Fractionation mechanism of stable isotope in evaporating water body

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Abstract: Under Rayleigh equilibrium condition, stable isotopic ratio in residual water increases with the decrease of the residual water proportion f exponentially, and the fractionation rate of stable isotopes is inversely proportional to temperature. However, under kinetic evaporation condition, the fractionation of stable isotopes is not only related to the phase temperature but also influenced by the atmospheric humidity and the mass exchange between liquid and vapor phases. The ratio δ in residual water will not change with f after undergoing evaporation of a long time for great relative humidity. The rate that the evaporating water body reaches isotopic steady state is mainly dependent on the relative humidity in atmosphere. The analysis shows that the actual mean linear variety rates, about -30.0, of the δ^{18} O in residual water versus the residual water proportion at Nagqu and Amdo stations are consistent with the simulated process under temperature of 20 °C and relative humidity of 50%. The distillation line simulated under Rayleigh equilibrium condition is analogous to the global meteoric water line (MWL) as the temperature is about 20 °C. Under non-equilibrium condition, the slope and constant values of distillation line are directly proportional to temperature and relative humidity. According to the basic data, the simulated distillation line is very consistent with the actual distillation line of Qinghai Lake.

Key words: stable isotope; evaporation; kinetic fractionation; distillation line; water body doi: 10.1360/gs050312

The variations of stable isotopes in atmospheric vapor and precipitation are caused by stable isotopic fractionation during phase changes in water cycle. The isotopic fractionation mainly happens in the mass transportation of stable isotopes from free water body pointing to air, such as the evaporation of water, and that from air pointing to land surface, such as the condensation of vapor or fall of condensates (Jouzel, 1986; Merlivat, 1978a). In water cycle, the stable isotopic species D (deuterium) and ¹⁸O respond to environmental change sensitively, and their variation features are linked to the formation of vapor, cloud and condensate, closely. With the constant improvements in mass spectrometric techniques since the mid-1950s, it is possible to measure stable isotopic components in water samples accurately, and thus, the technique on stable isotopic analyses is widely used in the study fields of hydrology and paleoclimatology (Dansgaad, 1964; Merlivat and Jouzel, 1979; Zhang, 1994; Zhang and Yao, 1997; Yao *et al.*, 1996).

Studying the vapor source (for example evaporation) and the vapor sink (for example precipitation) in the vapor transportation process on local and global scales according to the analyses of stable isotopic change in water cycle has the important significance. The variation of stable isotopic components in the evaporation process, similar to that in the condensation process, provides the knowledge of understanding the fractionation mechanism of stable isotopes

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in phase change, based on the mass transfer (Craig and Gordon, 1963; Saxena, 1987). The fractionation of stable isotopes in evaporating water body is attributed to the difference of the saturated vapor pressure e, between light and heavy isotopes, showing as the $e(H_2^{16}O)$ greater than the $e(H_2^{18}O)$ and the $e(HD^{16}O)$. Therefore, the light molecule will evaporate preferentially and the components of heavy molecule will increase in liquid phase, whereupon the liquid phase gets more and more enriched.

The estimate of the evaporation in water body, using the analyses of stable isotopes, is based on the mechanism of stable isotopic fractionation. A simple tool describing stable isotopic fractionation in the evaporation process is Rayleigh model (Craig and Gordon, 1963; Dansgaad, 1964; Tian *et al.*, 2000). In this model, it is assumed that the equilibrium fractionation happens between liquid and vapor phases and the phase change takes place in the equilibrium condition, and that the vapor escapes from the system at once, as soon as it is evaporated. Therefore, the temperature is the only external factor controlling the stable isotopic fractionation in evaporating water body. The equilibrium fractionation process is dependent on the temperature absolutely.

Krabbenholf *et al.* (1990) estimate the evaporation of water body using the stable isotopic mass balance and the water balance methods. In their calculations, the stable isotopes in lake water are assumed to be in equilibrium state. Gibbson *et al.* (1993) calculate the evaporation in lake according to the relationship between D and ¹⁸O. Although considering the influences of other controlling factors including temperature, they still assume the stable isotopes in atmospheric vapor and precipitation to be in the equilibrium state.

