

STRUCTURAL AND CHEMICAL EFFECTS ON THE SiK_β X-RAY LINE FOR SILICATES

E. W. WHITE, *Materials Research Laboratory*

AND

G. V. GIBBS, *Department of Geochemistry and Mineralogy*
The Pennsylvania State University
University Park, Pennsylvania.

ABSTRACT

A study has been made of the SiK_β X-ray emission band for some 45 silicates using an electron microprobe. The data reported as SiK_β peak shifts (Δ) were measured with respect to a standard peak position obtained from quartz. In the case of those silicates for which precise crystal structure analyses have been made, a strong correlation is observed between Δ and mean Si-O bond length. Because the mean Si-O bond length is closely related to structure-type, one can use the measured Δ to predict the degree of polymerization of the SiO_4 tetrahedra. Among the framework silicates, a correlation is also observed between Δ and the atomic ratio (Al/Si) where the aluminum is tetrahedrally coordinated and where the mean Si-O bond length is essentially constant. This technique provides a method for characterizing unknown silicates and will be especially useful in studies of glasses, gels and fine-grained powders which are not amenable to precise structural refinements.

INTRODUCTION

There has been considerable interest over the past few years in the study of the "chemical effect" on X-ray emission spectra. It has been of particular interest to us to be able to use the chemical effect for the determination of such crystal chemical parameters as valence, coordination number and short-range order of unknown materials regardless of the perfection of long range order or regardless of the chemical complexity of the material. This has involved the study of shifts in X-ray emission lines generated by X-ray fluorescence and studies of electron-excited x-ray emission spectra using the electron microprobe.

Figure 1 shows the results obtained in an earlier study of the SiK_β line from elemental silicon, quartz and stishovite (White *et al*, 1962). The peak position shifts about 0.02 Å between quartz and elemental silicon and about 0.005 Å between quartz and stishovite. Since that study it has been discovered that the SiK_β peak position from the silicon in silicates varies in the range between quartz and stishovite (White and Gibbs, 1965). It is the purpose of this paper to describe the procedure for precise measurement of the SiK_β peak shift with an electron microprobe and to correlate these shifts with such parameters as structure-type, mean Si-O bond distance and the effect of aluminum substitution for silicon for a number of silicates.

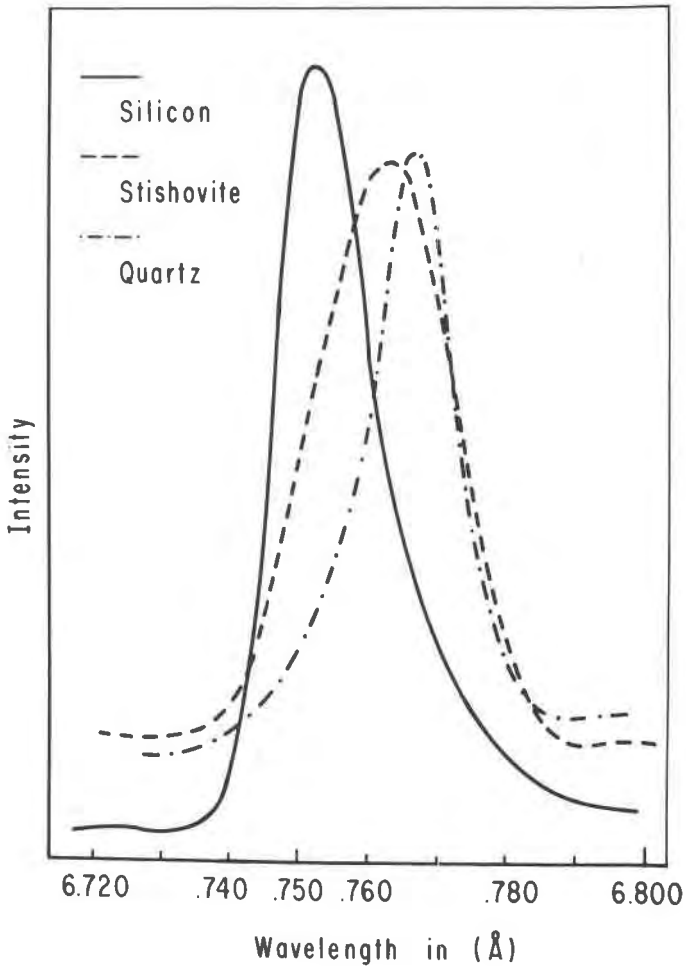


FIG. 1. The $\text{SiK}\beta$ lines from elemental silicon, low-quartz and stishovite.

