Isotopic fractionation in open systems: application to organic matter decomposition in ocean and land

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Stable isotopic evolution of a reservoir from which material is continuously removed with isotopic fractionation is generally described by the Rayleigh equation, widely used in geochemical research to describe two-component systems. It has been extended to the case of multi-component sources as well. Here we present an equation describing isotopic fractionation in open systems, wherefrom material is not only removed with isotopic fractionation, but fresh material of a different isotopic composition is added from an external source, at a given rate, and some examples where this equation is applicable.

Keywords: Denitrification, isotope fractionation, Rayleigh equation, soil organic matter.

LET R be the (non-radiogenic) stable isotopic ratio under consideration (e.g. $^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$, etc.), denoted by N^*/N, where N^* and N are respectively the number of molecules containing the heavier and lighter isotopes of a given mass of the same element (e.g. oxygen; $H_2{}^{18}O$ and $H_2{}^{16}O$; $N^* \ll N$; typical values in the ocean are 2000 and 10^6 respectively, in $\sim 3 \times 10^{-17}$ g of water). Taking the logarithm and differentiating, we obtain

$$dR/R = dN^*/N^* - dN/N = dN^*/(RN) - dN/N. \qquad (1)$$

At any instant dN_e^* and dN_e of the isotopically heavier and lighter molecules, respectively, are being removed by some physical process (e.g. evaporation from a lake) during an infinitesimal time interval Δt. Isotopic fractionation implies that dN_e^* is not equal to dN_e. In such a case, we define a fractionation factor between the material leaving (e.g. vapour) and the material left behind (e.g. water) as $\alpha = [dN_e^*/dN_e]/R$. In per mil units (‰), this fractionation factor is represented by $\varepsilon = (\alpha - 1) \times 10^3$. We restrict our consideration to isothermal processes where α and ε are constants. As in the case of Rayleigh fractionation[1-11], we assume that the reservoir remains isotopically homogeneous and has no isotopic gradients within, at any time. Let dN_r^* and dN_r of the heavier and lighter molecules be added to the reservoir during the interval Δt, but without fractionation (i.e. dN_r^*/dN_r is the same as N_r^*/N_r, the isotopic composition of the contributing source, which remains a constant $R_r \neq \alpha R$). Therefore, the net changes in the numbers of heavier and lighter isotopic

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molecules during Δt are $dN^* = dN_r^* - dN_e^*$ and $dN = dN_r - dN_e$ respectively, and their ratio,

$$dN^*/dN = (\beta R_r - \alpha R)/(\beta - 1), \qquad (2)$$

where β is dN_r/dN_e, the ratio of the amount of material added to that lost (the case $\beta = 1$ causes a singularity in eq. (2) and is discussed as a special case later). Integrating eq. (2) using eq. (1), with initial value of R as R_0, we obtain (see Appendix 1 for details):

$$R = R_0 f^\rho + [\beta R_r/(\alpha + \beta - 1)][1 - f^\rho], \quad \text{when } \beta \neq 1. \quad (3)$$

Here f is the fraction of the material left in the reservoir relative to its initial amount, i.e. $(N^* + N)/(N_0^* + N_0)$, approximated as (N/N_0), and $\rho = \alpha/(1 - \beta) - 1$. When $\beta = 0$, i.e., when these are only loss of material and no addition, this reduces to $R = R_0\, f^{\alpha-1}$, the classical Rayleigh fractionation equation. Using the δ notation for isotope ratios, taking the initial composition R_0 of the reservoir to be the reference value relative to which all other δ values are expressed, we have $\delta = (R/R_0 - 1)10^3$‰ and $\delta_r = (R_r/R_0 - 1)10^3$‰. With this standard notation eq. (3) becomes

$$\delta = [1 - f^\rho](\beta\delta_r - \varepsilon)/(\alpha + \beta - 1), \quad \text{when } \beta \neq 1. \quad (4)$$

