PEGMATITIC MUSCOVITES: EFFECT OF COMPOSITION ON

OPTICAL AND LATTICE PARAMETERS

by

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(ABSTRACT)

Twenty-five muscovites have been systematically studied chemically, optically, and structurally. Multiple linear regressions were performed on these data to determine the correlations of the compositional components with both the optical properties and the unit cell parameters. The results of this study indicate refractive indices increase to the extent Fe and Ti constitute the octahedral cations, and to the extent OH rather than F coordinates to these cations. The optic angle $2V_x$ decreases nearly linearly with the Ti content. The $\underline{b}$ cell edge follows a near linear trend with $\Sigma(Mg + Fe_{(total)})$, similar to that found by Guidotti (1984).

ACKNOWLEDGEMENTS

I wish to thank my chairman Donald Bloss, and committee members Paul Ribbe and Jesse Brown, for all their help and support in seeing this project to completion. Additional thanks to Dr. Li Zhe of Institute of Geology, Academia Sinica, for the 5 Mossbauer analyses and interpretations he provided.

Many faculty and staff were of great assistance to me, but most importantly I would like to acknowledge   for his technical assistance,   for both the samples he provided and for offering his time and interest in many aspects of the analytical procedures, and finally, for providing his machining skills as needed.

Very special thanks go to all of my friends, especially   , all who were invaluable for emotional and spiritual support and a ready ear.

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INTRODUCTION

A crystal's structure, its component atoms or ions, and the nature of the bonding among these components control its optical properties. Consequently, given a suite of $2M_1$ muscovites within which the optical properties differ significantly, these optical differences will reflect compositional differences plus the attendant minor variations in the structure, namely in cation-to-oxygen distances, caused when one ion substitutes for another. Although $KAl_2(AlSi_3)O_{10}(OH,F)_2$ represents the ideal formula for muscovite, numerous substitutions are possible. Thus, as noted by Deer et al. (1962), Na^+ is the principal substituent for K^+ in the interlayer site whereas Rb^+, Cs^+, Ca^{2+} and Ba^{2+} represent minor substituents. Substituents for Al^{3+} in the octahedral sites are Mg^{2+}, Fe^{2+}, Fe^{3+} and, much less importantly, Li^+, Ti^{4+}, Mn^{2+}, and other transition metal ions. In the tetrahedral sites the ratio of Si^{4+} to Al^{3+} may vary from Si_6Al_2 to Si_7Al.

Early studies of the variation in the optical properties and chemical compositions of muscovite failed to establish any precise correlations. Heinrich et al. (1953) surveyed the optical properties and chemical analyses of muscovites from many sources and concluded that neither direct nor inverse relationships could be shown between the optical prop-

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erties and the percentages of given oxides. Correlations have been attempted by Volk (1939), Winchell and Winchell (1951), and others. Some of the earlier studies probably suffered from less precise optical data than are desirable, from unsatisfactory methods of chemical analysis, and from inability to discern which polytype was being studied.

In addition to the optical properties, the crystal's cell dimensions are affected by variations in chemistry. The interrelationships between unit cell parameters and composition in muscovite have been studied by Radoslovich and Norrish (1962), Ernst (1963) and more recently, Guidotti (1984). Attempts have been made to predict unit cell parameters, especially the $\underline{b}$ parameter, the $d_{(002)}$ spacings, and the cell volumes by considering the substitutions of the interlayer cations and the octahedral cations. The regression equations developed by Guidotti (1984) are examined in light of data from the present study.

TECHNIQUES AND SAMPLE SELECTION

Previous studies commonly made use of oil immersion techniques in the measurement of optical properties. Refractive index measurements performed on sheet silicates in this manner yielded indices for the two principal vibration directions in the cleavage plane, Y and Z. However, the X direction, which is approximately perpendicular to the cleavage, was usually omitted from the measurements. In addition, because the refractive indices could not all be determined from a single flake, the optic angle 2V, if calculated from these indices, commonly differed by several degrees from 2V observed. The introduction of the spindle stage and the Abbe refractometer as tools for measuring optical properties of sheet silicates eliminated these problems and provided a complete set of optical data for individual flakes.

In the past, compositional analyses were usually performed on bulk samples by wet chemical techniques. This not only caused an averaging of any compositionally nonhomogeneous areas, but as is now known, the grinding of muscovites to powder, unless performed in acetone, oxidized Fe^{2+} to Fe^{3+}. Thus, a comparison of the optical data obtained on a small flake of muscovite and the bulk chemistry

composition determined by wet chemistry did not necessarily reflect the true relationship between optics and chemistry in the muscovites.

In the present study, techniques similar to those described by Hurlbut (1984), but with substitution of a much more precise Bellingham and Stanley refractometer for the jeweler's refractometer, were employed to measure with sodium light (589.3 nm) the principal refractive indices α, β, and γ of 25 muscovites. The value of 2V calculated from these indices usually agreed within three degrees of the value measured for the same flake using a universal stage. The muscovite flakes measured optically were then analyzed chemically by electron microprobe, thus reducing the problems associated with nonhomogeneous compositions.

SAMPLE SELECTION

The samples used in this study were taken from large sheets of high grade pegmatitic muscovite (Table 1). Special attention was given to avoiding inclusions and weathered areas. The samples were cut to 15 x 15 mm and cleaved down to ~0.025 mm in thickness. Each crystal was then viewed conoscopically under a polarizing microscope for signs of twinning or other optical discontinuity using the procedure described by Bloss et al. (1963). At the same time, this

TABLE 1. Sample Localities*

sample	locality
1	Madagascar (courtesy T.N. Solberg)
2	Ben Murphy Mine, Howard county, MD
3	Ben Murphy Mine, Howard county, MD
4	Earth Products Co., Montgomery county, MD
5	Ben Murphy Mine, Howard county, MD
6	Barron's Mine, Thomaston, GA
7	Battle Mine, GA
8	Brown's Mine, GA
9	Toonigh, GA
10	Hazelwood, Big Ridge, NC
11	Hazelwood, Big Ridge, NC
12	Barnes Mine, Alexander county, NC
13	Boyd Knob Mine, NC
14	Belden Mine, NH
15	Reynold's Mine, NH
16	New Haven, NH
17	Alexandria, NH
18	Star Mica Mining Co., NH
19	Star Mica Mining Co., NH
20	Tripp Mine, Alstead, NH
21	United Mica Co., Grafton county, NH
22	Haddam, CT
23	CT
24	CT
25	Ceylon (courtesy T.N. Solberg)

*Muscovite samples 2 through 24 represent pegmatitic micas collected by Waldemar T. Schaller from 1910 to 1918. No further locality information is available.

examination allowed the optic plane to be identified so that a line representing its trace could be scribed onto the surface of the flake.

OPTICAL DETERMINATIONS

After selection of the flake and location of its optic plane, each muscovite's principal refractive indices were then determined on a Bellingham and Stanley High Precision Refractometer (Model HR/60) illuminated by sodium light. A small drop of oil greater in refractive index than γ for muscovite was centered on the surface of the refractometer's upper prism, and a flake was pressed against the droplet. An area 15 x 15 mm proved to be the minimum necessary for reliable readings. Special care was taken to emplace the flake so that the scribed trace of the optic plane was either (1) N-S or (2) E-W, where we assume the observer, looking routinely down the eyepiece, faced "north." In each position, two dark-light boundaries could be observed in the eyepiece field of view. For position (1) the one boundary corresponded to β and the other to α for the muscovite being measured. For position (2) the dark-light boundaries corresponded to γ and α', a non-principal refractive index. A cap analyzer with pin-hole cover was placed over the refractometer's eyepiece and rotated so as to eliminate one

of the dark-light boundaries, remove dark interference fringes, and sharpen the other. Thus, one could measure β and α with the crystal in position (1), and α' and γ with the crystal in position (2) for the sodium light being used. A third boundary corresponded to the refractive index of the oil drop used to maintain optical continuity between the flake and the refractometer prism.

