TETRAHEDRALLY COORDINATED ALUMINUM IN SOME NATURAL BIOTITES: AN INFRARED ABSORPTION ANALYSIS

HOMER C. LIESE, *Department of Geology, University of Connecticut, Storrs, Connecticut.*

ABSTRACT

Infrared spectra (8 to 18.2 μ region) of eight chemically-analyzed natural biotites have been obtained, and variations in absorption intensities in the 13 to 15 μ region may be related to corresponding variations in the calculated tetrahedrally-coordinated aluminum. However, positive assignment of these specific spectral variations with corresponding changes in Y-number still requires more extensive and detailed study, primarily because of the apparent complicating spectral effects of MgO and FeO variations in octahedral coordination.

Infrared spectra (8 to 18.2 μ region) also have been obtained for eleven unanalyzed biotites separated from silicic igneous rocks of Utah and Nevada, and variations in absorption intensities within the 13 to 15 μ region have been tentatively interpreted as variations in the amount of tetrahedral aluminum. The results show a general decrease in the interpreted tetrahedral aluminum as the rock textures change from granitoid to porphyritic.

Three factors which influence tetrahedrally-coordinated aluminum in biotite (*i.e.*, temperature, pressure and composition), are briefly discussed.

INTRODUCTION

Previous infrared investigations, which specifically concern aluminum substitution for silicon[1] in the phlogopite-biotite series, have not been numerous. Lyon and Tuddenham (1960) observed changes in "shapes" of infrared absorption bands in the 8.5 to 11 μ region for these minerals, most of which were chemically analyzed. They concluded from their calculations and deductions, which were based largely on similar data from other mica types, that this change in shape reflects the amount of tetrahedrally-coordinated aluminum. Stubican and Roy (1961) observed systematic variations in the infrared spectra of synthetic phlogopite-biotite samples when the amount of tetrahedral aluminum was varied. Specifically, according to them, as the amount of tetrahedrally coordinated aluminum increased: (1) a sharp band at 14.77 μ (668 cm^{-1}) was replaced by a series of weak maxima between 16.66 μ (600 cm^{-1}) and 12.82 μ (780 cm^{-1}); and (2) a new band appeared at about 830 cm^{-1}. (Based on observation of their published spectra, the author finds that the reverse is more true with respect to statement (1), and that the "new band" in statement (2) merely represents a gradual shift in wavelength.)

---

[1] In previous studies, aluminum substitution for silicon in micas has been referred to as tetrahedrally-coordinated aluminum, tetrahedral aluminum, or the "Y-number." These designations are maintained herein.

It was the purpose of this investigation to: (a) obtain infrared spectra for a group of chemically-analyzed biotites, for which the Y-number could therefore be calculated, in order to verify the pertinent results of the previous work done by Lyon and Tuddenham (1960) and Stubican and Roy (1961); (b) obtain infrared spectra for a series of unanalyzed biotites, separated from selected silicic igneous rocks, and deduce the approximate Y-number (if possible) from the results obtained in (a) above and in previous studies; and (c) attempt to evaluate the relative significance of three environmental factors which probably influence the amount of tetrahedral aluminum in biotite (*i.e.* temperature, pressure, and composition), based chiefly upon the data obtained in this study.

EXPERIMENTAL PROCEDURE

The sample preparation method essentially followed in the infrared analysis is the potassium bromide technique, described independently by Stimson and O'Donnell (1952) and Scheidt (1952), and modified by French *et al.* (1954).

The biotite samples[1] were manually ground in an agate mortar until a fine powder was obtained. Eight to fifteen drops of isopropyl alcohol were then added, and a more gentle grinding continued until evaporation was complete. Then, 2.5 mg of sample were weighed out, to which was added one gram of KBr of infrared quality. The mixture was then placed in a plastic vial and mechanically blended for one minute with a "Wig-L-Bug" amalgamator. Discs of 1.4 mm and 0.5 mm in thickness were then prepared by utilizing 505 mg and 175 mg of mixture, respectively. These amounts were each placed in an infrared die, 12.5 mm in diameter. Evacuation for two to three minutes under a pressure of 7,000 psi resulted in relatively clear, uncracked discs. Standard discs of pure KBr were prepared by the same method, and run with all samples.

