of valley at stations Cholpon-Ata, Pokrovka, and Bolshaya Kyzyl-Su.

Variation of isotopic composition of the river water due to evaporation can be observed when examining, as an example, the Nile River (Friedman et al. 1964). During flood periods, the relative D content in river water near Khartoum is -23‰ and near Cairo it is -21‰ . By the calculations of Friedman, the data correspond to R/R_0 value of 1.002 and a value of 0.97 for the fraction of remaining water. Thus, the Nile appears to have lost about 3% of its water by evaporation between Khartoum and Cairo ($\sim 3,000$ km). At low water, these values are $+15\text{‰}$ and $+16\text{‰}$ respectively. Again, evaporation loss is about 3%. In Friedman's opinion, the difference in δ values reflects the fact that at high water the Blue Nile is the dominant water source and at low water the Wight Nile predominates.

Another example, illustrating conditions of isotopic composition formation and the influence of evaporation in a large continental water system, is the Great Lakes basin and that of the St. Lawrence River in North America.

Figure 5.4 shows the data obtained by Brown (1970) on D content in the St. Lawrence River and in the main tributaries of the system and also the data on D content in precipitation. As the author has pointed out, the D concentration in this water system is the highest compared to all the other reservoirs of water in Canada due to intensive evaporation of water and its enrichment with heavy isotopes. Within the range of these lakes, there is a slight (up to 10‰) enrichment in D when water flows from one lake to another. Down the river course, the D content drops due to the dilution of its water with higher waters from the tributaries and also due to the discharge of groundwaters of the valley. After Quebec (see Fig. 5.4, after point 21) the D content increases due to contributions of sea waters from the gulf mixing with the river water. Further (after point 18), some variations of isotopic composition are observed, being lower than those in the ocean water.

The following main principles of isotopic composition formation of continental surface waters in a regional scale should be pointed out. Since, surface continental waters are represented by a number of separate regional basins in the framework of which accumulation, mixing, and run-off of atmospheric precipitation in the ocean occur, the isotopic content of surface inland waters reflects some average

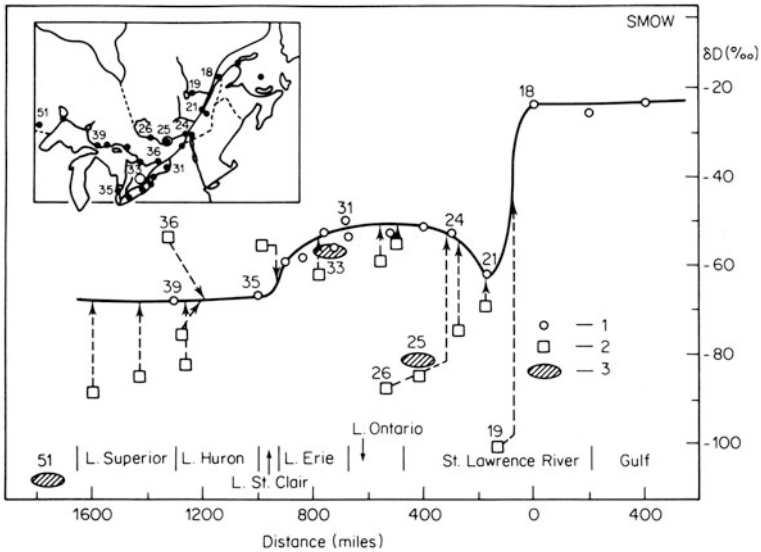


Fig. 5.4 D concentrations along the Great Lakes–St. Lawrence system in October 1967. Numbers refer to the points of investigation. 1 main stream; 2 tributaries; 3 precipitation. (After Brown 1970)

regional isotopic ratios in precipitation during a certain period of time. The isotopic composition of water of the basin may reflect both average annual isotopic ratios and seasonal variations in precipitation, which depend upon the climate zone, size of the basin, and the supply conditions. A rather important factor in the formation of the isotopic composition of water is the evaporation of water from the basin and the catchment area. This process has particular importance for conditions in lakes where heavy isotope content is always higher than in the source.

