# Isotopic Fractionation in a Thermal Ion Source

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Isotopic fractionation behavior in a thermal ion source was theroretically studied. An equation relating to the observed isotope ratio with the evaporated fraction of the sample was derived under conditions where two kinds of chemical species, atomic (atomic ions and neutral atoms) and molecular (molecular ions and molecules) species, simultaneously evaporate from the filament. It was demonstrated that integrations of all ion currents for two isotopes do not necessarily give a true ratio of the two isotopes in the sample when two evaporating chemical species are ionized at different rates. Isotopic fractionation curves for halides and elements of lithium, potassium, and rubidium are presented.

Fractionation effects in a thermal ion source are a serious problem in mass spectrometry, especially in isotope ratio measurements. In order to obtain the precise isotope ratios of samples, attempts have been made by many investigators[1,2] to estimate the degree of fractionation and to find appropriate correction methods.

The quantitative analyses of Eberhardt *et al.*[3] showed that evaporation of sample in a single filament ion source follows the Rayleigh distillation formula[4] and that atomic species (atomic ions and neutral atoms) are the only species evaporating from the filament. Their treatment, however, is insufficient in that the results can not be applied to a multiple filament ion source in which not only atomic but also molecular species (molecular ions, neutral molecules and their fragments) evaporate from the filament.

The isotopic fractionation factor in the evaporation of molecular species differs greatly from that of atomic species so that the net fractionation depends to a great extent on the molar ratio of atomic species to molecular species in the vapor leaving the filament. By taking this into account quantitative analysis seems to be helpful for clearing the extent of fractionation and improving mass spectrometric techniques and correction methods for precise isotope ratio measurements.

In this paper, variation of observed isotope ratio with percentage of the evaporated sample was theoretically calculated under conditions where both atomic and molecular species simultaneously evaporate from the filament, and it was shown that integrations of all ion currents for two isotopes do not necessarily give the true ratio of the two isotopes in the sample when two evaporating chemical species, atomic species and molecular species, are ionized at different rates.

## Theoretical

When the vapor pressure of an isotopic substance is of the order of magnitude such that the chance of an evaporated atom or molecule returning to the filament is very small, the total mass of vapor escaping from the unit area of surface in unit time is given by Langmuir's equation[5]

$$\mu = p\cdot c\left(\frac{M}{2\pi \boldsymbol{R}T}\right)^{1/2} \tag{1}$$

where $p$ is vapor pressure of an evaporating isotopic substance in pure state, $c$, its molar concentration in a sample on the filament, $M$, its molecular (or atomic) weight, $\boldsymbol{R}$, gas constant, and $T$, absolute temperature. Thus the number of moles $N$ evaporating per unit area in unit time is

$$N = \mu/M = p\cdot c(2\pi M\boldsymbol{R}T)^{-1/2} \tag{2}$$

For a mixture of two isotopic chemical species of masses $M_1$, $M_2$, concentrations of $c_1$, $c_2$, evaporating from a surface of filament, the numbers of moles of the two isotopes evaporating will be

$$\begin{aligned} N_1 &= p_1\cdot c_1(2\pi M_1\boldsymbol{R}T)^{-1/2} \\ N_2 &= p_2\cdot c_2(2\pi M_2\boldsymbol{R}T)^{-1/2} \end{aligned} \tag{3}$$

At such high temperatures as in thermal ion sources, the difference of vapor pressures between two isotopic substances will be negligibly small, so that

$$p_1 = p_2 \tag{4}$$

Hence the ratio of the molar concentrations of two isotopic species in the vaporized vapor (isotope ratio in the vapor) is given by

$$r = \frac{N_1}{N_2} = \frac{c_1}{c_2}\left(\frac{M_2}{M_1}\right)^{1/2} = \gamma\cdot R \tag{5}$$

where $\gamma$ $(=(M_2/M_1)^{1/2})$ is a fractionation factor, and $R$ $(=c_1/c_2)$ is the isotope ratio of the sample remaining on the filament. Accordingly, when some fractions of the sample on the filament are thermally decomposed into atomic species (or molecular fragments) and vaporization takes place in both atomic species $A$ and molecules $B$, isotope ratios of the vapors A and B just evaporating from the filament are

$$\begin{aligned} r_a &= \alpha R \\ r_b &= \beta R \end{aligned} \tag{6}$$

where

$$\begin{aligned} \alpha &= \sqrt{\frac{MA_h}{MA_l}} \\ \beta &= \sqrt{\frac{MB_h}{MB_l}} \end{aligned} \tag{7}$$

