THE AMERICAN MINERALOGIST, VOL. 56, NOVEMBER–DECEMBER, 1971

IMPROVED ELECTRON MICROPROBE ANALYSIS AT LOW OPERATING VOLTAGE: I. SILICON, MAGNESIUM AND ALUMINUM[1]

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ABSTRACT

Quantitative electron microprobe analysis of Si, Mg, and Al in silicates and light-element oxides demonstrates that theoretical and empirical corrections commonly applied to these elements for operating voltages of 15 kV are significantly reduced or virtually eliminated for these elements by using much lower operating voltages.

INTRODUCTION

For a variety of common rock-forming silicates we show that at an operating voltage of 6 kV, the relationship, counts/weight percent, for Si, Mg, and Al is virtually constant over a wide concentration range within the limitations of sample homogeneity and overall precision.

Many investigations of geologic materials, as well as ceramic studies, deal chiefly with silicates or glasses where SiO_2 is the major constituent and is combined with elements of atomic number 26 (Fe) or lower which are present as major or minor constituents. Typically in quantitative microprobe studies of silicate minerals and glasses, an operating voltage of 15 or 20 kV is used (Smith, 1965; Knowles *et al.*, 1969; Beaman and Isasi, 1970; Albee and Ray, 1970) even though the K_α excitation potential of Fe, the element with the highest atomic number routinely studied, is 7.1 kV. Smith (1965), in early studies of experimental techniques of quantitative electron microprobe analysis of rock-forming minerals, generally used an operating voltage of 15 kV. In most later analytical studies performed in his laboratory, a 15-kV operating voltage was also used for determination of concentrations of major elements ($Z=11$–26) (Smith, 1966a, 1966b; Smith and Ribbe, 1966; Ribbe and Smith, 1966; Howie and Smith, 1966). An operating voltage of 15 kV has been generally adopted as standard for quantitative electron microprobe analysis of silicates, as indicated by the survey of Beaman and Isasi (1970).

Selection of operating voltage is presumably based on optimizing counting rates for maximum precision while minimizing absorption and fluorescence effects; the latter two generally increase with the increasing operating voltage. In all quantitative analysis, the concentration of an element in the unknown material is determined by comparing the X-ray intensity of a standard with that of an unknown, thus determining the measured X-ray intensity ratio, k. This determination is the first approximation upon which all subsequent corrections are based; therefore,

[1] Publication authorized by the Director, U. S. Geological Survey.

this first approximation is critical. When standards are used whose elemental concentrations are very similar to those of the unknowns, the first approximation, based on *k*, is generally considered to produce a satisfactory final result for the unknown. However, for operating conditions of 15 kV and above, the first approximation is virtually never satisfactory as a final result when standards and unknowns differ significantly in composition. In the latter case, which is common to many electron microprobe laboratories, sophisticated computer corrections have been developed to determine the 'true' concentration in the unknown by corrections applied to the first approximation (Beaman and Isasi, 1970).

Divergence in philosophy of selection of reference standards is extreme. Some analysts believe it is essential to have an extensive collection of standards for the study of common rock-forming silicates; ideally, this should consist of suites of well-analyzed mineral groups (*e.g.*, garnets, feldspars, olivines, pyroxenes, etc.) as in the case of Smith's and associates studies cited previously. On the other hand, Bence and Albee (1968) and Albee and Ray (1970) use analytically well-known, but simple oxides (*e.g.*, Mg_2SiO_4, $FeSiO_3$, etc.) as standards. Albee and Ray (1970) have recently presented new correction factors for use of such standards at operating voltages of 15 and 20 kV in analysis of oxides, carbonates, phosphates, and sulfates. Obtaining homogeneous standards of appropriate composition is expensive and time-consuming, and it requires a major effort for each electron microprobe laboratory. It is almost impossible to have standards similar to all the unknown materials to be analyzed, and only the best equipped and well-staffed laboratories can even afford to strive for this position. To circumvent these limitations we reduce the magnitude of corrections applied to the first approximation of line intensity by selection of operating voltages, according to the element(s) being determined.