For the case where $\beta = 1$, we cannot express the isotopic ratio of the reservoir as a function of f because it remains constant at unity (i.e. N remains as N_0), as the amount of material lost is compensated exactly by the incoming material from the source. A different approach is therefore necessary. The change in the number of heavier molecules is given, as before, by $dN^* = dN_r^* - dN_e^*$, while the change in the number of lighter molecules is $dN = dN_r - dN_e = 0$, as $\beta = dN_r/dN_e = 1$. Therefore, the change in the isotopic ratio of the reservoir is $dR = R_r(dN_r/N) - \alpha R(dN_e/N)$ (mass balance is used: $R dN = 0$ as $dN = 0$). This can be rewritten as

$$dR/(R_r - \alpha R) = dN_r/N_0. \qquad (5)$$

Integrating this with initial value of R as R_0, we get:

$$R = R_0 \exp[-(\alpha N_r/N_0)] + (R_r/\alpha)\{1 - \exp[-(\alpha N_r/N_0)]\}. \qquad (6)$$

Here N_r indicates the total number of lighter isotopic molecules added thus far. In the δ notation, eq. (6) becomes:

$$\delta = \{(\delta_r - \varepsilon)/\alpha\}\{1 - \exp[-(\alpha N_r/N_0)]\}. \qquad (7)$$

It is clear that for large mixing (i.e. $N_r \gg N_0$), the reservoir isotopic composition (δ) saturates to $(\delta_r - \varepsilon)/\alpha$, rather than δ_r expected in the case of simple mixing, as

here both mixing and removal by fractionation occur simultaneously. However, when α is small (e.g. close to unity), thus δ reaches $\delta_r - \varepsilon$. We note that eq. (4) was derived in another form by Mook[4]. The case of alteration of radiogenic stable isotopes undergoing isotopic exchange with meteoric water was treated similarly by Albarede[12]. On the other extreme, when $N_r \ll N_0$, $\delta \approx (\delta_r - \varepsilon)(N_r/N_0)$.

Figure 1 shows an example of the isotopic (δ) evolution of a reservoir as a function of the fraction (f) left of the initial amount. The fractionation factor α has been taken as 1.01 (i.e. $\varepsilon = 10‰$) and isotopic composition of the source contributing to the reservoir, as $-10‰$. As the material lost from the reservoir is isotopically heavier in this example (i.e. $\alpha > 1$), the isotopic composition of the remaining material rapidly decreases and reaches close to $-46‰$ (from a value of 0), when f becomes small (~ 0.01); this is the Rayleigh case where no material is added to the reservoir ($\beta = 0$ in Figure 1). As β values increase, the reservoir δ value is brought up higher and higher, as the source steadily contributes material with a constant isotopic composition (δ_r) of $-10‰$. The saturation value is $\delta_r - \varepsilon = -10-10 = -20‰$, as expected from eq. (7).
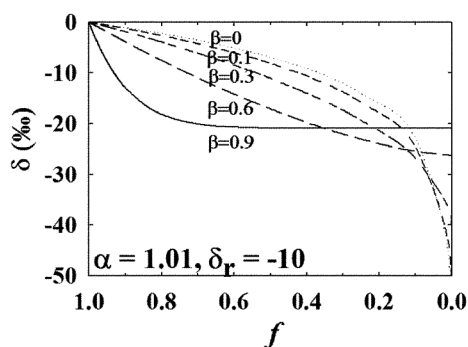

Figure 1. An example of the evolution of the isotopic composition (δ) of a reservoir as a function of the fraction (f) of the original material left, for different values of β, the ratio of instantaneous amount added to that lost ($\beta \neq 1$). The isotopic composition of the external source is taken as $-10‰$ and the fractionation factor, 1.01.
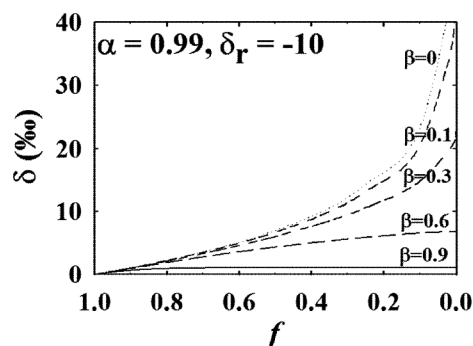

Figure 2. An example of the evolution of the isotopic composition (δ) of a reservoir as a function of the fraction (f) of the original material left, for different values of β, the ratio of instantaneous amount added to that lost ($\beta \neq 1$). The isotopic composition of the external source is taken as $-10‰$ and the fractionation factor, 0.99.