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[1] S. Taniguchi, O. Toyama, and T. Hayakawa, *Mass Spectrometry*, **10**, 91 (1962).

[2] M. H. Dodson, *J. Sci. Instr.*, **40**, 289 (1963).

[3] A. Eberhardt, R. Delwiche, and J. Geiss, *Z. Naturforschg.*, **19a**, 736 (1964).

[4] Lord Rayleigh, *Phil. Mag.*, **42**, 493 (1896).

[5] I. Langmuir, *Phys. Z.*, **14**, 1273 (1913).

Here $MA$ and $MB$ are the molecular (or atomic) weights of vapors A and B, and the subscripts $h$ and $l$ denote heavy and light isotopes, respectively. In the case of lithium iodide, A and B may be either $\mathrm{Li}^{(0,+)}$ or LiI. It is also assumed that the residual sample on the filament undergoes continuous and complete mixing and that there is no isotopic fractionation between chemical species $A$ and $B$.

Now we consider the course of evaporation. If the chemical species $A$ and $B$ simultaneously evaporate from the filament, the material balance requires

$$\mathrm{d}A + \mathrm{d}B = \mathrm{d}Q \tag{8}$$

where d$A$ and d$B$ are the amounts (in moles) of $A$ and $B$ evaporating from the filament in a time interval from $t$ to $t + \mathrm{d}t$, and d$Q$ is the corresponding change (in moles) of the sample on the filament.

Let us denote the mole fractions of lighter isotopic species of the vapors A and B by $n_a$ and $n_b$, and of the residual sample by $n_c$, respectively. Then the molar quantities of the lighter isotopic species of $A$ and $B$ just escaping from the filament will be given by $n_a\mathrm{d}A$ and $n_b\mathrm{d}B$. Thus we get

$$n_a\mathrm{d}A + n_b\mathrm{d}B = \mathrm{d}(n_cQ) \tag{9}$$

and

$$r_a = \frac{n_a}{1-n_a},\quad r_b = \frac{n_b}{1-n_b},\quad R = \frac{n_c}{1-n_c} \tag{10}$$

For the sake of simplicity we assume that molar quantity of vapor $B$ is always $k$ times as much as that of vapor A throughout the course of evaporation, *viz.*,

$$\mathrm{d}B = k\mathrm{d}A \tag{11}$$

Combining this relation with Eqs. (6), (8), (9), and (10), we obtain the following differential equation

$$\frac{1}{k+1}\left(\frac{\alpha R}{1+\alpha R}+\frac{\beta k R}{1+\beta R}\right)\mathrm{d}Q = \frac{R\mathrm{d}Q}{1+R}+\frac{Q\mathrm{d}R}{(1+R)^2} \tag{12}$$

The solution is

$$\log\left(\frac{Q}{Q_0}\right) = a\log\left(\frac{R}{R_0}\right) + \log\left(\frac{R+1}{R_0+1}\right) + b\log\left(\frac{c+dR}{c+dR_0}\right) \tag{13}$$

where

$$\begin{aligned} a &= (k+1)/\{(\alpha-1) + (\beta-1)k\} \\ b &= (\alpha-\beta)^2k/(cd) \\ c &= (\alpha-1) + (\beta-1)k \\ d &= (\alpha-1)\beta + \alpha(\beta-1)k \end{aligned}$$

and $Q_0$ is the initial quantity and $R_0$ the isotope ratio (true isotope ratio) of the sample. When $\alpha=\beta$, this equation becomes

$$(\alpha-1)\log\left(\frac{Q}{Q_0}\right) = \log\left(\frac{R}{R_0}\right) + (\alpha-1)\log\left(\frac{R+1}{R_0+1}\right) \tag{14}$$

which is the well-known Rayleigh distillation formula.