The natural evaporation process was originally modeled by Craig and Gordon (1963). They think that the liquid-vapor interface is bounded on either side (in each phase) by a laminar layer, in which the transport is predominantly governed by molecular diffusion. Beyond these laminar layers, there is a region dominated by turbulence. This was shown experimentally subsequently by Merlivat and Coantic (1975).

However, the enrichment of stable isotopic components in water body is very different from the result described by Rayleigh evaporation process in actual evaporation. The influence from kinetic effect caused by the differences of molecular diffusion, and interaction and mass exchange between stable isotopic components in evaporating water body and in atmosphere cannot be neglected (Jouzel and Merlivat, 1984; Merlivat, 1978b; Zhang *et al.*, 1998; Zhang and Yao, 1994). The study quantificationally analyses the interaction between evaporating water body and atmosphere, and the influences of different factors on the evaporation by probing into the fractionation mechanism of stable isotope as water body is vaporized under kinetic non-equilibrium and by comparing the kinetic fractionation model with the Rayleigh equilibrium model.

1 Fractionation of stable isotopes in Rayleigh evaporation process

Considering a system where water is slowly evaporating, the vapor is assumed to be removed immediately from the system such that equilibrium exists or virtually exists at the water-vapor interface. Let n_i and n_i be the number of heavy and light molecules in the liquid phase, respectively. Similarly, let n_v' and n_v be the number of heavy and light molecules in the vapor phase. The ratio of heavy to light components in the liquid phase $R_i = n'_i/n_i$ and the corresponding ratio in the vapor phase $R_v = n'_v/n_v$. Since the system is in equilibrium, we can get

$$R_{l} = R_{0} f^{\frac{1}{\alpha} - 1}$$
(1)

where $f = n_1/n_0$ is the residual water proportion; n_0 is the total number of molecules in the liquid phase initially, and R_0 the initial ratio of heavy to light isotopes; α is the fractionation factor of stable isotopes that is temperature dependent.

If using δ , deviated from the standard mean ocean water (SMOW) (= $R/R_{SMOW} - 1$, R_{SMOW} is the stable isotopic ratio in SMOW), stands for the degree of stable isotopic components, it can

be obtained

$$\delta_{i} = (\delta_{0} + 1)f^{\frac{1}{\alpha} - 1} - 1 \qquad (2)$$

The equation is called as Rayleigh distillation formula that describes the ratio in the liquid as a function of the residual water proportion f when the evaporation proceeds in a system under equilibrium condition.

It is assumed that the water in evaporating the water body originates from atmospheric precipitation, and the stable isotopes D and ¹⁸O in the water undergo equilibrium all the fractionation process as condensing and have such a relation, $\delta D =$ $8.0\delta^{18}O + 10.0$, namely the global MWL (Craig, 1961). Setting the initial ratio $\delta^{18}O = -10.0\%$ and δD = -70.0‰, the simulated variations with f, of stable isotopic ratios in the residual water and the simulated relationship between δ^{18} O and δ D are obtained under different temperature conditions (Figure 1).

It can be seen from the figure:

(1) Stable isotopic ratios in residual water increase with the decrease of the residual water proportion f exponentially in the Rayleigh fractionation process.

(2) The fractionation rate of stable isotopes is inversely proportional to temperature under



Figure 1 Variations of stable isotopic ratios in residual water under equilibrium condition

equilibrium condition. The higher the temperature is, the less the fractionation factor α is, and thus the lower the stable isotopic ratio in residual water is, corresponding to the same f, because the fractionation factor of stable isotopes is inversely proportional to temperature.

(3) The simulated Rayleigh distillation line, namely the relationship between δ^{18} O and δ D, changes with temperature. The higher the temperature is, the less the slope and the constant of the distillation line are. The simulated distillation line is near global MWL as the temperature is about 20 °C.

