

# A New Statistical Model and a Redefinition of Isotopic Ratio: Correction and Evaluation in Ultra-microanalysis

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## Abstract

Ultra-microanalysis of isotopes is required to clarify the origin, structure, and history of extremely small samples, for example micrometeorites and aerosols. However, a decrease in the number of measured atoms reveals a serious problem in the concept of isotopic ratio. The first fundamental defect of the isotopic ratio concept is imperfect reversibility of numerator and denominator, leading to two isotopic compositions inconsistent with each other. Secondly, the probability distribution of isotopic ratio is not the same as the binominal distribution, indicating that the mean isotopic ratio is systematically higher than the true isotopic ratio. Since these demerits should be avoided in ultra-microanalysis as much as possible, isotopic abundance or relative isotopic abundance should be used rather than isotopic ratio. The concept of isotopic ratio is, however, widely used in geochemical and cosmochemical fields, making it very difficult to abandon. Therefore, the potential uncertainty of isotopic ratio and the gap between the obtained isotopic ratio and the true one deriving from the number of sampling atoms and the isotopic ratio are vigorously evaluated here. In addition, a confirmation requirement for confirming an anomalous isotopic ratio is provided. The statistical model shown in the present work clearly indicates that the major isotope must be set as the denominator of isotopic ratio, i.e. isotopic ratio must be below 1, to reduce the effects of distorted probability distribution of isotopic ratio. In the precise measurement of isotopes, the potential error and disagreement with the true value must be tested when the number of sampled atoms is extremely few. Serious problems have not been occurred in research up to the present even in the case of NanoSIMS measurements, but this is because a sufficient number of atoms was analyzed and only extremely large isotopic anomalies were investigated. The correction and evaluation methods established in this paper will be required for accurate ultra-microanalysis.

## 1. Introduction

The conception of isotopic ratio has been developing with the history of isotopic chronology research for about 80 years. Recently, extremely small amounts of isotopes in minute samples can be measured with highly sensitivity and low background thanks to the development of new mass spectroscopic technology, e.g. secondary ion mass spectrometry (SIMS), inductively coupled plasma mass spectrometry (ICP-MS), thermal ionization mass spectrometer (TIMS), and noble gas mass spectrometer. Indeed,

$5 \times 10^{-20}$  mol of Xe can be detected by a modified VG-5400 noble gas mass spectrometer, as reported in my previous papers [1-4]. Such ultra-microanalyses have also been conducted by other methods, for example, TIMS measurement for  $<1 \mu\text{m}$  uranium particles [5], and measurements of oxygen, carbon, and nitrogen isotopes in interplanetary dust particles (IDPs) using NanoSIMS [6,7].

However, potential statistical error caused by the detected number of isotopes cannot be ignored in the future if technology of mass spectrometry is to further

evolve. In this paper, the fundamental concept of isotopic ratio and potential uncertainties of isotopic ratio are discussed, and correction and evaluation techniques are established.

## 2. What is isotopic ratio?

Since the discovery of ionium ( $^{230}\text{Th}$ ) by Boltwood in 1906, isotopes have been used in various research and industry fields. In geochemistry, it is utilized to clarify the origin of terrestrial and extraterrestrial materials, determine the formation age of rock materials and cosmic-ray exposure age of meteorites, and elucidate an ancient climate. Such geochemical and cosmochemical approaches are based on an important concept, isotopic ratio. We can obtain a lot of valuable information on an object by comparing its isotopic ratio with the normal isotopic ratio with regard to each element. Although the conception of isotopic ratio is basic and planetary scientists and geochemists often use it, it is firstly required that the conception of isotopic ratio be strictly defined. Isotopic ratio can be expressed in three ways, as follows.

- (1) Isotopic ratio is the ratio of the numbers of isotopes  $X_1$  and  $X_2$  of element  $X$  contained in a certain sample.
- (2) Isotopic ratio is the ratio of the abundance of isotope  $X_1$  and  $X_2$  of element  $X$  contained in a certain sample.
- (3) Isotopic ratio is a ratio of the probability of sampling  $X_1$  and  $X_2$  when one atom is sampled at random from the population of  $X$  in a certain sample. (statistical definition)

The three definitions have the same meaning, though the expressions are slightly different, and it would seem that each is entirely adequate. However, when the number of atom is extremely few, these definitions are clearly imperfect. For instance, when 1001 atoms of element  $X$  exist in a sample and the number of atoms of isotope  $X_1$  and  $X_2$  are 1 and 1000, respectively, the isotopic ratio of  $X_1/X_2$  based on these definitions is precisely 0.001. The determined isotopic ratio of 0.001 is completely correct and it has no uncertainty. If the normal isotopic ratio of  $X$  is 0.0001, I can thus conclude that the sample has ten times higher isotopic ratio than the standard sample. But still, common intuition tells us that this conclusion is quite strange because if another 1001 atoms of  $X$  in another sample

are measured,  $X_1$  might well not exist. In other words, the isotopic ratio obtained here (0.001) might not accurately reflect the isotopic ratio of the  $X$  population when the set of 1001  $X$  is a subset of the entire  $X$  population. Therefore, I redefined the isotopic ratio here to give generality as follows.

*Isotopic ratio is a probability distribution function of the ratio of the number of isotope  $X_1$  and  $X_2$  of element  $X$  contained in a certain sample. The isotopes are randomly selected from a population of element  $X$  that is composed of a finite but very large number of atoms.*

Thus the ratio for a sample has an inevitable potential uncertainty, but this is lowered by increasing the number of sampled atoms and has no relation with measurement accuracy at all. This definition asserts that isotopic ratio is not one numerical value but a distribution with inevitable uncertainty even if all atoms in a sample can be detected completely. If enormously large number of atoms is measured, the uncertainty will almost become 0 and the distribution will converge upon a value. However, the inevitable uncertainty cannot become exactly 0, since an infinite number of atoms cannot be measured. If there were an infinite number of atoms in the population, there would be no way to determine the isotopic ratio because one would never finish counting the atoms. Isotopic ratio is thus defined for a countable number of atoms, indicating that the ratio always has dispersion. This inevitable incertitude is detailed in the following chapters.

## 3. Indeterminacy probability

In the previous chapter I started that the isotopic ratio for a sample of infinite atoms couldn't be determined. Another indeterminate case is discussed here, i.e. where only one isotope atom exists in a sample. When some atoms are randomly sampled from a population, the indeterminacy probability  $P_i$  is calculated by the equation below.

$$P_i = \left(\frac{R}{1+R}\right)^n + \left(\frac{1}{1+R}\right)^n \quad (1)$$

where  $n$  is the number of sampled atoms and  $R$  is the

isotopic ratio of the population. Because the number of atoms in the population is enormously large, the probability of sampling isotope  $X_1$  is always the same. The relationship between the number of sampling atoms and the indeterminacy probability is presented in Fig. 1. This probability provides a minimum requirement for isotope analysis.

