

# OXYGEN AND HYDROGEN ISOTOPES IN THE HYDROLOGIC CYCLE

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## ABSTRACT

Changes of the isotopic composition of water within the water cycle provide a recognizable signature, relating such water to the different phases of the cycle. The isotope fractionations that accompany the evaporation from the ocean and other surface waters and the reverse process of rain formation account for the most notable changes. As a result, meteoric waters are depleted in the heavy isotopic species of H and O relative to ocean waters, whereas waters in evaporative systems such as lakes, plants, and soilwaters are relatively enriched. During the passage through the aquifers, the isotope composition of water is essentially a conservative property at ambient temperatures, but at elevated temperatures, interaction with the rock matrix may perturb the isotope composition. These changes of the isotope composition in atmospheric waters, surface water, soil, and groundwaters, as well as in the biosphere, are applied in the characterization of hydrological system as well as indicators of paleo-climatological conditions in proxy materials in climatic archives, such as ice, lake sediments, or organic materials.

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## 1. INTRODUCTION

The basic tenet of the hydrologic cycle as expounded by the preacher, that “into the sea all the rivers go and yet the sea is never filled, and still to their goal the rivers go” (The Jerusalem Bible, English translation, 1970), remains valid until today. However, the simple concept of a steady-state one-cycle

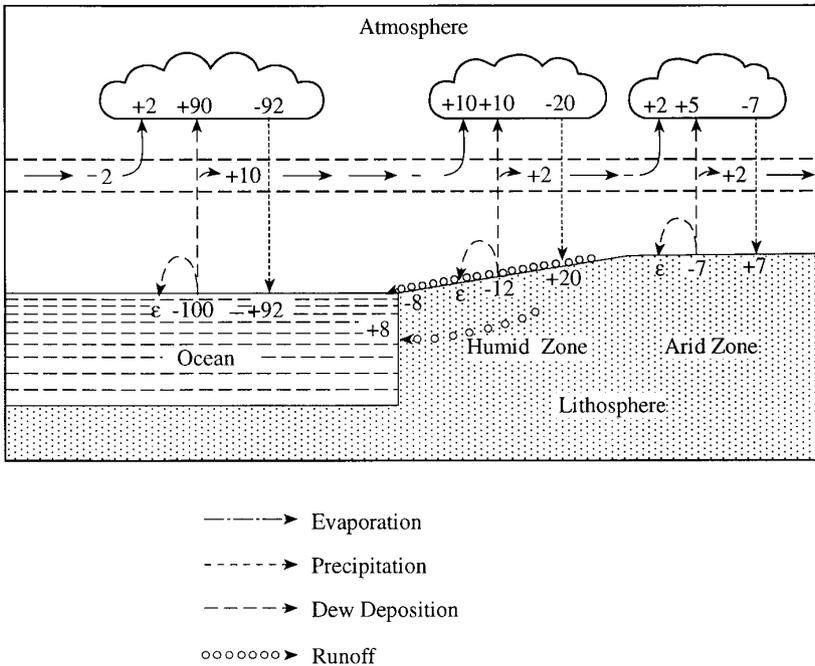


Figure 1 The hydrologic cycle, in relative flux units (100 units equals the marine evaporation flux). Figures have been rounded up. (Adapted from Chow 1964.)

system needs to be qualified. As shown schematically in Figure 1, the marine part of the cycle, namely the evaporation from the ocean and the return flux by atmospheric precipitation into the ocean, accounts for close to 90% of the annual flux. However, in the remaining continental part of the cycle, the precipitated water is recycled by evapo-transpiration a number of times before returning to the oceans as river and groundwater runoff. Moreover, intermediate storage reservoirs such as glaciers and deep groundwater systems are changeable on a variety of time scales, in response to a changing climate.

Compared to the  $1.35 \times 10^9 \text{ km}^3$  of oceanic waters, the groundwater and ice reservoirs on land are estimated at  $82 \times 10^6$  and  $27.5 \times 10^6 \text{ km}^3$ , respectively. Atmospheric moisture constitutes only about  $10^{-5}$  of the volume of the ocean waters.

Measurements of the isotope composition of water in the various components of the water cycle has enabled the identification of different water masses and the tracing of their interrelationships. Furthermore, measured variations (in time) of the isotopic composition (of proxy materials) in climatic archives such

as in ice cores, lake and ocean sediments, and of plant material, have proven useful for paleoclimate reconstructions.

The abundance of the isotopes  $^2\text{H}$  (deuterium, also marked as D) and  $^{18}\text{O}$  in ocean waters is close to  $\text{D}/\text{H} = 155.95 \times 10^{-6}$  (Dewit et al 1980) and  $^{18}\text{O}/\text{O} = 2005.2 \times 10^{-6}$  (Baertschi 1976), respectively, where H and O without a mass assignment stands for the natural assembly of all isotopic species. Another natural oxygen isotope,  $^{17}\text{O}$ , occurs at an abundance of about 1/10 that of  $^{18}\text{O}$ , but because its variations in the water cycle parallels that of the heavier isotope (at 1/2 the extent) it has not been measured as a rule.

Abundance variations of  $\pm 30\%$  for deuterium and  $\pm 5\%$  for  $^{18}\text{O}$  have been measured in natural waters (Boato 1961). These variations are only to a negligible degree the result of nuclear interactions that produce or consume these isotopes; they rather result primarily from the fractionation of the isotopic water species in isotopic exchange reactions (equilibrium isotope effects) or in chemical or biochemical reactions involving the isotopic species (kinetic and vital effects), or as a result of different diffusion rates of the isotopic water molecules (transport effects). In the water cycle, the most significant process in this respect is that of phase changes, from vapor to liquid or ice and vice versa.

The ocean, being the largest water reservoir and relatively homogeneous, was chosen as the reference standard for the  $\delta$  scale of both oxygen and hydrogen isotopes in water samples (Craig 1961a). The  $\delta$ -(permil) value is defined as  $\delta\text{‰} = (R_x/R_{\text{std}} - 1) \times 10^3$ , where  $R$  is the atom ratio  $\text{D}/\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$ , respectively. Positive  $\delta$  values thus signify an enrichment of the heavy isotopic species relative to the standard (SMOW); negative values indicate their depletion. Because the variability in  $\delta(\text{D})$  is typically larger by almost an order of magnitude than that of  $\delta(^{18}\text{O})$ , the usual way of presenting isotope data of water samples is on a  $\delta(\text{D})$  vs  $\delta(^{18}\text{O})$  diagram with the  $\delta(\text{D})$  scale compressed by a factor of ten.

Ever since the earliest measurement of isotopic abundance in the 1930s in Europe and Japan (Rankama 1954) and by the Chicago school of HC Urey, using the Nier-McKinney double-inlet, double-collector mass-spectrometer (Nier 1947, Mckinney et al 1950), it has been observed that freshwater samples are depleted in the heavy isotopes, whereas the residue of evaporating surface waters such as African lakes are enriched (Craig 1961b). A correlation between the depletion of the deuterium and oxygen-18 in freshwaters was established; the locus line of such samples in  $\delta$ -space was defined as  $\delta(^2\text{H}) = 8\delta(^{18}\text{O}) + 10(\text{‰})$ . This line is now known as the Global Meteoric Water Line (GMWL).

## 2. ISOTOPE FRACTIONATION IN THE WATER CYCLE

### 2.1 *Fractionation Factors*

The strength of chemical bonds involving different isotopes of an element differ slightly, with the bond involving the lighter isotope usually weaker and easier to disintegrate. The rate of chemical reactions in which such a bond is broken will then show a (kinetic) isotope effect (Melander 1960). Similarly, and based on the general thermodynamic principle that equilibrium systems tend toward a state of minimum energy, the heavy isotopes will favor that part of the system in which they are more strongly bound. This principle applies as well to equilibrium between different phases. These are quantum effects, which are appreciable at low temperatures and disappear at higher temperatures.

One defines a unit isotopic fractionation factor ( $\alpha$ ) in a system of two molecular species, A and B, with a common element or in two coexisting phases of some material as follows:

$$\alpha_{A-B} = \frac{R_A}{R_B} = \frac{(N_i/N_j)_A}{(N_i/N_j)_B},$$

where  $N_i$  and  $N_j$  are the amounts of the isotopes of the common element and  $R = N_i/N_j$ .

When the system is in isotopic equilibrium, one denotes the fractionation factors as either  $\alpha^+$  or  $\alpha^-$ , where by the convention introduced by Craig & Gordon (1965),  $\alpha^* < 1$ ;  $\alpha^+ > 1$  so that  $\alpha^+ = 1/\alpha^-$ . The values of such an equilibrium fractionation factor depend only on the molecules and isotopes involved and are strongly temperature dependent, following a rule such as

$$\ln \alpha^* = \frac{C_1}{T^2} + \frac{C_2}{T} + C_3.$$

Equilibrium fractionation factors can be calculated based on spectroscopic data using the partition functions of the molecules concerned. A number of reviews on this subject have been published (Bigeleisen & Mayer 1947, Urey 1947, Boato 1961, Bigeleisen et al 1973).

In a more general manner, an isotopic fractionation factor can be defined for a system from which there is an outgoing flux with different isotope ratios than in the bulk of the material:

$$\alpha_K = \frac{dN_i/dN_j}{N_i/N_j}.$$

One uses  $\alpha_K$  to distinguish this case from one where an equilibrium fractionation factor applies.

Such a formulation applies when part of the system is removed by a chemical reaction (in which case  $\alpha_K$  can be called a *kinetic* fractionation factor), but it will

also apply to the case where material is removed by diffusion or outflow, e.g. by effusion through an aperture. In the latter cases the term *transport* fractionation factor may be preferred. Unlike true kinetic fractionation factors, which like the equilibrium factors are strongly temperature dependent, the transport factors show only slight (positive) temperature coefficients.

The values of the equilibrium fractionation factors ( $\alpha^+$ ) for the water-vapor phase transition are given by Majoube (1971) as 1.0098 and 1.084 at 20°C and 1.0117 and 1.111 at 0°C, respectively, for  $^{18}\text{O}$  and D. For the ice-liquid transition the values of  $\alpha^+$  (at 0°C) are 1.0035 for  $^{18}\text{O}$  and 1.0208 for D (Arnason 1969).

## 2.2 The Rayleigh Equations

If material is removed from a (mixed) system containing  $N_i$  and  $N_j$  molecules, respectively, of two isotopic species and if the fractionation accompanying the removal process at any instance is described by the unit fractionation factor  $\alpha$ , then the evolution of the isotopic composition in the remnant material is described by the following equations, assuming  $N \gg N_i$ , where  $N_i + N_j = N$ , so that it follows that  $N \simeq N_j$  (which holds for the natural isotope abundance of the lighter elements, e.g. H, N, C, and O):

$$\frac{dR}{dN} = \frac{1}{N} \left( \frac{dN_i}{dN} - \frac{N_i}{N} \right) = \frac{R}{N} (\alpha - 1) \quad (1a)$$

and

$$\frac{d(\ln R)}{d(\ln N)} = (\alpha - 1). \quad (1b)$$

Equation 1a can be immediately integrated from an initial condition ( $R_0, N_0$ ) to any given stage, provided  $\alpha$  does not change during the course of the process:

$$R = R_0 \left( \frac{N}{N_0} \right)^{(\alpha-1)} = R_0 \cdot f^{(\alpha-1)}, \quad (3)$$

where  $f = N/N_0$  is the fraction of the material remaining.

