

Compositional Averaging of Backscatter Intensities in Compounds

John J. Donovan,^{1*} Nicholas E. Pingitore Jr.,² and Andrew Westphal³

¹Department of Geological Sciences, The University of Oregon, Eugene, Oregon 97403-1272, USA

²Department of Geological Sciences, The University of Texas at El Paso, El Paso, Texas 79968-0555, USA

³Department of Physics, The University of California, Berkeley, California 94720, USA

Abstract: We present high-precision measurements of pure element stable isotope pairs that demonstrate mass has no influence on the backscattering of electrons at typical electron microprobe energies. The traditional prediction of average backscatter intensities in compounds was pragmatically based on elemental mass fractions. Our isotopic measurements establish that this approximation has no physical basis. We propose an alternative model to mass fraction averaging, based on the number of electrons or protons, termed “electron fraction,” which predicts backscatter yield better than mass fraction averaging. We also present an improved backscatter (electron loss) factor based on a modified electron fraction average for the ZAF atomic number correction that provides a significant analytical improvement, especially where large atomic number corrections are required.

Key words: averaging, \bar{z} , electron scattering, mean atomic number, average atomic number, mass averaging, mass effect, mass fraction, atomic fraction, electron fraction, multielement compounds, backscatter, elastic scattering, microanalysis, quantitative microanalysis, atomic number correction, ZAF

INTRODUCTION

Calculations of average backscatter (or electron loss) for compounds in electron probe microanalysis (EPMA) have traditionally utilized mass fraction averaging (Goldstein et al., 1981). For multielement samples, the calculations of average mass absorption coefficients and average stopping power are properly formulated using mass fractions in traditional expressions because the terms are grounded in mass units. The same cannot be said of the average backscattering loss factor, R , which is generally assumed to be mass dependent by Castaing (1960), Heinrich (1966), Duncumb and Reed

(1968), and Joy (1995) for interelement effects by the use of the expression

$$R_i = \sum_j c_j R_{ij}, \quad (1)$$

where c_j is the mass fraction and R_{ij} is the backscatter loss factor for element i in the presence of element j in a multielement sample. This correction, though usually smaller than other matrix corrections, for example, the absorption correction, in certain cases, as demonstrated below, is not always a small correction to the intensities.

Although there have been attempts in the literature to find alternative methods based on various formulations involving atomic fractions, these have consistently yielded

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*Corresponding author. E-mail: donovan@oregon.uoregon.edu

even worse results. Reports of difficulty (Myklebust and Newbury, 1991) with certain Si-Pb and other compounds where a large atomic number correction is necessary suggest a reexamination of mass fraction averaging.

Physics of Electron Backscatter

Electron backscatter is primarily the result of the electrostatic interaction of incident electrons with the Coulombic field of the atom (essentially the positive charge of the nucleus), which in turn is produced by the total charge of the protons (partially modified by the screening effect of the inner orbital electrons), which is related to the number of each, that is Z . The electromagnetic dipole component is unlikely to provide more than a negligible contribution to backscatter, especially in nonmagnetic materials, where this property is effectively randomized. Therefore some variety of Z -based averaging should, in principle, apply for calculations involving multielement compounds. That is to say, neutrons, which have no electric charge, only mass, should have no effect on productions of this type at typical electron probe microanalysis (EPMA) energies and precision levels. But mass fraction averaging is based on atomic weight, which is the total mass of the protons, electrons, and neutrons.

Furthermore, from a physical perspective, it is unlikely for incident electrons at energies typically attained in EPMA to measurably interact with the neutron of an atom. In fact, the wavelength of a 100-keV electron is some 10^4 times larger than the interaction volume of the neutron. Even more to the point, it is uncontroversially accepted that electromagnetic effects dominate over gravitational effects (the only known intrinsic property of mass besides nuclear spin) in this atomic regime by a factor of approximately 10^{40} .

Backscatter R loss differs from normal backscatter in that R loss involves only those backscattered electrons that still retain sufficient energy to cause an X-ray ionization, for a given X-ray line. For that reason, the process also contains an inelastic component and is not solely dependent on elastic scattering models. But regardless of the model used to explain R loss, we only claim that these atomic processes are affected only by the electron energy, E , and atomic number, Z , and not by atomic weight, A .

Scope of This Study

In an effort to detect any possible effect due solely to atomic weight, as opposed to atomic number, we performed high-

precision measurements of absorbed current in samples in which the *only* difference was mass, that is the number of neutrons. Specifically, we examined stable isotopes of the same element. For this experiment, we compared samples of normal Cu (mass 63.54), and enriched ^{65}Cu ; normal Ni (mass 58.71) and enriched ^{60}Ni ; and normal Mo (mass 95.94) and enriched ^{100}Mo .

If mass, represented by the presence of the neutron, affects the production of backscatter, then we would expect to see a measurable difference in the absorbed currents between these stable isotope pairs. Absorbed current is, of course, related to backscatter by the simple relation

$$\eta = 1 - \frac{i_{\text{absorbed}}}{i_{\text{beam}}}, \quad (2)$$

where i_{beam} is the measured beam current and i_{absorbed} is the measured absorbed or specimen current.

High precision measurements were also performed on a variety of pure elements and simple stoichiometric compounds to evaluate a number of expressions used to predict average backscatter yield using both interpolation from pure end members and atomic number averaging.

EXPERIMENTAL

Electron Microprobe Conditions

All measurements were made on a Cameca SX-51 electron microprobe at the University of California at Berkeley, Department of Earth and Planetary Science. The conditions for the absorbed and beam current measurements were 15 keV, 100 nA. A total of 15 measurements were averaged for each data point plotted and each measurement is itself the average of five A/D current conversions. Where error bars are not shown in the data figures, one standard deviation is smaller than the symbol size.

