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MASS FRACTIONATION AND ENERGY DISTRIBUTION OF SPUTTERED MONATOMIC POSITIVE IONS

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Abstract

Secondary ion yields in sputtering depend significantly on the mass of the emitted species. Ionization as observed by secondary ion mass spectrometry is characterized by isotope fractionation; the yield of an isotope ion of mass  $M_i$  being proportional to  $M_i^{-\alpha}$ , where  $\alpha$  varies with the emitted species, its kinetic energy  $E_k$ , and the matrix.

By means of SIMS, isotope ratios have been measured for ions at energies up to ca 120 eV in different metallic matrices. For singly charged positive monatomic ions,  $\alpha$  has been found to range between 0 and ca 4. While  $\alpha$  may drop steeply at low or moderate  $E_k$ , at higher energies the gradient decreases and usually becomes positive. To some extent the trends of  $\alpha$  are complementary to those of the energy dependence of elemental ion yields.

In the present work, the main tendencies are surveyed for pure element matrices as well as for several elements sputtered from a given metallic matrix. It is attempted to correlate  $\alpha$  with the energy distributions of ionic yields. Isotope effects appear inherent in all three basic mechanisms of ion emission, i.e., in sputter yield, ionization, and charge survival.

KEY WORDS: Sputtering, ionization, isotope effects, ion mass, ion energy distribution, secondary ion mass spectrometry.

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Introduction

Efficient employment of secondary ion mass spectrometry (SIMS), e.g. in geo-cosmology /9,10, 2/ or in atomic transport studies /20, 21/, is conditional on the accuracy in the determination of isotope ratios. It has been pointed out in recent years /18, 19, 10, 16, 12, 20, 15/ that the role of isotope mass in the ion yields of sputtering is by no means negligible. The yields in SIMS are found to decrease with increasing isotope mass to a degree often higher than in other mass spectrometric techniques. The mass fractionation may be expressed by a factor, defined by

$$R_i/R_0 \propto M_i^{-\alpha}, \quad (1)$$

where  $M_i$  is the mass of the isotope  $i$ ,  $R_i$  is its apparent abundance as observed via the ion current ratios in SIMS, and  $R_0$  the true abundance of  $i$ . The pioneering discussion of the significance of  $\alpha$  has been given by Slodzian and co-workers /18, 19, 10/, who also contributed pilot experimental evidence, chiefly from work on minerals. Thorough experimental studies on pure element isotopic matrices have been carried out by Shimizu and Hart /16/. New studies of isotope fractionation in sputtering were made both on minerals /12/ and on pure element targets /20, 15/.

The extent of isotope fractionation depends on the nature of the matrix and of the emitted ion as well as on the kinetic energy  $E_k$  of the emitted species. Theoretical considerations /18, 19/ imply interrelations between  $\alpha$  on one hand, elemental ionizabilities on the other. The study of such relations may be expected to yield significant information on the mechanisms of ion emission and detection in SIMS.

Hitherto only few determinations of  $\alpha$  have been made at energies above ca 70 eV. Below ca 10 eV the results may at times have been affected by artifacts such as spectral contamination or the effects of finite width of energy pass window. In the present paper, isotope fractionation data are to be given for ions from pure elements as obtained at kinetic energies up to ca 120 eV. Furthermore, results are to be reported for several elements sputtered from a metal glass matrix. The behavior of  $\alpha$  is to be correlated with the ionizabilities of different elements at different kinetic energies  $E_k$ .

Experimental Principles

The measurements were performed with a Cameca IMS-3F secondary ion mass spectrometer. Primary ions,  $O_2^+$  or  $O^-$ , accelerated through ca 10 kV, were focused to an adjustable area on the target. The current density could be varied by different raster, and in each case the analyzed area was chosen so as to assure sufficient counting statistics also for the least abundant isotopes. Both the primary current density and the pressure of  $O_2$  backfill were used to vary the oxygen saturation of the target.

The position of the energy pass band (window width EWW) for acceptance of secondary ions into the analyzer was controlled by h.v. offset in specimen potential (OFS eV; the energy window extended  $\frac{1}{2}$  EWW on each side of OFS). Windows of 0.5 - 5 eV were employed for the recording of energy distributions and for isotope studies at the lowest  $E_k$ , while at higher energies and for low-abundance isotopes EWW values up to 40 eV were used.