The samples were analyzed using a Perkin-Elmer model 421 grating spectrophotometer. The specific instrumental conditions were as follow:

Slit program: 1000
Gain: 4
Attenuator speed: 1100
Suppression: 4
Scanning speed: fast (internal setting); 32 (external setting)
Expansion: 0.25×
Compression: 50%
Source intensity: 0.4 ampere
Scale factor: 0.5×

---

[1] Final selection of the biotite separated from the silicic igneous rocks was made under the binocular microscope. The resultant sample appeared to be essentially 95% pure, with observed tolerated contaminators being inclusions of apatite and magnetite and chloritic alteration minerals.

All samples were run from 8 to 18.2 μ (1250 to 550 cm^{-1}), with an initial transmittance of 90%. The two figures contained herein represent the spectra obtained from the 505 mg discs. The thinner 175 mg discs were run through the 8 to 11.76 μ (1250 to 850 cm^{-1}) region for all the samples, but no significant changes in absorption intensity or frequency were observed after comparison with the spectra obtained with the thicker 505 mg discs in that region.

Large particle size may result in infrared scattering, and yield poorly defined absorption bands (Launer, 1952). Since no special screening procedure was followed in order to minimize this possible effect, several samples of muscovite and fluorphlogopite were prepared and analyzed. The resultant infrared spectra compared favorably with published spectra for these minerals.

Variation in particle size may yield different infrared spectra for the same sample (Tuddenham and Lyon, 1960). Therefore, several samples of the same biotite specimen were prepared and analyzed, and reproducibility of spectra was readily obtained. This was interpreted as evidence supporting uniformity of particle size.

Polystyrene contamination, through usage of plastic vials in the sample disc preparation, may result in absorption peaks in the spectral region which the author considers significant for biotites, such as 690 to 696 cm^{-1}. However, similarly-prepared standard discs should compensate for the polystyrene in the sample discs. Secondly, if contamination was effective, other major polystyrene absorption peaks should appear in the spectra, such as those near 775 cm^{-1} and 905 cm^{-1}, and no such effects have been observed. Finally, if contamination was effective, consequent changes in absorption spectra would probably be relatively constant in magnitude, and any regular variations in the spectra would probably be due to causes other than polystyrene contamination.

PRESENTATION AND INTERPRETATION OF DATA

Infrared analysis was first conducted for eight chemically-analyzed biotites. Table I gives the chemical analyses of these biotites, their corresponding code numbers and analysts, and the amount of tetrahedral aluminum as calculated according to the method proposed by Shell and Craig (1956).

The 8 to 18.2 μ region of the spectra obtained for these biotites are shown in Fig. 1. In the region extending from about 12.82 to 15.3 μ (780 to 650 cm^{-1}), there exists, in general, a subtle but systematic variation in absorption intensities which *may* be related to a corresponding change in the amount of tetrahedral aluminum. (It may also be related to variation in octahedral composition, *i.e.* FeO and MgO, *or* a combination of

octahedral and tetrahedral variations.) Specifically, the intensities of the absorption troughs centered near 14.49 μ (690 cm^{-1}) and 13.2 μ (758 cm^{-1}) generally increase as the calculated Y-number increases. These results agree in general with those *observed* within the same region of the infrared spectra obtained by Stubican and Roy (1961). However, no "new band" appeared at about 830 cm^{-1}, as obtained in their spectra of