When the isotopic species removed at every instant are in *thermodynamics equilibrium* with those remaining in the system, we have the circumstances of the so-called Rayleigh distillation. Under these conditions, the unit separation factor will be a thermodynamic equilibrium constant  $\alpha^*$ , i.e. the vapor pressure ratio of the isotopic water molecules for the liquid to vapor transitions or the equilibrium constant of an isotopic exchange reaction.

The isotopic composition  $R$  of the remaining material, as a function of  $f$ , when subject to Rayleigh fractionation, is shown in Figure 2. Obviously, the isotope composition of the material that is removed at every instance describes

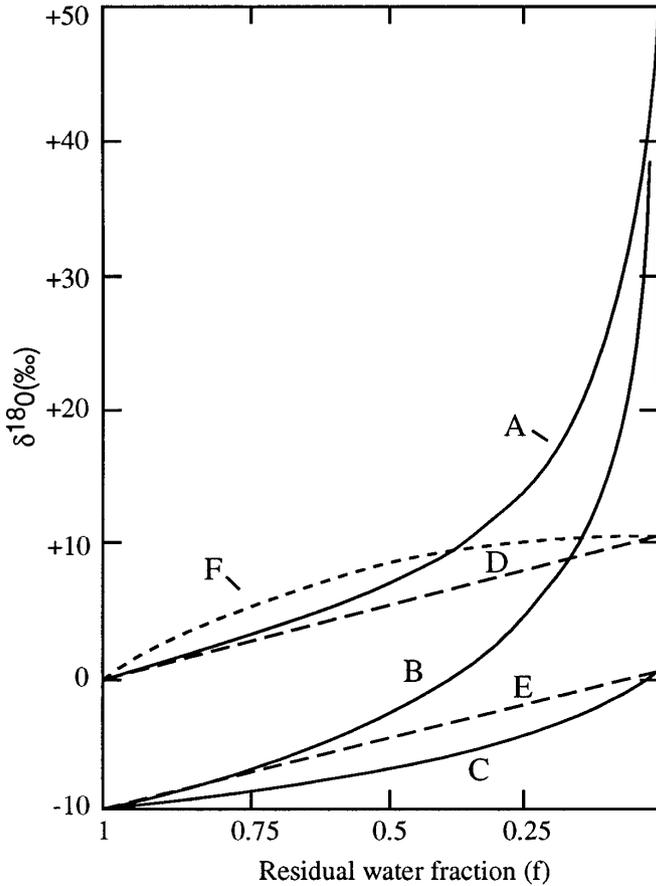


Figure 2 Isotopic change under Rayleigh, closed, and steady-state conditions for fractionation processes with a unit fractionation factor of  $\alpha = 1.01$  for initial liquid composition of  $\delta = 0$ . A, B, C: Rayleigh conditions for residual water, continuously removed vapor, and total vapor removed, respectively; D, E: liquid and vapor for two coexisting phase systems; F: liquid approaching steady state (time axis not in proportion).

a curve parallel to that of the remaining fraction. The integrated curve, giving the isotopic composition of the accumulated material thus removed, is also shown. Material balance considerations require that the isotope content of the total accumulated amount of the removed material approaches  $R_0$  as  $f \rightarrow 0$ .

### 2.3 *Isotope Fractionation in Open, Closed, and Steady-State Systems*

The system for which the Rayleigh equations apply is an open system from which material is removed continuously under condition of a fixed fractionation factor. However, other systems can be envisaged, to which the same unit fractionation factor applies but under other boundary conditions for the integration of the unit process. One such system is the so-called closed system (or two-phase equilibrium model), first described by S Epstein (unpublished lecture notes), where the material removed from one reservoir accumulates in a second reservoir in such a manner that isotopic equilibrium is maintained throughout the process. An example would be the condensation of vapor to droplets in a cloud.

If the time  $t = 0$  all material is in reservoir #1, then

$$N_2 = N_{1,0} - N_1, N_{i_2} = N_{i_{1,0}} - N_{i_1},$$

and also

$$\frac{R_2}{R_1} = \alpha.$$

Defining  $f = \frac{N_1}{N_{1,0}}$ , then

$$R_f = \frac{R_0}{\alpha - f(\alpha - 1)} \quad (3a)$$

or in  $\delta$ (‰) nomenclature

$$\delta_f = \frac{\delta_0 - \varepsilon(1 - f)}{\alpha - f(\varepsilon/10^3)}. \quad (3b)$$

Unlike in the open system,  $\delta_{f \rightarrow 0} \rightarrow (\delta_0 - \varepsilon)/\alpha$ , limiting the degree of isotope enrichment.

A third model is that of a throughflow system in which the outgoing (fractionated) flux is replaced by an inflow with isotope composition  $\delta_{in}$ . At steady state, the isotope composition of in- and outflowing fluxes are obviously equal. If the outflowing flux is related to the reservoir's isotope composition by a fractionation factor  $\alpha$ , then the steady-state isotopic composition in the reservoir

will be  $\delta_{ss} = (\delta_{in} - \varepsilon)/\alpha$ , while the approach to steady-state composition can be expressed as (Zimmermann 1979)

$$\frac{\delta_{ss} - \delta}{\delta_{ss} - \delta_0} = \exp(-\alpha^{t/\tau}), \quad (4)$$

where  $\tau$  is the characteristic turnover time of the system, given by the volume to flux ratio ( $\tau = V/F$ ).

Note that for the same unit fractionation factor the resultant evolution of the isotopic composition is quite different under these different circumstances, as shown in Figure 2.

In all examples given so far, a constant unit fractionation factor is assumed to apply throughout the process. This is not, however, always the case. For example, as will be discussed, the rainout from an air mass is usually the result of a continuous cooling of the parcel of air concerned; the cooling results in a change of the unit fractionation factor for the vapor-to-water (or vapor-to-ice) transition during the evolution of the precipitating system. Although the differential form of the Rayleigh equation (Equation 1a) still applies, the integration obviously has to be carried out for a prescribed change of  $\alpha$  throughout the process [as was first demonstrated by Dansgaard (1964)].

Another conspicuous example of a changing "effective" fractionation factor is that of the evaporation of water from a surface water body into the atmosphere. In this case, the change is the result of the changing boundary conditions (of the isotopic gradient, primarily) rather than a change of the unit fractionation factors themselves.

## 2.4 *Isotope Fractionation Accompanying Evaporation of Surface Waters*

Water-air interaction balances two opposing water fluxes, one upward from the surface and the other a downward one of atmospheric moisture. At saturation, i.e. when atmospheric humidity is 100% in terms of the saturation vapor pressure at the liquid surface, this interaction will bring the liquid water and air humidity into isotopic equilibrium with one another. Such a situation apparently occurs at cloud base between the falling rain droplets and the ascending air.

When the air is undersaturated, a net evaporation flux results, in which the rate-determining step is the diffusion of water vapor across the air boundary layer in response to the humidity gradient between the surface and the fully turbulent ambient air. Three factors are involved in determining the overall isotope fractionation: 1. the equilibrium isotope fractionation of the liquid to vapor phase transition, 2. a fractionation resulting from the diffusion across the air boundary layer, and 3. the back flux of the atmospheric moisture.

The most useful model for the isotope fractionation during evaporation, which has stood the test of time, is that of Craig & Gordon (1965). The model is based on the Langmuir linear-resistance model for evaporation and is schematically shown in Figure 3. The following assumptions underlie this model:

- (a) equilibrium conditions at the air/water interface, so that the relative humidity is  $h = 1$  and  $R_V = \alpha^* R_L$ ;
- (b) a constant vertical flux, i.e. no divergence or convergence in the air column; and
- (c) no isotopic fractionation during a fully turbulent transport.

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

$$E = (1 - h)/\rho; \rho = \rho_M + \rho_T$$

and

$$E_i = (\alpha^* R_L - h \cdot R_a)/\rho_i; \rho_i = \rho_{i,M} + \rho_{i,T}$$

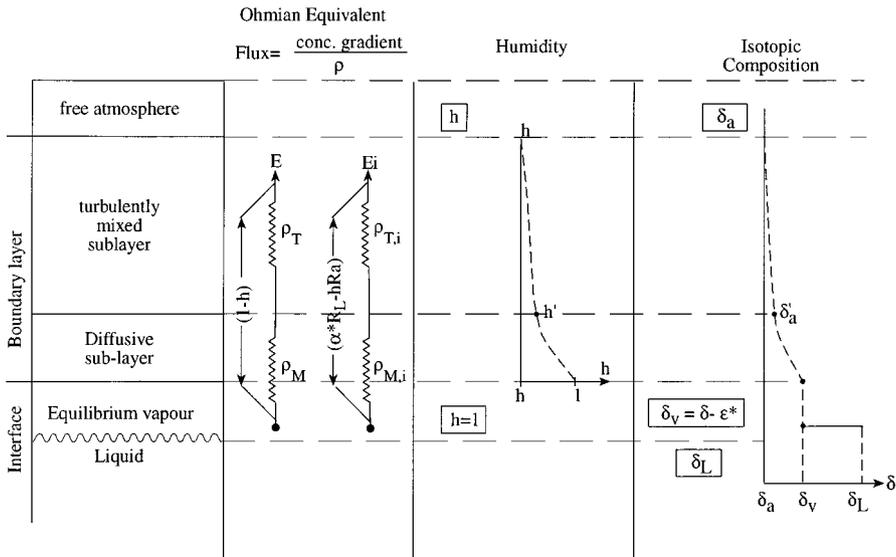


Figure 3 The Craig-Gordon evaporation model.

The  $\rho$  terms are the appropriate resistances as shown in Figure 3; subscripts M and T signify the diffusive and turbulent sublayer, respectively. Subscript a refers to a free atmosphere above the evaporating surface.