All comparative isotope measurements were performed with given ion-optic apertures, i.e., at a constant solid angle of exit for the analyzed sputtered ions.

All isotopes of each relevant element were recorded cyclically together as in-depth profiles; only those parts of the profiles that showed nearly constant intensities were used for calculations. Whenever an element with more than two isotopes was studied, it was checked that, within experimental accuracy, the same  $\alpha$  was obtained for all mass combinations. Spectral background on all relevant peaks was checked by means of high resolution spectra, and in most cases was found to be negligible.

The following matrices were investigated: elemental Cu, Ag, B, Ge, Sn, Mo, W; metal glass  $Fe_{73}B_{16}W_{11}$ .

The determination of  $\alpha$  was affected, in line with earlier work /10, 20, 15/, by comparing the isotope abundances  $R_i$ , as obtained via secondary ion currents in SIMS, with those listed as "true" isotope abundances  $(R_0)_i$  of elements in standard tables. In this work the critically evaluated isotope tables by de Bièvre and Barnes /3/ were used for all relevant elements.

From eq.(1) (where  $\alpha$  is defined similarly as in ref./10/, but assuming the mass difference  $M_j - M_i$  of two isotopes to be much less than their mean mass) it follows that

$$d \ln(R/R_0)_i / d \ln M_i = -\alpha \quad (2)$$

and so the fractionation factor is conveniently obtained as the gradient of the log-log diagram of  $R/R_0$  versus  $M_i$ . This is illustrated in fig.1 for the Sn isotopes emitted from tin metal /20/.

If the ionic yield of element L at isotopic mass  $M_i$ , measured at kinetic energy  $E_k$ , is  $Y_L$ , then

$$\alpha = -(d \ln Y_L / d \ln M_i)_{E_k} = \text{const} \cdot \quad (3)$$

Similarly one may express the measured ion yield gradient of the energy distribution curve for element L as

$$\beta = -(d \ln Y_L / d \ln E_k)_{M_i} = \text{const} \cdot \quad (4)$$

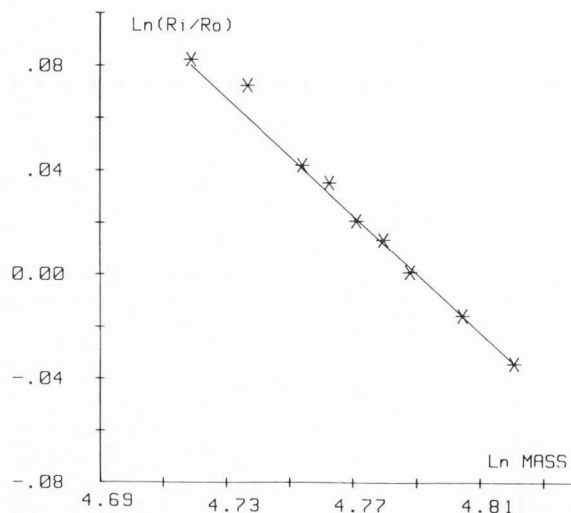


Fig.1. Isotope fractionation,  $Sn^+$  from tin metal. Energy range: 90-110 eV. Slope of line yields the parameter  $\alpha$ .

Results

In Table 1, the most recent results on  $\alpha$  in element matrices are listed together with those of earlier studies. Where comparison can be made, it is seen that the present work on the whole confirms previous data, although in the earlier references the conditions of chemical enhancement by oxygen were not as a rule specifically stated. It is seen in Table 1 that the oxidation effect is of significance for  $\alpha$  in most cases. Generally there is a lowering of  $\alpha$  at low or intermediate energies if oxygen saturation is not reached. At higher  $E_k$  the role of oxygen appears to decrease. Fig.2 represents the  $\alpha$  values as functions of  $E_k$  in the present study on element surfaces with an oxygen backfill of  $2 \times 10^{-5}$  torr.

At low  $E_k$  the different matrices are seen to exhibit considerable variation in the behavior of  $\alpha$ . At higher energies the plot of  $\alpha$  versus  $E_k$  appears to settle in a moderate gradient, usually positive (except W and Mo).

