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ANALYTICAL ELECTRON MICROSCOPY AND THE PROBLEM OF POTASSIUM DIFFUSION[1]

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Abstract—Diffusion of K during analytical electron microscopy (AEM) results in anomalously low count rates for this element. As the analysis area and specimen thickness decrease, count rates become disproportionally lower. Adularia and muscovite show different diffusion profiles during AEM; for muscovite a strong dependence of diffusion on crystallographic orientation has been observed. Conditions giving rise to reliable chemical data by AEM are the use of a wide scanning area (>800 × 800 Å) and/or large beam size to reduce the effect of diffusion of alkali elements, a specimen thickness greater than about 1000 Å, constant instrument operating conditions, and the use of a homogeneous, well-characterized standard sample. The optimum thickness range was obtained by determining the element intensity ratio vs. thickness curve for given operating conditions. The standard and unknown should have a similar crystal structure and, especially for strongly anisotropic minerals such as phyllosilicates, a similar crystallographic orientation with respect to the electron beam.

Key Words—Adularia, Analytical electron microscopy, Diffusion, Muscovite, Potassium, Transmission electron microscopy.

INTRODUCTION

The diffusion of alkali elements, such as Na and K, may cause significant analytical problems in the electron microprobe analysis of geological specimens (see, e.g., Craw, 1981). Conventional scanning-transmission electron microscopy (STEM), which utilizes much higher voltages (100–200 kV) than electron microprobe analysis (15–20 kV) has the same problem (see, e.g., Knipe, 1979; Lee *et al.*, 1986), but the factors affecting the accuracy of the analytical data are less well known. Ahn *et al.* (1986) showed that alkali element concentrations of micas change significantly during exposure to the electron beam. The effect was particularly marked in Na- and K-muscovites and gave rise to characteristic mottled or fissured textures. Similar effects were observed by Knipe (1979). White and Johnston (1981), on the other hand, observed little or no evidence for K diffusion in their study of cleavage lamellae in slates.

In the course of routine analytical electron microscopy (AEM) of illite and other phyllosilicates in shales and slates, anomalously low K/Si intensity ratios were encountered relative to those predicted from Si/Al ratios, especially if a very small diameter electron beam was used. Because such ratios may lead to gross inaccuracy in element determinations, the relationships between element intensity ratio and beam size and other related variables were therefore investigated to determine optimal operating conditions for elemental analysis.

In this paper the problems associated with AEM analysis for K in silicates are presented, especially the variation of results as a function of the size of the analysis area, the specimen thickness, and the crystallographic orientation of the sample with respect to the electron beam. Standardless analyses were carried out, and, hence, the results are interpreted only in terms of the relative variation in element ratios. A preferred procedure for obtaining accurate data is also presented.

METHOD

A JEOL JEM-100CX scanning-transmission electron microscope (STEM) equipped with a horizontally mounted, solid-state, energy-dispersive X-ray spectroscopy (EDX) detector was used for this study. The instrument was intensively modified to optimize the resolution and accuracy of the analytical data (for details, see Blake *et al.*, 1980; Allard and Blake, 1982). The X-ray spatial resolution of the instrument as determined by Isaacs *et al.* (1981) was reported to be ~300 Å in the spot-count mode for conditions similar to those used in this study.

After preparation of a petrographic thin section for optical and electron microprobe examination, a 3-mm thick Al retaining washer was glued to the thin section and then detached from the slide glass with the sample attached. The sample was then ion-thinned using an ion mill and coated with a layer of carbon. It was then mounted in a graphite boat and placed in a copper specimen holder. Ion thinning gave rise to a thickness gradient varying from thin-section thickness (about 30 μm) at the outer diameter to very thin edges (<1000 Å) near the hole at the center. Counts obtained from

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Table 1. Bulk wet chemical data (1) and recalculated wet chemical data (2) in %-oxides for the muscovite samples used in this study.[1]

Bulk wet chemical data (1) and recalculated wet chemical data (2) in %-oxides for the muscovite samples used in this study.	(1)	(2)
SiO_2	46.30	48.87
Al_2O_3	31.80	33.56
Fe_2O_3	3.68	3.88
MgO	0.83	0.88
CaO	0.13	0.14
Na_2O	0.98	1.03
K_2O	10.60	11.19
TiO_2	0.46	0.49
H_2O	5.39	
Total	100.14	

[1] Wet chemical data from R. J. Knipe, University of Leeds, Leeds, United Kingdom, personal communication 1983.

