3 STABLE ISOTOPE PROCESSES IN THE WATER CYCLE

In this section we will discuss the isotopic composition of the various elements in the global water cycle in a kind of natural order. Water is evaporating from the sea. The marine vapour for a large part precipitates over the oceans, as it is transported to higher latitudes and altitudes, where the vapour cools down and condenses. Part of the vapour is brought to the continents where it precipitates and forms different modes of surface- and groundwater. The "last" marine vapour is precipitated as ice over the Arctic and the Antarctic.

Compared to the waters of the ocean, the *meteoric waters* (i.e. the atmospheric moisture, the precipitation and ground- and surface water derived from them) are mostly depleted in the heavy isotopic species: ^{18}O, ^{17}O and ^2H. The main reason for depleted values of meteoric water is the Rayleigh rainout effect, operating on a limited water (vapour) reservoir in the atmosphere. The average ocean composition is accepted as the reference standard for these isotopes (Sect.2.1) so that $\delta_{SMOW} = 0‰$ by definition (Craig, 1961b).

All $^2\delta$ and $^{18}\delta$ values of water are given relative to the VSMOW standard.

The δ values of the meteoric waters are thus negative numbers. An extreme value is the composition of Antarctic ice with $^{18}\delta = -50‰$ (Epstein et al., 1965). The weighted mean $^{18}\delta$ of all water in the hydrosphere can be estimated to be about −0.64‰, assuming $^{18}\delta \sim -30‰$ as the average of ice accumulation (Craig and Gordon, 1965) and $^{18}\delta = -7‰$ as the average value of groundwater. Melting of the ice-caps would change the ocean water isotopic composition to an average of $^{18}\delta = -0.6‰$. On the other hand, at the maximum extent of glaciation at the peak of the last ice age the mean ocean water composition was estimated to have been $^{18}\delta = +1‰$, thus making the total "glacial increment" about 1.6‰. This number is of great interest for the palaeo-temperature effect in deep-sea carbonate cores.

Our picture about the global distribution of isotopes in meteoric waters is derived from the data of GNIP (the Global Network of Isotopes in Precipitation) established by the IAEA in co-operation with WMO in 1961 (see Box). In this program, monthly pooled samples of precipitation are collected world-wide and then analysed for their ^{18}O, ^2H and ^3H content. The annually averaged $^{18}\delta$ values are shown in Fig.3.1 (Dansgaard, 1964; Rozanski et al., 1993). The degree of depletion is related phenomenologically to geographic parameters such as latitude, altitude and distance from the coast and to the fraction precipitated from a vapour mass content, each of which is discussed in more detail in Chapter 4.

> The Global Network of Isotopes in Precipitation, GNIP
>
> In the early 1960ies a precipitation sampling network was established by the International Atomic Energy Agency (IAEA) in Vienna and the World Meteorological Organisation in Geneva with the view of documenting the isotopic parameters, $^2H/^1H$, $^{18}O/^{16}O$ and ^3H, together with some meteorological parameters of the input into the hydrological systems. The network consisted of about 100 sampling sites world-wide, including marine, coastal and inland stations. Samples are still being collected monthly and analysed, although the network has been slightly reduced and modified over the years. Also some local and regional networks and stations were added over shorter periods of time.
>
> Results have been evaluated by Dansgaard (1964), Yurtsever (1975) and Rozanski et al. (1993). The relevant data have been published regularly in the Technical Report Series of the IAEA, but have lately become available on Internet as *GNIP Data* (look at <www.iaea.org/programs/ri/gnip/gnipmain.htm>. It is advised to download per WMO Region).
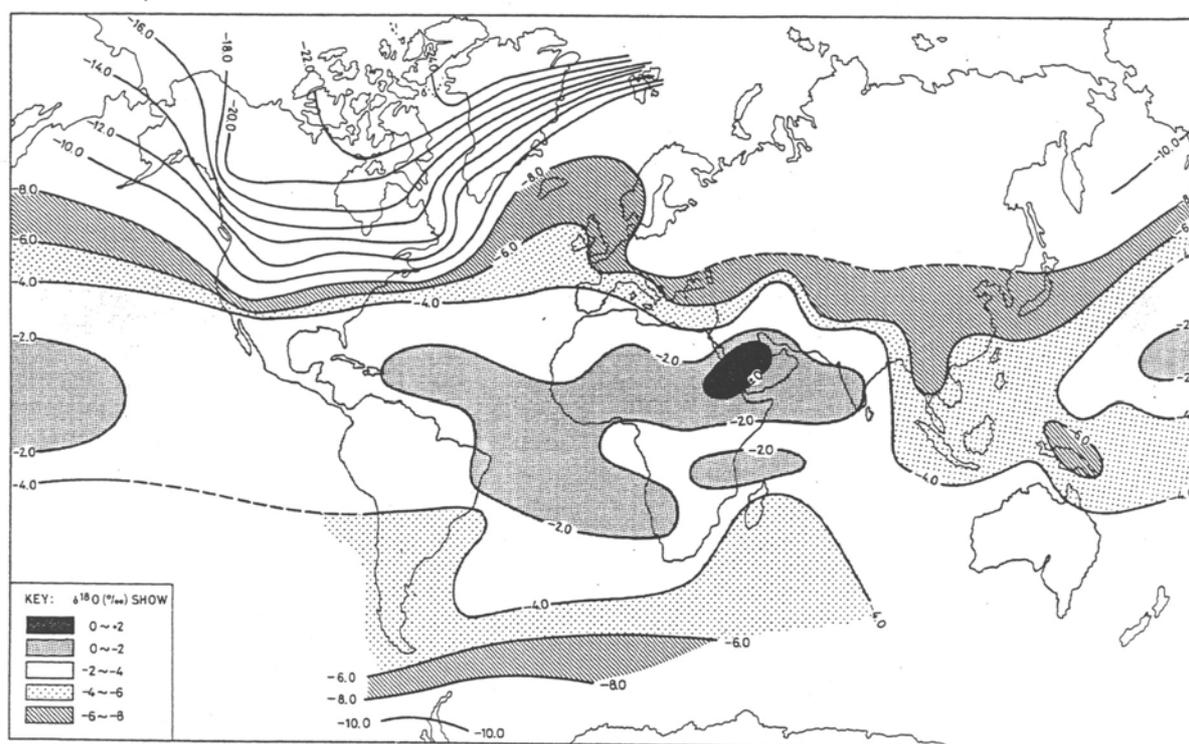

Fig.3.1　　World-wide distribution of the annual mean of $^{18}\delta$ in precipitation, based on the GNIP data set (Yurtsever and Gat, 1981).

While the monthly sampling regime can serve the purposes of specifying the inputs into larger hydrological systems, more detailed sampling may be required for regional water studies. Furthermore, more detailed data on precipitation and atmospheric moisture will be necessary in order to understand the effect of changes in climate and of the surface/atmosphere interaction pattern on the isotopic signal of these lumped monthly data.
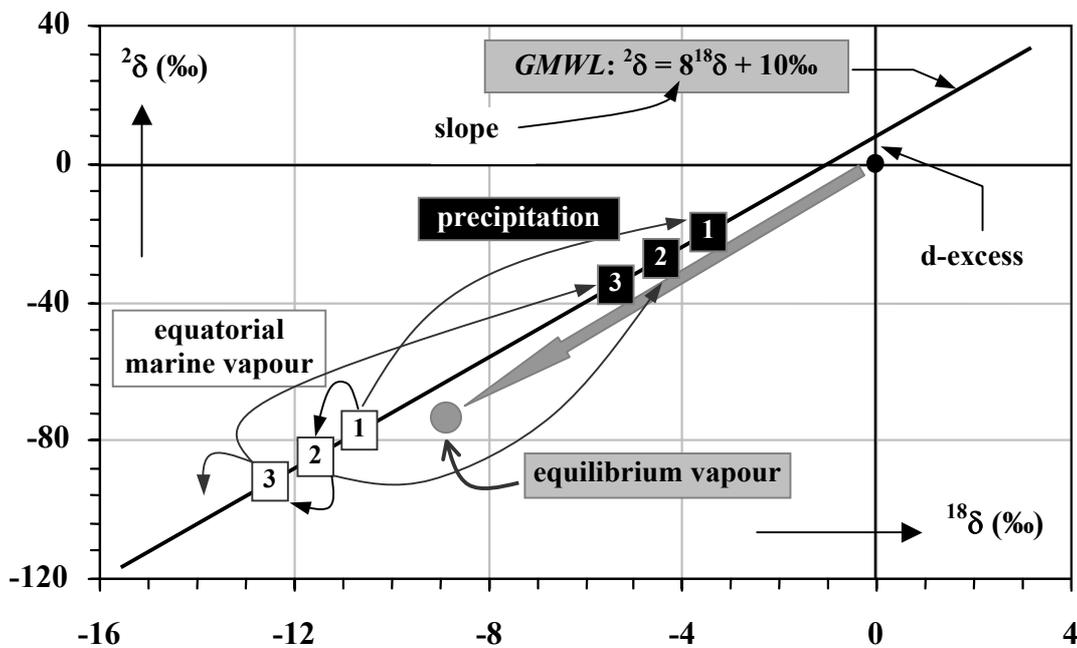

Fig.3.2   Schematic representation of the isotopic consequences of (non-equilibrium) evaporation from the oceans (black slice at (0,0)) forming the marine atmospheric vapour (white squares). Hypothetical equilibrium fractionation (grey arrow) would have resulted in a smaller fractionation (grey slice). The figure furthermore shows the progressive depletion of the vapour mass and thus of the precipitation (stippled squares) by the (here stepwise) condensation process, preferentially removing the ^{18}O and ^{2}H isotopes from the vapour (in the ($^{18}\delta$, $^{2}\delta$) plot the $^{2}\delta$ axis is usually compressed by a factor of 10, due to the larger variations).