The  $\alpha$  values of W, mean mass 184, lie on an average ca 6 times higher than those of B, mean mass 11.5. The other systems, too, seem to suggest a mainly positive correlation between  $\alpha$  and the element mass, despite considerable fluctuations.

Fig.3 shows the variation of  $\alpha$  with  $E_k$  for ions of B, Fe and W, as emitted from a metal glass matrix, sputtered with oxygen leak (whole-drawn) and without  $O_2$  (dotted). The qualitative tendencies are seen to be similar as in fig.2, in regard to the oxygen effect as well as the dependence on element mass. Although matrix effects obviously do affect the quantitative behavior of all the elements, the main comparative trends between the elements remain the same.

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Table 1. Measured values of the isotope fractionation parameter  $\alpha$  for ions sputtered from pure elemental matrices. Positive singly charged ions at different kinetic energies  $E_k$ .

Element	$\alpha_{E_k=0}$	$\alpha_{E_k=15}$	$\alpha_{E_k=30}$	$\alpha_{E_k=60}$	$\alpha_{E_k=120 \text{ eV}}$	Reference
Cu (with oxygen leak)	0.6	1.05	1.0	0.9	1.05	This work
Cu (no O <sub>2</sub> )	0.95	1.0	0.8	0.75	0.85	" "
Cu	0.7	0.9	0.95	1.0		16
Cu		0.9				10
Ag (with oxygen leak)	1.6	1.6	1.7	1.75	2.0	This work
Ag (no O <sub>2</sub> )	1.85	1.7	1.7	1.8	2.05	" "
Ag			1.2			16
Mg		0.3	0.05	0.1		16
B (with oxygen leak)	0.2	0.05	0.2	0.35	0.65	This work
B (no O <sub>2</sub> )	0.55	0.1	0.15	0.4	0.7	" "
B	0.65	0.15	0.2	0.5		16
Si	1.05	0.75	0.75	0.5	0.75	16
Si		0.75				10
Ge (with oxygen leak)	1.0	0.8	0.9	1.1	1.4	This work
Ge (no O <sub>2</sub> )	0.6	0.8	0.9	1.1	1.25	" "
Ge	0.6	0.65	0.85	0.95		16
Ge		0.5	0.6	1.0		15
Sn (with oxygen leak)	0.55	0.75	0.85	0.95	1.05	This work
Sn		0.5	0.5	0.75		15
Pb	0.55	0.6	0.95	1.0		16
Sb	1.2	1.15	1.1	0.95		16
Cr	0.75	0.35	0.1	0.2		16
Mo (with oxygen leak)	1.05	1.4	1.35	0.75	0.4	This work
Mo	0.25	0.5	0.9	0.75		16
Mo		0.45	1.0	0.8	0.7	15
W (with oxygen leak)	2.35	2.4	2.6	2.7	2.0	This work
W (no O <sub>2</sub> )	2.15	2.2	2.35	2.45	2.1	" "
Ni	0.85	0.9	0.7	0.95		16
Ni (with oxygen leak)		0.9				10
Ni (no O <sub>2</sub> )		0.6				10
Pd		1.1	1.3	1.6		15

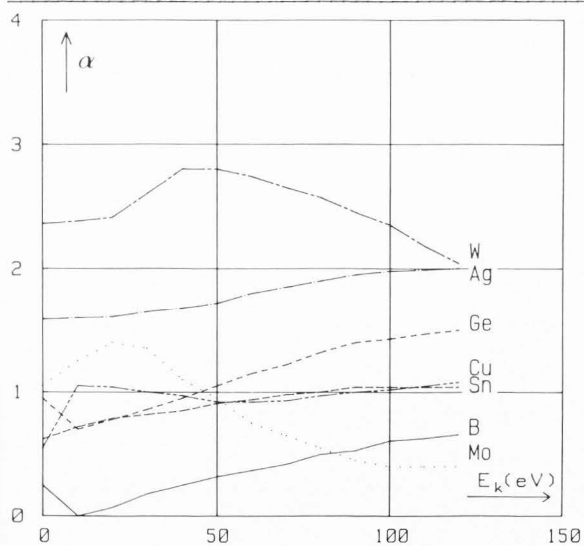


Fig.2. Isotope fractionation versus kinetic energy. Element matrices. O<sub>2</sub>-leak used during sputtering.

