

2-12-1988

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Recommended Citation

Metson, J. B.; Tui, D. L.; Muir, I. J.; and Bancroft, G. M. (1988) "High Energy Secondaries for the Quantitative Secondary Ion Mass Spectrometric Analysis of Minerals," *Scanning Microscopy*. Vol. 2 : No. 2 , Article 5.

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HIGH ENERGY SECONDARIES FOR THE QUANTITATIVE SECONDARY ION MASS SPECTROMETRIC ANALYSIS OF MINERALS

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(Received for publication March 16, 1987, and in revised form February 12, 1988)

Abstract

The major hurdle in quantitative analysis by SIMS is the inconsistency and non-predictability of ion yields, particularly their sensitivity to sample matrix. High energy (100-500 eV) secondary ions have been shown to be considerably less susceptible to matrix effects than low energy secondary ions, particularly in mineral analysis. Therefore ion yields of some sixty elements were measured utilizing very high energy secondaries (~ 500 eV), from a standard silicate glass. They show a broad ionization potential dependence and a mass (or velocity) dependency, which is not removed by the application of a $M^{\frac{1}{2}}$ or M factor. The modification of yields with conventional thermodynamic partition functions, improves but does not clearly define agreement with the inverse exponential relationship observed by others, for low energy secondaries sputtered from oxygen rich matrices. The reproducibility of ion yields of high energy secondaries suggests empirical approaches to quantitative analysis are well justified; however the poor agreement of ion yields with an inverse exponential relationship, suggests that ion yielding mechanisms are somewhat different to those proposed in the low energy regime.

Introduction

Although Secondary Ion Mass Spectrometry (SIMS) has been applied successfully to many analytical problems, they have almost exclusively been applications where comparative intensities of ion signals have provided the required information. In depth profiles, identification of contaminants etc., it is sufficient to know only that secondary ion intensities are proportional to the level of the element in the sputtered matrix and that for a given matrix, ion yields do not change dramatically as a function of sputtering time. However to truly exploit the sensitivity of SIMS - particularly in mineral analysis - the quantitative analysis of unknown samples is the critical hurdle and it is yet to be satisfactorily overcome. The difficulty is the absence of a coherent theory of secondary ionization with the ability to predict the ion yield of a given element, from the sample and instrumental information available to the analyst. It must also be acknowledged that the limited applications of SIMS in geochemical analysis has resulted from the marked reluctance of geochemists to adapt in the absence of such a theory, even in applications where reproducibility and accuracy are acceptable - for example in the analysis of rare-earth elements in minerals [Zinner and Crozaz (1986), MacRae and Metson (1985)]. Electron probe microanalysis, it must be remembered, despite the relatively sophisticated understanding of the factors controlling X-ray yields has been and still often is, refined on the basis of exhaustive comparison with known standards of similar matrix.

Secondary ions are however a rather more complex breed. In a conventional SIMS experiment, secondary ions are emitted from a surface under bombardment by a focused beam of primary ions. The secondaries emitted display an energy distribution with its peak at very low energies (2-10 eV), relative to the very substantial energies of the bombarding species (1-20 kV) and a tail extending many hundreds of eV's above this peak. This extended tail shows a dependence on energy which is difficult to define, largely because it is a combination of two sample dependent factors (total sputtered yield and ionization probability) and several instrument dependent factors (e.g. transmission of the mass spectrometer).

KEY WORDS: Secondary Ion Mass Spectrometry, Ion Yields, High Energy Secondaries.

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The importance of this high energy tail is however quite considerable. The elemental ion/molecular ion discrimination advantages of analyzing higher energy secondaries have been thoroughly demonstrated, particularly in mineral analysis [Ray and Hart (1982), Zinner and Crozaz (1986), Nesbitt et al. (1986)]. The question remains however, does the analysis of high energy secondaries offer other advantages in addition to eliminating molecular ions? Of most interest is whether such a strategy contributes any useful simplification of the elusive model for the prediction of ion yields.