HISTORICAL

The chemical effect on X-ray emission spectra was discovered by Lindh and Lundquist in 1924. Since their discovery numerous studies have been reported in the literature in which X-ray emission line changes were observed among various compounds of a given element (Yakowitz and Cuthill, 1962). Faessler (1963) and Cauchois (1954), among others, have reported the effect of valence on characteristic x-ray lines. In 1958 White *et al* reported the relation between $\text{AlK}\alpha$ peak shift and aluminum coordination number in several silicates and oxides. Several investi-

gators have subsequently adopted this technique to determine the average coordination number of aluminum in fine-grained silicates, gels, glasses and solutions (Brindley and McKinstry, 1961; Day, 1963; De Kimpe *et al.*, 1961, 1964).

EXPERIMENTAL PROCEDURE

Forty-three silicates representing a wide range of structure types and compositions were selected for study. Whenever possible, those silicates were included for which precise 3D crystal structure analyses have been completed. The samples, imbedded in $\frac{1}{4}$ in. diameter plastic molds, were carefully polished to a one micron diamond finish and mounted in brass holders, each containing one polished quartz standard and four silicates. The samples were then coated with 200–500 Å of vacuum evaporated carbon to serve as an electrically conductive overcoat.

The measurements were made with an ARL electron microprobe operated at 30KV and 0.05 μ A using a 75 μ diameter electron spot size. A four-inch (radius of focusing circle) ADP spectrometer equipped with a 0.001 inch beryllium window flow proportional counter and P-10 gas was used. Pulse height selection reduced interference from the second order CaK α (6.719 Å); however, this was not adequate when calcium was a major constituent. An EDDT crystal, having the advantage that the second order CaK α line is only weakly diffracted, was used to record the peaks for several samples, thus effectively eliminating the calcium interference.

Line profiles were scanned at a rate of 0.02 Å/min. and recorded on a five-inch strip chart recorder with a chart speed of an inch per minute. Peak count rates varied from 50 to 500 cps. Individual peak positions, measured at the point of maximum intensity, were determined with a precision of ± 0.0005 Å (± 0.13 eV). A minimum of four measurements was made on each sample. Averaged values are reported in Table 1.

The performance of the spectrometer used in this investigation has been further evaluated by comparison of results with those obtained from the high precision flat crystal vacuum X-ray spectrograph in the Materials Laboratory at Wright-Patterson Air Force Base, Ohio, the results being in good agreement with respect to peak shifts, widths and shapes. We are indebted to W. L. Baun for providing the measurements for this comparison. The Δ -values are also in general agreement with results reported by Koffman and Moll (1965).

The following five precautions must be taken to insure valid measurements with the microprobe: (1) Each specimen must be precisely positioned on the spectrometer focusing circle by very carefully adjusting each specimen to the focal plane of the light microscope; (2) The spectrometer and strip chart recorder drives must be accurately synchronized; (3) Spectral interferences must be eliminated; (4) Any drift in the spectrometer alignment must be recorded and compensated for by frequent reference to a standard specimen (low-quartz in this case); (5) The ratemeter time constant must be set at one second or less to prevent artificial displacement of peak positions.

Lack of suitable wavelength standards in the region of the SiK β line make it impractical to assign accurate wavelength values to each peak. Therefore it was decided to report all measurements as shifts in peak position calculated with respect to the measured peak from quartz. This shift, called delta (Δ), is defined as

$$\Delta = \lambda_{\text{SiK}\beta}(\text{Quartz}) - \lambda_{\text{SiK}\beta}(\text{Silicate})$$

where λ is the measured wavelength of the line in 10^{-4} Angstrom units.