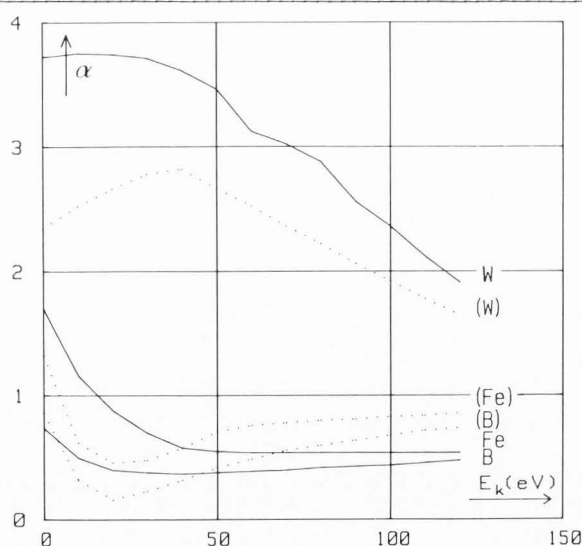


Fig.3. Isotope fractionation versus kinetic energy. Element ions sputtered from Fe<sub>73</sub>B<sub>16</sub>W<sub>11</sub> metal glass.

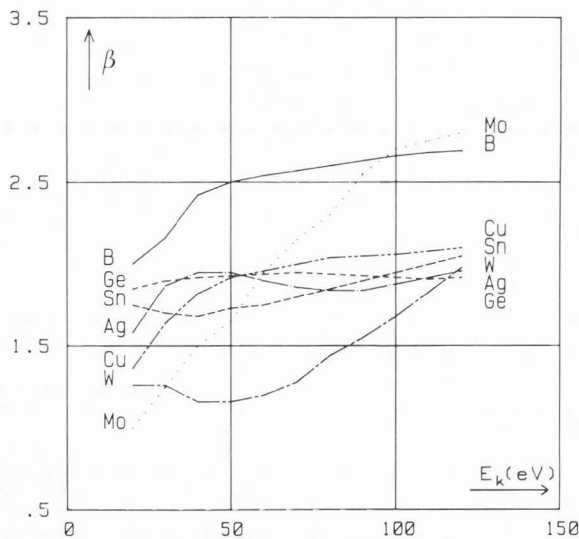


Fig. 4. Gradient  $\beta$  of energy distribution, versus kinetic energy. Element Matrices.  $O_2$ -leak used during sputtering.

In figs. 4 and 5, the energy distribution gradient parameters, defined by eq.(4), are plotted for the corresponding ions and matrices. The systematics of  $\beta$  appear, to some extent, opposite to those of  $\alpha$ ; e.g., the gradient factor first shows a fast increase at low  $E_k$ , then rises slower or possibly decreases. Also, the elements of high mass yield relatively low values of  $\beta$ .

Discussion

The considerations of the present paper are restricted to singly charged positive secondary ions in the positive range of kinetic energy  $E_k$ . The different terms entering the total ion yield of sputtering have been studied by numerous workers /4-6, 11, 13, 17, 25/. If one employs the formalism of Garrett et al. /4/, who investigated the dependence of elemental ion yield,  $Y_L$ , on kinetic energy  $E_k$  and exit angle  $\theta$ , then

$$Y_L \propto N_L(E_k, \theta, M_i) \cdot R_L^+(E_k, \theta, M_i) \cdot P_L^+(E_k, \theta, M_i) \quad (5)$$

where  $N_L$  denotes the total sputter yield of element L,  $R_L^+$  its probability of ionization in the sputtering cascade, and  $P_L^+$  the probability that the ion will survive and be detected far from the surface.

The angular dependence, although reported as relatively slight under the present conditions of SIMS analysis (performed with fairly high primary ion energies), is probably a non-negligible factor both in ion emission and in its isotope effect. In the geometry of the present work the exit angle is to be considered as constant and near-zero. The pilot discussion can therefore be limited to variations with  $E_k$  and with  $M_i$ .