If the residence time of vapor A and B in the ion source is short enough to prevent the cross mixing of the vapors at different instances, the mean isotope ratio of the vaporized species in the ion source can be expressed in terms of $\alpha$, $\beta$, $k$, and $R$ as follows.

$$\begin{aligned} r_m &= \frac{n_a\mathrm{d}A+n_b\mathrm{d}B}{(1-n_a)\mathrm{d}A+(1-n_b)\mathrm{d}B} \\ &= \frac{(\alpha+\beta k)R+\alpha\beta(k+1)R^2}{(k+1)+(\beta+\alpha Rk)} \end{aligned} \tag{15}$$

Furthermore, if the ionization efficiencies[6] of the chemical species $A$ and $B$ have the same value, the observed isotope ratio ($r_{ob}$) is equal to $r_m$, and if the ionization efficiency of vapor A is much greater than that of $B$, $r_{ob}$ is approximately equal to $r_a$. This is summarized as follows

$$\begin{aligned} r_{ob} &= r_m \quad (\text{when } I_a = I_b) \\ r_{ob} &= r_a \quad (\text{when } I_a \gg I_b) \\ r_{ob} &= r_b \quad (\text{when } I_a \ll I_b) \end{aligned}$$

where $I_a$ and $I_b$ are the ionization efficiencies of vapors A and B, respectively.

## Calculation and Discussion

Calculations have been made for lithium, potassium and rubidium when halides of these elements are adopted as the working material. The calculated observable isotope ratios ($r_{ob}$) for iodides of these elements are shown in Figs. 1, 2, and 3 as a function of the fraction of the sample remaining on the filament. In these calculations it is implicitly assumed that chemical forms of vapor species are either $\mathrm{M}^{(0,+)}$ or MI, and that ionization efficiencies of both vapor species are identical (M=Li, K, and Rb, I is iodine). As shown in Figs. 1, 2, and 3, the isotope ratio to be observed significantly deviates from the true isotope ratio when the fractions of atomic species $\mathrm{M}^{(0,+)}$ in vaporizing substances are large and the fraction evaporated is large or small.

It is of importance to know how much is evaporated when the observed isotope ratio gives the true isotope ratio of the sample.

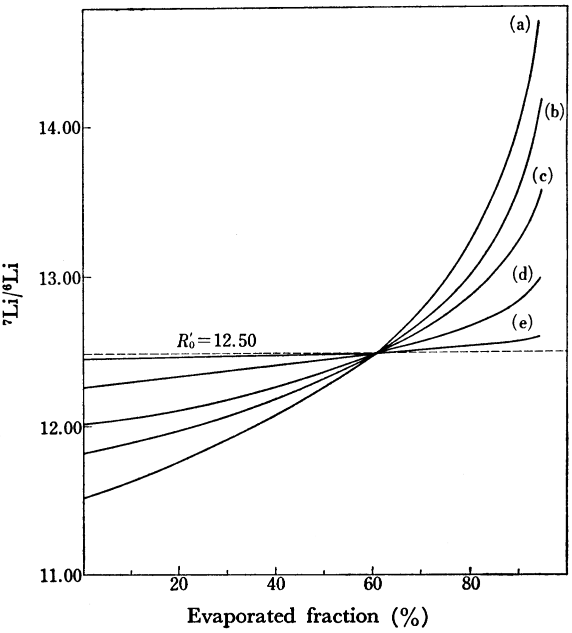

Fig. 1. Variation of $^7\mathrm{Li}/^6\mathrm{Li}$ with composition of vaporizing species.
(a) $k=0.00$ (b) $k=0.40$ (c) $k=1.00$ (d) $k=4.00$
(e) $k=\infty$
A: $\mathrm{Li}^{(0,+)}$ $\alpha=1.080000$ B: LiI $\beta=1.00376$

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[6] Ionization efficiency is regarded as the production rate of atomic ions $M^+$ from vapor A or B.

