

STABLE ISOTOPE THEORY: KINETIC FRACTIONATION AND THE HYDROLOGIC SYSTEM

KINETIC FRACTIONATION

Kinetic effects are normally associated with fast, incomplete, or unidirectional processes like evaporation, diffusion and dissociation reactions. As an example, recall that temperature is related to the average kinetic energy. In an ideal gas, the average kinetic energy of all molecules is the same. The kinetic energy is given by:

$$E = \frac{1}{2}mv^2 \quad 26.1$$

Consider two molecules of carbon dioxide, $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$, in such a gas. If their energies are equal, the ratio of their velocities is $(45/44)^{1/2}$, or 1.011. Thus $^{12}\text{C}^{16}\text{O}_2$ can diffuse 1.1% further in a given amount of time at a given temperature than $^{13}\text{C}^{16}\text{O}_2$. This result, however, is largely limited to ideal gases, i.e., low pressures where collisions between molecules are infrequent and intermolecular forces negligible. For the case of air, where molecular collisions are important, the ratio of the diffusion coefficients of the two CO_2 species is the ratio of the square roots of the reduced masses of CO_2 and air (mean molecular weight 28.8):

$$\frac{D_{^{12}\text{CO}_2}}{D_{^{13}\text{CO}_2}} = \frac{\sqrt{\mu_{^{12}\text{CO}_2\text{-air}}}}{\sqrt{\mu_{^{13}\text{CO}_2\text{-air}}}} = \frac{17.561}{17.406} = 1.0044 \quad 26.2$$

Hence we would predict that gaseous diffusion will lead to only a 4.4‰ fractionation.

In addition, molecules containing the heavy isotope are more stable and have higher dissociation energies than those containing the light isotope. This can be readily seen in Figure 25.1. The energy required to raise the D_2 molecule to the energy where the atoms dissociate is 441.6 kJ/mole, whereas the energy required to dissociate the H_2 molecule is 431.8 kJ/mole. Therefore it is easier to break bonds such as C-H than C-D. Where reactions go to completion, this difference in bonding energy plays no role: isotopic fractionations will be governed by the considerations of equilibrium discussed in the previous lecture. *Where reactions do not achieve equilibrium the lighter isotope will be preferentially concentrated in the reaction products*, because of this effect of the bonds involving light isotopes in the reactants being more easily broken. Large kinetic effects are associated with biologically mediated reactions (e.g., bacterial reduction), because such reactions generally do not achieve equilibrium (the existence of reduced carbon in a O_2 -bearing atmosphere is a non-equilibrium condition). Thus ^{12}C is enriched in the products of photosynthesis in plants (hydrocarbons) relative to atmospheric CO_2 , and ^{32}S is enriched in H_2S produced by bacterial reduction of sulfate.

We can express this in a more quantitative sense. The rate at which reactions occur is given by:

$$R = ke^{-E_b/kT} \quad 26.3$$

where k is a constant and E_b is the barrier energy. Referring to Figure 25.1, the barrier energy is the difference between the dissociation energy and the zero-point energy. The constant k is independent of isotopic composition, thus the ratio of reaction rates between the HD molecule and the H_2 molecule is:

$$\frac{R_D}{R_H} = \frac{e^{-(\epsilon - \frac{1}{2}h\nu_D)/kT}}{e^{-(\epsilon - \frac{1}{2}h\nu_H)/kT}} \quad 26.4$$

or

$$\frac{R_D}{R_H} = e^{(\nu_H - \nu_D)h/2kT} \quad 26.5$$

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Substituting for the various constants, and using the wavenumbers given in the caption to Figure 25.1 (remembering that $\omega = cv$ where c is the speed of light) the ratio is calculated as 0.24; in other words we expect the H_2 molecule to react four times faster than the HD molecule, a very large difference. For heavier elements, the rate differences are smaller. For example, the same ratio calculated for $^{16}O_2$ and $^{18}O^{16}O$ shows that the ^{16}O will react about 15% faster than the $^{18}O^{16}O$ molecule.

The greater translational velocities of lighter molecules also allows them to break through a liquid surface more readily and hence evaporate more quickly than a heavy molecule of the same composition. Thus water vapor above the ocean typically has $\delta^{18}O$ around -13 per mil, whereas at equilibrium the vapor should only be about 9 per mil lighter than the liquid.