The GNIP data pertain to precipitation samples. The atmospheric vapour is always much more depleted in the heavy isotopic species, by close to 10‰ in $^{18}\delta$ on the average. In a continental setting, in the temperate and humid regions, the air moisture and precipitation are found to be close to isotopic equilibrium with each other at the prevailing temperature. This is not strictly true close to the vapour source, i.e. in a maritime or coastal setting (Matsui et al., 1983; Tzur, 1971), nor under dry conditions when the droplets below the cloud base are subject to evaporation, as will be discussed below.

3.1 RELATION BETWEEN ^{18}O/^{16}O AND ^{2}H/^{1}H IN NATURAL WATERS

The changes of ^{18}O and ^{2}H concentrations in meteoric waters were shown to be fairly well correlated (Friedman, 1953; Craig, 1961a; Dansgaard, 1964; Yurtsever, 1975) so that in the ($^{2}\delta$,$^{18}\delta$) graph the isotopic compositions of precipitation are aligned along what is referred to as a *Meteoric Water Line* (MWL) for which a global average is $^{2}\delta = 8 \cdot ^{18}\delta + 10‰$ (then called the *GMWL*).

The variations in $^{18}\delta$ and $^{2}\delta$ can be better understood if we consider the two main processes in the global water cycle:

1) evaporation of surface ocean water, and

2) the progressive raining out of the vapour masses as they move towards regions with lower temperatures, i.e. higher latitudes and altitudes.

These processes and the resulting isotope effects are (irrealistically) visualised stepwise in Fig.3.2. The evaporation of seawater is in part a non-equilibrium process. This results from the fact that the air above the sea surface is under-saturated with respect to water vapour, and that the rate-determining step is one of diffusion from the surface to the marine air. If it were saturated, the isotopic composition ($^{18}\delta$, $^{2}\delta$) would move along the grey arrow, as determined by the equilibrium fractionations for ^{18}O and ^{2}H (Table 3.1).

Table 3.1   Hydrogen and oxygen isotope fractionation in the equilibrium system liquid water (l) and water vapour (v); $\varepsilon_{v/l}$ represents the fractionation of v relative to l (details in Volume I).

t (°C)	$^{2}\varepsilon_{v/l}$ (‰)	$^{18}\varepsilon_{v/l}$ (‰)	$^{2}\varepsilon_{v/l} / ^{18}\varepsilon_{v/l}$
0	−101.0	−11.55	8.7
5	− 94.8	−11.07	8.5^5
10	− 89.0	−10.60	8.4
15	− 83.5	−10.15	8.2^5
20	− 78.4	− 9.71	8.1
25	− 73.5	− 9.29	7.9
30	− 68.9	− 8.89	7.7^5
35	− 64.6	− 8.49	7.6
40	− 60.6	− 8.11	7.4

Once the (non-isotopic-equilibrium) vapour has been formed (open square numbered 1), the rainout process proceeds in isotopic equilibrium, as the vapour is then saturated. Removing the "first" rain (black square nr.1) causes the remaining vapour (nr.2) to be depleted in both

isotopes. This process continues: vapour and condensate (= rain) become progressively depleted, the isotopic compositions "move" along a meteoric water line (black line in Fig.3.2), of which the slope is given by the ratio of $^2\varepsilon_{v/l}$ / $^{18}\varepsilon_{v/l}$ (see also Sect.3.6.1).

In (surface) water subject to evaporation the conditions concerning the ($^{18}\delta$, $^2\delta$) relation are such that the slopes of the evaporation lines are generally different from 8. A schematic view is given in Fig.3.3 and will be discussed in the next section.
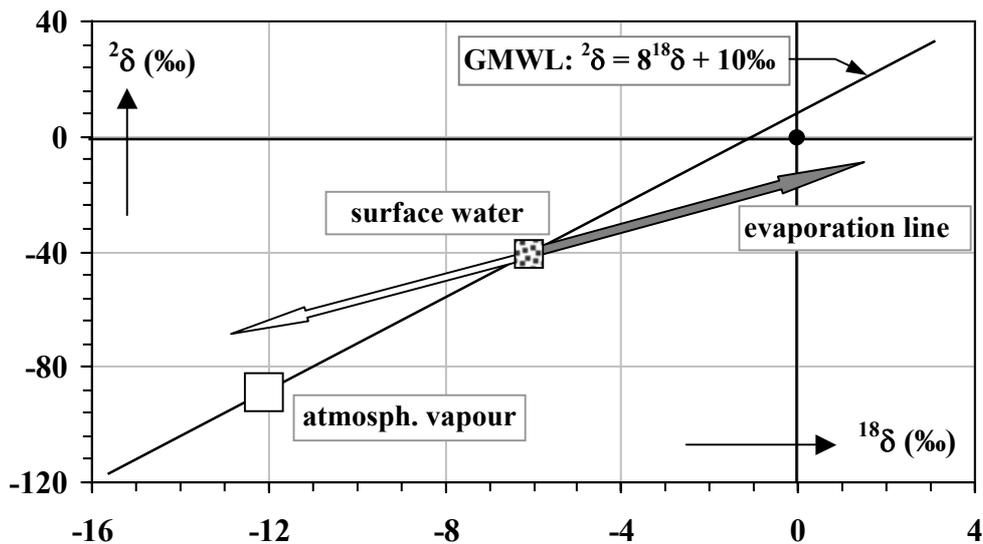

Fig.3.3   Relation between the ($^{18}\delta$, $^2\delta$) values of meteoric water which undergoes evaporation, the vapour leaving the water and the residual water following evaporation, described by the *evaporation line*, compared with the relationship between atmospheric water and precipitation described by the meteoric water line (cf. Fig.3.2). The relatively "light" (depleted) water vapour leaves the water reservoir (open arrow) causing the residual water to become enriched (grey arrow).

3.2   EVAPORATION

3.2.1   THE CASE OF COMPLETE MIXING OF THE LIQUID RESERVOIR

The source of water in the atmosphere is the evaporation of water on the surface of the Earth, foremost from the oceans and open water bodies. To a lesser extent, evaporation from the plants (referred to as transpiration) and from the soil adds to the evaporation flux into the atmosphere. The isotope fractionation which accompanies the evaporation process is one important factor in the variability of isotopic composition within the water cycle.

Evaporation into the (under-saturated) air above the water is rate-limited by the transport of vapour from the air layer near the surface into the ambient atmosphere (Brutsaert, 1965). Compared to this, the establishment of liquid-vapour equilibrium at the water-air interface is rapid; isotopic equilibrium between the surface waters (L) and the saturated vapour (V) can

thus be assumed at the interface, i.e. $\delta_V = \delta_L + \varepsilon_{V/L}$ where the equilibrium isotopic fractionation term depends only on the temperature and salinity of the water (Sect.2.2.1).

The mechanism and rate of transport from the saturated "layer" at the interface into the ambient atmosphere depends on the structure of the air boundary layer and the airflow pattern. For the simple case of a stagnant air layer (as applies for evaporation from within the soil as well as for the case of water loss from plants through the stomata openings), where the transport is by molecular diffusion, a fixed (linear) concentration profile is established. The flux of water and its isotopic species is then determined by their respective diffusion coefficients through air, D_m, as given in Sect.2.2.3.

On the other hand, for an open interface under strong wind conditions most of the transport is by turbulent diffusion and molecular diffusion through a non-steady variable air layer plays a role only close to the surface. The transient-eddy model of Brutsaert (1965) is then be applied, where the diffusion flux is proportioned to $D_m^{-1/2}$. At more moderate wind speed a transition from the proportionality of $D_m^{-1/2}$ to $D_m^{-2/3}$ is to be expected (Merlivat and Contiac, 1975).

Craig and Gordon (1965) suggested a model for the isotope fractionation during evaporation as shown in Fig.3.4 (see also Volume III). The model is based on the Langmuir linear-resistance model (Sverdrup, 1951), and in addition to the assumption of an equilibrium condition at the air/water interface, it is assumed that there is no divergence or convergence in the vertical air column and no isotopic fractionation during a fully turbulent transport. In the model the vapour flux is described in terms equivalent to an Ohmian law so that the vapour flux equals the quotient of the concentration difference (expressed as the humidity difference) and the transport resistance.

The appropriate flux equations for the water substance (E) and isotopic molecules (E_i, either for $^1H^2H^{16}O$ or $^1H_2^{18}O$) are then:

$$E = (1 - h_N)/\rho \quad \text{with } \rho = \rho_M + \rho_T \tag{3.1}$$

and

$$E_i = (\alpha_{V/L} R_L - h_N R_A)/\rho_i \qquad \text{with } \rho_i = \rho_{Mi} + \rho_{Ti} \tag{3.2}$$

The ρ terms are the appropriate resistances as shown in Fig.3.4. Subscripts M and T signify the *diffusive* and *turbulent* sub-layers, respectively. Subscript A refers to a free atmosphere far above the evaporating surface and subscript L to the liquid (surface). $R = N_i/N$ is the isotope ratio (N_i and N being number of the isotopic species, N_i representing the less abundant isotope; for the light elements hydrogen, nitrogen, carbon and oxygen: $N \gg N_i$); h_N is the relative humidity, normalised with respect to the saturated vapour pressure for the temperature and salinity conditions at the surface.