At least six readings were taken for each boundary observed. The data were averaged and converted to refractive index values for sodium light, and 2V was calculated from the measured indices. The optic angle 2V was then measured for each flake on the universal stage, providing a check on the accuracy of the refractive indices by comparing calculated values and observed 2V data.

CHEMICAL ANALYSES

The muscovite compositions were determined by electron microprobe analysis using an automated ARL SEMQ for Si, Al, Ti, Mg, Mn, Fe, Rb, Sr, K, Na, Ba, Ca, F, and Cl. Data were reduced on-line by the method of Bence and Albee (1968). Replicate analyses collected on each muscovite flake were used to determine the homogeneity. The average compositions are reported and used for all statistical analyses.

The oxide weight percentages were recalculated to the chemical formulas using SUPERRECAL (Rucklidge, 1971) based on the presence of 24 (O+ F + OH); no Cl was found. Because ferric iron is present in small percentages, some error is inherent in the calculations. F was then subtracted out in an iterative process to determine the H_2O content.

Lithium was determined by Specific Ion Electrode Analyses for thirteen of the original muscovite samples, and these results have been incorporated and included in the recalculated formulas for those samples.

MOSSBAUER ANALYSES

Mossbauer analyses on randomly oriented powders of five specimens were performed at room temperature by Dr. Li Zhe at the Institute of Geology, Academia Sinica, Beijing, China. An FH Mossbauer spectrometer was used in conjunction with an FH 451 1024 multichannel analyzer (Li, personal communication). The source consisted of 25 Mc of ^{57}Co in rhodium. The spectra were filtered to Lorentzian lines using the computer program written by Li Shi et al. (1983). Intensities were constrained to remain equal for each doublet, and line widths for all Fe^{2+} doublets were also constrained to be equal, as were those for Fe^{3+} (Li, personal communication).

The ratio of Fe^{3+} to Fe^{2+} provided by the Mossbauer re-
sults was then used in conjunction with total Fe from the
microprobe data to determine the formula numbers for Fe^{3+} and
Fe^{2+} for each of the five muscovites analyzed.

LATTICE PARAMETER DETERMINATION

For each of the suite of pegmatitic muscovites studied
here, powder diffraction data for unfiltered CuKα radiation
were collected and interpreted by an automated powder
diffractometer. After the digital data on peak maxima lo-
cations were corrected relative to a CaF_2 internal standard,
the peaks were indexed. For each muscovite the 2θ values for
at least ten uniquely indexed reflections were submitted to
the least-squares refinement program of Appleman (1973). Us-
ing standard $2M_1$ muscovite cell dimensions and space group
symmetry as starting points, positions of all permissible
maxima in the 2θ range from 20° to 75° were calculated. The
observed peaks deviated in position from those calculated by
less than 0.025° 2θ. From the d-spacing and reflection in-
dices for the observed peaks, the unit cell dimensions for
each muscovite were then calculated.

In a survey of data from many available sources of the optical properties of muscovite, Heinrich et al. (1953) found no convincing evidence for either a direct or an inverse relationship (other than general trends) between the optical properties and percentages of oxides. Previous attempts to correlate the two had been made by other researchers. Thus, Volk (1939) concluded that refractive index increased with ferric iron content which is consistent with the findings of Winchell and Winchell (1951). In addition, Deer et al. (1962) reported that refractive indices for muscovite increase "with increase in iron (particularly Fe^{3+}) and Mn content" and with decrease in Al. They also noted that specimens "with least Mg and Fe" have the largest optical angles 2V. Wilcox (1984) reported that, in general, refractive indices are increased by substitution of Fe^{2+}, Fe^{3+}, Mn, Zn, and/or Ti for Al, and of Ca for K (where the valence is compensated by substitution of Al for Si). These and other studies have yet, however, to establish any precise correlations. A major barrier toward this goal continues to be the multiplicity of substituents and their possible inter-correlations.

All the optical data from the 25 muscovites here studied are presented in Table 2. The microprobe and Li Ion Electrode analyses are summarized in the form of formula

numbers and given in Table 3. General linear models were generated for the refractive indices and for the optic angle each as the dependent variable versus formula numbers for the individual ions. In particular, the Statistical Analysis System (SAS, 1976) procedure, MAXIMUM R^2 IMPROVEMENT (MAXR^2), was employed to select from the compositional (independent) variables submitted — namely, K, Na, Si, Al^{vi}, Mg, Ti, Fe, OH, and F — the best combinations of variables needed to produce models that best "explained" the effect of composition on the given optical parameter, α, β, γ, or 2V, selected as the dependent variable. This procedure looks for the "best" single independent variable model, the "best" two independent variable model, etc. Thus, it first produces a one variable model by finding that independent variable that produces the highest r^2 value. It then examines all two variable combinations and produces that model with the highest r^2. It repeats the process to determine the "best" three variable model, etc. For each model, in addition to calculating r^2, it calculates the standard errors for the intercept and regression coefficients determined for the model.

TABLE 2. Observed refractive indices and $2V_x$ for sodium light

sample	α	β	γ	$2V_{obs}$*	$2V_{calc}$**
1	1.5696	1.6089	1.6136	35.3	33.0
2	1.5615	1.5954	1.6004	41.3	43.8
3	1.5645	1.5989	1.6047	43.5	40.5
4	1.5664	1.6028	1.6079	41.1	40.0
5	1.5648	1.5995	1.6051	42.4	43.0
6	1.5620	1.5965	1.6011	39.3	40.3
7	1.5632	1.5984	1.6023	37.2	36.2
8	1.5620	1.5971	1.6015	40.5	38.6
9	1.5698	1.6088	1.6123	34.6	32.7
10	1.5637	1.5972	1.6032	41.8	45.2
11	1.5637	1.5982	1.6027	39.0	39.0
12	1.5613	1.5940	1.6003	42.7	46.7
13	1.5637	1.5980	1.6024	38.7	38.6
14	1.5605	1.5934	1.5989	43.2	43.8
15	1.5608	1.5936	1.5987	41.7	42.3
16	1.5625	1.5953	1.6014	44.0	45.8
17	1.5595	1.5925	1.5981	44.2	44.0
18	1.5607	1.5939	1.5990	44.3	41.9
19	1.5599	1.5940	1.5987	43.9	40.1
20	1.5604	1.5935	1.5985	42.3	42.0
21	1.5604	1.5692	1.5999	38.4	35.2
22	1.5587	1.5915	1.5970	42.3	43.9
23	1.5587	1.5912	1.5961	42.6	41.5
24	1.5590	1.5923	1.5975	43.0	42.2
25	1.5594	1.5914	1.5975	43.9	46.5

* Determined by universal stage

** Calculated from refractive indices at left

TABLE 3. Muscovite compositions from microprobe and specific ion electrode
Formula numbers based on 24 O, OH, and F.