Let's explore this example a bit further. An interesting example of a kinetic effect is the fractionation of O isotopes between water and water vapor. This is another example of Rayleigh distillation (or condensation), as is fractional crystallization. Let A be the amount of the species containing the major isotope, $H_2^{16}O$, and B be the amount of the species containing the minor isotope, $H_2^{18}O$. The rate at which these species evaporate is proportional to the amount present:

$$dA = k_A A \quad 26.6a$$

and

$$dB = k_B B \quad 26.6b$$

Since the isotopic composition affects the reaction, or evaporation, rate, $k_A \neq k_B$. We'll call the ratio of the rate constants, k_B/k_A , α . Then

$$\frac{dB}{dA} = \alpha \frac{B}{A} \quad 26.7$$

Rearranging and integrating, we have

$$\ln \frac{B}{B^\circ} = \alpha \ln \frac{A}{A^\circ} \quad \text{or} \quad \frac{B}{B^\circ} = \left(\frac{A}{A^\circ} \right)^\alpha \quad 26.8$$

where A° and B° are the amount of A and B originally present. Dividing both sides by A/A°

$$\frac{B/A}{B^\circ/A^\circ} = \left(\frac{A}{A^\circ} \right)^{\alpha-1} \quad 26.9$$

Since the amount of B makes up only a trace of the total amount of H_2O present, A is essentially equal to the total water present, and A/A° is essentially identical to f , the fraction of the original water remaining. Hence:

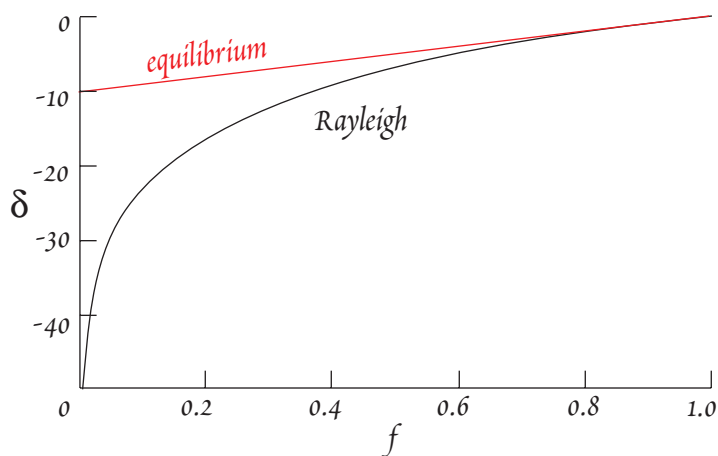


Figure 26.1. Fractionation of isotope ratios during Rayleigh and equilibrium condensation. δ is the per mil difference between the isotopic composition of original vapor and the isotopic composition after fraction F has condensed.

$$\frac{B/A}{B^\circ/A^\circ} = f^{\alpha-1} \quad 26.10$$

Subtracting 1 from both sides, we have

$$\frac{B/A - B^\circ/A^\circ}{B^\circ/A^\circ} = f^{\alpha-1} - 1 \quad 26.11$$

Comparing the left side of the equation to 25.1, we see the permil fractionation is given by:

$$\delta = 1000(f^{\alpha-1} - 1) \quad 26.12$$

Of course, the same principle applies when water condenses from vapor. Assuming a value of α of 1.01, δ will vary with f , the fraction of vapor remaining, as shown in Figure 26.1.

Even if the vapor and liquid remain in equilibrium throughout the condensation process, the isotopic composition

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of the remaining vapor will change continuously. The relevant equation is:

$$\delta = \left(1 - \frac{1}{(1-f)/\alpha + f} \right) \quad 26.13$$

The effect of equilibrium condensation is also shown in Figure 26.1.

