β-DECAY AND THE ORIGIN OF OPTICAL PURITY

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Abstract. Improving Keszthelyi's simple model the evolutionary appearance of concentration difference of enanthiomeric compounds due to their differential decomposition by β-rays is investigated taking into account the racemization as well. It is shown that if the difference in the cross sections is very small then the resulting concentration difference will never exceed the statistical fluctuations, while in the case of a sufficiently large difference in the cross sections the concentration difference can overgrow the statistical fluctuations in an evolutionary reasonable period of time. The relative difference of the concentrations, however, will be generally much smaller than that of the cross sections. Therefore some other, amplifying mechanism must be postulated in order to explain the optical purity of living beings.

In a recent paper Keszthelyi (Keszthelyi, 1976) estimated the time necessary for the appearance of the optical activity above the statistical fluctuations, supposing the decomposition of enantiomeric molecules by β-particles being different. He derived the following system of equations:

$$\begin{aligned} \dot{n}_L &= k - \epsilon(1-\delta)n_L\,, \\ \dot{n}_D &= k - \epsilon(1+\delta)n_L\,, \end{aligned} \tag{1}$$

where n_L and n_D are the number of L and D molecules in a volume of 1 liter sea water (1 cm^2 x 10 m) at surface, k (denoted by α/l in Keszthelyi's paper) is the rate of appearance of L or D molecules in this volume, ϵ is the mean cross section for decomposition by β-particles, δ is the relative difference in the cross sections for L and D molecules.

He obtained for the time in question

$$t \approx \sqrt[3]{\frac{2}{k\epsilon^2\delta^2}}\,. \tag{1a}$$

For the quantities in Equation (1) the following estimates were selected from the literature: $k \approx 10^{10}\ \mathrm{s}^{-1}$, $\epsilon \approx 5 \times 10^{-19}\ \mathrm{s}^{-1}$.

With these data (1a) gives

$$t \approx 10^9 \delta^{-2/3}\ \mathrm{s}$$

which means that even for $\pi = 10^{-9}\,\Delta t$ is less than 15 million years, a rather short period on the evolutionary time scale.

We refine this model taking into account the spontaneous racemization.

Denoting the rate constant of racemization by r (the corresponding time constant is

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$\tau = 1/r$) the following system of equations is obtained:

$$\begin{aligned} \dot{n}_L &= k - \epsilon(1-\delta)n_L - rn_L + rn_D, \\ \dot{n}_D &= k - \epsilon(1+\delta)n_D - rn_D + rn_L. \end{aligned} \tag{2}$$

Introducing the difference and the sum of the number of L and D molecules

$$\Delta = n_L - n_D,$$
$$\Sigma = n_L + n_D.$$

Equation (2) can be transformed into

$$\begin{aligned} \dot{\Sigma} &= 2k - \epsilon\Sigma + \epsilon\delta\Delta, \\ \dot{\Delta} &= \epsilon\delta\Sigma - (2r+\epsilon)\Delta. \end{aligned} \tag{3}$$

Under the initial conditions $\Sigma(o) = \Delta(o) = 0$ the solution of Equation (3) is

$$\Sigma = \Sigma_\infty(1 - (1-A)e^{\lambda_1 t} - Ae^{\lambda_2 t}),$$
$$\Delta = \Delta_\infty(1 - (1+B)e^{\lambda_1 t} + Be^{\lambda_2 t}),$$

where

$$\Sigma_\infty = \frac{2k(2r+\epsilon)}{\epsilon(2r+\epsilon-\epsilon\delta^2)} \quad \text{and} \quad \Delta_\infty = \frac{2k\delta}{2r+\epsilon-\epsilon\delta^2}$$

are the asymptotic values of Σ and Δ,

$$\lambda_{1,2} = -\epsilon - r \pm r\sqrt{1 + \left(\frac{\epsilon\delta}{r}\right)^2},$$

$$A = \frac{\dfrac{2k}{\Sigma_\infty} + \lambda_1}{\lambda_1 - \lambda_2} = \frac{1}{2}\left(1 - \frac{1 + \dfrac{\epsilon^2\delta^2}{r(2r+\epsilon)}}{\sqrt{1+\left(\dfrac{\epsilon\delta}{r}\right)^2}}\right),$$

$$B = \frac{-\lambda_1}{\lambda_1 - \lambda_2} = -\frac{1}{2}\left(1 - \frac{1 + \dfrac{\epsilon}{r}}{\sqrt{1+\left(\dfrac{\epsilon\delta}{r}\right)^2}}\right).$$