The isotopo composition of the evaporation flux is

$$R_E = E_i/E = \frac{(\alpha^* R_L - h R_a)}{(1-h) \cdot \rho_i/\rho}. \quad (5a)$$

This can be translated into  $\delta$  units,  $\delta = (R/R_{\text{std}} - 1)$ , to give

$$\delta_E = \frac{\alpha^* \delta_L - h \delta_a - \varepsilon^* - \Delta\varepsilon}{(1-h) + \Delta\varepsilon/10^3} \approx \frac{\delta_L - h \delta_a - \varepsilon^* - \Delta\varepsilon}{(1-h)}, \quad (5b)$$

where

$$\varepsilon^* = (1 - \alpha^*) \cdot 10^3$$

and

$$\Delta\varepsilon = (1-h) \left( \frac{\rho_i}{\rho} - 1 \right) \times 10^3.$$

The term  $[(\rho_i/\rho) - 1]$  can be evaluated as follows: In the linear resistance model  $\rho_i = \rho_{i,M} + \rho_{i,T}$  and  $\rho = \rho_M + \rho_T$ ;

$$\begin{aligned} \frac{\rho_i}{\rho} &= \frac{\rho_{M,i} + \rho_{i,T}}{\rho_M + \rho_T} = \frac{\rho_M}{\rho} \cdot \frac{\rho_{M,i}}{\rho_M} + \frac{\rho_T}{\rho} \cdot \frac{\rho_{i,T}}{\rho_T}, \\ \left( \frac{\rho_i}{\rho} - 1 \right) &= \frac{\rho_M}{\rho} \left( \frac{\rho_{M,i}}{\rho_M} - 1 \right) + \frac{\rho_T}{\rho} \left( \frac{\rho_{i,T}}{\rho_T} - 1 \right). \end{aligned}$$

The second term on the right-hand side is eliminated on the assumption that  $\rho_{i,T} = \rho_T$ , so that

$$\frac{\Delta\varepsilon}{10^3} = (1-h) \left[ \frac{\rho_M}{\rho} \left( \frac{\rho_{M,i}}{\rho_M} - 1 \right) \right]. \quad (6a)$$

For the case of a fully developed diffusion layer  $\rho_M \propto D_m^{-1}$ , where  $D_m$  is the molecular diffusivities of water in air. For a rough interface under strong (turbulent) wind conditions, the transient eddy model of Brutsaert (1965) can be applied, with  $\rho_M \propto D_m^{-1/2}$ . At more moderate wind speeds a transition from the proportionality of  $D^{-2/3}$  to  $D^{-1/2}$  can be expected (Merlivat & Contiac 1975).

The ratio of the molecular diffusivities in air, of the pairs  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  and  $^1\text{HDO}/^1\text{H}_2\text{O}$ , has been determined by Merlivat (1978) as 0.9723 and 0.9755, respectively. Note that these values differ from those calculated by simple gas kinetic theory, based on the molecular weights only, apparently due to some hydrogen bonding in the gas phase. Accordingly, the  $\Delta\varepsilon$ -term is expressed as

$$\Delta\varepsilon = (1-h) \cdot \theta \cdot n \cdot C_D \cdot 10^3, \quad (6b)$$

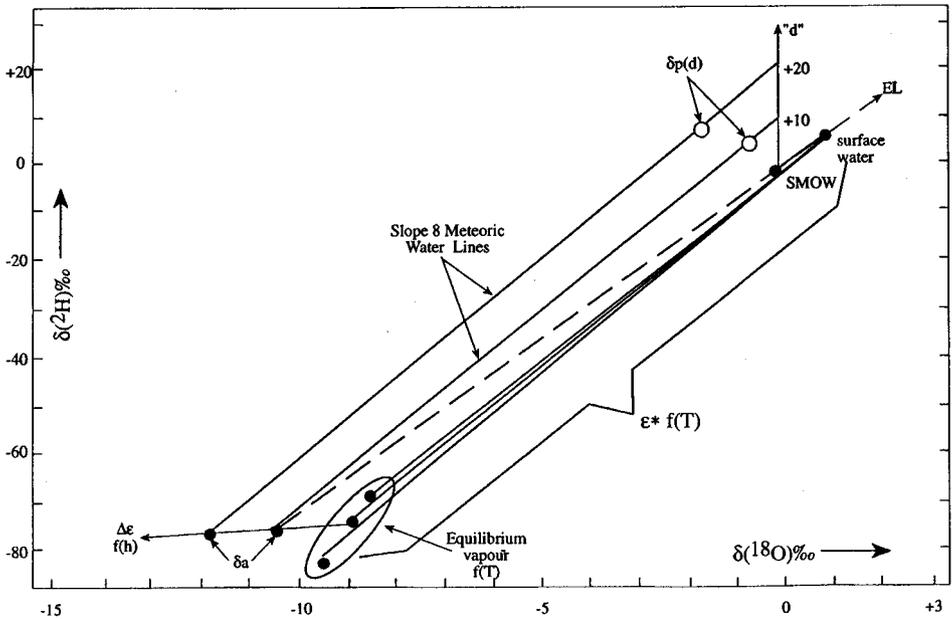


Figure 4 The marine evaporation process in terms of the  $\delta$ -diagram.

where  $0.5 \leq n \leq 1$ ;  $C_D(^{18}\text{O}) = 28.5.5\text{‰}$  and  $C_D(\text{D}) = 25.115\text{‰}$ . The weighting term,

$$\theta = \frac{\rho_M}{\rho} = \frac{(1 - h')}{1 - h},$$

(see Figure 3) can be assumed equal to 1 for a small body of water whose evaporation flux does not perturb the ambient moisture significantly (Gat 1995); however,  $\theta$  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 1995). 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 & Allison 1988) or leaves (Allison et al 1985), a value of  $n \sim 1$  fits the data well.

Figure 4 shows in schematic manner the  $\delta(\text{D}) - \delta(^{18}\text{O})$  relationships in this process.  $\delta_E$  and  $\delta_L$  define a line in  $\delta(^{18}\text{O})$  vs  $\delta(\text{D})$  space, called the evaporation line (EL) whose slope is given by

$$S_{E(\delta)} = \frac{[h(\delta_a - \delta_L) + \varepsilon]_{2\text{H}}}{[n(\delta_a - \delta_L) + \varepsilon]_{18\text{O}}}. \tag{7}$$

As shown in Figure 4, from material balance considerations, both the initial water composition, the evaporated moisture, and the remnant liquid (such as lake waters, surface ocean water, or soil waters) all lie on this line. Obviously the humidity, the isotope composition of the air humidity, and the fractionation factors  $\varepsilon^*$  and  $\Delta\varepsilon$  [which in turn are temperature (for  $\varepsilon^*$ ) and mechanism (for  $\Delta\varepsilon$ ) dependent] determine the slope. A special case is presented when  $\delta_L$  and  $\delta_a$  are in isotopic equilibrium with each other for both isotopic species (H and O), in which case  $S_E = (\varepsilon^* + \theta n C_D)_{2H} / (\varepsilon^* + \theta n C_D)_{18O}$ , independent of  $h$ . This slope is  $S = 3.54$  when  $\theta = 1$  and  $n = 1/2$  and is lower for the case of the fully developed boundary layer, when for  $n = 1$  the equilibrium slope can be calculated to be  $S_E = 2.69$ . Having  $\theta < 1$  will increase the slope of the relevant evaporation line, as will be the case where  $\delta_L - \delta_a > -\varepsilon^*$ .

The Craig-Gordon model does not account for the case where evaporation of droplets and spray contribute to the evaporation flux. Furthermore, if surface waters are not well mixed so that a concentration gradient can build up between the evaporating surface skin and the bulk water, this needs to be taken into account by introducing a resistance in the liquid into the linear evaporation model (Craig & Gordon 1965).

### 3. THE ISOTOPIC COMPOSITION OF ATMOSPHERIC MOISTURE AND OF PRECIPITATION

To a first rough approximation, as shown in Figure 1, the water cycle can be described by its marine part, which accounts for 90% of the water flux. Craig & Gordon (1965) in their first attempt to describe the isotopes of the ocean-atmosphere system indeed modeled the marine atmosphere as a closed cycle (Figure 5a) assuming  $\delta_E = \delta_p$  (where  $\delta_p$ , which is close to  $\delta(^{18}\text{O}) = -4\%$  and  $\delta(\text{D}) = -22\%$ , is the worldwide average of precipitation) and that 2/3 of the moisture in the ascending air is rained out, resulting in air with a mean humidity of 75%. The marine moisture's isotopic composition is neither that of the evaporative flux ( $\delta_E$ ), nor is it in equilibrium with the ocean surface water; in the model it is assumed to be in isotopic equilibrium with the precipitation.

The isotope data of marine precipitation, collected by the IAEA-WMO precipitation network from island stations and weatherships (an excerpt of which is shown in Figure 6), show that marine air is not uniform and that a mean isotopic value for marine precipitation is  $\delta(^{18}\text{O}) = -2.5$  to  $-3.0\%$ , with variable  $\delta_D$  values, rather than that assumed in the above-mentioned model. The more realistic, though still grossly simplified model, shown in Figure 5b, assumes a value of  $\delta_p(^{18}\text{O}) = -3\%$ ;  $\delta(\text{D}) = -14\%$  for marine precipitation, which accounts for 90% of the evaporative flux. Solving Equation 5b for both the

isotopes and assuming marine air in equilibrium with the marine precipitation at a temperature of 20°C (with the humidity  $h$  and the factor  $\theta$  as open parameters) yield very reasonable values of  $h = 0.743$  and  $\theta = 0.48$ . This value of  $\theta \sim 0.5$  should be noted, as one encounters this value repeatedly over large evaporative systems (Gat et al 1995) as noted above.

As the marine air then moves over the coast and into the continents, the different marine air parcels appear to mix and homogenize, resulting in precipitation that is closely aligned along the so-called meteoric water lines (MWL). These are the lines in  $\delta$ -space whose formula is  $\delta(D) = 8\delta(^{18}O) + d$ , where  $d$  has been named the “deuterium excess” parameter by Dansgaard (1964); obviously the GMWL (Craig 1961b) is one such meteoric water line with  $d = 10\text{‰}$ . The further removed from the vapor source, the more depleted the isotopic values of the precipitation on each of these lines. Dansgaard (1964) recognized four parameters that determine this depletion in the isotopic values, including an altitude effect, a distance from the coast, and a latitude effect. All of these are basically related to the wringing out of moisture from the atmosphere as a result of cooling of the air mass, and indeed the correlation with the temperature appears as the overriding factor (Yurtsever 1975). Only the fourth parameter described by Dansgaard, the “amount effect,” has a more complicated structure (Gat 1980). Figure 7 shows the worldwide distribution of the oxygen-18 values in annual precipitation.

To explain these findings of terms of the Rayleigh equations described above, the early concepts on the evolution of the isotopic composition of “meteoric” waters envisaged an air mass (with water vapor mass  $N$  and a given isotopic composition  $R_v$ ) from which precipitation is derived by equilibrium condensation, so that at any time:  $R_p = \alpha^* R_v$ . The system then follows a “Rayleigh law,” according to Equation 1b, with the fractionation factor of  $\alpha^*$ . In integrated form  $\lambda = \lambda_0 + \varepsilon^* \ln f$ , with  $\lambda \equiv \ln R$ ;  $(\alpha^* - 1) \equiv \varepsilon^*$  and  $f$  is the fraction of remaining water vapor in the system ( $f = N/N_0$ ).