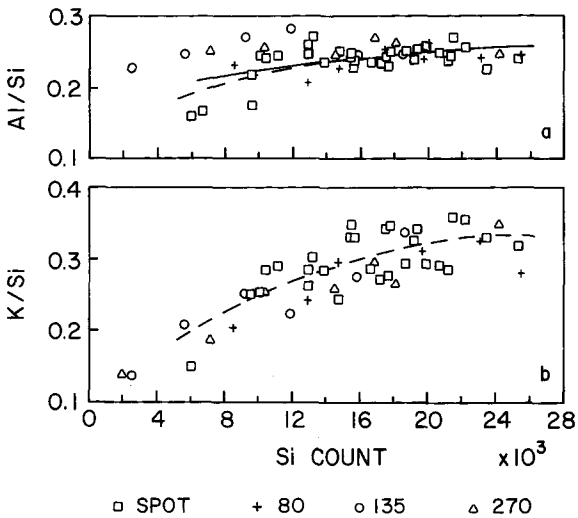


Figure 1. Intensity ratios of (a) Al/Si and (b) K/Si vs. total Si count in Gotthard adularia; total Si count is a measure of foil thickness, but is also dependent on the analysis size area. Four analysis size areas are plotted: spot, 800 × 800, 1350 × 1350, and 2700 × 2700 Å. The dashed and continuous lines are the best-fit, second-order polynomials for the spot mode and 800 × 800 Å size area, respectively. See text for discussion.

traverses over this gradient correspond to thin-film, non-ZAF conditions to thick areas requiring substantial ZAF corrections. The sample was placed inside the STEM column so that the Al-washer side of the sample faced away from the beam in order to avoid beam-washer interaction. The sample was tilted toward the X-ray detector by 40° for analysis, and beam conditions of 100 kV and 100-μA emission current were obtained using a W filament for the adularia data and a LaB_6 filament for the muscovite data. The fixed #1 condenser lens (CL1) was modified as described in Allard and Blake (1982), and the current was set manually at 170 mA for all analyses to enhance the count rate. A thick CL2 aperture of 200-μm diameter and a removable 'hard X-ray' aperture were used. These instrumental conditions were maintained throughout all analyses. Spectra were accumulated for 100 and 150 s for adularia and muscovite, respectively, using three different scanning areas, 2700 × 2700, 1350 × 1350, and 800 × 800 Å, and the spot mode. The spectra were mathematically filtered for background subtraction, which, at the light end of the spectrum, often led to determinations that did not produce meaningful peaks.

Two silicates (adularia and muscovite) having different crystal structures but which contain major amounts of the elements under consideration (i.e., K, Al, and Si) were used for this study. Adularia ($KAlSi_3O_8$), which is homogeneous in composition as determined by electron microprobe analysis, has been used as a standard for AEM analysis of K and Al in several previous studies (e.g., Ahn and Peacor, 1986; Lee *et al.*, 1986). For the present study, traverses were made from thin edges toward thick areas (thickness ≤ 0.4 μm) in the same specimen. The role of the crystallographic orientation in the analytical procedure was examined using muscovite. In Table 1, the wet chemical analysis and recalculated wet chemical analysis of the muscovite sample are given. From these data a K/Si ratio of 0.3 and an Al/Si ratio of 0.8 were obtained. Two samples were prepared, in which the muscovite basal planes were parallel and perpendicular to the specimen surface, respectively. Parallel traverses using different analysis size areas were made from thin to thick edges, as for adularia.

