

Quantitative Electron Probe Analysis

QUANTITATIVE ANALYSIS OF SILICATE AND OXIDE MATERIALS: COMPARISON OF MONTE CARLO, ZAF, AND $\phi(\rho z)$ PROCEDURES

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Geological applications of electron microprobe analysis are widespread and often require high degrees of precision and accuracy. New generation electron-beam instruments, with their improved electronics, superior beam stabilization, lower-noise and higher-sensitivity detectors, and sophisticated computer control, have

enabled analyses of much higher precision than previously possible. However, some investigators appear to have confused this improved precision with improved accuracy. Conventional ZAF correction procedures produce systematic errors in the analysis of silicate materials, particularly when standards of greatly different composition (such as simple oxides) are employed.¹ Recent attempts to refine quantitative analysis correction procedures have generally involved comparison with data sets of metal alloy analyses rather than analyses of materials similar to those commonly encountered in geological applications. As a result, some of the newer correction algorithms produce poorer results in the analysis of silicate and oxide minerals than some of the earlier corrections. In the present study, data sets of analyses of silicate and oxide standards are compared with series of ZAF and $\phi(\rho z)$

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TABLE 1.--Correction procedures and parameters tested.

Code	Correction	Ref.	Code	Correction	Ref.
Absorption corrections:			Continuum fluorescence correction:		
A --	Philibert	3	U --	Henoc et al.	22
B --	Heinrich	4			
C --	Love and Scott	5			
D --	Sewell, Love, Scott	6			
E --	Packwood and Brown	7			
F --	Armstrong	8			
G --	Bastin et al., I	9			
H --	Bastin et al., II	10			
I --	Riveros et al.	11			
J --	Monte Carlo, mult. scat.	2			
K --	Monte Carlo, sing. scat.	2			
Atomic number corrections:					
L --	Duncumb and Reed	13			
M --	Philibert and Tixier	14			
N --	Love, Cox, Scott	15			
O --	$\Phi(\rho z)$ integration	7-11			
P --	Monte Carlo, mult. scat.	2			
Q --	Monte Carlo, sing. scat.	2			
Characteristic fluorescence corrections:					
R --	Reed	17			
S --	Armstrong-modified Reed				
T --	Armstrong and Buseck	18			
Combined corrections considered:					
Name: Table 3-5 -- Corr. codes			Name: Table 3-5 -- Corr. codes		
Phil-DR	---	ALSa	Bast-I	---	GOScfh
Hein-DR	---	BLSa	Bast-II	---	HOScfh
NBS-COR	---	AMRUa	Riveros	---	IOSafi
Love-Sc	---	CNSafh	MCms-GC	---	JQSaj
Sewl-LS	---	DNSafh	MCms-WT	---	JQSak
Pack-Br	---	EOSafh	MCms-Hu	---	JQSsal
Arms-DR	---	FLSaeg	MCms-Gz	---	JQSsam
Arms-LS	---	FNSafh	MCms-Fa	---	JQSsan

correction procedures as well as with recent Monte Carlo calculations.

Correction Procedures Tested

The correction procedures and parameters evaluated in this study are listed in Table 1. In a companion paper, the accuracy of α -factor correction procedures is evaluated.² Typically, the largest correction in the analysis of silicates and oxides is that for primary absorption. The various absorption corrections examined³⁻¹¹ employ different assumptions regarding the distribution with depth of the primary x-ray production.¹² The conventional Philibert correction assumes an exponential distribution with depth and no x-ray production at the surface. The Heinrich correction uses a quadratic equation to fit the absorption parameter $f(\chi)$. The Love-Scott correction assumes constant production from the surface to a mean depth and no production below that (the so-called box model). The Sewell-Love-Scott correction fits measured $\phi(\rho z)$ curves to a quadratic model. The remaining corrections, the so-called $\phi(\rho z)$ corrections, employ a Gaussian equation to express the depth distribution of primary x-ray production:

$$\phi(\rho z) = \quad (1)$$

$$\gamma_0 \exp[-\alpha^2(\rho z)^2] [1 - \{(\gamma_0 - \phi(0))/\gamma_0\} \exp(-\beta \rho z)]$$

Equations of this form have been shown to fit well experimentally determined $\phi(\rho z)$ distributions. The various Gaussian corrections employ different equations to express α , β , and γ_0 . The original model proposed by Packwood and Brown⁷ was parameterized on the basis of a simple physical model and some fitting to the measured $\phi(\rho z)$ curves. The subsequent models were more or less altered to better fit analytical data; those of Bastin et al.^{9,10} are heavily parameterized to fit binary metal alloy data; that of Armstrong⁸ makes minor adjustments to the Packwood and Brown expressions to optimize silicate and oxide analyses.