TABLE I. CHEMICAL ANALYSES OF THE BIOTITES; THEIR CALCULATED
Y NUMBER; ANALYSTS; AND CORRESPONDING CODE NUMBERS

	1	2	3	4	5	6	7	8
SiO_2	36.70	36.70	36.11	33.60	34.64	34.24	36.64	33.09
Al_2O_3	16.10	15.10	18.50	16.79	20.31	18.28	19.36	17.65
Fe_2O_3	3.37	2.83	1.46	4.59	1.39	1.83	0.62	2.42
FeO	18.68	15.90	16.62	23.83	20.76	21.89	17.18	29.22
CaO	0.00	0.03	0.00	0.09	0.04	0.54	0.09	0.10
MgO	9.16	11.82	10.50	4.61	5.95	6.30	9.59	2.83
Na_2O	0.05	0.13	0.10	0.23	0.25	0.20	0.31	0.13
K_2O	9.39	9.42	9.54	9.17	9.37	8.51	9.03	9.04
TiO_2	2.83	4.10	2.63	2.39	3.01	3.29	3.00	1.30
H_2O^+	2.90	2.64	3.05	3.18	3.44	4.03	3.26	2.92
H_2O^-	0.10	0.06	0.05	0.36	0.14	0.08	0.08	0.04
MnO	0.23	0.21	0.33	0.53	0.24	0.35	0.05	0.04
F	0.31	0.59	0.55	0.33	0.24	0.35	0.05	0.04
Cl					0.06		0.05	1.11
Less 0=F	0.13	0.25	0.23	0.14	0.11	0.08	0.12	0.34
Total:	99.91	99.61	99.40	99.70	99.88	99.88	99.83	99.97

1. Y=1.09 B141-Analysts: Courville & Bender
2. Y=1.11 B140-Analysts: Courville & Bender
3. Y=1.17 B142-Analysts: Courville & Bender
4. Y=1.23 R1844-Analyst: Maxwell
5. Y=1.24 R2270-Analyst: Rock Analysis Lab., U. of Minnesota
6. Y=1.25 KA235 (Kaavi biotite)-Analyst: Ingamells
7. Y=1.15 60-1138 (MIT biotite)-Analyst: Ingamells
8. Y=1.23 R2208 (Idaho biotite)-Analyst: Goldich