	1	2	3	4	5	6	7	8	9	10	11	12	13
Si	6.40	6.26	6.26	6.33	6.34	6.27	6.26	6.25	6.33	6.26	6.32	6.24	6.24
Al^{iv}	1.60	1.74	1.74	1.66	1.65	1.73	1.74	1.75	1.67	1.75	1.68	1.76	1.76
Al^{vi}	3.16	3.61	3.67	3.46	3.57	3.60	3.57	3.57	3.33	3.55	3.53	3.64	3.58
Ti	0.09	0.03	0.01	0.03	0.02	0.05	0.08	0.06	0.10	0.05	0.06	0.02	0.07
Fe	0.61	0.20	0.32	0.45	0.33	0.23	0.20	0.25	0.45	0.25	0.22	0.25	0.19
Mg	0.31	0.25	0.10	0.16	0.10	0.20	0.22	0.19	0.21	0.24	0.20	0.15	0.22
Li	-	-	-	0.01	0.01	-	0.01	-	0.01	-	-	0.02	-
K	1.79	1.65	1.67	1.75	1.78	1.66	1.70	1.71	1.78	1.70	1.75	1.69	1.69
Na	0.11	0.20	0.15	0.16	0.19	0.18	0.18	0.17	0.14	0.16	0.16	0.20	0.18
F	0.03	0.04	0.06	0.06	0.10	0.03	0.05	0.06	0.04	0.03	0.02	0.06	0.04
H	3.97	3.96	3.94	3.94	3.90	3.97	3.95	3.94	3.96	3.97	3.99	3.94	3.96

	14	15	16	17	18	19	20	21	22	23	24	25
Si	6.24	6.29	6.28	6.25	6.22	6.23	6.27	6.27	6.31	6.30	6.29	6.21
Al^{iv}	1.76	1.72	1.72	1.76	1.78	1.77	1.73	1.73	1.69	1.70	1.71	1.79
Al^{vi}	3.78	3.66	3.63	3.68	3.73	3.75	3.67	3.65	3.61	3.62	3.65	3.80
Ti	0.01	0.03	0.00	0.01	0.02	0.01	0.03	0.07	0.02	0.02	0.02	0.01
Fe	0.19	0.21	0.42	0.24	0.18	0.17	0.20	0.16	0.29	0.28	0.27	0.17
Mg	0.08	0.13	0.05	0.13	0.14	0.12	0.15	0.13	0.11	0.10	0.11	0.07
Li	-	0.02	0.03	0.03	-	-	-	0.01	0.08	0.08	0.04	0.01
K	1.64	1.69	1.67	1.67	1.63	1.67	1.65	1.74	1.73	1.72	1.70	1.63
Na	0.20	0.20	0.19	0.22	0.20	0.19	0.18	0.16	0.18	0.18	0.18	0.22
F	0.08	0.12	0.21	0.16	0.05	0.04	0.08	0.11	0.22	0.28	0.20	0.16
H	3.91	3.88	3.79	3.84	3.95	3.96	3.92	3.88	3.78	3.72	3.80	3.84

: Li analyses determined by specific ion electrode.

REFRACTIVE INDEX

Applied to the refractive index and compositional data for the 25 muscovites studied (Tables 2 and 3), the SAS MAXR^2 procedure disclosed that, of the compositional variables K, Na, Si, Al^{vi}, Mg, Ti, total Fe (Fe$_T$), OH, and F, the Fe$_T$, Ti, and OH gave statistically the most significant multiple variable model. The models which follow give the best three variable models for the individual principal refractive indices:

$$\alpha = 1.485 + 0.019Fe_T + 0.028Ti + 0.018(OH) \tag{1}$$
$$(0.010) \quad (0.002) \quad (0.007) \quad (0.003) \quad r^2 = 0.93$$

$$\beta = 1.491 + 0.028Fe_T + 0.059Ti + 0.025(OH) \tag{2}$$
$$(0.013) \quad (0.002) \quad (0.010) \quad (0.003) \quad r^2 = 0.95$$

$$\gamma = 1.493 + 0.030Fe_T \div 0.035Ti + 0.025(OH) \tag{3}$$
$$(0.012) \quad (0.002) \quad (0.008) \quad (0.003) \quad r^2 = 0.96$$

(

For these models, the standard errors are given in parentheses directly below the value to which they refer.

In Equations (1) to (3), we assume that the magnitudes of the coefficients for the independent variables — Fe$_T$, Ti, and OH — indicate how strongly these independent variables increase the dependent variable. Under this assumption, the

refractive indices β and γ increase more with increasing Fe_T and Ti, and perhaps OH, than does α. In particular, Ti significantly increases β. These trends appear consistent with the influence of muscovite's crystal structure upon its optics. The polarizability of the OH and O ions constituting the close-packed sheets in muscovite would likely be increased by the entry of the transition metal ions, Fe and Ti, into the octahedral sites. Moreover, this effect would be increased to the extent that these sheets contained OH rather than the less polar F ions. Because α vibrates approximately normal to these sheets, it is less affected by increase in the Fe, Ti, and/or OH content.

Comparison of the observed refractive indices to those calculated from Equations (1), (2), and (3) shows good agreement (Figures 1, 2, and 3). Indeed, if we apply these models to the compositional data for the Methuen muscovite studied by Hurlbut (1956), namely, Fe = 0.0, Ti = 0.0, OH = 4.135, the resultant calculated refractive indices 1.560, 1.592, and 1.599 agree closely with those (1.5595, 1.5930, and 1.5991) which Hurlbut determined by Emmons double variation method.

Thus, the extent to which Fe and Ti constitute the octahedral cations, plus the extent to which OH rather than F coordinates to these octahedral cations, appear to dominate the effect of composition on refractive index for muscovites.

For five muscovites, the amount of Fe^{3+} versus Fe^{2+} was determined by Mossbauer techniques. Results of these analyses, kindly supplied by Dr. Li, are summarized in Table 4. The Fe^{2+}/Fe^{3+} ratio calculated from Mossbauer spectra together with total Fe from microprobe analyses yielded the formula numbers presented in Table 5. Admittedly this sample number is small; nevertheless, the SAS procedure CORR showed that Fe^{3+}, compared to Fe^{2+}, had a greater positive correlation with the principal refractive indices (Table 6). The results for Fe^{3+} agree then with the reports by both Deer et al. (1962) and Wilcox (1984) and are consistent with the influence of crystal structure on optics.

TABLE 4. Mössbauer parameters of the muscovites[*]

sample	I.S(mm/s)	Q.S(mm/s)	Γ(mm/s)	Assignments	%Fe	Fe^{2+}/Fe^{3+}	x^2
9	1.13(1)	3.01(2)	0.36(2)	M1(Fe^{2+})	17		
	1.08(2)	2.17(4)	0.36(2)	M2(Fe^{2+})	12	0.41	266
	0.38(2)	0.71(3)	0.67(3)	M1(Fe^{3+})	65		
	0.51(12)	1.65(24)	0.67(3)	M2(Fe^{3+})	6		
1	1.31(1)	2.98(1)	0.35(1)	M1(Fe^{2+})	21		
	1.14(1)	2.10(1)	0.35(1)	M2(Fe^{2+})	14	0.54	251
	0.35(1)	0.80(1)	0.64(1)	M1(Fe^{3+})	65		
10	1.11(1)	3.01(1)	0.37(1)	M1(Fe^{2+})	21		
	1.15(1)	2.24(2)	0.37(1)	M2(Fe^{2+})	17	0.61	241
	0.33(3)	0.84(6)	1.31(19)	M1(Fe^{3+})	62		
11	1.10(1)	2.98(1)	0.34(1)	M1(Fe^{2+})	35		
	1.11(1)	2.14(1)	0.34(1)	M2(Fe^{2+})	28	1.70	259
	0.25(2)	0.69(4)	0.78(8)	M1(Fe^{3+})	37		
13	1.14(1)	2.95(1)	0.37(1)	M1(Fe^{2+})	40		
	1.13(1)	2.00(1)	0.37(1)	M2(Fe^{2+})	26	1.94	244
	0.37(2)	0.82(3)	0.79(7)	M1(Fe^{3+})	34		

* This data and table were kindly supplied by Dr. Li Zhe of the Institute
  of Geology, Academia Sinica, Beijing, China.