Figure 2 shows another example where fractionation factor has been taken as 0.99 ($\varepsilon = -10‰$) and isotopic composition of the source contributing to the reservoir, as $-10‰$. As the material lost from the reservoir is isotopically lighter in this example (i.e. $\alpha < 1$), the isotopic composition of the remaining material rapidly increases and reaches close to $+47‰$ (from a value of 0), when f becomes small (~ 0.01); this is the Rayleigh case where no material is added to the reservoir (closed system, $\beta = 0$ in Figure 2). As β increases, the reservoir δ value is lowered further and further, as the source steadily contributes material with a constant isotopic composition (δ_r) of $-10‰$. The saturation value is $\delta_r - \varepsilon = -10-(-10) = 0‰$, as expected from eq. (7).

We further discuss a general example for a special case of $\beta = 1$, i.e. the rates of addition and removal of material remain same at any instant. Figure 3 shows the isotopic (δ) evolution of a reservoir as a function of N_r/N_0 (ratio of lighter isotopic molecules being added by some source to the number of initial lighter isotopic molecules of the reservoir) for different combinations of enrichment factor (ε) and isotopic composition of material being added (δ_r). Initial isotopic composition of the reservoir is taken 5‰. The enrichment factor ε has been taken as $-25‰$ and $-22‰$ and δ_r as 10‰ and 5‰. Keeping δ_r constant, δ in the case of more negative ε increases faster than in the case of less negative ε. While keeping ε constant, δ in the case of higher δ_r increases faster than that in the case of lower δ_r.

We now discuss some examples where the given equations are applicable: ocean denitrification and soil organic matter decomposition. Data on both processes are limited. We extracted the data on isotopic composition (δ) and f values from the literature using origin package.

Primary productivity in surface ocean is generally limited due to unavailability of nutrients. However, some parts of the world oceans are highly productive due to nutrient inputs by upwelling, riverine inputs, etc. Decom-
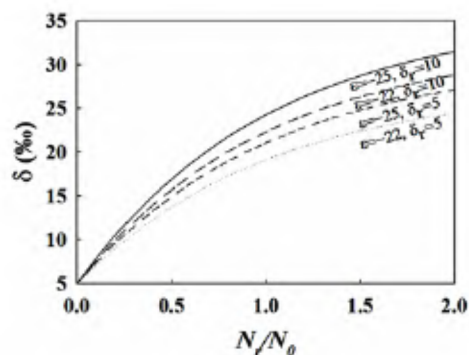

Figure 3. An example (for $\beta = 1$, i.e. the rate at which material is being added is equal to the removal rate) of the evolution of the isotopic composition (δ) of a reservoir as a function of N_r/N_0 (ratio of the total number of lighter isotopic molecules being added from an external source to the number of initial lighter isotopic molecules of the reservoir) for different combinations of ε and δ_r.

position of organic matter in these regions at intermediate ocean depths (~500 m) leads to oxygen deficiency at these depths. In such regions microorganisms use nitrate as an oxidant to decompose organic matter and produce N_2O and N_2 gases ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$). This microbially catalysed multi-step process is known as denitrification[13,14]. Ocean loses bioavailable nitrogen (NO_3^-) through this process. Denitrification occurs in oxygen minimum zones (OMZ) of the world oceans, e.g. the eastern tropical North Pacific and the Arabian Sea[15,16]. During denitrification, the nitrate concentration, [NO_3^-], in OMZ (generally 150–1000 m depth) decreases, i.e. f decreases. Denitrifying bacteria reduce lighter nitrate ($^{14}NO_3$) preferentially; hence the remaining NO_3^- gets enriched in heavier isotopes (^{15}N). At the same time, NO_3^- is being added by settling organic matter from above, by decay. If this is unaccounted for, the isotopic composition of the NO_3^- reservoir can be significantly different from that expected from a simple Rayleigh model. Unlike earlier studies, we apply eq. (4), which takes this effect into account, to understand the isotopic evolution of nitrate in the OMZ of the Arabian Sea using literature data[17].