The isotopic composition of the evaporation flux is now:

$$R_E = E_i / E = \frac{(\alpha_{V/L} R_L - h_N R_A)}{(1 - h_N) \rho_i / \rho}$$ **(3.3)**
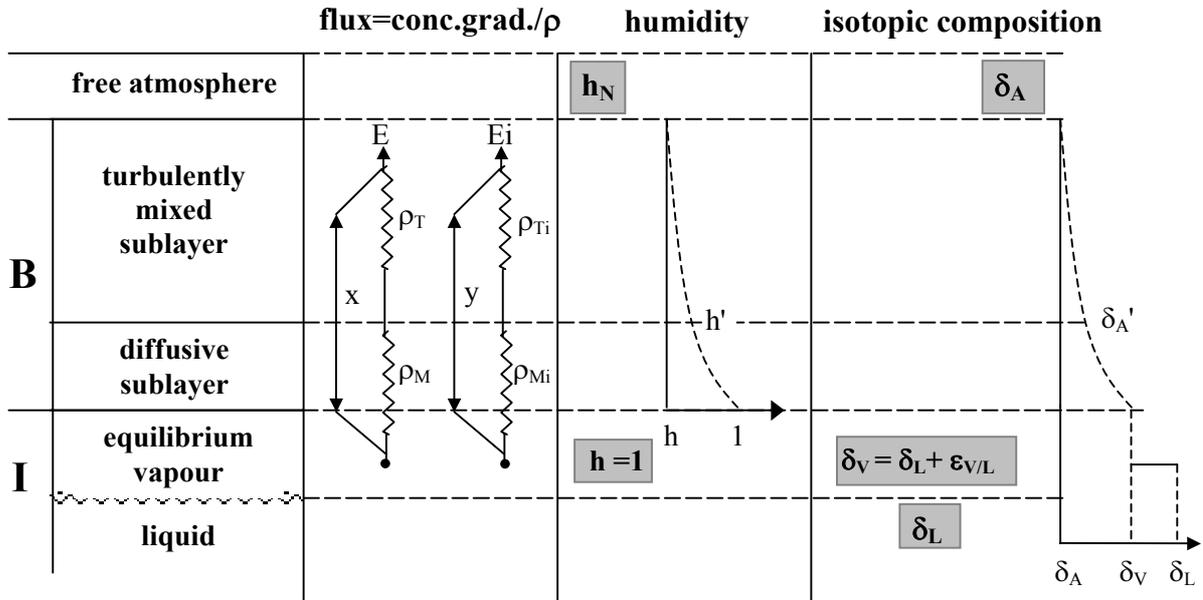

Fig.3.4 The Craig-Gordon isotopic evaporation model. I and B signify the surface inter-phase zone and the atmospheric boundary layer, respectively; $x = 1 - h_N$, and $y = \alpha_{V/L} R_L - h_N R_A$, where h_N is the relative humidity normalised to the saturated vapour pressure at the temperature and salinity conditions of the water surface; δ_A' is the isotopic composition of the air moisture at the boundary of the diffusive sublayer and h_N' is the corresponding relative humidity.

Written in δ values (by substituting each R by the respective $(1 + \delta)$):

$$\delta_E = \frac{\alpha_{V/L} \delta_L - h_N \delta_A + \varepsilon_{V/L} + \varepsilon_{diff}}{(1 - h_N) - \varepsilon_{diff}}$$ **(3.4)**

and approximately

$$\delta_E \approx \frac{\delta_L - h_N \delta_A + \varepsilon_{V/L} + \varepsilon_{diff}}{1 - h_N}$$ **(3.5)**

where

$$\varepsilon_{diff} \equiv (1 - h_N)\left(1 - \frac{\rho_i}{\rho}\right)$$ **(3.6)**

(cf. $\varepsilon_{\text{diff}} \equiv -\Delta\varepsilon$ as used by Craig and Gordon, 1965).

The total fractionation consists of two steps, as shown in Fig.3.4:

$$\varepsilon_{\text{tot}} = \varepsilon_{\text{V/L}} + \varepsilon_{\text{diff}} \tag{3.7}$$

Each ε is < 0: the overall process results in an isotopic depletion, for ^{18}O as well as for ^{2}H.
(on the contrary, Craig and Gordon defined ε values such that they are always positive).

In the linear resistance model $\rho_i = \rho_{\text{Mi}} + \rho_{\text{Ti}}$ and $\rho = \rho_M + \rho_T$. Thus:

$$\frac{\rho_i}{\rho} = \frac{\rho_{\text{Mi}} + \rho_{\text{Ti}}}{\rho_M + \rho_T} = \frac{\rho_M}{\rho} \cdot \frac{\rho_{\text{Mi}}}{\rho_M} + \frac{\rho_T}{\rho} \cdot \frac{\rho_{\text{Ti}}}{\rho_T}$$

The term $(1 - \rho_i/\rho)$ can thus be written as:

$$1 - \frac{\rho_i}{\rho} = \frac{\rho_M}{\rho}\left(1 - \frac{\rho_{\text{Mi}}}{\rho_M}\right) + \frac{\rho_T}{\rho}\left(1 - \frac{\rho_{\text{Ti}}}{\rho_T}\right)$$

The second term on the right-hand side can be eliminated on the assumption that $\rho_{\text{Ti}} = \rho_T$, so that substitution into the expression for $\varepsilon_{\text{diff}}$ results in:

$$\varepsilon_{\text{diff}} = \left(1 - h_N\right)\left[\frac{\rho_M}{\rho}\left(1 - \frac{\rho_{\text{Mi}}}{\rho_M}\right)\right]$$

As discussed before $\rho_M \propto D_m^{-1}$ for a stagnant air layer, where D_m is the molecular diffusivity of water in air. For a rough interface under strong (turbulent) wind conditions, $\rho_M \propto D_m^{-1/2}$ and at more moderate wind speed a transition from the proportionality of $D^{-1/3}$ to $D^{-2/2}$ can be expected. Accordingly $\left(1 - \dfrac{\rho_{\text{Mi}}}{\rho_M}\right)$ can be written as $\left(1 - \dfrac{D_m^n}{D_{\text{mi}}^n}\right)$, where $1/2 < n \leq 1$. Since $\left(1 - \dfrac{D_m}{D_{\text{mi}}}\right) = \Delta_{\text{diff}}$ is a very small number:

$$\left(1 - \frac{D_m^n}{D_{\text{mi}}^n}\right) \approx n\left(1 - \frac{D_m}{D_{\text{mi}}}\right) = n\,\Delta_{\text{diff}}$$

(cf. Craig and Gordon (1965): $C_m = D_{\text{mi}}/D_m - 1$, so that: $\Delta_{\text{diff}} \equiv 1/(1+1/C_m)$; $C_m > 0$, whereas here $\Delta_{\text{diff}} < 0$, consistent with $\varepsilon_{\text{diff}} < 0$).

Furthermore, by defining $\dfrac{\rho_M}{\rho} \equiv \Theta$ the diffusional fractionation $\varepsilon_{\text{diff}}$ is expressed as:

$$\varepsilon_{\text{diff}} = n\,\Theta(1 - h_N)\,\Delta_{\text{diff}} \tag{3.8}$$

(Because the diffusion coefficient of the light/abundant molecule is the largest, $\varepsilon_{\text{diff}} < 0$, as mentioned above).

The weighting term, which according to Fig.3.4 is given by $\Theta = (1 - h_N')/(1 - h_N)$, can be assumed equal to 1 for a small water body whose evaporation flux does not perturb the ambient moisture significantly (Gat, 1995). However, Θ has been shown to have a value of 0.88 for the North American Great Lakes (Gat et al., 1994) and a value of close to 0.5 for evaporation in the eastern Mediterranean Sea (Gat et al., 1996). This value of $\Theta = 0.5$ appears to be the limiting value for large water bodies.

For an open water body under natural conditions, a value of $n = 1/2$ seems appropriate. In contrast, in the case of evaporation of water through a stagnant air layer, such as from the soils (Barnes and Allison, 1988) or leaves (Allison et al. 1985), a value of $n \sim 1$ fits the data well. The ratio of the molecular diffusivities in air, of the pairs $H_2^{18}O/H_2^{16}O$ and $^1H^2HO/^1H_2O$, has been determined by Merlivat (1978) as $(D_i/D)_m = 0.9723$ and 0.9755, respectively (Sect.2.2.3), so that for ^{18}O: $^{18}\Delta_{diff} = -28.5‰$ and for ^2H: $^2\Delta_{diff} = -25.1‰$.

Fig.3.3 shows in a schematic manner the $(^{18}\delta, ^2\delta)$ relationships in this process. δ_E and δ_L define a line called the *evaporation line* (EL) of which the slope is given by:

$$S_E = \frac{h_N(^2\delta_A - {}^2\delta_L) - {}^2\varepsilon_{tot}}{h_N(^{18}\delta_A - {}^{18}\delta_L) - {}^{18}\varepsilon_{tot}} \tag{3.9}$$

As shown in Fig.3.3, the initial water composition, the evaporated moisture and the isotopic composition of the remnant liquid (such as lake waters, surface ocean water, or soil waters) all lie on this line, as is obvious from material balance considerations.

The humidity, the isotopic composition of the air vapour, and the fractionations $\varepsilon_{L/V}$ and ε_{diff} - which in turn depend on temperature and mechanism, respectively- determine the slope, as shown in Fig.3.5.. A special case is presented when δ_L and δ_A are in isotopic equilibrium with each other for both the hydrogen and oxygen isotope, in which case, S_E is independent of h_N:

$$S_E^* = \left(^2\varepsilon_{V/L} + n\Theta\,^2\Delta_{diff}\right)/\left(^{18}\varepsilon_{V/L} + n\Theta\,^{18}\Delta_{diff}\right) \tag{3.10}$$

This slope is $S_E^* = 3.82$ when $\Theta = 1$, $n = 0.5$ and $\varepsilon_{V/L}$ is given in Table 3.1. It is lower for the case of the stagnant boundary layer; when $n = 1$ the equilibrium slope can be calculated to be $S_E^* = 2.72$. If $\Theta < 1$ the slope of the relevant evaporation line will be increased, as is the case where

$$\delta_L - \delta_A > \varepsilon_{L/V}$$

The Craig-Gordon model does not account for the case where evaporation of droplets and spray contribute to the evaporation flux.