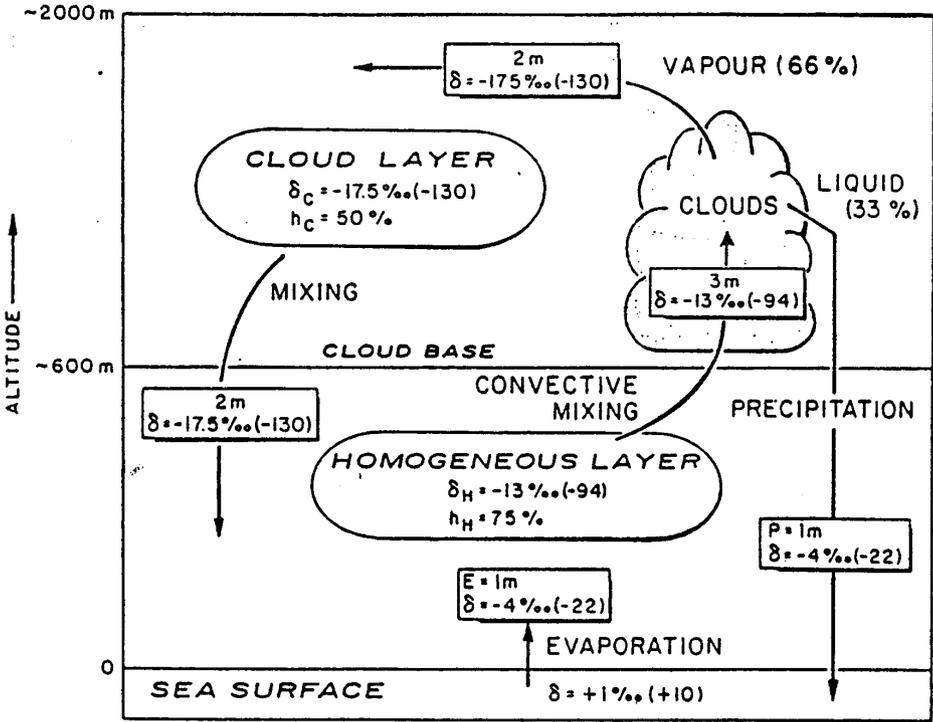
This equation establishes a linear relationship in  $\lambda_D$ - $\lambda_{18}$  space under isothermal conditions, i.e. when  $\alpha^*$  remains fixed throughout the process. The slopes of such Rayleigh lines in  $\lambda$ -space vary from the value of  $S_\lambda = \varepsilon_D^*/\varepsilon_{18}^* = 8.22$  to a value of  $S_\lambda = 9.6$  over the temperature range of 30°C to 0°C, according to the fractionation factors as given by Majoube (1971).

The  $\lambda$ - and  $\delta(\text{‰})$ -space are related by the equations:

$$\frac{R}{R_{\text{std}}} = \left(1 + \frac{\delta}{10^3}\right)$$

and

$$d\lambda = d[\ln(1 + \delta/10^3)] = \frac{d\delta/10^3}{(1 + \delta/10^3)}.$$



(a)

Figure 5 (a) The marine-atmosphere isotope model of Craig & Gordon (1965). The first of the  $\delta$  values refers to  $\delta(^{18}\text{O})$ , while the value in parenthesis refers to the value of  $\delta(\text{D})$ .

Translation of the Rayleigh lines into  $\delta(\text{‰})$ -space then imposes a deviation from linearity as the system becomes further removed from the zero of the  $\delta$ -scale. In  $\delta$  units the Rayleigh law is expressed in the following form:

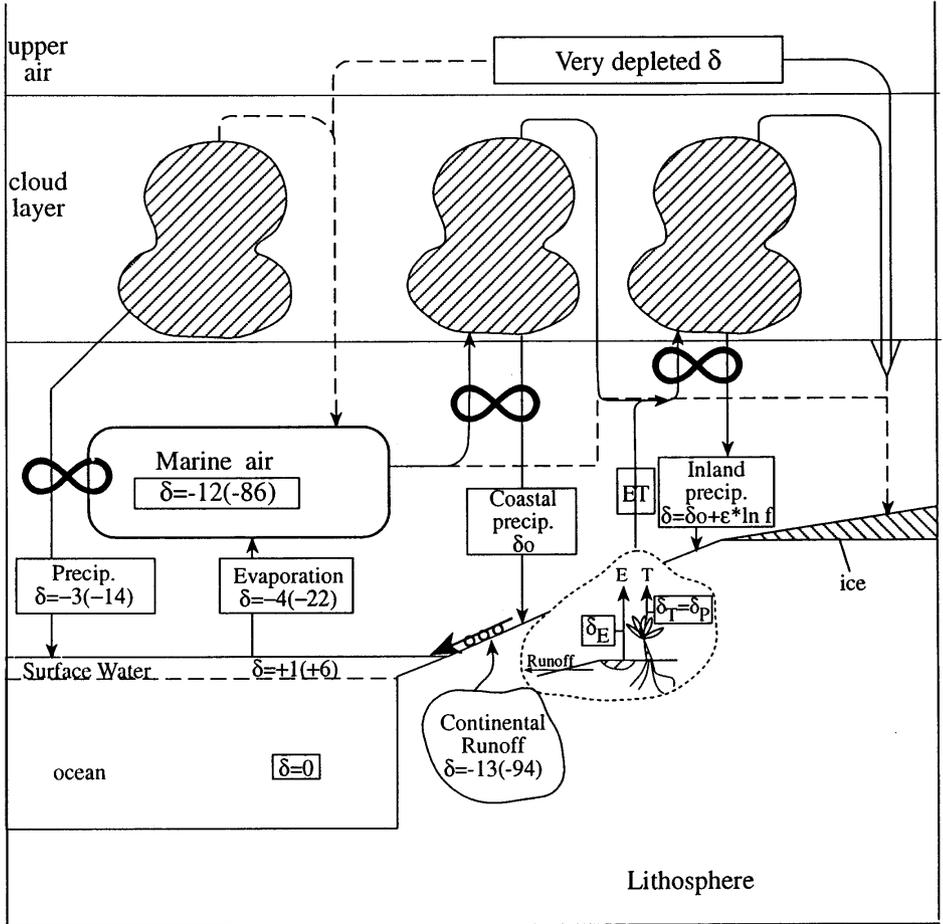
$$\frac{d\delta/10^3}{(1 + \delta/10^3)} = \epsilon^* d \ln f$$

and the Rayleigh slope in  $\delta$ -space will then be given by

$$(S_\delta)_{\text{Rayl.}} = \frac{\epsilon_D^* (1 + \delta_V/10^3)_D}{\epsilon_{18}^* (1 + \delta_V/10^3)_{18\text{O}}}$$

where  $\delta$  values refer to the vapor phase.

This slope is not a constant, but changes with the magnitude of  $\delta(^{18}\text{O})$  and  $\delta(\text{D})$ . The correction term  $(1 + \delta_V/10^3)$  becomes significant as the system is removed from its original state and acquires large negative  $\delta$  values, as is the case especially for the hydrogen isotopes. It is often neglected in other cases.



(b)

Figure 5 (b) Adaptation of the Craig-Gordon marine model to account for the terrestrial part of the hydrologic cycle.  $\infty$  indicates isotopic equilibrium between the vapor and precipitation fluxes.

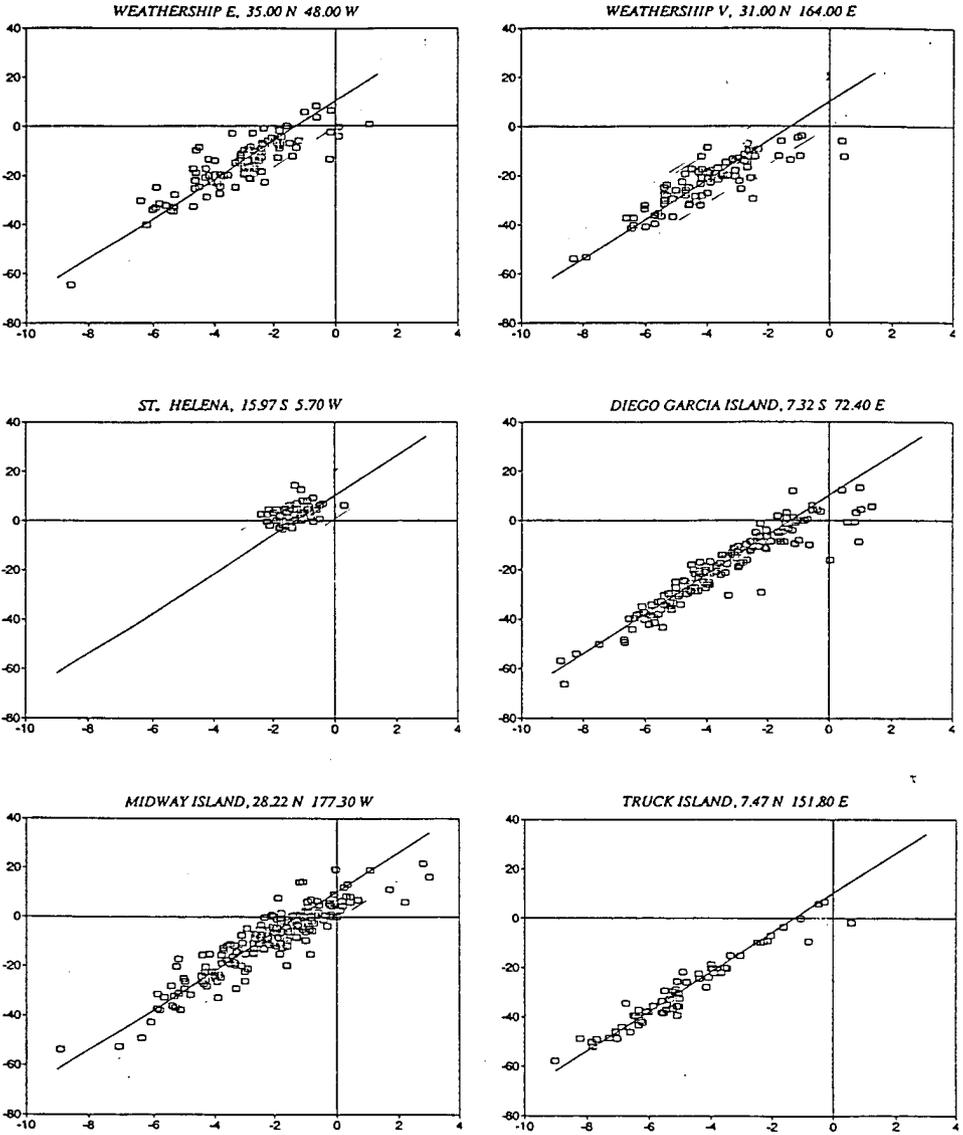


Figure 6 Monthly precipitation values at selected marine stations, based on data of the IAEA network on a  $\delta(D)$  vs  $\delta(^{18}O)$  diagram (Rosanski et al 1992).