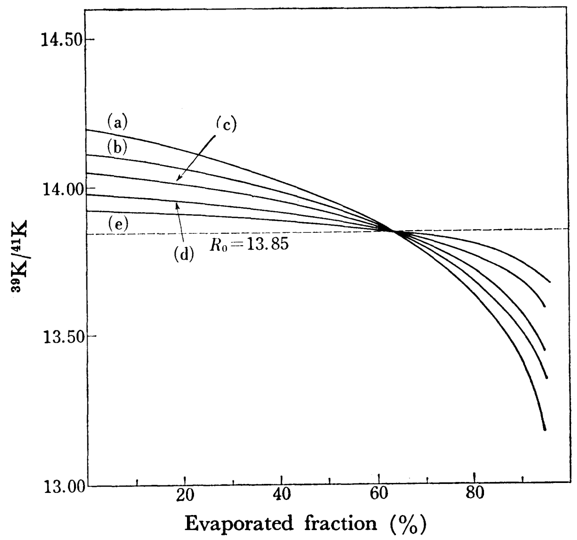

Fig. 2. Variation of $^{39}K/^{41}K$ with composition of vaporizing species.
(a) $k=0.00$ (b) $k=0.40$ (c) $k=1.00$ (d) $k=4.00$
(e) $k=\infty$
A: $K^{(0,+)}$ $\alpha=1.02532$ B: KI $\beta=1.00605$

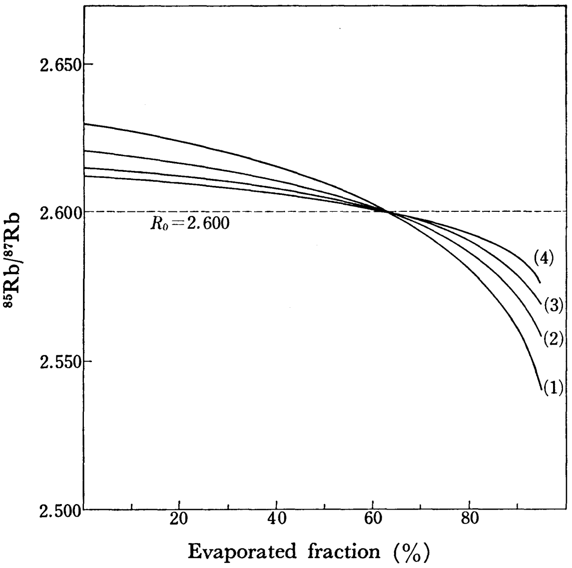

Fig. 3. Variation of $^{85}Rb/^{87}Rb$ with composition of vaporizing species.
(a) $k=0.00$ (b) $k=0.40$ (c) $k=1.00$ (d) $k=4.00$
(e) $k=\infty$
A: $Rb^{(0,+)}$ $\alpha=1.01169$ B: RbI $\beta=1.00470$

When $\alpha=\beta$, we get from Eq. (15)

$$r_{ob} = \alpha R = R_0$$

Substituting this relation into Eq. (14), we have

$$(\alpha-1)\log\left(\frac{Q}{Q_0}\right) = -\log\alpha + (\alpha-1)\log\frac{R_0+\alpha}{\alpha(R_0+1)}$$

