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A Possible Method for Obtaining Precise Isotope Ratio of the Element Having Only Two Isotopes

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As an extension of the atomic/molecular vaporization model, a new method is presented for correcting the isotopic fractionation effects in the multiple filament thermal ionization source (MFTIS). It is applicable to the isotope ratio measurements of the element having only two observable isotopes.

It is well known that the isotope ratio observed in a thermal ionization mass spectrometry is "fractionated"[1–7] due to the isotope effects in the vaporization process of the sample. As the correction methods for elements having more than three isotopes, normalization and double spike techniques[8–12] are usually adopted to obtain "precise" isotope ratio capable to interlaboratory comparison and geochemical uses. However, when the element in question has only two stable isotopes, it is almost impossible to estimate the extent of isotopic fractionation in an observed isotope ratio.

In this paper I propose a new method which may be used to overcome the limitation inherent to the element having only two isotopes for obtaining precise isotope ratio.

Theoretical

In a multiple filament thermal ionization source (MFTIS), sample evaporates in both atomic and molecular species

$$\mathrm{MX_{(s)}} \longrightarrow \mathrm{M_{(g)}} + \mathrm{X_{(g)}}$$
$$\mathrm{MX_{(s)}} \longrightarrow \mathrm{MX_{(g)}}$$

and ionization occurs at or near the ionizing filament,

$$\mathrm{M} \longrightarrow \mathrm{M^+}$$
$$\mathrm{MX} \longrightarrow \mathrm{M^+} + \mathrm{X^{(0,-)}}$$
$$\searrow \mathrm{MX^+}.$$

If molecular ions are stable enough to be observed as mass spectra and if metal counterpart (X in this case) consists of more than two isotopic species, we will observe (at least) following four peaks in the mass spectra of molecular ions

$$\mathrm{M_lX_l^+},\ \mathrm{M_lX_h^+},\ \mathrm{M_hX_l^+},\ \text{and}\ \mathrm{M_hX_h^+}$$

where h and l denote heavy and light isotopes of the element M and its counterpart X. It is to be noted that the overlapping of mass peaks may sometimes occur due to the particular combination of mass numbers of M and X. In addition to these mass peaks, we can also get isotope ratio of the element M as usual from mass peaks of $\mathrm{M^+}$ ions. Combination of isotope ratios of molecular ions and atomic ions may resolve the fractionation problem. This is shown in the following way. As in the previous analysis,[5] we assume that the molar quantity of MX (vapor B) is always k_m times as much as $\mathrm{M^{(0,+)}}$ (vapor A) and k_x times as much as $\mathrm{X^{(0,+,-)}}$ (vapor C). Thus we get

$$\mathrm{d[B]} = k_\mathrm{m}\mathrm{d[A]}$$
$$\mathrm{d[B]} = k_\mathrm{x}\mathrm{d[C]} \tag{1}$$

where [Y] is the molar quantity of the vapor Y. It is easily seen from Eq. 1 that k_m is equal to k_x in the ideal case. For the simplicity of the discussion, we further assume that (1) the residual sample on the filament undergoes complete and continuous mixing and there is no isotopic fractionation between the compounds (chemical species) on the filament and (2) the residence time of the vapor in the ion source is short so that there are no isotopic exchanges in the successively evaporating chemical species. Here we assume that the element M and its counterpart X consist each of only two isotopes (isotopic species). The isotopic fractionation factors are defined as follows;

$$\alpha = (\mathrm{M_h/M_l})^{1/2},\quad \beta = (\mathrm{M_h\bar{X}/M_l\bar{X}})^{1/2},$$
$$\gamma_1 = (\mathrm{\bar{M}X_h/\bar{M}X_l})^{1/2},\quad \gamma_2 = (\mathrm{X_h/X_l})^{1/2} \tag{2}$$

where $\mathrm{\bar{M}}$ and $\mathrm{\bar{X}}$ are the average mass of the element M and its counterpart X, respectively. The isotope ratios R_a and R_b of the element M in the vapor A and vapor B evaporating from the filament are given by

$$R_\mathrm{a} = \alpha R \ \text{and}\ R_\mathrm{b} = \beta R \tag{3}$$

where R is the isotope ratio of the element M in the sample remaining on the filament.