Because silicates are the most abundant group of minerals, intensity ratios for the emission lines of given elements to that of Si are most often used in AEM studies. This ratio is a linear function of the weight fraction ratio (Cliff and Lorimer, 1975; Lorimer, 1987) within the limits in which the "thin film" criterion applies and, thus, in which ZAF effects are insignificant (Goldstein *et al.*, 1977).

In the present study ratios of intensity of a given element to that of Si were used, rather than the inverse values as used by Cliff and Lorimer (1975). Furthermore, for convenience the molecular ratio of the element (E) analyzed relative to that of Si was used, rather than the weight fraction ratio. These modifications provided a direct measure of the relative number of atoms in the chemical formula of the mineral analyzed. The standard ratio of Cliff and Lorimer (1975), k, which is calculated using the following equation:

$$k_{(E,Si)} = \frac{C_E}{C_{Si}} \cdot \frac{I_{Si}}{I_E}$$

was thus modified to be k′:

$$k'_{(E,Si)} = \frac{M_{Si}}{M_E} \cdot \frac{I_E}{I_{Si}},$$

where C_E/C_{Si} = weight fraction ratio, I_{Si}/I_E = intensity

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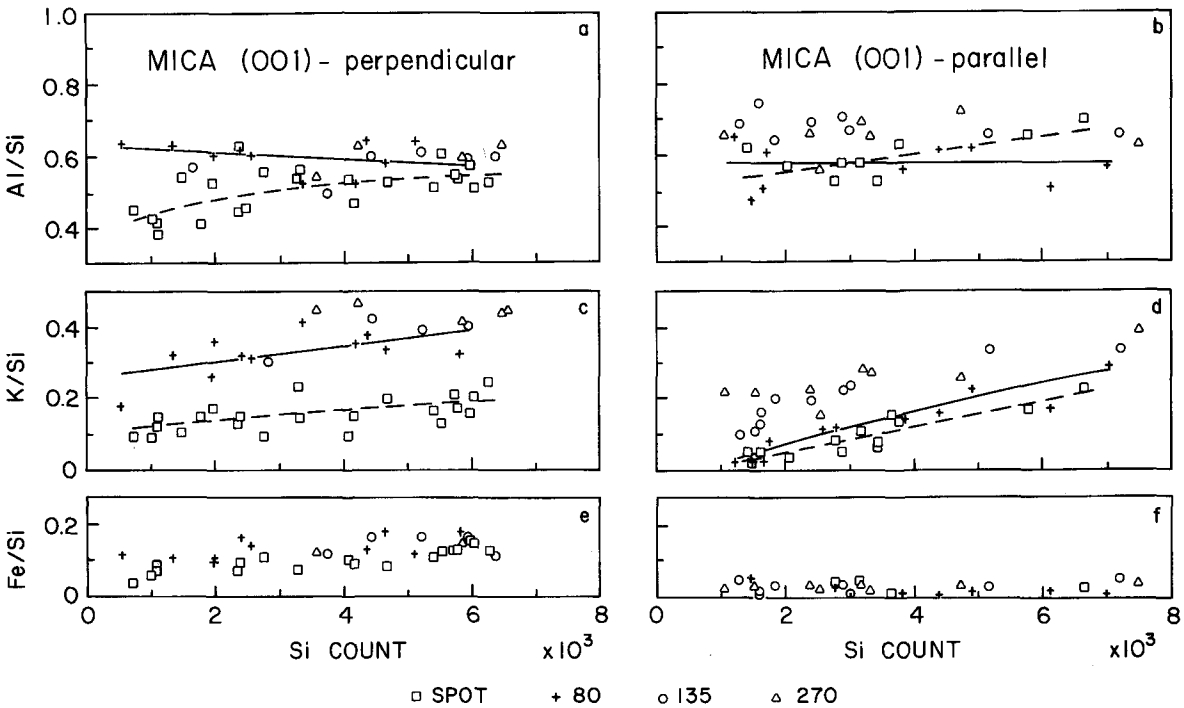