synthetic phlogopite-biotite members. In addition, no significant or systematic change in the "shape" of the main Si-O absorption band, centered around the 10 μ region, was observed (even when using the thinner 175 mg discs), which would thus correspond to a change in Y-number as proposed by Lyon and Tuddenham (1960). This probably signifies that the Si-O absorption in the 10 μ region is too strong to detect minor variations in tetrahedral aluminum, at least under the experimental conditions of this study.
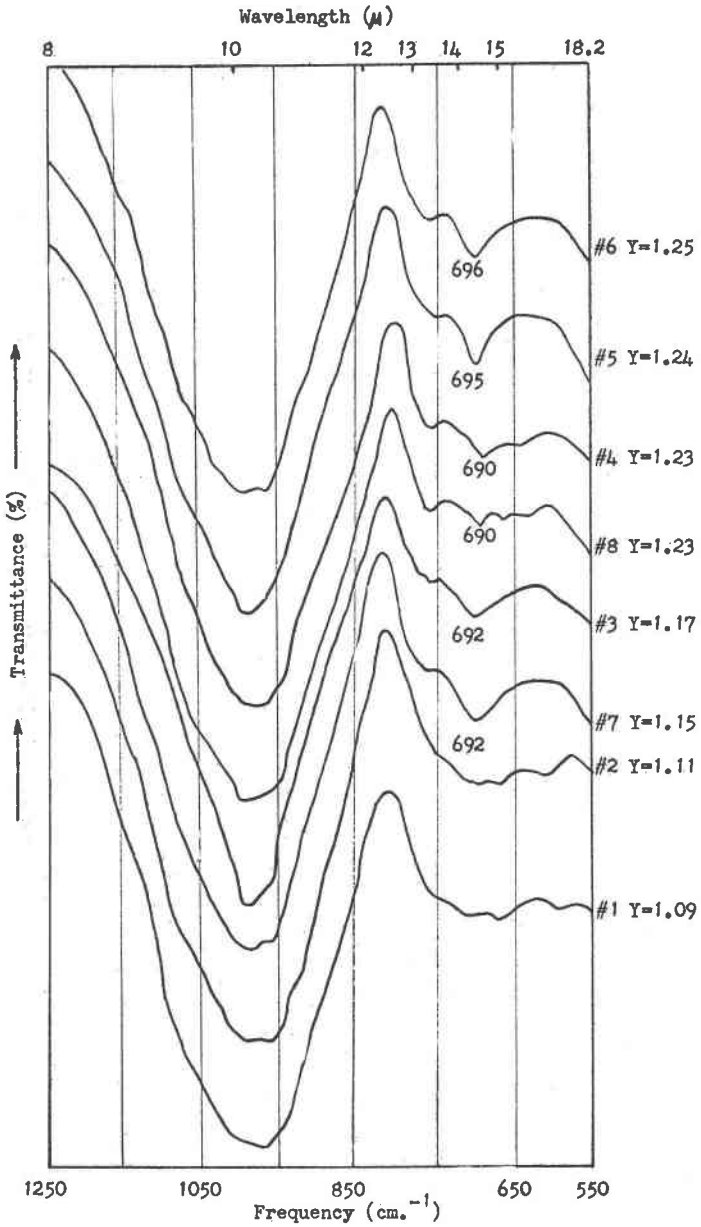
FIG. 1. Tracings of infrared absorption spectra (8 to 18.2μ) of eight chemically analyzed biotites, with calculated tetrahedral aluminum (Y-number).

The above information does not represent conclusive evidence, and positive assignment of a change in specific absorption spectra with a corresponding change in tetrahedrally coordinated aluminum in biotites still requires more extensive and detailed study. This uncertainty is primarily due to the fact that there are several closely interrelated geochemical factors which influence infrared absorption intensities and/or frequencies as pointed out in the studies by Miller and Wilkins (1952), Launer (1952), Setkina (1959), Dachille and Roy (1959), Saksena (1960) and Stubican and Roy (1961). The resultant complexity would be especially pronounced when dealing with naturally-occurring, heterodesmic phyllosilicates.

However, the spectra obtained for the eight chemically analyzed biotites do reveal certain variations which may be related to variations of the calculated tetrahedral aluminum (limited Y-number spread from 1.09 to 1.25). Thus, tentative interpretations of Y-number are now applied to the infrared spectra obtained for eleven unanalyzed biotites which have been separated from silicic igneous rocks located in the Basin and Range Province of Utah and Nevada (Fig. 2).

Almost all of these spectra show a distinct decrease in absorption intensity of the band *near* the 14.5 μ (690 cm^{-1}) region as the rock types change from more granitoid to more porphyritic in texture. This is tentatively interpreted to mean a corresponding slight decrease in tetrahedral aluminum (and/or change in octahedral composition). The spectra obtained for both the north and south ends of the quartz monzonite porphyry dike, Lone Mountain, Nevada (an intervening distance of 3 miles), are essentially identical. This suggests no change in the amount of tetrahedral aluminum (and/or octahedral composition), thus indirectly providing evidence that there exists compositional variations for most of the biotites from the other sample localities in which rock types of varying textures are represented.

Shifts of Si-O bands to longer wavelengths have been noted in micas by Mg replacement of Al (Saksena, 1960) and Fe^{2+} replacement of Mg (Tuddenham and Lyon, 1959) in octahedral coordination. Similar frequency shifts in some of the infrared spectra obtained in this study are believed in part due to the above replacements, but are possibly somewhat influenced by minor chloritic alteration as well.