2 Fractionation of stable isotopes in kinetic evaporation process

The kinetic process assumes that the mass transport in the liquid-vapor interface is predominantly governed by molecular diffusion (Jouzel and Merlivat, 1984; Merlivat, 1978a; Zhang *et al.*, 1998). And it is defined that F_{la} and F_{al} stand for the flux of lighter component from liquid to gaseous phase and from gaseous to liquid phase, respectively, F_{la} and F_{al} for that of heavier

component; $E' = F_{la} - F_{al}$ is the net flux of heavier component from liquid to gaseous phase and $E = F_{la} - F_{al}$ is that of lighter component from liquid to gaseous phase; $R_e = E'/E$ stands for the ratio of heavy to light component in the net flux from liquid to gaseous phase.

As evaporation proceeds, the change in the heavier component in liquid phase is given by $dn'_{l} = d(R_{l}n_{l}) = E'/Edn_{l}$

or
$$\frac{d(\ln R_l)}{d(\ln n_l)} = \frac{R_e}{R_l}$$

(3)

If the relative humidity is h, then the flux from gaseous to liquid phase can be expressed as $F_d = hF_{la}$

When h = 1, $F_{al} = F_{lao}$ there is no net flux across the interface. If h = 0, then $F_{al} = 0$, and there is no flux from gaseous to liquid phase, while for $h \ge 1$, the gaseous phase is condensing.

Experiment proves that the flux F_{la} is directly proportional to n_l (Merlivat, 1978a; Saxena, 1987), hence

$$F_{la} = k_{la} n_l$$
 and $F_{al} = k_{al} n_a$
similarly

- 1

 $F'_{la} = k'_{la}R_{ln}$ and $F'_{al} = k'_{al}R_{an}$

where k'_{la} and k_{la} are the resistances to the flow of the heavy and light components from liquid to gaseous phase respectively; k'_{a} and k_{a} are the corresponding resistances from gaseous to liquid phase. Therefore,

$$E' = F_{la} - F_{al} = k'_{la}R_{l}n_{l} - k'_{al}R_{a}n_{a} \quad \text{or} \quad E' = \frac{k'_{la}R_{l}F_{la}}{k_{la}} - \frac{k'_{al}R_{a}F_{al}}{k_{al}}$$

From the definition of E, we have $E = (1 - h)F_{la}$. Substituting

$$\gamma_{la} = \frac{k'_{la}}{k_{la}}$$
 and $\gamma_{al} = \frac{k'_{al}}{k_{al}}$

 γ_{la} is the ratio of the resistances of the interface to molecules of the heavy and light components from liquid to gaseous phase. γ_{a} can be similarly defined. Then,

$$R_{e} = \frac{E'}{E} = \frac{\gamma_{la}R_{l}F_{la} - \gamma_{al}R_{a}F_{al}}{(1-h)F_{la}} = \frac{\gamma_{la}R_{l} - \gamma_{al}R_{a}h}{(1-h)}$$

During evaporation, $\alpha = \gamma_{al}/\gamma_{la}$ (Saxena, 1987) and

$$R_{e} = \frac{E'}{E} = \frac{\frac{1}{\alpha}R_{l} - R_{a}h}{\beta(1 - h)}$$
If writing in terms of the δ value, and substituting $\beta = 1/\gamma$, then
(4)

If writing in terms of the δ value, and substituting $\beta = 1/\gamma_{a}$, then

$$\delta_e = \frac{\frac{1}{\alpha}(1+\delta_l) - h(1+\delta_a)}{\beta(1-h)} - 1$$
(5)

Gat finds (1970), by experiment, that the magnitude of β (> 1) is related to wind speed. If keeping the other conditions unchanged, the greater the wind speed, the stronger the evaporation, the lower the β , and thus the higher the δ_e . On the contrary, the smaller the wind speed, the higher the β_e and thus the lower the δ_e .

From equations (4) or (5), the net evaporation E = 0 and h = 1 as liquid and vapor reach kinetic equilibrium, and thus

 $\frac{1}{\alpha}R_l - R_a = 0 \qquad \text{or} \qquad R_l = \alpha R_a$

which as expected is also the expression for the phase transition equation.

As liquid evaporates in the environment of h = 0, equation (4) becomes into

$$R_e = \frac{R_l}{\alpha \beta}$$

substituting R_e in equation (3), then $\frac{d(\ln R_l)}{d(\ln n_l)} = \frac{1}{\alpha\beta} - 1$

It has the same form as Rayleigh distillation formula, but the extra term β displays that the fractionation of system is speeded.

