

The heavy isotope enrichment of water in coupled evaporative systems*

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Abstract—The enrichment of heavy isotopic species of hydrogen and oxygen in a coupled series of evaporative steps is limited by the feedback of atmospheric moisture. A number of feedback schemes involving the admixture of evaporated moisture into the atmosphere is examined. The humidity is found to be the controlling parameter, so that high degrees of enrichment of the heavy isotopes are an attribute of the arid zones. The relation $\delta_L - \delta_a = \frac{\epsilon}{h}$ describes a limiting situation, beyond which no further heavy isotope enrichment can occur.

INTRODUCTION

THE CHANGES IN the isotopic composition of a water body exposed to evaporation are well documented (DINCER, 1968; MERLIVAT, 1970; GAT, 1981, 1991; GONFIANTINI, 1986). The evaporation flux is depleted in the heavy isotopic species $H_2^{18}O$ and HDO relative to the water pool; as a result, the residual waters are enriched in the heavy isotopes. The isotopic composition is expressed in δ units in per mil relative to mean ocean water (CRAIG, 1961), using the notation δ_{18} for the heavy oxygen species and δ_D for the hydrogen isotopes.

Based on the Craig-Gordon linear resistance model (CRAIG and GORDON, 1965), the isotopic composition of the evaporating flux is given as

$$\delta_E = \frac{\alpha^* \delta_L - h \delta_a - \epsilon}{(1-h) + \Delta\epsilon/1000} \sim \frac{\delta_L - h \delta_a - \epsilon}{(1-h)} \quad (1)$$

where h is the relative humidity, normalized to the saturated vapor pressure at the surface of the liquid; δ_a is the isotopic composition of atmospheric moisture, δ_L that of the liquid and α^* the equilibrium fractionation factor from which the value of ϵ^* is derived as follows: $\epsilon^* = (1 - \alpha^*) 10^3$; $\epsilon = \epsilon^* + \Delta\epsilon$ where $\Delta\epsilon = (1-h)C_K$, and C_K is a parameter which expresses the nonequilibrium fractionation which occurs at the air/water interface due to the diffusion of the isotopic water molecules.

Equation (1) can be rewritten in the following form:

$$\delta_E - \delta_L \sim \frac{h(\delta_L - \delta_a) - \epsilon}{(1-h)} \quad (1a)$$

from which it is apparent that there cannot be any further fractionation due to the evaporation process once

$$\delta_L - \delta_a \geq \epsilon/h. \quad (1b)$$

This interesting relation will be further discussed below.

If F_+ stands for the influx and δ_+ is the weighted average isotopic composition of F_+ —if further, E is the evaporation flux and F_- is the outflow which is assumed to be unfractionated with respect to the water body's isotopic composition so that $\delta(F_-) = \delta_L$ —then the isotopic balance of the water body (of volume V) is given at hydrologic steady state, when $V = \text{constant}$ and $F_+ = F_- + E$, by the expression

$$V \frac{d\delta_L}{dt} = F_+ \delta_+ - F_- \delta_L - E \delta_E \quad (2)$$

On introducing the value for δ_E from Eqn. (1) into Eqn. (2) one obtains

$$\frac{d\delta_L}{dt} = \frac{F_+}{V} (\delta_+ - \delta_L) - \frac{E}{V} \frac{[h(\delta_L - \delta_a) - \epsilon]}{(1-h)} \quad (3)$$

whose steady-state solution (from the isotopic point of view) yields the following expression for the enrichment of the heavy isotopes in the water body relative to the influx:

$$\Delta = \delta_{ss} - \delta_+ = \frac{\left\{ \delta_a - \delta_+ + \frac{\epsilon}{h} \right\}}{\left[1 + \frac{F_+ (1-h)}{E h} \right]}. \quad (4)$$

According to this equation and for given values of δ_a and δ_+ , the determining parameters for the heavy isotope enrichment are, on the one hand, the inherent fractionation factors associated with the

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phase transition, namely ϵ^* and C_K , and, on the other hand, the humidity term which is the only ambient parameter which appears explicitly in this formulation. However, the ambient temperature appears in a hidden way since both ϵ^* and h are a function of the prevailing temperature at the surface. Moreover, the wind and turbulence regime at the water/air interface controls the value of parameter C_K (MERLIVAT and COANTIC, 1975).

In an isolated evaporating system which does not influence its environment, h and δ_a are fixed by the meteorological situation. The value of δ_+ is determined by the hydrologic setting of the lake or system. In the case of a midcontinental setting, the precipitation and runoff (which together make up the δ_+ term) and the atmospheric moisture are often in isotopic equilibrium (CRAIG and HORIBE, 1967; MATSUI *et al.*, 1983), so that $\delta_a = \delta_+ - \epsilon^*$.

Equation (4) can then be further simplified:

$$\Delta = \delta_{ss} - \delta_+ = \frac{(1-h)(\epsilon^* + C_K)}{\left[h + (1-h) \frac{F_+}{E} \right]} \quad (4a)$$

In this paper, however, we will be discussing coupled systems which are not isolated, but where a feedback between the evaporation process and the environment takes place through either one or both of the following coupling mechanisms:

- the introduction of the heavy waters from one such evaporative system into a downstream water body;
- admixture of the evaporated moisture into the ambient air, which then affects downwind evaporative systems.