Atomic number corrections tested include the conventional Duncumb and Reed¹³ and Philibert and Tixter¹⁴ corrections, as well as the Monte Carlo calculation-based Love and Scott¹⁵ correction. In typical silicate analyses, the magnitude of the atomic-number correction is not great and these three corrections give similar results. The other atomic-number corrections examined are those based on integration of the Gaussian $\phi(\rho z)$ expressions:

$$I_p = \int_0^{\infty} \phi(\rho z) d(\rho z) \quad (2)$$

This author urges caution in the use of the Gaussian $\phi(\rho z)$ expressions for atomic-number corrections. Use of these expressions for the absorption correction requires only that the shapes of the curves be correct, not their absolute magnitudes. Use of them for the atomic-number correction, however, requires correct proportionality between the total integrals of

$\phi(\rho z)$ curves from different matrices. In experimental terms, this means that the thicknesses of the tracer films and the normalizing thin films used in the $\phi(\rho z)$ experiments for different matrices must be known with a high degree of accuracy--a difficult restriction, particularly when results from different investigators are compared. In addition, virtually no work has been done in determining experimental $\phi(\rho z)$ curves for multielement specimens; the atomic-number dependence is calculated strictly by comparison of different combinations of tracers and pure elements.

Monte Carlo calculations of electron trajectories were performed based on both multiple-scattering and single-scattering models to calculate $\phi(\rho z)$ distributions. These $\phi(\rho z)$ distributions were then used to calculate both absorption and atomic-number corrections. The programs employed were modifications of the programs created by Joy.¹⁶ The details of the algorithms used in these calculations are given in a companion paper.² Unlike for the Gaussian $\phi(\rho z)$ corrections, there is no a priori reason that the Monte Carlo calculations might be suspect for use in a combined absorption and atomic-number correction.

The characteristic fluorescence corrections considered include the conventional correction of Reed¹⁷ and the integral $\phi(\rho z)$ expression of Armstrong and Buseck.¹⁸ Evaluation of the commonly used correction of Reed shows that some of the approximations (made with metal analyses in mind) are inappropriate for silicates. Reed assumed that the absorption-edge jump ratio factor $(1 - r)/r$, was constant with a value of 0.88 for K-lines and 0.75 for L-lines. The jump ratio is actually a regularly variable function of Z as seen in Fig. 1 for K-lines (based on the mass absorption coefficient data of Heinrich¹⁹). The jump ratio factor is underestimated by about 10% for Mg, Al, or Si, which means that the fluorescence correction calculated for these elements is also underestimated from this factor by about 10%. Similarly, the L-line jump ratio factor for $Z = 30$ is about 0.875 instead of 0.75, which results in underestimation of fluorescence by a factor of over 10%. The jump ratios for K- and L-lines can be accurately expressed by the equations:

$$r_K = 53.46Z - 18.01 \quad (3)$$

$$(r_L - 1)/r_L = 0.9548 - 0.0026Z \quad (4)$$

In the ZAF corrections given in this paper, these equations have been used in the Reed correction.

Other simplifications in the Reed equation results in underestimation of light element fluorescence. Both Monte Carlo calculations and experimental measurements of the relative intensities of a series of pure element and compound standards made at 15 and 20 keV (Fig. 2) suggest that the Green and Cosslett²⁰ expression for the relative number of inner-shell ionizations per atom of elements A and

K-shell Abs. Edge Jump Ratio Factors

Heinrich MAC Data

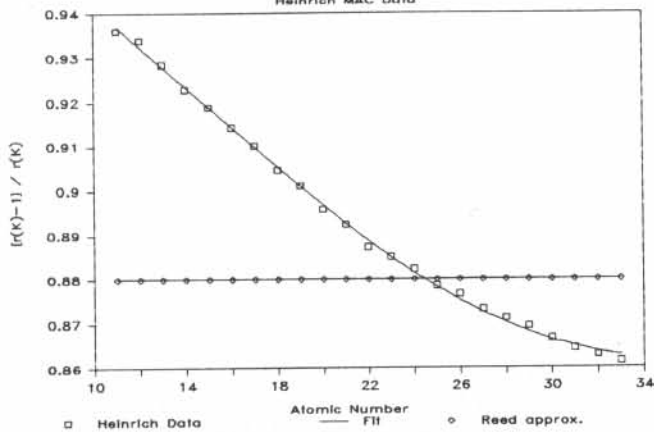


FIG. 1.--Plot of K-line absorption edge jump factor vs atomic number based on Heinrich's mass absorption coefficient data.