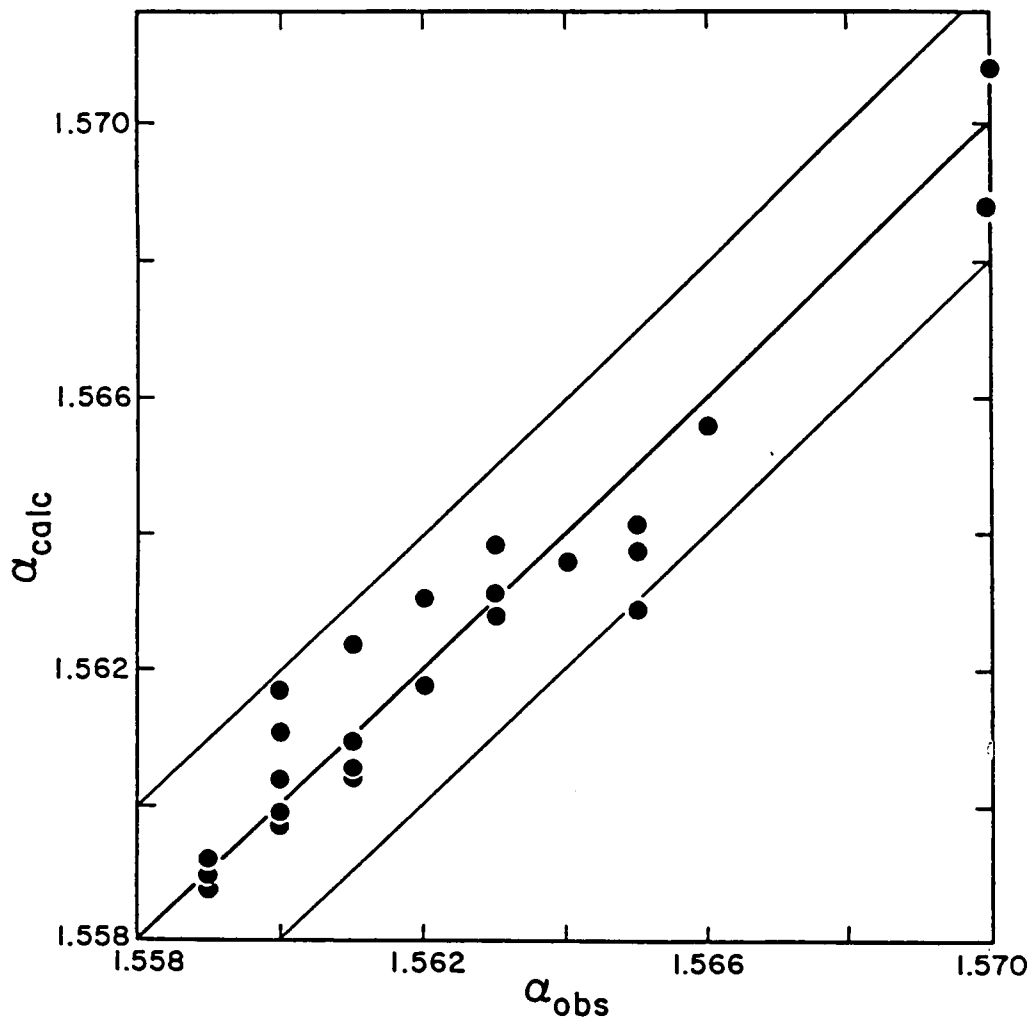# CALCULATED VERSUS OBSERVED REFRACTIVE INDEX α

Figure 1: Calculated versus observed refractive index α. Calculated values are from Equation (1). The boundaries drawn represent the intervals at n ±0.002.
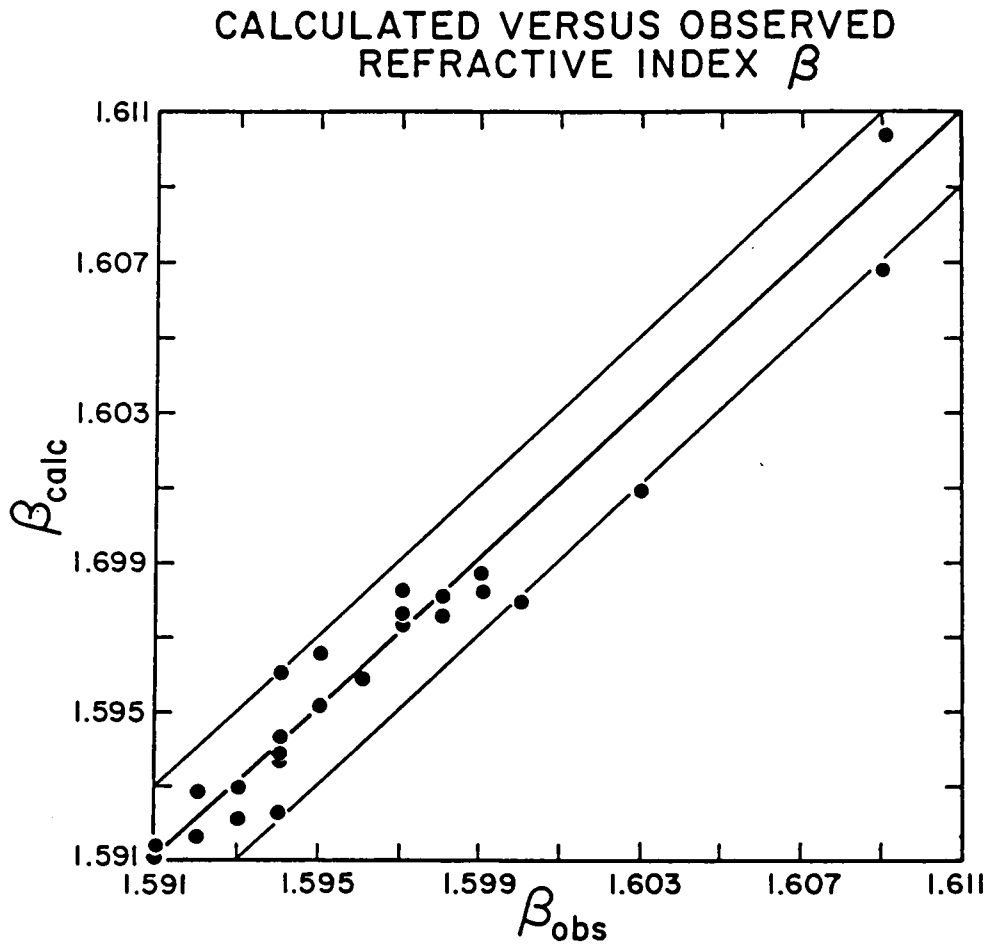
Figure 2: Calculated versus observed refractive index β. Calculated values are from Equation (2). The boundaries drawn represent the intervals at n ±0.002.

