Rayleigh Distillation Equation

\[ R = R_0 f^{\alpha - 1} \]

for constant \( \alpha \)

- \( R_0 \) = initial isotopic ratio
- \( R \) = instantaneous remaining ratio
- \( f \) = fraction of initial substance remaining
- \( \alpha \) = fractionation factor

slide from Clark and Aravena
Rayleigh model

The condensed phase is assumed to form in isotopic equilibrium with the surrounding vapor and to be removed immediately from the parcel.

Under these assumptions, the isotope content of this precipitation is a unique function of the initial isotope mass and water vapor mass within the air parcel and of the water vapor mass remaining when the precipitation forms.

This model quite satisfactorily explains the main features of the global distribution of isotopes in precipitation (seasonal and spatial characteristics, the observed relationships with local temperature or precipitation amount, and the strong link between $\delta D$ and $\delta^{18}O$).

Some factors determining $\delta^{18}O/\delta D$ in global precipitation in any given location

- latitude
- altitude ("altitude effect")
- distance to the coast ("continental effect")
- amount of precipitation ("amount effect")
- air temperature
- Changes in seasonality and intermittency of precipitation fallout

Out of these, two factors are of special significance: temperature and the amount of precipitation. The best temperature correlation is observed in continental regions nearer to the poles, whereas the correlation with amount of rainfall is most pronounced in tropical regions.

Dansgaard, [1964]; Jouzel et al., 1997; 2003

Continental and altitude effect for $\delta^{18}O$ in precipitation
Seasonal effect for $\delta^{18}O$ in precipitation

1) Seasonally changing temperature at mid and high latitudes
2) Seasonally modulated evapotranspiration flux over continents
3) Seasonally changing source areas of the vapor and/or different storm trajectories

“The Amount Effect”

(a) Long term monthly and annual mean $\delta^{18}O$ values for tropical island stations of the IAEA/WMO global network (20°S to 20°N), plotted as a function of mean monthly and mean annual precipitation

(b) plotted as a function of mean monthly and annual surface temperature

Rozanski et al., 1993
Kinetic Fractionation Effects

In reality, we cannot consider the process to be always at equilibrium between vapor and condensate…

The kinetic effect is due to the fact that molecular diffusivities in air are lower for isotopically heavier molecules, which induces an additional effect for non-equilibrium processes

The equilibrium isotopic effect is 8-10 times higher for deuterium than for O-18, whereas the kinetic effects are of the same order.

*Example:*

Kinetic isotope fractionation in molecular diffusion:

\[ K.E. = \frac{1}{2} m v^2 \]
Kinetic Fractionation Effects Related to the Hydrologic Cycle

Nonequilibrium isotopic fractionation often accompanies dynamic processes that are fast, incomplete, or unidirectional

Examples:
Fast evaporation: lightest isotopes preferentially break through the liquid surface and escape into the atmosphere during their fall to the ground, raindrops are subjected to evaporation and exchange with the surrounding vapor, evaporation is relatively high in dry air so that the process probably proceeds under non-equilibrium conditions

The existence of large drops: which are out of isotopic equilibrium, prevents the application of these simple Rayleigh distillation models to large convective systems, such as those occurring in tropical and equatorial regions.

$\delta D - \delta^{18}O$ relationship

Global Meteoric Water Line (GMWL): [Craig, 1961]

$\delta D = 8 \times \delta^{18}O + 10$

Global relationship between long-term annual (a) and monthly (b) means of $\delta^{18}O$ and $\delta D$ in precipitation derived for all stations in the IAEA/WMO global network. Heavey lines indicate the position of the GMWL.

Rozanski et al., 1993
“Deuterium Excess”

\[ d = \delta D - 8^{18}O \]

Dansgaard, 1964

\( d \) varies under non-equilibrium conditions, providing information not available from \( \delta^{18}O \) or \( \delta D \) alone.