The differential equation describing the change in the isotope ratio R in the course of evaporation is

$$\frac{1}{k_\mathrm{m}+1}\left(\frac{\alpha R}{1+\alpha R}+\frac{\beta k_\mathrm{m} R}{1+\beta R}\right)\mathrm{d}Q = \frac{R\mathrm{d}Q}{1+R}+\frac{Q\mathrm{d}R}{(1+R)^2} \tag{4}$$

where Q is the amount of sample on filament. The integration of Eq. 4 gives

$$\ln\left(\frac{Q}{Q_0}\right) = a_\mathrm{m}\ln\left(\frac{R}{R_0}\right) + \ln\left(\frac{R+1}{R_0+1}\right) + b_\mathrm{m}\ln\left(\frac{c_\mathrm{m}+d_\mathrm{m}R}{c_\mathrm{m}+d_\mathrm{m}R_0}\right) \tag{5}$$

where Q_0: amount of sample originally on filament,
R_0: true isotope ratio of the sample at Q_0,
$a_\mathrm{m} = (k_\mathrm{m}+1)/c_\mathrm{m}$, $b_\mathrm{m} = (\alpha-\beta)^2k_\mathrm{m}/(c_\mathrm{m}d_\mathrm{m})$,
$c_\mathrm{m} = (\alpha-1) + (\beta-1)k_\mathrm{m}$,
$d_\mathrm{m} = (\alpha-1)\beta + \alpha(\beta-1)k_\mathrm{m}$.

When we measure the metal ions $\mathrm{M^+}$ for obtaining isotope ratio of the element M, the observed isotope ratio (R_ob) will be the mean isotope ratio of the vapor A and vapor B as expressed by

$$R_\mathrm{ob} = \frac{(\alpha+\beta k_\mathrm{m}I_\mathrm{m})R+\alpha\beta(k_\mathrm{m}I_\mathrm{m}+1)R^2}{(k_\mathrm{m}I_\mathrm{m}+1)+(\beta+\alpha k_\mathrm{m}I_\mathrm{m})R} \tag{6}$$

where $I_\mathrm{m} = I_\mathrm{a}/I_\mathrm{b}$ and I_a and I_b are the ionization efficiencies (production rate of metal ion $\mathrm{M^+}$) of the vapor A and vapor B, respectively.

Next we consider the change of isotope ratio of X during the course of evaporation of the sample MX. The isotope ratios r_b and r_c of X in the vapor B and vapor C (MX and X) are given by

$$r_b = \gamma_1 R_x \text{ and } r_c = \gamma_2 R_x \qquad (7)$$

where R_x is the isotope ratio of X in the sample remaining on the filament. The equation corresponding to Eq. 4 is

$$\frac{1}{k_x+1}\left(\frac{\gamma_1 R_x}{1+\gamma_1 R_x}+\frac{\gamma_2 k_x R_x}{1+\gamma_2 R_x}\right)\mathrm{d}Q_x = \frac{R_x \mathrm{d}Q_x}{1+R_x}+\frac{Q_x \mathrm{d}R_x}{(1+R_x)^2} \qquad (8)$$

where Q_x is the amount of the sample (X-containing chemical species) remaining on the filament, and Eq. 8 is integrated to give

$$\ln\left(\frac{Q_x}{Q_0}\right) = a_x \ln\left(\frac{R_x}{R_x^\circ}\right) + \ln\left(\frac{R_x+1}{R_x^\circ+1}\right) + b_x \ln\left(\frac{c_x+d_xR_x}{c_x+d_xR_x^\circ}\right) \qquad (9)$$

where R_x°: the initial isotope ratio of X on the sample filament,

$a_x = (k_x+1)/c_x, \quad b_x = (\gamma_1-\gamma_2)^2 k_x/(c_x d_x),$

$c_x = (\gamma_1-1) + (\gamma_2-1)k_x,$

$d_x = (\gamma_1-1)\gamma_2 + \gamma_1(\gamma_2-1)k_x.$

Thus the observed isotope ratio of X in the vapor of molecular ions MX^+ will be

$$r_{ob} = \frac{[M_lX_h{}^+]+[M_hX_h{}^+]}{[M_lX_l{}^+]+[M_hX_h{}^+]} = \gamma_1 R_x. \qquad (10)$$

Here [Z] represents the peak height of mass spectrum at the mass number Z. If we use the sample MX as a working material in which the initial isotope ratio of X is precisely known, we can monitor the amount of the sample remaining on the filament Q_x (or Q) from the measured r_{ob} value, initial isotope ratio R_x° and the k_x value using Eqs. 7 and 9. Evaluation of k_m and k_x may be achieved by either calibration curve or thermodynamic studies on vapor composition in a thermal ion source. Recently Heald has attempted the computer calculation of equilibrium compositions of vapor species in a thermal ionization mass spectrometer.[13] Once we get Q_x ($Q_x \simeq Q$) value, it is easy to get the "precise" isotope ratio R_0 of the element M by use of Eqs. 5 and 6, evaluated k_m value and observed R_{ob} value.