Experimental Methods

A three-spectrometer, A.R.L. (Applied Research Laboratories, Inc.) electron microprobe equipped with LiF/ADP, LiF/ADP, and ADP/KAP analyzing crystals and utilizing two sealed proportional counters and one flow counter was used for the present study. The same spectrometer was used for a given element at different operating voltages. Fixed-beam current termination was used with a counting time of 10.0 ± 0.5 seconds for each observation. Sample current was referenced on benitoite, and a 5-micron-diameter electron beam was used. Twenty reference materials, consisting of Al_2O_3, MgO, SiO_2, and chemically well-known silicate minerals and glasses, were analyzed at operating votlages of 15 kV, 10 kV, and 6 kV. Except for MgO and Al_2O_3, these materials are listed on Figure 1.

	15 kV and 10 kV, 2×10^{-8} A			6 kV, 4×10^{-8} A		
Spect. No.	1	2	3	1	2	3
	$Fe_{K\alpha}$-LiF	$Al_{K\alpha}$-ADP	$Mg_{K\alpha}$-KAP	$Ca_{K\alpha}$-LiF	$Si_{K\alpha}$-ADP	$Mg_{K\alpha}$-KAP
	$Ca_{K\alpha}$-LiF	$Si_{K\alpha}$-ADP	$Mg_{K\alpha}$-KAP	$Si_{K\alpha}$-ADP	$Al_{K\alpha}$-ADP	$Mg_{K\alpha}$-KAP

Using the relationship S = counts/weight-percent concentration, as a measure of sensitivity, one can evaluate the magnitude of absorption, atomic number, and fluorescence effects for a sample at different voltages. The constancy of S for an element in a series of samples for a particular operating voltage is, of course, indicative of the linearity of the relationship between element concentration and X-ray intensity.

X-ray intensity for each element in the samples is based on averaged counts from 10 observations at different points. The estimate of precision, which is calculated from the standard deviation, includes sources of variation such as sample inhomogeneity as well as counting error.

Table 1.--Typical X-ray intensity (counts)-versus-concentration data for SiO_2, MgO, and Al_2O_3 in silicates and oxides at operating voltages of 15, 10, and 6 kV. (Average counts per weight percent oxide--$\bar{S}$, σ, and CV (coefficient of variation) combine count data for all samples. C_{DL} refers to minimum detection limits in parts per million (ppm), at the 99-percent confidence level.)

15 kV				10 kV				6 kV			
SiO_2											
$\bar{S}$ cts. per %	σ	CV	C_{DL} (ppm)	$\bar{S}$ cts. per %	σ	CV	C_{DL} (ppm)	$\bar{S}$ cts. per %	σ	CV	C_{DL} (ppm)
346.4	23.5	6.45	339±192	205.6	7.06	3.43	565±305	158.7	4.4	2.77	908±500
σ at 100% SiO_2 = 0.62				σ at 100% SiO_2 = 0.73				σ at 100% SiO_2 = 1.0			
MgO											
$\bar{S}$ cts. per %	σ	CV	C_{DL} (ppm)	$\bar{S}$ cts. per %	σ	CV	C_{DL} (ppm)	$\bar{S}$ cts. per %	σ	CV	C_{DL} (ppm)
461.4	40.8	8.84	491±250	328.1	10.8	3.29	514±342	307.7	11.3	3.67	709±363
σ at 100% MgO = 0.46				σ at 100% MgO = 0.52				σ at 100% MgO = 0.45			
Al_2O_3											
$\bar{S}$ cts. per %	σ	CV	C_{DL} (ppm)	$\bar{S}$ cts. per %	σ	CV	C_{DL} (ppm)	$\bar{S}$ cts. per %	σ	CV	C_{DL} (ppm)
239.0	14.6	6.1	816±432	137.8	4.5	3.27	1009±539	127.4	2.5	1.96	1111±604
σ at 100% Al_2O_3 = 1.05				σ at 100% Al_2O_3 = 1.01				σ at 100% Al_2O_3 = 1.38			

RESULTS

Table 1 presents typical results for SiO_2, MgO, and Al_2O_3. $\bar{S}$ is the average of sensitivities for all sample concentrations of each oxide, σ is the standard deviation, CV the coefficient of variation, and C_{DL} the minimum detectability level at 3 σ above background (99 percent confidence level). The σ at 100 percent indicated for SiO_2, MgO, and Al_2O_3 is listed in Table 1 for determination of precision and accuracy, and is based entirely on each series of 10 observations taken on the pure oxides. In general, we note that precision is slightly better at 15 kV, compared to the lower operating voltages, but rarely is the same σ obtained for the same sample during different periods of analysis. Six separate series of