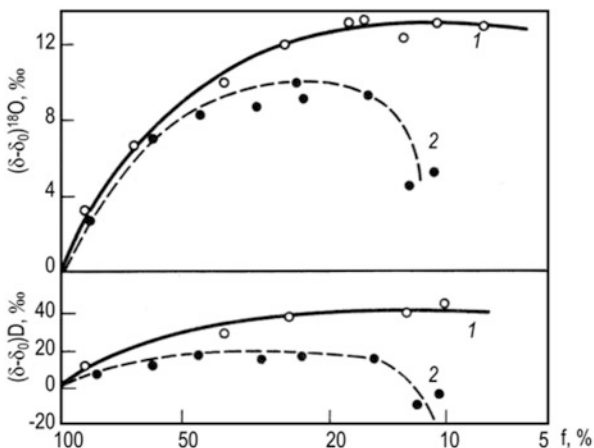
The latitudinal and altitudinal effects, which are a feature of isotopic variations in precipitation, are also valid for the surface waters. In high latitudes, the river and lake waters are depleted in heavy isotopes compared to those in low latitudes. Rivers and lakes of the arid zones, being fed by water from high mountain glaciers and snow melting, are distinguished by lower values of heavy isotopes. In contrast, the drying rivers and lakes of the arid zone have excessive heavy isotopic contents.

It should be noted that when considering the difficulty of the formation of isotopic composition of surface continental waters, one of the main problems is to establish a genetic relationship between the isotopic composition of the surface waters in a given region and that of precipitation. This problem, which should be based on the development of regional water exchange models, awaits solution.

5.3 Isotopic Composition of Water in Evaporating Basins

The problem of D accumulation in closed evaporating basins connected genetically with ocean waters is of great theoretical and practical interest. The study of D behavior during the evaporative concentration of sea water is important to answer

Fig. 5.5 D and ^{18}O concentration changes at evaporation of distilled (1) and normal sea (2) waters. (After Gonfiantini 1965)



paleogeological questions, since the formation of thalassogenic sedimentary waters might occur not only from basin waters with normal salinity but also from concentrated lagoon brines, shallow bays, etc. If the subsurface waters of connate marine basins can be adequately identified by their 'marine' D content, the history of sedimentary waters formed from waters of saline basins becomes ambiguous. There is an opinion (Polivanova 1970) that brines which are formed during continuous evaporation from reservoirs have the same isotopic content as infiltration waters. If this is true then, the D content serves as indicator of the marine origin of subsurface brines.

As shown above, the accumulation of D in nature does not follow Rayleigh's equation but is complicated by kinetic factors and by isotopic exchange between liquid and atmospheric moisture vapor. Whilst studying the behavior of heavy isotopes of hydrogen and oxygen during the evaporation of sea water Gonfiantini (1965) found an inversion of the isotopic content in the water-vapor system when the water body has decreased 10 times (Fig. 5.5). He correctly explained this phenomenon in terms of the increasing influence of the condensing vapor of atmospheric moisture when the rate of evaporation of the solution decreases due to decrease in the water activity provided by increases in the concentration of salts. Such an approach provides explanation of the observed phenomenon of the process studied, but the equation derived by Gonfiantini contains several assumptions which preclude its use to describe the evaporation of very small amounts of sea water.

Because of this, Polivanova (1970) concluded that the D content of water with high salinity may decrease sharply, attaining magnitudes characteristic for meteoric waters. Polivanova tried to confirm this hypothesis by considering theoretical variations in the activity coefficient of magnesium chlorides and also by the changes in water chemistry. She did not take into account the role of evaporation rates in formation of the isotopic composition of the liquid being evaporated, although Craig (1963), Lloyd (1966), and Gonfiantini (1965) showed this effect to be of great importance.

While studying the process of accumulation of heavy isotopes of oxygen during the evaporation of sea water, Lloyd (1966) came to the conclusion that changes in the