Brandes et al.[17] obtained values for the enrichment factor (ε) and initial isotopic composition of nitrate (δ_0) of –22‰ and 6‰, respectively, in the Arabian Sea using a simple Rayleigh model and the measured $\delta^{15}N$ values of dissolved NO_3. We know that organic matter steadily rains down to the deeper ocean and therefore treating this system with a simple Rayleigh equation may lead to an incorrect estimation of the fractionation factor. This is borne out by laboratory derived ε values, which show large variations –17‰ to –29‰ (refs 18–20). We use different combinations of ε (–22‰ and –10‰) and δ_r values (5‰ and 10‰) to understand the isotopic evolution of nitrate and estimate the fraction of material added. β values are taken as 0, 0.2, 0.5 and 0.8. As the data are from Brandes et al.[17], for ε = –22‰, it shows no addition from an external source (Figure 4 a), even by changing the δ_r value 10‰ to 5‰ as f decreases from 1 to 0.75 (Figure 4 a and c). But when f decreases further (0.75–0.70), ~20% contribution from external source is observed. In Figure 4 b and d, when ε value is –10‰, results show that ~50% of the nitrate that is lost during denitrification is compensated by organic matter raining from above, for a small initial decrease in f; if f decreases further, this contribution rises to ~80%. Thus by fixing β, the ratio of the rates of nitrate release due to fresh organic matter getting oxidized and the in situ denitrification, we can constrain the fractionation factor better with the eq. (4). In this special case $\delta_r = \delta_0$.

Now we discuss another example where soil organic matter (SOM) is decomposed by bacteria up to 100 cm depth. Similar to oceanic denitrification, these decomposing organisms also preferentially release lighter isotopic molecules (^{12}C) for respiration and hence remaining SOM

enriched in heavier isotopes (^{13}C) (refs 21 and 22). Decrease in the total carbon content and increase in $\delta^{13}C$ are signatures of fractionation during decomposition of SOM. There is a supply of organic matter from above by diffusion/leaching, so eq. (4) is suitable to characterize this process[23]. Surface isotopic composition of SOM is taken as initial isotopic composition (δ_0; freshly deposited organic matter). The remaining fraction f of SOM is cal-
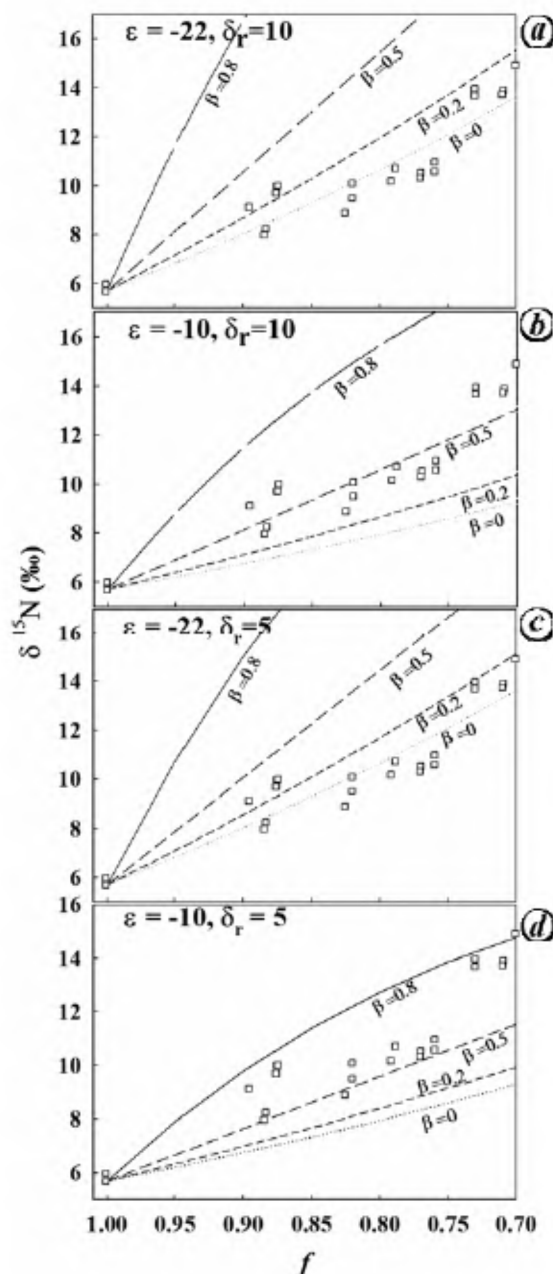