B as a function of the overvoltage

$$U_A = E / E_{c,A}$$

$$I_B'' / I_A'' = (U_B - 1)^{1.67} / (U_A - 1)^{1.67} \quad (5)$$

significantly overestimates the difference when the two overvoltages are large and similar. The new data suggest the following alternative equations:

$$I_B'' / I_A'' = (U_B - 1)^{1.59} / (U_A - 1)^{1.59} \quad (6)$$

for $(U_B - 1) / (U_A - 1) < 2/3$ and

$$I_B'' / I_A'' = 1.87(U_B - 1)^{3.19} / (U_A - 1)^{3.19} \quad (7)$$

for $(U_B - 1) / (U_A - 1) > 2/3$. For elements like Mg, Al and Si at 15 keV, the new data suggest that the conventional Green/Cosslett expression underestimates the amount of fluorescence by another 10%. Finally, the data of Armstrong and Buseck¹⁸ suggest that the simple $\phi(\rho z)$ model employed by Reed underestimated the magnitude of emitted fluorescence radiation in silicates by still another 10%. In all, the magnitude of characteristic fluorescence of the major light elements in silicates may be underestimated in the Reed correction by a factor as large as 30-40% relative. Even though the absolute value of the fluorescence correction in silicates is low (typically <4%), an error of this magnitude can be of some significance.

Most ZAF correction programs do not correct for fluorescence due to the continuum, in large part due to the complexity of the correction equations. In this study, the continuum fluorescence correction of Henoc et al.²² was calculated for selected specimens to evaluate its significance. For elements lower in energy than Ti K α , the correction in typical silicates and oxides is negligible (<0.2% relative) for $E_0 = 10-20$ keV. For higher-energy lines, the

correction can start to become significant. For example, when one analyzes for Fe in $Mg_{1.85}Fe_{0.16}SiO_4$ using Fe in Fe_2SiO_4 as a standard, the magnitude of the characteristic fluorescence correction is 1.5% at 20 keV, 1.8% at 15 keV, and 2.2% at 10 keV (for $\psi = 40^\circ$).

The parameters used in the ZAF corrections can be as important as the corrections themselves. In the atomic-number correction and Monte Carlo calculation, and important parameter is the mean ionization potential. The expressions of Berger and Seltzer, Duncumb and Da Casa, Ruste, and Springer were tested and significant differences were found in the results depending on the expression used. (A comparison of the algorithms with the original references can be found in Heinrich.²³) Duncumb and Da Casa developed their expression specifically to optimize experimental results using the Duncumb-Reed atomic-number correction; the expression should be probably employed only for that correction. The authors of the other atomic-number corrections generally stated a preference in the mean ionization potential to be used; those preferences were adhered to in this evaluation.

The Gaussian $\phi(\rho z)$ and Love-Scott and Sewell-Love-Scott corrections make use of backscatter coefficients and $\phi(0)$ expressions. The various coefficients tested are given in Table 1. Variation of these parameters typically does not significantly affect the absorption or atomic number corrections and the preferences of the various authors of the corrections were adhered to. In the Monte Carlo calculations, a critical parameter is the ionization cross section $Q(E)$. Expressions evaluated were those of Green and Cosslett, Worthington and Tomlin, Hutchins, Gryzinski, and Fabre as tabulated and referenced by Powell.²⁷ Significant differences were seen in the results depending on the $Q(E)$ and, as seen below, the data suggest that optimal $Q(E)$ expressions can be chosen for silicates. Finally, the tabulated mass absorption coefficients of Heinrich¹⁹ were used in the comparisons.