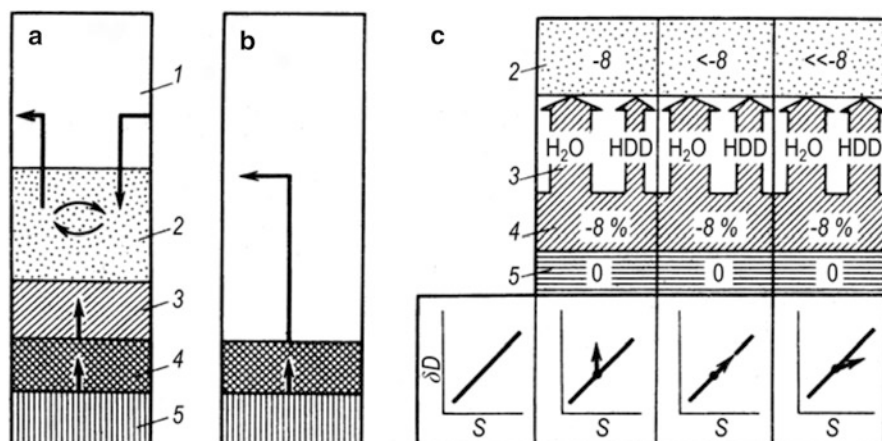


Fig. 5.6 Sverdrup (a), equilibrium (b), and deviating from equilibrium (c) models of water evaporation: 1 atmosphere; 2 mixed layer; 3 diffusion layer; 4 equilibrium layer; 5 liquid water

isotopic composition of liquids may be explained by Sverdrup's evaporation theory which, unlike the equilibrium evaporation theory, assumed the presence of diffuse and mixed layers (Fig. 5.6a, b). A somewhat modified scheme of Lloyd is pictured in Fig. 5.6c, illustrating the influence of the isotopic composition of vapor of mixed layer on the formation of isotopic composition of evaporating water. If the content of HDO in the mixed layer is greater than, or equal to, their equilibrium concentration with respect to the evaporating liquid (which, at 20°C, corresponds to a depletion in the D vapor by approximately 80‰ in comparison with the liquid), then the outflow of HDO vapor through the diffuse layer occurs less intensively than the outflow of H₂O vapor. In this case, the Rayleigh's process would predict.

The change in concentration of heavy isotopes in vapor of mixing layers (the degree of deviation of this concentration from the equilibrated value) provides for deviations in the accumulation of D in evaporating water on both sides of the line described by Rayleigh's equation (see Fig. 5.6c).

In natural conditions, the D concentration in mixed layer (in atmospheric moisture), as a rule, is appreciably lower than that in equilibrium, which results in a negative deviation from the Rayleigh's law. The influence of the isotopic composition of atmospheric moisture vapor upon the isotopic composition of evaporated water is clearly illustrated by Lloyd's scheme but according to this scheme it is practically impossible to explain inversions in the changes of isotopic composition being conditioned by the increase of saline concentration in the solution. Undoubtedly the rate of evaporation and the isotopic composition of atmospheric moisture are important factors in the formation of isotopic composition of evaporating liquids (Craig et al. 1963; Gonfiantini 1965; Sofer and Gat 1975; Polyakov and Seletsky 1972; Gutsalo 1980).

The isotopic composition of the atmospheric moisture can be considered in laboratory experiments to be independent of the isotopic composition of the evaporating

liquid. This is also true within certain assumptions for natural evaporating basins (e.g., where the lagoon is isolated from the sea). In this case, the evaporating rate of the liquid will be proportional to the difference between the equilibrium pressure of vapor above the liquid and the vapor pressure of the atmosphere:

$$G = k(p_1 - p_a), \quad (5.17)$$

where G is the rate of liquid evaporation; p_1 is the equilibrium pressure of vapor above the liquid; p_a is the vapor pressure of the atmosphere; k is the coefficient of proportionality.

According to Raule's law, $p_1 = p_1^0 a$, (where p_1^0 is the activity of water in the solution). If we assume $p_a = p_1^0 h$ (where h is relative humidity), then

$$G = k p_1^0 (a - h) k (p_1 / p_1^0) - h. \quad (5.18)$$

The activity of water in the solution remains constant during the evaporation of pure water or saturated solutions ($a = 1$ for pure water and $a \approx 0.8$ for saturated solution of NaCl).

If the evaporation led to an accumulation of salts in the reservoir to such an extent that the vapor pressure above the liquid equals to the pressure of vapor of the atmospheric moisture ($a = h$), then the final isotopic composition of the reservoir water by Eq. 5.15 will be equal to $R_L = R_a a$, that is the reservoir will be in equilibrium with atmospheric moisture. If water loss from the reservoir is due only to evaporation and the water body is decreasing, then the isotopic composition of the remaining liquid can be calculated by the equation

$$R_L = \frac{[R_0(a/\alpha k - a + h) - h R_a/k](V/V_0)^{(a/\alpha k - a + h)/(a - h)} + h R_a/k}{a/\alpha k - 1 + h}, \quad (5.19)$$

where a is the activity of water being changed by evaporation; V/V_0 is the remaining body fraction of the solution; V_0 is the initial volume; R_0 is the initial isotopic ratio of the liquid.