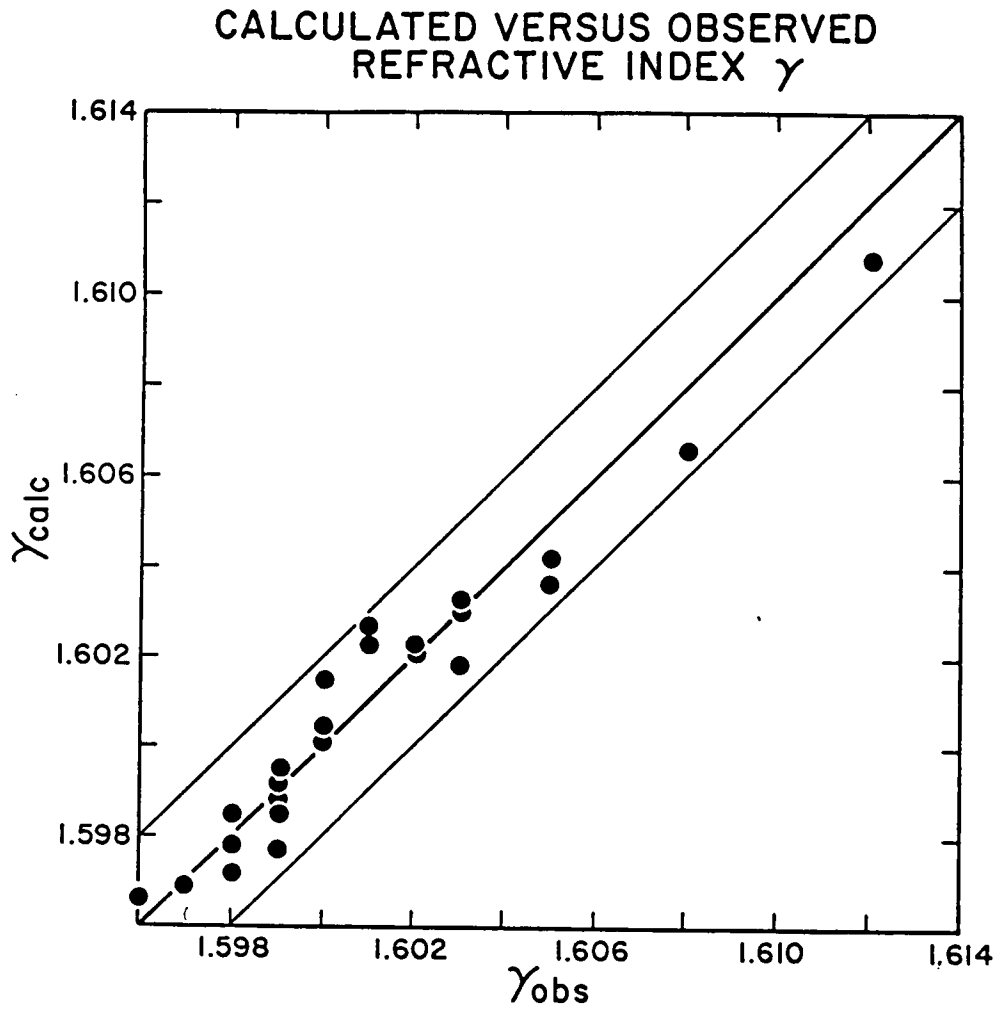# CALCULATED VERSUS OBSERVED
REFRACTIVE INDEX γ

Figure 3: Calculated versus observed refractive index γ. Calculated values are from Equation (3). The boundaries drawn represent the intervals at n ±0.002.

TABLE 5. Formula numbers for Fe^{3+} and Fe^{2+}
based on 24 anions *

	MUSCOVITE SPECIMENS				
	9	1	10	11	13
Fe^{3+}	0.397	0.321	0.157	0.083	0.064
Fe^{2+}	0.215	0.131	0.095	0.140	0.124

* Formula numbers calculated from total Fe
  determined by microprobe and Fe^{2+}/Fe^{3+} ratio,
  calculated from Mössbauer spectra.

TABLE 6. CORRELATION MATRIX for Fe^{3+}, Fe^{2+}, and
the principal refractive indices*

	α	β	γ
Fe^{3+}	0.93 (0.02)	0.93 (0.02)	0.96 (0.01)
Fe^{2+}	0.63 (0.26)	0.69 (0.19)	0.71 (0.18)

* Correlation coefficients are based on five samples.
  Probability of no correlation given below.

OPTIC ANGLE

The compositional variables, K, Na, Si, Al^{vi}, Mg, Fe_T, Ti, OH, and F, were entered as independent variables in the SAS variable selection procedure $MAXR^2$ with the optic angle 2V as the dependent variable. Surprisingly, of the "best" single variable, the "best" two variable, the "best" three variable, etc. models produced as a result of $MAXR^2$, the single variable model appeared to be the most statistically significant. The regression equation which obtained for the single variable model is:

$$2V = 44.7 - 92.5Ti \qquad\qquad (4)$$
$$(0.3) \quad (6.0) \qquad r^2 = 0.91$$

where Ti is the formula number of Ti ions based on 24 oxygens. Standard errors are given in parentheses below the value to which they refer.

Figure 4 and Equation (4) both show that Ti causes 2V to decrease nearly linearly for the 25 muscovites here studied. The Ti ion enters the octahedral site in muscovite substituting for Al^{vi}. Of the octahedral Al substituents, namely — Mg, Ti, Fe^{2+}, and Fe^{3+} — the Ti^{4+} is the most highly charged cation and causes the greatest increase in the refractive indices, especially β (compare coefficients of Fe_T

and Ti in Equations (1), (2), and (3)). By increasing β more than γ, Ti decreases ($\gamma - \beta$) and thereby decreases $2V_X$. In addition, because Ti^{4+} and Mg^{2+} and/or Fe^{2+} are possible substituents for two octahedral Al^{3+}, the trend reported by Deer et al. (1962) for low Mg and Fe muscovites to have large 2V values may result because such muscovites may also be low in Ti.