Figure 7 Distribution of the annual mean  $\delta(^{18}\text{O})$  value in precipitation, based on the IAEA network data. (From Yurtsever & Gat 1981.)

An isothermal situation, however, is not a realistic model for continuous rainout as required by the Rayleigh formulation. The only close-to-isothermal natural system is the tropical rain forest, where  $T \sim 26^\circ\text{C}$ . In this case the abundant rain feeds on evapo-transpired (recycled) moisture so that the Rayleigh plot does not adequately describe the isotopic relationship (Salati et al 1979, Gat & Matsui 1991).

A more generally realistic hydro-meteorological model is that of an air-mass that loses part of its water content during a continental passage as a result of cooling by an orographic or latitudinal effect (Dansgaard 1953). The isotopic evolution of the precipitation derived from such an air mass can then be calculated under the assumption of vapor/liquid equilibrium during rainout, which, however, occurs at progressively lower temperatures. In this case the isotope composition of the precipitation closely follows the linear relationship of the MWL, as a consequence of the opposing effects of the  $(1 + \delta/10^3)$  correction term (which increases as the isotopic values are more depleted) and the increased isotopic fractionation factor (the  $\varepsilon^*$  term), as a result of the lower temperatures, as Taylor (1972) has shown.

The additive parameter in the meteoric water lines (which was defined as “d”) is evidently inherited from the air masses’ initial isotopic composition, as determined by the air-sea interaction regime: It remains relatively invariant during the Rayleigh rainout. Different air-sea interaction conditions at the source result in a series of parallel meteoric water lines (each of slope 8), for which the d-parameter in each case is related to the source of moisture (Gat 1981), in particular to the moisture deficit above the interface at the site where the air-masses’ water content is acquired (Merlivat & Contiac 1975). Particular regional lines relating to some locally effective moisture sources have been recognized, such as the eastern Mediterranean–MWL of  $d \sim 20\text{‰}$  (Gat & Carmi 1970) and a western Australian line with  $d \sim 14\text{‰}$ , etc.

The meteoric water lines discussed so far, which in essence are “Rayleigh lines,” obviously describe a spatially distributed data set, which describes the evolution of a particular precipitating air mass. They also apply to different air masses, with similar initial properties (water content, temperature, and  $\delta_{v,0}$ ), formed under comparable circumstances.

The physical reality behind the Rayleigh formulation of the rainout process is the isotopic exchange between the falling droplets and the ascending air in the cloud (Bolin 1959, Friedman et al 1962), resulting in precipitation that essentially “forgets” the isotopic label of very depleted isotopic values imprinted by the in-cloud processes, establishing isotopic equilibrium with the ambient air. 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 & Magaritz 1983). This simple scenario, which generally fits the data rather well, is modified under exceptional circumstances, namely,

- in the case where snow or hail reaches the ground; the isotopic exchange then does not occur, with the result that the precipitation is more depleted than in the equilibrium situation. Often, in addition, the solid precipitation forms show higher d-values due to nonequilibrium condensation during the growth of ice particles (Jouzel & Merlivat 1984).
- in the case of precipitation from strongly convective systems [thunder clouds, cold fronts, and tropical clouds associated with the ITCZ (intertropical convergence zone)] which are characterized 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.

In the two cases cited above, 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.

An additional process that can affect the isotopic composition of precipitation and of the atmospheric moisture is the evaporation from falling rain droplets beneath the cloud base or from surface waters. Evaporation from the falling rain results in the enrichment of the heavy isotopic species in the remnant drop along the so-called evaporation line; since these usually have a slope of less than 8 in  $\delta(D)$  vs  $\delta(^{18}O)$  space, the resulting precipitation shows a smaller d-value than at the cloud base. On the other hand, as shown in Figure 8, the evaporated moisture's isotope composition is characterized by larger d-excess value, so that the precipitation derived from an air mass into which the reevaporated moisture is admixed is also characterized by a large d-excess (Dansgaard 1964). A similar effect occurs with the evaporated flux from surface waters (Goodfriend et al 1989, Gat et al 1994).

The d-excess parameter has been shown to be a diagnostic tool for measuring the contribution of evaporated moisture to the downwind atmosphere (Gat et al 1994). The scaling factor for judging a change in the d-value of the perturbed atmosphere is given by

$$(d_E - d_a) = \frac{(d_L - d_a)}{1 - h} + (C_{D(D)} - C_{D(^{18}O)}) \times \theta \times n,$$

with subscripts E, a, and L standing for the evaporation flux, the ambient moisture, and the liquid, respectively.

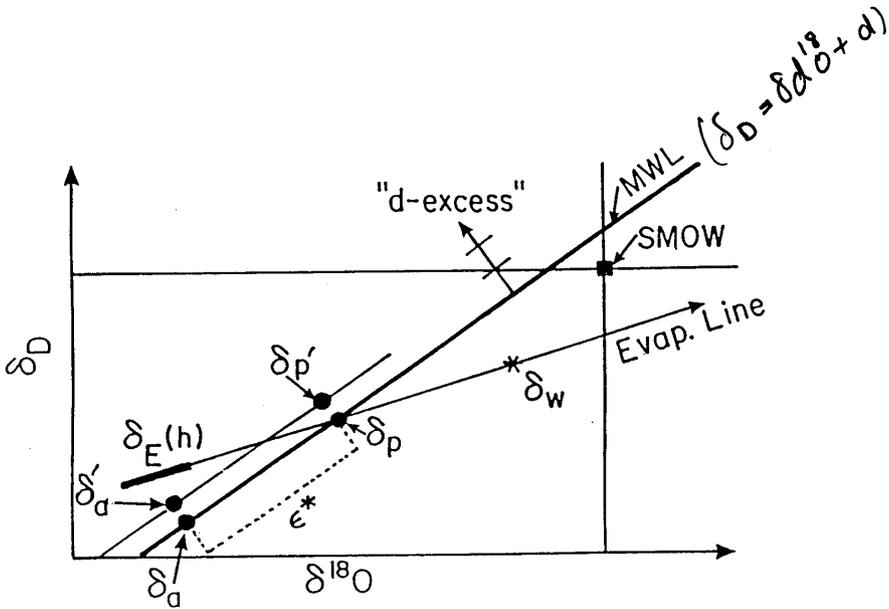


Figure 8 Schematics of the addition of evaporated moisture from surface water into the ambient atmosphere on the  $\delta$ -diagram.  $\delta_p = \delta$  value of precipitation;  $\delta_w = \delta$  value of the residual water after evaporation;  $\delta_E =$  the evaporation flux;  $\delta_a$  and  $\delta'_a$  are the atmospheric moisture before and after mixing with  $\delta_E$ .

Transpired moisture, in contrast, is usually not fractionated relative to soil moisture, so that if the latter is derived from precipitation, the transpired flux does not perturb the d-value of the atmospheric moisture (Salati et al 1979).

Some authors have attempted to fit a linear relationship (in  $\delta$ -space) to precipitation data from a particular station (usually the monthly averaged values as reported for the IAEA sampling network; IAEA 1992), naming such lines "local meteoric water lines." Such a procedure is not always meaningful, for instance when the various precipitation events are related to air masses with different source characteristics or to different synoptic patterns, especially during different seasons.

### 3.1 Seasonal and Short-Term Variation in the Isotopic Composition of Precipitation

As seasons change, the isotopic composition of rain at any site will reflect two basic changes in the rain pattern. The first is the change of the source characteristics over the ocean due to the seasonal change in ocean temperature

and air-sea interaction conditions. This affects the d-value primarily. Furthermore, different seasons have different degrees of rainout as dictated by the temperature along the air mass trajectory (which fixes the position along the “Rayleigh” line). In addition, the deviation from the Rayleigh relationship by either evaporative enrichment from falling raindrops, the admixture of reevaporated moisture, or the effects of snow and hail are also different for the different seasons.

A typical seasonal march of precipitation values is shown in Figure 9, based on data provided by the IAEA precipitation network (IAEA 1992). Both the heavy isotope content and the d-parameter vary over a yearly cycle, with the d-values for the winter precipitation usually somewhat higher. Evidently, the

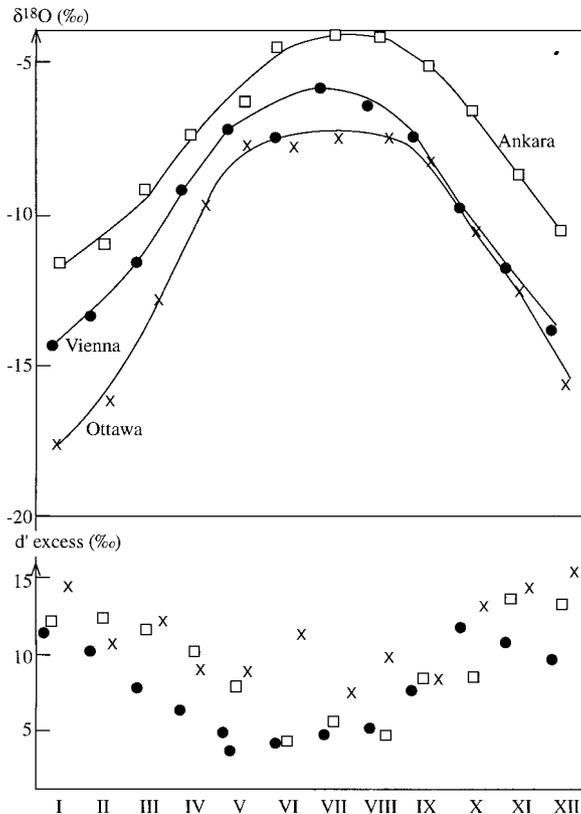


Figure 9 Seasonal change of  $\delta(^{18}\text{O})$  and  $d$  for selected continental stations, based on IAEA network data (IAEA 1992).

effect of high d-values in snow (Jouzel & Merlivat 1984) and the reduced degree of evaporation from falling rain droplets in winter when compared to the summer conditions usually override the effect of higher humidity at the oceanic source areas, which would result in the opposite effect (Merlivat & Jouzel 1979).

There are still insufficient data to fully characterize shorter term isotopic changes during a storm or in between individual precipitation events. It appears that such variations span a wide range of  $\delta$ -values, up to  $\pm 10\%$  in  $\delta^{18}\text{O}$  at times. Some early studies by Epstein (1956), Bleeker et al (1966), and Matsuo & Friedman (1967) indicated differences between rain produced by warm front uplifting or cold fronts and associated thunder clouds. These studies also showed that the beginning part of most rainshowers are 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, Gedzelman et al 1989, Rindsberger et al 1990, Pionke & Dewalle 1992, McDonnel et al 1990) make it appear that these differences reflect mainly the source of moisture and its rainout history, and only to a lesser extent the local rain intensity (EM Adar, unpublished data from the Negev). However, a notable exception to this rule is given by very strong tropical rains, associated with the ITCZ and its towering clouds, when precipitation with extremely depleted isotopic values are found at the peak of the downpour (Matsui et al 1983).