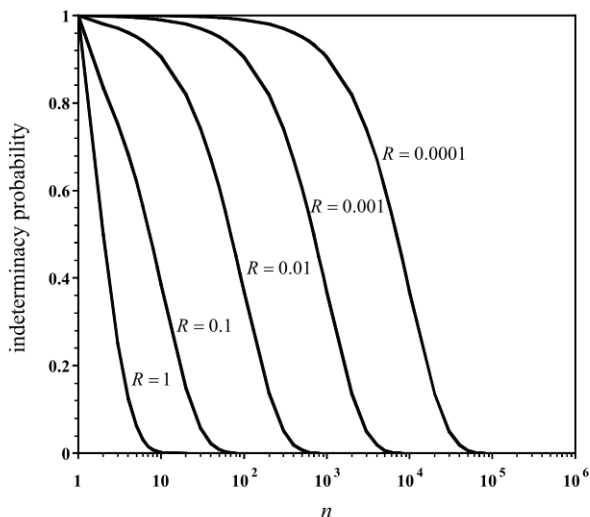


Fig. 1: Indeterminacy probability versus the number of atoms.

4. Fundamental demerits of isotopic ratio

This section indicates two fundamental defects of isotopic ratio and provides a strategy consisting of a statistical model to remedy them. Fig. 2 shows a chart of this model. When  $n$  atoms are extracted at random from a population which has an isotopic ratio of  $R$  ( $X_1/X_2$ ), the isotopic ratio of extracted atoms ( $R_m$ ) has a statistical dispersion which is dependent on  $n$  and  $R$ . If the number of atoms in the population is  $N$  and all atoms are sampled,  $R_m$  will accurately be equal to  $R$  with no uncertainty, with a probability of 1. However, it is impossible to sample all atoms because  $N$  is a nearly infinite number practically speaking, in spite of its countability as mentioned above. The probability that number of  $X_1$  atoms are sampled ( $x_1$ ) is expressed by the binominal distribution shown below.

$$f(x_1) = {}_n C_{x_1} \left(\frac{R}{1+R}\right)^{x_1} \left(\frac{1}{1+R}\right)^{n-x_1} \quad (2)$$

The average ( $\bar{x}_1$ ) and variance ( $s_1^2$ ) of the binominal

distribution are shown below.

$$\bar{x}_1 = \sum_{x_1=0}^n x_1 {}_n C_{x_1} \left(\frac{R}{1+R}\right)^{x_1} \left(\frac{1}{1+R}\right)^{n-x_1} = \frac{nR}{1+R} \quad (3)$$

$$s_1^2 = \sum_{x_1=0}^n x_1^2 {}_n C_{x_1} \left(\frac{R}{1+R}\right)^{x_1} \left(\frac{1}{1+R}\right)^{n-x_1} = \frac{nR}{(1+R)^2} \quad (4)$$

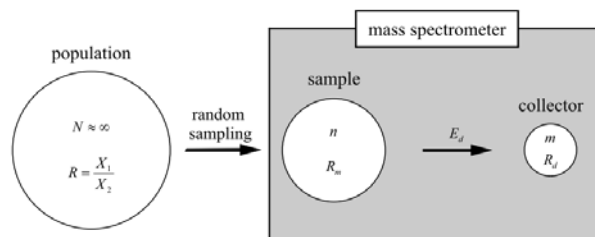


Fig. 2. Conceptual diagram of the model.  $n$  atoms are randomly extracted from the population, whose isotopic ratio is  $R$ , and some of the atoms in the sample are ionized and transported to the collector. The obtained isotopic ratio by the measurement ( $R_d$ ) is statistically distributed by two-step sampling. The unavoidable uncertainty of isotopic ratio depends on the number of atoms in the sample ( $n$ ) and detection efficiency ( $E_d$ ). Even if all atoms in the sample can be detected,  $R_m$  has inevitable deviation because  $n$  is much fewer than  $N$ . The final goal of this model is to estimate the true isotopic ratio ( $R$ ) from known parameters.

Therefore, relative standard deviation  $D_I$  can be computed from expressions (3) and (4) as shown below.

$$D_1 = \frac{s_1}{\bar{x}_1} = \frac{\sqrt{nR}}{1+R} \cdot \frac{1+R}{nR} = \frac{1}{\sqrt{nR}} \quad (5)$$

The  $D_I$  shows the inevitable uncertainty of the number of  $X_1$  in a sample. In a similar procedure, relative standard deviation of the number of  $X_2$  in the sample is expressed as below.

$$D_2 = \frac{s_2}{\bar{x}_2} = \frac{\sqrt{nR}}{1+R} \cdot \frac{1+R}{n} = \sqrt{\frac{R}{n}} \quad (6)$$

However, the probability distribution of isotopic ratio cannot be expressed by such a simple binominal distribution, and the average isotopic ratio ( $\overline{R}_m$ ) is always higher than the isotopic ratio of the population ( $R$ ).

$$\overline{R}_m = \sum_{x_1=0}^{n-1} \left( \frac{x_1}{n-x_1} \right)^n C_{x_1} \left( \frac{R}{1+R} \right)^{x_1} \left( \frac{1}{1+R} \right)^{n-x_1} > R \quad (7)$$

Note that the expression is not the sum from 0 to  $n$  but 0 to  $n-1$  because isotopic ratio cannot be defined when  $x=n$  and at any rate the possibility of  $x=n$  is extremely low. Fig. 3 presents an example of the probability distribution of isotopic ratio when  $R=1$  and  $n=500$ . Although  $R$  coincides with the mode of the distribution when  $n$  is large, as proved in the next section,  $\overline{R}_m$  is systematically higher than  $R$  due to the form of the distribution function. This property of isotopic ratio is a fatal defect for the detailed investigation of isotopic composition through ultra-microanalysis because we cannot obtain the true isotopic ratio ( $R$ ) from the average of measured values. The gap between  $R$  and  $\overline{R}_m$  is controlled by the number of sampled atoms and  $R$ . Fig. 4 shows the relationship between  $\overline{R}_m/R$  ratio and  $n$ . When sampled atoms are few and isotopic ratio is high, the gap between  $R$  and  $\overline{R}_m$  becomes significantly large. Note that  $\overline{R}_m/R$  ratio is quite different in the cases of  $R=0.1$  and 10, although they indicate the same isotopic composition. The result implies another demerit of isotopic ratio, which is the imperfect reversibility of numerator and denominator. This is demonstrated in the inequality below, which also shows that the arithmetic mean is always higher than the harmonic mean.

$$\frac{\sum_{x=1}^l R_x}{l} \geq \frac{l}{\sum_{x=1}^l \frac{1}{R_x}} \quad (8)$$

$R_s$  is isotopic ratio for each measurement step and  $l$  shows the number of measurement steps. The expression means that the average of isotopic ratios (left-hand side) is always higher than the reciprocal of the average of reciprocal of isotopic ratios (right-hand

side), showing that reversing numerator and denominator leads to different conclusions. The inequality (8) is proved by Cauchy's inequality.