When Ti enters the octahedral site in muscovite, its higher charge likely polarizes the OH and O anions more than the other possible occupants, Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, normally would. Because OH has a higher polarizability than the O anion, this effect would cause more polarization in the direction of the a-axis in muscovite since the concentration of OH anions is greatest along $\underline{a}$ (Fig. 5). The principal refractive index β is most nearly parallel the a-axis in muscovite, and therefore the concentration of the highly polarized OH anions associated with $\underline{a}$ should be expected to increase β, more so than γ. Thus it appears, the extent to which Ti occupies the octahedral site determines the decrease in ($\gamma - \beta$) and, in turn, the decrease in $2V_X$.
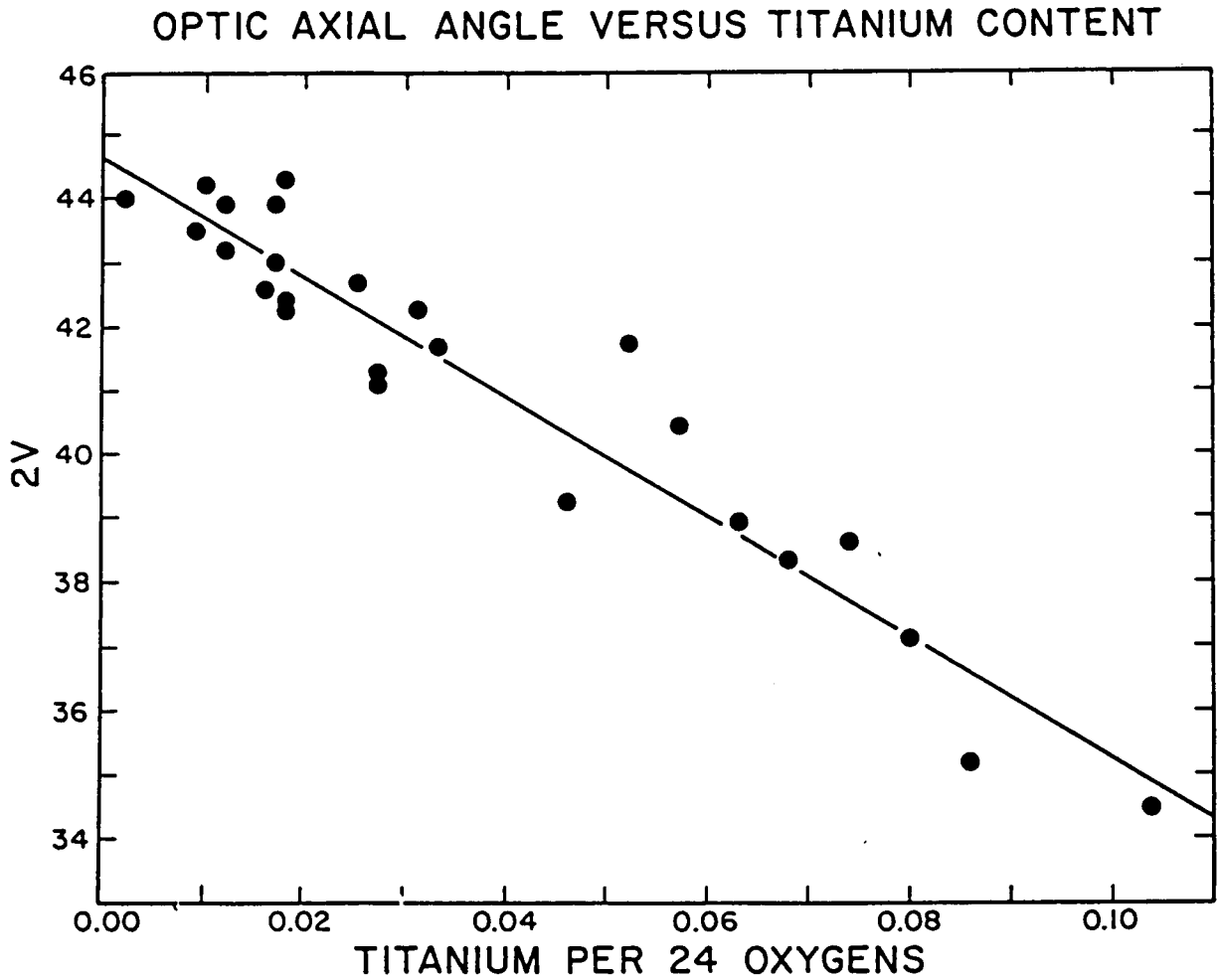
FIGURE 4. The 25 muscovites of this study reveal optic angle 2V
decreases nearly linearly with titanium content.

COMPOSITION VERSUS UNIT CELL PARAMETERS

Many attempts have been made to show the dependence of
the unit cell parameters of muscovites upon composition.
Radoslovich and Norrish (1962) showed that compositional
variations of the octahedral layers principally controlled
the cell dimensions of micas. Ernst (1963) noted that re-
placement of Al by Mg and Fe in the octahedral sites in-
creased the $\underline{b}$ cell edge. This in turn reduced the
tetrahedral rotation causing decreased $\underline{c}$ sinβ values by re-
ducing the degree to which the interlayer cations, Na and/or
K, propped apart the successive layers. More recently,
Guidotti (1984) has considered the relationships between
composition and unit cell parameters for muscovites in which
the Na/(Na + K) ratios ranged from 0 to 0.38 and for natural
samples wherein ΣAl per 22 oxygens usually exceeded 5.60.

RELATIONSHIP TO COMPOSITION

The unit cell parameters for each of the suite of
pegmatitic muscovites studied here were determined by powder
diffraction techniques. These measured cell dimensions with
their estimated standard deviations are presented in Table
7. Multiple linear regressions, employing these unit cell

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PROJECTION DOWN [001]   - two octahedral layers
● octahedral cations of both upper and lower layers
◯ (OH) ions - stippled ions belong to lower layer
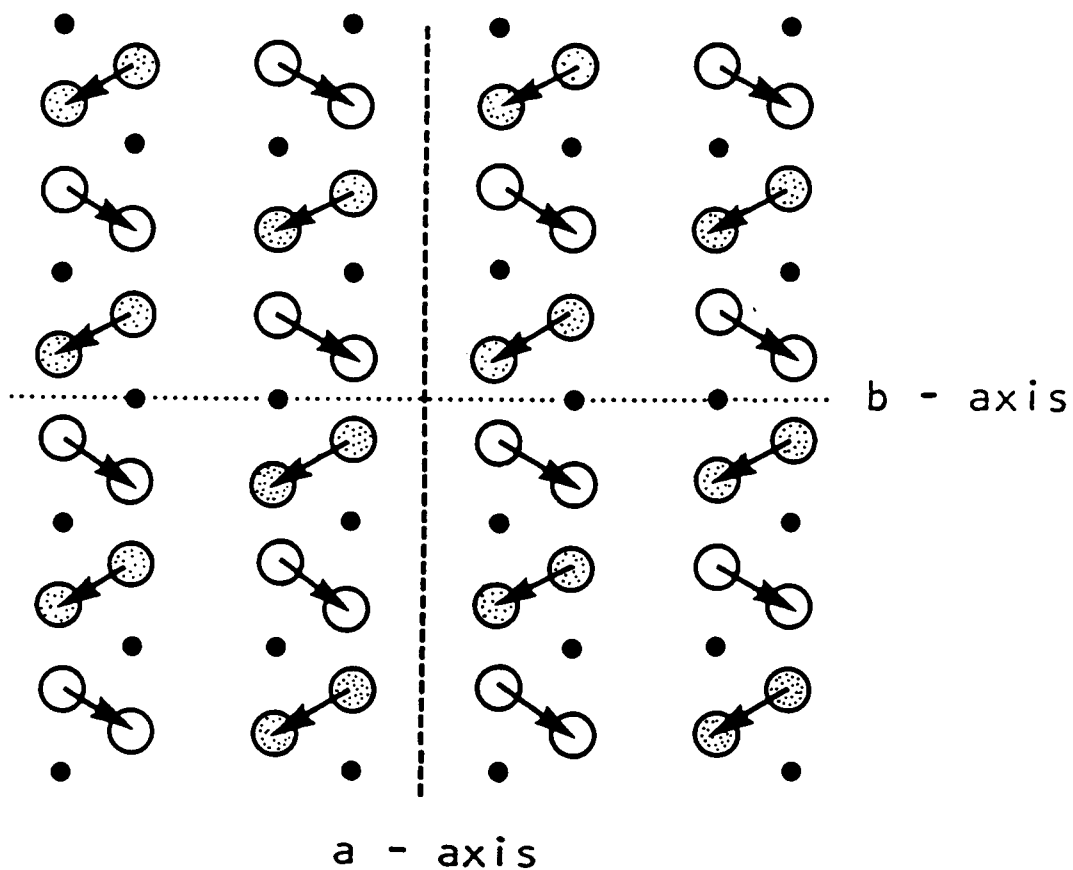arrows indicate the stacking direction

b - axis

a - axis

FIGURE 5.