Backscatter Measurements

Care was taken to reduce or correct for both the additional contribution of absorbed current from reabsorbed secondary electrons produced by backscattered electrons striking the sample chamber walls and the loss of secondary electrons from the target area. This was accomplished by the use of a small bias of 22.5 V applied to a separately insulated

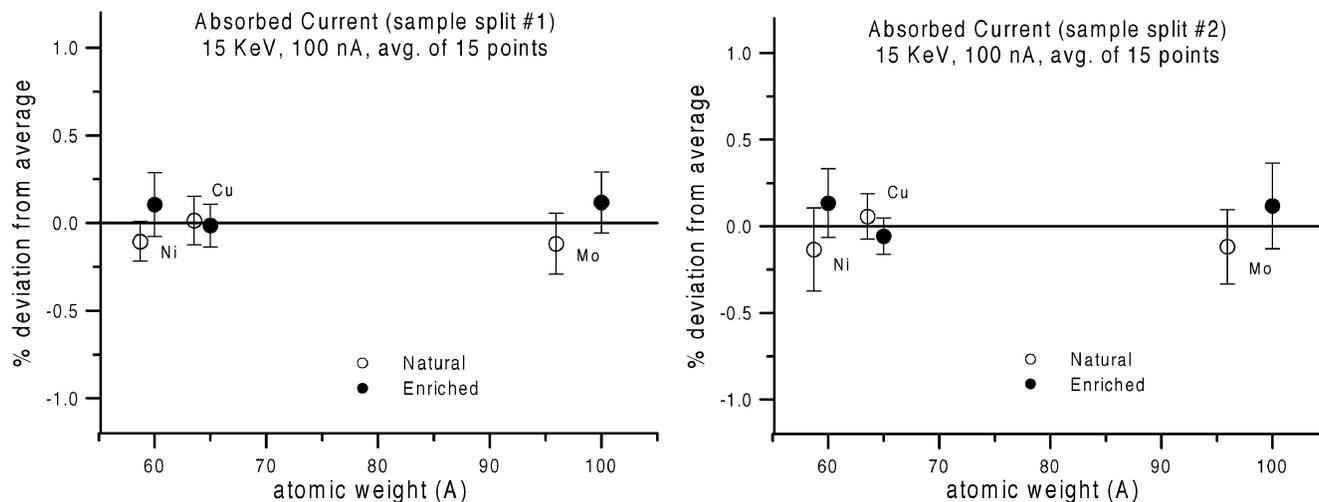


Figure 1. Absorbed current intensities (which acts as a proxy for backscatter yield) acquired on three stable isotope/natural abundance pairs. The fractional atomic weight numbers are averages for natural abundance isotopic mixtures, presented for comparison with masses for enriched isotopes. Each point represents an average of 15 measurements, shown relative to the average intensity measured for both natural and enriched isotopes; each error bar is one standard deviation. The complete analysis (sample split #1) was repeated for verification on a second probe mount of a separate set of isotope pairs, and this second set of results is presented as sample split #2. Note that all the measurements fall within 0.25% of the respective average of each isotope pair, and that even the one-standard-deviation error bars are within 0.5% of the average. This result indicates that any possible mass effect on the production of backscatter electrons is significantly less than the difference in mass between the isotope pairs.

area surrounding the sample (Heinrich, 1966) which Heinrich showed was sufficient to compensate for this effect.

From this and other experiments, it is clear that sample voltage biasing is necessary for accurate determination of absolute backscatter coefficients. However, to simply compare the relative merit of various average atomic number models, we found that the precision of the measurement is much more critical. Since the contribution of secondary electrons is very small for electrically insulated targets of minimal size ($<10 \text{ mm}^3$) and also fairly constant over large ranges of atomic number, we established that sample biasing was unnecessary in comparing stable isotope pairs where the atomic numbers (and hence the nuclear charges) are *exactly* the same.

In fact, we found that even when evaluating a mixed set of compounds and pure elements, all measured under the same conditions and sample configuration, the observed trends between the various models were consistently reproducible *whether the samples had a voltage bias applied or not*. In this article, results reported in absorbed current were generally not acquired using a voltage-biased sample mount, while those results reported in backscatter coefficient, (η), were acquired using a voltage-biased sample mount.

It should be noted that the R loss factor is related to backscatter by the loss of those backscattered electrons from the sample surface which contain sufficient energy to have caused an X-ray ionization had they remained in the sample. This may be denoted by the symbol, η_X , which is similar but slightly smaller in magnitude to the backscatter coefficient, η , depending on the sample-detector geometry and the energy of the X ray that is being observed.

Because of the close connection between backscatter and R loss, relative trends in backscatter from compounds and elements can be useful in developing new R loss models, and this assumption is borne out by the quantitative measurements presented in this article.

RESULTS

Figure 1 presents high-precision results for absorbed current, measured on two different sample splits of the isotope pairs. The variation ($\sim 0.2\%$) within the pairs is similar to the precision level, that is, roughly an order of magnitude smaller than the differences in mass between the isotope

pairs. The differences in atomic weight between the natural abundance and enriched isotopes range from 2.2 to 4%.

If mass did affect pure element backscatter intensities, one might have expected an increase in backscatter of about 2.2% per atomic mass unit (AMU) in the region of Ni and Cu (based on pure Fe and Cu measurements) and about 0.22% per AMU in the region of Mo (based on Cu and Ag measurements). Given the respective differences in the Ni, Cu, and Mo isotope pairs of 1.29, 1.46, and 4.06 AMUs, we might have expected to observe backscatter intensity differences on the order of 2.8%, 3.2%, and 0.9% for Ni, Cu, and Mo, respectively.

The observed differences in the isotope pairs were approximately 5 to 15 times *smaller* than these mass-effect calculations suggest. Furthermore the minuscule variation of backscatter with mass appears random, and likely represents experimental error. We must conclude that mass, represented here by the additional atomic mass of neutrons, does not affect backscattering of electrons under microprobe conditions. Mass therefore should not appear as a mathematical term in EPMA models that predict average backscatter.

DISCUSSION

Averaging from Pure Elements to Predict Properties of Compounds

It is well known that atomic-fraction averaging (the ratio of the number of atoms in a compound) poorly predicts the properties of compounds under electron bombardment. For example, uranium sulfide, US, exhibits properties more similar to those of uranium than those of sulfur, even though the atomic proportion of the two elements is 1:1. Mass-averaging of element properties became established early in the history of electron probe microanalysis because of its reasonable success in predicting the properties of compounds from the observed properties of the relevant pure elements.

Electron Fraction Averaging

Physical considerations and the isotope data presented above suggest the use of electron fraction based averaging (Donovan and Pingitore, 1998; Pingitore et al., 1999; Donovan and Westphal, 2000; Donovan and Pingitore, 2002). The electron fraction is the fraction of the electrons, or protons,

in a compound contributed by each of the elements present. The electron fraction is calculated as

$$z_i = \frac{a_i Z_i}{\sum_{i=1}^n a_i Z_i}, \quad (3)$$

where a_i is the atomic fraction and Z_i is the atomic number of element i in the compound. The difference between this expression and mass fraction is the substitution of atomic number for atomic weight.