Generally $\alpha$ is nearly equal to unity, *i.e.*, $\alpha=1+\varepsilon$ and $\varepsilon\ll1$, thus

$$\frac{R_0+\alpha}{R_0+1}\approx 1, \qquad \log\alpha\approx\varepsilon$$

which leads to

$$Q = Q_0/e \approx 0.37Q_0$$

When $\alpha\neq\beta$ but $I_a=I_b$, the same result is also deduced if only $\alpha$ and $\beta$ are nearly unity. We see that when the fraction evaporated being near 63% ($Q\approx0.37\,Q_0$), observed isotope ratio ($r_{ob}$) can be regarded as the true isotope ratio ($R_0$) of the sample material, and that when $Q<0.37Q_0$, $r_{ob}$ is larger than $R_0$ and when $Q<0.37\,Q_0$, $r_{ob}$ is smaller than $R_0$. However, it should be pointed out that when $\alpha\neq\beta$ and $I_a\neq I_b$ (probably this is the usual case in a multiple filament ion source) the above relation is not realized as will be shown later.

Fractionation curves of the halides and elements of lithium, potassium and rubidium are presented in

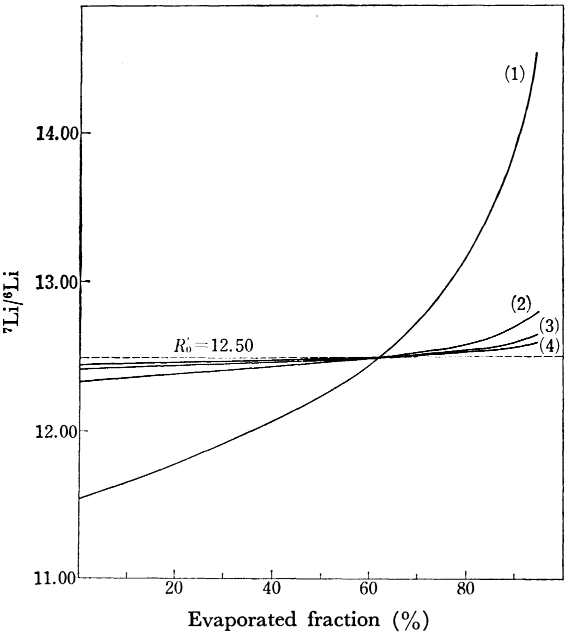

Fig. 4. Fractionation curves for lithium.
(1) $^6Li$-$^7Li$: 1.0800 (2) $^6LiCl$-$^7LiCl$: 1.01200
(3) $^6LiBr$-$^7LiBr$: 1.00581 (4) $^6LiI$-$^7LiI$: 1.00376

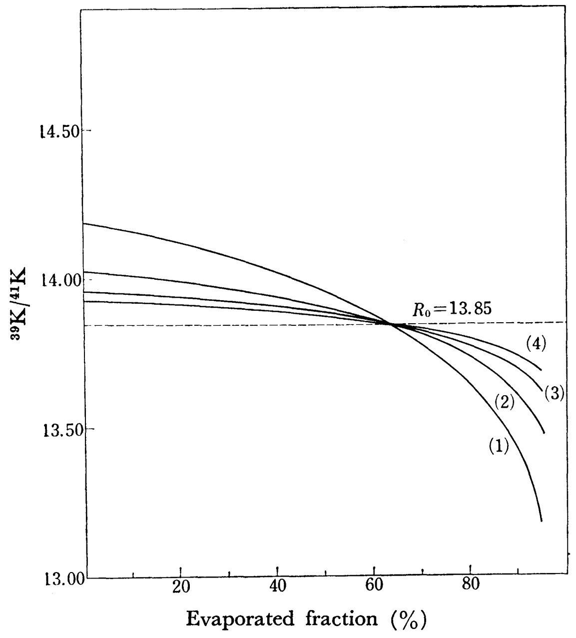

Fig. 5. Fractionation curves for potassium.
(1) $^{39}K$-$^{41}K$: 1.02532 (2) $^{39}KCl$-$^{41}KCl$: 1.01334
(3) $^{39}KBr$-$^{41}KBr$: 1.00837 (4) $^{39}KI$-$^{41}KI$: 1.00605