TABLE 7. Observed cell parameters and calculated[*] cell volumes

sample	a	b	c	β	V
1	5.226(5)[**]	9.053(8)	20.020(5)	95.73(3)	942.8
2	5.202(4)	9.009(6)	20.038(4)	95.80(3)	934.8
3	5.200(5)	9.033(7)	20.039(5)	95.80(3)	936.9
4	5.188(1)	9.026(3)	20.050(2)	95.77(2)	934.6
5	5.192(5)	9.032(5)	20.045(5)	95.82(3)	935.7
6	5.194(2)	9.037(7)	20.044(3)	95.78(2)	936.5
7	5.196(2)	9.027(4)	20.036(2)	95.75(3)	935.9
8	5.197(3)	9.025(7)	20.041(5)	95.73(3)	935.7
9	5.220(3)	9.039(4)	20.032(3)	95.78(2)	940.9
10	5.202(1)	9.030(5)	20.030(3)	95.77(2)	939.9
11	5.198(4)	9.032(3)	20.036(3)	95.80(3)	936.4
12	5.203(2)	9.019(3)	20.049(4)	95.78(3)	936.5
13	5.194(2)	9.029(5)	20.031(6)	95.82(3)	935.1
14	5.188(3)	9.019(7)	20.062(6)	95.83(5)	934.4
15	5.203(3)	9.025(3)	20.042(5)	95.75(5)	936.9
16	5.207(1)	9.024(3)	20.040(3)	95.80(2)	937.3
17	5.191(2)	9.024(4)	20.046(2)	95.77(1)	934.8
18	5.189(1)	9.011(4)	20.057(3)	95.75(2)	933.6
19	5.189(2)	9.021(3)	20.055(2)	95.75(2)	934.5
20	5.197(4)	9.023(3)	20.044(4)	95.75(3)	935.7
21	5.196(1)	9.020(2)	20.062(3)	95.73(1)	936.0
22	5.193(2)	9.022(4)	20.037(4)	95.73(2)	934.5
23	5.195(2)	9.023(4)	20.044(3)	95.78(2)	935.3
24	5.194(2)	9.027(4)	20.038(4)	95.77(3)	935.2
25	5.191(1)	9.023(3)	20.068(2)	95.75(2)	935.7

* Calculated from measured cell parameters

** Estimated standard deviations in parentheses refer to the least
   units cited. Thus, 5.226(5) represents an esd of 0.005.

parameters as the dependent variable and the various compositional parameters, in turn, as the independent variables, were performed using the SAS procedure GENERAL LINEAR MODEL (GLM). Models like those developed by Guidotti (1984) were tested, but with some caution according to the compositional restrictions employed by Guidotti when these equations were developed. For Al-rich muscovites wherein the $\Sigma(Mg + Fe_T)$ content was small, Guidotti maintained that volume and the parameter $\frac{1}{2}\underline{c}$ sinβ were largely dependent on the Na/(Na + K) ratio. In addition, the relationships were modeled from samples covering a Na/(Na + K) range of 0.0 to 0.38. The regression equation for volume that he obtained is:

$$V = 934.92 - 0.23X - 0.0069X^2 \tag{7}$$

where V is cell volume in A^3 and X is the Na/(Na + K) in atomic per cent. A second equation he obtained is:

$$\frac{1}{2}\underline{c} \ \sin\beta = 10.00 - 0.00217X - 0.0000259X^2 \tag{8}$$

The b cell edge he relates to $\Sigma(Mg + Fe_T)$ in atoms per 22 oxygens, where Fe_T represents total iron atoms. His regression equation for b is:

$$b = 8.990 + 0.04 \; \Sigma(Mg + Fe_T) \tag{9}$$

The greater scatter of his observations relative to Equation (9) he attributed to the influence of the $Na/(Na + K)$ ratio on b. Thus he notes, "The $Na/(Na + K)$ ratio has a small but as yet unquantified effect on b."

In the 25 pegmatitic muscovites here studied, ΣAl per 22 oxygens ranged from 4.76 to 5.59 (Table 3), most falling considerably below the minimum of 5.60 considered to be Al-rich, and the ratio of $Na/(Na + K)$ covered the narrow range of only 0.05 to 0.11. With this in mind, the following are results from the SAS procedure GLM for the volume and $\frac{1}{2}c \sin\beta$ parameters from this study. The best fit equation for volume using X and X^2 (as previously defined) is:

$$V = 972.104 - 6.808X + 0.313X^2 \tag{10}$$
$$(7.919) \quad (1.751) \quad (0.096) \qquad r^2 = 0.68$$

An examination of Equation (10) indicates it to be inappropriate, probably because the range for X was so limited in

the samples studied. To illustrate its inadequacy, note that for a "pure" K-rich muscovite, Equation (10) predicts $V = 972$ A^3 whereas a volume of 935 A^3 has been determined from synthetic end-member muscovite and from Guidotti's model (Eq.(7)). The necessity for an additional compositional term accounting for the octahedral variation to further explain changes in volume is apparent. However, in the limited range of Na/(Na + K) values, all attempts to include the variable $\Sigma(Mg + Fe_T)$, or squared and cubed terms, failed to produce a reasonable regression equation.

The same compositional variables were modeled to the dependent variable, $\frac{1}{2}c \sin\beta$. Again, no significant regression equation could be fit to the data, although other compositional variables were later added and tested. This model suffers from the same inadequacies associated with that of Equation (10) above.

Guidotti modeled the $\underline{b}$ cell edge using a sample population whose atomic per cent Na/(Na + K) < 12.5. The 25 muscovites of this study conform to this population. Accordingly his model, Equation (9), was applied to the present data to calculate $\underline{b}$ and the differences $(\underline{b}_{obs} - \underline{b}_{calc})$. The calculated $\underline{b}$ values were found to be too high with differences ranging from 0.01 to 0.03 A (Table 8). When the SAS procedure GLM was applied to the present data, this time with

$\underline{b}$ as the dependent variable and $\Sigma(Mg + Fe_T)$ as the independent parameter, the following model resulted:

$$\underline{b} = 9.007 + 0.048 \; \Sigma(Mg + Fe_T) \tag{11}$$
$$(0.004) \quad (0.009) \qquad\qquad r^2 = 0.52$$

The r^2 value for Equation (11) indicated that the variable $\Sigma(Mg + Fe_T)$ might not be the best independent variable to explain the $\underline{b}$ cell edge. However, further testing of the compositional variables X, Si, Al^{iv}, Al^{vi}, Fe_T, Mg, Ti, OH, and F using SAS procedure $MAXR^2$, produced no model which yielded a statistically superior correlation.

The statistics for Guidotti's model were unavailable, therefore to compare Equation (7) with Equation (11), Guidotti's plot of $\Sigma(Mg + Fe_T)$ per 22 oxygens versus $\underline{b}$ has been reproduced with the points from this study (symbolized by +) added to the original data set (Fig. 6). From his plot, it is clear that, to a close approximation, the $\underline{b}$ value is a linear function of $\Sigma(Mg + Fe_T)$. Indeed, Guidotti produced the regression equation (Eq. (9)) previously discussed. However, Guidotti's regression line, which was not originally included on the published plot, has been drawn onto the diagram. This resulted in an obvious discrepancy between the regression line and the data reported on his plot. Presently, this incongruity is not understood. The regression line for

Equation (11) obtained from data of the present study is also included on Figure 6.