According to established model /22, 17/, the sputter yield may be satisfactorily expressed as

$$N(E_k) \propto E_k / (E_k + E_B)^{-3} \quad (6a)$$

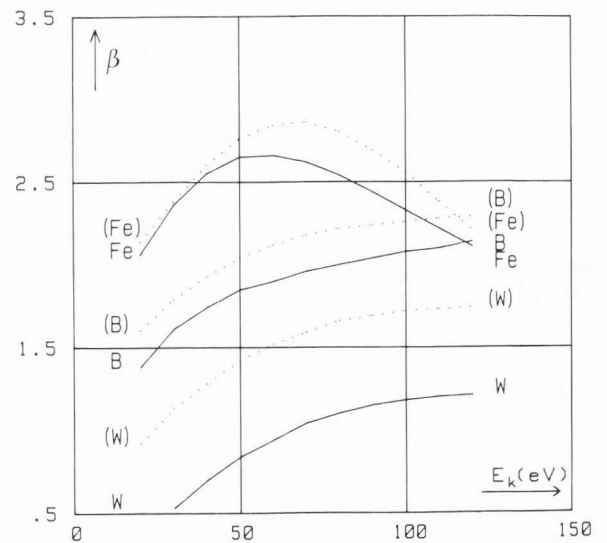


Fig. 5. Gradient  $\beta$  of energy distribution, versus kinetic energy. Ions sputtered from a metal glass,  $Fe_{73}B_{16}W_{11}$ . Whole drawn: with  $O_2$ -leak. Dots: no  $O_2$ .

where  $E_B$  is the surface binding energy, of the order of 1 to 5 eV. Attempts have been made (e.g., ref./23/) to deduce the mass effect from detailed considerations of energy partitioning in a sputter cascade. At this stage, however, simple kinetic arguments may be adequate for a first phenomenological model. When the atom of mass  $M_i$  is ejected as the last step of a cascade, the process might be considered as momentum transfer from an effective mass  $M_N$  (proportional to the mean atom mass of matrix), and consequently

$$N(E_k, M_i) \propto (E_k M_N / M_i) (E_k M_N / M_i - E_B)^{-3} \quad (6b)$$

Logarithmic differentiation yields, via eqs. (3) and (4), the following contributions to  $\alpha$  and  $\beta$ :

$$\alpha_N = -\beta_N = 1 - 3E_k / (E_k + E_B M_i / M_N) \quad (7)$$

This term drops from +1 at  $E_k=0$  to ca -2 at high kinetic energies. The drop is particularly fast if the value of  $E_B M_i / M_N$  is small.

The mechanisms of ionization and of charge survival are still largely a matter of speculation. Usually the ingoing terms are treated either as proportional to a power of  $E_k$ , or as exponential functions of inverse exit velocity of the ion. In the first form,

$$R^+ P^+ \propto E_k^n \quad (8a)$$

The exponent  $n$  as derived in literature ranges within a factor of ca 3 about unity.

The alternative form is

$$R^+ P^+ = A' \cdot \exp(-v_0/v) \quad (8b)$$

where  $A'$  is a constant of the order of unity;  $v = (2E_k/M_i)^{1/2}$  is the normal component of the exit velocity; and the matrix term  $v_0$  is usually assumed to contain the difference between the first ionization potential  $E_i$  and the work function  $\phi$ .

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Experimentally it has been found /24/ that at moderate  $E_k$  the ion yields can be fairly well represented by straight lines when plotting  $\ln(R^+P^+)$  either versus  $\ln E_k$  (yielding  $n$  in the order of unity), or versus the inverse of  $v$  (with  $v_0$  in the order of  $5 \times 10^5$  cm/s). However, the predictions of (8a) or (8b) are too high by 2 or 3 powers of ten; further, both expressions formally fail at energies below some 15 eV.

For the problem of isotope yields, it can easily be shown that both expressions are incompatible with the present results: eq.(8a) would predict constant fractionation,  $\alpha = +n$ , for all systems, and from (8b) would follow  $\alpha = \frac{1}{2}v_0/v$ , decreasing monotonically over the whole range of  $E_k$  for positive  $v_0$ , or negative if  $v < 0$ .