HYDROGEN AND OXYGEN ISOTOPE RATIOS IN THE HYDROLOGIC SYSTEM

We noted above that isotopically light water has a higher vapor pressure, and hence lower boiling point than isotopically heavy water. Let's consider this in a bit more detail. Raoult's law states that the partial pressure, p , of a species above a solution is equal to its molar concentration in the solution times the standard state partial pressure, p° , where the standard state is the pure solution. So for example:

$$p_{\text{H}_2^{16}\text{O}} = p_{\text{H}_2^{16}\text{O}}^\circ [\text{H}_2^{16}\text{O}] \quad 26.14a$$

and

$$p_{\text{H}_2^{18}\text{O}} = p_{\text{H}_2^{18}\text{O}}^\circ [\text{H}_2^{18}\text{O}] \quad 26.14b$$

Since the partial pressure of a species is proportional to the number of atoms of that species in a gas, we can define α , the fractionation factor between liquid water and vapor in the usual way:

$$\alpha_{l/v} = \frac{p_{\text{H}_2^{18}\text{O}} / p_{\text{H}_2^{16}\text{O}}}{[\text{H}_2^{18}\text{O}] / [\text{H}_2^{16}\text{O}]} \quad 26.15$$

By solving 26.14a and 26.14b for $[\text{H}_2^{16}\text{O}]$ and $[\text{H}_2^{18}\text{O}]$ and substituting into 26.15 we arrive at the relationship:

$$\alpha_{l/v} = \frac{p_{\text{H}_2^{18}\text{O}}^\circ}{p_{\text{H}_2^{16}\text{O}}^\circ} \quad 26.16$$

Interestingly enough, the fractionation factor for oxygen between water vapor and liquid turns out to be just the ratio of the standard state partial pressures. The next question is how the partial pressures vary with temperature. According to classical thermodynamics, the temperature dependence of the partial pressure of a species may be expressed as:

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2} \quad 26.17$$

where T is temperature, ΔH is the enthalpy or latent heat of evaporation, and R is the gas constant. Over a sufficiently small range of temperature, we can assume that ΔH is independent of temperature. Rearranging and integrating, we obtain:

$$\ln p = \frac{\Delta H}{RT} + \text{const} \quad 26.18$$

We can write two such equations, one for $[\text{H}_2^{16}\text{O}]$ and one for $[\text{H}_2^{18}\text{O}]$. Dividing one by the other we obtain:

$$\ln \frac{p_{\text{H}_2^{18}\text{O}}^\circ}{p_{\text{H}_2^{16}\text{O}}^\circ} = A - \frac{B}{RT} \quad 26.19$$

where A and B are constants. This can be rewritten as:

$$\alpha = a e^{B/RT} \quad 26.20$$

Over a larger range of temperature, ΔH is not constant. The fractionation factor in that case depends on the inverse square of temperature, so that the temperature dependence of the fractionation factor can be represented as:

$$\ln \alpha = A - \frac{B}{T^2} \quad 26.21$$

Figure 26.2 shows water-vapor and ice-vapor fractionation factors for oxygen. Over a temperature range relevant to the Earth's surface, the fractionation factor for oxygen shows an approximately inverse dependence on temperature. Hydrogen isotope fractionation is clearly non-linear over a large range of temperature.

Given the fractionation between water and vapor, we might predict that there will be considerable variation in the isotopic composition of water in the hydrologic cycle, and indeed there is. Furthermore, these variations form the basis of estimates of paleotemperatures and past ice volumes. Let's now consider the question of isotopic fraction in the hydrosphere in greater detail.

As water vapor condenses, the droplets and vapor do not remain in equilibrium. So the most accurate description of the condensation process is Rayleigh distillation, which we discussed above. To a first approximation, condensation of water vapor will be a function of temperature. As air rises, it cools. You may have noticed the base elevation of clouds is quite uniform on a given day in a given locality. This elevation represents the isotherm where condensation begins. At that height, the air has become supersaturated, and condensation begins, forming clouds. Water continues to condense until equilibrium is again achieved. Further condensation will only occur if there is further cooling, which generally occurs as air rises. The point is that the parameter f , the fraction of vapor remaining, can be approximately represented as a function of temperature. To explore what happens when water vapor condenses, let's construct a hypothetical model of condensation and represent f as hypothetical function of temperature such as:

$$f = \frac{T - 223}{50} \quad 26.22$$

Since T is in kelvins, this equation means that f will be 1 at 273 K (0°C) and will be 0 at 223 K (-50°C). In other words, we suppose condensation begins at 0°C and is complete at -50°C. Now we also want to include temperature dependent fractionation in our model, so we will use equation 26.20. Realistic values for the con-