The first of these effects we can call a "string-of-lakes" effect, which exercises its control through the influx term δ_+ . The second mechanism obviously constitutes a coupling by means of the atmosphere, affecting the parameters h and δ_a . Either of these feedbacks changes the value of $(\delta_a - \delta_+)$, and thus, according to Eqn. (4), the degree of enrichment of the heavy isotopic species in an evaporative element which is situated downstream (or downwind), will be smaller than if such an element were situated in an unperturbed environment.

Figure 1 shows a number of feedback schemes for a series of evaporative ponds. Three variants of hydrologically coupled strings-of-lakes with different atmospheric feedbacks are shown, as well as systems which are coupled only atmospherically but which differ in the composition of the liquid input to the downwind evaporation systems.

In the following sections the direction and mag-

nitude of the isotopic changes in these systems will be discussed.

THE "STRING-OF-LAKES" EFFECT

Let us consider a series of evaporating elements, numbered $1 \cdots n$, whose outflow constitutes the influx into the consecutive element in the series. Examples of such a system are a series of lakes or reservoirs situated along a river, or the case of arid zone hydrologic systems where water moves from the rain, through stages of surface flows and soil waters into either plants, discharge ponds, or groundwaters, with some evaporation occurring all along the hydrologic path. Let us assume further, as a first approximation, that the evaporation exerts a negligibly small effect on the atmospheric moisture, so that each of the evaporation elements interacts with an atmosphere characterized by a given value of humidity "h" and of the atmospheric moisture's isotopic composition, δ_a (model C, Fig. 1). It is then evident from Eqn. (4), which describes the buildup of the heavy isotopes in each evaporation step, that the heavy isotope enrichment downstream falls short of that of the primary element, for the simple reason that the term $(\delta_a - \delta_{+,n}) < (\delta_a - \delta_{+,0})$ because $\delta_{+,n}$, the δ value for the input to the n th element, is a larger number than $\delta_{+,0}$.

The enrichment in the heavy isotopic species of the n th element of such a series, according to Eqn. (4), and assuming that $\delta_{+,n} = \delta_{L,(n-1)}$, is given by the expression

$$\Delta_{n,n-1} = \delta_{L,n} - \delta_{L,n-1} = \frac{\left(\delta_a - \delta_{L,n-1} + \frac{\epsilon}{h} \right)}{\left[1 + \frac{F_+}{E} \frac{(1-h)}{h} \right]} \quad (5)$$

Using the shorthand notation of $a \equiv \frac{F_+}{E} \frac{(1-h)}{h}$, this value of $\Delta_{n,n-1}$ is related to the first element in the series $\Delta_{1,0}$ in the following manner:

$$\Delta_{n,n-1} = \left[\prod_{x=1}^{(n-1)} \frac{a_x}{1+a_x} \right] \Delta_{1,0} \quad (5a)$$

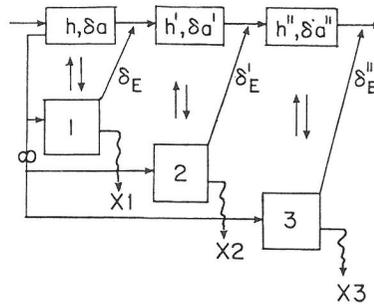
If one can assume in a simplified version that all elements are similar in the hydrologic sense so that $a_1 = a_2 = \cdots$, then Eqn. (5a) simplifies and becomes a power series:

$$\Delta_{n,n-1} = \left(\frac{a}{1+a} \right)^{n-1} \Delta_{1,0} \quad (5b)$$

The overall, summed-up enrichment of the heavy isotopic species along the series is given by the expression

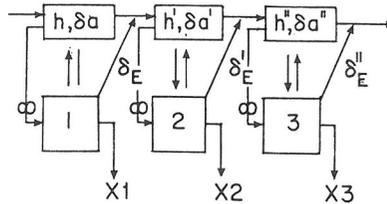
Model A

Feedback to atmosphere:
constant input



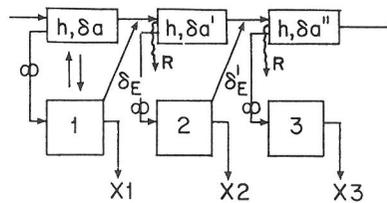
Model B1

Feedback to atmosphere:
equilibrium input at each stage



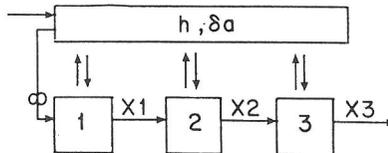
Model B2

With Rayleigh rainout



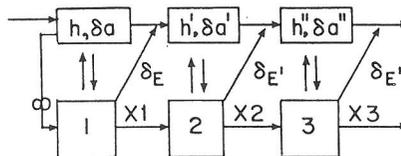
Model C

String-of-lakes, no feedback
to atmosphere



Model D1

String-of-lakes, with feedback
to atmosphere



Model D2

String-of-lakes with counter-
current atmospheric flow

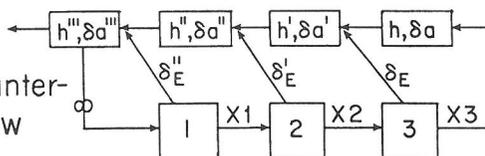


FIG. 1. Flow schemes for coupled evaporation elements with varied feedback loops. In each scheme the upper series of boxes represents the atmospheric reservoir and the lower series of boxes (numbered consecutively) represent the evaporation elements.