\( d \) mainly reflects kinetic fractionation occurring during non-equilibrium processes (such as evaporation above the ocean surface) due to the difference in diffusivity between heavy and light molecules.

Generally thought that polar \( d \) values contain information on meteorological conditions at evaporative source regions, such as sea surface temperature (SST) and humidity.

Global mean \( d = 10^{10} \) today, but large variability between different samples and environments.

Weighted annual \( d \)-excess in precipitation

**Using \(d\)-excess to improve \(\Delta T\) estimates**

\(d\)-excess provides information on meteorological and oceanic characteristics of the water source region (in particular, their temperature and relative humidity).

Obliquity (41 ka periodicity) is significant for \(d\)-excess, with a strong anti-correlation for the past 150 ka (affecting the insolation gradient).

They argue that the high \(d\) values are driven by relatively less moisture from high latitudes, and more from low latitudes.

This increases glacial-interglacial \(\Delta T\) by about 15% [Vimeux et al., 2002]

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**Orbital Variations**

Obliquity (tilt)

...strongly modulates annual insolation (incoming solar radiation that reaches a particular latitude)
The $\delta^{18}$O – T correlation in precipitation

Slope $\approx 0.7$‰/°C

Empirical observations do show that mean annual $\delta^{18}$O values and mean annual temperatures are strongly correlated in the spatial domain. **Whether this relationship can be applied to the temporal domain is an important issue!**

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Glacial-interglacial $\delta^{18}$O and T differences

Based on 0.7‰/°C slope

<table>
<thead>
<tr>
<th>Location</th>
<th>$\Delta\delta^{18}$O(‰)</th>
<th>$\Delta\delta^{18}$O*(‰)</th>
<th>$\Delta T$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camp Century, Northern Greenland</td>
<td>11</td>
<td>12</td>
<td>~17</td>
</tr>
<tr>
<td>Dye 3, Southern Greenland</td>
<td>6</td>
<td>7</td>
<td>~10</td>
</tr>
<tr>
<td>Byrd Station</td>
<td>5</td>
<td>6</td>
<td>~9</td>
</tr>
<tr>
<td>Vostok, Antarctica</td>
<td>5</td>
<td>6</td>
<td>~9</td>
</tr>
</tbody>
</table>

*Corrected for change in the isotopic composition of sea water

from “The Glacial World According to Wally”
Interpreting paleo-temperatures using the $\delta$/$T$ relationship

Does the present day spatial relationship of 0.7‰/°C apply in the past?

What could change the slope?:
- Seasonality (timing) of precipitation
- Evaporative origin
- Sea-ice extent
- Evaporative source temperature changes

Temporal variations of the $\delta$-T relationship

Temporal slope estimates tend to be lower than the present day spatial slope, and yield ~0.5‰/°C

How can we estimate the temporal relationship?
- $N_2$ (δ$^{15}$N) and Ar (δ$^{40}$Ar) isotopes in ice core gas bubbles
- Borehole paleothermometry
- Empirical calibration using snow pit δ values and the rather short instrumental temperature record
- Modeling of δ in precipitation using GCMs
Firn-Ice Transition

**Firn**: porous, unconsolidated layer of snow on top of polar ice sheets

Gases diffuse throughout the layer of firn and fractionate due to gravity, and temperature and concentration gradients

Ice: air bubbles are closed off

from “The Glacial World According to Wally”

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**Thermal fractionation of N₂ and Ar in Ice Cores**

Thermal Diffusion: gas separation due to temperature gradient

- **Warm**
  - Light ($^{28}$N₂, $^{36}$Ar)
  - Diffusion coefficient varies with $T$
- **Cold**
  - Heavy ($^{29}$N₂, $^{40}$Ar)

Works for rapid climate changes only.

Severinghaus et al., 1998
Estimating Rapid Climate Change based on Thermal Fractionation of Gases in Firn

Severinghaus et al., 1998