The variation in A/Z in natural elements is as much as 30% (over several hundred percent for hydrogen and helium). Some elements have more neutrons (and hence more mass) than might be expected from their atomic number, while others have fewer neutrons (and hence less mass) than expected.

Mass fraction averaging in traditional models thereby imposes a systematic error on backscatter averaging, an error that is described by the variation of A/Z versus Z for the natural elements. This mass-induced (or neutron induced) error depends on the specific ratios of A/Z for the elements of the compound in question. The difference between the mass fraction and electron fraction for many compounds is 1 to 3%, but it can exceed 20 to 25%, as in, for example, lead sulfide or uranium carbide (Table 1).

Ways to Compare Mass and Electron Fraction Averaging for Backscatter Prediction

There are two distinct approaches to comparing the relative merit of the two fractional models. One is to predict the property of the compound from the weighted (by mass, electron, or whatever) average of the properties of the relevant pure elements, and compare this to the value of the property measured on the compound. This *property averaging* method has been widely used in estimations of average backscatter, based on mass averaging, by many early experimenters, although it was usually limited to mixtures of two elements.

The other method is to plot a series of measurements of the property versus calculated hypothetical average atomic numbers and observe the smoothness of fit to a simple polynomial or exponential curve. We term this *atomic number averaging*.

We present both approaches to evaluate the predictive powers of mass fraction and electron fraction averaging. We

Table 1. Comparison of Mass Fraction and Electron Fraction for a Number of Compounds^a

Compound	Element	Mass fraction	Electron fraction	Relative difference (%)
AuCu	Au	0.756	0.731	-3.3
	Cu	0.244	0.269	10.2
PbS	Pb	0.866	0.837	20.4
	S	0.134	0.163	21.6
NaCl	Na	0.393	0.393	0.0
	Cl	0.607	0.607	0.0
UN	U	0.944	0.929	-1.6
	N	0.056	0.071	26.7
MgO	Mg	0.603	0.600	-0.50
	O	0.397	0.400	0.75
ThSiO ₄	Th	0.7159	0.6618	-7.6
	Si	0.0867	0.1029	18.6
	O	0.1975	0.2353	19.1
UC ₂	U	0.983	0.8846	-10.0
	C	0.0917	0.1154	25.8

^aThe relative difference between the two calculations depends on the A/Z ratio of the elements in the compound and is due solely to the effect of the neutron mass of the atom.

also present an additional technique for predicting backscatter, based on elastic cross section averaging.

Backscatter Prediction from Property Averaging

Predictions of the backscatter from intermediate compositions made using property averaged measurements from pure elements are performed using the expression for mass fraction (Heinrich, 1963; Duncumb and Reed, 1968):

$$\bar{\eta}_{C_{AB}} = c_A \eta_A + c_B \eta_B, \quad (4)$$

where c_A and c_B are the mass fractions of elements A and B in the binary compound and η_A and η_B are the backscatter ratios of the pure elements. The electron fraction property averaging expression for intermediate compositions derived from measurements on pure elements is similarly assumed to be

$$\bar{\eta}_{Z_{AB}} = z_A \eta_A + z_B \eta_B, \quad (5)$$

where z_A and z_B are the electron fractions of elements A and B in the binary compound from equation (3). In all cases, it is assumed that the mixing of binary end-member properties is on a straight line.

In Figure 2a,b, mass and electron fraction property predictions give similar results, with a slightly better prediction from the mass fraction average.

Backscatter Prediction Based on Elastic Cross Section Averaging

Backscatter is an elastic scattering process, to a first order dependent on the number of protons in the nucleus and to a second order on its effective nuclear charge. At typical energies utilized in EPMA, there is no interaction with neutrons, as demonstrated by the isotope data previously shown. The word *effective* denotes that the total nuclear charge is not involved in elastic scattering of incident electrons, especially for atoms of higher atomic number due to screening of the nucleus by the inner orbital electrons. Because of this nuclear screening effect, the effective charge of the nucleus is reduced and a correction is required to account for this.

The use of mass fraction for average backscatter calculations contains a fortuitous bias for nuclear screening due to the nonlinearity of atomic weight with respect to Z . (A increases faster than Z , especially at high Z .) This atomic weight scaling effect is produced by the additional mass of the neutron, and is completely unrelated to elastic scattering of electrons at EPMA energies.

Armstrong (1991) noted that the ratios of elastic scattering cross section and atomic mass to atomic number correlate fairly well. Since the elastic scattering term is essentially the size of the target atom as seen by an electron beam (for backscattered electrons), Armstrong felt this might explain the observed correlation of various electron–solid interactions with mass fraction. Thus, the correlation of mass fraction with electron backscatter yield, demonstrated by Heinrich (1963) and Colby (1966), may be accidental. In fact, during efforts to create more physically based electron interaction models, this relative elastic scattering ratio has been suggested by others as one possible basis for calculating the elemental proportioning of electron backscatter in multielement compounds, rather than the traditionally utilized mass fraction basis from Castaing (1960) and Heinrich.

Armstrong (1991) used the following expression for single elastic scattering that produces results that vary only slightly with the energy of the incident beam:

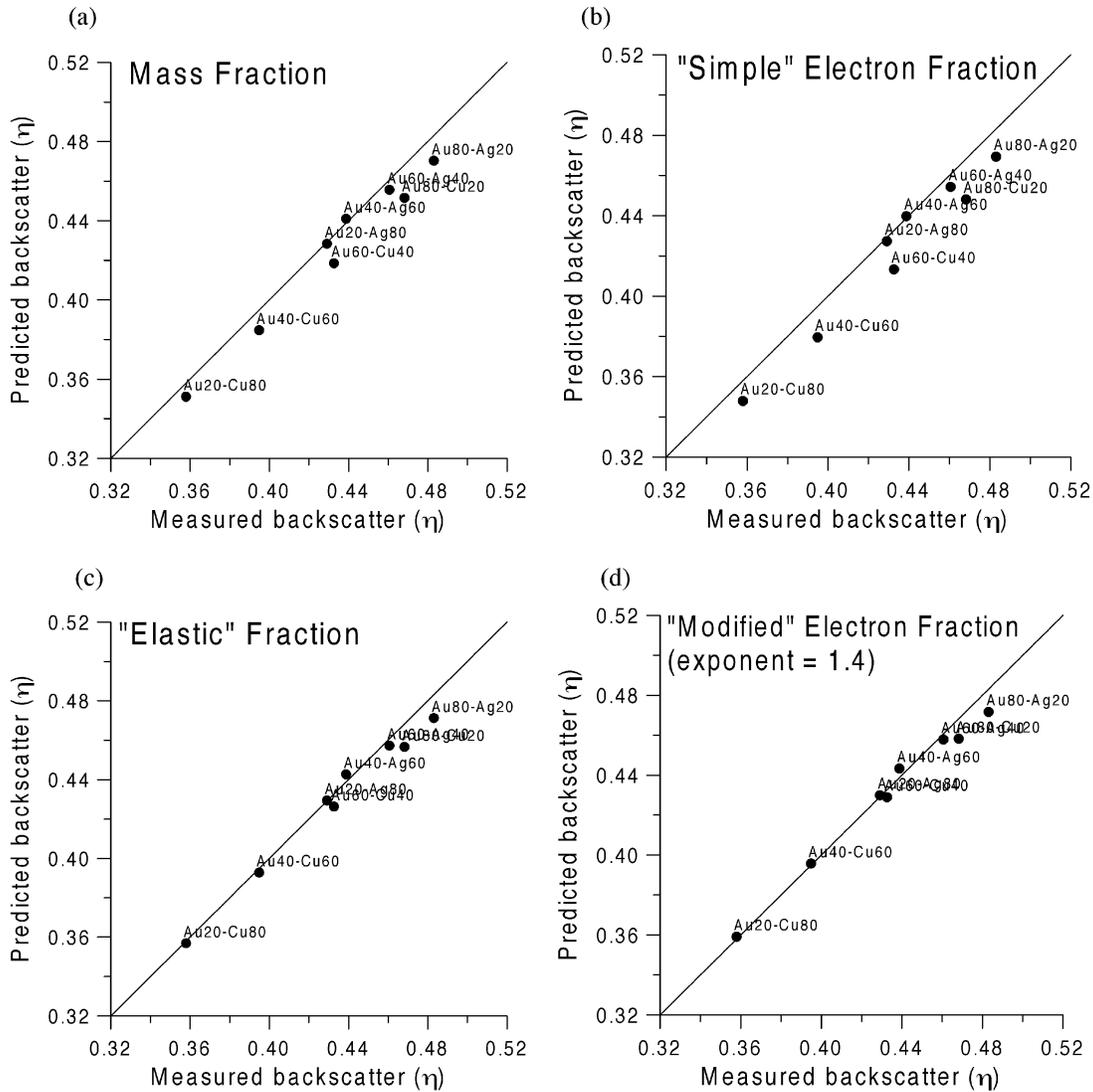


Figure 2. Property average predictions from pure element backscatter intensities versus backscatter measurements on NIST SRM 481/482 Au/Ag/Cu binary alloys (20 keV, 100 nA, average of 10 measurements per point, 22.5 V sample bias) for (a) mass fraction, equation (4), (b) simple electron fraction, equation (5), (c) elastic fraction, equation (9), and (d) “modified” electron fraction, equation (11). Both the elastic fraction and modified electron fraction predictions give good results to the data. The parameterized elastic fraction is mathematically equivalent to a $Z^{1.35}$ function and therefore similar to a modified electron fraction using a Z exponent of 1.4, as is seen from the similarity of the two plots.

$$\sigma^E = 5.21 \times 10^{-21} \frac{Z^2}{E^2} \frac{4\pi}{\alpha(1+\alpha)} \left(\frac{E + m_0 c^2}{E + 2m_0 c^2} \right)^2, \quad (6)$$

where E is the electron energy in kiloelectron volts, Z is the atomic number, $m_0 c^2 \approx 511$ keV, and α is an effective nuclear charge screening factor,

$$\alpha = 3.4 \times 10^{-3} \frac{Z^{0.67}}{E} \quad (7)$$

from Newbury et al. (1980). To calculate an elastic scattering cross section fraction, we assume that the averaging is based on the additivity of the elastic scattering weighted atom proportion of each element in the compound. The elastic scattering fraction, σ_i , is therefore,

$$\sigma_i = \frac{a_i \sigma_i^E}{\sum_{i=1}^n a_i \sigma_i^E}, \quad (8)$$

where a_i is the atomic proportion of the element in the compound, and σ_i^E is the total elastic scattering cross section for element i as defined in equation (6).

We calculate the elastic scattering cross section average, derived from Armstrong (1991), as

$$\bar{\eta}_{\sigma_{AB}} = \sigma_A \eta_A + \sigma_B \eta_B, \quad (9)$$

where σ_A and σ_B are the elastic fractions of elements A and B in the binary compound from equation (8). It is assumed that the mixing of properties is on a straight line between pure element end members.

In Figure 2a,b,c, the best prediction is given by the elastic scattering fraction average, based on equation (9), derived from Armstrong (1991).

Modified Electron Fraction Averaging

The simple (Z^x , where $x = 1.0$) electron fraction model does not predict property averaged backscatter production in compounds quite as well as the elastic scattering fraction model. Nuclear screening by the inner orbital electrons, especially in nuclei of the higher Z elements, limits the performance of simple electron fraction averaging. The simple electron fraction model assumes that all protons (whose Coulombic field is the contributing factor for elastic scattering) are of equal influence. But as the inner orbital electrons screen the nucleus with increasing efficiency, the rate of increase in backscatter yield decreases significantly for the higher Z elements. Since the elastic scattering fraction formulation includes a correction for this, it predicts backscatter better. The mass fraction includes a bias in the proper direction due to the increase in neutron count in higher atomic number elements, and so partially compensates for the screening effect, as noted by Armstrong (1991).

With this screening effect in mind, we adjust the electron fraction calculation to compensate for a variation in scattering with Z . The calculation of this modified electron fraction is

$$z_i^{(x)} = \frac{a_i Z_i^x}{\sum_{i=1}^n a_i Z_i^x}, \quad (10)$$

where x is an exponent generally close to 1.0. The exponent (x) in parentheses simply indicates the derivation of the modified term. To utilize the modified electron fraction adjusted for nuclear screening effects in the calculation of property averaging, we use the following expression:

$$\bar{\eta}_{Z_{AB}^{(x)}} = z_A^{(x)} \eta_A + z_B^{(x)} \eta_B, \quad (11)$$

where $z_A^{(x)}$ and $z_B^{(x)}$ are the modified electron fractions of elements A and B in the binary compound from equation (10).

Figure 2d reveals that a good fit can be obtained with this simple adjustment where the best fit is obtained with an electron fraction exponent of Z^x , where $x = 1.4$ for the NIST SRM 481/482 Au-Ag-Cu alloys and pure elements.