The first question to answer is whether the concentration shift can overgrow the fluctuations at all, i.e. whether $|\Delta| > \sqrt{\Sigma}$ for some t. Since it can be proved that Δ^2/Σ is monotonously increasing with time we need to consider only the asymptotic value of this ratio. The concentration difference can exceed the statistical fluctuations at least m times if and only if

$$\frac{\Delta_\infty^2}{\Sigma_\infty} > m^2, \tag{3a}$$

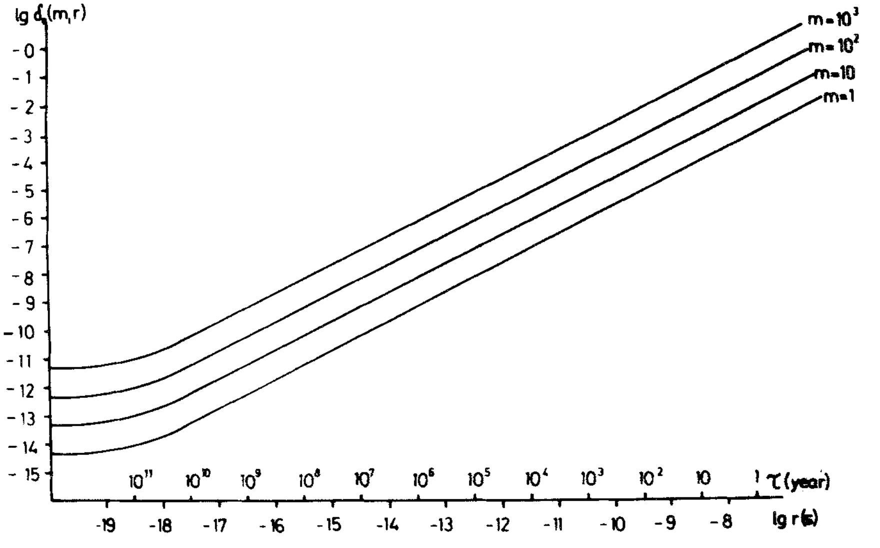

Fig. 1. Dependence of $\delta_0(m,r)$ on the racemization rate r, for several values of m. The concentration difference asymptotically exceeds m-fold the level of statistical fluctuations if and only if $\delta > \delta_0(m,r)$. On the abscissa $\tau = 1/r$ is also shown.

i.e.,

$$\delta^2 > \frac{m^2(2r+\epsilon)^2}{\epsilon(2k+m^2(2r+\epsilon))} = \delta_0^2(m,r)\,,$$

where $\delta_0(m,r)$ is the minimal allowable value for δ. The plot of $\delta_0(m,r)$ vs r is given in Figure 1. It can be seen that for $r \geqslant \epsilon$ (that is for $\tau \leqslant 10^9$ yr)

$$\delta_0(m,r) \approx 2 \times 10^4 \text{ mr}\,.$$

while for $r = 0$

$$\delta_0(m,0) \approx 5 \times 10^{-15} \text{ m}\,.$$

This means that for $\delta < \delta_0(m,o)$ the difference will not exceed the statistical fluctuations, even if there is no racemization.

Even though the concentration shift reaches the level of statistical fluctuations it might require an enormously long period of time. In this case the process can not explain the origin of optical purity in the biosphere. Therefore it is necessary to estimate the time elapsing before the concentration difference grows out of the statistical noise. Since Δ^2/Σ is monotonously increasing in time there is a definite moment of time (t_0) where the concentration difference meets the level of statistical fluctuations (or, more generally, m times this level). As the equation

$$\Delta = m \cdot \sqrt{\Sigma}$$

is a transcendental one that seems to have no explicit expression for its solution, we give here only an upper and a lower limit for t_0.

After some algebra one arrives at

$$\frac{1}{\lambda_1}\ln\left(\frac{2k+m^2(2r+\epsilon)}{2k}\right)\left(1-\left(\frac{\delta(m,r)}{\delta}\right)^2\right)<t_0$$

$$<\frac{1}{\lambda_1}\ln\left(\frac{1}{1+B}\left(1-\frac{m^2\dfrac{r}{\epsilon\delta}+\sqrt{\left(m^2\dfrac{r}{\epsilon\delta}\right)^2+m^2\dfrac{2k}{2r+\epsilon-\epsilon\delta^2}}}{\Delta_\infty}\right)\right).$$

For $r \gg \epsilon$ both the upper and the lower limit depend only on δ/m.

