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SUPPLEMENTAL DATA ON THE CORRELATION OF INFRARED ABSORPTION SPECTRA AND COMPOSITION OF BIOTITES

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As part of a concurrent study involving the petrologic significance of compositional characteristics of selected minerals, approximately sixty biotites were analyzed routinely employing a Perkin-Elmer model 621 infrared grating spectrophotometer. (Details of the experimental procedure appear in Liese, 1967*a*). After spectrogram examination, six of the biotites were selected for chemical analysis; the basis for the selection being consistent and substantial modifications of certain absorption bands.

This note presents, very briefly, data supplemental to a previous publication (Liese, 1963) on the correlation of specific spectral changes with specific changes in biotite composition. It is hoped that this information will be of use to the increasing number of workers who have been involved in various aspects of spectral determinations of phyllosilicates, as well as those concerned with petrologic (and pedologic) interpretations based on compositional characteristics.

From an examination of the spectra (1100 to 300 cm^{-1}) of the six biotites (Fig. 1) and their chemical composition (Table 1), it is clear that a considerable increase in total Fe (and decrease in Mg) causes several definite changes in the spectra. Primarily, as the total Fe content increases substantially, a new band develops near 340 cm^{-1}. This is accompanied by a frequency shift from 352 to 330 cm^{-1}. This band is possibly an Fe-O-Al(?) bending or deformation vibration owing to its small magnitude, sensitivity to the environment, and its absence in quartz, presence in hematite and ilmenite, and variable development in some feldspars. Spectra for these appear in Liese, 1967*a* and 1967*b*.

In addition, the frequency of the band near 450 cm^{-1} shifts substantially from 454 to 440 cm^{-1}.

This considerable increase in total Fe is also accompanied, secondarily, by changes in the bands near 670 cm^{-1} and at 715 cm^{-1}. Based on the study by Stubican and Roy (1961), much of the observed increase in intensities here are interpreted as being due to an (corresponding) increase in tetrahedral Al. The substantial shift to lower frequencies is probably a "secondary" effect of the substantial increase in octahedral Fe. The 715 cm^{-1} band was observed to shift similarly in other spectra of unanalyzed biotites, and is thought to be generally related to probable Fe variations. In addition, there is no consistent or substantial effect on the Si-O-Si stretching band near 1000 cm^{-1} that can be related to total Fe

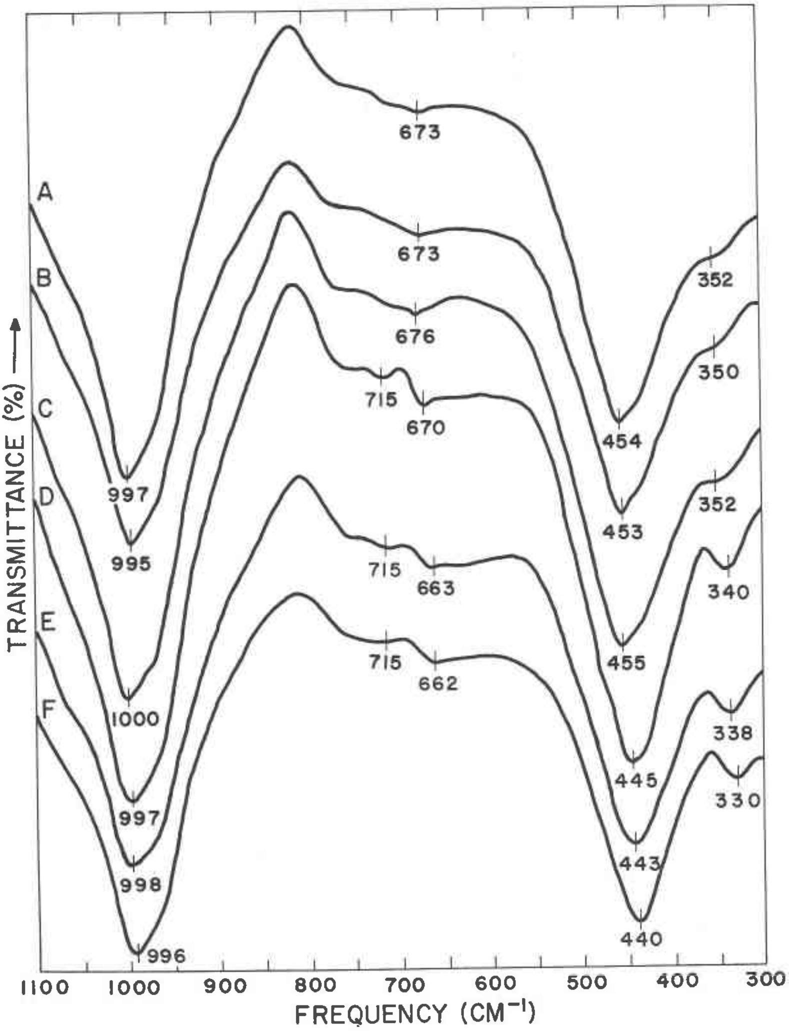

FIG. 1. Spectrogram tracings of the six chemically analyzed biotites.