Measurements

Replicate analyses of a large series of oxide and silicate natural and synthetic mineral standards were performed on a five-crystal spectrometer JEOL 733 electron microprobe (take-off angle = 40°) at 10, 15, and 20 keV. Space does not permit inclusion of all of the data. Table 2 lists the compositions of selected primary and secondary standards used in this study. The accuracy of the accelerating potential was determined by careful EDS determination of the Duane Hunt limit. The absence of sample tilt effects was determined by the performance of replicate analyses with the samples rotated in different orientations. Samples were repolished, recoated, and reanalyzed to determine that there were no charging or surface-hydration artifacts. Correct background settings were determined by analysis of

METAL & OXIDE PRIMARY INTENSITY RATIOS

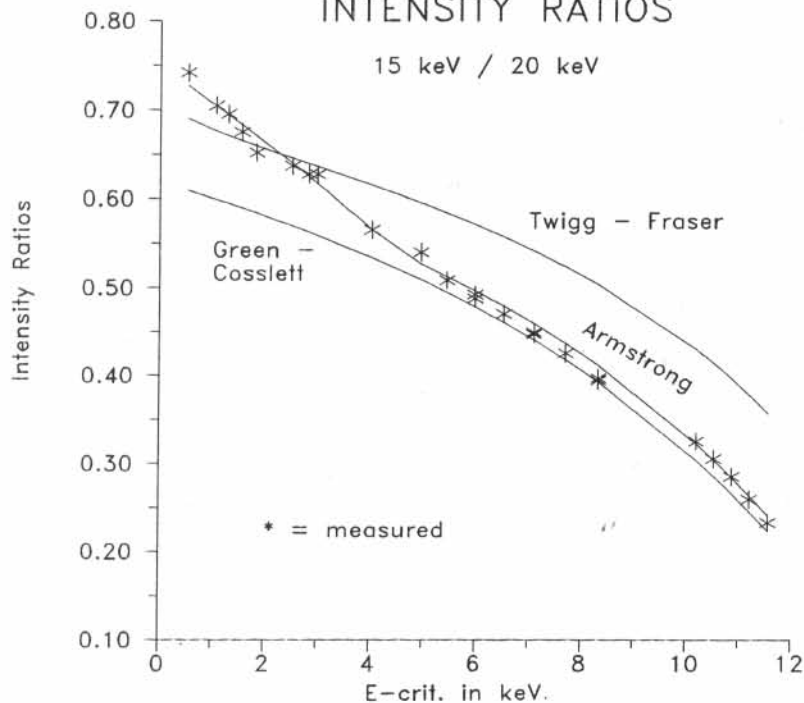


FIG. 2.--Plot of ratio of metal and oxide beam-normalized intensities (corrected for absorption) at 15 keV to those measured at 20 keV vs critical excitation potential. For high E_c , data approach equation of Green and Cosslett;²⁰ for low E_c equation of Twigg and Fraser.²¹ Equations (6) and (7) do better job of fitting data than either of above expressions.

"blank" standards, and deviations from zero background were less than 100 ppm. Deadtime was measured periodically on all spectrometers and determined reproducibly to 0.1 μ sec. Gain-shift artifacts were avoided as the output pulse energy for all elements was kept at 3 ± 0.08 V. Replicate analyses were performed at various beam currents (10-60 nA) to confirm that there were no artifacts due to counting nonlinearities or radiation damage.

Measurements were typically taken to a relative precision of 0.2%; only samples that appeared to be homogeneous at that level were considered. Effects of wavelength shift or peak shape changes for light elements were determined by repetitive high-precision wavelength scanning and peak integration. Small differences in the energy splitting between the $K\alpha_1$ and $K\alpha_2$ lines can result in significant differences in the ratio of the peak maximum to the net peak area for elements like Al and Si. The peak integration measurements made on the analyzed standards indicated that the maximum variation due to peak shape change was at or below the 1% relative level.

Elements were analyzed simultaneously with the same type of crystals on different spectrometers to check for geometry or crystal problems. Surprisingly, significant (1 to 2%) differences in k-ratios of sample to standard were detected for simultaneous analysis of Na, Mg, Al, and Si $K\alpha$ on three TAP-crystal spectrometers, and up to 5% differences were measured for Cu $L\alpha$ in Cu and 80% Au-20% Cu alloy. These differences follow the crystal when it is moved from one spectrometer to another. The measured values for a series of tested TAP crystals are almost bimodal, and the data given in this paper are from the most numerous set of crystals, the set that appears to agree most

closely with measurements made on other instruments. (The reason for this variability in crystal response is still under active investigation.)