TABLE 1. SILICON X-RAY LINE SHIFT IN SILICATES

Name	Ideal composition	Δ	Mean Si-O where known
<i>FRAMEWORK STRUCTURE</i>			
Low quartz	SiO ₂	0	1.607 Å
Beryl	Be ₃ Al ₂ Si ₆ O ₁₈	0	1.610
Amelia albite	NaAlSi ₃ O ₈	15	1.613
Oligoclase	Ab ₉₀ An ₁₀ to Ab ₇₀ An ₃₀	21	
Andesine	Ab ₇₀ An ₃₀ to Ab ₅₀ An ₅₀	27	
Amorphite	CaAl ₂ Si ₂ O ₈	33	1.614
Leucite	KAlSi ₂ O ₆	24	
Haddam cordierite	Mg ₂ (Be,Al,Si) ₉ O ₁₈	27	1.614
Synthetic corderite	Mg ₂ (Mg,Al,Si) ₉ O ₁₈	33	
Sanidine	KAlSi ₃ O ₈	17	
Microcline	KAlSi ₃ O ₈	19	1.613
Orthoclase	KAlSi ₃ O ₈	17	
Orthoclase	KAlSi ₃ O ₈	20	
Intermediate microcline	KAlSi ₃ O ₈	21	1.612
Danburite	CaB ₂ Si ₂ O ₈	28	1.619
<i>SHEET STRUCTURE</i>			
Muscovite	K(Al,Mg,Fe ₂ AlSi ₃ O ₁₀ (OH) ₂	20	
Muscovite	(K,Na,Ca)(Al,Fe,Mg) ₂ AlSi ₃ O ₁₀ (OH) ₂	25	
Biotite	K(Fe,Mg,Al)AlSi ₃ O ₁₀ (OH,Cl) ₂	25	
Lepidotite	KLiAl ₂ Si ₄ O ₁₀ (OH,F) ₂	25	
M.I.T. biotite	K(Mg,Fe,Al,Ti) ₃ AlSi ₃ O ₁₀ (OH,F) ₂	25	
Fluorophlogopite	KMg ₃ AlSi ₃ O ₁₀ F ₂	28	
<i>CHAIN STRUCTURE</i>			
Protoamphibole	(Li,Mg) ₇ Si ₈ O ₂₂ F ₂	25	1.617
Crossite	Na ₂ (Fe,Mg) ₃ (Al,Fe) ₂ Si ₈ O ₂₂ (OH) ₂	28	
Richterite	Na ₂ CaMg ₅ Si ₈ O ₂₂ (OH) ₂	23	
Wollastonite	CaSiO ₃	40	1.626
Spodumene	LiAlSi ₂ O ₆	44	
Tourmaline	NaMg ₃ B ₃ Al ₆ Si ₆ O ₂₇ (OH) ₄	25	1.621
Jadeite	NaAlSi ₂ O ₆	29	1.623
Axinite	HCa(Mn,Fe)Al ₂ B(SiO ₄) ₄	34	
Pyroxene	(Ca,Na,Fe,Al,Mg) ₂ Si ₂ O ₆	38	
Pyroxene	(Ca,Fe,Mg,Mn) ₂ Si ₂ O ₆	25	
<i>ISOLATED TETRAHEDRA</i>			
Spessartite	Mn ₃ Al ₂ (SiO ₄) ₃	40	
Almandite	Fe ₃ Al ₂ (SiO ₄) ₃	40	
Pyrope	Mg ₃ Al ₂ (SiO ₄) ₃	36	1.635
Almandite	Fe ₃ Al ₂ (SiO ₄) ₃	50	
Uvarovite	Ca ₃ Cr ₂ (SiO ₄) ₃	49	
Fayalite	Fe ₂ SiO ₄	40	1.633
Forsterite	Mg ₂ SiO ₄	40	1.634
Monticellite	CaMgSiO ₄	55	
Vesuvianite	Ca ₁₀ Al ₄ (Mg,Fe) ₂ Si ₉ O ₃₄ (OH) ₄	54	
Kyanite	Al ₂ SiO ₅	33	1.628
Zircon	ZrSiO ₄	37	1.612(2D)
Topaz	Al ₂ SiO ₄ (F,OH) ₂	45	
Titanite	CaTiSiO ₅	49	
Andalusite	Al ₂ SiO ₅	34	1.628
<i>MIXED TYPES</i>			
Epidote	Ca ₂ (Al,Fe) ₃ (SiO ₄) ₃ (OH)	46	1.634(2D)