Figure 2. Intensity ratios of (a, b) Al/Si, (c, d) K/Si and (e, f) Fe/Si vs. total Si count as a measure of foil thickness in two muscovite samples. In (a), (c), and (e) the muscovite basal planes were oriented perpendicular to the foil surface; in (b), (d), and (f) the (001) planes were parallel to the foil surface. Same analysis size areas as in Figure 1. The dashed and continuous lines are best-fit, first- or second-order polynomials for the spot mode and 800 × 800 Å size area, respectively. See text for discussion.

ratio calculated after subtracting background from both peak profiles, and M_{Si}/M_E = mole ratio.

The K/Si and Al/Si intensity ratios for both minerals and the Fe/Si ratio for muscovite were plotted as a function of total Si counts (Figures 1 and 2); in Table 2 the observed ranges and associated k′ and k values are listed. The Si count rate was chosen because, to a first approximation, it is proportional to the volume of excitation and, thus, to the thickness of a given material if other conditions are constant, and because total Si counts could be easily monitored during the analysis procedure. Note that because analyses from different size areas were combined in the plots, the total Si counts are not representative of a single specimen thickness.

RESULTS

Adularia

Figure 1 shows the change in Al/Si and K/Si intensity ratios with increasing specimen thickness (as a function of total Si count) for four different sizes of the analysis area. The measured intensity ratios of Al/Si in the three analysis size areas (800 × 800, 1350 × 1350, 2700 × 2700 Å; Figure 1a) generally ranged from 0.22 to 0.26; however, in the spot mode (beam diameter ~25 Å and

Table 2. Calculated k′ and k values from E/Si ratios of adularia and muscovite.

Sample[2]	I_K/I_{Si}	k′	k	I_{Al}/I_{Si}	k′	k
Adularia (spot)	0.33–0.15	0.99–0.45	1.01–2.22	0.25–0.17	0.75–0.51	1.33–1.96
Adularia (800 × 800 Å)	0.32–0.20	0.96–0.60	1.04–1.67	0.26–0.22	0.78–0.66	1.28–1.52
Mica-perp (spot)	0.19–0.10	0.65–0.34	1.54–2.92	0.55–0.40	0.68–0.49	1.48–2.04
Mica-perp (800 × 800 Å)	0.35–0.18	1.20–0.62	0.84–1.62	0.57–0.62	0.70–0.76	1.43–1.31
Mica-par (spot)	0.23–0.03	0.79–0.10	1.27–9.75	0.65–0.55	0.77–0.68	1.29–1.48
Mica-par (800 × 800 Å)	0.28–0.03	0.96–0.10	1.04–9.75	0.57–0.56	0.70–0.69	1.43–1.45

[1] Spot-mode data from the 800 × 800 Å analysis size area in Figures 1 and 2. At optimal operating conditions for analytical electron microscopy analysis the k values for Al/Si and K/Si are about 1.4 and 1.0, respectively, in excellent agreement with other published k values (e.g., Lorimer and Cliff, 1976).

[2] Mica-perp = oriented perpendicular to (001). Mica-par = oriented parallel to (001).

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X-ray spatial resolution ~300 Å), they were considerably smaller at low Si counts. The latter corresponded to the thinnest parts of the sample. The values increased from 0.17 to 0.25 at total Si counts of 11,000, but were constant at higher counts. These data indicate that the diffusion of Al generally was not significant for determinations in the area count modes. Only in the spot mode was a minor, but detectable, loss of Al noted.