Selected results of the analyses are given in Tables 3 to 5 and shown in Figs. 3 to 5. Tables 3 to 5 compare the analytical results with those calculated by the various Monte Carlo, ZAF, and $\phi(\rho z)$ corrections. The data are presented as the ratio of concentration relative to the standard divided by the intensity relative to the standard; i.e., $(C/K)_{\text{sample}} / (C/K)_{\text{standard}}$. The measured data for Fe and Ni has been back-corrected for fluorescence by the continuum, by use of the correction of Henoc et al.²² As can be seen in the tables, there is a significant difference in the accuracy of the different correction procedures; the mean error for the corrections tested varies by over a factor of 5. At 15 keV, the corrections that agree best with the experimental data are the Armstrong-Duncumb/Reed, Armstrong-Love/Scott, and Love-Scott corrections, with mean relative errors of 0.5-0.6%. Next best are the Philibert-Duncumb/Reed ZAF correction and the Monte Carlo multiple scattering corrections with the Hutchins, Fabre, and Gryzinski $Q(E)$ expressions, which have mean relative errors of 0.8 to 0.9%. Following them are the Sewell-Love/Scott, NBS COR2 (Philibert-Philibert/Tixier), and Monte Carlo-Green/Cosslett expressions with mean relative errors of 1.1-1.3%. Trailing the list are the $\phi(\rho z)$ corrections of Packwood and Brown, Bastin (I and II), and the Riveros and the Monte Carlo-Worthington/Tomlin expression with mean relative errors of 1.5-2.5%. The data shows that several of the corrections diverge from the measured data in higher-Z matrices.

TABLE 2.--Compositions of analyzed standards.

A. Primary standards (oxide wt %)

Elem	Std	MgO	Al2O3	SiO2	CaO	MnO	FeO	NiO	Total
Mg	MgO	100.0							100.0
Al	Kyan		62.78	37.07			0.13		100.0
Si	Qtz			100.0					100.0
Ca	Wo	0.04	0.08	51.69	48.17		0.02		100.0
Fe	Fa			29.49			70.51		100.0
Ni	NiO							100.0	100.0

B. Secondary standards (oxide wt %)

Std	MgO	Al2O3	SiO2	CaO	MnO	FeO	NiO	Total
Cor		100.0						100.0
Mel	14.79		44.08	41.13			0.01	100.0
Anor		36.65	43.19	20.16				100.0
Gros		22.63	40.02	37.35				100.0
Fo	57.30		42.70					100.0
Oliv	51.63		40.85		0.07	7.23	0.30	100.1
NiOl			28.68				71.32	100.0

TABLE 3.--Analytical results at 15 keV: (C/K)_{smp}/(C/K)_{std}.