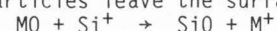
Most investigations of ion yields have centred on low energy secondaries simply because to exploit the sensitivity of SIMS, their abundance makes such ions the obvious analytical population. Perhaps of just as much significance, they are also the only population conveniently analyzable by quadrupole mass spectrometers.

Several reviewers have addressed the critical problem of identifying ion yielding mechanisms in the light of available experimental evidence [for example, Williams 1979, Wittmaack 1980]. However the conclusion remains that mechanisms are extraordinarily difficult to convert into quantitative predictions of relative ion yields. In particular the influence of matrix effects including, for example, chemical modification of the sputtered zone due to the accumulation of strongly electropositive or electronegative elements [Williams, 1979], is profound and as yet has been little studied. Thus it is important to establish whether yields of higher energy (> 100 eV) secondaries are less sensitive to the environment from which they are sputtered than are low energy secondaries (0-20 eV). Mineral analysis should present fewer problems in this respect than many other materials, simply because the matrix is in most cases already oxygen rich. Combined with use of an oxygen primary beam, this provides saturation levels of oxygen in the sputtered zone (evidenced by the stability of ion signals), and undoubtedly the optimum combination of sensitivity and stability available in conventional SIMS analysis.

Despite this, Steele et al. (1981) noted acute matrix problems in attempting the quantitative analysis of olivines and pyroxenes. However, their instrument was optimised solely to analyse peak intensities i.e. low energy secondaries were sampled, and under these conditions, maximum matrix sensitivity would be expected.

On the other hand, there is considerable evidence that these effects are much less apparent in the higher energy secondary ion population. Ray and Hart (1982) were quite successful using energy offsets, in empirical calibration of ion yields using standards to analyse a number of glass and mineral specimens. It is worth noting that they conclude improved reproducibility was obtained by the use of more energy filtering (i.e. analyzing higher energy secondaries than was

necessary simply to eliminate molecular ions, which has been the usual reason for using energy filtering). Shimizu (1986a) describes the influence of Si levels on yields of Ca and Al from calcium aluminosilicate glasses (a similar effect to that observed by Steele et al. 1981) but also notes this influence is negligible when 80 ± 10 eV secondaries are analysed. Shimizu (1986b) proposes a binary collision mechanism involving both charge and oxygen transfer and occurring as sputtered particles leave the surface i.e.,



Shimizu then observes that the abundance of M^+ will be determined by the relative strengths of the MO and SiO bonds and the abundance of Si in the target. However this mechanism also affects the shape of the observed energy distribution of M^+ , which if silicon levels are high, will resemble the shape of the MO distribution rather than that normally expected from M^+ . When analyzing 80 ± 10 eV secondaries, linear relationships between observed ion intensity and atomic abundance in the sample are observed. Thus the more rapidly ejected secondaries are not as susceptible to such binary collisions above the surface. The Specimen Isolation (SI) method, which gives access to considerably higher energy secondaries (500 ± 100 eV), has proved extremely useful in trace analysis of minerals [for example Nesbitt et al. 1986], because again linear relationships between observed intensity and abundance are in general, observed.

The tempting conclusion is that yields of higher energy secondaries, in the absence of such binary interactions at the surface, are progressively less susceptible to matrix influences. If then the intensity loss is not prohibitive as demonstrated for example by MacRae and Metson (1985) in sub ppm rare earth analysis, is there any advantage in using extreme energy filtering, as the SI method induces rather than the 80 ± 10 eV suggested from Shimizu's work, for the quantitative analysis of minerals? Or, more significantly for the development of SIMS in general, can ion yields be predicted under these conditions?