In contrast, the K/Si intensity ratio (Figure 1b) varied markedly as a function of specimen thickness for determinations in the spot as well as the area count modes. In the thinnest portions of the foil the K/Si ratios were as low as 0.15, but with increasing thickness (i.e., Si counts >15,000) they leveled out at about 0.3, with a relatively large scatter of data points. No significant difference was observed in element intensity ratios after 30- and 100-s counting periods for measurements made in the spot mode, implying that the diffusion of K was so fast that it was largely completed during the early stages of counting. Finally, the K data points in Figure 1 are scattered over a much larger area than those for Al, which reflects the greater diffusion of K relative to Al, as is well known from electron microprobe analyses.

Muscovite

The data for the mica specimen are compiled in Figure 2. Muscovite samples having their basal planes oriented (1) perpendicular (a, c, e) and (2) parallel (b, d, f) to the specimen surface were prepared to examine the effect of crystallographic orientation in strongly layered minerals on element diffusion. These configurations are referred to below as (001)-perpendicular and (001)-parallel orientations, respectively. Note that in most slate and shale studies the muscovite basal planes have been typically oriented at a high angle to the sample surface in order to observe deformation microstructures and interlayering (e.g., White and Knipe, 1978; Lee *et al.*, 1986). During the analysis of the muscovite the characteristic mottling effect of micas was observed as a result of beam interaction; this mottling effect has been associated with diffusion of K by Ahn *et al.* (1986).

Similar trends of Al/Si ratios were observed for both the (001)-perpendicular and (001)-parallel muscovite. Only in the spot mode of samples in which the mica basal planes were oriented perpendicular to the specimen surface were low Al/Si ratios found (0.40; Figure 2a). These limited data, however, did not allow the significance of the Al diffusion to be determined. An alternative interpretation for these low ratios is the effect of electron channeling. In all area modes the Al/Si ratio was about 0.6. The calculated k value of about 1.4 is in very good agreement with other published data for Al by AEM (e.g., Lorimer and Cliff, 1976).

In contrast to Al, K showed strong evidence for diffusion. For the thicker portions of the (001)-perpendicular specimen analyzed in the area mode, K/Si ratios of about 0.3 were measured (Figure 2c); for determinations in the spot mode this value was never obtained, and the ratios dropped to about 0.1. K diffusion was most noticeable in the (001)-parallel specimen (Figure 2d). All area analyses, including the largest size area, generally gave values considerably less than 0.3, and only for the thickest portions of the foil were the ratios comparable to those of the (001)-perpendicular specimen. In general, increasing the size of the analysis area yielded larger K/Si ratios. The calculated k values for the (001)-perpendicular and the (001)-parallel specimens ranged from 0.84–2.92 and 1.04–9.75, respectively. The lower values, which were obtained using the 800 × 800-Å size area and/or greater specimen thickness, correspond well with **k** values (about 1.0) determined by Lorimer and Cliff (1976).

The variation in the Fe/Si ratio was difficult to assess because the small percentage of Fe gave rise to low count rates and, hence, imprecise ratios. The Fe/Si ratios seemed to follow the same trend as Al (Figure 2e and 2f). The difference in average Fe/Si ratio between the two muscovite specimens was either due to a slight difference in original Fe content or was caused by electron channeling effects.

DISCUSSION

The two probable mechanisms responsible for the observed variation in intensity ratios as a result of specimen-beam interaction are (1) a preferential loss of elements due to sputtering and (2) a loss due to element diffusion within the specimen. In diffusion, elements migrate away from the irradiated area, but do not leave the specimen as in sputtering. To distinguish between these two mechanisms, spectra from the same area of the specimen were obtained before and after a spot mode analysis in the center of the particular area of interest. The count rates, and thus element ratios, in both area analyses were similar; however, the spot mode analysis produced ratios, in particular K/Si, which were considerably different from the ratios obtained in the area analyses. These differences suggest that, although sputtering (and, thus, specimen thinning) cannot be entirely excluded, the main mechanism responsible for the observed variation in element ratios in conventional STEM analysis was element diffusion.