$$\Delta_{n,0} = \delta_{L_n} - \delta_{+,0} = \left[1 + \sum_1^{n-1} \left(\frac{a}{1+a} \right)^x \right] \Delta_{1,0}. \quad (6)$$

The buildup of isotopically heavy species as a function of the humidity for different values of F_+/E (up to the limiting case of $F_+/E \rightarrow 1$) is shown in Fig. 2.

Evidently, not only is the heavy isotope enrichment of a single evaporation element a function of the parameters that make up "a," but also the amplification of the heavy isotope enrichment in a series of evaporative elements.

The maximum heavy isotope enrichment achieved in an infinite series of elements is simply

$$\Delta_{\infty,0} = (1+a)\Delta_{1,0} = (\delta_a - \delta_{+,0}) + \frac{\epsilon}{h}. \quad (6a)$$

Not too surprisingly, this corresponds to the condition set forth in Eqn. (1a). This final degree of heavy isotope enrichment is no longer a function of the hydrologic parameters F_+/E . However, as shown in Fig. 3, the rate at which this limiting value is approached bears an inverse relation to "a" (or to F_+/E for a given value of h).

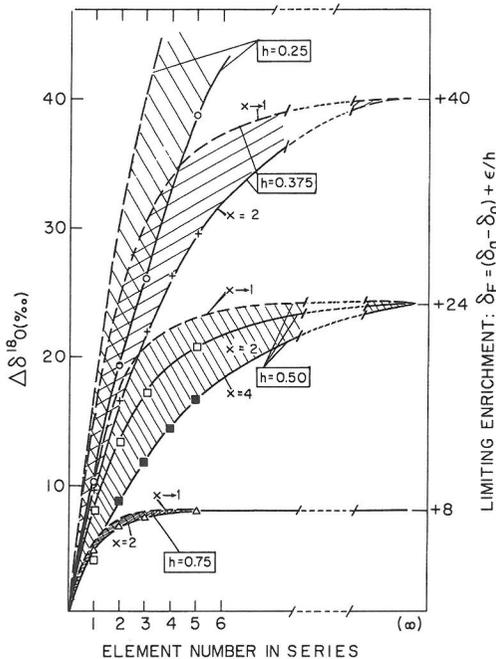


FIG. 2. ^{18}O enrichment along the elements of an evaporative series (string-of-lakes) for different humidity values and a range of $X = F_+/E$; open symbols—for $X = 2$; filled symbols—for $X = 4$; the limits of $X \rightarrow 1$ (terminal lakes' system) are shown by stippled lines. The ultimate enrichment obtainable as $n \rightarrow \infty$ is shown on the right-hand margin: $\delta_r = (\delta_a - \delta_{0,+}) + \epsilon/h$.

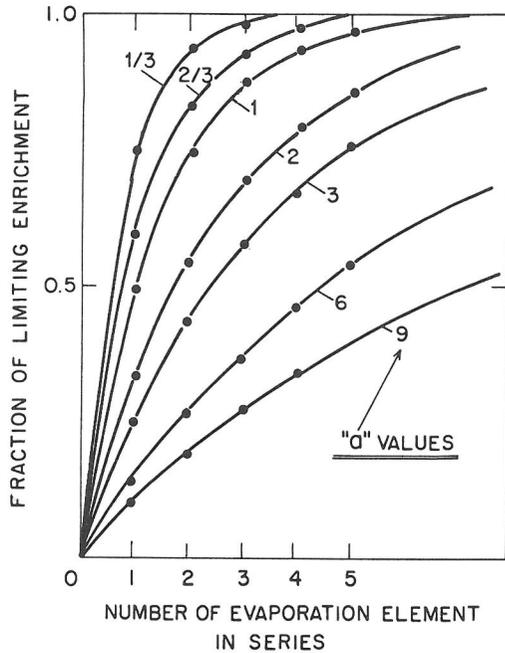


FIG. 3. The fraction of the ultimate enrichment achieved along a string-of-lakes, for a range of values of a according to the formula: $f(n) = \sum_{x=1}^{x=n} \frac{a^{(x-1)}}{(1+a)^x}$.

The ultimate heavy isotope enrichment is very considerable when humidity is low but is more restrained at humidities above 50%, when the atmospheric flux becomes increasingly important. Indeed, humidity is the controlling parameter, and already the second or third evaporation element of a series (provided that evaporation is a dominant component of the water balance in each of them) enables one to assess the humidity rather accurately, as can be seen in Fig. 2. This attribute of the string-of-lakes effect makes the isotopic composition of remnants of highly evaporative systems, such as desert plants or carbonate nodules, valuable paleoclimatic indicators, since they provide a rather clear indication of the prevailing humidity with relatively little interference from other changeable climate parameters.