We have therefore set out to investigate: (1) whether ion yields at 500 eV differ significantly from those measured under low energy and conventional offset (< 100 eV) conditions; (2) whether relatively simple models can be fitted to experimental ion yield data from this energy region, and (3) if any unique information on the nature of secondary ion emission is available from yields under specimen isolated conditions. This paper addresses the latter two points. The first question is answered in the paper of Muir et al. (1987), who observed relatively small differences (up to a factor of 2) for most elements, in the yields from crystalline and glassed material of a $CaTiSiO_5$ composition. Muir et al. concluded that high energy (~500 eV) conditions offered significantly greater molecular ion suppression, without cost in sensitivity, but at the expense of spatial resolution, when compared to conventional energy filtering (100 eV). The similarity in yields from glasses and crystalline material of the same composition

High energy secondary ions for analysis

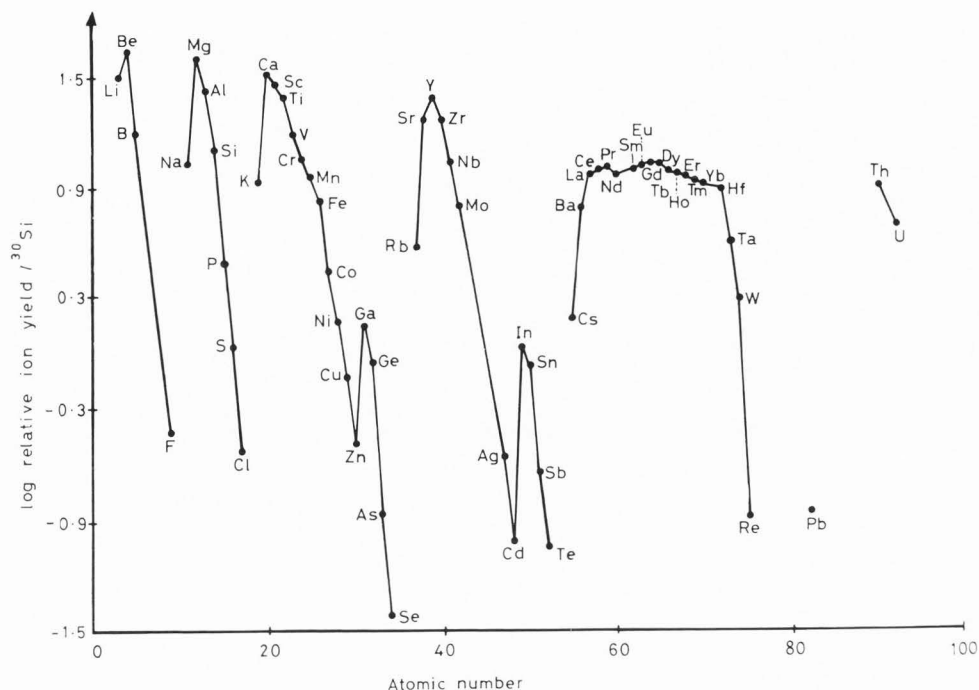


Figure 1. Relative ion yields measured from NBS 610 under Specimen Isolated (SI) conditions, using ³⁰Si as an internal reference.

suggested the absence of a structural matrix effect and thus the suitability of glasses as standards under these conditions.

Experimental

Much reference will be made to the energy of ejected secondary ions. Thus it is necessary to define exactly the energy regimes we are referring to. Low energy secondaries refer to those (the vast majority) leaving the surface with energies in the 0-20 eV range. Conventional energy filtering (as applied to the Cameca IMS 3f on which these results were obtained) refers to rather higher energies, up to ~ 100 eV. Energy window widths of ~ 20 eV were used. Specimen Isolated conditions select secondary ions of high energy (~ 500 eV) and a full width (± 65 eV) energy window is used for analysis, to compensate for the associated drop in intensity (Metson et al. 1985).

A primary beam of mass filtered ¹⁶⁰- was used in all experiments at a net accelerating voltage of approximately 16 kV. The ion yield results were obtained from an NBS standard silicate glass (SRM 610) containing ~ 500 ppm of a broad range of trace elements. Nominal concentrations were used for most elements, however for approximately 20 of the elements, measured concentrations were used - these rarely deviated from nominal values by more than ~ 15%. Thus there is some error associated with the nominal values but this should be insufficient to affect the conclusions drawn from the data. This is the same glass used by Morgan and Werner (1977) in a "Local Thermal Equilibrium" approach to

quantitative analysis and its complete composition is listed in that reference.