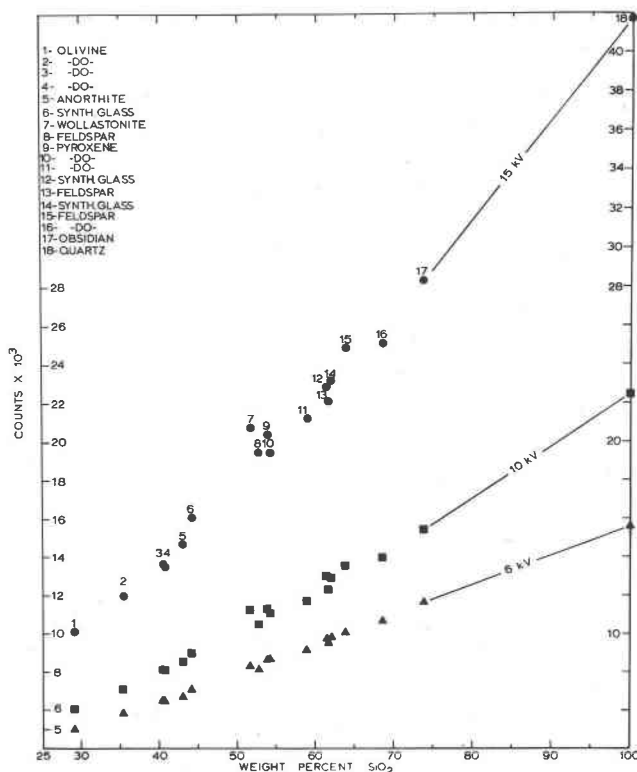

FIG. 1. Concentration of SiO_2 versus X-ray intensity (net counts) for 18 samples analyzed at 15, 10, and 6 kV, respectively. Size of data points is greater than 2 σ (95% confidence).

analysis of Si taken on quartz at 6 kV over a period of 2 months produced σ for SiO_2 ranging from 0.5–1.1 and averaging 0.86 weight percent.

Figure 1 presents the average background-corrected counts versus the weight percent SiO_2 reported chemically for each of 18 samples which range from 29.24 to 100 weight percent SiO_2. Count data for each point are corrected only for background, which did not exceed 25 counts in any series of determinations. We have chosen to evaluate linearity, or constancy of S, at the three operating voltages in terms of coefficient of variation—CV. We assume, therefore, that the lowest coefficient of variation indicates maximum linearity. Inspection of Figure 1 and evaluation of the SiO_2 data in Table 1 reveal that at 6 and 10 kV, the counts versus weight percent relationship is significantly more linear than at 15 kV. Deviation(s) from linearity at 15 kV are attributed chiefly to mass absorption effects. Average atomic number ($\overline{Z}$) versus counts/weight