	Mg in		Al in			Si in				
	Fo	Oliv	Me	Cor	Anor	Gros	Wo	Me	Gros	Anor
Measured:	1.044	1.119	1.179	0.981	1.047	1.058	1.026	1.080	1.114	1.172
Correction										
MCms-Hu			1.173	0.990	1.031		1.026	1.080		1.183
MCms-Fa			1.177	0.990	1.032		1.026	1.082		1.186
MCms-Gz			1.180	0.990	1.032		1.027	1.082		1.187
MCms-GC			1.183	0.990	1.033		1.028	1.085		1.194
MCms-WT			1.188	0.989	1.034		1.030	1.088		1.199
Phil-DR	1.047	1.122	1.178	0.987	1.034	1.060	1.027	1.084	1.127	1.186
NBS-COR			1.194	0.988	1.040		1.039	1.095		1.191
Love-Sc	1.045	1.119	1.168	0.989	1.029	1.052	1.022	1.076	1.117	1.176
Sewl-LS	1.043	1.113	1.157	0.990	1.027	1.048	1.019	1.073	1.113	1.173
Arms-LS	1.044	1.119	1.172	0.990	1.031	1.055	1.026	1.078	1.118	1.173
Arms-DR	1.044	1.119	1.176	0.989	1.031	1.057	1.025	1.078	1.118	1.173
Pack-Br	1.042	1.106	1.140	0.990	1.018	1.031	0.995	1.050	1.090	1.153
Bast- I	1.044	1.120	1.157	0.995	1.018	1.033	1.003	1.062	1.109	1.179
Bast-II	1.044	1.118	1.150	0.995	1.016	1.028	0.998	1.058	1.105	1.176
Riveros	1.041	1.104	1.139	0.990	1.020	1.036	1.005	1.060	1.100	1.163
	Si in			Ca in			Fe in		Ni in	
	Fa	Oliv	Fo	Kyan	NiOl	Me	Gros	An	Oliv	NiOl
Measured:	1.202	1.232	1.230	1.284	1.297	1.002	1.005	1.015	1.077	1.050
Correction										
MCms-Hu	1.207			1.313		1.002		1.014		
MCms-Fa	1.212			1.318		1.002		1.015		
MCms-Gz	1.214			1.320		1.002		1.015		
MCms-GC	1.223			1.331		1.002		1.015		
MCms-WT	1.231			1.340		1.002		1.015		
Phil-DR	1.200	1.248	1.249	1.308	1.315	1.003	1.004	1.016	1.070	1.035
NBS-COR	1.231			1.307		1.003		1.014		
Love-Sc	1.194	1.236	1.237	1.298	1.301	1.004	1.005	1.017	1.085	1.041
Sewl-LS	1.163	1.234	1.237	1.297	1.244	1.004	1.005	1.019	1.086	1.041
Arms-LS	1.214	1.232	1.229	1.288	1.328	1.004	1.004	1.017	1.084	1.040
Arms-DR	1.207	1.230	1.229	1.288	1.319	1.003	1.004	1.014	1.069	1.035
Pack-Br	1.133	1.213	1.219	1.274	1.232	1.008	1.010	1.032	1.124	1.068
Bast- I	1.199	1.244	1.245	1.315	1.257	1.008	1.015	1.039	1.087	1.055
Bast-II	1.189	1.242	1.244	1.314	1.286	1.008	1.015	1.039	1.084	1.046
Riveros	1.139	1.222	1.231	1.286	1.234	1.005	1.007	1.022	1.086	1.032

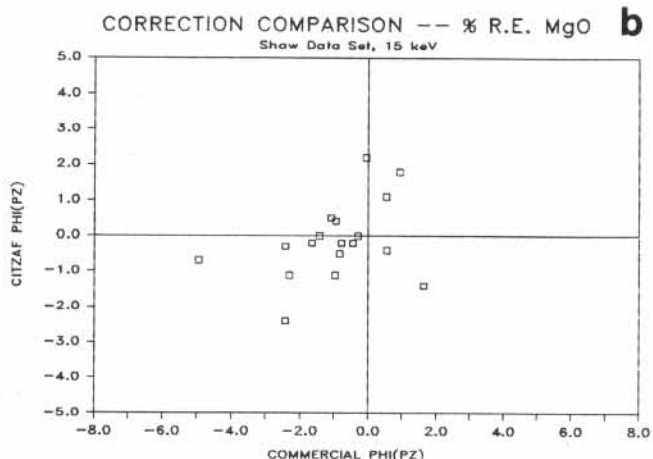
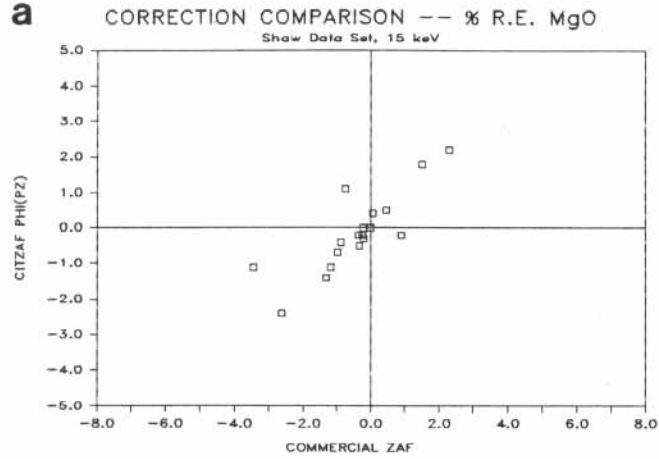


FIG. 3.--Plot of percentage relative errors for MgO in set of standard silicates and oxides based on Armstrong/Love-Scott correction procedure, CITZAF $\phi(\rho z)$, vs that based on (a) commercial ZAF program, (b) commercial $\phi(\rho z)$ program,