Reproducibility and sample homogeneity were checked by analyzing several points on the uncoated glass in each experimental run and repeating the measurements on at least two days for each element. No evidence of intrasample inhomogeneity was found. Elements were analyzed in groups of seven with ³⁰Si as an internal standard. NBS 610 contains ~ 33% Si and an additional correction for Si abundance in the sample was made. Relative yields were calculated from:

$$\frac{M^+}{Si^+} = \frac{I_{M^+}}{I_{Si^+}} \times \frac{Ab_{Si}}{Ab_M} \times \frac{100}{C_M} \quad (1)$$

where Ab_{Si} = natural abundance of the silicon isotope used as an internal standard

Ab_M = natural abundance of the isotope of element M used for analysis

C_M = The concentration of element M in NBS 610

standard deviations for M^+ were typically 3 → $\overline{Si^+}$

6% but ranged up to ~ 15% for several of the rare earths. The energy offset achieved under SI conditions was determined using the method described in Lau et al. (1985) and was always between 450 and 550 eV.

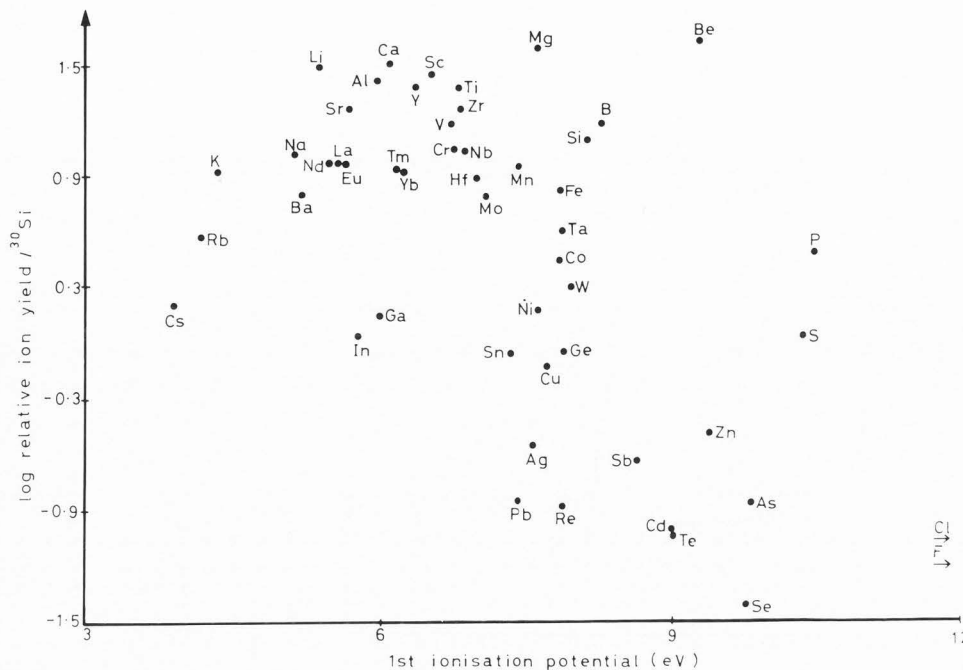


Figure 2. A semilog plot of relative ion yields from NBS 610 under SI conditions, versus first ionization potential.

Results and Discussion

Relative ion yields under SI conditions for some sixty elements are shown in Figure 1. We sought to fit these yields to the parameters which, in an ideal electronic excitation process, should correlate with ion yields. The only generally agreed conclusion with regard to positive ion yields under oxygen bombardment, is that they follow an inverse exponential dependence on ionization potential, of the form:

$$M^+ \propto \exp(-AE_{Ip}) \quad (2)$$

where A is a constant and E_{Ip} is the first ionization potential of M (Wittmaack 1980). A semilog plot should then result in a straight line for yields under common conditions. However such a plot (Figure 2) reveals poor agreement, particularly for those elements bordering the periodic table.