To obtain accurate analyses in analytical electron microscopy, a standard curve should be established for each element (as in Figures 1 and 2) and the optimum thickness range for the required resolution (analysis area) must be determined. The main advantage of using counts and count rates instead of actual specimen thicknesses is that counts can be measured at the time of analysis. These counts can then be related to the true thickness of the sample once the relation between

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thickness and count rate for different analysis areas has been established. The thickness of a sample can be determined by using the distance between the carbon contamination spots at the top and bottom of the foil at 0° tilt. For example, for adularia, the optimum thickness range started at about 900 Å. The same count rates for mineral standard and unknown under similar analysis conditions do not necessarily mean that these analyses are for the same specimen thickness, unless the specimens have the same composition. The relationship between count rates for the same thickness of standard and unknown, however, can be qualitatively estimated by comparing their average atomic number and can be more accurately estimated by measuring the actual thicknesses for different count rates. The most reliable results are obtained if the standard and the unknown are chemically similar.

The K diffusion data for muscovite were strongly dependent on the crystallographic orientation of the specimen. The count rates for K were considerably smaller if the mica basal planes were parallel to the specimen surface than if they were perpendicular (Figures 2c and 2d). Lower count rates for Al and Fe were only observed in the spot mode and in the thinnest portions of the samples. These data, however, do not allow conclusions to be drawn on the role of crystallographic orientation in diffusion of these two elements (see the previous section).

The measured dependence of K diffusion on the crystallographic orientation was most likely a result of the layered structure of the mica. The mobility of alkali ions was probably facilitated by diffusion pathways within the (001) alkali atom planes, but was probably nil across the tetrahedral and octahedral sheets. Veblen and Buseck (1980) and Ahn and Peacor (1986) suggested that pathways ("tunnels") exist parallel to layer terminations, which may also facilitate diffusion. If the specimen surface of the mica examined in the present study was perpendicular to the mica basal planes, element mobility was apparently limited by the thickness of the specimen and approached that of a one-dimensional diffusion pathway (intersection between the basal planes and specimen surface) in thin foils. On the other hand, if the surface and the basal planes were parallel, the diffusion paths were also parallel to the specimen surface; hence, element mobility was greatly facilitated (two-dimensional situation), as shown by the data in Figure 2. Thus, element ratios should have increased here also near the thinnest portions of a specimen that were unfavorably oriented for diffusion. Because of the inherently low count rates in thin areas, however, an accurate element ratio was generally not obtained, and this relationship was not observed in the present study. From the above data we conclude that, in addition to the need for similarity in chemistry, the crystal structure and the crystallographic orientation of the standard and the unknown should also be similar.

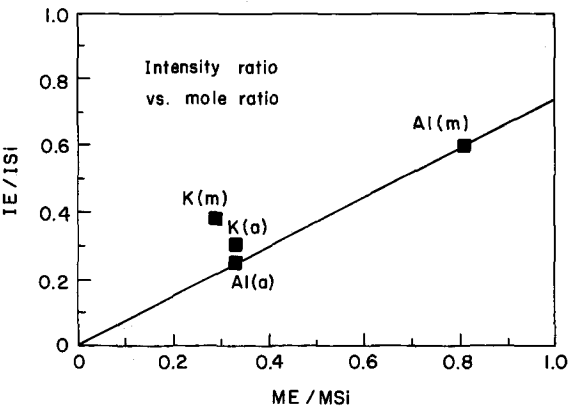


Figure 3. Al (Al) and K (K) intensity ratios I_E/I_{Si} vs. mole ratios M_E/M_{Si} for adularia (a) and (001)-perpendicular muscovite (m) using the 800 × 800-Å analysis area ratios from Figures 1a and 2a.