δ_E is the (isotopic) source term for the atmospheric moisture. It is only under very unusual conditions, namely if $\delta_A = \delta_L + \varepsilon_{V/L} + \varepsilon_{diff}$, that $\delta_E = \delta_A$. More commonly, as shown in

Fig.3.3, the evaporate differs from the isotopic composition of the ambient air so that its admixture changes the isotopic composition of the atmospheric moisture, usually increasing the d-excess value. At the same time the isotopic composition of the evaporating waters also changes, increasing the content of the heavy isotopes in the residual liquid. The degree of such an enrichment depends on the relative magnitude of the evaporation flux to the amount of water in the evaporating water pool and whether the system is open or closed (see further Volume III on Surface Waters).
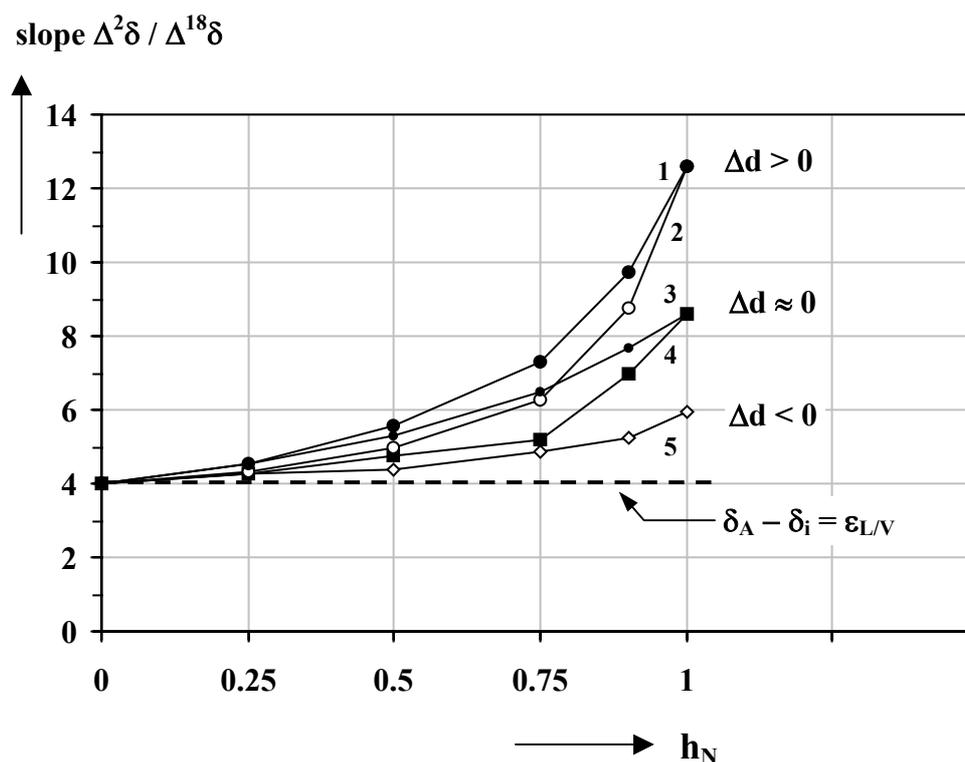

Fig.3.5   Slopes of the evaporation lines for an open water body as a function of the ambient humidity, for a number of assumptions concerning the ambient moisture. Calculations are based on an initial isotopic composition of the water body of $^{18}\delta_o = -5‰$ and $^2\delta_o = -30‰$; the d-excess = 10‰ and the temperature 20°C. The dashed line represents the condition of isotopic equilibrium between water and the ambient vapour, which at this temperature gives a difference of $\Delta d = -0.8‰$ between the δ values of the water and vapour (see Table 3.1). Line 1: moisture is derived from the evaporate with $\Delta\delta = +18‰$; line 2: data for a mixture of ambient and evaporated moisture with $\Delta\delta = +10‰$; line 3: $\delta_A = \delta_0$ and $\Delta\delta = 0‰$; line 4: $\delta_A = \delta_0 + \varepsilon_{V/L}$ and $\Delta\delta = -2.8‰$; line 5: the case where the air moisture is in equilibrium with ocean water at 20°C and $\Delta d = -10.8‰$.

3.2.2   THE CASE OF INCOMPLETE MIXING OF THE LIQUID RESERVOIR

The formulations given above can be applied to a well-mixed (homogeneous) water body, where at all times $\delta_{L,surface} = \delta_{L,bulk}$. This is not necessarily true for either an open-water body

under no-wind conditions, or for waters evaporating from within a porous medium, e.g. soil. Incomplete mixing then results in the surface water being enriched in the heavy isotopic species relative to the bulk of the liquid, and the establishment of a concentration gradient in the liquid boundary layer which opposes the fractionation in the air above.

In the Craig-Gordon model this needs to be taken into account by introducing an additional resistance ρ_L. Its maximum magnitude was found to be $\rho_L/\rho = 0.2$ (Siegenthaler, 1975).

On the assumption of a constant depth surface boundary layer, the flux through this layer is formulated as:

$$E_i = ER_L - \frac{R_S - R_L}{\rho_L}$$

Substituting this into Eq.3.3 (noting that R_L has to be substituted by R_S, the isotopic composition of the surface layer of the water):

$$E_i = \left[\alpha_{V/L}R_L\left(1 + E\rho_L\right) - h_N R_A\right] / \left(\rho_{Ai} + \alpha_{V/L}\rho_L\right)$$

so that

$$\frac{d \ln R_L}{d \ln N} = \frac{h_N\left(R_L - R_A\right)/R_L - \varepsilon_{V/L} - \varepsilon_{diff}}{\left(1 - h_N\right) - \varepsilon_{diff} + \alpha_{V/L}E\rho_L} \qquad \textbf{(3.11)}$$

compared to

$$\frac{d \ln R_L}{d \ln N} = \frac{h_N\left(R_L - R_A\right)/R_L - \varepsilon_{V/L} - \varepsilon_{diff}}{\left(1 - h_N\right) - \varepsilon_{diff}} \qquad \textbf{(3.12)}$$

if there is no liquid resistance.

Obviously when $\rho_L \neq 0$ the isotopic change is slowed down.

3.3   CLOUDS AND PRECIPITATION

3.3.1   IN-CLOUD PROCESSES

The formation of precipitation comes about as a result of the lifting of an air mass (dynamically or orographically). Due to adiabatic expansion, the air mass then cools until the dew point is reached. Provided appropriate condensation nuclei are present, cloud droplets are formed. These are believed to be in local isotopic composition with the moisture in the warm part of the cloud due to a rapid exchange which takes place between the droplets and the air moisture. In the cold part of the cloud, however, an additional isotope fractionation occurs due to the diffusion of the isotopic vapour molecules to the solid ice particles (Jouzel and Merlivat, 1984). This may then be conserved in the frozen cloud elements which are not subject to the isotopic exchange. As droplets coalesce and start to fall to the ground against

the rising air, further isotopic exchange takes place, which amplifies the fractionation between the liquid and gas phase. A number of authors have thus modelled clouds as a multistage vertical distillation column (Kirschenbaum, 1951; Tzur, 1971). Ehhalt (1967) found the vertical in-cloud gradient of isotopic composition to be described rather well by an ideal Rayleigh law (Chapter 2). At high levels of the clouds the depletion in the heavy isotopes becomes extreme, and values of $^2\delta \sim -450‰$ were measured on the top of the troposphere (Ehhalt, 1974). Only snow or hail keep a record of the isotopic composition of upper air, and hail is being used as a probe of a cloud's internal structure (Facy et al., 1963; Bailey et al., 1969; Macklin et al., 1970; Jouzel et al., 1975). The measured stable isotope content in the different layers of the hailstone can then be matched to a vertical isotope profile as predicted by a Rayleigh law (Volume I and Sect.3.1.5.1).

As far as the isotopic composition of the air under the cloud itself is concerned, all these models lead to the conclusion that *rain is close to equilibrium with the moisture in surface air*. This was indeed confirmed, on land, by the simultaneous collection of surface air moisture and precipitation (Craig and Horibe, 1967; Jacob and Sonntag, 1991; Rozanski et al., 1982; Matsui et al., 1983).

3.3.2 INTERACTION BETWEEN RAIN DROPLETS AND AMBIENT MOISTURE

A closer look at precipitating weather systems shows that the simplified view expressed above needs some qualification. First, it is obvious, that the different sizes of raindrops will represent equilibration with lower or higher levels in the cloud. Moreover, during the fall of the raindrops to the ground beneath the cloud base (where the air is undersaturated) some evaporation occurs, resulting in enrichment in the heavy isotopes. The degree of enrichment is a function of the size of the drop and thus of the rainfall intensity. Another factor to consider is the downdraft of air from higher levels, besides the cloud or within it, which will impart a negative isotopic signal. An extreme case is presented by the huge tropical clouds associated with the Intertropical Convergence Zone (ITCZ) (Salati et al., 1979).

The exchange of water molecules between a liquid drop and the ambient water vapour results in the establishment of isotopic equilibrium in those cases where the air is saturated with respect to the liquid at the prevailing temperature. Evaporation or condensation of water occurs if the air is undersaturated- or oversaturated, respectively. with respect to the saturated vapour pressure, accompanied by isotope fractionation characteristic of these processes. Once equilibrium has been established, a dynamic exchange of water molecules continues, without leading to a visible change.

The kinetic of the exchange process involves a few steps: a very rapid process at the very surface of the liquid, and much slower processes of diffuse mixing into the air and bulk of the liquid, controlled by the convective currents and turbulence in both these media. The situation

of a falling drop through the air, accompanied by currents engendered by this, enhances the efficiency of both of the latter processes.

The overall kinetics of the exchange process, like all exchange processes, follows first-order kinetics and can thus be characterised by a half-life or a relaxation time, i.e. the time to achieve 1/e of the final equilibrium state. For the case of falling droplets the size of the drop is a determining parameter, as it affects both the speed of fall and the size of the water reservoir involved. For raindrops falling at terminal free-falling velocities (at 10^oC) the data given in Table 3.2 can serve as guidelines (Bolin, 1958; Friedman et al. (1962).

When the ambient air is under-saturated, evaporation of the droplets occurs. As a result there is an isotope enrichment of the water in the liquid phase, usually along ($^{18}\delta,^2\delta$) evaporation lines with slopes smaller than 8, causing a shift in the d-excess value. Rain samples will then not necessarily represent the in-cloud composition. Bolin (1958) calculated that only the heaviest showers, in excess of 10mm/hour, represent the relatively unmodified composition of the precipitation at cloud base, when that is up to an elevation of about 1000m above ground.