It should be noted that a desert river which continually loses water by evaporation, such as described by FONTES and GONFIANTINI (1967), can be considered an example of a "string-of-lakes" of infinite extent. Such a system finally approaches high δ values even though each incremental element shows a high throughflow ratio and a small enrichment.

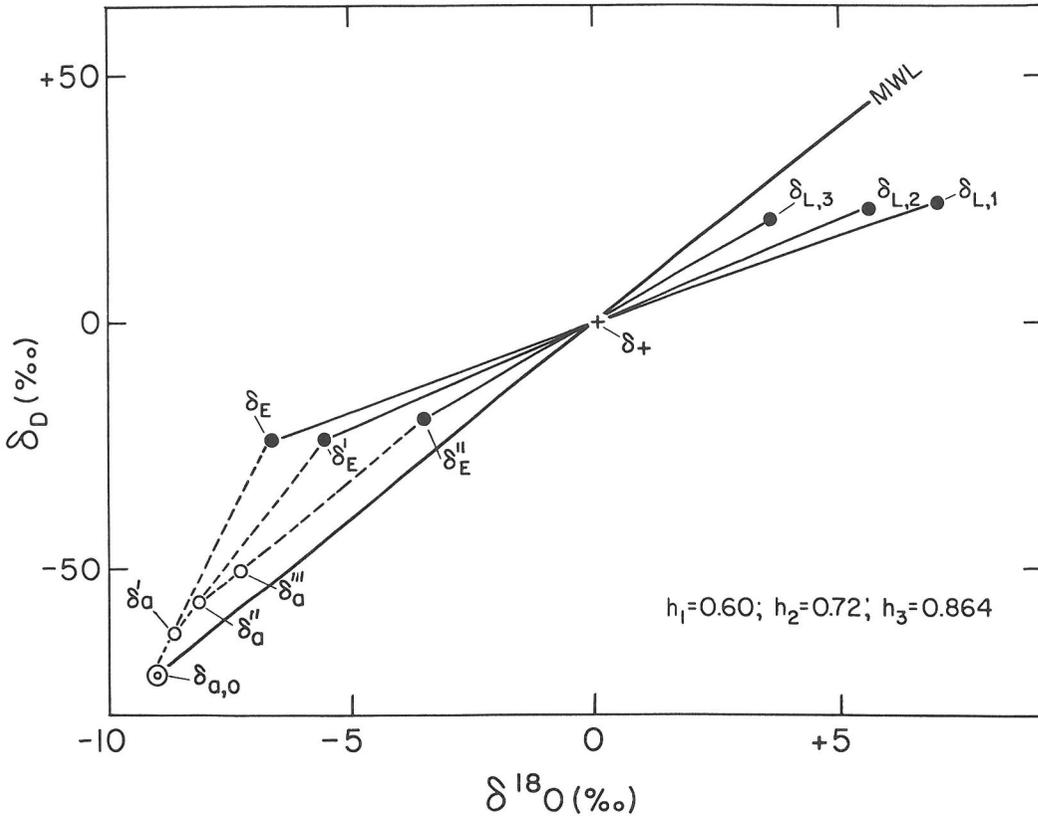


FIG. 4. $\delta_D - \delta_{18}$ plot of the steady-state isotopic values in consecutive evaporation elements $n = 1 \dots 3$, for a group of lakes which are all fed by the same input water (δ_+), with buildup of atmospheric humidity by the evaporation flux (δ_E) according to model scheme A; for $X = 2$ and $b = 1.2$.

The value of the ultimate enrichment of the heavy isotopic species given by the relation $\delta_1 = (\delta_a - \delta_{+,0} + \epsilon/h)$ depends on the value of the atmospheric parameters h and δ_a , but one also must take note of the mechanism of fractionation of the final stage of enrichment, as this determines the value of $\Delta\epsilon$, specifically the value of C_K . As shown by ALLISON *et al.* (1983), the value of C_K is considerably larger when evaporation takes place through a fully developed boundary layer. Such is the case when evaporation occurs from within the soil column or from leaves, and C_K may then be doubled compared to the case of evaporation occurring from a freely exposed water surface. This effect is very pronounced for the enrichment in ^{18}O , whereas the deuterium values are relatively less affected: the range of $(\epsilon^* + C_K)$ for the two extreme mechanisms of evaporation vary between the values of $C_K^{18} = 24\text{--}39$ per mil for ^{18}O , and within the limits of $C_K^D = 85\text{--}98$ per mil in the case of deuterium. The last evaporation stage plays a most pronounced role in the string-of-lakes.

In $\delta_{18} - \delta_D$ space, the changing isotopic com-

positions along the series of evaporative elements describe an "evaporation line," whose slope can be derived from Eqn. (4) as

$$S = \frac{\left[\delta_a - \delta_+ + \frac{\epsilon}{h} \right]_D}{\left[\delta_a - \delta_+ + \frac{\epsilon}{h} \right]_{18}} \quad (7)$$

As described by GAT (1971) this slope becomes independent of h when the atmospheric moisture and the inflow are in isotopic equilibrium; under these conditions the slope merges into the value

$$S = \frac{(\epsilon^* + C_K)_D}{(\epsilon^* + C_K)_{18}} \quad (7a)$$

Obviously, then, the shift in the relative values of C_K as the evaporative mechanism changes, as discussed in the last section, will manifest itself in a change of slope of the evaporation line.

