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"The Rayleigh Equation"

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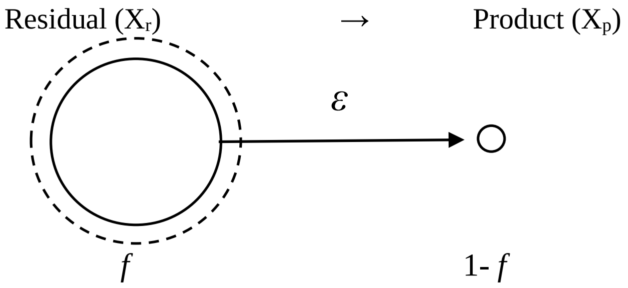
1. The Rayleigh Equation *(Fractional Distillation of Mixed Liquids)*

Lord Rayleigh, one of great minds in the history derived an equation to express the case of fractional distillation of mixed liquids. (Highly likely that he loved drinking liquor: ~~*Scotch Whiskey*~~). In isotope geochemistry, the expression of kinetic isotope fractionation adopted Lord Rayleigh's idea to describe the partitioning of isotopes between two different reservoirs containing the same element (or between two phases) as one reservoir decreases in size.



$X_{r,0}$ (initial amount of residual at t = 0) = $X_r + X_p$
ε is the isotope fractionation factor (= α-1)

There are few assumptions to derive this cool, fancy "The Rayleigh Equation". They are…

(1) Material is continuously removed from a mixed system containing molecules of two or more isotopic species (e.g., Hydrogen with H and D, or Sulfide with ^{32}S and ^{34}S).

(2) The fractionation accompanying the removal process at any instance is described by the fractionation factor α, which is

$$\alpha = \frac{X_{H,p}/X_{L,p}}{X_{H,r}/X_{L,r}}$$

(where subscript *H* means heavier isotope which is usually rare one, *L* means lighter isotope which is usually abundant, *p* means product and *r* means residual)

(3) The fractionation factor α is constant during the process.

Alright… where should we start from? We should start from the isotope fractionation factor *α!*

$$\alpha = \frac{X_{H,p}/X_{L,p}}{X_{H,r}/X_{L,r}} = \frac{R_p(t)}{R_r(t)}$$

where we denote R as an isotope ratio of each reservoir,

$$R_r = \frac{X_{H,r}}{X_{L,r}+X_{H,r}} \approx \frac{X_{H,r}}{X_{L,r}} \ (\because \text{usually}, X_{L,r} \gg X_{H,r})$$

(isotope ratio of the residual reservoir, for example)

Since the size of the residual is relatively much bigger than that of the product reservoir, we can replace R_r as the isotope ratio of the increment of product in an infinitely short time at time t.

$$\alpha = \frac{dR_p(t)}{R_r(t)} = \frac{dX_{H,p}/(dX_{L,p}+dX_{H,p})}{X_{H,r}/X_{L,r}} \approx \frac{dX_{H,p}/dX_{L,p}}{X_{H,r}/X_{L,r}} \ \ (\because \text{usually}, dX_{L,p} \gg dX_{H,p})$$

At the same time,

$$dX_{H,p} = -dX_{H,r} \ and \ dX_{L,p} = -dX_{L,r}$$

Thus,

$$\alpha = \frac{dX_{H,r}/dX_{L,r}}{X_{H,r}/X_{L,r}}$$

This can be manipulated into

$$\alpha * \frac{dX_{L,r}}{X_{L,r}} = \frac{dX_{H,r}}{X_{H,r}}$$

Since α is constant from the assumption, if you integrate both sides from t=0 to time *t*,

$$\alpha * ln\frac{X_{L,r}}{X_{L,r,0}} = ln\frac{X_{H,r}}{X_{H,r,0}}$$

($X_{L,r,0}$ and $X_{H,r,0}$ will be the initial amount of each isotope)

Since *f* is the fraction of residual at the time *t*,

$$f = \frac{X_{L,r} + X_{H,r,0}}{X_{L,r,0} + X_{H,r,0}} \approx \frac{X_{L,r}}{X_{L,r,0}}$$

$$(\because \text{ usually}, X_{L,r} \gg X_{H,r})$$

The equation can be expressed as below,

$$(\alpha - 1) * lnf = ln\frac{X_{H,r}}{X_{H,r,0}} - lnf$$

Using isotope ratio notation R,

$$(\alpha - 1) * lnf = ln\frac{R_r}{R_{r,0}}$$

Finally, we can get *the equation of Rayleigh Fractionation* as below,

$$f^{\alpha-1} = \frac{R_r}{R_{r,0}} \tag{1}$$

From this equation, we can apply small delta notation used in isotope geochemistry.
First, according to *mass balance equation*.

$$X_{L,r,0} = X_{L,r} + X_{L,p}$$
$$X_{H,r,0} = X_{H,r} + X_{H,p}$$

And as mentioned above, *f* is the fraction of residual at time *t*. Surely, 1-*f* will be the fraction of product at time *t*. Then…

$$X_{L,r} + X_{H,r} : X_{L,p} + X_{H,p} = f : 1 - f \approx X_{L,r} : X_{L,p} \quad (\because \text{ usually}, X_L \gg X_H)$$

Also, as mentioned above, R is an isotope ratio of each reservoir,

$$R_r = \frac{X_{H,r}}{X_{L,r}+X_{H,r}} \approx \frac{X_{H,r}}{X_{L,r}} \quad (\because \text{ usually}, X_{L,r} \gg X_{H,r})$$

(isotope ratio of the residual reservoir, for example)

If you combine these relationships above, you can get,

$$R_r * f + (1-f) * R_p = R_{r,0} \tag{2}$$

And since

$$\delta^H X_p = \frac{R_p}{R_{r,0}} - 1 \tag{3}$$

If you plug equation (3) into equation (2),

$$R_r * f + (1-f) * \delta^H X_p * R_{r,0} = R_{r,0}$$

$$\therefore\ \delta^L X_r = \frac{f-1}{f} * \delta^H X_p \tag{4}$$

From equation (1),

$$\frac{R_r}{R_{r,0}} = \delta^L X_r + 1 = f^{\alpha-1}$$

If we apply natural logarithm on both sides,

$$(\alpha-1)lnf = \ln(\delta^L X_r + 1)\ \approx \delta^L X_r\ \ (\because \text{usually}, \delta^L X_r \ll 1)$$

$$(\alpha-1)lnf = \delta^L X_r \tag{5}$$

If you plug (4) into equation (5),

$$\epsilon = \alpha - 1 = \frac{f-1}{f*lnf} * \delta^H X_p \tag{6}$$

2. References

Mariotti et al., 1981, "Experimental Determination of Nitrogen Kinetic Isotope Fractionation: Some Principles; Illustration for the Denitrification and Nitrification processes"