As
$$0 < h < 1$$
, substituting equation (5) in equation (3)

$$\frac{d(\ln R_l)}{d(\ln n_l)} = \frac{\frac{1}{\alpha} - \frac{R_a}{R_l}h}{\beta(1-h)} - 1$$
or $d\delta_l = \frac{\frac{1}{\alpha}(1+\delta_l) - h(1+\delta_a) - \beta(1-h)(1+\delta_l)}{\beta(1-h)} d(\ln n_l)$

$$= (\delta_e - \delta_l)d(\ln n_l) = (\delta_e - \delta_l)d(\ln f)$$
(6)

The equation describes the change in δ values of a water body evaporating under constant humidity and constant temperature.

When water body has evaporated long enough and the stable isotopic ratio in the net evaporated water, δ_e , is equal to the stable isotopic ratio in water body, δ_l , the fractionation effect disappears, $d\delta_l = 0$. So

$$\delta_l = \frac{h(1+\delta_a)}{\frac{1}{\alpha} - \beta(1-h)} - 1 \tag{7}$$

Furthermore, if the atmospheric conditions remain constant, the δ value in residual water will not change with evaporation.

3 Simulation of stable isotopic change in kinetic evaporation process

It is different from that by Rayleigh equilibrium model that the stable isotopic ratio in residual water, besides being influenced by temperature, is also influenced by relative humidity h and stable isotopic ratio in atmospheric vapor δ_a , in kinetic evaporation process. Comparing with the studies on the stable isotopes in precipitation, few surveys and studies on δ_a are conducted in the world, especially in China, the study gaps have not filled so far. However, according to the limited records (Jacob and Sonntag, 1991; Saxena, 1987; White and Gedzelman, 1984), there is the good positive correlations between δ_a and air temperature. In this study, the survey results of δ_a from Jacob and Sonntag (1991) are used in the kinetic simulation processes

$$\delta^{18}O_{a}(\%) = 0.39T(^{6}C) - 22.8$$

 $\delta D_{a}(\%) = 3.0T(\%) - 169.0$

(8)

In addition, the initial stable isotopic ratios in liquid are the same as the assumption under Rayleigh equilibrium condition. Based on the above assumption, the variations of stable isotopic ratios in residual water are simulated under different evaporation conditions.

3.1 Variations of stable isotopic ratio in residual water with f

In Rayleigh model, the δ values are uniquely determined by f under constant temperature. However, the relationship between δ and f changes with the relative humidity in the kinetic evaporation process. Figure 2 shows the variations of δ with f corresponding to different relative humidity conditions as the temperature is 20 °C. Furthermore, in order to compare two kinds of fractionation effects, the figure also gives the result simulated by Rayleigh equilibrium model under the same temperature.

From the simulated results, the less the h is, the quicker the variation rate with f, of stable isotopic ratios in residual water is. For great h, the ratio δ in residual water will not change with f after undergoing the evaporation of a long time, namely isotopic components in residual water reach the steady state $\delta_e = \delta_l$. The rate that the evaporating water body reaches isotopic steady state is mainly dependent on the relative humidity in atmosphere. Such a phenomenon has been proved by Saxena through actual evaporation experiments made in different evaporating pans (Saxena, 1987). His experiment results show that the atmospheric relative humidity governs the rate of pan water reaching isotopic steady state. Similarly, Craig and Gordon (1963) find that the heavy isotopic components in residual water will gradually tend to their limit values as water body evaporates in moist air.

Compared with the evaporation processes simulated by Rayleigh equilibrium model. the isotopic enrichment in residual water is markedly higher the kinetic in process, evaporation but lower for the evaporating water body of having reached steady state for small h.

It can be deduced, from Figure 2, that Rayleigh model is not a special case of kinetic model as h = 1.

3.2 Relationship between stable isotopic ratio in residual water and temperature



Figure 2 Variations with f, of stable isotopic ratios in residual water under different relative humidity conditions (T = 20 °C)

Here, the initial conditions and the variations of δ_{α} are the same as the former. Setting h = 50%, the relationship between δ in residual water and f in the kinetic evaporation process is shown in Figure 3 for T = 10 °C, 20 °C and 30 °C respectively.