The study of both angular dependence and energy dependence of ionic yields /4/ has suggested that both forms of eqs.(8) might meaningfully be combined in the total expression, such that

$$R^+ \propto (E_k + E_B)^n \quad (9)$$

and

$$P^+ \propto \exp(-v_0/v) \quad (10)$$

where, however,  $v_0$  should depend on energy according to

$$v_0 = A + A^* \cdot E_k^\delta \quad (11)$$

with the orders of magnitude of  $5 \times 10^5$  cm/s for  $A$ ,  $10^{17}$  (erg) $^{-1}$  for  $A^*$ , and unity for  $\delta$ .

The empirical expression (11) does not take into account the influence of isotope mass, and for the present first treatment it may be tentatively replaced by the form

$$v_0 = A + CE_k^\delta M_i^\gamma \quad (12)$$

where the arbitrary parameter  $\gamma$  should be obtainable from the results of isotope experiments.

If  $\alpha$  and  $\beta$  are to be expressed on the basis of this more elaborate formalism, logarithmic differentiation of (9) and (10, 12) yields

$$\alpha_R = -\beta_R = nE_k(E_B M_i / M_n + E_k)^{-1} \quad (13)$$

and

$$\alpha_P = \frac{1}{2}A(M_i/2E_k)^{\frac{1}{2}} + 2^{-\frac{1}{2}}C(\gamma + \frac{1}{2}) \cdot M^{\gamma + \frac{1}{2}} E_k^{\delta - \frac{1}{2}} \quad (14a)$$

$$\beta_P = -\frac{1}{2}A(M_i/2E_k)^{\frac{1}{2}} + 2^{-\frac{1}{2}}C(\delta - \frac{1}{2}) \cdot M^{\gamma + \frac{1}{2}} E_k^{\delta - \frac{1}{2}} \quad (14b)$$

It is of interest now to compare the model expressions for total  $\alpha$  and  $\beta$ , as obtained by adding together the terms with index  $N$ ,  $R$  and  $P$ , i.e. eqs. (7), (13) and (14), with the experimental results of the present pilot study. Relevant for a first comparison is the sum of the two parameters,

$$\alpha + \beta = 2^{\frac{1}{2}}C(\gamma + \delta) M_i^{\gamma + \frac{1}{2}} E_k^{\delta - \frac{1}{2}} \quad (15)$$

as the expression only contains the second term in eq.(14), and so may be suited for a determination of the arbitrary parameters  $\gamma$ ,  $\delta$ , and  $C$ .

Table 2 lists the parameter ( $\alpha + \beta$ ) at two values of  $E_k$  for the systems studied with respect both to isotope fractionation and energy dependence, as shown in figs. 2-5. A comparison of  $\alpha + \beta$  for the 3 elements sputtered from the metal glass (asterisks in Table 2) may furnish reasonable orientation on the mass exponent  $\gamma$  ( $W$ ,  $Fe$  and  $B$  having about the same ionization potential). The comparison of the two columns in Table 2 ( $\alpha + \beta$  being, on an average, by a factor 1.15 higher at 80 eV than at 20 eV) should yield the mean energy exponent  $\delta$ . With the

Table 2. Experimental values of ( $\alpha + \beta$ ) at two kinetic energies, for ions sputtered from element matrices and (marked with \*) from a metal glass.

Element	$\alpha + \beta$	$\alpha + \beta$	Ratio
	20 eV	80 eV	
Cu	2.4	3.05	1.25
Ag	3.15	3.7	1.15
B	2.05	3.1	1.5
Ge	2.55	3.15	1.25
Sn	2.45	2.9	1.2
Mo	2.1	3.05	1.45
W	3.6	3.95	1.1
B*	1.8	2.45	1.35
Fe*	2.8	3.2	1.15
W*	3.5	3.7	1.05

knowledge of the exponents, an average value of  $C$  is readily obtained. The results, from Table 2, are:  $\gamma = -0.30 \pm 0.08$ ;  $\delta = +0.6 \pm 0.2$ ;  $C = 4.5 \pm 1.5$ .