The relatively low yield of the alkali metals (as shown in Figure 1) is consistent with the energy distribution (both of ions and to a lesser extent sputtered yield) being strongly weighted to low energies by their susceptibility to direct ionic emission from the lattice as suggested in bond breaking models [Slodzian 1975]. The yield of the halogens is clearly enhanced by the effects of electron stimulated desorption [see for example Lodding et al., (1984)].

Despite the fall from grace of the thermal emission models such as the "Local

Thermal Equilibrium" model, the significance of the Boltzmann type relationship is acknowledged in contributing to the success achieved using this approach (Wittmaack 1980). However the inclusion of electronic partition functions [Morgan and Werner (1976), Lodding et al. (1984)] to improve agreement is more difficult to justify. Wittmaack (1980) suggested temperature and electron density (of the hypothetical plasma) should be more appropriately considered as "fitting parameters". Morgan and Werner (1977) obtained a temperature of 8840 K to 0-105 eV secondaries and a temperature of 13,730 K from the yields of 40-105 eV secondaries from NBS 610, which suggests T for 500 eV secondaries should be at least 20,000 K. This is far beyond the range for which the functions used were calculated (De Galan et al., 1968) and the parameter bears no apparent relation to the processes occurring at the surface. Neither low temperature (1500 K - Figure 3) nor high temperature (7,000 K) partition functions significantly improve the agreement with the Boltzmann relationship. We conclude there is little justification for including them, in "correcting" the yields of high energy secondaries.

Odelius et al. (1985) examined the correlation between "corrected ion yields" (using the LTE method) for some twenty elements sputtered from standard glasses. They similarly concluded that although the correlation was satisfactory at low energy, there was evidence of departure from Ionization Potential dependence when higher energy (mean 60v) secondaries were analyzed.

High energy secondary ions for analysis

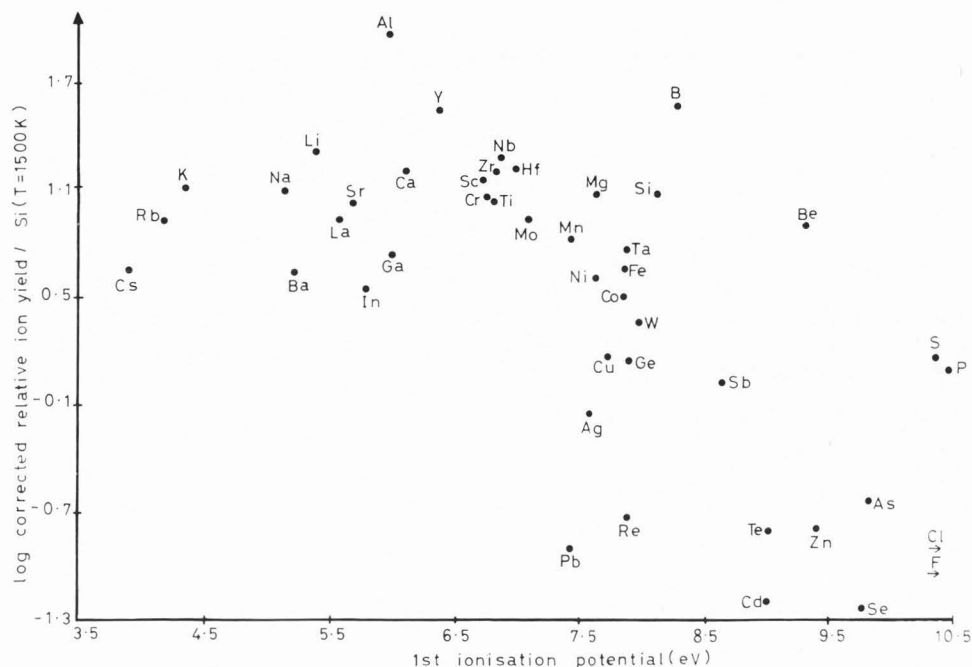


Figure 3. Relative Ion yields from NBS 610, corrected by using thermodynamic partition functions (de Galan et al. 1968) calculated for $T = 1500$ K, plotted against first ionization potential.