It will be shown below that this rule of a single evaporation line for a string-of-lakes is violated once an atmospheric feedback occurs. Indeed, this is one

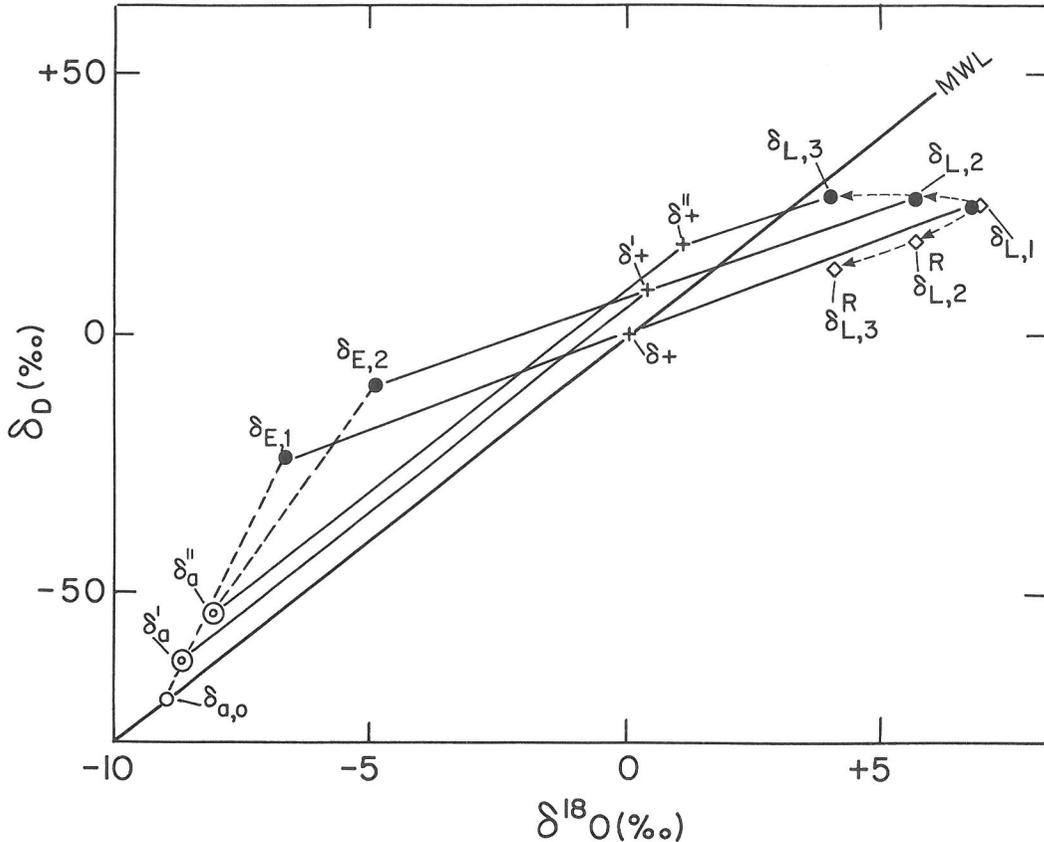


FIG. 5. Isotopic relation for evaporating systems which are coupled through an atmospheric feedback, and with isotopic equilibrium between the liquid input ($\delta_{+,n}$) and atmospheric moisture ($\delta_{a,n}$). Dots correspond to model B1 with an increasing humidity of $h_{(1)} = 0.6$, $h_{(2)} = 0/72$, and $h_{(3)} = 0.864$ (i.e., $b = 1.2$) and for $X = F_+/E = 2$. Diamonds indicate system with "Rayleigh" rainout at constant humidity of $h = 0.6$ (model B2).

property of the system that can be used as a diagnostic for the occurrence of such feedbacks.

COUPLING OF EVAPORATION SYSTEMS THROUGH ATMOSPHERIC FEEDBACK MECHANISMS

Since atmospheric moisture plays a dominant role in the isotopic change which accompanies the evaporation process, especially at high humidities where it limits the isotopic buildup, it is not surprising to find that the incorporation of the evaporated moisture flux into the atmosphere affects the buildup of heavy isotopes in an evaporating system. Furthermore, it has been shown that such a process imprints on the meteoric waters an isotopic signature which enables one to quantify this feedback interaction.

In principle, one can conceive of a large variety of air-water interaction schemes between atmo-

spheric moisture and evaporating waters. We will first discuss just a few representative and idealized systems, shown in Fig. 1, which span the situations actually encountered. Subsequently, some real systems will be discussed in light of these models.

Constant input model

The simplest model is that of a group of lakes situated downwind one from another, each of which is being fed by a stream of identical isotopic composition (Scheme A, Fig. 1). Although not too realistic from a hydrological point of view, we will use this scheme to explore the dependence of the heavy isotope enrichment on the feedback parameters (since in this scheme it is only the atmospheric component which changes along the flowpath).