In the limiting case of $V/V_0 \rightarrow 0$, the final isotopic composition of water will be equal to:

$$R_L = \frac{h R_a/k}{a/\alpha k - a + h}. \quad (5.20)$$

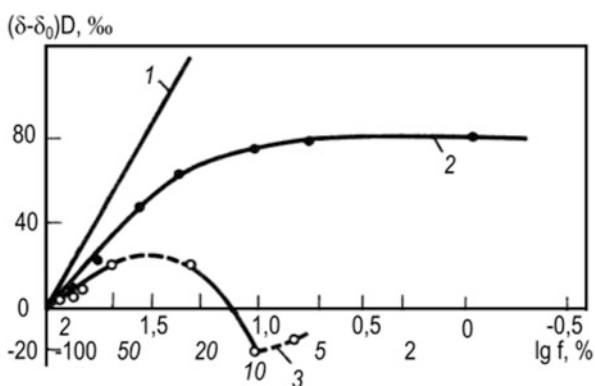
This formula is similar to Eq. 5.15 but the former takes into account the activity of water in the solution, where the value of $a \neq 1$.

It follows from Eq. 5.19 that the limiting isotopic composition obtained by evaporating distilled water ($a = 1$) and saturated salt solution ($a < 1$) are not the same as those discovered by experimentation. If water activity in the solution during experiment (during the sea-water evaporation) is not a constant, then the rate of evaporation by Eq. 5.18 will be equal to zero.

Inserting the value $a = h$ in Eq. 5.20, one obtains

$$R_L = a R_a, \quad (5.21)$$

Fig. 5.7 Air moisture influence on the D accumulation in liquid at the evaporation of water with marine salinity (from Atlantic ocean): 1 Rayleigh distillation case; 2 the experimental data at air relative moisture equal to 40–50%; 3 the data at relative air moisture equal to 70–80%



that is the limiting isotopic composition of liquid with respect to vapors of atmospheric moisture will be at equilibrium. This result is similar to that obtained from Eq. 5.13 since in both cases it is assumed that the water reservoir is in dynamic equilibrium with atmospheric moisture vapor.

It follows from sea-water evaporation experiments (Fig. 5.7) that the isotopic composition of water being evaporated under certain conditions may undergo inversion. This is caused by a decrease in the evaporation rate due to decreasing activity of water in the liquid phase (Polyakov and Seletsky 1972). When $V \rightarrow 0$, the D content tends to a stationary value at which $R_L = aR_a$.

In natural evaporating basins with initially normal sea-water salinity, the consequent sedimentation of minerals and the increase in the salt concentration in the residue of the solution occur due to the evaporation of water. The changes in the composition of salts of sea-water at different stages of concentration are given in Table 5.2 (data obtained by Galakhovskaya 1967).

It is evident from Table 5.2 that at the stage of halite sedimentation, a gradual change in the water salt composition occurs (the sodium chloride water transforms into magnesium chloride water). If evaporation continues, the water activity also changes (from 0.8 at the stage of halite sedimentation to ~ 0.6 at the stage of bischofite sedimentation), resulting in a decrease in the evaporation rate of the brine at the final

Table 5.2 Sea-water composition changes at different stages of concentration

Stage of concentration	Liquid content relative initial volume (%)	Density (g/cm^3)	Ion composition (mass %)						$\sum \text{ions}^a$
			SO_4^{2-}	Cl $^-$	Ca $^{2+}$	Mg $^{2+}$	K $^+$	Na $^+$	
Calcium carbonate	25	1.10	1.00	7.31	0.12	0.50	0.16	4.05	13.1
Gypsum	15	1.16	1.28	11.36	0.07	0.75	0.25	6.36	19.90
Halite	13	1.21	1.67	15.44	0.03	1.10	0.36	8.52	27.31
Epsomite	1.0	1.30	6.33	14.37	0.11	4.80	1.86	2.16	29.83
Silvine	1.6	1.30	5.53	18.21	0.01	6.39	2.22	1.25	34.44
Bischofite	0.7	1.35	3.03	23.58	–	8.81	0.02	0.28	36.25
Carnollite	0.9	1.32	4.35	19.59	0.03	6.95	1.82	0.77	33.88