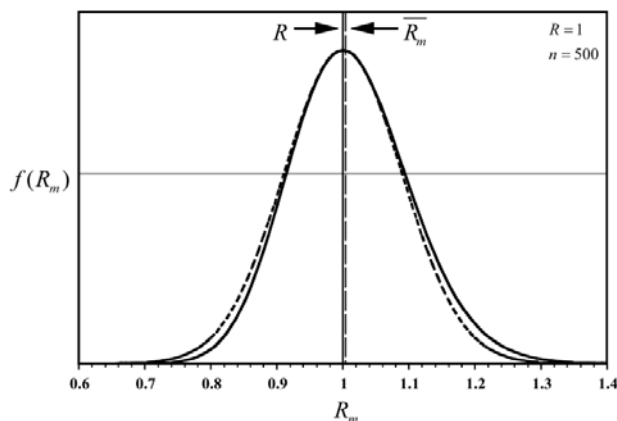


Fig. 3: The distribution function of  $R_m$ .  $R$  and  $n$  are set to be 1 and 500. The dotted curve shows a normal distribution as reference. It is clear that the mean of  $R_m$  is systematically higher than  $R$  due to the disagreement with normal distribution.

Since researchers search for the true isotopic composition of measured sample, it is a significant problem that the calculated isotopic composition is different depending on the isotope selected as the denominator. Moreover, the average of isotopic ratios is systematically higher than the true isotopic ratio as presented in expression (7). These two faults are remedied by using isotopic abundance instead of isotopic ratio. The probability distribution of isotopic abundance is displayed by a binominal distribution and its mean exactly coincides with  $R$ . The problem of the numerator and denominator can completely be avoided because the reciprocal of isotopic abundance is not used and the expression below is applicable to the inequality (8).

$$A_i = \frac{x_i}{\sum_{i=1}^m x_i} \quad (9)$$

$$\frac{\sum_{x=1}^l A_x}{l} = 1 - \frac{\sum_{x=1}^l (1 - A_x)}{l}$$

$x_i$  shows the number atoms of isotope  $X_i$ . If all isotopes

of an element cannot be measured, it is advisable to measure partial isotopic abundance, which is defined as the ratio of the abundance of a certain isotope to all measured isotopes. In this way, isotopic abundance or partial isotopic abundance which is preferable to isotopic ratio for detailed microanalysis can be measured. Isotopic ratio, however, has been conventionally used for a long time, so that now it is completely established as a standard concept. I shall thus discuss here the limits of the determination of isotopic ratio and provide an appropriate correction and evaluation method. When isotopic ratio is used, it is very important to select the major isotope as the denominator of isotopic ratio because otherwise the distortion of the probability distribution function becomes large as seen in Fig. 4. It is a mistake to define an isotopic ratio which will be over 1. This important suggestion conflicts with some traditional manner of expression, in which the minor isotope is generally set to in the denominator of isotopic ratio, for example,  $^{40}\text{Ar}/^{36}\text{Ar}$  [8].

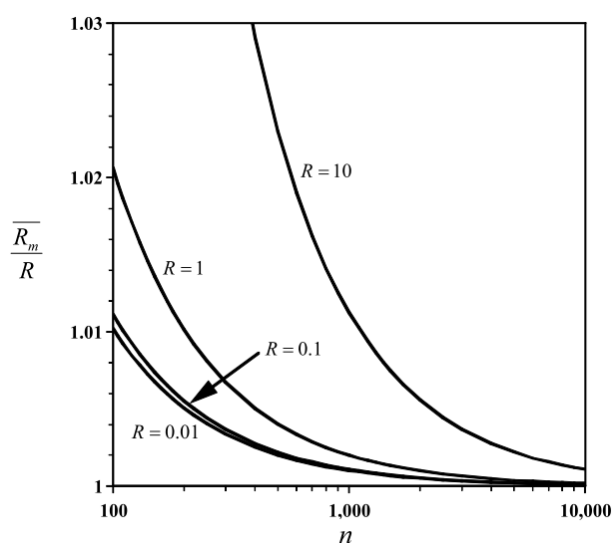


Fig. 4: The ratio between  $R$  and  $\overline{R}_m$  plotted against the number of atoms and different values of  $R$ . When  $R$  is high and  $n$  is small, the disagreement is not negligible. This characteristics of isotopic ratio has a grave effect on the reliability of conclusions.

### 5. Inevitable uncertainty of isotopic ratio

To estimate the inevitable uncertainty of isotopic ratio,

the distribution function of isotopic ratio has to be formulated using an approximation technique. Because a binominal distribution can be approximated with a normal distribution using Laplace's theorem, the distribution function of isotopic ratio of a sample ( $R_m$ ) is expressed by the following equation using equation (3) and (4).

$$g(R_m) = \frac{1+R}{\sqrt{2\pi \cdot nR}} \cdot e^{-\frac{(1+R)^2}{2nR} \left( \frac{nR_m}{1+R_m} - \frac{nR}{1+R} \right)^2} \quad (10)$$

Since this function is not normalized, its integral value doesn't become 1. Normalized probability density function is obtained by the following expression.

$$f(R_m) = \left( \int_0^\infty g(R_m) dR_m \right)^{-1} g(R_m) \quad (11)$$

This is the probability distribution function of  $R_m$ . Differential of the expression (10) is shown below.

$$g'(R_m) = \frac{(1+R)^2}{\sqrt{2\pi \cdot nR}} \cdot \frac{n(R-R_m)}{R(1+R_m)^3} \cdot e^{-\frac{(1+R)^2}{2nR} \left( \frac{nR_m}{1+R_m} - \frac{nR}{1+R} \right)^2} \quad (12)$$

When  $g'(R_m)$  is 0,  $R_m$  becomes maximum, i.e. the mode of the probability distribution. Because the value of equation (12) is 0 when  $R_m=R$ , the mode of  $R_m$  thus coincides with  $R$ . The average of  $R_m$  ( $\overline{R}_m$ ) and variance ( $s_{R_m}^2$ ) are defined by the following expressions using the functions of  $x_1$  obtained from the equation (3) and (4).

$$\overline{R}_m = \sum_{x_1=0}^{n-1} \frac{x_1}{n-x_1} {}_n C_{x_1} \left( \frac{R}{1+R} \right)^{x_1} \left( \frac{1}{1+R} \right)^{n-x_1} \quad (13)$$

$$\approx \frac{1+R}{\sqrt{2\pi \cdot nR}} \int_0^{n-1} \frac{x_1}{n-x_1} \cdot e^{-\frac{(1+R)^2}{2nR} \left( x_1 \frac{nR}{1+R} \right)^2} dx_1$$

$$s_{R_m}^2 = \sum_{x_1=0}^{n-1} \left( \frac{x_1}{n-x_1} \right)^2 {}_n C_{x_1} \left( \frac{R}{1+R} \right)^{x_1} \left( \frac{1}{1+R} \right)^{n-x_1} - \overline{R}_m^2 \quad (14)$$

$$\approx \frac{1+R}{\sqrt{2\pi \cdot nR}} \int_0^{n-1} \left( \frac{x_1}{n-x_1} \right)^2 \cdot e^{-\frac{(1+R)^2}{2nR} \left( x_1 \frac{nR}{1+R} \right)^2} dx_1 - \overline{R}_m^2$$