Table 3.2 Relaxation time and distance for the exchange process between falling water droplets and the ambient air moisture.

Drop radius (cm)	Relaxation distance (m)	Relaxation time (sec)
0.01	5.1	7.1
0.05	370	92.5
0.10	1600	246

The exchange and evaporation of the falling droplets is probably an important factor in the fact that in more arid regions the best fit Local MWLines show a slope smaller than 8. This effect may also explain the observed correlation between drop size and the depletion of their ^{2}H content (Woodcock and Friedman, 1963), and is responsible, in part, for the amount effect as discussed in Sect.4.5.

3.3.3 EVOLUTION OF THE ISOTOPIC COMPOSITION DURING A SHOWER

The evolution of the isotopic composition during a shower takes on many forms, and is intimately coupled with the synoptic pattern. There are still insufficient data to fully characterise shorter term isotopic changes during a storm or in between individual precipitation events. Such variations span a wide range of δ values, at times up to about 10‰ in $^{18}\delta$. Early studies by Epstein (1956), Bleeker et al. (1966), and Matsuo and Friedman (1967) indicated differences between rain produced by warm front uplifting or cold fronts and associated thunder clouds. These studies also showed that the early part of most rain showers is more enriched in the heavy isotopes, due to partial evaporation during the fall of rain

droplets through the air column. Later studies (Leguy et al., 1983; Rindsberger and Magaritz, 1983; Gedzelman et al., 1989; Rindsberger et al., 1990; Pionke and Dewalle, 1992; McDonnel et al., 1990) make it appear that these variations reflect mainly the source of moisture and its rainout history, and only to a smaller extent the local rain intensity. However, a notable exception to this rule is given by very strong tropical rains, associated with the ITCZ and its towering clouds, mentioned above, when precipitation with extremely depleted isotopic values is found at the peak of the downpour (Matsui et al., 1983). Some typical isotope patterns during a shower are shown in Fig.4.7.

3.4 SEAWATER AND THE MARINE ATMOSPHERE

As expected, surface waters of the world's oceans are slightly enriched in the heavy isotopes in those areas where E/P>1, whereas in estuaries and in polar regions the δ values become slightly negative. The highest degrees of enrichments are obtained in evaporative basins such as the Red Sea and the Mediterranean, where values go up to $^{18}\delta = +2‰$ (Craig, 1966; Pierre et al., 1986).
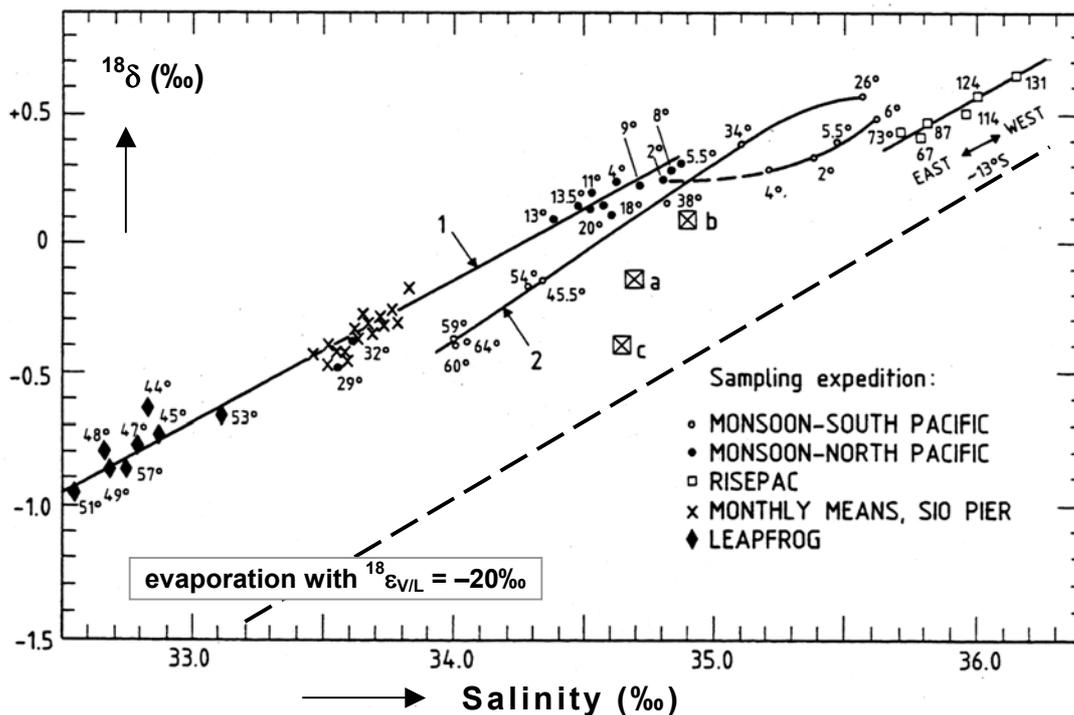

Fig.3.6   The isotopic composition of oceanic surface waters as a function of salinity; the degree of latitude is shown for some stations (from Craig and Gordon, 1965). If the seawater were evaporating with an ^{18}O fractionation of –20‰, the relation between $^{18}\delta$ and salinity would show the slope as indicated by the solid line.

The $^{18}\delta$ and $^{2}\delta$ values are usually well correlated with one another as well as with the salinity. $\Delta^{2}\delta/\Delta^{18}\delta$ is found to be 7.5, 6.5 and 6.0 for the North Pacific and North Atlantic (Craig and Gordon, 1965; Ferronski and Brezhgunov, 1989) and the Red Sea (Craig, 1966), respectively.

The Mediterranean Sea is an exception, portraying a relatively wide range of $^{18}\delta$ values with no commensurate increase in $^{2}\delta$ (= 8 ± 1‰) (Gat et al. 1996). The changes in the stable isotopic composition of the surface waters result from the interplay of the air-sea interaction process which determines the value of δ_E on the one hand and the δ value of the precipitation (and runoff) on the other. The latter more or less balances the evaporation flux.

The correlation with salinity is shown in Fig.3.6. The figure also contains a line indicating the slope of $^{18}\delta$ versus S in case the seawater is evaporating with an oxygen isotope fractionation of $^{18}\varepsilon = -20‰$.

There are very few direct measurements of the isotopic composition of the moisture in the marine atmosphere. Craig and Gordon (1965) report two profiles collected at mast height above the surface on a south-to-north track in the northern Pacific (Expedition Monsoon) and an east-to-west transect along latitude 20°N (Expedition Zephyrus) in the Atlantic. In both cases the $^{18}\delta$ value of the collected vapour was between -10.5‰ to -14‰, which is depleted by 3 to 4‰ relative to the value expected for equilibrium with the surface waters.

The fact that the marine vapour is neither constituted simply of the evaporation flux from the ocean, nor in local equilibrium with the surface ocean water was explained on the global scale as shown in Fig.3.7.

Because of the scarcity of vapour data one generally attempts to infer the isotopic composition of the atmospheric moisture based on the precipitation data, on the assumption of isotopic equilibrium between them. Unlike the case in a mid-continental location where the fact of such an equilibrium is fairly well established (Craig and Horibe, 1967; Jacob and Sonntag, 1991; Rozansky et al., 1982), one cannot rely on this as strictly over the oceans which are a source of vapour, so that a gradient upwards from the sea-surface is to be expected. A systematic difference in the isotopic composition of vapour collected at deck (20.35 m) and mast (27.9 m) height was reported for the 1995 cruise in the Mediterranean Sea by the RV METEOR.

3.5   THE CONTINENTAL ATMOSPHERE

3.5.1   THE RAYLEIGH REGIME

The further removed from the water source, the more depleted in the heavy isotopes are the meteoric waters. As described in Sect.3.2, the so-called *altitude*, *latitude* and *distance-from-coast* effects have been identified (Dansgaard, 1964). All of these effects are basically related

to the wringing out of moisture by cooling of the air masses and indeed the correlation with temperature appears as the overriding factor.
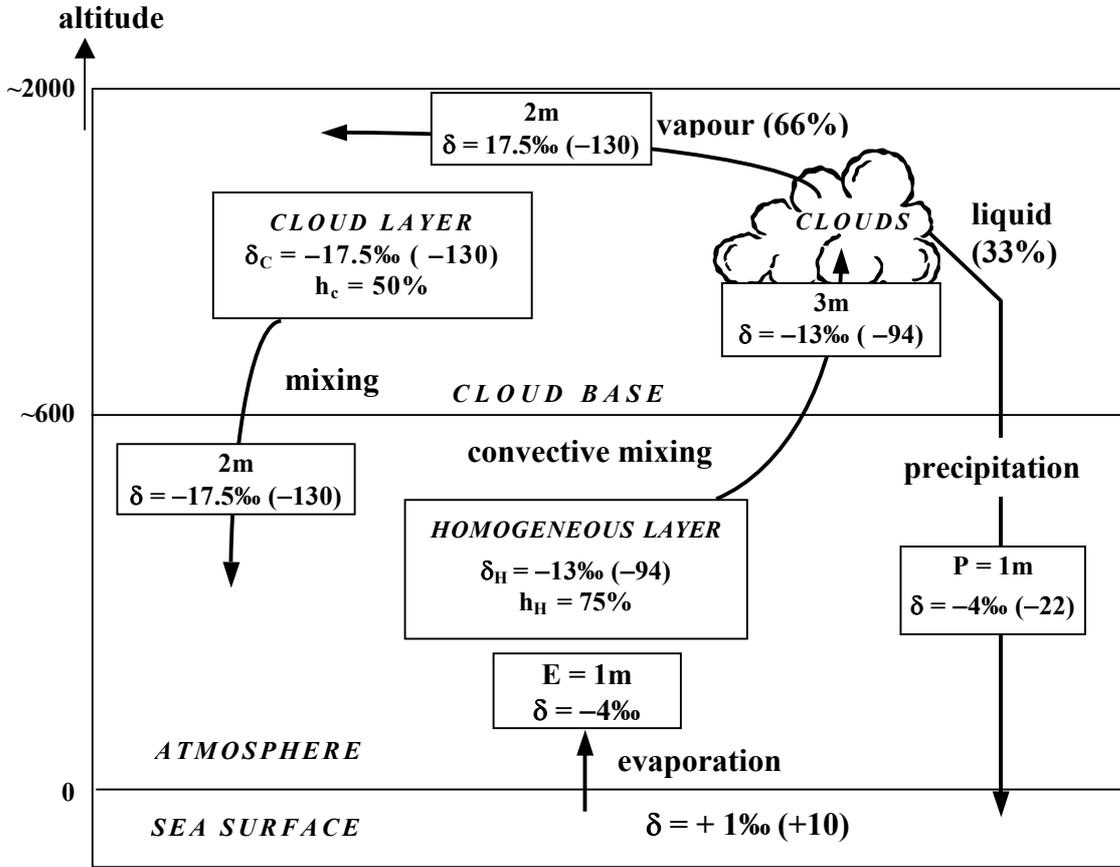

Fig.3.7 The marine-atmosphere isotope model of Craig and Gordon (1965) for the marine atmosphere. The δ values refer to $^{18}\delta$; $^{2}\delta$ is shown in parenthesis. The water transport fluxes are given in amounts of liquid water equivalents units of meter/year.