Figure 4. An example of denitrification in the sea: open squares in all the plots show the variation of $\delta^{15}N$ of dissolved NO_3 with f (fraction of NO_3 remaining) from experimental data[17]. Initial isotopic value of nitrate (δ_0) is 5.7‰ and β values are taken as 0, 0.2, 0.5 and 0.8. Dotted and solid lines are plotted using eq. (4) for different β values. *a*, ε = –22‰ and δ_r = 10‰; *b*, ε = –10‰ and δ_r = 10‰; *c*, ε = –22‰ and δ_r = 5‰; *d*, ε = –10‰ and δ_r = 5‰.

culated as the ratio of carbon content at a particular depth and the surface[23]. Accoe et al.[23] have estimated an ε value −2.3‰ using the simple Rayleigh model. We use four different combinations of ε (−2.3‰ and −1‰) and δ_r (−25‰ and −30‰) values in eq. (4) to analyse the same data. In Figure 5 a and b, when δ_r remains constant (−25‰), an

increase in enrichment factor shows that contribution of SOM from above increases (i.e. β value increases). In Figure 5 c, when f decreases from 1 to 0.7, no external contribution ($\beta = 0$) is seen. Further decrease in f shows $\beta = 0.2$. When $\varepsilon = −1‰$ and $\delta_r = −30‰$ (Figure 4 d), data points are difficult to explain especially when f decreases from 0.7 to 0.0. This happens because unlike all other cases, here δ value of the external source is less than the initial reservoir value. While increasing β, isotopic composition of the resultant SOM cannot be increased, therefore it saturates. This can be used as an indication of absence of carbon percolation from above.

Appendix 1

We consider a reservoir that loses material due to any physicochemical process with isotopic fractionation at a constant temperature. At any instant the stable isotope ratio is given by

$$R = \frac{N^*}{N}. \tag{1A}$$

Taking logarithm of both sides of eq. (1A)

$$\ln R = \ln N^* - \ln N. \tag{2A}$$

After differentiating, eq. (2A) becomes

$$\frac{dR}{R} = \frac{dN^*}{N^*} - \frac{dN}{N} = \frac{dN^*}{NR} - \frac{dN}{N}. \tag{3A}$$

At any instant, let dN_r^* and dN_e are being lost and dN_r^* and dN_r are being added to the reservoir. So the net change in N^* and N is

$$dN^* = dN_r^* - dN_e^*, \tag{4A}$$

$$dN = dN_r - dN_e. \tag{5A}$$

Dividing eq. (4A) by eq. (5A)

$$\frac{dN^*}{dN} = \frac{dN_r^* - dN_e^*}{dN_r - dN_e} = \frac{\dfrac{dN_r^*}{dN_r} \times \dfrac{dN_r}{dN_e} - \dfrac{dN_e^*}{dN_e}}{\dfrac{dN_r}{dN_e} - 1} \tag{6A}$$