We assume, as before, that the lake system is in hydrologic and isotopic steady state for a through-

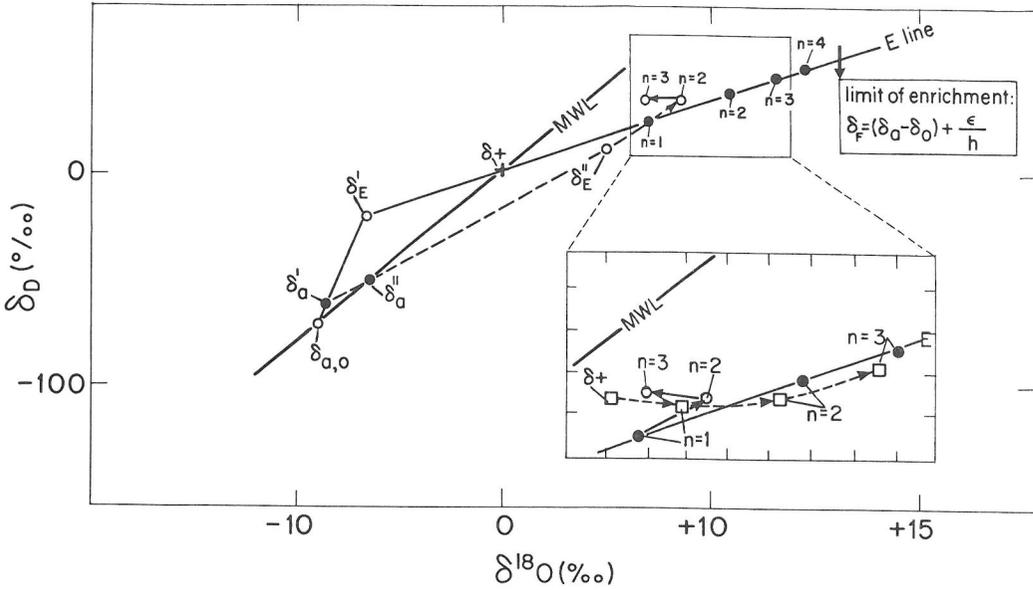


FIG. 6. Steady-state heavy isotope enrichment along a string-of-lakes, assuming $X = 2$, $h_{\text{initial}} = 0.6$, and with the initial inflow (δ_+) in isotopic equilibrium with atmospheric water vapor ($\delta_{a,0}$). Filled circles: δ_{ss} values for model C (without humidity buildup). Open circles: δ_{ss} values for model D1, with humidity buildup due to the evaporation flux, for $b = 1.2$. The atmospheric δ values (δ_E and δ_a) correspond to the case of model D1. Open squares are δ_{ss} values for the reverse, countercurrent system (model D2) (shown in inset only).

flow ratio $F_+/E = X$. For the sake of simplicity, it is assumed that the input (δ_+) is in isotopic equilibrium with the atmospheric humidity in the first

element $\delta_a^{(1)}$; i.e., $\delta_+ = \delta_a^{(1)} + \epsilon^*$. It is also assumed that the difference ($h' - h$) is made up of evaporated moisture of composition δ_E where $b = h'/h$ is the ratio of the humidity in successive elements. The following set of equations then describes the heavy isotope buildup in the different elements of the system:

for element $n = 1$

$$\delta_L^{\text{ss}} = \frac{(1-h)(\epsilon^* + C_K)}{[h + (1-h)X]} + \delta_+ \quad (8)$$

$$\delta_E = \frac{[\delta_L^{\text{ss}} - h\delta_a^{(1)} - \epsilon^* - (1-h)C_K]}{(1-h)} \quad (9)$$

for the n th element

input value (as before): $\delta_+ = \delta_a^{(1)} + \epsilon^*$

atmospheric moisture: $\delta_a^{(n)}$

$$= \frac{1}{b} \delta_a^{(n-1)} + \left(1 - \frac{1}{b}\right) \delta_E^{(n-1)} \quad (10)$$

$$h^{(n)} = b_n h^{(n-1)} \quad (11)$$

$$\delta_{\text{ss}}^n = \frac{h^{(n)}(\delta_a^n) + \epsilon^* + (1-h^{(n)})C_K}{h^{(n)} + (1-h^{(n)})X_n} + \delta_+ \quad (12)$$

Solutions for the case of $X = 2$ and $b = 1.2$ are

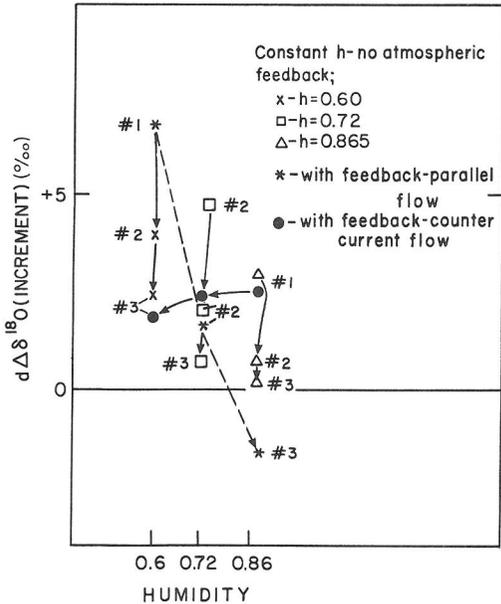


FIG. 7. The incremental enrichment along a string-of-lakes for the case of parallel and countercurrent air and water flow as a function of humidity.