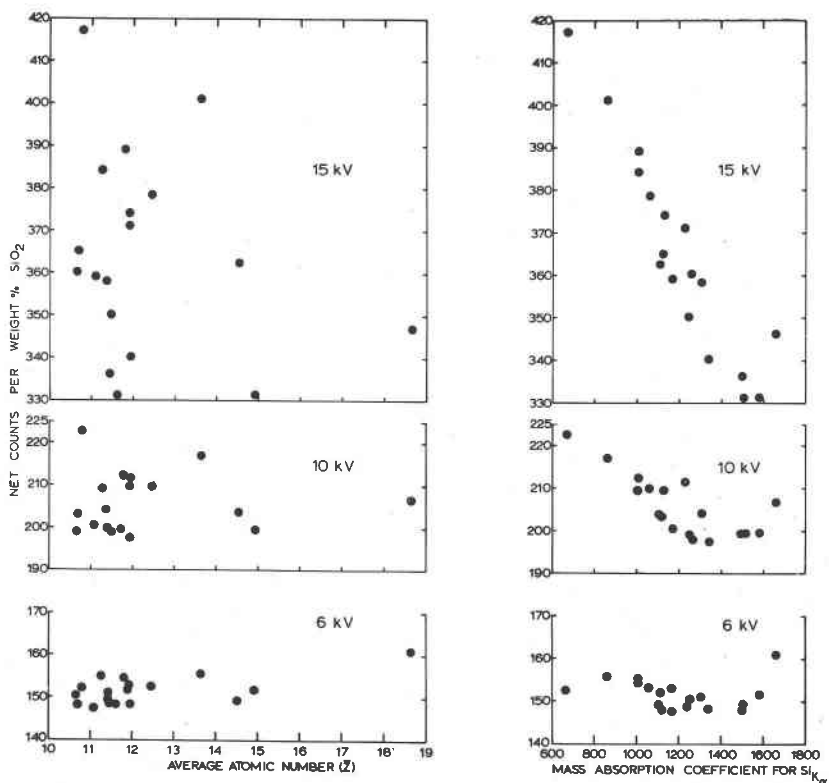

FIG. 2a (left). Average atomic number ($\bar{Z}$) versus net counts per weight percent SiO_2 for 18 samples analyzed at 15, 10, and 6 kV. Size of data points is greater than 2 σ (95% confidence).

Fig. 2b (right). Mass absorption coefficient (μ/ρ) for $Si_{K\alpha}$ versus net counts per weight percent SiO_2 for 18 samples, analyzed at 15, 10, and 6 kV. Size of data points is greater than 2 σ (95% confidence).

percent for each sample and mass absorption coefficient ($\bar{\mu}/\bar{\rho}$) versus counts/weight percent for each sample, at each operating voltage, are shown on Figures 2a and 2b. At 15 kV, counts/weight percent SiO_2 for the samples is influenced appreciably by mass absorption effects; the lowest values correspond to samples with highest $\bar{\mu}/\bar{\rho}$. However, at 6 kV, counts/weight percent show no apparent dependence on either $\bar{Z}$ or $\bar{\mu}/\bar{\rho}$. We believe this demonstrates that, at the lower operating voltages, the major correction (mass absorption coefficient) of X-ray intensity data for Si in silicates may be significantly reduced or virtually eliminated.

Variations of X-ray intensity output at 15, 10, and 6 kV for MgO in

nine samples ranging from 3.89 to 100 weight percent are summarized in Table 1. These samples consisted of three synthetic glasses, two pyroxenes, three olivines, and periclase. The same conclusion is reached for MgO as for SiO_2—specifically, that the linearity of X-ray intensity versus concentration is significantly improved at 10 kV and at 6 kV. Appreciable deviations from linearity at both 15 and 10 kV are chiefly the result of the influence of mass absorption variation (proved by graphical methods but not illustrated here). At 6 kV the small deviations from linearity show no apparent dependence on either mass absorption or atomic number effects.

The relationships of Al_2O_3 concentration to X-ray intensity output for 15, 10, and 6 kV were determined in the same manner as those for SiO_2 and MgO. Ten samples, consisting of two synthetic glasses, one obsidian, five feldspars, one pyroxene, and one corundum, were used. These ranged in concentration from 4.36 to 100 weight percent Al_2O_3. Examination of the data in Table 1 reveals that the linearity of X-ray intensity versus concentration increases with decreasing voltage. Deviations from linearity at 15 and 10 kV have been shown to result almost entirely from mass absorption effects.

Ten samples listed on Fig. 1 with a concentration range of 1.72 to 67.57 weight percent FeO, and seven samples containing 5.00 to 47.84 percent CaO have coefficients of variation for $\overline{S}$ for Fe and Ca showing linearity regardless of the operating conditions used; *i.e.*, for 15, 10, and 6 kV.

The obvious advantage in the use of low operating voltage is the linearity obtained. Comparisons are particularly compelling for important light elements such as Al, Mg, and Si for which mass absorption effects are most significant. Low operating voltages could eliminate the need for many standards. The collection of scattered X-rays from adjacent materials is also reduced and increased filament life results when using lower voltages. Sampling of a smaller volume because of decreased penetration of the electron beam, at lower operating voltage, may be either an advantage or disadvantage depending upon whether the material to be analyzed is small and is underlain by other phases, or whether it is large and homogeneous.

Disadvantages in the use of low operating voltage are a low detection limit and a lower count rate with greater time required to obtain satisfactory counting precision.

ACKNOWLEDGMENTS

We are grateful to J. M. Tripp for computer data reduction, and we thank D. R. Beaman, A. Chodos, G. K. Czamanske, K. F. J. Heinrich, and G. A. Izett for critical reviews.

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Manuscript received, May 21, 1971; accepted for publication, May 27, 1971.