DISCUSSION OF INFLUENTIAL FACTORS

Aluminum, having an ionic radius of 0.51 Å (Ahrens, 1952), can occur in both tetrahedral and octahedral coordination with oxygen. In high temperature minerals, such as feldspars, aluminum tends to assume a tetrahedral coordination, whereas in low temperature minerals, such as
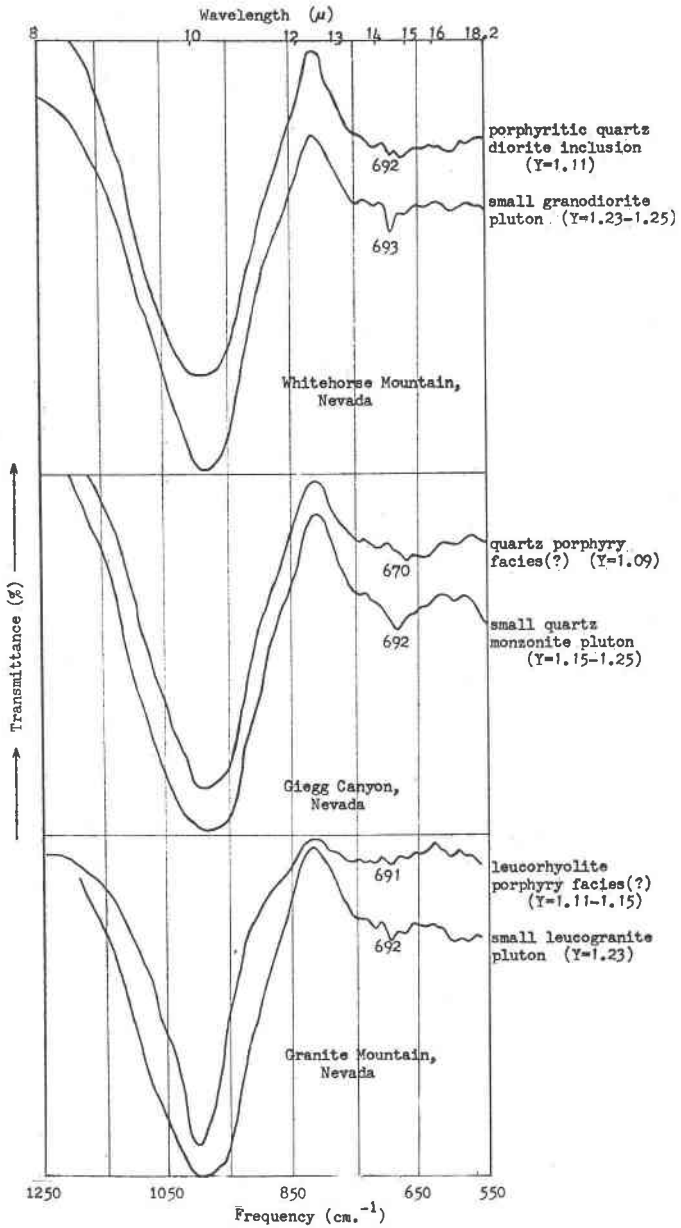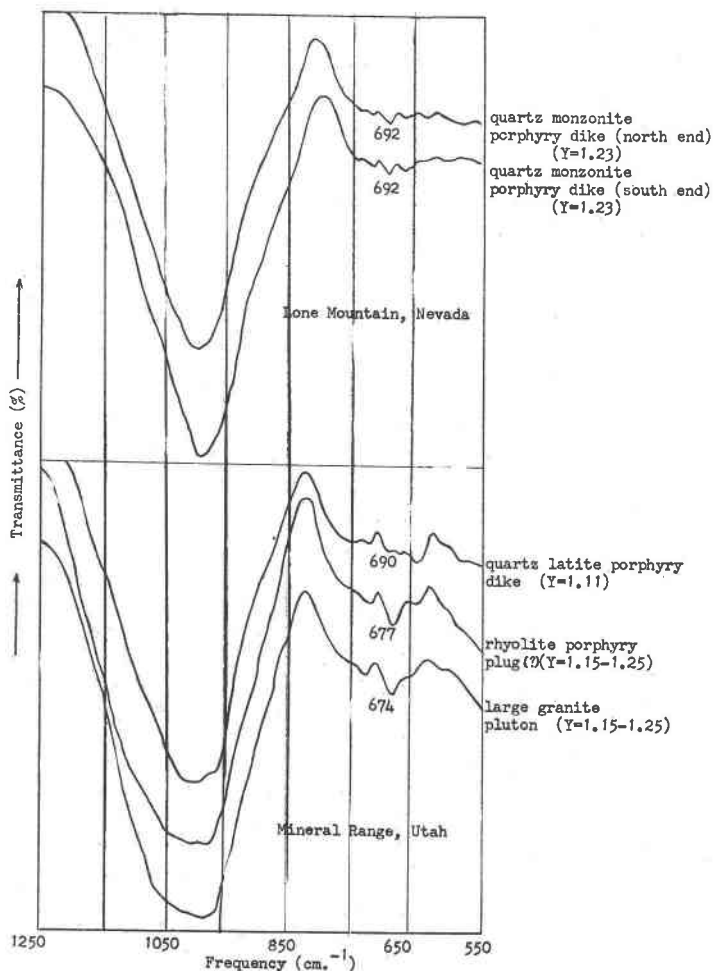
FIG. 2. Tracings of infrared absorption spectra (8 to 18.2μ) of biotites from selected silicic igneous rocks, with interpreted tetrahedral aluminum (Y-number)