Obviously, the inverse question is more interesting: for which values of δ will the concentration difference reach m times the level of statistical fluctuations in a period of time not longer than T (say, 100 million years)? In other words when will be $t \leqslant T$, or when will be

$$\left.\frac{\Delta^2}{\Sigma}\right|_{t=T}=\frac{\Delta_\infty^2}{\Sigma_\infty}\frac{(1-(1+B)e^{\lambda_1 T}+Be^{\lambda_2 T})^2}{1-(1-A)e^{\lambda_1 T}-Ae^{\lambda_2 T}}\geqslant m^2.$$

If $r \gg \epsilon$ and $r \gg 1/T$ we can write it as

$$\frac{\Delta_\infty^2}{\Sigma_\infty}(1-e^{\lambda_1 T})\geqslant m^2. \tag{3b}$$

(It can be shown that the relative error of this substitution is about $\tau/(T-\tau)$ whenever $\tau \ll T$). As Equation (3b) is analogous to Equation (3a) the following condition has to be fulfilled:

$$\delta \geqslant \delta_0\left(\frac{m}{\sqrt{1-e^{\lambda_1 T'}}}r\right). \tag{4}$$

For $T \gg \tau$ this is a necessary and sufficient condition, for $\tau > T$ it is a necessary but not sufficient one.

For 10^6 yr $\leqslant T \leqslant 10^9$ yr Equation (4) further simplifies to

$$\frac{\delta_0}{m}\approx 2\times 10^{13} r\sqrt{\frac{2}{T}}.$$

δ_0/m vs r is shown in Figure 2 for several values of T. From the data it can be decided whether at any given racemization rate the concentration shift reaches the desired level above the noise within a given T.

The final problem is the extent of this concentration shift. The relative difference in the number of the two enantiomers is

$$\frac{n_L-n_D}{n_L+n_D}=\frac{\Delta}{\Sigma}\leqslant\frac{\Delta_\infty}{\Sigma_\infty}=\frac{\epsilon}{\epsilon+2r}\delta.$$

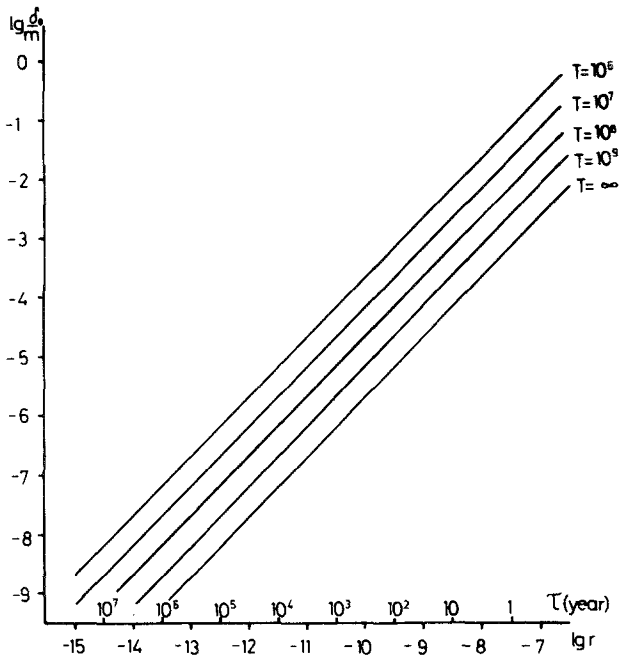

Fig. 2. Dependence of δ_0/m on r, for several values of T. The concentration difference overgrows m-fold the level of statistical fluctuations, in a period of time not longer than T, if and only if $\delta > \delta_0$.

For $r = 0$ (no racemization)

$$\frac{n_L - n_D}{n_L + n_D} = \delta \ .$$

For $r > 0$:

$$\frac{n_L - n_D}{n_L + n_D} < \delta \ ,$$

and for $r \gg \epsilon$ the relative difference will be smaller than δ by many orders of magnitude. This means that, although the difference in the cross sections can manifest itself as a concentration difference, if there is a not too slow racemization then this mechanism is of very low yield. Therefore some different, amplifying mechanism is necessary to explain the observed optical purity of the biosphere.

Reference

Keszthelyi, L: 1976, *Origins of Life* 7, 349.