$$= \frac{\beta R_r - \alpha R}{\beta - 1},$$
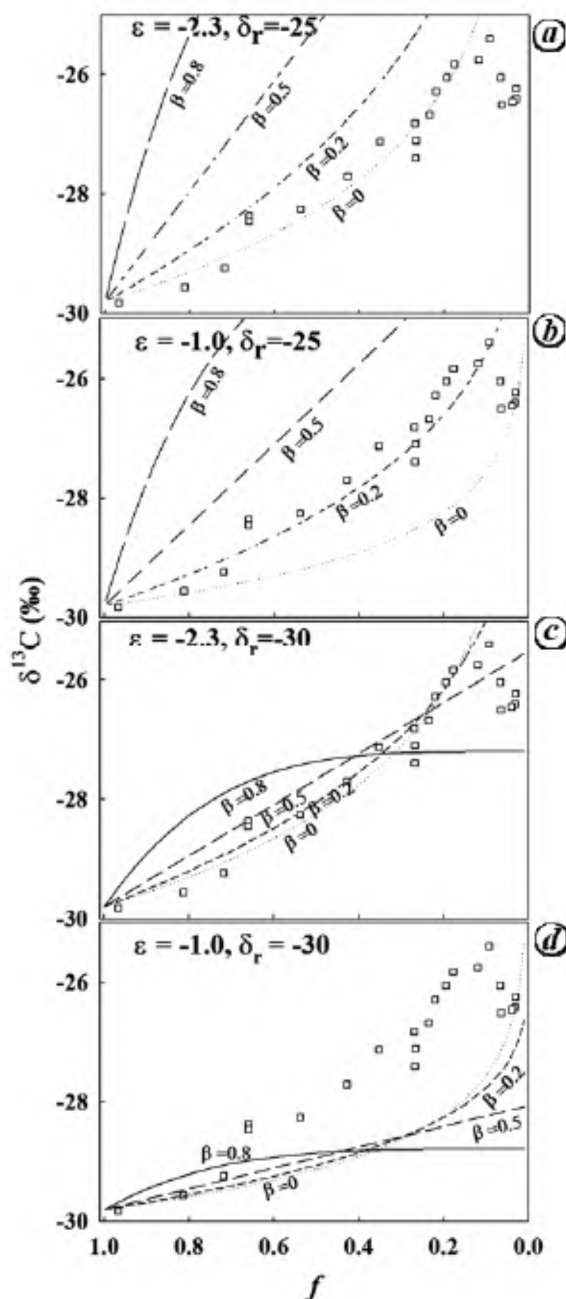
where α is defined as $(dN_e^*/dN_e)/(N^*/N)$.

Figure 5. Example where soil organic matter (SOM) is decomposed by microorganisms: open squares in all the plots show the variation of $\delta^{13}C$ of SOM variation with f (fraction of SOM remaining) from experimental data[23]. Initial isotopic value of SOM (δ_0) is −29.8‰ and β values are taken as 0, 0.2, 0.5 and 0.8. Dotted and solid lines are derived using eq. (4) for different β values. **a**, $\varepsilon = −2.3‰$ and $\delta_r = −25‰$; **b**, $\varepsilon = −1‰$ and $\delta_r = −25‰$; **c**, $\varepsilon = −2.3‰$ and $\delta_r = −30‰$; **d**, $\varepsilon = −1‰$ and $\delta_r = −30‰$.

Substituting the value of dN^* from eq. (6A) to eq. (3A)

$$\frac{dR}{R} = \left(\frac{\beta R_r - \alpha R}{\beta - 1}\right)\frac{dN}{NR} - \frac{dN}{N} = \frac{dN}{N}\left(\frac{\beta\dfrac{R_r}{R}}{\beta - 1} - \frac{\alpha}{\beta - 1} - 1\right)$$

or

$$\frac{dR}{\left(\dfrac{\beta R_r}{\beta - 1} - \left(\dfrac{\alpha}{\beta - 1} + 1\right)R\right)} = \frac{dN}{N}. \tag{7A}$$

Take integration on both sides

$$\frac{1}{-\left(\dfrac{\alpha}{\beta - 1} + 1\right)}\int\frac{d\left\{\dfrac{\beta R_r}{\beta - 1} - \left(\dfrac{\alpha}{\beta - 1} + 1\right)R\right\}}{\left\{\dfrac{\beta R_r}{\beta - 1} - \left(\dfrac{\alpha}{\beta - 1} + 1\right)R\right\}} = \int\frac{dN}{N}. \tag{8A}$$

Condition for integrating this equation is

$$\frac{\beta R_r}{\beta - 1} \neq \left(\frac{\alpha}{\beta - 1} + 1\right)R, \text{ it gives } \frac{dN_r}{dN_e} \neq \left(\frac{\alpha - 1}{\dfrac{R_r}{R} - 1}\right). \tag{9A}$$

At $\beta = 1$, this equation is not solvable, hence first we take the case where $\beta \neq 1$.