Although some deviation for the high Au compositions in the predicted backscatter data may be noted due to slight surface contamination of the pure Au standard by Cu and Ag during polishing ($\sim 1\%$ Cu as bulk analysis), this is in close agreement with the numerical solution to the expression for single elastic scattering used by Armstrong, which yields approximately $Z^{1.35}$.

It must be emphasized that exponents are adjusted to obtain the best prediction solely to demonstrate that the variation of backscatter production, in materials of differing composition, can be adequately described by a simple function of atomic number.

Backscatter Atomic Number Averaging

The calculation of average atomic number is straightforward. For the mass fraction average atomic number or “ Z -bar” (\bar{Z}), the expression

$$\bar{Z}_{(c_i Z_i)} = \sum_{i=1}^n c_i Z_i \quad (12)$$

is usually seen (Goldstein, 1992), where c_i is the mass fraction and Z_i is again the atomic number of element i of each element in the compound. The electron fraction \bar{Z} , that we propose, is calculated from

$$\bar{Z}_{(z_i Z_i)} = \sum_{i=1}^n z_i Z_i, \quad (13)$$

where z_i is the electron fraction from equation (3). For the sake of symmetry, we can also compare the elastic scattering cross section average Z , which could be calculated from

$$\bar{Z}_{(\sigma_i Z_i)} = \sum_{i=1}^n \sigma_i Z_i, \quad (14)$$

where σ_i is the elastic scattering cross section fraction of element i in the compound as defined in equation (8), and Z_i is the atomic number of element i .

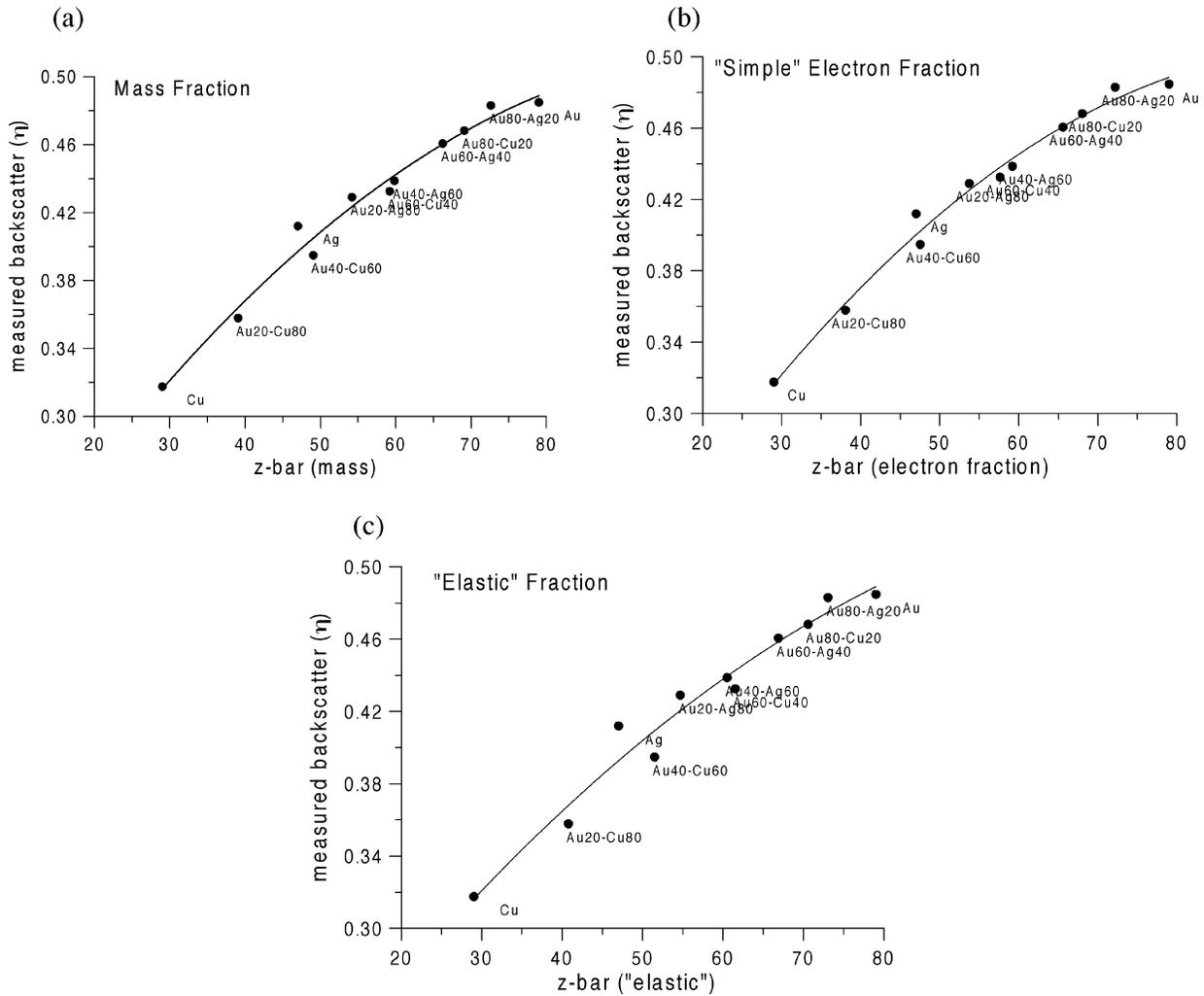


Figure 3. Backscatter yield from the Au/Ag/Cu NIST 481/482 data set (20 keV, 100 nA, average of 10 measurements per point, 22.5 V sample bias) versus average atomic number calculations using (a) mass fraction, equation (12), (b) simple electron fraction, equation (13), and (c) elastic fraction, equation (14). The mass and simple electron fractional methods give similar results with a slight improvement for the electron fraction average \bar{Z} -bar. Note that no correction for nuclear charge screening has been applied to the simple electron fraction expression, while the mass fraction expression contains a serendipitous built-in bias for nuclear screening due to the nonlinearity of atomic weight with respect to Z , a bias produced by the additional mass of the neutron which has no actual effect on electron–solid interactions in EPMA.

In Figure 3a,b,c, we can see backscatter fit results for these three expressions (equations (12), (13), and (14)) plotted using the high Z data set. Interestingly, now the best prediction is given by the simple electron fraction average atomic number expression. This is opposite from the result that we obtained from the property-averaged data in the previous section using equations (4), (5), and (6). A discussion of this result will appear in the next section.