It can be seen from Figure 3 that the isotopic fractionation rate is directly proportional to temperature, the higher the temperature is, the faster the isotopic fractionation rate is, which is absolutely contrary to the result of the Rayleigh fractionation.

In kinetic fractionation model, the impact of temperature on the stable isotopic ratio in residual water $\Delta \delta_l = \delta_l(T_2) - \delta_l(T_1)$ can be divided into two parts:

$$\Delta \delta_l \propto (1 + \overline{\delta_l}) \Big[\frac{1}{\alpha(T_1)} - \frac{1}{\alpha(T_2)} \Big] + h[\delta_a(T_2) - \delta_a(T_1)] = A + B$$

where δ_l is the mean stable isotopic ratio under the mean temperature $(T_1 + T_2)/2$; $a(T_1)$, $\delta_a(T_1)$ and $a(T_2)$, $\delta_a(T_2)$ stand for the fractionation factor of stable isotopes and stable isotopic ratio in atmospheric vapor as the temperature is T_1 and T_2 , respectively.

As $T_2 > T_1$, α (T_2) < α (T_1), then A < 0, but $\delta_a(T_2) > \delta_a(T_1)$ because δ_a is directly proportional to temperature, thus B > 0. If B > |A|, then $\delta_i(T_2) > \delta_i(T_1)$, showing that δ_a in atmospheric vapor will increase because of the increase of temperature, and thus the flux of heavy isotopic components from gaseous to liquid phase increases and may counteract the decrement of δ_i caused by the decreasing fractionation factor owing to the increase of temperature. Therefore, the impact of temperature on δ_i under kinetic fractionation should be attributed to the contribution of δ_{a} .

In addition, B = 0 if δ_a is invariable with temperature, then $\delta_l(T_2) < \delta_l(T_1)$ as $T_2 > T_1$ under the conditions of the same h and the same f. Such a result is the same as that simulated by Rayleigh distillation formula.

The linear variety rates of the δ^{18} O in residual water versus the residual water proportion f are -28.27 for T = 30 °C, -30.40 for T = 20 °C and -32.70 for T = 10 °C respectively as setting h = 50% (Figure 3).

3.3 Comparison between actual and simulated $\delta^{18}O-f$ relationship

A study on the stable isotopic fractionation during water evaporating was conducted on the

central Tibetan Plateau in the summer of 1998. In order to eliminate the influence of precipitation replenishment on evaporation, two evaporation pans were put under plastic awnings with ventilative around, respectively, at Nagqu and Amdo (Figure 4).

The evaporation pans with water were weighed before experiment beginning and after every sampling. The evaporated water in the pans was sampled 10:00 AM every day. at Usually, an experiment would undergo a few days as less water was remained in. Two sets of evaporation experiments, 10 ones for each station, were done during the season. Because the sampling interval was one day, the experiment length would be dependent on air humidity. The wetter the air



Figure 3 Simulated variations with f, of stable isotopic ratios in residual water for different temperature (h = 50%)

is, the longer the time that experiments undergo and vice versa. All collected water samples were sealed in plastic bottles and measured for their stable oxygen isotopic ratios by the Delta-Plus mass spectrometer, at the Key Laboratory of Ice Core and Cold Regions Environments, Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Sciences. The measured ratio of the stable oxygen isotope in samples ¹⁸O/¹⁶O is expressed as parts per thousand of their deviation relative to the SMOW.

The results of evaporation fractionations for these experiments are displayed in Figure 5. It can be found that the δ^{18} O in residual water is linearly increased with the deceasing residual water proportion f.

water proportion f, actual basically, in evaporation processes. In this figure, the simulated process under the temperature of 20 °C, δ^{18} O = -30.40f + 20.28, is given (the dashed line in Figure 5). Because of different initial δ^{18} O values and weather processes. the evaporation actual processes are also different. However, the actual mean linear variety rates of the $\delta^{18}O$ in residual water versus the residual water -30.0 proportion, about



Figure 4 Map showing the location of the evaporation experimental stations on the central Tibetan Plateau

(Tian *et al.*, 2000), are consistent with the simulated result, which illuminates that the kinetic distillation model can accurately simulate the variations of stable isotopic ratios in residual water in actual evaporation process.