FIG. 2—*Continued*

kaolinite, it prefers the octahedral coordination. According to Buerger (1948), aluminum may have both four- and six-fold coordination in minerals of intermediate temperature, such as biotite. Therefore, the amount of aluminum in tetrahedral coordination may be a function of temperature of formation, and accordingly, an increase of aluminum in tetrahedral coordination may suggest an increase in the temperature of formation.

In a recent study by Liese (1963), temperature interpretations based on the deduced variation in tetrahedral aluminum in nine of the eleven

unanalyzed biotites examined herein were correlated with temperature interpretations based on: (1) variation in titanium content in magnetite; (2) order-disorder in potassium feldspars; and (3) order-disorder in sodic plagioclases—all correlations being made on minerals separated from the same rocks. The correlated temperature interpretations for the variation in tetrahedral aluminum in the biotites showed only a 50% agreement with the other methods of investigation, and this was interpreted as a weakening of its geothermometric value. If the other methods of temperature estimation are valid (especially those concerning magnetite and potassium feldspar), and the work of others as well as that by Liese suggest they are, the amount of tetrahedral aluminum in biotites (as deduced by this infrared method) does not seem to be *primarily* a function of temperature.

If we relate variations of MgO, FeO, and SiO_2 in the eight chemically-analyzed biotites (Table I), it is found that those biotites having slightly higher SiO_2 also contain higher MgO and lower FeO, and moreover, have a slightly lesser amount of calculated tetrahedral aluminum. Thus, the variations in infrared spectra, tentatively interpreted as being due to variation in tetrahedral aluminum, may also be explained by the amount of Mg or Fe influencing the octahedral positions.

Low pressures, like high temperatures, promote more open structures. Infrared absorption spectra for almost all the separated biotites that were analyzed in this investigation show an interpreted slight decrease in tetrahedral aluminum as the silicic rocks become more porphyritic. It is thus suggested that biotites may be especially pressure-sensitive owing perhaps to their pronounced anisotropism relative to bond strength, and may undergo a significant distortion of structure as the pressure varies. This structural variation may be related to variation in tetrahedral aluminum. In an x-ray study by Crowley and Roy (1960), evidence is presented revealing a change in the b and c directions of the unit cell of several phyllosilicates (but not synthetic phlogopite) as a function of pressure—whereas temperature appeared to have little effect on the cell dimensions.