variations (See Tuddenham and Lyon, 1958; Lyon and Tuddenham, 1960).

Although not shown here, it was also observed that an increase in the intensity and number of bands in the 3700 to 3500 cm^{-1} region (specifically, near 3660, 3586, and 3550 cm^{-1}) usually accompanied the considerable increase in total Fe (Vedder, 1964).

Owing to the considerable change in Fe:Mg ratio, and the accompany-

Table 1. Chemical Analyses of the Six Biotites[1]

	A	B	C	D	E	F
SiO_2	35.0	35.4	35.1	34.8	34.8	32.0
Al_2O_3	19.1	20.0	19.9	17.1	17.3	15.3
Fe_2O_3	6.3	6.8	7.1	12.6	13.6	15.3
FeO	16.0	15.0	16.8	19.2	18.7	20.6
MgO	10.2	9.7	6.8	1.5	1.2	0.5
CaO	0.1	0.5	0.08	0.2	0.2	0.2
Na_2O	0.06	0.08	0.03	0.1	0.08	0.12
K_2O	8.5	8.2	9.0	7.9	7.5	7.5
H_2O^+	4.7	4.4	4.4	4.2	4.5	4.0
H_2O^-	0.6	0.6	0.6	0.6	0.6	0.6
TiO_2	0.2	0.2	0.3	0.08	0.1	3.5
CO_2	0.0	0.0	0.0	0.0	0.0	0.0
MnO	0.1	0.09	0.1	0.09	0.4	0.1
Total	100.9	101.0	100.2	98.4	99.0	99.7

[1] Analyzed by Earth Sciences, Inc. (Golden, Colorado).
A—Glastonbury Gneiss (Connecticut).
B—Middletown Gneiss (Connecticut).
C—Canterbury Gneiss (Connecticut).
D—Scituate Granite Gneiss (Rhode Island).
E—Granite Augen Gneiss (Hoadley Neck, Connecticut).
F—Conway Granite (New Hampshire).

ing change in spectra, biotites A and F were run routinely on an X-ray diffractometer. Changes in diffraction line intensity, but not in spacings, were observed.

Other less consistent (even inconsistent) and less substantial variations in the spectra are probably related to the variations of lesser magnitude in other octahedral and tetrahedral cations or by trivalent *vs* divalent cations in octahedral coordination (or quadrivalent *vs* trivalent in tetrahedral coordination). One interesting comparison, in addition to those involving Fe^{3+} and Fe^{2+}, is the spectral effect of appreciably lower SiO_2 and Al_2O_3 and higher Fe_2O_3+FeO and TiO_2 in biotite F.

It is this type of minor variation, especially when dealing with cations that are capable of tetrahedral as well as octahedral coordination, that prevents the precise quantitative analysis of major ratio variations (*e.g.*, Fe:Mg). Relatively accurate semiquantitative results still seem possible, but additional work must be done on more chemically analyzed samples before the spectral effects of specific combinations of minor constituents can be evaluated fully.

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ZIRCON STABILITY AND THE ZrO_2-SiO_2 PHASE DIAGRAM

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INTRODUCTION

The compound $ZrSiO_4$ makes up 98 percent or more, by weight, of the mineral zircon. In view of the petrological and technological importance of this mineral, accurate information on the thermal stability of $ZrSiO_4$ is highly desirable. Yet even in the most recent studies there is no general agreement as to the temperature or the manner of breakdown of $ZrSiO_4$. Table 1 lists the stability data of various investigators.

The uncertainty regarding the thermal stability of $ZrSiO_4$ is reflected in the published phase diagrams for the system ZrO_2-SiO_2. Thus far, three fundamentally distinct configurations have been presented. The diagrams of Washburn and Libman (1920) and of Zhirnowa (1934) depict zircon as a congruently-melting compound, the melting point being given

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