Discussion

The crucial point of this method is whether the sample MX can form stable molecular ions to be observed as mass spectra. There have been only a few studies on the stability and intensity of molecular ions in a thermal ionization ion source as atomic ions have exclusively been the only target for observations in most isotope ratio measurements.[14–16] However, there is much evidence for the existence of molecular ions as well as atomic metal ions in a thermal ionization ion source.[14–18] Together with the high-temperature vaporization data of inorganic salts by Knudsen-cell effusion method,[19,20] recent extensive studies by NBS group[7] support the above contention. It is very common to observe not only atomic ions M^+ but also oxide ions such as MO^+ in the isotope ratio measurements of rare earth elements when nitrates or perchlorates are used as a chemical form of the sample.[14,15] In the experimental work by Gensho and Honda,[18] they used M_2BO_3 (M=Li, Na, K, and Rb) as a working material for obtaining precise isotopic abundance ratio of boron ($^{11}B/^{10}B$). When the metal M consists of more than two isotopes such as Li, K, and Rb, we can obtain more than three $M_2BO_2{}^+$ ion peaks. This makes it possible to evaluate the discrimination factor which would otherwise be unobtainable from only two peaks ($M_2{}^{10}BO_2{}^+$ and $M_2{}^{11}BO_2{}^+$). The merits of using M_2BO_3 (M=Li, K, and Rb) instead of Na_2BO_3 as a sample in measuring isotope ratio of boron are summarized by Gensho and Honda as follows: (a) three or more mass peaks are observable from the combination of isotopes of boron and alkali metal (Li, K, and Rb), (b) the discrimination factor (including fractionation effect) may be obtained using a synthetic mixture of isotopes of alkali metal, and (c) the relative peak heights can be adjusted by using a synthetic isotope mixture so as to minimize the reading error (the error arising from using different ranges for recordings of two peaks having a large difference in intensities).

It is important to know how high precision we have to evaluate Q_x (Q) for getting "precise" isotope ratio R_0 of M. The main sources for errors possibly caused in evaluating Q_x come from the evaluation of k_x and the measurement of R_x. From Eqs. 4 and 8, we obtain

$$\frac{\Delta Q}{Q} = \frac{(k_m+1)(\alpha R+1)(\beta R+1)}{(R+1)(c+\mathrm{d}R)}\,\frac{\Delta R}{R},$$

$$\frac{\Delta R_x}{R_x} = \frac{(R_x+1)(c_x+d_xR_x)}{(k_x+1)(\gamma_1 R_x+1)(\gamma_2 R_x+1)}\,\frac{\Delta Q_x}{Q_x}.$$

Combination of these two equations with Eqs. 5 and 9 gives the magnitude of error permissible to the observed R_x or to the evaluation of Q as a function of Q (or Q_x). Table 1 shows an example of calculations for ΔR_x and ΔQ under the conditions: $k_m=k_x=1$, $Q=Q_x$, and $\Delta R/R=0.05\%$.

Remarkable points of the calculations are that relative

TABLE 1. THE RELATIVE ERROR PERMISSIBLE TO THE EVALUATION OF Q OR R_x AS A FUNCTION OF Q

Q/Q_0	R ($^{39}K/^{41}K$)	$\Delta Q/Q$ (%)	R_x ($^{35}Cl/^{37}Cl$)	$\Delta R_x/R_x$ (%)
1.00	13.850	—	3.1248	—
0.95	13.837	2.64	3.1215	0.05_4
0.90	13.822	2.64	3.1181	0.05_4
0.80	13.792	2.64	3.1106	0.05_4
0.70	13.757	2.64	3.1021	0.05_4
0.60	13.717	2.64	3.0924	0.05_4
0.50	13.669	2.64	3.0809	0.05_4
0.40	13.612	2.64	3.0669	0.05_4
0.30	13.537	2.64	3.0489	0.05_4
0.20	13.434	2.64	3.0238	0.05_4
0.10	13.258	2.64	2.9813	0.05_4
0.05	13.085	2.64	2.9394	0.05_4

R_0 ($^{39}K/^{41}K$) = 13.850, R_x° ($^{35}Cl/^{37}Cl$) = 3.1248, α=1.02532, β=1.01334, γ_1=1.01339, γ_2=1.02816, $Q=Q_x$, $k_m=k_x$= 1.0, $I_m=I_x$=1.0, $\Delta R/R$=0.05%.

error permissible to the evaluation of Q is rather constant and large as expected and that the precision required to the measurement of R_x is comparable to the precision of the isotope ratio of M which we intend to obtain. The accuracy of the evaluation of Q_x (Q) can be improved by the least-squares curve fitting of several sets of Q and R_x data so that a lower accuracy for each R_x may be tolerable to get the required accuracy of Q. Probably the calibration curve which may be constructed by use of the synthetic isotope mixtures of both metal M and its counterpart X suffices this object because most accurate Q value is obtainable from the comparison of the calibration curve and observed R_x of the sample.