^aTogether with the other ions not shown in the table

stage of evaporation. Under conditions of high humidity, this process might cause a certain decrease in D concentration in the solution. The magnitude of this decrease depends on the relative humidity, isotopic composition of atmospheric moisture, and also on the evaporation rate of the solution. If relative air humidity during evaporation is 70–80%, then obviously sea water cannot be evaporated to the stage of bischofite sedimentation and the stationary isotopic composition of the solution $R_L = aR_a$ will be attained at earlier stages of evaporation.

In coastal regions (if the saline basin is marine lagoon), the isotopic composition of vapor R_a will be close to that in equilibrium with sea water, that is equal to R_s/a (where R_s is the isotopic composition of sea water).

During the condensation of vapor, the liquid phase is enriched with heavy isotopes of hydrogen by a factor α , that is the isotopic composition of the coastal evaporating basin, in any case, does not differ considerably from the isotopic composition of sea-water and will be in isotopic equilibrium with the marine water vapor ($\delta D \approx -94\text{‰}$, $\delta^{18}\text{O} \approx -13\text{‰}$, see Chap. 3). For small inland saline basins (saline lakes), the isotopic composition can differ considerably from the marine one, being depleted in heavy isotopes for two reasons. Firstly, such basins could be fed by groundwaters with an isotopic composition lower than that of seawater. Secondly, the isotopic composition of the vapor of atmospheric moisture is much lower than that in equilibrium with ocean water. Besides, precipitation greatly influences the isotopic composition of some of these basins because of their small storage in comparison with large evaporating basins of marine origin. Precipitation is decreasing in response to a decrease in the vapor condensation temperature.

These conclusions were confirmed by model calculations reported by Vlasova and Btegunov (1978) for brines with certain isotopic composition formed from standard seawater at different stages of evaporation. Two models have been considered by these authors such as the one assumes a constant storage (with replenishment) and the exhaustion model (the model of a drying basin). Calculations have been carried out using formulae similar to Eqs. 5.13 and 5.19 taking into account the changes in the water activity in the solution during evaporation. Substituting the isotopic ratios in the replenishing water R_I , in the basin R_L , in the vapor outflow from the basin R_E ($R_E = R_I$) and in the vapor of the atmospheric moisture R_a with the corresponding $1 + \delta_i$ values, an expression is obtained which permits the calculation of the liquid's isotopic composition in relative units for given values of air humidity h , activity of water in the solution a , isotopic composition of the inflowing water δ_I and the isotopic composition of atmospheric moisture vapor δ_a :

$$\delta_L = \frac{\alpha[k(1 + \delta_I)(a - h) + (1 + \delta_a)h]}{a} - 1. \quad (5.22)$$

The α -values for a given temperature were taken from reference books and the values of k were taken to be $k_D = 1.009$ and $k_{18\text{O}} = 1.016$.

In the case of a drying basin, calculations have been made using the formula

$$\delta_L - \delta_L^0 = \frac{h[\delta_a - k\delta_L^0 - (k - 1)] - \Delta\varepsilon_a(1000 + \delta_L^0)}{hk + \Delta\varepsilon_a} [1 - f^{hk + \Delta\varepsilon_a/k(a-h)}], \quad (5.23)$$