In these expressions,  $x_1=n$  is excluded because isotopic ratio cannot be determined in this case. When  $n$  is large enough ( $>ca$  one thousand), and  $R$  is lower than 1,  $\overline{R}_m$  can be approximated with high accuracy by the following simple equation.

$$\overline{R}_m \approx R \left( 1 + \frac{1+R}{n} \right) \quad (15)$$

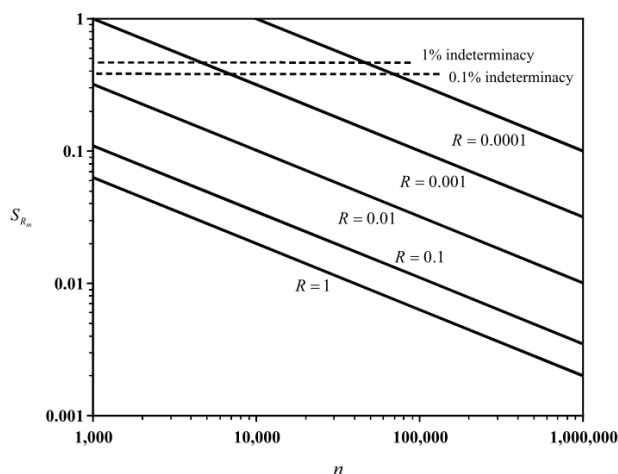


Fig. 5: Inevitable uncertainty of isotopic ratio inherent in the number of sampled atoms and the isotopic ratio of the population. Two dotted lines represent indeterminacy probabilities of 1% and 0.1%. Since the uncertainty is unavoidable, it provides a fundamental limit of measurement accuracy.

Derivation of this approximation is detailed in the appendix. If the distribution function of isotopic ratio coincides with the normal distribution, the standard deviation can be easily calculated. However, the function (10) is an asymmetrical distribution, and it is very difficult to solve the equation (14). Nevertheless, the variance of isotopic ratio can be approximated by a simple expression when  $n$  is large and  $R$  is lower than 1. A formula for approximate standard deviation of isotopic ratio is obtained from equations (3) and (4) as follows.

$$s_{R_m} \approx \frac{1}{2} \left( \frac{\overline{x}_1 + s_1}{n - (\overline{x}_1 + s_1)} - \frac{\overline{x}_1 - s_1}{n - (\overline{x}_1 - s_1)} \right) = \frac{\sqrt{nR}(1+R)}{n-R} \quad (16)$$

$$\frac{s_{R_m}}{R_m} \approx \frac{n\sqrt{nR}(1+R)}{R(n+R+1)(n-R)} \quad (17)$$

When  $n \gg R$ , the expression (17) is simplified as below.

$$\frac{s_{R_m}}{R_m} \approx \frac{1+R}{\sqrt{nR}} \quad (18)$$

Fig. 5 shows the relationship between the number of atoms and relative standard deviation of isotopic ratio. The diagram indicates that the measured isotopic ratio always has potential error, which does not depend on experimental uncertainties at all.

### 6. Confirmation requirement for isotopic anomaly

It is important to judge whether an obtained isotopic ratio is anomalous or not. Since the isotopic ratio unavoidably has statistical uncertainty which is estimated by expression (16), the anomaly of isotopic ratio has to be evaluated from the probability density function. When the level of significance is set to be 0.05 and  $R_n$  is normal isotopic ratio, the requirement for anomaly with regarded to the relation  $\overline{R}_m > R_n$  or  $\overline{R}_m > R_n$  is approximately expressed as follows.

$$\begin{aligned} \left| \overline{R}_m - R_n \right| &> \frac{1}{2} \left( \frac{\overline{x}_1 + 1.645 \cdot s_1}{n - (\overline{x}_1 + 1.645 \cdot s_1)} - \frac{\overline{x}_1 - 1.645 \cdot s_1}{n - (\overline{x}_1 - 1.645 \cdot s_1)} \right) \\ &= \frac{1.645 \cdot \sqrt{nR}(1+R)}{n - 1.645^2 \cdot R} \quad (19) \end{aligned}$$

If  $n$  is large enough compared with  $R$ ,  $\overline{R}_m$  is almost equal to  $R$  and the requirement (19) can be simplified to the inequality below.

$$\left| \overline{R}_m - R_n \right| \approx |R - R_n| > 1.645 \cdot s_{R_m} \approx 1.645 \cdot \frac{\sqrt{nR}(1+R)}{n} \quad (20)$$

This is the convenient expression of the confirmation requirement for isotopic anomaly. In the expression (20),  $R$  and  $R_n$  are mutually exchangeable and thus another important expression is produced.

$$|R_n - R| > 1.645 \cdot \frac{\sqrt{nR_n(1+R_n)}}{n} \quad (21)$$

The inequality provides the requirement for an isotopic ratio ( $R$ ) to be confirmed anomalous as compared with a normal isotopic ratio ( $R_n$ ). The relationship between this requirement and number of atoms is shown in Fig. 6. If the difference between  $R$  and normal isotopic ratio of  $R_n$  is larger than the corresponding curve in the diagram, significant isotopic fractionation is detectable. On the other hand, if the composition of  $n$  or  $R$  doesn't satisfy this requirement, i.e. its plotted position is under the curve, it is impossible to prove an isotopic anomaly even though the isotopic ratio in a sample is completely determined by an all-powerful mass spectrometer, because the uncertainty derives from the number of sampled atoms.

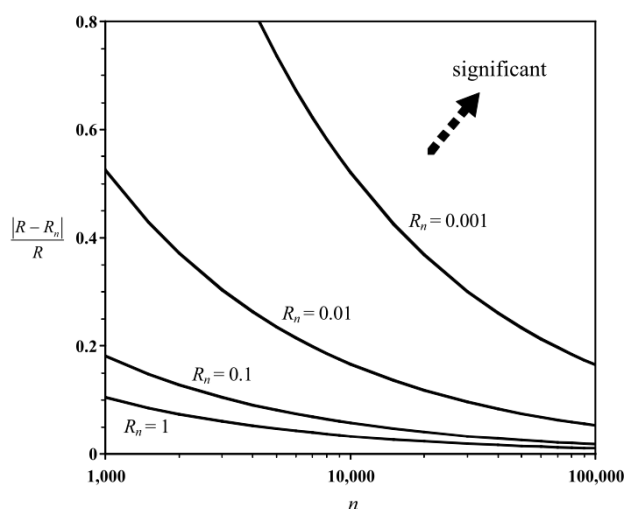


Fig. 6: Confirmation requirement for isotopic anomaly. Because isotopic ratio has inevitable uncertainty, a certain number of atoms is required to prove a significant isotopic anomaly.

Table 1 presents the minimum atomicity of each element needed to confirm 1 and 10% isotopic anomaly calculated from expression (21). The listed numbers have two significant digits. Although current mass spectrometers cannot investigate such small numbers of isotopes accurately, the confirmation limits shown in this table are fundamental barriers to precise isotopic analysis in future.