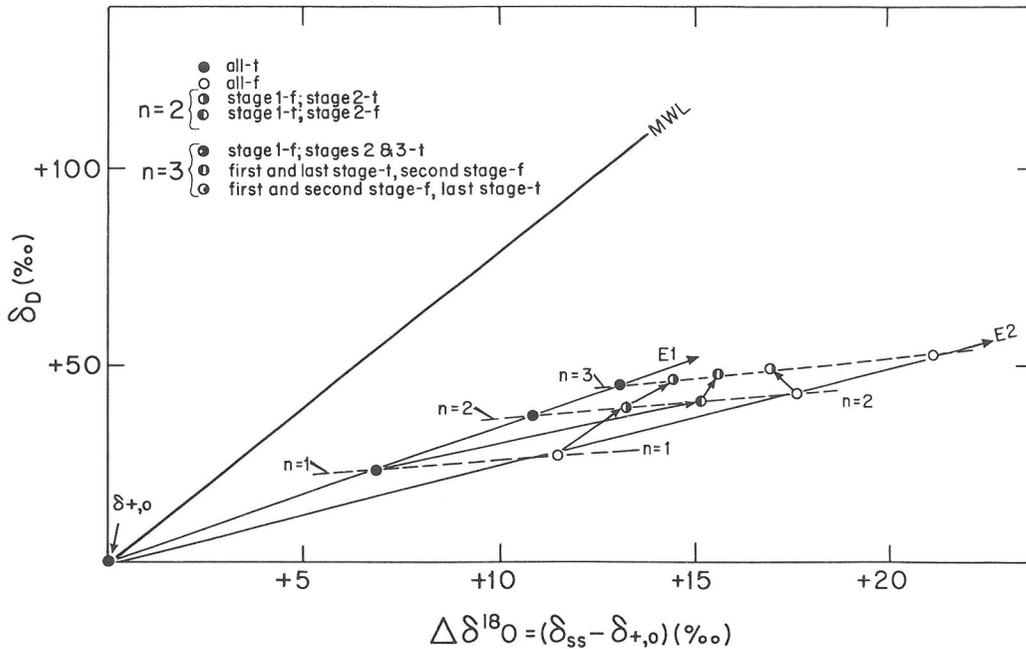


FIG. 8. The heavy isotope enrichment along a series of evaporation elements with different evaporation mechanism, *i.e.*, a turbulent (t) or fully developed (f) boundary layer. Line #1 (with filled circles) is the evaporation line for open water surface elements (t); line #2 (open circles) is the evaporation line for systems with a diffusive (f) boundary layer. Note the locus lines for successive stages of the evaporative series, from $n = 1 \dots 3$, etc.

shown on a δ_D versus δ_{18O} diagram in Fig. 4. Evidently the controlling parameter in this case is the humidity; as the humidity increases, the heavy isotope buildup in the evaporation system is reduced. Most interesting, however, is the increase of the deuterium excess value of atmospheric moisture (“*d*”—defined by DANSGAARD, 1964, as $d = \delta_D - 8\delta_{18}$), which initially increases (by about 8 per mil for elements $n = 2, 3$) but then reverses its value and at the limit of $h \rightarrow 1$ returns to the initial Meteoric Water Line.

One can note further that the initial increase in “*d*” of the atmospheric reservoir is inversely related to the ratio of influx to evaporation, *i.e.*, the value of X . Somewhat counter-intuitively, the “*d*” value of the evaporated moisture is largest for a through-flow system with a large Fx/E ratio, whereas at the lower limit, as $X \rightarrow 1$ (which is the situation of a terminal lake system) the isotopic composition of re-evaporated moisture is located on the MWL; obviously then, $\delta_E = \delta_+$ (at steady state).

The slope of the evaporation line increases for each successive element, and it is once more the increasing humidity which is the dominant parameter in this respect.

Atmosphere/input equilibrium systems

Scheme B (Fig. 1), where the input into any downwind evaporation element is in isotopic equilibrium with the local (higher) moisture, is a more realistic model. This scheme can be considered in two variants, namely with a continuous humidity buildup from element $n = 1$ to n , and a second one of more or less constant humidity, due to rainout of the added moisture. In the latter case it is, of course, reasonable to assume that the isotopic composition changes according to a Rayleigh law as rainout proceeds. Since in this scheme the input into each of the evaporation elements is in isotopic equilibrium with the atmospheric waters, the mathematical formulation of δ_L is even more simple than in the previous model (Table 1, GAT, 1991).