Equation (11) predicts that a muscovite with $\Sigma(Mg + Fe_T)$ = 0.0 will have a $\underline{b}$ cell dimension of 9.007 A, slightly greater than Guidotti's value of 8.990 A (Eq. (9)). For synthetic potassic micas, Velde (1980) plots the $\underline{b}$ cell edge versus the muscovite-celadonite content and for a "pure" muscovite wherein $\Sigma(Mg + Fe_T)$ = 0.0, the $\underline{b}$ value is between 9.005 and 9.01 A. Velde's data indicate the predicted value from Equation (11) is a better estimate. In order to further test Equation (9) and Equation (11), both were then applied to data from two samples in the literature, each with a precise crystal structure and compositional analysis. Sample 1 is from Richardson and Richardson (1982), and sample 2 is from Rothbauer (1971). The results are given in Table 9. In each case Equation (11), despite its poor r^2, yielded better agreement than Equation (7).

TABLE 8. Observed and calculated $\underline{b}$ values

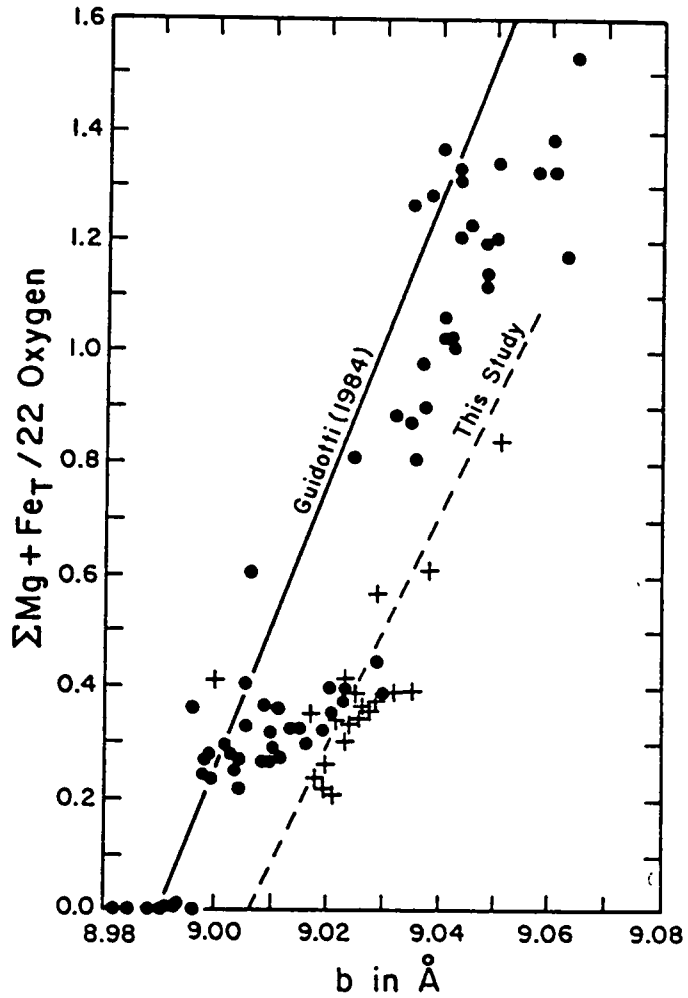| sample	$\underline{b}$	THIS STUDY		GUIDOTTI'S MODEL	
		$\underline{b}_{calc}$	$\underline{b}_{obs} - \underline{b}_{calc}$	$\underline{b}_{calc}$	$\underline{b}_{obs} - \underline{b}_{calc}$
1	9.052	9.047	0.005	9.024	0.028
2	9.009	9.027	-0.018	9.006	0.003
3	9.033	9.026	0.007	9.005	0.028
4	9.026	9.034	-0.008	9.013	0.013
5	9.032	9.026	0.006	9.006	0.026
6	9.037	9.026	0.010	9.006	0.031
7	9.027	9.025	0.002	9.005	0.022
8	9.025	9.026	-0.001	9.006	0.019
9	9.039	9.036	0.003	9.014	0.025
10	9.030	9.029	0.001	9.008	0.022
11	9.032	9.026	0.006	9.005	0.027
12	9.019	9.025	-0.006	9.005	0.014
13	9.029	9.025	0.004	9.005	0.024
14	9.019	9.019	0.000	9.000	0.019
15	9.025	9.022	0.003	9.002	0.023
16	9.024	9.027	-0.003	9.007	0.017
17	9.024	9.023	0.001	9.004	0.020
18	9.011	9.021	-0.010	9.001	0.010
19	9.021	9.018	0.003	8.999	0.022
20	9.023	9.022	0.001	9.003	0.020
21	9.020	9.020	0.000	9.001	0.019
22	9.022	9.024	-0.002	9.004	0.018
23	9.023	9.024	-0.001	9.004	0.019
24	9.027	9.024	0.003	9.004	0.023
25	9.023	9.018	0.005	8.999	0.024

FIGURE 6. A plot of $\Sigma(Mg + Fe_T)$ per 22 oxygens versus the b cell edge for muscovites of this study and Guidotti (1984). Solid circles and a solid regression line are after Guidotti (1984). Crosses and broken regression line represent the present study.

TABLE 9. Predicted $\underline{b}$ cell edge from $\Sigma(Mg + Fe_T)$ values

	MUSCOVITE SPECIMENS	
	Richardson and Richardson (1982)	Rothbauer (1971)
Fe_T^*	0.259	0.282
Mg^*	0.117	0.028
b_{obs}	9.0266 A	9.0153 A
b_{calc} (this study)	9.0250 A	9.0219 A
b_{calc} (Guidotti, 1984)	9.0050 A	9.0020 A

* Formula numbers per 22 oxygens

CONCLUSIONS

1. The Abbe refractometer represents an invaluable aid in the collection of refractive index data for the micas.

2. The collection of optical, compositional, and structural data should be performed on a single flake or grain (to the extent this is possible) before determining the dependencies of one parameter on another from the experimental data.

3. The extent to which Fe and Ti constitute the octahedral cations, and the extent to which OH rather than F occurs in the closely packed layers, appear to dominate the effect of composition on refractive index for muscovites.

4. Multiple linear regressions wherein independent variables Fe_T, Ti, and OH were modeled to explain variation in the principal refractive indices, indicate that Ti increases the refractive indices more than Fe_T or OH, and it increases β more than either α or γ. This may be because the Ti^{4+} is such a highly charged cation that it increases the polarizability of the closely packed O and OH anions.

5. The correlation coefficients for Fe^{2+} and Fe^{3+} (based on five Mossbauer data points) indicate Fe^{3+} strongly increases refractive indices in muscovite, whereas Fe^{2+} increases them to a lesser extent.

6. The optic angle 2V varies nearly linearly and inversely with the Ti content in the 25 muscovites presently studied. The high correlation of Ti and 2V is a result of its increasing β more than γ.

7. The effect of Ti on 2V agrees with the trend reported by Deer et al. (1962) for low Mg and Fe muscovites to have the largest 2V values since such muscovites are also low in Ti.

8. The b cell edge is, to a close approximation, a linear function of $\Sigma(Mg + Fe_T)$.

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