The conventional scenario envisages that, as the air mass cools, precipitation is formed in isotopic equilibrium with the vapour, At thermodynamic equilibrium between vapour and water the latter has a higher ^{18}O and ^{2}H content. Thus, the remaining vapour is continuously and thus progressively depleted in the heavy isotope. Fig. 3.8 presents the simple box model for this process. N_V is the number of water molecules, which closely equals that of the abundant, isotopically lighter molecules; R_V is the ratio of the isotopic molecules for either $^{2}H/^{1}H$ or $^{18}O/^{16}O$.

When dN_V molecules are removed with an accompanying fractionation factor $\alpha_{L/V}$ (=$1/\alpha_{V/L}$), the rare isotopic mass balance for the transported vapour is now written as:

$$R_V N_V = (R_V - dR_V)(N_V - dN_V) + (\alpha_{L/V}/R_V)dN_V \tag{3.13}$$

resulting in:

$$dR_V/R_V = (\alpha_{L/V} - 1)(dN_V/N_V)$$

and, if we assume that the number of isotopically light molecules, N_V, equals the total amount of molecules, the solution for this equation is:

$$R_V / R_{V0} = (N_V / N_{V0})^{\alpha_{L/V} - 1} \tag{3.14}$$

where the subscript "$_0$" refers to the initial conditions, i.e. the source region of the water vapour.
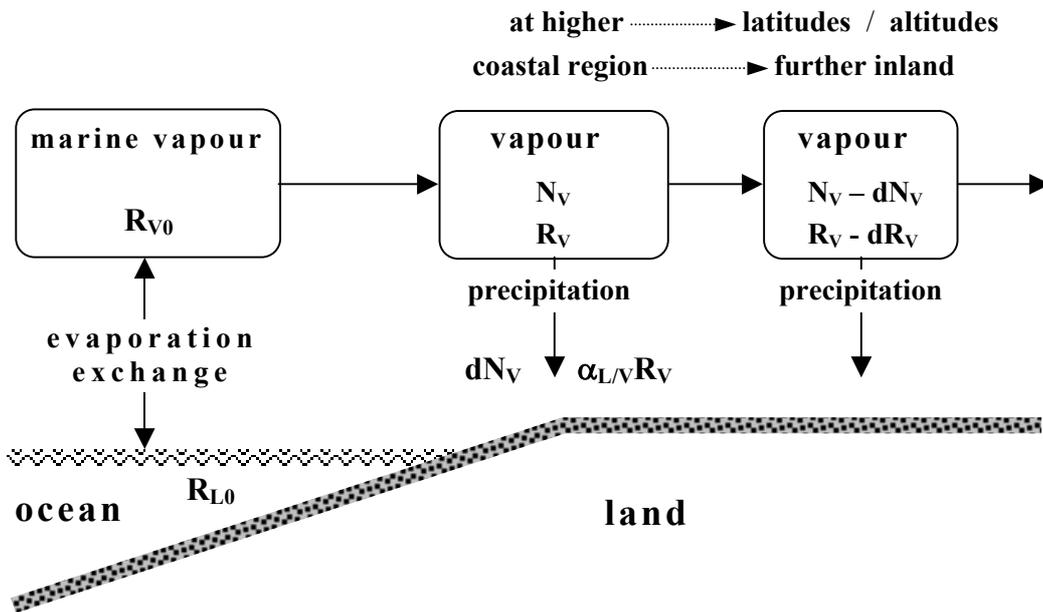

Fig.3.8   Schematic representation of a simplified (non-recycling) Rayleigh model applied to evaporation from the ocean and global precipitation. Water vapour originating from oceanic regions with strong evaporation moves to higher latitudes and altitudes with lower temperatures. The vapour gradually condenses to precipitation and loses $H_2^{18}O$ more rapidly than $H_2^{16}O$, because of isotope fractionation, causing the remaining vapour and also the "later" precipitation to become more and more depleted in both ^{18}O and ^2H.

For isobaric cooling the relative change in the amount of vapour is taken equal to the relative change in the saturated vapour pressure p_V:

$$dN_V/N_V = dp_V/p_V$$

Further, the relation between vapour pressure and temperature for an isobaric condensation process is presented by the law of Clausius Clapeyron:

$$p_V = C \exp(-D/T) \tag{3.15}$$

where   L = molar heat of evaporation = 44.4×10^3 J/mole

G = gas constant = 8.3J/Kmole

D = L/G = 5349K

T = absolute temperature = t(^{o}C) + 273.15K

C = constant for water (value here irrelevant)

From this we have:

$$dN_V/N_V = (D/T^2)dT$$

or:

$$N_V/N_{V0} = p_V/p_{V0} = expD(1/T_0 - 1/T)$$

so that

$$R_V/R_{V0} = exp\{-D(1/T - 1/T_0)(\alpha_{L/V} - 1)\} \quad (3.16)$$

where T refers to the temperature of the sampling station, T_0 to the source region of the water vapour.

For the temperature dependence of the fractionation between water vapour and liquid we choose the exponential equation (cf. Volume I, Sect.4.4):

$$\alpha_{L/V} = A \, exp(B/T) = 0.9845 \, exp(7.430/T) \quad (3.17)$$

(exponential adjustment made from data by Majoube, 1971).

The use of this temperature relation is a refinement of the calculation by Dansgaard (1964), who used an average $^{18}\alpha$ value over the temperature range between source region and precipitation areas.

The isotopic ratio of the precipitation condensing from atmospheric water vapour is: $R_L = \alpha_{L/V}R_V$ where $\alpha_{L/V}$ is determined by the condensation temperature or rather the temperature at the cloud base. Combining Eqs.3.16, 3.17 and the value for $R_{V0} = R_{VSMOW}(1 + {}^{18}\delta_{V0})$ with $^{18}\delta_{V0} = -12‰$ (Sect.3.5) and considering that $R_{L0} = R_{VSMOW}$ leads to:

$$\delta_{prec. \, at \, temp \, t} = \delta_L = \alpha_{L/V} \frac{R_V}{R_{V0}} \frac{R_{V0}}{R_{L0}} - 1 \quad (3.18)$$

This equation permits us to calculate curves of $^{18}\delta$ values versus temperature (Fig.3.8), which is to be compared with the observed variations in average annual $^{18}\delta$ values with latitude (Sect.4.1). Of course the model is too simple, as it is assumed that all vapour originates from regions around the thermal equator and all ocean evaporation at higher latitudes is neglected.

Using the above equations the temperature dependence of the latitude effect ranges from +0.8‰/^{o}C at 0°C to +0.5‰/^{o}C at 20°C (Fig.3.8).

The applicability of the Rayleigh relationship is based on the fact of the isotopic exchange between the falling droplets and the ascending air in the cloud, resulting in precipitation

which essentially "forgets" the isotopic label of very depleted isotopic values imprinted by the in-cloud processes, establishes isotopic equilibrium with the ambient air (Friedman et al., 1962). Indeed to a good approximation, the depletion in isotopic composition in precipitation correlates well with the near-ground temperature, as shown by Dansgaard (1964) and Yurtsever (1975), or more precisely with the temperature at the cloud base (Rindsberger and Magaritz, 1983). The result is to be compared with the observed values as presented in Sect.4.2.

This simple scenario which generally fits the data rather well, is modified under exceptional circumstances, namely:

1) in the case where snow or hail reaches the ground; the isotopic exchange between the air moisture and the precipitation element then does not occur, with the result that the precipitation is more depleted than in the equilibrium situation. Often, in addition, the solid precipitation shows higher d-values due to non-equilibrium condensation during the growth of ice particles (Jouzel and Merlivat, 1984);

2) in the case of precipitation from strongly convective systems (thunder clouds, cold fronts and tropical clouds associated with the ITCZ) which are characterised by strong local downdrafts. As a result the raindrops do not interact with an averaged sample of the ambient air but only with a portion of the in-cloud air.
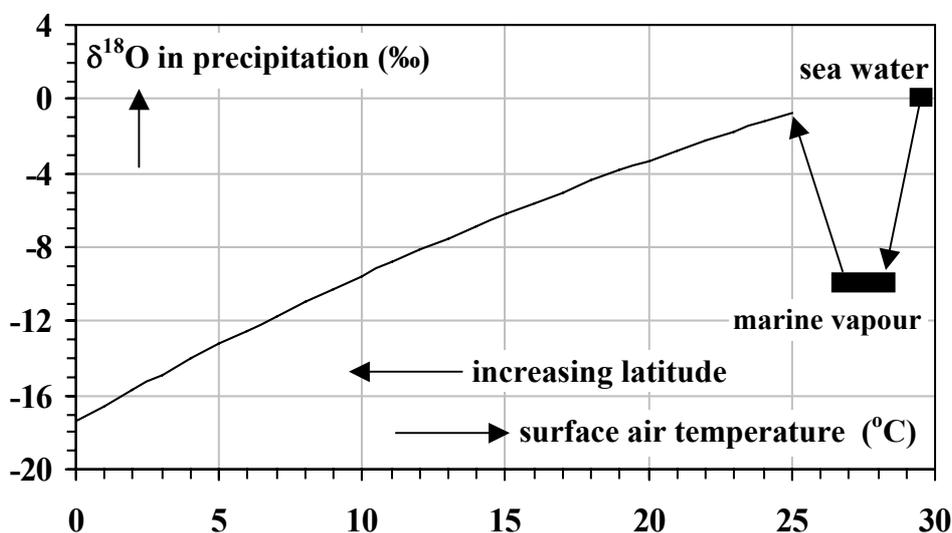

Fig.3.9   Result of calculating the temperature dependence of the latitude effect according to the simplified model of Fig.3.8 and Eq.3.18 ($^{18}R_{V0}/^{18}R_{L0}$ is taken 0.99, i.e. $^{18}\delta$ of the original marine vapour −10‰, and the evaporation temperature 25°C). The right-hand side of the drawing refers to the formation of water vapour from seawater and the subsequent condensation to form precipitation.