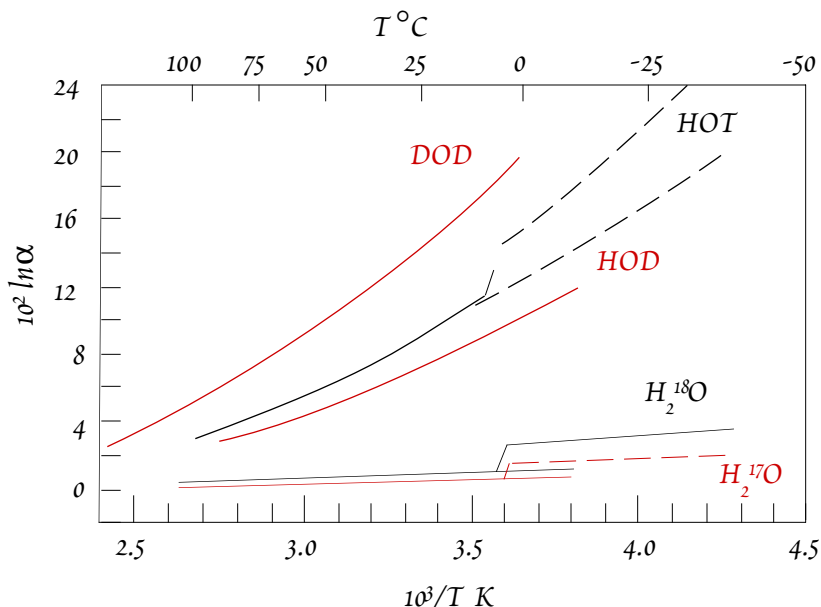


Figure 26.2. Temperature dependence of fractionation factors between vapor and water (solid lines) and vapor and ice (dashed lines) for various species of water.

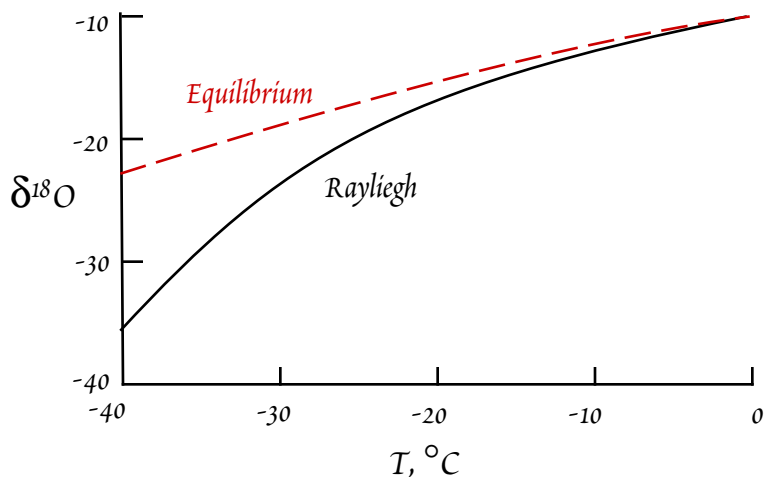


Figure 26.3. Calculated dependence of $\delta^{18}\text{O}$ on temperature based on equ. 26.24. We assume the water vapor starts out 10 per mil depleted in $\delta^{18}\text{O}$.

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stant a and B are 0.9822 and 15.788 respectively, so that 26.20 becomes:

$$\alpha = 0.9822 e^{15.788/RT} \quad 26.23$$

Substituting 26.22 and 26.23 into equation 26.12, our model is:

$$\delta^{18}\text{O}_v = 1000 \left(\left[\frac{\{T - 223\}}{50} \right]^{0.9822 e^{\frac{7.9448}{T}} - 1} - 1 \right) \quad 26.24$$

So we predict that the isotopic composition of water vapor should be a function of temperature. We can, of course, write a similar equation for equilibrium condensation. Figure 26.3 shows the temperature dependence we predict for water vapor in the atmosphere as a function of temperature (we have assumed that the vapor begins with $\delta^{18}\text{O}$ of -10 before condensation begins).