In the discussions above, measurement error, which originates in the structure and instability of the

analytical device, is completely ignored. When the measurement error is described as  $s_m$ , total uncertainty of isotopic ratio ( $s_{total}$ ) is simply expressed as follows due to the law of propagation of errors.

$$s_{total} = \sqrt{s_m^2 + s_{R_n}^2} \approx \sqrt{s_m^2 + \frac{nR(1+R)^2}{(n-R)^2}} \quad (22)$$

$s_m$  is derived from various causes, the main ones being related the structure of the measuring equipment. In general, atoms introduced into the mass spectrometer are ionized in the ion source, resolved according to mass, and finally detected by collectors. Since an ion source cannot ionize all isotopes and all ions cannot reach the collectors, the number of detected isotopes is always smaller than the total number of isotopes in a sample. If the sampling in the mass spectrometer is done at random, detection efficiency ( $E_d$ ) is determined by the ionization efficiency ( $E_i$ ) and transporting efficiency ( $E_t$ ).

$$E_d = E_i \cdot E_t \quad (23)$$

If the detection probability is constant, the probability distribution function of detected number of atoms ( $m$ ) is expressed by a binominal distribution.

$$f(m) = {}_n C_m (E_d)^m (1 - E_d)^{(n-m)} \quad (24)$$

On the other hand, the probability distribution of the number of detected isotope  $X_1$  ( $y_1$ ) is a hypergeometric distribution, which can be approximated by binominal distribution when the number of atoms in the sample ( $n$ ) is large.

$$f(y_1) = \frac{{}^{nR_m} C_{y_1} \cdot {}^n C_{m-y_1}}{{}^n C_m} \quad (25)$$

$$\approx {}_m C_{y_1} \left( \frac{R_m}{1+R_m} \right)^{y_1} \left( \frac{1}{1+R_m} \right)^{m-y_1}$$

$R_m$  shows the isotopic ratio of the sample. Since the equation (25) can be approximated by a normal

distribution, the distribution function of the isotopic certain  $R_m$  by equation (24) and (26) becomes the

Table 1. Confirmation requirement for isotopic fractionation of selected elements.

Element	Isotope combination	Normal isotopic ratio	Confirmation requirement			
			10% anomaly		1% anomaly	
			number of atoms	weight ( $10^{-15}$ g) <sup>a</sup>	number of atoms	weight ( $10^{-15}$ g) <sup>a</sup>
H	H/D	0.000150	1,900,000	3.2	190,000,000	320
He	<sup>3</sup> He/ <sup>4</sup> He	0.00000134	210,000,000	351	21,000,000,000	35000
Li	<sup>6</sup> Li/ <sup>7</sup> Li	0.0821	3,900	0.0065	390,000	0.65
B	<sup>10</sup> B/ <sup>11</sup> B	0.248	1,700	0.0028	170,000	0.28
C	<sup>13</sup> C/ <sup>12</sup> C	0.0108	26,000	0.044	2,600,000	4.4
N	<sup>15</sup> N/ <sup>14</sup> N	0.00365	75,000	0.13	7,500,000	13
O	<sup>18</sup> O/ <sup>16</sup> O	0.00205	140,000	0.23	14,000,000	23
	<sup>17</sup> O/ <sup>16</sup> O	0.000381	720,000	1.2	72,000,000	120
Ne	<sup>21</sup> Ne/ <sup>20</sup> Ne	0.00298	92,000	0.15	9,200,000	15
	<sup>22</sup> Ne/ <sup>20</sup> Ne	0.102	3,300	0.0055	330,000	0.55
Mg	<sup>25</sup> Mg/ <sup>24</sup> Mg	0.127	2,800	0.0047	280,000	0.47
	<sup>26</sup> Mg/ <sup>24</sup> Mg	0.139	2,600	0.0044	260,000	0.44
Si	<sup>29</sup> Si/ <sup>28</sup> Si	0.0508	5,900	0.010	590,000	0.99
	<sup>30</sup> Si/ <sup>28</sup> Si	0.0335	8,700	0.015	870,000	1.46
S	<sup>33</sup> S/ <sup>32</sup> S	0.00790	35,000	0.059	3,500,000	5.9
	<sup>34</sup> S/ <sup>32</sup> S	0.0447	6,700	0.011	670,000	1.1
	<sup>36</sup> S/ <sup>32</sup> S	0.000105	2,600,000	4.4	260,000,000	440
Ar	<sup>36</sup> Ar/ <sup>40</sup> Ar	0.00338	81,000	0.14	8,100,000	14
	<sup>38</sup> Ar/ <sup>40</sup> Ar	0.000635	430,000	0.72	43,000,000	72
K	<sup>40</sup> K/ <sup>39</sup> K	0.000125	2,200,000	3.7	220,000,000	370
	<sup>41</sup> K/ <sup>39</sup> K	0.0722	4,400	0.0074	440,000	0.74
Fe	<sup>54</sup> Fe/ <sup>56</sup> Fe	0.0637	4,900	0.0082	490,000	0.82
	<sup>57</sup> Fe/ <sup>56</sup> Fe	0.0231	13,000	0.022	1,300,000	2.2
	<sup>58</sup> Fe/ <sup>56</sup> Fe	0.00307	89,000	0.15	8,900,000	15
Pb	<sup>204</sup> Pb/ <sup>208</sup> Pb	0.0267	11,000	0.018	1,100,000	1.8
	<sup>206</sup> Pb/ <sup>208</sup> Pb	0.460	1,300	0.0022	130,000	0.22
	<sup>207</sup> Pb/ <sup>208</sup> Pb	0.422	1,300	0.0022	130,000	0.22
U	<sup>234</sup> U/ <sup>238</sup> U	0.0000544	5,000,000	8.4	500,000,000	837
	<sup>235</sup> U/ <sup>238</sup> U	0.00726	38,000	0.064	3,800,000	6.4

Level of significance is set to be 0.05

Experimental uncertainties are completely ignored

(a) Total weight of two isotopes

ratio of detected isotopes is expressed as follows.

$$g(R_d) = \frac{1 + R_m}{\sqrt{2\pi \cdot mR_m}} \cdot e^{-\frac{(1+R_m)^2}{2mR_m} \left(\frac{mR_d}{1+R_d} - \frac{mR_m}{1+R_m}\right)^2} \quad (26)$$

This is the same expression as equation (10). Since this equation is a function of both  $m$  and  $R_m$ , all cases have to be considered. The distribution function of  $R_d$  for a

following expression.

$$G(R_d, R_m) = \sum_{m=1}^n \{f(m)g(R_d)\} \\ = \sum_{m=1}^n \left\{ {}_n C_m (E_d)^m (1 - E_d)^{n-m} \frac{1 + R_m}{\sqrt{2\pi \cdot mR_m}} \cdot e^{-\frac{(1+R_m)^2}{2mR_m} \left(\frac{mR_d}{1+R_d} - \frac{mR_m}{1+R_m}\right)^2} \right\} \quad (27)$$