In these two cases the isotopic value in the precipitation is more depleted than the true equilibrium precipitation. These situations are then less effective in isotopic fractionation during rainout than the Rayleigh process proper, moderating the extent of isotopic depletion as a function of the rainout.

The meteoric water lines discussed so far, which in essence are Rayleigh lines, obviously describe a spatially distributed data set, describing the evolution of a particular precipitating air mass. They may also apply to different air masses with similar initial properties (water content, temperature and δ_{V0}), formed under comparable circumstances.

3.5.2 EVAPORATION AND TRANSPIRATION; RECYCLING OF MOISTURE OVERLAND

As rain falls on the ground it is partitioned into stagnant water pools and fluxes of surface runoff and of infiltration into the soil. As shown in Fig.3.10, part of the meteoric water is re-introduced into the atmosphere by virtue of direct evaporation or transpiration by the intermediary of the plant cover. Indeed some degree of evaporation already occurs as raindrops fall to the ground beneath the cloud base.

The largest share of the evapo-transpiration flux is carried by the transpiration of the plant cover, with evaporation from water intercepted on the canopy also accounting for an important share, up to 35% in the tropical rain forest (Molion, 1987). The total amount of re-evaporated water from the plants, from the soil and from open waters accounts in most cases for close to 50% of the incoming precipitation and approaches 100% in the arid zone. On a globally averaged basis the incoming moisture is recycled 1.5 times over the continents. Unlike the situation for transpired waters, evaporation from an open water body does not restore the ambient moisture's isotopic composition, since $\delta_E \neq \delta_P$. Moreover, it changes the d-excess of the atmospheric waters as explained below. However, complete drying-up of a surface water pool, as well as a terminal lake at hydrologic steady state, restores all of the incoming precipitation to the atmosphere so that the isotopic composition remains unchanged.

From the isotopic point of view, the transpiration flux is essentially non-fractionating (see Volume I, Sect.4.4.3), so that the addition of the transpired water restores the humidity lost by precipitation without a change in the isotopic composition. However, since the transpiration flux utilises the soil waters on a seasonally selective basis, and since usually there is a large seasonal cycle in the isotopic composition of precipitation, one finds a value different from the annual average, due to the selective utilisation of part of the rain (Sect.3.5.3).

The expression for the isotopic composition of the evaporate, given in Eq.3.5, depends among other factors on the composition of the water body which is evaporating. The value of δ_E in the δ^2 vs. $^{18}\delta$ graph is usually situated above the MWL, depending on how far the enrichment of the residual surface waters has progressed relative to the initial conditions.
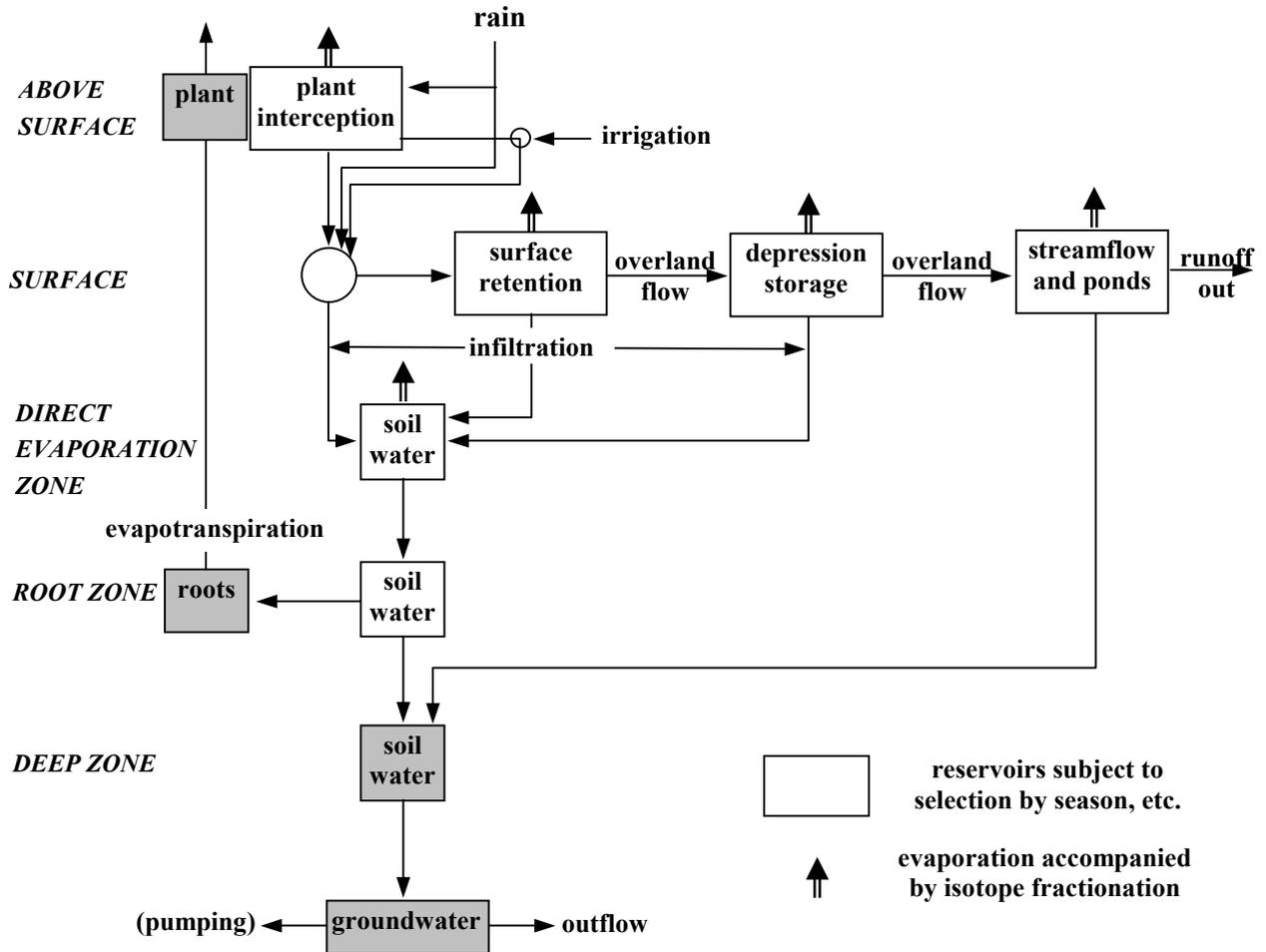
Fig.3.10 Scheme of the atmosphere/land surface interface, based on Gat and Tzur (1976). The backflux of water into the atmosphere by evapo-transpiration consists of 3 variants: 1. evaporation from open-water bodies with isotope fractionation; 2. transpiration from plants without isotope fractionation; 3. periodic evapo-transpiration from reservoirs where selection by season or based on rain amounts takes place (see also Sect.3.1.5).

As shown in Fig.3.3, when the isotopic composition of the residual waters is further and further removed from that of the initial (precipitation) value, then it is to be noted that the isotopic composition of the return flux to the atmosphere (δ_E) approaches that of the inflow (δ_{in}) and under terminal-lake conditions, when $\delta_E = \delta_{in}$, material balance considerations dictate that $\delta_E = \delta_{in}$. Thus, paradoxically, at the time that the effect on the isotopic composition of the lake water is maximal, the effect of the evaporation flux on the isotopic composition of the air moisture vanishes.

Writing Eq.3.6 for both the oxygen and hydrogen isotopes and remembering that

$$d = {}^2\delta - 8 \cdot {}^{18}\delta$$

we obtain an expression for d_E, the *d-excess value for the evaporation flux*, as follows:

$$d_E = \left\{ d_w - h_N d_A - (^2\varepsilon_{L/V} - 8\,^{18}\varepsilon_{L/V}) - (^2\varepsilon_{diff} - 8\,^{18}\varepsilon_{diff}) \right\} / (1 - h_N) =$$

(3.19)

$$= \frac{d_w - h_N d_A - (^2\varepsilon_{L/V} - 8\,^{18}\varepsilon_{L/V})}{1 - h_N} - n\Theta(^2\Delta_m - 8\,^{18}\Delta_m)$$

where d_E, d_w and d_A are the d-excess values of the evaporation flux, the surface water and the atmospheric humidity, respectively.

The term $(^2\varepsilon_{L/V} - 8\,^{18}\varepsilon_{L/V})$ is close to zero in all cases; $n(^2\Delta_m - 8\,^{18}\Delta_m) = -100.3‰$ when $n = \frac{1}{2}$, as applies to an open water body. Thus:

$$d_E - d_A \approx \frac{(d_w - d_A)}{(1 - h_N)} + 0.1 \times \Theta$$

(3.20)

The value of $(d_E - d_A)$ does not depend on the discrete δ_A values. This is a very fortunate feature, since the value of d_A is never in doubt by more than a few ‰, even in the case where the values of δ_A may be uncertain due to the variable rainout history of the air masses (Gat, 1980) or due to the possibility of admixture of transpired water from the vegetation-covered continental areas (White and Gedzelman, 1984).