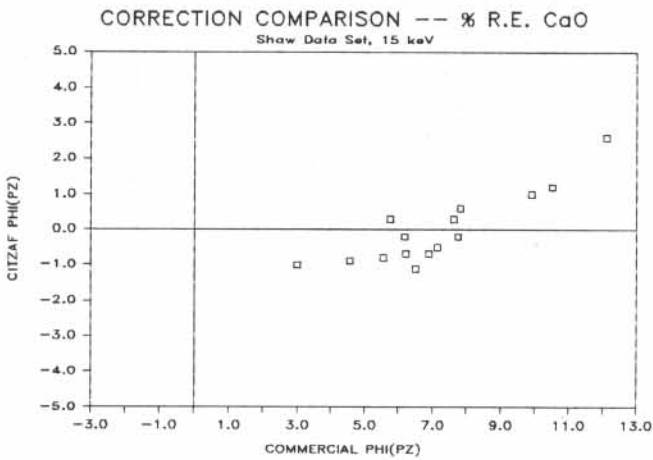
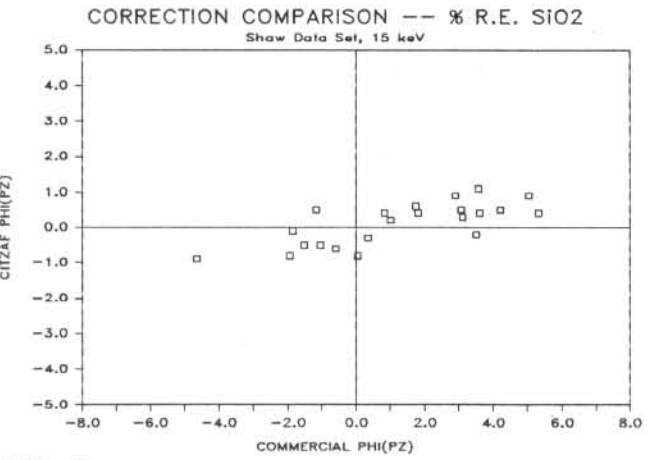
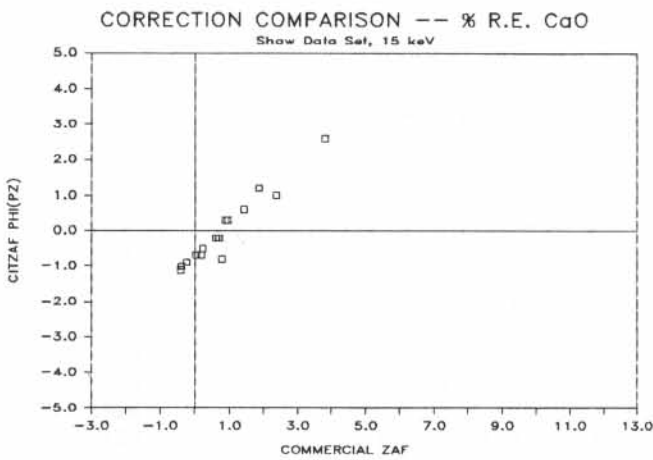
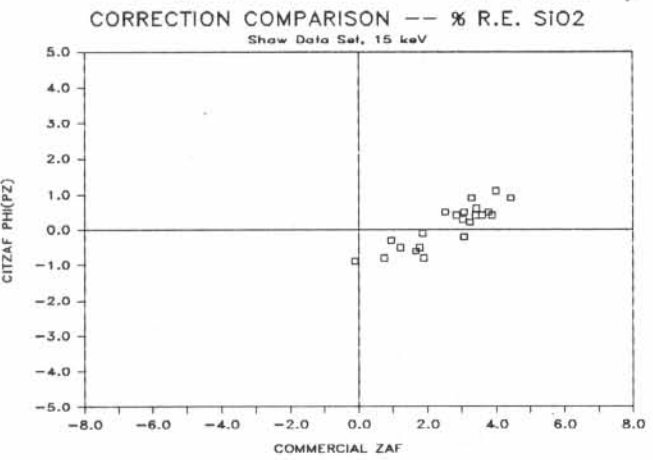


FIG. 4.--Same as Fig. 3, for SiO₂.

FIG. 5.--Same as Fig. 3, for CaO.