In fig.6 are plotted the values of the parameter  $\alpha = \alpha_N + \alpha_R + \alpha_P$  for  $W$ ,  $Fe$  and  $B$  from the metal glass matrix, as calculated from eq.(7) with  $E_B = 5$  eV, eq.(13) with  $n = 0.5$ , and eq.(14a) with  $A = 5 \times 10^5$  cm/s and with the above values of  $\gamma$ ,  $\delta$ , and  $C$ . The plots of calculated  $\alpha$  vs  $E_k$  are seen to be in qualitative or semi-quantitative agreement with the whole-drawn experimental curves of fig.3. It is evident that for ions from a given matrix, particularly at low or moderate  $E_k$ ,  $\alpha$  is dependent on element mass. Experimentally a similar mass dependence is seen also from the results on pure elements (fig.2); however, the comparison between elemental matrices is likely to be more complex due to differences e.g. in work functions, ionization potentials and binding energies /1, 7-8, 14/.

The model leading to the curves in fig.6 also predicts that  $\alpha$  should first drop steeply at low energies, then go through a minimum, and then exhibit a slow rise with increasing  $E_k$ . For elements similar in  $E_i$  and emitted from given matrix, the

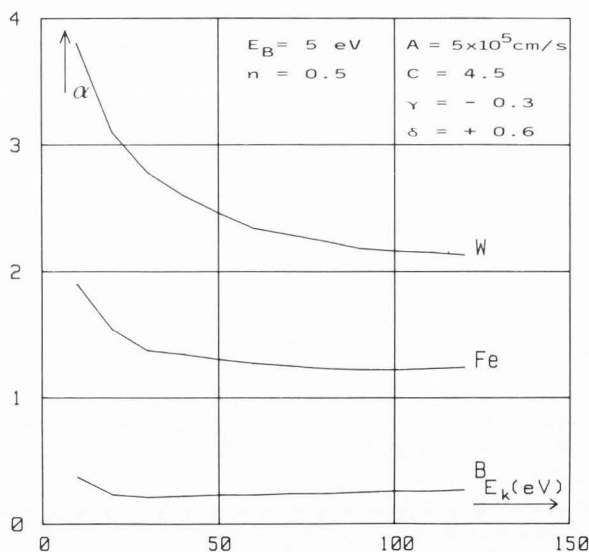


Fig.6. Isotope fractionation as calculated via an ionization model; ions sputtered from  $Fe_{73}B_{16}W_{11}$  metal glass.



position of the minimum should depend on the mass; for the heaviest elements in fig.6, tungsten, the minimum is not yet reached at 120 eV. The negative gradient for Mo in fig.2 could be due to a similar circumstance. That in fig.2 several elements show only a rise of  $\alpha$  with  $E_k$  might indicate particular dominance of the second term in eq.(14a) over the first term, which is likely to depend on  $E_i$  and  $\phi$ .

The plateau in  $\alpha$  observed at low energies for W in figs. 2 and 3 is not expected on the basis of the model. It seems probable that the experimental curve shape is to some extent connected with the fact that the SIMS yield of  $WO^+$  and  $WO_2^+$  ions, particularly at low  $E_k$ , is higher than that of  $W^+$ .

In conclusion, it appears likely that the behavior of  $\alpha$  may be understood in terms of a relatively simple model, such as that expressed in eqs. (5), (6b), (9), (10) and (12). Although such a model of ionization necessarily contains adjustable parameters, these parameters can in principle be evaluated by the study of ion yields as functions of kinetic energy, exit angle and isotope mass.

The behavior of the isotope fractionation parameter  $\alpha$  is seen to be in several aspects related to that of the gradient parameter calculated from the energy distribution plot. However, the relation  $\beta = -\alpha$  does not apply to a term in the charge survival mechanism; this term in  $P^+$ , similar to one discovered in recent studies of the angular dependence of ion yields /4/, appears to steer the behavior of  $\alpha$  especially at high kinetic energies.

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Discussion with Reviewers

R.Gijbels: Is it your opinion that, under the operating conditions of SIMS, the specific ion yield is not significantly dependent on the angle of ejection? This would mean that no isotope fractionation would be caused by reflective collisions and screening surface layers with enriched heavy isotope. Now if we scan through the literature, we encounter the following observations:

1) G.K.Wehner; Appl.Phys.Lett. 30, 185-187 (1977): "... in low energy sputtering ( $E_p = 100$  eV) the low mass species should have a lower probability of being ejected normal to the target surface than the heavier atoms in the matrix."