However, it must be mentioned that other expressions for the calculation of average atomic number and electron backscatter yield, cited by Muller (1954), Herrmann and

Reimer (1984), and Howell et al. (1998), can be found in the literature. For example, we note

$$\bar{Z}_{(a_i, Z_i^2)} = \frac{\sum_{i=1}^n a_i Z_i^2}{\sum_{i=1}^n a_i Z_i} \quad (15)$$

from Saldick and Allen (1954), given without theoretical explanation for use in calculating the average atomic number backscatter for measurement of sulfate solutions, while

Joyet et al. (1953), Hohn and Niedrig (1972), and Büchner (1973) proposed

$$\bar{Z}_{(\sqrt{a_i Z_i^2})} = \sqrt{\sum_{i=1}^n a_i Z_i^2}, \quad (16)$$

where it was assumed that backscatter is primarily caused by large angle Rutherford scattering, and Everhart (1960) and also Danguy and Quivy (1956) utilized

$$\bar{Z}_{(c_i Z_i^2)} = \frac{\sum_{i=1}^n c_i Z_i^2}{\sum_{i=1}^n c_i Z_i}, \quad (17)$$

where it was proposed that backscatter is the outcome of two processes, continuous energy loss and a single large angle scattering event. In all expressions, c_i is, again, the weight fraction, a_i is the atomic fraction, and Z_i is the atomic number of element i .

Because the isotope data demonstrate backscatter is independent of mass, we immediately suspect equation (17), since it contains a mass fraction term. Indeed, the Everhart (1960) or Danguy and Quivy (1956) model performs worse than the simple mass fraction averaging model. Buchner (1973) found good results with Cu-Au alloys with equation (16), while recently Howell et al. (1998) found a generally poor fit to all three models for very low atomic number compounds. The best fit was from equation (15) of Saldick and Allen (1954), using an SEM operating at 20 keV and only 0.5 nA of beam current on polymers. However, since Howell et al. could only obtain average image “gray levels” from their instrument, we feel that the measurements in the present paper provide a higher precision test for the various formulations.

These various expressions are plotted in Figure 4 with both the low Z and high Z absorbed current data sets ($\bar{Z} < 30$ and $\bar{Z} > 30$). All three expressions fit these data reasonably well, but the fit to the Saldick and Allen (1954) formulation for $\bar{Z}_{(a_i Z_i^2)}$ from equation (15) is significantly better, and is, in fact, even better than the fit to the mass fraction $\bar{Z}_{(c_i Z_i^2)}$, as shown in Figure 4a.

Saldick and Allen (1954) gave no explanation for the theoretical basis or origin of this Z -based expression in their paper, although Herrmann and Reimer (1984) showed that a similar expression might be derived by constructing a ratio of the elastic backscatter loss to the inelastic energy loss.

Table 2 summarizes these results by comparing both data sets for each model for atomic number averaging of the backscatter data and chi-squared fits, which show that equation (13) for the electron fraction $\bar{Z}_{(z_i Z_i)}$ and the Saldick and Allen (1954) $\bar{Z}_{(a_i Z_i^2)}$ equation (15) give exactly the same results. These expressions are algebraically equivalent, since substituting equation (3) for z_i in equation (13) we obtain

$$\bar{Z}_{(z_i Z_i)} = \sum_{i=1}^n \frac{a_i Z_i}{\sum_{i=1}^n a_i Z_i} Z_i \quad (18)$$

or

$$\bar{Z}_{(z_i Z_i)} = \frac{\sum_{i=1}^n a_i Z_i^2}{\sum_{i=1}^n a_i Z_i}, \quad (19)$$

which is exactly the same as equation (15).

However, once again we can provide an adjustment to the simple electron fraction model to compensate for the nuclear screening effect, using the average Z -calculated modified electron fraction, by substituting $z_i^{(x)}$ from equation (10), for z_i in equation (13), yielding the expression,

$$\bar{Z}_{(z_i^{(x)} Z_i)} = \sum_{i=1}^n z_i^{(x)} Z_i \quad (20)$$

where the exponent has been adjusted to give a smooth fit using a simple polynomial. We can see the results in Figure 5, where, using an electron fraction, $\bar{Z}_{(z_i^x Z_i)}$, where the z_i^x exponent x is about 0.8, we obtain a very smooth fit. This best fit exponent is obtained from selecting the best fit (smallest chi-square) from a range of exponents as seen in Figure 6 for both the low and high Z data sets.

Comparison of Property and Atomic Number Averaging

In the backscatter data sets, efficacy of the different fractional averaging methods is different for property-averaged and atomic-number-averaged evaluations. In Fig. 2a,b,c and Fig. 3a,b,c, the proficiencies of mass versus electron versus elastic fraction averaging are almost exactly opposite. Atomic number averaging and property averaging produce different results, from the same data set, because the two approaches are mathematically discrete and not directly comparable. This may explain some of the confusion in the literature in