This equation considers all the cases of  $m$ . Since the distribution function of  $R_m$  is obtained by equation (10), the distribution function of  $R_d$  finally develops as follows.

$$G(R_d) = \int_0^\infty g(R_m) \sum_{m=1}^n \{f(m)g(R_d)\} dR_m$$

$$= \int_0^\infty \frac{1+R}{\sqrt{2\pi \cdot nR}} \cdot e^{-\frac{(1+R)^2 \left( \frac{nR_m}{1+R_m} - \frac{nR}{1+R} \right)^2}{2nR}} \cdot \sum_{m=1}^n \left\{ {}_n C_m (E_d)^m (1-E_d)^{n-m} \frac{1+R_m}{\sqrt{2\pi \cdot mR_m}} \cdot e^{-\frac{(1+R_m)^2 \left( \frac{mR_d}{1+R_d} - \frac{mR_m}{1+R_m} \right)^2}{2mR_m}} \right\} dR_m$$

(28)

The probability distribution function is obtained if this function is normalized as in the case of equation (11). Because this function is very complex, another approach is adopted here as an approximate calculation. The mean and variance of  $y_1$  and  $y_2$  can be presented as follows because of their hypergeometric distribution.

$$\bar{y}_1 = \frac{mR_m}{1+R_m} \quad (29)$$

$$\bar{y}_2 = \frac{m}{1+R_m}$$

$$s_{y_1}^2 = s_{y_2}^2 = m \frac{nR_m}{n(1+R_m)} \cdot \frac{n}{n(1+R_m)} \cdot \frac{n-m}{n-1} = \frac{mR_m(n-m)}{(n-1)(1+R_m)^2}$$

(30)

The standard deviation of  $R_d$  ( $s_{R_d}$ ) is approximately calculated from the expressions (29) and (30) in the same way as equation (16).

$$s_{R_d} \approx \frac{1}{2} \left\{ \frac{\bar{y}_1 + s_{y_1}}{m - (\bar{y}_1 + s_{y_1})} - \frac{\bar{y}_1 - s_{y_1}}{m - (\bar{y}_1 - s_{y_1})} \right\} \quad (31)$$

$$= \frac{(1+R_m)\sqrt{mR_m(n-m)(n-1)}}{m(n-1) - R_m(n-m)}$$

The mean of the  $s_{R_d}$  ( $\bar{s}_{R_d}$ ) can be calculated from

$$\int_0^\infty f(R_m) \left\{ \sum_{m=1}^{n-1} f(m)s_{R_d} \right\} dR_m$$

using the equations (11) and (24). However, a more simple method is adopted here to avoid this complex computation.  $\bar{s}_{R_d}$  is approximated substituting  $m$  for

the mean of  $m$  ( $\bar{m} = nE_d$ ) in the expression (31), although this approximated value is always slightly lower than the true  $\bar{s}_{R_d}$ .

$$\bar{s}_{R_d} \approx \frac{(1+R_m)\sqrt{E_d R_m (1-E_d)(n-1)}}{E_d(n-1) - R_m(1-E_d)} \quad (32)$$

When  $n$  is large and  $E_d$  is high, the approximation has high accuracy. In the same way, if  $R_m$  is substituted for  $\bar{R}_m$  using equation (15), the expression (32) is described in terms of  $n$ ,  $R$ , and  $E_d$  as follows.

$$\bar{s}_{R_d} \approx \frac{(1+R)(n+R)\sqrt{nRE_d(1+n+R)(1-E_d)(n-1)}}{nE_d(n-1) - R(1+n+R)(1-E_d)} \quad (33)$$

When  $n \gg 1 > R$ , this can be simplified to

$$\bar{s}_{R_d} \approx \frac{(1+R)\sqrt{nRE_d(1-E_d)}}{nE_d - R(1-E_d)} \quad (34)$$

This expression can be utilized to estimate the inevitable uncertainty of isotopic ratio, due to  $n$ ,  $R$ , and  $E_d$ . It is important to keep in mind that the detection efficiency strongly affects the error.

In the isotopic measurement, detectable uncertainty does not, however, coincide with the estimated error for two reasons. First, the sample had already been selected before the measuring process, meaning that  $R_m$  and  $n$  are initially fixed and potential error due to sampling from a population, which is shown by the equation (14), is not detectable. Second, measurement error is generated by the fluctuation due to the instability of the analytical device. If the contribution of the fluctuation of the equipment ( $f$ ) is taken into consideration, the standard deviations of the numbers of detected isotopes ( $\sigma_{y_1}$  and  $\sigma_{y_2}$ ) become the equations below using the equation (30) derived from the law of propagation of errors.

$$\sigma_{y_1} = \sigma_{y_2} = \sqrt{s_{y_1}^2 + f^2} = \sqrt{\frac{m^2 R_m^2 (n-m)^2}{(n-1)^2 (1+R_m)^4} + f^2} \quad (35)$$

$s_{y_1}$  and  $s_{y_2}$  are given by the equation (30).  $f$  is set to be constant here. The approximated standard deviation of  $R_d$  is, therefore, calculated by the same procedure for expression (31).

$$\begin{aligned} \sigma_{R_d} &\approx \frac{1}{2} \left\{ \frac{\bar{y}_1 + \sigma_{y_1}}{m - (\bar{y}_1 + \sigma_{y_1})} - \frac{\bar{y}_1 - \sigma_{y_1}}{m - (\bar{y}_1 - \sigma_{y_1})} \right\} \\ &= \frac{m\sigma_{y_1}}{(m - \bar{y}_1)^2 - \sigma_{y_1}^2} \\ \sigma_{R_d} &\approx \frac{nE_d\sigma_{y_1}}{(nE_d - \bar{y}_1)^2 - \sigma_{y_1}^2} \end{aligned} \quad (36)$$

This is the total detectable uncertainty of isotopic ratio. The confirmation requirement for isotopic anomaly is shown below.

$$|\bar{R}_d - R_n| > 1.645 \cdot \sigma_{R_d} \approx 1.645 \cdot \frac{nE_d\sigma_{y_1}}{(nE_d - \bar{y}_1)^2 - \sigma_{y_1}^2} \quad (37)$$

Because  $R_m$  and  $n$  are constant,  $E_d$  and  $f$  control the detected error. However, the  $\sigma_{R_d}$  cannot be regarded as the measurement error itself in most cases, because it expresses the potential error of only one measurement of  $m$  atoms, which means that  $\sigma_{R_d}$  predicts a potential error for a one-step isotopic measurement. In general, more than eight measurements are carried out to measure an isotope ratio, and the standard deviation is calculated. Therefore, when  $l$  step measurements are carried out,  $m$  has to be substituted with  $m/l$  in the expression (36). The average of the measurement error is described as follows.

$$\begin{aligned} \bar{s}_m &\approx \frac{\frac{nE_d}{l} \sqrt{\frac{n^2 E_d^2 R_m^2 (nl - nE_d)^2}{l^4 (n-1)^2 (1+R_m)^4} + f^2}}{\left( \frac{nE_d}{l} - \frac{nE_d R_m}{l(1+R_m)} \right)^2 - \frac{n^4 E_d^2 R_m^2 (l - E_d)^2}{l^4 (n-1)^2 (1+R_m)^4} - f^2} \end{aligned} \quad (38)$$

This expression predicts average error derived from  $n$ ,  $l$ ,  $E_d$ ,  $f$ , and  $R_m$ . The error is the detectable error obtained by measurement. If the calculated  $\bar{s}_m$  is larger than the obtained measurement error when 0 is substituted for  $f$ , it cannot be adopted as a plausible

uncertainty because the calculated  $\bar{s}_m$  reflects the inevitable error caused by  $E_d$ .