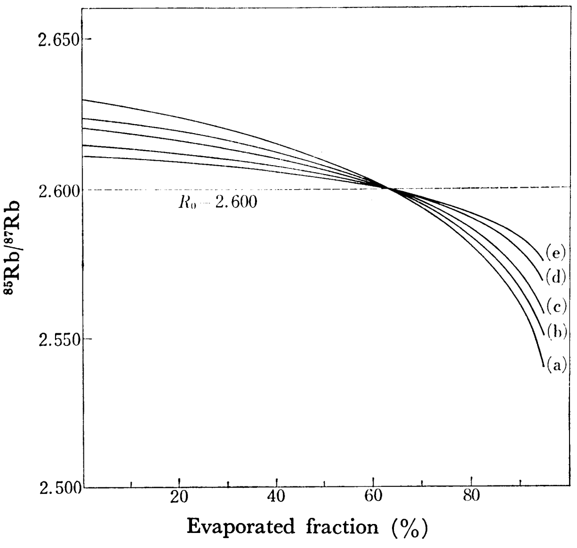

Fig. 6. Fractionation curves for rubidium.
(1) $^{85}$Rb-$^{87}$Rb: 1.01169 (2) $^{85}$RbCl-$^{87}$RbCl: 1.00826
(3) $^{85}$RbBr-$^{87}$RbBr: 1.00604 (4) $^{85}$RbI-$^{87}$RbI: 1.00470

Figs. 4, 5, and 6. It is apparent from these figures that fractionation of lithium iodide is the smallest. If most of the vaporizing species are molecules and molecular ions, isotopic fractionation of lithium can be reduced to minimum by adopting lithium iodide as the working material. On the other hand, in the cases of potassium and rubidium the deviations from the true isotope ratios are larger than those of lithium when the bromides or iodides of these elements are used for the isotope ratio measurements. This stems from the fact that the mass difference of potassium (or rubidium) isotopes is twice as much as that of lithium isotopes. Thus fractionation factor of lithium is more effectively decreased with the use of a heavy compound as a working material than potassium and rubidium. In other words, in the case of lithium the error from fractionation can be reduced to a considerable extent by only adopting a heavy compound as a sample and making lithium emit from the filament as a high mass molecule or molecular ion. The latter condition is practically effected by using a multiple filament ion source. This shows that elements having isotopes of large mass differences are difficult for overcoming the fractionation problem. For example, in measurements of lead where hydroxide, nitrate and sulfide are usually adopted as chemical forms of the sample, and of rare earth elements such as gadolinium and neodymium where nitrate and perchlorate are used, fractionation factors do not decrease so effectively as expected because the vaporizing species from the filament are considered to be either atomic species or decomposed molecular fragments such as $MO^{(0,+)}$ and $M_2O_3$. Thus in measurements of these elements we must make some other corrections for fractionation to obtain precise isotope ratios.[7,8]

As a matter of fact, the partial mixing of the successively vaporizing substances occurs in an ion source, and the actually observed deviations from the true isotope ratio may not be so large as expected from Eq. (14).

Eberhardt *et al.*[3] observed that different chemical forms and different filament materials yield differences in the observed isotope ratios, and stated that measured isotope ratios of rubidium increased in the order: sulphate on tungsten-sulfate on tantalum-chloride on tungsten-chloride on tantalum. Ozard and Russel[9] have observed in their lead isotope ratio measurement that the fractionation pattern of a rhenium filament is different from that of a tantalum filament. These observations may be partly explained by the fact that both the composition of vaporizing species and their ionization efficiencies are greatly influenced by the chemical form of the sample, condition of filament surface (temperature of filament, filament material), type of ion source (single or multiple filament ion source) and impurities in the sample and filament. It is well known that ionization of lead is significantly reduced by large alkali ions arising from contaminations.

In the calculations presented in Figs. 1, 2, and 3, ionization efficiencies of vapors A and B were assumed to be the same. However, in actual cases in a multiple filament ion source this is rare so that observed fractionation also varies with the change of ionization efficiencies of the vapors.