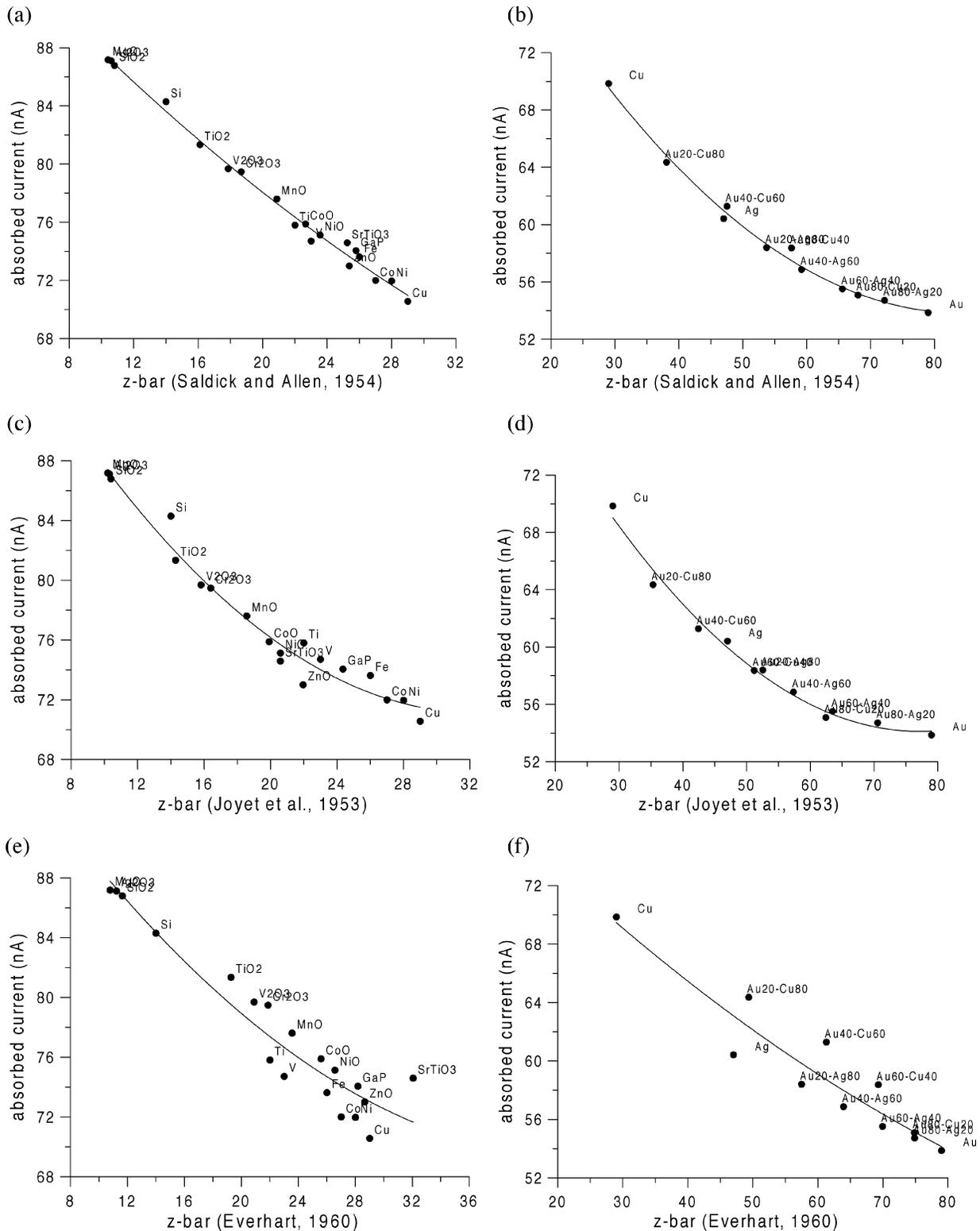


Figure 4. Absorbed current measurements from both the MgO-Cu and Au/Ag/Cu NIST 481/482 data sets (20 keV, 100 nA, average of 10 measurements per point, no sample bias on MgO-Cu, 22.5 sample bias on Au/Ag/Cu NIST 481/482) versus average atomic number calculations using expressions from (a) and (b) Saldick and Allen (1954), equation (15), (c) and (d) Joyet et al. (1953), equation (16), and (e) and (f) Everhart (1960), equation (17). The fit for all three expressions are reasonable, although the expression of Saldick and Allen is noticeably better and is, in fact, algebraically equivalent to the simple electron fraction expression, equation (13), proposed by us for average atomic number calculations.

Table 2. Second Order Polynomial Fit Sum of Squares Residuals, $r_{ss} = \sum_{i=1}^n (y_i - y_{\text{exp}})^2$, for Both Absorbed Current in Nanoamperes (20 keV, 100 nA, No Sample Bias Voltage) for the $\bar{Z} < 30$ (MgO-Cu) and $\bar{Z} > 30$ (NIST SRM 481/482) Data Sets, for the Various z -bar Models Discussed in the Text

Fractional z -bar model	Expression	χ^2 fit for $\bar{Z} < 30$ (MgO-Cu)	χ^2 fit for $\bar{Z} > 30$ (SRM 481/482)
Atomic	$\bar{Z}_{(a_i, Z_i)} = \sum_{i=1}^n a_i Z_i$	46.89	14.11
Mass, equation (12)	$\bar{Z}_{(c_i, Z_i)} = \sum_{i=1}^n c_i Z_i$	5.419	2.776
Simple electron, equation (13) ^a	$\bar{Z}_{(z_i, Z_i)} = \sum_{i=1}^n z_i Z_i$	4.021	1.796
Elastic scattering, equation (14)	$\bar{Z}_{(\sigma_i, Z_i)} = \sum_{i=1}^n \sigma_i Z_i$	12.03	5.453
Saldick and Allen (1954), equation (15) ^a	$\bar{Z}_{(a_i, Z_i^2)} = \frac{\sum_{i=1}^n a_i Z_i^2}{\sum_{i=1}^n a_i Z_i}$	4.021	1.796
Joyet et al. (1953), equation (16)	$\bar{Z}_{(\sqrt{a_i, Z_i^2})} = \sqrt{\sum_{i=1}^n a_i Z_i^2}$	14.14	2.875
Everhart (1960), equation (17)	$\bar{Z}_{(c_i, Z_i^2)} = \frac{\sum_{i=1}^n c_i Z_i^2}{\sum_{i=1}^n c_i Z_i}$	42.58	25.58

^aNote that the Saldick and Allen and the simple electron fraction expressions are equivalent and both give the best fit to both data sets.

evaluating the two methods for describing elemental averaging in compounds.

The Atomic Number Matrix Correction

The stopping power calculation in the atomic number matrix correction for multielement compounds is correctly formulated in mass fractions because the terms contain mass normalized terms. However, the backscatter loss calculation is not mass dependent, and is improperly averaged using mass fractions. The approximate error produced by the discrepancy between mass and electron fractions for compounds that contain, say Si and Pb, is 3–4% (for a backscatter correction of 15% and a 20–25% difference in mass versus electron fraction averaging).

The standard form of the electron backscatter loss equation as seen in equation (1) using mass fraction can be altered to utilize a modified electron fraction:

$$R_i^{(x)} = \sum_j z_i^{(x)} R_{ij}, \quad (21)$$

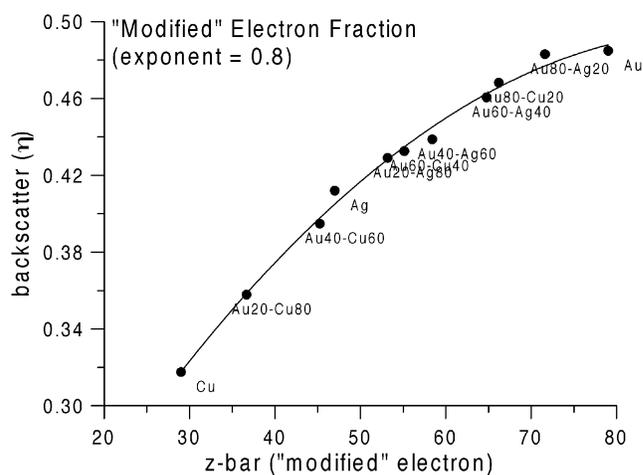


Figure 5. Backscatter yield from the Au/Ag/Cu NIST 481/482 data set (20 keV, 100 nA, average of 10 measurements per point, 22.5 V sample bias) versus average atomic number calculations using a modified electron fraction expression for average atomic number, equation (20). An electron fraction exponent of around 0.7 or 0.8 provides the best fit. A very similar result is obtained for the low Z MgO-Cu data set and as seen in the comparison of chi-square versus electron fraction exponent shown in Figure 6.