The following are the relevant formulations of the isotopic composition for these two variants of the scheme. In both cases the equations for δ_L^{ss} , δ_E , and δ_a in the first element ($n = 1$) are the same as in scheme A, given above. For the case of a humidity buildup downwind, so that $h^{(n)} = bh^{(n-1)}$, the following equations apply to element “*n*” in the series:

atmospheric input:

$$\delta_a^{(n)} = \frac{1}{b} \delta_a^{(n-1)} + \left(1 - \frac{1}{b}\right) \delta_E^{(n-1)}; \quad h^{(n)} = bh^{(n-1)}$$

liquid input:

$$\delta_+^{(n)} = \delta_a^{(n)} + \epsilon^*$$

$$\delta_{L,ss}^{(n)} = \frac{(1 - h^{(n)})(\epsilon^* + C_K)}{[h^{(n)} + (1 - h^{(n)})X_n]} + \delta_+^{(n)} \quad (13)$$

$$\delta_E^{(n)} = \frac{\delta_{L,ss}^{(n)} - h^{(n)}\delta_a^{(n)} - \epsilon}{(1 - h^{(n)})}. \quad (14)$$

For the case where rainout keeps the humidity constant, the expression for the atmospheric input is changed (according to a Rayleigh formulation): atmospheric input:

$$\delta_a^{(n)} = \frac{1}{b} \delta_a^{(n-1)} + \left(1 - \frac{1}{b}\right) \delta_E^{(n-1)} + \epsilon^* \ln\left(\frac{1}{b}\right); \quad h^{(n)} = h$$

liquid input:

$$\delta_+^{(n)} = \delta_a^{(n)} + \epsilon^*$$

Figure 5 shows the data for the singular case of the parameter $X = 2$ and $b = 1.2$ for these two situations. It is to be noted that the buildup of the “ d ” excess is larger compared to model A, simply because the inflow term δ_+ is already characterized by a high “ d ” value. Being equilibrium systems, the slopes of the evaporation lines are fixed by Eqn. (7a) and do not vary as a function of humidity.

Fully coupled systems

The effect of humidity buildup along a string-of-lakes, in parallel to the streamflow, is shown in Fig. 6. In comparison to the system without the atmospheric buildup it is evident that the humidity buildup (and to a lesser extent the change in the value of δ_a) limits the heavy isotope enrichment in the downstream elements. Actually, a reversal in the trend of increasing δ_{18} values is noted further downstream.

In contrast, when the air and runoff streams run countercurrently (as is the case of the Amazon basin; GAT and MATSUI, 1991), the final heavy isotope enrichment approaches that of the string-of-lakes without feedback. The process of heavy isotope enrichment is reversed, however, with the larger increases occurring in the final stages of the flow-system, where humidity is lower (Fig. 7).

This latter case exemplifies once more the overriding importance of humidity on the degree of heavy isotope enrichment in these evaporative systems.

DISCUSSION: EVAPORATIVE SYSTEMS IN THE ARID ENVIRONMENT

The high enrichment of heavy isotopic species of water is an attribute of rather dry and warm climates. The buildup of high atmospheric moisture levels is not likely in arid zones, and evaporation can play a major role in every link of the hydrologic cycle. Indeed, very heavy waters have been described in the arid environment, such as residual surface waters in the desert (FONTES and GONFIANTINI, 1967) or the water in fruits and leaves of arid zone plants (NISSENBAUM *et al.*, 1974).

A closer look at these systems reveals that they represent a series of linked evaporative systems. In the case of the very heavy water in plants, for example, these evaporation steps occur consecutively: during the fall of rain droplets to the ground, on the surface and within the soil column, during the irrigation process when it applies (evaporation from either sprinkler droplets or from flooded surface plots), and finally during the transpiration process by the stomata-mediated evaporation processes. Two of these steps, namely evaporation from within the soil column and evaporation from leaves, occur through a “fully developed” boundary layer (as defined by ALLISON *et al.*, 1983) which favors ^{18}O enrichment relative to that of the deuterium.

As a general rule one can observe a monotonous heavy isotope enrichment along the hydrologic path. Yet at times a reversal of the enrichment process can be observed even under arid conditions. The most commonly encountered situation is that related to the buildup of salinity, in which case humidity (apparently) increases due to the salt effect on the saturated vapor pressure over the evaporating waters, an effect discussed before, *e.g.*, by GONFIANTINI (1965), GAT (1979), and others. The relatively low heavy isotope enrichment in a terminal evaporative system such as the Dead Sea (where one could have expected some extremely positive δ values) is one illustration of this effect (GAT, 1984).

Another situation where a reversal in the heavy isotope enrichment occurs along the flow path is in the case where the mechanism of evaporation changes, *i.e.*, where an evaporation step with a fully developed boundary layer precedes evaporation from an open water surface, as shown in Fig. 8.

CONCLUSION

Even though possible scenarios for linking lake and evaporation systems are numerous, it is found that heavy isotope enrichment in such coupled systems is severely constrained by the atmospheric

feedback loop. Evidently, in addition to the hydrologic setting of the evaporation process it is mainly the humidity which controls the degree of heavy isotope enrichment, and hence it is the latter for which the enrichment is a measure. In any event, the value defined in Eqn. (1b) remains as the ultimate enrichment barrier regardless of circumstances.

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