Figures 3 to 5 show the difference in mean percentage relative errors in the analyses of a series of Mg-Ca-Al-silicate standards processed with the Armstrong-Love/Scott correction and two commercial correction programs, one conventional ZAF and other $\phi(\rho z)$. The errors are much smaller for the Armstrong-Love/Scott correction than for either of the commercial programs. Indeed, the commercial programs perform worse than our evaluation of the

equations on which they are based, suggesting that some compromising parameterization has been used in these programs.

Conclusions

There are significant differences in the ability of the several ZAF, $\phi(\rho z)$, and Monte Carlo programs properly to correct analyses of silicate and oxide minerals. The corrections that appear to work best at present are the

TABLE 4.--Analytical results at 10 keV: (C/K)_{smp}/(C/K)_{std}.

	Mg in		Al in		Si in		Ca in			
	Me	Cor	Anor	Wo	Me	Anor	Fa	Kyan	Me	Anor
Measured:	1.090	0.986	1.039	0.999	1.025	1.066	1.054	1.134	1.008	1.012
Correction										
Phil-DR	1.088	0.992	1.015	1.004	1.036	1.091	1.067	1.156	1.003	1.012
Love-Sc	1.074	0.994	1.011	0.997	1.024	1.074	1.044	1.133	1.004	1.014
Sewl-LS	1.066	0.994	1.009	0.994	1.023	1.075	1.011	1.138	1.004	1.016
Arms-LS	1.080	0.994	1.012	0.999	1.027	1.077	1.059	1.136	1.004	1.015
Arms-DR	1.078	0.994	1.012	1.001	1.029	1.078	1.060	1.135	1.003	1.011
Pack-Br	1.054	0.994	1.001	0.973	1.004	1.063	0.996	1.130	1.007	1.025
Bast- I	1.060	1.001	0.998	0.978	1.010	1.079	1.047	1.154	1.008	1.033
Bast-II	1.056	1.001	0.997	0.975	1.008	1.077	1.044	1.154	1.008	1.032
Riveros	1.060	0.994	1.005	0.987	1.017	1.072	1.015	1.137	1.004	1.014

TABLE 5.--Analytical results at 20 keV: (C/K)_{smp}/(C/K)_{std}.

	Mg in		Al in		Si in		Ca in			
	Me	Cor	Anor	Wo	Me	Anor	Fa	Kyan	Me	Anor
Measured:	1.283	0.976	1.056	1.052	1.140	1.304	1.341	1.482	1.005	1.028
Correction										
Phil-DR	1.262	0.981	1.052	1.057	1.142	1.294	1.365	1.478	1.004	1.023
Love-Sc	1.271	0.983	1.050	1.051	1.138	1.304	1.377	1.510	1.004	1.024
Sewl-LS	1.259	0.984	1.047	1.046	1.132	1.296	1.342	1.502	1.005	1.026
Arms-LS	1.271	0.984	1.051	1.054	1.137	1.288	1.400	1.474	1.004	1.022
Arms-DR	1.275	0.984	1.052	1.058	1.140	1.290	1.405	1.474	1.004	1.020
Pack-Br	1.234	0.985	1.037	1.022	1.104	1.261	1.299	1.450	1.008	1.039
Bast- I	1.261	0.989	1.039	1.033	1.123	1.299	1.383	1.513	1.009	1.046
Bast-II	1.236	0.989	1.036	1.026	1.117	1.295	1.366	1.512	1.009	1.047
Riveros	1.224	0.985	1.037	1.028	1.112	1.271	1.290	1.465	1.008	1.031

Armstrong-Duncumb/Reed, Armstrong-Love/Scott, and Love/Scott corrections. Those that work worst are a series of $\phi(\rho z)$ expressions optimized for metal analyses, at least when they are used for both the absorption and atomic-number corrections. A simple Monte Carlo multiple scattering model works well in correcting for absorption and atomic-number effects in silicates (when the ionization cross section expressions of Fabre, Gryzinski, or Hutchins are employed), although not quite as well as the best ZAF or $\phi(\rho z)$ corrections.

The characteristic fluorescence correction of Reed significantly underestimates the amount of fluorescence produced in the lighter elements in silicates, although the magnitude of the error is usually not significant, since the amount of actual fluorescence is still small. The Reed equation can be easily modified to correct most of the underestimation. Finally, although the amount of fluorescence by the continuum of lines of energy less than that for Ti $K\alpha$ is negligible in most silicates, the continuum fluorescence correction can be significant for the higher energy lines, such as Fe and Ni $K\alpha$, and should be evaluated.

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