Case I: On integrating eq. (8A), we get

$$-\frac{1}{\left(\dfrac{\alpha}{\beta - 1} + 1\right)}\ln\left\{\frac{\beta R_r}{\beta - 1} - \left(\frac{\alpha}{\beta - 1} + 1\right)R\right\} = \ln N + k. \tag{10A}$$

After applying boundary conditions, at $t = 0$, $N = N_0$, $R = R_0$, we evaluate k and substitute in eq. (10A); we get

$$-\frac{1}{\left(\dfrac{\alpha}{\beta - 1} + 1\right)}\ln\left\{\frac{\dfrac{\beta R_r}{\beta - 1} - \left(\dfrac{\alpha}{\beta - 1} + 1\right)R}{\dfrac{\beta R_r}{\beta - 1} - \left(\dfrac{\alpha}{\beta - 1} + 1\right)R_0}\right\} \tag{11A}$$

$$= \ln\frac{N}{N_0} = \ln f.$$

Further simplifying eq. (11A) becomes

$$R = R_0 f^{-\left(\frac{\alpha}{\beta - 1} + 1\right)} + \frac{\beta}{\alpha + \beta - 1}R_r\left[1 - f^{-\left(\frac{\alpha}{\beta - 1} + 1\right)}\right]. \tag{12A}$$

From the standard definition of δ, we write $R = (1 + \delta \times 10^{-3})R_0$, we get the final equation

$$\delta = \frac{\beta\delta_r - \varepsilon}{\alpha + \beta - 1}\left(1 - f^{-\left(\frac{\alpha}{\beta - 1} + 1\right)}\right). \tag{13A}$$

Substituting $\beta = 0$, eq. (13A) converts to the simple Rayleigh equation, which cross-checks the derivation.

Case II: When $\beta = 1$, $dN = 0$ hence from eq. (5A), $dN_r = dN_e$. Equation (3A) becomes

$$dR = \frac{dN_r^* - dN_e^*}{N} = R_r\frac{dN_r}{N} - \alpha R\frac{dN_e}{N}$$
$$= \left(\frac{R_r - \alpha R}{N}\right)dN_r = \left(\frac{R_r - \alpha R}{N_0}\right)dN_r. \tag{14A}$$

After rearranging and integrating, this becomes

$$-\frac{1}{\alpha}\int\frac{d(R_r - \alpha R)}{R_r - \alpha R} = \frac{1}{N_0}\int dN_r. \tag{15A}$$

After solving fully and applying boundary conditions as in the previous case, we get

$$\delta = \frac{(\delta_r - \varepsilon)}{\alpha}\left(1 - e^{-\alpha\frac{N_r}{N_0}}\right). \tag{16A}$$

Equations (13A) and (16A) express the resultant isotopic composition after addition and removal of isotopic molecules for $\beta \neq 1$ (when input and output fluxes are different) and $\beta = 1$ (when these fluxes are the same), respectively.

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Thermal conductivity estimates in the Niger Delta using lithologic data and geophysical well logs

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Thermal ock properties and heat flow were determined from 260 wells in the Niger Delta. The thermal conductivity data provides inputs for the determination of heat flow and for thermal evaluation of the Niger Delta basin. A map has been constructed using lithologic data and geophysical well logs to give an overview of its distribution. The thermal conductivity for sand and shale, the predominant lithology in the Niger Delta, shows wide variations from one well to another. In the Benin Formation, thermal conductivity has an average value of 8 W/mK. The lowest values are found offshore westward, while highest values occur northward. The conductivity values, however, decrease towards the marine paralic section, with an average value of 5 W/mK, the region of highest interest. The thermal conductivity values have been used in calculating heat flow. A significant regional trend of relatively low (20–30 mW/m^2) heat flow at the central part of the delta, increases both seaward and northward (40–55 mW/m^2). The lowest values of heat flow as low as 20 mW/m^2 are recorded in the central part of the delta while the highest values exceeding 50 mW/m^2 are recorded in the northern part of the delta. Knowledge of thermal properties has direct relevance for hydrocarbon exploration. It has been established that the bulk of hydrocarbon accumulation in the Niger Delta is of thermal origin, hence the importance of this findings.

Keywords: Heat flow, temperature, thermal conductivity, sand percentage.

THE thermal conductivity of rocks is one of the major factors that affect temperature in sedimentary basins and therefore, should be addressed in basin analysis; its effect on the temperature distribution is significant, up to the order of 50–80%[1]. As a result of thermal conductivity, thermal structure of a basin may change laterally and vertically even if the heat flow into the basin is regionally the same[2].

The variability of heat flow in most basins must arise from some combination of at least the following four principal influences: heat redistribution by migration of formation fluids (hydrodynamic effect); variations in conductivity and heat generation in the sedimentary