CONCLUSIONS

Based on the results of this limited study, the following tentative conclusions are summarized:

(1) Variation in tetrahedrally coordinated aluminum in natural biotites *may* be revealed in the 13.0 to 15.0 μ region of infrared absorption spectra, although its precise detection therein is probably primarily complicated by the spectral effects in MgO and FeO variations in octahedral coordination.

(2) Absorption is too strong in the 9 to 11 μ region to detect minor changes in tetrahedrally coordinated aluminum, at least under the experimental conditions of this study.

(3) If the spectral changes do signify changes in tetrahedral aluminum, then pressure (rather than temperature) along with composition may be the environmental factors which primarily influence the amount of tetrahedral aluminum in biotites.

Positive assignment of variations in infrared spectra to corresponding variations in tetrahedral aluminum in biotites still requires more extensive and detailed studies, which should include samples with a wider range of calculated tetrahedral aluminum (1 to 1.5), as well as spectrophotometric conditions which permit analyses beyond 25 microns.

Acknowledgments

References

Buerger, M. J. (1948) The role of temperature in mineralogy. *Am. Mineral.* **33**, 101.

Crowley, M. S. and R. Roy (1960) The effects of formation pressures on sheet structures—a possible case of Al-Si ordering. *Geochim. Cosmochim. Acta,* **18**, 94–100.

Dachille, F. and R. Roy (1959) The use of infrared absorption and molar refractivities to check coordination. *Zeit. Kristall.* **111**, 462–470.

French, R. O., M. E. Wadsworth, M. A. Cook, and I. B. Cutler (1954) The quantitative application of infrared spectroscopy to studies in surface chemistry. *Jour. Phys. Chem.* **58**, 805–811.

Launer, P. J. (1952) Regularities in the infrared absorption spectra of silicate minerals. *Am. Mineral.* **37**, 764–784.

Liese, H. C. (1963) A correlative geothermometric mineral study. *Am. Jour. Sci.* (in press).

Lyon, R. J. P. and W. M. Tuddenham (1960) Determination of tetrahedral aluminum in mica by infrared absorption analyses. *Nature,* **185**, 374–375.

Miller, F. A. and C. H. Wilkins (1952) Infrared spectra and characteristic frequencies of inorganic ions. *Anal. Chem.* **24**, 1253–1294.

Saksena, B. D. (1960) Infrared absorption studies of some silicate structures. *Proc. Indian Acad. Sci.,* 242–258.

Scheidt, U. (1952) On the infrared spectroscopy of amino acids. I. A new preparation technique for infrared spectroscopy of amino acids and other polar compounds. *Zeit. Naturforsch.* **7b**, 270.

Setkina, O. N. (1959) Infrared spectra of minerals and their practical application. *Zapiski Vsesoivznogo Mineral. Obshohestva,* **88**, 39–47.

Shell, H. R. and R. L. Craig (1956) Synthetic mica investigations: VII, chemical analysis and calculation to unit formula of fluorsilicates. *U. S. Bureau Mines, Rpt. Invest.* **5158**.

Stimson, M. M. and M. J. O'Donnell (1952) The infrared and ultraviolet absorption

spectra of cytosine and isocytosine in the solid state. *Jour. Am. Chem. Soc.* **74,** 1805.

STUBICAN, V. AND R. ROY (1961) Isomorphous substitution and infrared spectra of the layer lattice silicates. *Am. Mineral.* **46,** 32–51.

TUDDENHAM, W. M. AND R. J. P. LYON (1959) Relation of infrared spectra and chemical analysis for some chlorites and related minerals. *Anal. Chem.* **31,** 377–380.

——— (1960) Infrared techniques in the identification and measurement of minerals. *Anal. Chem.* **32,** 1630–1634.