However figure 2 also suggests a systematic mass dependence of ion yields. Morgan and Werner (1977) applied an $M^{1/2}$ factor as an "instrumental factor" presumably to account for the transmission characteristics of the mass spectrometer. However Vasile (1983) investigated the velocity dependence of ion yields and found a v^{-1} dependence. Thus as we are analyzing ions of constant energy, the so called mass dependence can in fact be viewed as a velocity dependence of ionization. The application of an $M^{1/2}$ factor to our data does not however remove the observed mass dependence and even an M factor does not eliminate this dependence over the entire mass range.

Once again, such a correction has been used by others (Morgan and Werner 1977, Shimizu et al. 1974) on the grounds that it "always improved the closeness of the fit" (to a Boltzmann-type relationship). However there is evidence the mass correction is rather more complex than this. Odelius et al. (1985) suggest the possibility of a mass dependent mass correction $(\frac{M}{M_{Si}})^n$ based again on improved

agreement of their data with LTE and evidence accumulated by others from isotope fractionation measurements. We have attempted to fit our data to a similar relationship by allowing n to vary, however there is no apparent systematic variation in n simply as a function of mass. Specimen Isolation conditions although they severely distort the extraction field around the sputtered zone (Lau et al. 1985) do not alter the pass energy of the mass

spectrometer, thus apart from possible detector sensitivity (Rudat and Morrison, 1978) there seems little basis for an arbitrary mass correction. An ion velocity correction may be a more plausible physical interpretation.

As pointed out by Vasile (1983) the LTE model predicts relatively weak velocity dependence for secondary ion survival, while Vasile observed a linear relationship between $\log M^+$ and v^{-1} . However although linearity is consistently observed in the low energy region, the relationship breaks down with a distinct change in slope at $E \sim 30$ eV for all the metals examined.

This agrees with the qualitative observation that the most dramatic changes in the energy distribution are observed in the low energy region and that energy distributions are largely parallel for $E > 100$ eV [see for example Odelius et al. (1985)]. Muir et al. (1987) observed very similar relative ion yields at 100 eV and 500 eV in a comparison of conventional energy filtering and Specimen Isolation analysis of glass, mineral and ceramic specimens of the same composition, indicating near parallel intensity versus ion energy curves over this relatively large range. Consistency over this energy range does not however imply predictability as the current study indicates, so further attempts to model yields on the basis of ionization mechanisms were considered.

Blaise and Slodzian (1973) have proposed a bond breaking model which assumes that the ionic character of the metal-oxygen bond allows