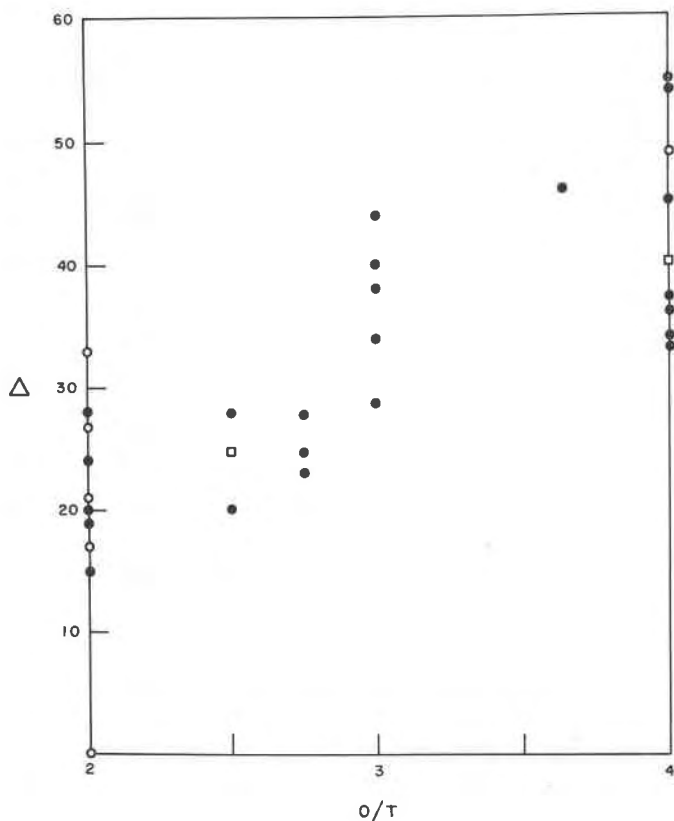


FIG. 2. Plot of ΔSiK_β versus O/T ratio for all silicates included in this study. The ratio of tetrahedral oxygen (O) to tetrahedrally coordinated cation (T) has been calculated assuming ideal compositions and structures. Open circles indicate that two values fall at the same point. Open squares indicate the occurrence of four values at one point on the plot.

RESULTS AND DISCUSSION

The measurements recorded in this study are enumerated in Table 1 according to structure type along with the corresponding mineral name, the idealized chemical formula and the mean Si-O bond distance (where available). The majority of the mean Si-O distances were taken from a review paper by Smith and Bailey (1963) in which they found correlations to exist between mean Si-O bond distance, O/T ratio and structure-type. Additional values were taken from Gibbs and Smith (pyrope, 1965), Prewitt and Burnham (jadeite, 1966), Gibbs *et al* (forsterite and fayalite, 1963 and in preparation), Meagher and Gibbs (cordierite, in preparation) and Gibbs *et al* (beryl, in preparation).

Figure 2 is a plot of Δ versus the ratio of oxygen to tetrahedrally coordinated atoms (O/T) for all the silicates tabulated in Table 1. Despite the spread of Δ values within each O/T group, there is an apparent correlation between Δ and O/T ratio. As the mean Si-O bond distance can be correlated with O/T ratio (Smith and Bailey, 1963), the relation between Δ and the mean Si-O distance was examined for those silicates for which precise 3D structural determinations have been completed. Unfortunately, for more than half of the silicates included in our study, precise Si-O distances are not available; however, a plot of those for which such information is available gives an apparent linear relation (Fig. 3) with a linear correlation coefficient of 0.85.

The Δ values of several of the framework structures, having essentially the same mean Si-O bond lengths, show departures from the linear plot that is outside the experimental error. As several of these compounds contain tetrahedrally coordinated aluminum in addition to silicon, a plot of Δ vs the Al/Si ratio was prepared (Fig. 5), permitting a correlation to be made between Δ and the Al/Si ratio. Actually, because the average T-O distance in a framework silicate is linearly related to the percentage of aluminum in tetrahedral coordination (Smith and Bailey, 1963), it follows perforce that a correlation exists between the mean T-O bond length and Δ as well. Figure 4 is a plot of Δ vs the mean Si-O bond length