If the potential error of  $R_m$  is taken into consideration, the total of detectable and undetectable uncertainty can be calculated by the equation (22). To compute the total error,  $R$  has to be expressed by  $\bar{R}_d$  in the equation. In the first step,  $R_m$  is expressed by  $\bar{R}_d$  referring to equation (15).

$$\begin{aligned} \bar{R}_d &\approx R_m \left( 1 + \frac{l(1+R_m)}{m} \right) \\ R_m &\approx \frac{-(m+l) + \sqrt{(m+l)^2 + 4ml\bar{R}_d}}{2l} \end{aligned} \quad (39)$$

Although this  $R_m$  is the isotopic ratio in the sample as deduced from  $\bar{R}_d$ ,  $R$  cannot be determined from the  $R_m$  because  $R_m$  is a probability distribution function. Only the plausible value with the highest possibility is, therefore, presented. If the  $R_m$  is regarded as  $\bar{R}_m$ , the most plausible  $R$  ( $R_{est}$ ) can be estimated.

$$\begin{aligned} R_{est} &= \frac{-(n+1)}{2} \\ &+ \frac{1}{2} \sqrt{(n+1)^2 + 2n \cdot \frac{-(m+l) + \sqrt{(m+l)^2 + 4ml\bar{R}_d}}{l}} \end{aligned} \quad (40)$$

The expression provides a practical method to estimate a plausible true isotopic ratio from  $n$ ,  $m$ ,  $l$ , and  $\bar{R}_d$ , all of which can be obtained by analytical procedures. The total uncertainty of isotopic ratio can thus be expressed using the  $R_{est}$ .

$$s_{total} = \sqrt{s_m^2 + \frac{nR_{est}(1+R_{est})^2}{(n-R_{est})^2}} \quad (41)$$

The last three equations are applicable to most mass spectrometry, although they have to be slightly amended in the case of a gas mass spectrometer, which can repeatedly detect atoms. In such case,  $m/l$  is replaced with the average of the number of detected atoms ( $\bar{p}$ ) in one measurement step in the equation (39).

$$R_m \approx \frac{1}{2} \left( -(\bar{p}+1) + \sqrt{(\bar{p}+1)^2 + 4\bar{p}\bar{R}_d} \right) \quad (42)$$

$$R_{est} = \frac{-(n+1)}{2} + \frac{1}{2} \sqrt{(n+1)^2 - 2n(\bar{p}+1) + 2n\sqrt{(\bar{p}+1)^2 + 4\bar{p}\bar{R}_d}} \quad (43)$$

The total of inevitable uncertainty in the two-step sampling procedure is calculated using equations (15), (31), (42), and (43).

$$S_{potential} = \sqrt{\frac{nR_{est}(1+R_{est})^2}{(n-R_{est})^2} + \left( \frac{(1+R_m)\sqrt{\bar{p}\bar{R}_d(n-\bar{p})(n-1)}}{\bar{p}(n-1)-R_m(n-\bar{p})} \right)^2} \quad (44)$$

This equation is available to estimate an expected inevitable error from  $n$ ,  $\bar{p}$  and  $\bar{R}_d$ . Fig. 7 presents a diagram  $R_{est}/\bar{R}_d$  versus  $\bar{p}$  when  $n$  is fixed to be 1,000,000. This figure can predict the required number of atoms to be detected before the measurement. If the content of the target element in a sample is known, it is also possible to calculate the required detection time.

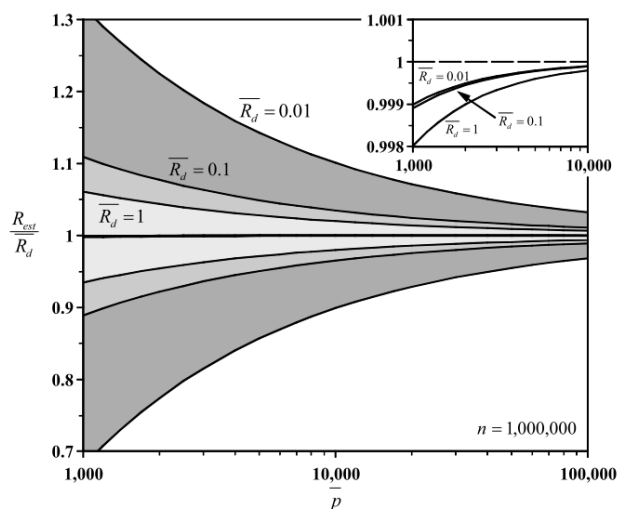


Fig. 7:  $R_{est}/\bar{R}_d$ , with  $R_{est}$  estimated from  $\bar{R}_d$  and  $\bar{p}$  using the equations (43) and (44).  $n$  is set to be 1,000,000. Shaded areas show the range of one sigma uncertainty.  $\bar{p}$  means the number of atoms detected in a step of measurement.

### 7. Correction using the standard

The isotopic ratio obtained by measurement is usually corrected using a mass bias coefficient determined by

analysis of the standard. If the same amount of the standard as the measured sample is used, the difference from the true isotopic ratio is counterbalanced by the bias coefficient because the coefficient expresses the effect causes the deviation from the true value. However, a standard much larger than the sample is generally analyzed to determine an accurate mass bias coefficient. When very large amount of the standard is used compared with that of the sample, the correction of isotopic ratio presented in the equation (40) or (43) is usable. In particular, the correction of isotopic ratio will be required in ultra-microanalysis.

### 8. The statistical effects on previously reported data

Recently, measurements of isotopic compositions of extremely small samples are reported using very sensitive mass spectrometers. Particularly, NanoSIMS, a new generation secondary ion mass spectrometer, allows isotopic imaging at a spatial scale of 50 nm and can detect around 6000 atomic ions with ionization of 0.005 and transmission of 100%. This apparatus is used in the field of cosmochemistry [9], geology [10], and biology [11]. In this section, I verify the validity of some reported data.