Plots of the intensity ratio, I_E/I_{Si}, vs. the mole ratio, M_E/M_{Si}, should fall on a straight line that passes through the origin for data points having different mole ratios, if the data points are accurate and free of ZAF corrections, i.e., if the thin-film criterion applies. The data for Al obtained in this study are plotted in Figure 3 using the intensity ratios for a 800 × 800 Å analysis area from Figures 1a and 2a. Because the linear relationship passes near the origin, this plot confirms that the values were free from anomalous effects. On the other hand, such a plot for K is inconclusive because of the similarity in the K/Si mole ratios for adularia and muscovite (Figure 3). Experience in the electron microscopy laboratory has shown that alkali ions are the only cations in phyllosilicates that present significant problems.

The present study did not consider the effect of crystal size and overall crystal-defect state, variables that may also be significant. For example, Lee *et al.* (1986) studied a series of illite-phengite samples having different dislocation densities from a shale-to-slate sequence. The shale illites, having relatively high dislocation densities, rapidly damaged in the electron beam, with loss of diffraction patterns within a minute or two, whereas relatively perfect phengites in the slate remained almost undamaged. Because diffusion is affected by both point and line defects, and because the vacancy state of illites in the alkali atom layers is known to vary, the diffusion of K may be a function of the defect state. This effect, however, remains to be investigated in a quantitative way.

SUMMARY AND CONCLUSIONS

Diffusion of elements as a result of the interaction between the electron beam and the specimen may cause significant errors in analytical electron microscopy. In general, diffusion is most pronounced for the alkali elements. The present study has found:

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1. Analyses for K, and to a much lesser degree for other elements, were different if the size of the analysis area was different. For example, the K/Si intensity ratio in muscovite decreased from about 0.4 for a 1350 × 1350 Å analysis area to about 0.1 for determinations made in the spot mode.

2. With decreasing specimen thickness, element diffusion increased. For example, in adularia the K/Si ratio changed from about 0.3 to about 0.15 with decreasing thickness for all analysis area sizes. This effect was less pronounced for thicker areas (i.e., for thicknesses >900 Å).

3. Spot mode counting, which uses the smallest analysis area, generally produced the lowest count rates for mobile elements. In muscovite, spot counting for K consistently gave low values, whereas Al and Fe values were slightly lower only in the thinnest portions of the specimens.

4. Most of the element diffusion took place in the early stages of spectra accumulation, i.e., well before meaningful count totals were obtained.

5. Diffusion of K in mica was greater in specimens in which the basal planes were oriented parallel to the specimen surface rather than perpendicular to the specimen surface. This demonstrates that diffusion pathways were a function of the crystal structure. For muscovite, and probably phyllosilicates in general, diffusion seems to be strongly facilitated by element migration parallel to the basal planes.

Therefore, to obtain the most accurate analytical data with the electron microscope, a traverse should be made on a mineral standard from thin to thick areas before each analysis of an unknown mineral to determine the relationship between specimen thickness and element ratio. The chemistry, crystal structure, and defect state of standard and unknown should correspond as closely as possible, and the instrumental conditions should be standardized. The specimen thickness range associated with a constant intensity ratio for each of the elements should be determined, and the corresponding count rates for the unknown and standard of the same thickness should be calibrated. Analyses within these optimum count rate ranges will give the most reliable values. Spot analyses should be avoided inasmuch as they strongly facilitate diffusion, especially in thin edges. Generally, satisfactory results can be obtained using analysis size areas greater than 800 × 800 Å. Each analysis should be preceded by inspection of the diffraction pattern to determine the crystallographic orientation of the specimen with respect to the electron beam, and results from the standard should be obtained using approximately the same crystallographic orientation. Finally, to monitor the instrumental conditions, the k′ (or k) values should be determined using the mineral standard both before and after analysis of the unknown.

Using this procedure, electron microscopy is a powerful technique that can yield accurate chemical as well as crystallographic data which cannot otherwise be obtained. Despite such care, analytical electron microscopy has a larger inherent standard error (scatter of data) for K and other mobile elements (such as Na) than many other techniques.

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