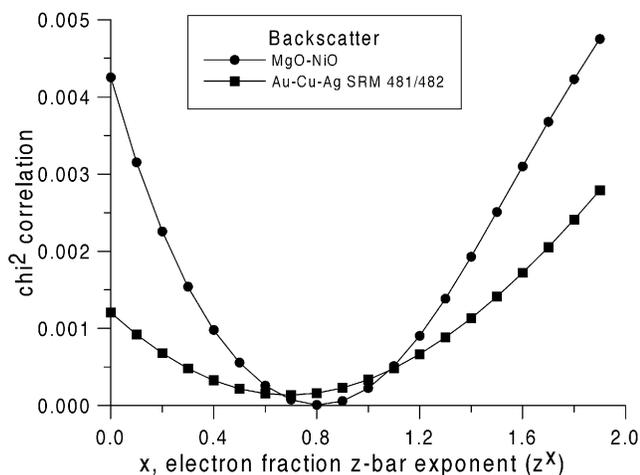


Figure 6. Plot of chi-square values from a range of modified electron fraction z -bar calculation exponents for best fit backscatter data seen in the previous figures, from equation (20), for both a low Z (MgO-Cu) data set and a high Z (NIST SRM 481/482) data set. The low Z data set gives a best fit modified electron fraction exponent of around 0.8, while the high Z data set fits best when the exponent is very slightly lower, around 0.7.

where $z_i^{(x)}$ is the modified electron fraction from equation (10) that utilizes the best fit exponent from Figure 6, which is around 0.8. The actual form of the atomic number correction is, therefore,

$$Z_i^{(x)} = \frac{R_i^{(x)} \int_{E_c}^{E_o} \frac{Q}{S} dE}{R_i^{(x)*} \int_{E_c}^{E_o} \frac{Q}{S^*} dE}, \quad (22)$$

where $R_i^{(x)}$ and $R_i^{(x)*}$ are the backscattering loss correction factors for element i for the standard and the unknown specimen using a modified electron fraction from equation (21), dE is the energy loss of an electron, Q is the ionization cross section defined as the probability per path length of a primary electron of a given energy causing an ionization event of the associated electron shell for the specified characteristic line, and S_i and S_i^* are the electron stopping power for the standard and unknown (calculated using mass fractions) from this expression,

$$S_i = \sum_j c_j S_{ij}. \quad (23)$$

This modified correction for the atomic number effect, as seen in equation (22), along with the traditional Duncumb

atomic number correction, was compared using a suite of silicate standards, where silicon was measured over a wide range of atomic numbers. Analyses using the Love–Scott atomic number correction (Scott and Love, 1983) gave similar but slightly worse results compared to the traditional mass averaged Duncumb–Reed atomic number correction. Table 3 shows that the improvement for compounds with large atomic number corrections is significant when using “modified” electron-fraction-based averaging for the backscatter loss factor, especially where compounds with disparate A/Z ratios are involved.

CONCLUSIONS

The isotope data do not support a mass effect in electron–solid interactions, at least to the fractional percent level. Prediction of electron backscatter in compounds should be based not on the mass fraction, but on the electron fraction, of the constituent elements times the backscatter measured in the respective pure element. The screening effect on the proton nuclear charge from the inner orbital electrons requires an adjustment to the simple electron fraction model.

Mass-fraction averaging has met some success in predicting electron backscatter because atomic mass happens to vary with Z in a manner that partially compensates for nuclear screening of the proton charge in atoms of higher atomic number elements.

The average backscatter loss factor can be more accurately calculated using a Z based modified electron fraction calculation and should be incorporated in existing matrix correction routines to allow for improved accuracy in cases where large atomic number corrections are involved.

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Table 3. Comparison of Calculated Compositional Results Using the Traditional Mass-Based Atomic Number Correction and a Modified Duncumb–Reed Atomic Number Correction Using a Z-Based (Modified Electron Fraction) Average R Loss Factor for Compounds^a

Compound ^b	Published (wt.% Si)	Trad. Duncumb–Reed	Rel. error	Mod. Duncumb–Reed (equation 22)	Rel. Error
SiO ₂ (std)	46.74	46.74	0.00%	46.74	0.00%
Mg ₂ SiO ₄	19.96	19.88	−0.40%	19.88	−0.38%
Mn ₂ SiO ₄	13.91	13.91	−0.92%	13.71	−1.37%
Fe ₂ SiO ₄	13.78	13.72	−0.50%	13.66	−0.94%
Co ₂ SiO ₄	13.38	13.23	−1.07%	13.17	−1.58%
Ni ₂ SiO ₄	13.41	13.27	−1.04%	13.21	−1.49%
ZrSiO ₄	15.32	15.41	0.56%	15.21	−0.73%
PbSiO ₃	9.91	10.55	6.41%	10.13	2.23%
ThSiO ₄ ^c	8.67	9.09	4.90%	8.67	−0.01%
ThSiO ₄ ^d	8.67	9.25	6.75%	8.81	1.76%

^aThe exponent of the Z-based correction factor (0.8) was adjusted based on the best fit to the Au–Ag–Cu alloy and the MgO–Cu as data sets discussed in the text. Note that the relative error for the traditional Duncumb–Reed mass-based atomic number correction increases generally with the size of the atomic number correction (and also with the size of the disparity of A/Z ratio for the elements in the compound).

^bAll silicate materials are synthetically grown except the PbSiO₃, which is from the Tsumeb locality and obtained from Mineralogical Research. The SiO₂ was hydrothermally grown and obtained from ESPI, the Mn₂SiO₄, Co₂SiO₄, and Mg₂SiO₄ were obtained from the Institute for Solid State Physics, University of Tokyo by H. Takei, the Ni₂SiO₄ was grown at Tokyo University by M. Ojima, the Fe₂SiO₄ was grown at Oak Ridge National Laboratory by L. Boatner, and the ZrSiO₄, the ThSiO₄ (Thorite structure), and the ThSiO₄ (Huttonite structure) were grown at George Washington University by John Hanchar.

^cThorite structure.

^dHuttonite structure.

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