Table 1 shows fractionation data of lithium iodide with the conditions (a) $k=1.0$ and $I(\text{LiI})=I(\text{Li})$, (b) $k=1.0$ and $I(\text{LiI})\gg I(\text{Li})$, and (c) $k=1.0$ and

TABLE 1. VARIATION OF EXPECTED ISOTOPE RATIOS ($r_{ob}$) WITH EVAPORATED FRACTION AND IONIZATION EFFICIENCY

| evaporated fraction(%) | Observed isotope ratio $^7$Li/$^6$Li[a)]<br>$I(\text{LiI})=I(\text{Li})$<br>$r'_{ob}$ | <br>$I(\text{LiI})\ll I(\text{Li})$<br>$r'_{ob}$ | <br>$I(\text{LiI})\gg I(\text{Li})$<br>$r'_{ob}$ |
|---|---|---|---|
| 5.0 | $12.02_4$ | $11.59_9$ | $12.48_0$ |
| 10.0 | $12.05_2$ | $11.62_5$ | $12.50_8$ |
| 15.0 | $12.08_0$ | $11.65_3$ | $12.53_8$ |
| 20.0 | $12.11_1$ | $11.68_2$ | $12.56_9$ |
| 25.0 | $12.14_3$ | $11.71_4$ | $12.60_3$ |
| 30.0 | $12.17_8$ | $11.74_7$ | $12.64_0$ |
| 35.0 | $12.21_6$ | $11.78_4$ | $12.67_9$ |
| 40.0 | $12.25_7$ | $11.82_3$ | $12.72_1$ |
| 45.0 | $12.30_1$ | $11.86_6$ | $12.76_7$ |
| 50.0 | $12.35_0$ | $11.91_3$ | $12.81_8$ |
| 55.0 | $12.40_4$ | $11.96_5$ | $12.87_4$ |
| 60.0 | $12.46_5$ | $12.02_4$ | $12.93_8$ |
| 65.0 | $12.53_5$ | $12.09_1$ | $13.01_0$ |
| 70.0 | $12.61_6$ | $12.16_9$ | $13.09_4$ |
| 75.0 | $12.71_2$ | $12.26_2$ | $13.19_3$ |
| 80.0 | $12.83_1$ | $12.37_7$ | $13.31_7$ |
| 85.0 | $12.98_5$ | $12.52_6$ | $13.47_7$ |
| 90.0 | $13.20_6$ | $12.73_9$ | $13.70_7$ |
| 95.0 | $13.59_3$ | $13.11_2$ | $14.10_8$ |

a) Initial isotope ratio (true isotope ratio) $^7\text{Li}/^6\text{Li}=12.50$.
$k=1.0$, A: Li $\alpha=1.08000$ B: LiI $\beta=1.00376$

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7) G. W. Wetherill, *J. Geophys. Res.*, **69**, 4403 (1964).

8) J. A. Cooper, P. H. Reynolds, and J. R. Richards, *Earth Planet. Sci. Lett.*, **6**, 467 (1969).

9) J. M. Ozard and R. D. Russel, *ibid.*, **8**, 331 (1970).

$I(\mathrm{LiI}) \ll I(\mathrm{Li})$. It should be noted that when $I(\mathrm{Li}) \gg I(\mathrm{LiI})$, $r'_{ob}$ $(=1/r_{ob})$[10] is lower than $R_0'$ $(=1/R_0)$ in the evaporated fraction ranging from 0 to 84% and that when $I(\mathrm{Li}) \ll I(\mathrm{LiI})$, $r'_{ob}$ is larger than $R_0'$ from 9 to 100%. Accordingly, this suggests that integrations of all ion currents for both isotopes do not necessarily give the true isotope ratio because of the fact that non-ionized vaporization also affects observed fractionation.

In conclusion, the theory presented here, though too much idealized to give a real picture of fractionation, is adequate to give the qualitative or even semi-quantitative behavior of fractionation in a thermal ion source, and therefore, the derived results are applicable to actual cases.

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[10] Lithium isotope ratio is usually presented as $^7\mathrm{Li}/^6\mathrm{Li}$.