First, I verify the carbon isotopic anomaly discovered in an IDP nicknamed Benavente, which contains a large ( $0.6 \times 1.8 \mu\text{m}^2$ ) region that is depleted in  $^{13}\text{C}$  ( $^{12}\text{C}/^{13}\text{C} = 96.6 \pm 1.3$ ;  $\delta^{13}\text{C} = -70 \pm 13\text{‰}$ ) [6]. Because these researchers obtained isotopic imaging at a spatial scale of 100 nm, it is assumed that there are 108 measured points ( $6 \times 18$ ). Thus an estimated isotopic ratio ( $R_{est}$ ) and total uncertainty ( $S_{total}$ ) are calculated from the equations (40) and (41) as a function of  $n$ . In the calculation,  $l = 108$  and  $m = nE_d = n \times 0.005$ . When the level of significance is set to 0.05, about 34,000,000 carbon atoms (170,000 detected atomic ions) are required to prove the anomaly with regard to the terrestrial carbon isotopic ratio of 89. This requirement is presumably satisfied because the isotopic anomaly is detected in carbonaceous material regions (in rough estimation, over 3% C is required). In another paper, Stadermann and Floss (2004) reported oxygen isotope anomaly in a noncluster IDP TIBERIUS, having a high  $^{17}\text{O}/^{16}\text{O}$  ratio of  $1.31 \pm 0.03 \times 10^{-3}$  in a well-defined individual grain that has a size of  $350 \times 600 \text{ nm}^2$  [12]. Only 1000 oxygen atoms are

needed to verify this anomalous isotopic ratio with regard to the terrestrial ratio of  $3.81 \times 10^{-4}$ , because the isotopic anomaly is significantly large.

I also checked several other papers and verify that the statistical effects on isotopic ratio did not strongly affect the conclusions reached, since a sufficient number of atoms was measured even in NanoSIMS and/or the isotopic anomaly was extremely large. I can thus conclude that fortunately no serious problem has occurred up to the present. However, if the measurement of a smaller number of atoms is required in the future, for example isotope analysis for a single presolar grain, it will be necessary to understand the statistical characteristics of isotopic ratio outlined in this paper and to carefully handle obtained data.

### 9. Conclusions

The statistical discussions presented in this paper provide several important conclusions, relating to the fundamental characteristics of isotopic ratio. The most significant defect of isotopic ratio is that the probability distribution function of isotopic ratio is not the same as the binominal distribution, suggesting that the average value of isotopic ratio always higher than the true one. When the isotopic ratio is over 1, the difference between the true and averaged isotopic ratio is not negligible, even if the number of measured atoms are large. Therefore, it is necessary to set the isotopic ratio lower than 1 to reduce this difference, showing another basic shortcoming of isotopic ratio, that is, the imperfect reversibility of numerator and denominator. Since these two fundamental characteristics cause intolerable inaccuracies in the analysis of extremely small numbers of atoms, isotopic abundance should be used rather than isotopic ratio.

However, it is difficult to stop use of isotopic ratio immediately because it is widely used in various fields of science and in the measurement by most types of mass spectrometer. Therefore, it is important to calculate the inevitable uncertainty and a plausible true isotopic ratio using the expressions presented in this paper. It is especially necessary for such the computations to be carried out when an extremely small sample is measured, e.g. spot analysis for a minute object using a precise mass spectrometer, although no serious problem was found in previous

such reports. In the future, functions for estimating potential uncertainty and correcting the isotopic ratio should be built in the measurement program of mass spectrometers because the technique of ultra-microanalysis will evolve in this century.

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## Appendix

The equation (13) can be transformed as follows.

$$\begin{aligned}
 \overline{R}_m &= \sum_{x_1=0}^{n-1} \frac{x_1}{n-x_1} {}_n C_{x_1} \left(\frac{R}{1+R}\right)^{x_1} \left(\frac{1}{1+R}\right)^{n-x_1} \\
 &= \sum_{x_1=0}^{n-1} \frac{x_1}{n-x_1} \frac{n!}{(n-x_1)!x_1!} \left(\frac{R}{1+R}\right)^{x_1} \left(\frac{1}{1+R}\right)^{n-x_1} \\
 &= \sum_{x_1=1}^{n-1} \frac{x_1}{n-x_1} \frac{n!}{(n-x_1+1)!(x_1-1)!} \frac{n-x_1+1}{x_1} \left(\frac{R}{1+R}\right)^{x_1} \left(\frac{1}{1+R}\right)^{n-x_1} \\
 &= \sum_{x_1=1}^{n-1} \frac{n-x_1+1}{n-x_1} {}_n C_{x_1-1} \left(\frac{R}{1+R}\right)^{x_1-1} \left(\frac{1}{1+R}\right)^{n-x_1+1} \left(\frac{R}{1+R}\right) (1+R) \\
 &= R \sum_{x_1=1}^{n-1} \left(1 + \frac{1}{n-x_1}\right) {}_n C_{x_1-1} \left(\frac{R}{1+R}\right)^{x_1-1} \left(\frac{1}{1+R}\right)^{n-x_1+1} \\
 &= R \left\{ 1 + \sum_{x_1=1}^{n-1} \frac{1}{n-x_1} {}_n C_{x_1-1} \left(\frac{R}{1+R}\right)^{x_1-1} \left(\frac{1}{1+R}\right)^{n-x_1+1} \right\} \\
 &= R \left\{ 1 + \sum_{x_1=1}^{n-1} \frac{1}{n-x_1} \frac{(n+1)!}{(n-x_1+2)!(x_1-1)!} \frac{n-x_1+2}{n+1} \left(\frac{R}{1+R}\right)^{x_1-1} \left(\frac{1}{1+R}\right)^{n-x_1+2} (1+R) \right\} \\
 &= R \left\{ 1 + (1+R) \sum_{x_1=1}^{n-1} \frac{n-x_1+2}{(n-x_1)(n+1)} {}_n C_{x_1-1} \left(\frac{R}{1+R}\right)^{x_1-1} \left(\frac{1}{1+R}\right)^{n-x_1+2} \right\} \\
 &= R \left\{ 1 + \frac{1+R}{n+1} + \frac{2(1+R)}{n+1} \sum_{x_1=1}^{n-1} \frac{1}{n-x_1} {}_n C_{x_1-1} \left(\frac{R}{1+R}\right)^{x_1-1} \left(\frac{1}{1+R}\right)^{n-x_1+2} \right\} \\
 &= R \left[ 1 + \frac{1+R}{n+1} + \frac{2(1+R)}{n+1} \left\{ \frac{1+R}{n+2} + \frac{3(1+R)}{n+2} \sum_{x_1=1}^{n-1} \frac{1}{n-x_1} {}_n C_{x_1-1} \left(\frac{R}{1+R}\right)^{x_1-1} \left(\frac{1}{1+R}\right)^{n-x_1+3} \right\} \right] \\
 \therefore \overline{R}_m &= R \left\{ 1 + \frac{1!(1+R)}{n+1} + \frac{2!(1+R)^2}{(n+1)(n+2)} + \frac{3!(1+R)^3}{(n+1)(n+2)(n+3)} + \frac{4!(1+R)^4}{(n+1)(n+2)(n+3)(n+4)} \dots \right\} \\
 &(45)
 \end{aligned}$$

Therefore, the average of  $R_m$  can be approximated by the equation (15) when  $n$  is large and  $R$  is lower than 1.

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