When molecules or molecular ions are the only entity of vaporizing species from sample filament, calculations become much simpler and easier. Equation 5 is reduced to

$$(\beta-1)\ln\left(\frac{Q}{Q_0}\right)=\ln\left(\frac{R}{R_0}\right)+(\beta-1)\ln\left(\frac{R+1}{R_0+1}\right)$$

and the observed isotope ratio of metal ions will be $R_{ob}=\beta R$. Equation 9 is also simplified to be

$$(\gamma_1-1)\ln\left(\frac{Q_x}{Q_0}\right)=\ln\left(\frac{R_x}{R_x^\circ}\right)+(\gamma_1-1)\ln\left(\frac{R_x+1}{R_x^\circ+1}\right)$$

and the observed isotope ratio of X in molecular ions MX^+ is $\gamma_1 R_x$. If we can observe X^{+or-} ions as mass peaks, the isotope ratio of X^{+or-} ions should be $\gamma_1 R_x$. The observation of X^{+or-} ions may be advantageous from the practical stand point as will be discussed later in more details.

In recent high precision mass spectroscopic studies, the synthetic mixture of isotopes from highly enriched isotopes plays an important role in getting high accuracy.[6] The use of a synthetic isotope mixture makes it feasible to apply the present method to various isotope ratio measurements. In fact, it is almost straightforward to make a rough estimation of Q value from the precisely known $R_x{}^\circ$ value and observed isotope ratio R_x of X. Furthermore, the isotope mixture of an appropriate composition can greatly improve the accuracy of isotope ratio of molecular ions, *e.g.*, if we use the sample of La_2O_3 in which the isotope ratio of $^{18}O/^{16}O$ is about 1122, we will have the comparable intensities for $^{139}La^{16}O^+$ ($m=155$) and $^{138}La^{18}O^+$ ($m=156$) peaks so that recording error will be minimized.

An alternative method for estimating Q is the measurements of isotope ratio of X by observing mass spectra of X ions. It is to be noticed that isotope ratios of chlorine and bromine can be obtained by measuring negative ions of these elements ionized in a thermal ionization ion source.[21,22] Chloride and bromide are the most common chemical form of the sample in a MFTIS. The advantage of measuring chloride or bromide ions is the possible applicability of the present method to most metal elements by adopting chloride or bromide as a chemical form of the sample. The simultaneous determinations of isotope ratios of M^+ and X^- in the same sample are attainable by simply changing polarity of the accerating voltage and magnetic current of a mass spectrometer. Instead of Eq. 10, the equation relating R_x and observed isotope ratio r_x in the vapor X^{-or+} is given by

$$r_x=\frac{(\gamma_1+\gamma_2k_xI_x)R_x+\gamma_1\gamma_2(k_xI_x+1)R_x^2}{(k_xI_x+1)+(\gamma_2+\gamma_1k_xI_x)R_x}$$

where $I_x=I_{xb}/I_{xc}$, and I_{xb} and I_{xc} are the ionization efficiencies of the vapor B and vapor C, respectively.

It is expected that the fractionation factor of $M\overline{X}$ (or $\overline{M}X$) varies according to the change in the average mass of $\overline{X}$ (or $\overline{M}$) as the sample evaporation proceeds. However, the change is usually so small that fractionation factors can be regarded constant in most cases without causing any detectable errors (Table 2).

TABLE 2. FRACTIONATION FACTORS OF KCl AS A FUNCTION OF AVERAGE MASS OF POTASSIUM OR CHLORINE

$R(^{39}K/^{41}K)$	$\overline{M}(K)$	$\gamma_1=(\overline{M}^{37}Cl/\overline{M}^{35}Cl)^{1/2}$
13.850	39.098_3	1.01339_2
13.700	39.099_6	1.01339_1
13.300	39.103_4	1.01339_1
12.900	39.107_4	1.01339_0
12.000	39.129_8	1.01338_5
$R_x(^{35}Cl/^{37}Cl)$	$\overline{X}(Cl)$	$\beta=(^{41}K\overline{X}/^{39}K\overline{X})^{1/2}$
3.1248	35.453_0	1.01333_9
3.0000	35.468_1	1.01333_6
2.8000	35.494_4	1.01333_2
2.5000	35.539_4	1.01332_4

As implicitly implied in the previous paper[5] and extensively studied by Moore *et al.*,[7] the change of k must be admitted during the vaporization process. In fact, not only k but also I varies in the actual experimental situation. In addition to the fractionation pattern, most anomalous phenomena associated with MFTIS may be explained by admitting the change in either k or I (or both) during analysis.[5,7] From the practical stand point, the entire fractionation curve can be constructed experimentally on a point-by-point basis with a standard sample in which initial isotope ratios of both M and X are precisely known. With experimental data of k and I (or the combination factor $L=k\ I$), incorporation of the changes of k and I will be made case by case by using Eqs. 4 and 8 as a starting point. Some examples of such attempts have been presented by Moore *et al.*[7]

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