2) R.R.Olson, M.E.King, G.K.Wehner; J.Appl. Phys. 50, 3677-3683 (1983): same reasoning, working with ion energies (Hg or Ar) at  $< 300$  eV.

3) J.C.Lorin, A.Havette, G.Slodzian; ref./10/ above: "... no clue regarding a possible dependence of the isotope effect on the secondary ion ejection angle" ( $E_p = 5.5$  keV;  $O_2^+$  or  $Ar^+$ ).

4) W.A.Russel, D.A.Papanastassiou, T.A.Tombrello; Rad.Effects 52, 41-52 (1980): "... the difference in the isotope ratio  $^{40}Ca/^{44}Ca$  over the angular range was ca 1.5%. This fractionation with angle of ejection persisted even when a quasi-steady state was reached after heavy bombardment, when the isotope composition of the material averaged over angle had become essentially indistinguishable from that of the pristine target." Conditions: normally incident low energy nitrogen beams, 130 keV  $N^+$  and 100 keV  $N_2^+$ .

What is your opinion on the statement of Russel et al.? If there is a real angular dependence even at high primary ion energy, how seriously will this influence your deductions?

Authors: We have no reason to doubt the results quoted by Russel and his coworkers. In fact we think that there may be a non-negligible angular dependence of  $\alpha$  even under normal SIMS conditions. In our experience we have seen changes in the recorded  $\alpha$  values when the exit selection apertures of the secondary ions were varied. In all measurements in the present paper, we kept our exit geometry constant. We are planning quantitative studies of the angular dependence. Meanwhile it seems not unlikely that some small positive contribution to  $\alpha$  should be included as a complement to the model arguments.

A.Havette: According to its definition  $\alpha$  is the relative deviation from the standard ratio, normalized to the relative mass difference between the isotopes. In your work, what is the physical significance of  $\beta$  ?

Authors: As expressed by eq.(4),  $\beta$  is, at constant isotope mass, the gradient of the secondary ion energy distribution, plotted as the logarithm of the ion yield versus the logarithm of the kinetic energy.

Reviewer III: How can one compare eqs. (7), (13) and (14) with experimental data without really knowing parameters such as  $n$ ,  $A$ ,  $C$ ,  $\gamma$  and  $\delta$  ? How can one evaluate the relative significance of the individual terms involved in  $\alpha$  ?

Authors: As for the  $\alpha_N + \alpha_R$  term, as discussed in text it should drop from unity at  $E_k=0$  to values of the order of -1 at high  $E_k$ . The decrease is steep at low  $E_k$ , especially for elements with low binding energies. Order-of-magnitude values of  $C$ ,  $\gamma$  and  $\delta$  can, as shown, be deduced from  $\alpha+\beta$ ; to some extent  $n$ ,  $C$  and  $\delta$  can also be compared with results of other kinds of investigations /4/. The parameter  $A$  is comparable to directly determined counterparts (ref./24/ above). Accordingly, the  $A$  containing term may dominate at low  $E_k$ , the  $C$  containing term at higher energies. The transition between the two regions is suggested by the present results, and has a direct bearing on the relative significance of the different terms in  $\alpha$ .

R.Gijbels: a) Was a deadtime correction necessary in your experiments? b) Is there any influence on the quantum efficiency of the detection system if different isotopes are collected? c) How did you deal with hydride interferences if any?

Authors: a) Deadtime correction was essential. We have a computer program based on the frequently checked deadtime (ca 15-40 ns) of our collector system. b) Isotope mass fractionation in the electron multiplier is indeed thought to be a part of the overall instrumental fractionation. The corresponding systematic positive contribution to  $\alpha$  should be of the order of 0.05 to 0.2 (see E.Zinner, A.J.Fahey, K.D.McKeegan; in: SIMS V, A.Benninghoven et al., /Eds./, Springer Ser.Chem.Phys. 44, 1986, pp 170-172). In most cases, however, one may assume that the same collector fractionation is also affecting the standard isotope ratio  $R_0$  used for comparison (our ref./3/) and thus does not influence the SIMS-specific  $\alpha$  value determined in the present paper. c) Hydride corrections were regularly performed by means of "isotope stripping".