Of course, ours is not a particular sophisticated model; we have included none of the complexities of the real atmosphere. It is interesting to now look at some actual observations to compare with our model. Figure 26.4 shows the global variation in $\delta^{18}\text{O}$ in precipitation, which should be somewhat heavier than vapor, as a function of mean annual air temperature. The actual observations show a linear dependence on temperature and a somewhat greater range of $\delta^{18}\text{O}$ than our prediction. This reflects both the *ad hoc* nature of our model and the complexities of the real system. We did not, for example, consider that some precipitation is snow and some rain, nor did we consider the variations that evaporation at various temperatures might introduce.

Along with these factors, distance from the ocean also appears to be an important variable in the isotopic composition of precipitation. The further air moves from the site

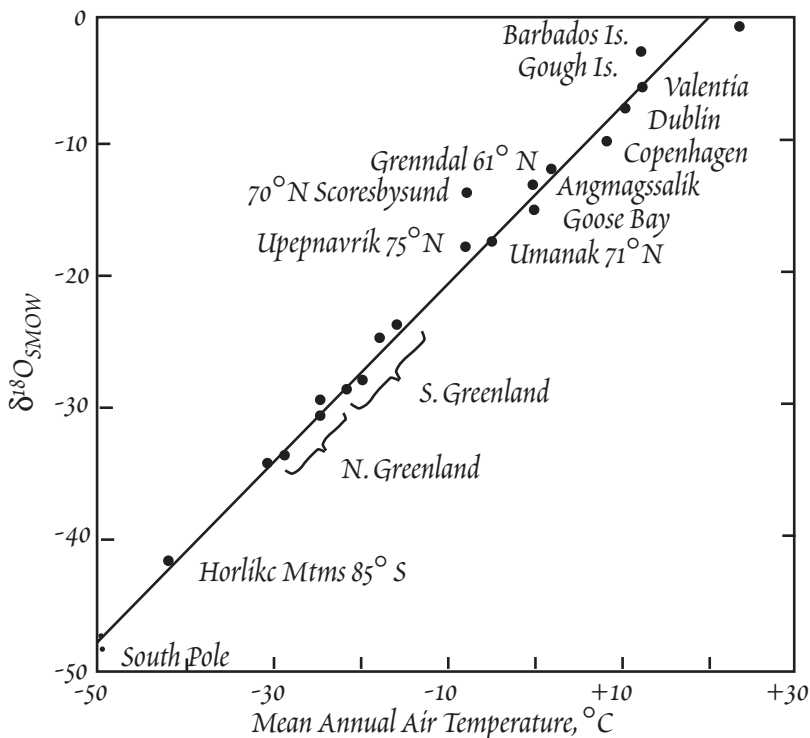


Figure 26.4. Variation of $\delta^{18}\text{O}$ in precipitation as a function of mean annual temperature.

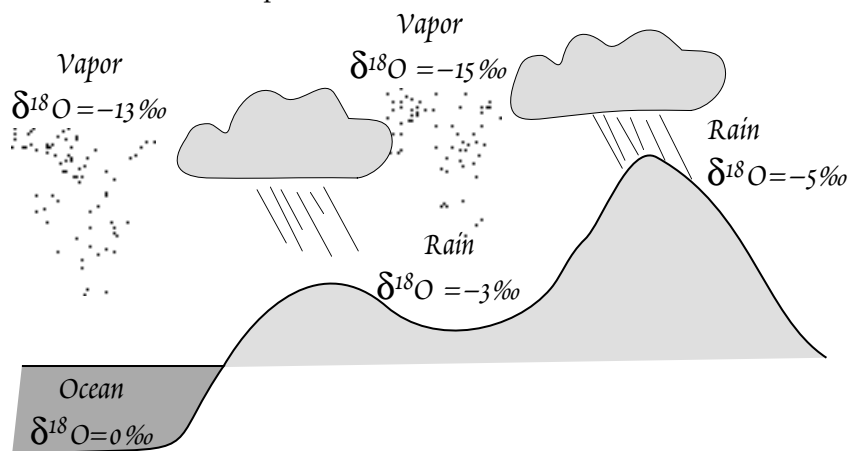


Figure 26.5. Cartoon illustrating the process of Rayleigh fractionation and the increasing fractionation of oxygen isotopes in rain as it moves inland.