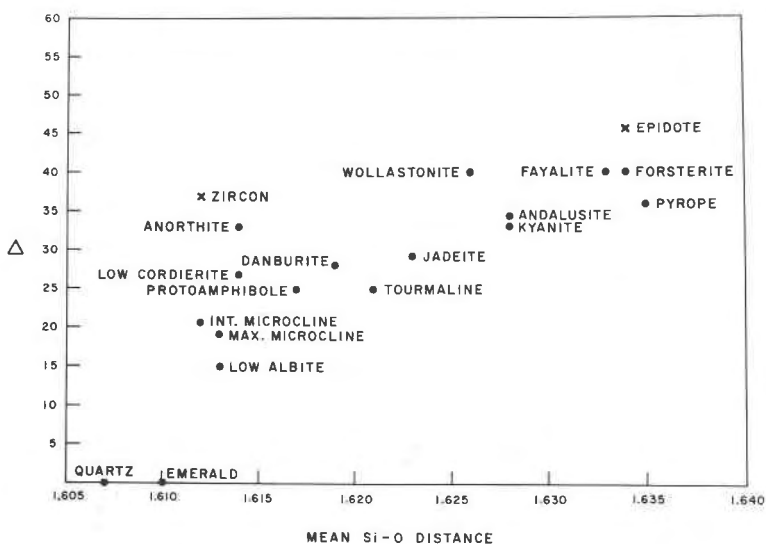


FIG. 3. Plot of Δ SiK β versus mean Si-O distance for silicates where accurate Si-O distances have been determined. Points indicated by an X refer to values calculated from two-dimensional intensity data.

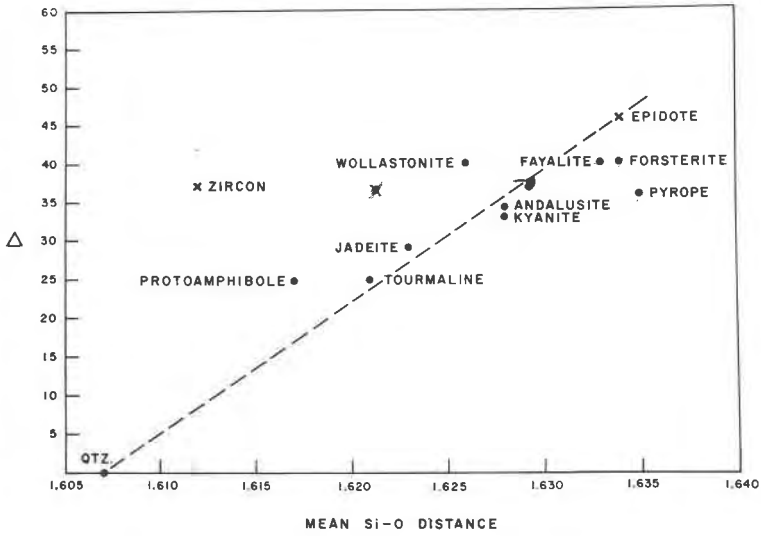


FIG. 4. Plot of Δ SiK β versus mean Si-O distance for those structures in which Si is the only cation in tetrahedral coordination.

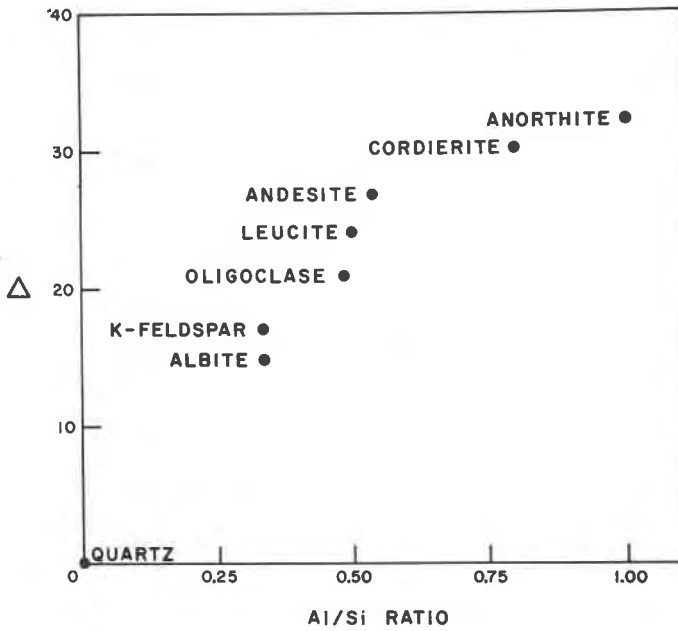


FIG. 5. Plot of Δ SiK β versus Al/Si ratio for framework structures where both the Al and Si are in tetrahedral coordination.

for those silicates which have only silicon in tetrahedral coordination. With the exception of zircon, the Δ 's and mean Si-O bonds lengths fall along a straight line within the experimental error of the measurements having a linear correlation coefficient of 0.93. As the structural determination of zircon was made from 2D data (Krstanovic, 1958) resulting in a standard error of 0.01 Å of the Si-O bond length, we have decided to carry out a refinement using 3D data to learn the source of discrepancy.