It is also of interest that in a continental setting the average air moisture and the daily precipitation are close to isotopic equilibrium with each another (Craig & Horibe 1967, Jacob & Sonntag 1991). This is not strictly true in a coastal setting or in regions of climate transition (Matsui et al 1983).

#### 4. PRECIPITATION-INFILTRATION-RUNOFF RELATIONSHIPS OVER LAND

##### 4.1 *Surface Interception of Precipitation*

As rain falls on the ground, a number of processes take place that modify the isotope composition of the incoming precipitation. Details of these processes depend on the nature of the terrain and on the characteristics of the rain, such as its amount and duration, intensity, and intermittency.

As shown in Figure 10 [which is an adaptation of an early model of Gat & Tzur (1967)], part of the incoming precipitation is intercepted on the canopy of the vegetation cover and in part lost by evaporation. Up to 35% of the precipitation is thus lost in tropical forests (Molion 1987) and 14.2 and 20.3%, respectively, on deciduous and coniferous trees in the Appalachian Mountains in the USA (Kendall 1993). While it evaporates, the water on the canopy,

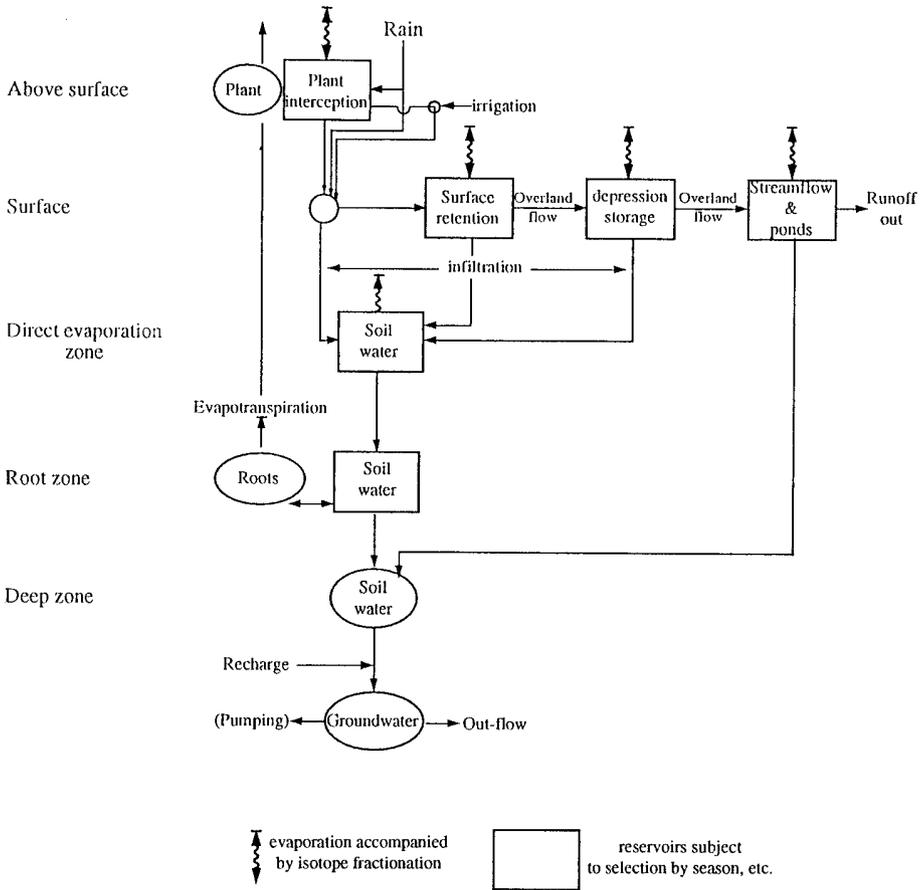


Figure 10 The interception reservoirs during the precipitation to runoff transition, based on Gat & Tzur (1967).

as well as in other surface reservoirs, is enriched in the heavy isotopes. If a further rainshower then follows before the canopy is dried up, this can flush the enriched residual of the partially evaporated waters to the ground.

In an attempt to recognize the isotopic signature imposed by the canopy interception, the isotopic composition of the throughflow under a tree was compared to that of the free-falling precipitation, as collected in a clearing of the forest (Leopoldo 1981, Saxena 1986, Dewalle & Swistock 1994). The results show that the expected isotopic enrichment in the throughflow is overshadowed by selection of part of the rainwater during the process. Apparently the less-

intense parts of the rainshower are preferentially lost. Since these usually constitute the isotopically most enriched part of the rain [corresponding to the amount effect of Dansgaard (1964)], this selection process introduces a negative bias that cancels the signature of the evaporation process.

The isotopic change on an interception volume  $V$ —where  $aV$  is the first rainshower,  $f$  is the fraction of  $V$  remaining after evaporative water loss, and  $bV$  is the follow-up shower—that results in throughflow when  $b > (1 - f)$  can be modeled with some simplifying assumptions. The isotopic composition of the throughfall is then

$$\delta_{\text{Th}} = \frac{f\delta_A + (b - 1)\delta_B}{(b + f - 1)} + \frac{f \int \varepsilon'(f) d \ln f}{(b + f - 1)}, \quad (8)$$

where

$$\frac{d\delta_f}{d \ln f} = \frac{h(\delta_f - \delta_{\text{atm}}) - \varepsilon}{(1 - h)} = \varepsilon'(f), \quad (9)$$

and  $\delta_A$  and  $\delta_B$  are the isotopic composition of the first and second rain events, respectively.

Whereas the first term is simply the weighted mean of the contribution of the first and second rainy spell, it is the second term that expresses the change in isotope composition due to evaporation. As was shown in a similar model applied to evaporation from the soil column (Gat 1987), this term has a maximum for  $f \sim 0.5$  and vanishes as  $f$  approaches either 0 or 1. Although the effect of evaporation from the canopy is thus difficult to quantify based on the local recharge flux, it is reflected in the downwind atmosphere in the form of an increase of the d-excess parameter of the atmospheric moisture. Gat & Matsui (1991) thus interpreted an increase of close to 3‰ in the value of d over the Amazon Basin as the cumulative effect of reevaporation from the canopy of the rainforest. The transpiration flux, while larger than that of the interception flux, is not expected to produce a change in d.

In the semi-arid zone the plant cover is less developed. Here the direct evaporation from temporary surface water impoundments that appear following stronger rains are expected to produce the largest isotopic signal. Gat & Tzur (1967) calculated the change between the isotopic composition of infiltrating water from such surface impoundments and the precipitation. For the climatic conditions of Israel the enrichment is less than 1‰ [in  $\delta(^{18}\text{O})$ ] on soils with infiltration capacity of  $< 2$  mm/hr in winter and  $\sim 2$ ‰ in summer. On heavy soils, higher distortions of up to 5‰ are expected. The effect is minimal on sandy soils where one does not encounter free surface waters. The effect of evaporation from within the soil column, and especially from well-ventilated sand, is discussed below.

## 4.2 *Surface Runoff*

Any water in excess of the holdup capacity of the surface reservoirs and of the infiltrability of the soil appears as surface runoff. Stable isotopes have played a decisive role in understanding the mechanism of their formation. A Canadian group pioneered this work (Fritz et al 1976). One chooses a particular rainfall event with extreme isotopic values and traces this pulse into the local and regional runoff. In the case of the temperate (wet) environment of Canada Sklash et al (1976) found that the antecedent wetness in the topsoil was involved in the runoff and that the last rainfall (which triggered the runoff event) was diluted by the past rainfalls of the season. Some degree of evaporative enrichment, presumably from waters in the topsoil, was detected (Fritz et al 1976). Similar results were reported from other localities (Mook et al 1974).

The situation is dramatically different in the arid zone. Here the deficiency of rainfall and long intervals between rain events result in a dry top layer, the absence of a continuous plant cover, and bare rock surfaces denuded of soils. Loess areas are baked dry to form a rather impermeable "desert pavement." Small amounts of rain that just wet the surface are then lost by complete evaporation. But even moderate rainfall events of just a few millimeters of precipitation result in local surface runoff from the hillsides. These combine, when the rain event is more continuous, to produce the phenomenal desert flash floods on a regional scale. Isotopic studies in the highlands of the Negev Desert have shown that the local runoff assumes the mean isotopic composition of the particular shower (Gat 1987) but that the large flash floods are consistently depleted in the heavy isotopes relative to the local rain (Levin et al 1980) which gives rise to them. This effect has been attributed to the intra-storm isotope variability where the most intense part of the shower shows depleted isotopic values (E Adar, unpublished data). Ehhalt et al (1963) have described a similar effect of depleted isotopic values in river runoff in South Africa.

The exception to these interrelationships are the sand dune areas in the dry zone, on which almost no surface flows occur because all incoming precipitation infiltrates into the open pore structure of the sand. The subsequent evaporation from within the sand column is another story.

## 4.3 *Lakes and Other Surface Waters*

The enrichment of the heavy isotopic species in residual surface waters as a result of the isotopic fractionation that accompanies evaporation was recognized long ago (Craig 1961b). This buildup of the isotopic enrichment and the recognizable isotopic signature of lake water is being utilized to establish the water balance of the lake, especially the ratio of inflow to evaporation fluxes, and as

a tool for studying mixing in the lake. It is also a useful tracer for detecting the addition of lake waters to adjacent groundwaters (Krabbenhoft et al 1994).

Under hydrologic steady-state conditions the isotopic buildup in a lake is given by

$$\Delta\delta = \delta_{L,SS} - \delta_{in} = \frac{(\delta_a - \delta_{in} + \varepsilon/h)}{\left[1 + \frac{F_{in}}{E} \cdot \frac{(1-h)}{h}\right]}, \quad (10)$$

where  $F_{in}$  and  $E$  are the influx and evaporation terms, respectively. Evidently, changes in either  $\delta_{in}$ ,  $\delta_a$ , the humidity ( $h$ ), or the hydrologic balance of the lake are determining parameters. Higher enrichments up to a limiting value of  $\delta_L = \delta_a + \varepsilon/h$  are possible for situations such as a string of lakes, i.e. when a number of evaporative elements act in series (Gat & Bowser 1991).

The subject of lakes, freshwater and saline ones, has been extensively reviewed over the years. Gat (1995) summarizes the state of the art in this respect.

#### 4.4 *Soilwaters*

Waters infiltrating from the surface drain through the void spaces in the soil, once the “field capacity,” i.e. the amount of water held against gravity on the grains of the soil by adsorption and capillary forces, is filled up. In very homogeneous soils one can recognize a piston flow pattern where the infiltrate of each season pushes the previous one ahead, as visualized by the tritium content of the moisture column (Dincer et al 1974, Gvirtzman & Magaritz 1990). In heterogeneous soils and fractured matrixes the pattern is more complicated.