Eq.3.20 provides a scaling factor against which one can compare the measured change of d resulting from the admixture of the evaporate.

Due to the above-mentioned processes, one typically finds an increase of d in an air mass along a continental passage, as observed, for example, in the Amazon basin (Gat and Matsui, 1991).

The recycling of water over the continents, just described, affect the total atmospheric water cycle. Fig.3.11 is an attempt to show how the basic Craig-Gordon model is modified by the terrestrial part of the water cycle (Gat, 1996).

3.5.3   SELECTION VERSUS FRACTIONATION

The isotopic composition of precipitation is the primary signal whereby the derived meteoric waters, be these surface, soil or groundwater, can be related to the precipitation input, geographically or temporally. Further, their subsequent change by evaporation, mixing or interaction with the lithosphere can then be utilised to trace or quantify these processes.

Only in exceptional cases is the transfer from one compartment or phase to another indiscriminate, so that the original isotopic composition is fully preserved. One such case is the direct rainout on a mixed surface water, another obviously the total transfer of water from one system to another as occurs when a pool of water dries up completely.
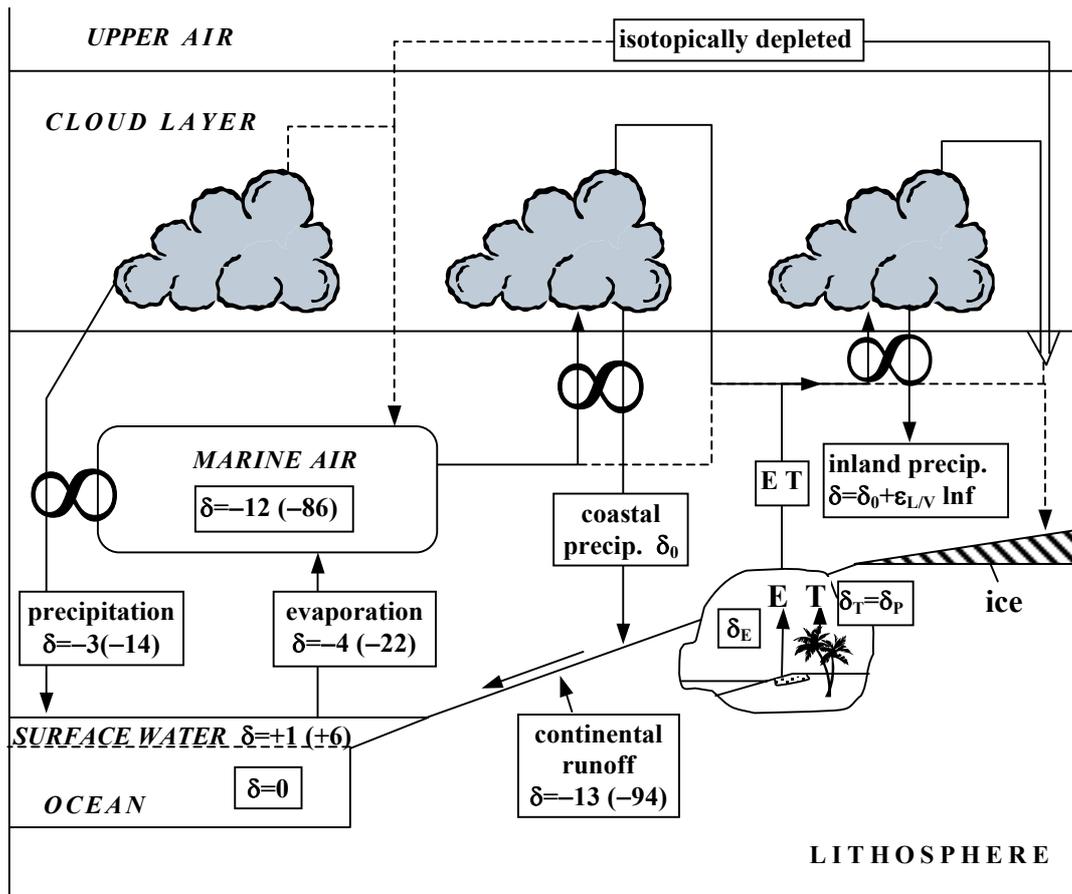
Fig.3.11   Adaptation of the Craig and Gordon model (Fig.3.7) to include the terrestrial part of the hydrological cycle. The double loop signifies that isotopic equilibrium is assumed between the precipitation and the ambient atmospheric moisture (Gat, 1996).

A difference in isotopic composition of the primary water pool to that transferred into another phase occurs, for example, by partial evaporation from an open-water body as discussed above or by uptake of water by plants from the soil during different parts of the year. These two examples differ, however, in that in the case of evaporation the different isotopic species of water, namely $^{1}H_{2}^{16}O$, $^{2}H^{1}H^{16}O$ and $^{1}H_{2}^{18}O$, partake at different rates in the evaporation, in which case a consistent isotope enrichment or depletion will occur. We have defined such a process as one with *isotope fractionation*. In the second case the momentary water transition is not fractionating with respect to the different isotopic species. However, the uptake can be unequal during different times of the year, e.g. favouring the growing season. Since the soil water pool is usually not a well mixed reservoir, and furthermore, since the isotopic composition of the precipitation varies seasonally, one will find a shift in isotopic composition in the remaining soilwater and its subsequent recharge to groundwater, based on a *selection* between rain events rather than on isotope fractionation directly. One more example out of many others is the favouring of intense rainfalls in the generation of surface

runoff, resulting in a selection based on the influence of the *amount effect* on the isotopic composition of the rain.

3.6 THE $^{17}O - ^{18}O$ RELATION

The two rare, heavy isotopes, of oxygen, ^{17}O and ^{18}O, occur with natural abundances of 0.037% and 0.204%, respectively (Table 2.1).

As must be clear from its omission in the preceding text, ^{17}O is hardly used, since nearly all ^{17}O and ^{18}O fractionation factors, and thus abundance variations have a fixed relation, independent of the (natural) processes and conditions that give rise to the fractionation:

$$\left(\frac{^{18}R_s}{^{18}R_r} \right) = \left(\frac{^{17}R_s}{^{17}R_r} \right)^{\theta} \tag{3.21}$$

In this expression, the R's stand for the isotope ratio $^{17}O/^{16}O$ or $^{18}O/^{16}O$, depending on the superscript, and the subscripts "s" and "r" stand for "sample" and "reference", respectively.

This expression is commonly referred to as *mass dependent fractionation*.

Theoretically, the exponent θ is expected to be somewhat smaller than 2, but for the sake of simplicity, $\theta = 2$ is commonly assumed (Volume I, Sect.3.7) (Craig, 1957, Mook and Grootes, 1973, Allison et al., 1995)

The only field in which always ^{17}O was studied in relation to ^{18}O is cosmochemistry, the research of extraterrestrial material such as meteorites (Clayton, 1993). In the early 1980's, however, attention was drawn to observations of non-mass-dependent oxygen isotope fractionation in stratospheric ozone (Mauersberger, 1981), and later also in other stratospheric molecules such as CO_2 (Thiemens et al., 1991). A fractionation behaviour was observed that either obeyed Eq.3.21, but with θ very different from 2, or did not obey Eq.3.21 at all (Krankowsky and Mauersberger, 1996).

These quite unexpected ^{17}O-^{18}O anomalies in the earth's atmosphere brought new attention to the relation Eq.3.21. Actually, until recently, this relation never had been checked properly for meteoric waters, mainly due to practical facts: in the common analytical technique, that of Isotope Ratio Mass Spectrometry (IRMS) applied to CO_2 gas, the ^{17}O ($^{12}C^{17}O^{16}O$) signal is obscured by the much more abundant ^{13}C one ($^{13}C^{16}O_2$), both having mass 45.

Recently, however, two studies appeared, in which the ^{17}O-^{18}O relation of terrestrial material has been carefully analysed. The first (Meijer and Li, 1998) was based on the electrolysis of water and subsequent IRMS analysis of the oxygen gas thus formed. The authors studied a wide variety of natural waters (meteoric, ocean and lake water, and even fruit juice), and found a ($^{17}\delta, ^{18}\delta$) relationship perfectly following Eq.3.21 with an exponent $\theta = 1.8936 \pm 0.00538$. Typical individual standard deviations of this study were 0.07 ‰ for $^{17}\delta$, and 0.10 ‰ for $^{18}\delta$ (note that the definitions of $^{18}\delta$ and $^{17}\delta$ are similar).

Miller et al. (1999) studied the ($^{17}\delta, ^{18}\delta$) relationship of a large suite of rock and mineral samples, using the fluorination technique. They also found a relationship according to Eq.3.21, with $\theta = 1.9069 \pm 0.0009$. The individual standard deviations in this study were 0.04‰, and 0.08‰ for $^{17}\delta$, and $^{18}\delta$, respectively.

Although research in this field has not yet fully matured, and the two values for θ reported seem significantly different, it is safe to say at this point that, at least for isotope hydrological applications, $^{17}O/^{16}O$ does not carry additional information.

Studying the global carbon cycle, however, a new application of ^{17}O has been demonstrated by Luz et al. (1999) and Luz and Barkan (2000). The stratospheric processes, leading to ^{17}O-^{18}O anomalies in ozone and other oxygen-containing species, also influence the ^{17}O-^{18}O relation in molecular oxygen (Thiemens et al., 1995). Using IRMS for whole-air samples, this small effect can still be observed in sea-level oxygen. The stratospheric ^{17}O-^{18}O anomaly, however, is washed out by plant activity: photosynthesis (CO_2 consumption) as well as respiration and combustion (CO_2 production) show a ^{17}O-^{18}O relation fully complient with Eq.3.21. From the competition between these effects, and thanks to the high precision of the measurements, independent numbers can be deduced for marine and terrestrial biological activity (see further the related subjects in Sect.6.7 on O_2/N_2 measurements and the Dole effect).

Chapter 3