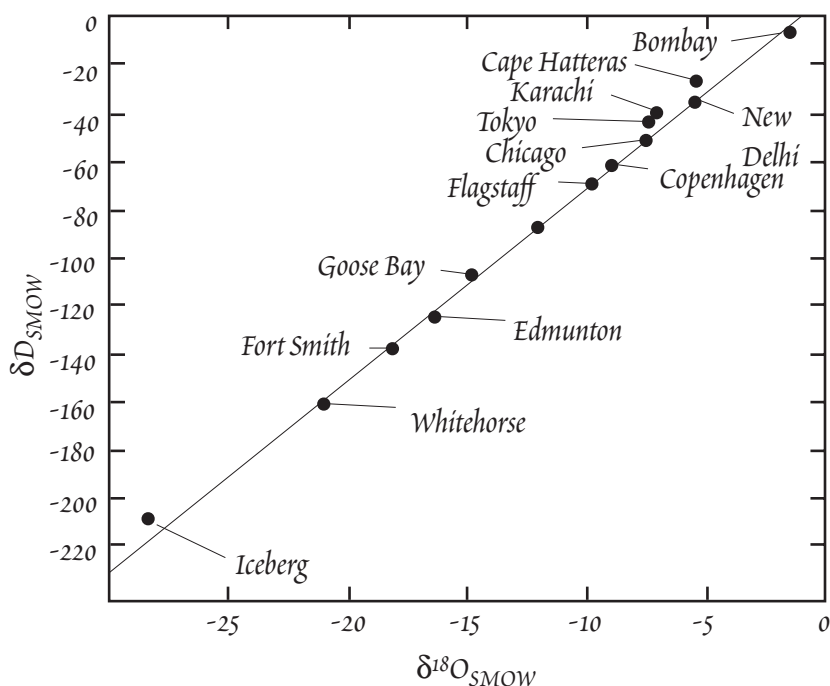


Figure 26.6. Northern hemisphere variation in δD and $\delta^{18}O$ in precipitation and meteoric waters. The relationship between δD and $\delta^{18}O$ is approximately $\delta D = 8\delta^{18}O + 10$. After Dansgaard (1964).

fractionation of hydrogen isotopes, however, is greater because the mass difference is greater.

Figure 27.6 shows the variation in oxygen isotopic composition of meteoric surface waters in the North America. The distribution is clearly not purely a function of mean annual temperature, and this illustrates the role of the factors discussed above. We will return to the topic of the hydrologic system in a future lecture when we discuss paleoclimatology.

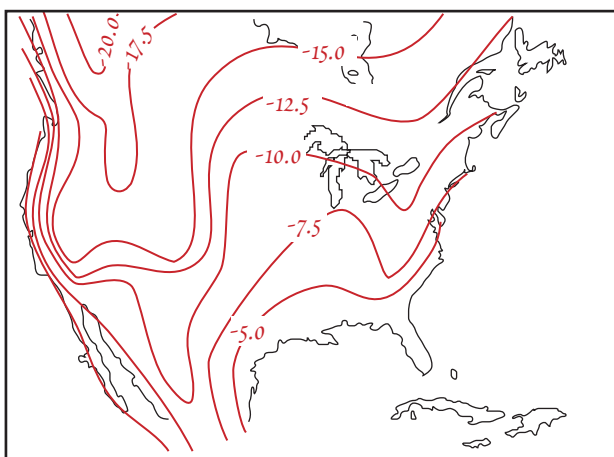


Figure 26.7. Variation of average $\delta^{18}O$ in precipitation over North America. $\delta^{18}O$ depends on orographic effects, mean annual temperature, and distance from the sources of water vapor.

of evaporation (the ocean), the more water is likely to have condensed and fallen as rain, and therefore, the smaller the value of f . Topography also plays an important role in the climate, rainfall, and therefore in the isotopic composition of precipitation. Mountains force air up, causing it to cool and the water vapor to condense. Thus the water vapor in air that has passed over a mountain range will be isotopically lighter than air on the ocean side of a mountain range. These factors are illustrated in the cartoon in Figure 26.5.

Hydrogen as well as oxygen isotopes will be fractionated in the hydrologic cycle. Indeed, $\delta^{18}O$ and δD are reasonably well correlated in precipitation, as is shown in Figure 26.6. The

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