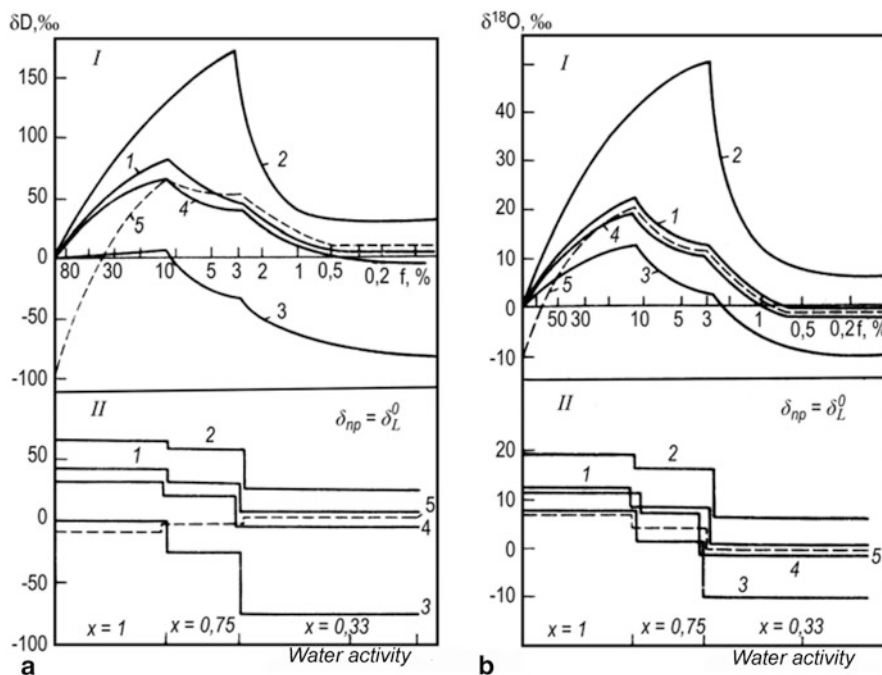


Fig. 5.8 Isotopic composition of **a** hydrogen and **b** oxygen of evaporated sea water for changed evaporation conditions (calculated curves): *I* exhaustion model; *II* constant level model

where δ_L^0 , δ_L , δ_a are the relative isotopic contents of water at the beginning of evaporation ($f = 1$), at an arbitrary moment after evaporation has begun, the vapor of atmospheric moisture, respectively; f is the degree of water loss, equal to the ratio of volume of the remaining water to the initial volume; $\Delta\varepsilon = 1/\alpha - k$; α is the equilibrium fractionation factor of isotopes at a given temperature; k is the kinetic fractionation factor.

Three constant values of water activity were taken in order to carry out the calculations: $a = 1$, corresponding to evaporation without precipitation of salts when the water body decreases from 100 to 12%; $a = 0.75$, corresponding to precipitation of halite when the water body decreases from 12 to 3%; $a = 0.33$, corresponding to precipitation of magnesium salts when the water body decreases from 3 to 0.1%.

Equations (5.22) and (5.23) were solved for the following parameter values: humidity $h = 25\%$, 50% , 75% ; temperature of evaporating water $t + 10^\circ\text{C}$, $+20^\circ\text{C}$, $+30^\circ\text{C}$; isotopic composition of the atmospheric vapor δ_a for $\delta D -70\text{‰}$, -150‰ , -200‰ and for $\delta^{18}O -10\text{‰}$, -20‰ , -40‰ ; isotopic composition of inflowing water for the model with a constant storage δ_I for $\delta D 0\text{‰}$, -50‰ , -100‰ and for $\delta^{18}O 0\text{‰}$, -5‰ , -10‰ .

The results of the calculations are given in Fig. 5.8 (Vlasova and Brezgunov 1978).

The following parameters were accepted to plot the graphs:

(a)					(b)				
	$h, \%$	$\delta_a, \text{‰}$	$t, \text{°C}$	$\delta_L^0, \text{‰}$		$h, \%$	$\delta_a, \text{‰}$	$t, \text{°C}$	$\delta_L^0, \text{‰}$
1	50	-10	20	0	1	50	-10	20	0
2	25	-10	20	0	2	25	-10	20	0
3	30	-150	20	0	3	50	-20	20	0
4	50	-10	30	0	4	50	-10	30	0
5	50	-10	20	-100	5	50	-10	20	-10

The results show that under natural conditions, the isotopic composition of evaporating basins may vary greatly depending on the conditions of evaporation. The climatic conditions of the formation of large saline basins from the sea restrict the range of δD and $\delta^{18}O$ variations. According to Vlasova and Brezgunov (1978), under less favorable conditions, the minimum D and ^{18}O content in brines of sea origin at the evaporation stage will not be less than $\delta D = -40\text{‰}$ and $\delta^{18}O = -3\text{‰}$.

These conclusions enable one to use isotopic data for estimating the genesis of connate brines. Theoretical and experimental data for modern saline basins have been reported to be in agreement with the author's conclusions. They are also in accordance with calculations made by Sofer and Gat (1975) and Gutsalo (1980).