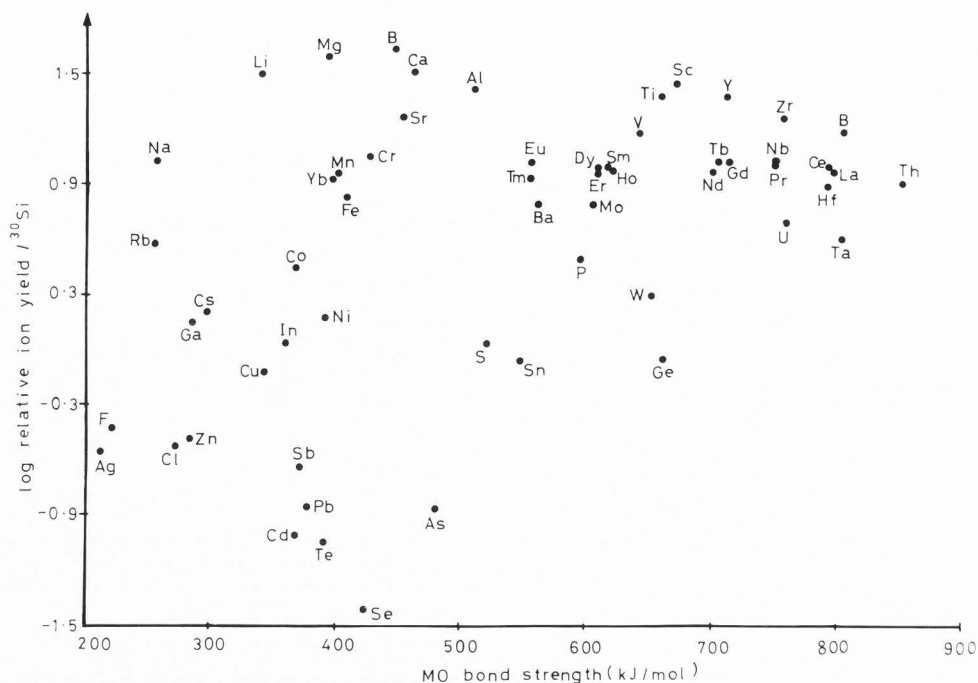


Figure 4. The relationship between oxide bond strengths and relative ion yields for the elements in NBS 610.

direct emission of ions. Thus the critical step in secondary ion emission (as it applies to oxygen saturated systems) is the breaking of a largely ionic metal-oxygen bond. This acts to effectively reduce the energy necessary for ionization of positive secondaries by an amount equal to the electron affinity of the oxygen atom. Although the model is qualitatively consistent with peak secondary ion intensities being observed at energies of several eV's, it is not as clear-cut in application to yields of higher energy secondaries. As Williams (1979) points out, if ion emission occurs through dissociation of pre-existing ion-pairs at the surface, high energy ionizing collisions are unnecessary. This provides (at least) a qualitative explanation of the anomalously low yields of the alkali metals observed in figure 1.

The bond-breaking model adequately accounts for the enhancing effect of oxygen on low energy secondary ion yields, but does not fundamentally alter the exponential dependence of yields on ionization potential. Thus the relationship sought in figure 2 should still be apparent. Shimizu's more subtle application of the binary collision [Shimizu 1986b] in explaining the shape and intensity of the low energy peak in the secondary ion energy distribution of ions sputtered from silicate glasses, again does not extend to higher energies. Because of the limited residence time of such ions at the surface and the presumably relatively narrow energy distribution of molecules leaving the surface, such binary collisions are limited to relatively low energies. The dominant collision considered by

Shimizu (1986b) for silicate glasses is :



The critical factor influencing M^+ is the relative stability of each side of the equation. We would thus expect in a silicon dominated matrix, a correlation between M^+ and oxide bond strength in the low energy spectrum, whereas from our data, there appears to be little relationship between oxide bond strengths and yields in the higher energy spectrum (figure 4). Thus we are left with no plausible mechanism to suggest any structural or chemical matrix effect should be observed for high energy secondary ions. Yet such secondary ions clearly do not conform to a simple exponential dependence on ionization potential.

Discussion thus far has been limited to the "ionization yield" from the total sputtered population. We have ignored the possibility of matrix modification of the energy distribution of the total sputtered yield. One potential stumbling block in prediction of high energy ion yields can be seen in the following argument. For a pure sample of element S

$$S^+(E) = N^+(E)/N_0(E) \quad (4)$$

where $S^+(E)$ = ion yield of element S at Energy E

$N^+(E)$ = rate of ion ejection at Energy E of element S

$N_0(E)$ = total no. of sputtered particles containing S ejected with Energy E.

$N^+(E)$ = is measured with the mass spectrometer but $N_0(E)$ is extremely difficult to determine. In general some model must be used to determine total sputtered yields and the model must define the energy dependence of the total yield. This is clearly predictable in the low energy region, for sputtering from pure metal substrates (Vasile 1983). However, this is the region of severe matrix sensitivity in ion yields from more complex targets, and it is not clear that the energy distributions of total sputtered yields $N_0(E)$ are not matrix dependent as well. Because of the much larger population of sputtered particles in the low energy spectrum, any perturbation in this yield will have profound effects on ion yields in the high energy secondary ion spectrum. To put it simply, the high energy ion yield cannot be divorced from the influence of the low energy ion and total sputtered yields. If the latter are matrix sensitive it seems there is little prospect of quantitative prediction of the former.