The holdup in the soil column and transport through it does not, in itself, affect the isotopic composition of the infiltrating waters, except as far as mixing between moving and standing water parcels occurs. However, when evaporation from within the topsoil occurs during dry intervals between rain events, this results in an enrichment of the heavy isotopes in the residual waters (Zimmerman et al 1967). At some depth beneath the surface an evaporating front develops: Above it water transport is predominantly in the gaseous phase through the air-filled intergranular space; below it laminar flow and molecular diffusion in the water-filled pore space dominate. An isotopic concentration profile develops, representing a balance between the upward convective flux and the downward diffusion of the evaporative signature (Barnes & Allison 1988). Isotopic enrichments of  $^{18}\text{O}$  in excess of 10‰ relative to the precipitation are found in desert soils. Because the isotope enrichment at the evaporating front occurs by diffusion through a stagnant air layer, Equation 6a with  $n = 1$  applies. The isotopic composition of the residual waters are characterized by their situation on a low-slope evaporation line (Figure 11). These enriched waters are then

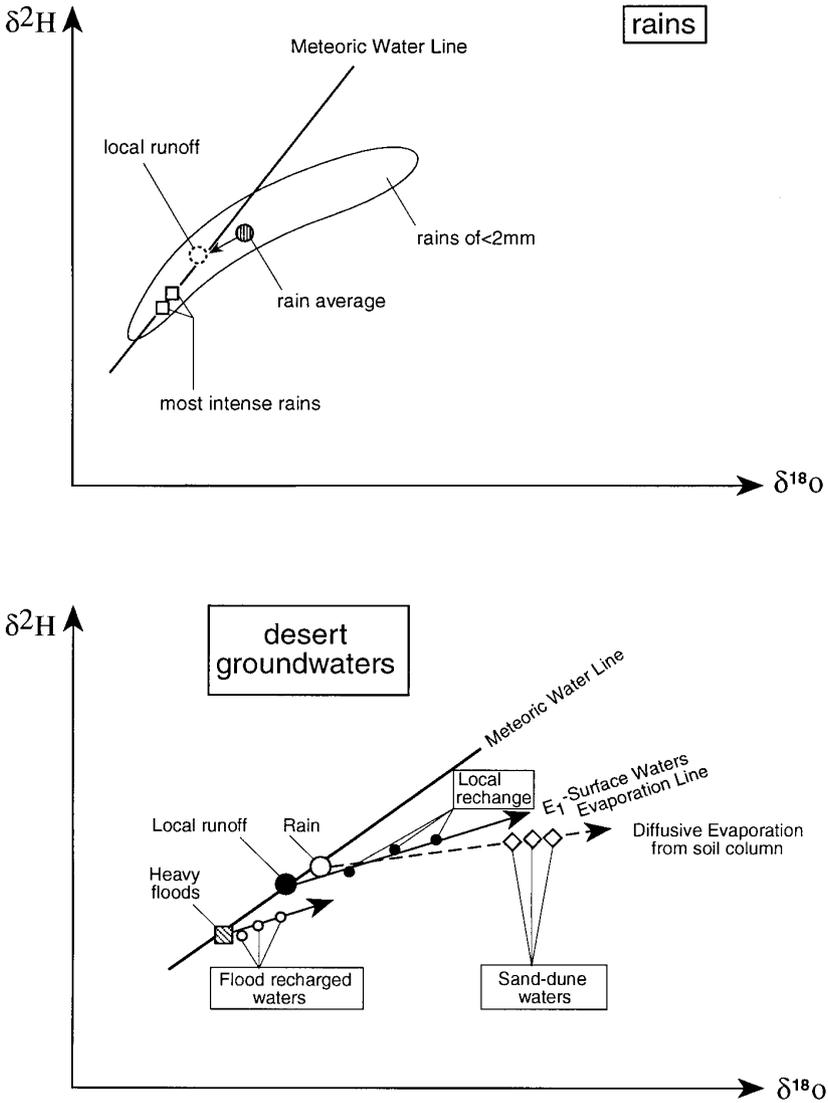


Figure 11 Isotopic relationships during the groundwater formation in the arid and semiarid zone.

flushed down by subsequent rains, imparting their evaporative isotope signature to the deeper soilwaters and groundwaters.

Direct evaporation from a bare soil surface is a factor in the water balance of an arid environment, in particular in sandy soils with a high water table [(e.g. dry lakes and diffuse groundwater discharge zones in the desert (Fontes et al 1986)]. In other areas it is the transpiration flux that accounts for the bulk of the evapo-transpiration flux from the soil. All evidence shows that there is no fractionation between isotopes as roots take up water. On the other hand, transpiration selectively utilizes the soilwaters during the growing period in spring and summer. If, as is typically the case, the seasonal input of precipitation is not yet mixed in the soil moisture of the root zone, this results in a selection of part of the seasonal cycle in the input to the groundwaters, resulting usually in more depleted isotope values in the deeper soil compared to the mean annual value. This property has been utilized to investigate the water balance of the groundwater recharge process, e.g. by Simpson et al (1970).

The two processes of direct evaporation from the soil and seasonal selection by transpiration have opposing isotopic signals. It is thus often difficult to use isotopic profiles in the soil as a measure of the evaporative history of a site. However, in combination with the salinity profile in the soil [salinity builds up as a function of the total evapo-transpiration flux (Eriksson & Khunakasse 1969)] more quantitative information can be resolved.

#### 4.5 *Water in Plants*

As discussed above, soilwater is taken up by the plants essentially unfractionated. This feature is used extensively to characterize the source of water for the plant and transpiration, whether soil- or riverwater (Dawson & Ehleringer 1991), snowmelt waters, or shallow or deep soilwaters in the arid zone where marked isotope gradients exist (Adar et al 1995). Yakir & Yehieli (1995) have also exploited this feature to distinguish between saline groundwaters and flash floods at the Dead Sea shore.

Leaves are the site of the evaporation front in the plant, specifically, the cells located near the stomata. These waters are highly enriched in the heavy isotopes (Gonfiantini et al 1965) when stomata are open, to an extent given by the steady-state isotope composition with respect to the evaporation process as given by the formula,  $\delta_{SS} = (1 - h)\delta_{in} + h\delta_a + \varepsilon$ , derived from Equation 4. Steady state can be practically achieved by virtue of the large flux/volume ratio in the transpiring leaves.

Allison et al (1985), Yakir et al (1990), and others who calculated the expected steady-state isotopic composition often found the overall enrichment in the leafwaters to fall short of the expected steady-state value. Allison interpreted such a difference to be the result of dilution by unfractionated source waters

in the veins of the leaves [amounting at times up to 30% of the total leafwater volume (Allison et al 1985)]. In the case of cotton plants, Yakir et al (1990), on the other hand, postulated that part of the leafwater (in the mesophyll cells) lags behind the steady-state enrichment due to a slow water exchange with the outer water sheath, which is assumed to be in momentary steady state relative to the evaporation process during the day and to take up unfractionated source water at night.

Under steady-state conditions obviously  $\delta_E = \delta_{in}$ , so that the transpiration flux is unfractionated with respect to the soilwater taken up by the plants.

The enriched isotopic values of plant waters is being used to check the authenticity of fruit products and distinguish them from those adulterated by water (Bricout et al 1972).

## 5. GROUNDWATERS

### 5.1 *Meteoric Waters*

The isotopic composition of groundwaters that are recharged by direct infiltration in the temperature zone follows that of the incident precipitation rather closely. The surface processes discussed above usually cause shifts in the isotope composition of less than 1‰ in  $\delta(^{18}\text{O})$  (Gat & Tzur 1967). The isotope composition of groundwaters are thus useful tools for identifying recharge sites (utilizing geographic effects on the isotopic composition of rain, such as the altitude effect), tracing mixing patterns and, in particular, for detecting the encroachment of lake waters (which are enriched in the heavy isotopes) (Payne 1970) of seawater and other extraneous water sources. In the arid zone, direct infiltration can result in recharge only on sand. In other cases some surface runoff is a necessary prerequisite for accumulating sufficient water depth to enable occurrence of recharge. Both small-scale local runoff, feeding locally important aquifer pockets in limestones and crystalline rocks, and large-scale regional flood flows, which recharge large deep regional aquifers, are important recharge mechanisms. Each of these recharge pathways imprints a distinguishable stable isotopic signature on the recharge waters (Figure 11).

In order to take full advantage of the possibilities of understanding groundwater formation, the detailed isotope effects of the recharge and runoff processes need to be established for different climate conditions and for each watershed. Such studies are still few and incomplete. When available, the changing isotope composition in groundwater recharge or runoff could be used as a sensitive monitor of climatic and anthropogenic changes in the watershed (Gat & Lister 1995).

Up to temperatures of about 60–80°C, the isotopic composition of groundwaters is conserved in the aquifer, so that even waters recharged in the Pleistocene

more than 10,000 years ago are still useful for climate reconstruction of these past conditions based on the isotopic composition of paleowaters (Fontes 1981). For example, the wetter climate of North Africa was established by interpreting paleowaters in the Nubian sandstone aquifers (Sonntag et al 1976). By virtue of the lower d-excess value of such waters ( $d \sim 7\text{‰}$ ), Merlivat & Jouzel (1979) established a higher humidity over the Atlantic at that time. However, the advantage of having a record for both oxygen and hydrogen isotopes in paleowaters (whereas most other climate proxies only give the  $^{18}\text{O}$  record) is offset by the difficulty of reliably dating such waters.

## 5.2 *Geothermal and Formation Water*

At elevated temperatures of more than  $80^\circ\text{C}$  the isotopic exchange between the groundwater and the host rock becomes noticeable, resulting in an “oxygen shift” towards more positive  $\delta(^{18}\text{O})$  values. However, extrapolation of the isotopic composition of such waters [at constant  $\delta(\text{D})$ ] enables one, in many cases, to identify the meteoric water origin of such waters. At still higher temperatures and when steam venting occurs, the isotopic exchange between water and the steam at these elevated temperatures causes changes of both oxygen and hydrogen isotopes. These relationships have been extensively utilized for the exploration of geothermal systems and reservoirs, as reviewed by Panichi & Gonfiantini (1981).

Below the cycling meteoric waters one often encounters brackish waters and brines in deeper geologic formations. The term “formation water” is used to denote such water that is obtained from a geologic formation and is representative of its fluid content. No a priori connotation concerning the origin of salinity or of water is intended.

The isotopic composition provides information about the origin and history of the water phase. Recent studies have indicated that in marine sediments on the continents, the original marine brines have as a rule been replaced by meteoric waters (Clayton et al 1966, Hitchon & Friedman 1969). Unfortunately, many aspects of the mechanism of movement of water and salt remain obscure. The evolution of such brines has been discussed by Fleisher et al (1977).