SUMMARY

A unique opportunity has been provided by the silicates for the examination of some of the more subtle aspects of the "chemical effects" on X-ray spectra. In these compounds the silicon plays a quasicontant role with respect to valence, coordination number and bond type which has facilitated the study of the short range order effects. It appears that Δ can be used to predict the mean Si-O distance with a precision close to that expected in a crystal structure analysis. As the degree of long range order does not affect Δ , one could use the technique to study amorphous and poorly crystallized materials which are not amenable to precise crystal structure analysis.

ACKNOWLEDGMENTS

The authors wish to thank Professor R. V. Dietrich of The Virginia Polytechnic Institute and C. O. Ingamells of The Pennsylvania State University for donating several of the silicates used in this study. The paper was critically reviewed by Dr. C. T. Prewitt of the E. I. du Pont de Nemours Central Research Department and Dr. P. H. Ribbe of The Virginia Polytechnic Institute. This study was supported by the Advanced Research Projects Agency (Grant SD-132) and National Science Foundation (Grant GP-3440).

REFERENCES

- BRINDLEY, G. W. AND H. A. MCKINSTRY (1961) The kaolinite-mullite reaction series: IV. The coordination of aluminum. *J. Amer. Ceram. Soc.* **44**, 506-507.
- CAUCHOIS, Y. (1954) Spectres et liaison chimique. *J. Chim. Phys.* **51**, D76-88.
- DAY, D. E. (1963) Determining the coordination number of aluminum ions by X-ray emission spectroscopy. *Nature* **200**, 649-651.
- DE KIMPE, D., M. C. GASTUCHE AND G. W. BRINDLEY (1961) Ionic coordination in aluminosilicic gels in relation to clay mineral formation. *Amer. Mineral.* **46**, 1370-1381.
- DE KIMPE, C., M. C. GASTUCHE AND G. W. BRINDLEY (1964) Low-temperature synthesis of kaolin minerals. *Amer. Mineral.* **49**, 1-16.
- FAESSLER, A. (1963) X-ray emission and the chemical bond In *Proceedings of the tenth colloquium spectroscopicum internationale*, ed. E. R. Lippincott and M. Margoshes, Spartan Books, Washington, D. C., 307-319.
- GIBBS, G. V., P. B. MOORE AND J. V. SMITH (1963) Crystal structure of forsterite and hortonolite varieties of olivine (abstr.). *Geol. Soc. Amer. Spec. Pap.* **74**, 66.
- GIBBS, G. V. AND J. V. SMITH (1965) Refinement of the crystal structure of synthetic pyrope. *Amer. Mineral.* **50**, 2023-2039.
- KOFFMAN, D. M. AND S. H. MOLL (1966) Effect of chemical combination on the X-ray

- spectra of silicon. *Advances in X-ray Analysis* 9, ed. Mallett, Fay and Mueller, Plenum Press, 323-328.
- KRSTANOVIC, I. R. (1958) Redetermination of oxygen parameters in zircon ($ZrSiO_4$). *Acta Crystallogr.* **11**, 896-897.
- LINDH, A. E. AND O. LUNDQUIST (1924) *Ark. Mat. Astron. Fys.* **18**, no. 3, 14, 35.
- PREWITT, C. T. AND C. W. BURNHAM (1966) The crystal structure of jadeite, $NaAlSi_2O_6$. *Amer Mineral.* **51**, 956-975.
- SMITH, J. V. AND S. W. BAILEY (1963) Second review of Al-O and Si-O tetrahedral distances. *Acta Crystallogr.* **16**, 801-811.
- WHITE, E. W., H. A. MCKINSTRY AND T. F. BATES (1958) Crystal chemical studies by X-ray fluorescence. *Proc. 7th Ann. Conf. Ind. Appl. X-ray Anal.*, ed. W. M. Mueller, University of Denver, 239-245.
- , H. A. MCKINSTRY AND RUSTUM ROY (1962) Use of electron probe analysis of Si and Al emission spectra in studies of microstructural relationships (abstr.). *Geol. Soc. Amer. Spec. Pap.* **73**, 261.
- AND G. V. GIBBS (1965) Estimation of mean Si-O bond lengths in silicates by X-ray emission (abstr.). *Geol. Soc. Amer. Spec. Pap.* **87**, 185.
- YAKOWITZ, H. AND J. R. CUTHILL (1962) Annotated bibliography on soft X-ray spectroscopy. *U. S. Nat. Bur Stand. Monogr.* **52**.

Manuscript received, July 15, 1966; accepted for publication, October 10, 1966.