Conclusion

The use of high energy (~ 500 eV) secondaries for mineral analysis has been demonstrated by a number of workers. It has also been observed that there is little difference in ion yields from glasses and crystalline materials in this energy region. Matrix effects on ion yields are generally agreed to be significantly reduced when analyzing higher energy secondaries. This has prompted the measurement of ion yields of a large number of elements under Specimen Isolated conditions i.e. ~ 500 eV secondaries, and attempts to fit these yields into models describing the ionization process.

An inverse exponential dependence on ionization potential is only loosely followed, with substantial deviations for the alkalis and a clear mass/velocity dependence apparent. The inclusion of an M^2 factor, as used by others or even M , improves the fit but does not eliminate this dependence. In this respect we must come to the same conclusion as Wittmaack (1980), that parameters such as mass dependence, represent "fitting factors" which can be used to constrain data to fit relationships which do not necessarily exist. Modifying yields through the use of thermodynamic partition functions also does not significantly improve the agreement with a simple inverse exponential dependence, irrespective of the temperature at which these functions are calculated. This simply confirms that ion emission is not a thermal process in this energy regime. Nor, it appears is there any contribution from the type of binary collisions invoked by Shimizu (1986b) in explaining matrix effects in the low energy spectrum.

What is clear is that ion yields in the high energy regime cannot be divorced from the factors which affect their yields in the low energy spectrum. To take the alkalis as an example, a strong bias towards emission of low

energy secondaries, consistent with a bond breaking model, correlates with their relatively low abundance in the high energy spectrum. This suggests that both ionization yield, and sputtering yield are biased towards low energies.

Such a "matrix effect" on the energy dependence of total sputtered yield would make it extremely difficult to successfully model ion yields in the high energy regime despite the near absence of matrix modification of ionization probability for these ions. The only way to test this is to examine the energy distributions of total sputtered yields over the rather large relevant energy range (0 → 500 eV). To do this with any accuracy is a rather daunting if not insurmountable experimental task.

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Discussion with Reviewers

ARE Lodding, In your text you criticize the use of an $M^{-\frac{1}{2}}$ proportionality for the yield of an ion of mass M, and point out that not even an M^{-1} relation appears adequate. Can you propose any other systematic mass dependence? Much work has been done in recent years on the isotope effects of SIMS ion emission /1,2,3/. The mass dependence is found to be significantly dependent on the element, the matrix, and the exit velocity. Such work has also been done on numerous isotopic elements in glasses /3/. At high offset energies the elemental mass effects seem to stabilize, often at n values, in M^{-n} , considerably above unity. It would be interesting to see if a correction by the experimental mass dependences would yield smoother curves than those in your fig 3.

Authors: We have found that the use of any fixed n value (in the M^{-n} factor) does not significantly improve the fit of our data to Ionization Potential dependence. The question of a mass dependent n then arises. If an exponential relationship is assumed and n allowed to vary to satisfy this relationship, there appears to be no systematic variation of n with M, although n was often consistent within individual groups. It is questionable whether we are in fact observing a mass effect or simply masking something else.

ARE Lodding: The bond-breaking model seems to be reasonably in agreement with experiments, at least qualitatively, for ionic exit energies between ca 5 and 30 eV. However, the dependence of the ion yield on v^{-1} seems to fail both at very low and at high energies /3,4,5/. From most evidence it appears likely that there are several ionization mechanisms competing. Is there, to your knowledge, any recent theoretical approach that would predict a mechanism particularly dominant at high ion exit energies?

Authors: No. The frustrating feature of studying high energy yields is the observation that most of the potential complications due to sputtering or closely post sputtering interactions appear to be eliminated by ~80 - 100 eV. Ion yields should then be determined by the probability of the excited sputtered particle choosing the decay pathway to the ion, a process the ionization potential might be expected to dominate. The relative stability of ion yields in this energy regime argues against competing ionization mechanisms, yet it still appears that some vestiges of chemical matrix effects remain, Nesbitt et al. (1986) and the observed yields do not seem to be amenable to any current theoretical interpretation.

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