Since chloride is the dominant anion of all these brines, it is reasonable to suppose that, initially, the salts were mainly of a marine origin.

The simplest initial solution to be considered is that of seawater or marine interstitial water. Another set of initial solutions that can be considered comprises continental surface waters. The origin of the dissolved salts in the formation waters may then be quite varied, ranging from marine salts to residual salts of continental weathering reactions. In another model, the sources of dissolved salts are minerals in the geologic formations, especially evaporites. In this

model, there is then no a priori relation between the dissolved salt composition and the isotopic composition of the water.

These initial solutions are then exposed to various processes. Three geochemical processes can be considered. The first process is surface exposure accompanied by evaporative water loss. According to Lloyd (1966), the isotope composition tends in this case towards an enriched value while salinity increases.

A second process is that of ultrafiltration by clay membranes. This process results in a slight enrichment of both  $^{18}\text{O}$  and D in the residual brine, corresponding to a parallel increase in salinity with a preferential increase of multivalent cations relative to sodium. The single stage isotope fractionation factors in dilute NaCl solutions as a result of this process are 0.9993 for  $^{18}\text{O}$  and 0.998 for deuterium (Coplen & Hanshaw 1973). The fractionation effect is thus smaller by one order of magnitude than the fractionation in the evaporation process. The relationships between the increase of salinity and increase in  $^{18}\text{O}$  content by ultrafiltration for the solutions considered by Coplen & Hanshaw (under conditions of Rayleigh fractionation) is given by the equation  $S = S_0 \exp(\Delta\delta^{18}/0.7)$ . If one assumes that the process starts with seawater pushed through a clay membrane filter until the dissolved salt increases by a factor of 4 to a concentration of 150 g/liter (which are concentrations typical of formation waters), then this relation predicts an enrichment of  $^{18}\text{O}$  in the water by + 1%. A parallel increase in the Ca/Na ratio would be expected (White 1965). If additional freshwater then flows through this system, a further increase of the Ca/Na ratio may result (forming a  $\text{CaCl}_2$  type water), accompanied, however, by a possible slight decrease in the concentration of total dissolved solids. The  $^{18}\text{O}$  content of the residual brine approaches in the steady-state limit an enrichment of 0.7‰ relative to the meteoric water (this being the single stage fractionation factor for this process).

A third process that can affect the isotopic composition of formation waters is interaction with minerals in the formation, especially at elevated temperatures. In this case the changes in the chemical and isotopic compositions depend on the nature of the minerals. One extreme case occurs when the fluid is in contact with limestones: The  $^{18}\text{O}$  content of the fluid increases by exchange, without significant change of the salinity. Another extreme occurs in the presence of anhydrous evaporite deposits, which when they dissolve, cause the salinity to increase without significantly changing the isotope composition of the fluid. White et al (1973) have claimed that in the presence of clays deuterium exchange can occur, resulting in a slight decrease of the  $\delta(\text{D})$  values.

The three processes mentioned result in increases of salinity and enrichment of  $^{18}\text{O}$  in the brine (Figure 12). Mixing with meteoric waters has the opposite effect, i.e. a decrease in salinity and depletion in  $^{18}\text{O}$ . The evidence of the

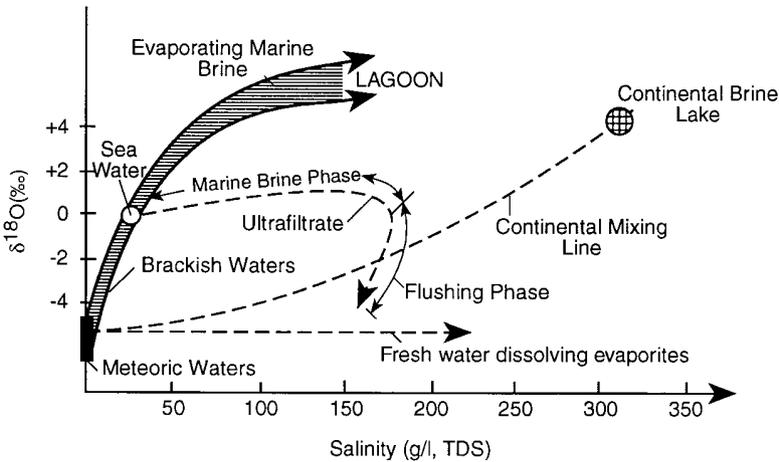


Figure 12 Isotopic changes of formation waters.

hydrogen isotopes is more ambiguous, since both exchange with clays and mixing with meteoric waters results in slightly depleted  $\delta(\text{D})$  values.

Figure 12 shows the changes in salinity and isotopic composition predicted for the waters, as these evolve through any of the processes described above or when mixing with meteoric waters occurs.

## 6. ICE AND SNOW

Ice and snow present a special situation in isotope hydrology. Unlike the liquid raindrop, the solid phases do not exhibit isotope exchange with atmospheric moisture but conserve the isotopic composition as formed in the cloud. Because of this, hailstones were used to probe the conditions within a thundercloud (Facy et al 1963, Macklin et al 1970, Jouzel et al 1975).

As shown by Jouzel & Merlivat (1984) the formation of snow shows a non-equilibrium effect that gives rise to precipitation with an elevated  $d$ -excess value. As an example, snow in Jerusalem was measured with a value of  $d = 32\text{‰}$ , compared to  $d \approx 20\text{‰}$  in the ambient air. The same effect is responsible for the seasonality of  $d$ -values in precipitation of the northern latitudes, e.g. in Canada (Fritz et al 1987), with higher values in winter. It has been noted above that the removal of snow or hail from an air mass with which it is not in isotopic equilibrium does not satisfy the conditions for a Rayleigh process.

The accumulation of snow on the ground, with each successive snowfall keeping its identity (with the exception of mixing caused by snowdrifts) has

enabled one to use cores in glaciers to establish the most reliable isotope record of precipitation as far back as the Pleistocene (e.g. Dansgaard et al 1969). The establishment of the isotope record in glaciers constitutes one of the highlights of isotope hydrology, which is not discussed further here in view of the many good descriptions available.

The sublimation of the ice removes the material layer by layer. It could be expected then that this process would not alter the isotopic composition of the remaining snowpack, unlike the situation in an evaporating water body in which the effect of surface fractionation is propagated into the residual liquid by mixing. However, this simple model is not realized in practice, apparently due to diffusion of vapor through the void spaces in the snow pack and also due to some surface melting and percolation of meltwaters into the remaining snow. As a result of such processes, which have been extensively explored (Moser & Stichler 1974, Whillans & Grootes 1985, Friedman et al 1991, also the review of Arnason 1981) meltwaters do not always show the same isotopic composition as that of the snow; the remainder of the snow pack shows increasing enrichment of the heavy isotopes and reduced values of the  $d$ -parameter. An extreme example is reported by Claassen & Downey (1995) in the canopy-intercepted snowfall on evergreens, where enrichments of up to 2‰ in  $\delta(^{18}\text{O})$  are found.

Another facet of solid-phase isotope hydrology is the constitution of the sea-ice cover and of lake ice. Merlivat (1978) has shown that a marine glacier is made up mostly of accumulated precipitation and that only the very bottom layers are frozen seawater. On a lake in northern Wisconsin, on the other hand, Bowser & Gat (1995) found the lower half of the ice cover to be ice grown in equilibrium with the lake water, which, however, is mixed with unfractionated lake water trapped in the ice during the freezing process. The upper 50% of the ice core is evidently made up of lake water that overflows on top of the subsiding ice layer, mixes with the accumulated snow on the surface, and is then refrozen.

## 7. APPLICATIONS TO PALEOCLIMATOLOGY

The usefulness of the changes in isotope composition in the hydrologic cycle for hydrological studies is self-evident. The essentially conservative behavior of the isotope in the subsurface, on the one hand, and the characteristic and well-documented changes in the atmospheric section of the cycle and at the surface-atmosphere interface, on the other hand, provide a reliable tracer (fingerprint). This tracer has been utilized to determine the origin of water bodies, to quantify the water balance of surface and subsurface reservoirs, and to trace the mechanisms of salinization of water resources (Gat 1975).

The isotope record in climatic archives is increasingly called upon to provide paleoclimatic information. This analysis is based on two premises: (a) that the

isotope composition of the proxy material can be related to that of the water cycle of past periods and (*b*) that from the latter one can evaluate the relevant climatic or hydrologic parameters. Both of these premises need a critical appraisal.

As for the first of these premises, the situation is fairly straightforward where the proxy material is the water substance itself, as in ice cores, paleowaters, or interstitial waters in sediment cores. However, the constancy of the isotopic record has to be addressed, whether with regard to diffusive mixing in the column, the interaction with the rock matrix or sedimentary material (affecting the oxygen isotopes primarily), or the effect of biogeochemical interactions that occur in porewaters, which affect mainly the hydrogen isotopes. The porewater system cannot be regarded as a closed one for more than a few thousand years at best because the older isotopic signals are erased by porewater diffusion (GS Lister, unpublished data).

In the case of proxy materials such as lacustrine carbonates, shells of land-snails (Goodfriend et al 1989), or plant materials (cellulose), the major issue is the relationship of the isotopic composition in the proxy to the environmental waters. Lake carbonate deposits are related to the lake waters through a temperature-dependent fractionation factor (often compounded by an additional "vital effect," i.e. a biochemical effect). The lake waters, in turn, are related to the inflowing waters isotope composition and to the degree of isotopic enrichment of the lake waters.

Thus both hydrological and climatic factors are involved, as well as ecological ones, as discussed by Talbot (1990) and Gat & Lister (1995).

Plant material, on the other hand, is related to the hydrological cycle through the soilwater taken up in the roots. The isotope composition is, however, modified by hydrological and physiological processes in the plant, such as water stress, ambient humidity, and also the timing of stomata openings.

In all these cases the isotope composition of the precipitation is thus modified by factors that are climatically and environmentally controlled and that need to be recognized in great detail under a variety of climatic conditions.

The second premise mentioned above—which concerns the interpretation of changes in the isotope composition of precipitation with time in terms of changing climate parameters, temperature in particular—is based on the strong correlation between the isotopic composition of precipitation and the ambient temperature in the present-day water cycle. Various authors have attempted to impose this relationship on the paleo-record. This obviously could be an illusive procedure when one considers that the sources and sinks of water as well as details of the global circulation undergo important changes over the periods concerned. The approach of modelers such as Joussaume & Jouzel (1993), who attempt to derive global isotope maps for past climate conditions

as reference points for the local climatic record, is a more promising approach. This effort, however, requires a rather detailed understanding of the boundary conditions both over the ocean and at the plant (soil)-atmosphere interface.

It is interesting to note that the interest in the paleoclimatic applications of isotope hydrology has been a stronger motivation for the study of stable isotopes in the hydrologic cycle (yielding much useful hydrological information as a by-product) than that provided by the hydrological sciences directly.

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