3.4 Simulation of distillation line

The distillation line of evaporating water body is analogous to the global MWL under the equilibrium fractionation condition and as the temperature being 20 °C (Figure 1). However, the relationship between D and ¹⁸O is changed under the impact of kinetic function. Figure 6 gives the variations of distillation line under different temperature and different relative humidity conditions.

It can be seen from Figure 6: (1) The slope and constant values of simulated distillation line are directly proportional to temperature. The higher the temperature is, the greater the slope and constant values are and vice versa, which is contrary with the results of Rayleigh evaporation. (2) The greater the relative humidity is, the greater the



Figure 5 Observed variations with f, of δ^{18} O in residual water at Nagqu and Amdo (The dashed line is the simulated process of the δ^{18} O in residual water versus f under T = 20 °C and h = 50%)

slope and constant values are and vice versa for the same temperature.

We have known, according to Figure 2, that the enrichment of ¹⁸O in water body for the evaporation in unsaturated atmosphere is usually higher than that by Rayleigh model. It is apparent that an excess fractionation mechanism operates the non-equilibrium evaporation. Its function is larger than that of equilibrium fractionation and is strengthened with the increase of temperature. Comparatively, the enrichment rate of ¹⁸O is faster than that of D (Eriksson, 1965; Jouzel, 1986), which will lead to the slope and constant of distillation line decreasing in actual evaporation.

The kinetic distillation model can be used to simulate the distillation line of the Qinghai Lake. According to the estimation of actual data, the initial stable isotopic ratios $\delta D = -60.6\%$ and $\delta^{18}O = -10.86\%$ in the water of the Qinghai Lake (Zhang, 1994); the mean annual temperature being -0.65 °C in this lake region and the relative humidity 55% (Qu *et al.*, 1994); setting $\beta = 1.006$ because of the strong average wind speed; assuming the same stable isotopic ratios in atmospheric vapor as equation (8). The simulated distillation line of the Qinghai Lake (the solid line in Figure 7) is

 $\delta D(\%) = 5.56 \delta^{18} O(\%) - 1.51$

It is very consistent with the actual distillation line of the Qinghai Lake (the dashed line in Figure 7)

 $\delta D(\%) = 5.55 \delta^{18} O(\%) - 0.30$

4 Conclusions

(1) In the equilibrium evaporation process, stable isotopic ratios in residual water increase with the decrease of the residual water proportion f exponentially, and the fractionation rate of

stable isotopes is inversely proportional to temperature.

(2) In the kinetic evaporation process, the fractionation of stable isotopes is not only related to phase temperature but also influenced by atmospheric humidity and mass exchange between liquid and vapor phases.

(3) In the kinetic evaporation process, the less. the relative humidity the quicker the is, variation rate with f, of stable isotopic ratios in residual water is. For the great relative humidity, the stable isotopic ratio in residual water will not change with f after long-time undergoing the evaporation. that the The rate evaporating water body reaches isotopic steady state is mainly dependent on the relative humidity atmosphere. The isotopic in enrichment in residual water, as setting the relative humidity being 50%, is higher than that by Rayleigh equilibrium model. The rate of enrichment is directly proportional to temperature. The analysis shows that the actual mean linear variety rates, about -30.0, of the δ^{18} O in residual water versus the residual water proportion at Nagqu and Amdo stations are consistent with simulated process under the temperature of 20 °C and relative humidity of 50%.

(4) The distillation line simulated equilibrium Rayleigh under condition is analogous to the global the meteoric water line as temperature is about 20°C. Under non-equilibrium condition, the slope and constant values of distillation line are directly proportional to temperature and relative humidity. According to the basic data, the simulated distillation line is very actual consistent with the distillation line of the Qinghai Lake.



Figure 6 Distillation lines simulated under different relative humidity and different temperature conditions



Figure 7 Comparison between the simulated and observed distillation lines in Qinghai Lake (after Zhang, 1994)

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