

DETERMINATION OF THE COMPOSITION OF PLAGIOCLASE FELDSPARS BY MEANS OF INFRARED SPECTROSCOPY

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ABSTRACT

A systematic variation in the infrared spectra of plagioclase feldspars throughout the albite-anorthite series indicates a definite correlation between the band positions, number of bands, and composition. A structural shift is indicated in the region $An_{31}-An_{33}$. Data are presented whereby composition may be determined by the wave length of the symmetry vibrational mode in the 15.4 to 16.2 micron region.

INTRODUCTION

The application of infrared spectroscopy to the study of inorganic systems has been very limited. The infrared spectra of a number of clay minerals have been studied in some degree (Adler, *et al.*, 1950; Keller and Pickett, 1950) and the applicability of the infrared method to other mineral systems has been demonstrated (Hunt, *et al.*, 1950; Keller, *et al.*, 1952; Hunt and Turner, 1953).

The possibility for the study of the plagioclase series was made apparent by the spectra published by Hunt, *et al.* (1950) of albite, oligoclase and anorthite which showed a marked difference in the number and positions of absorption bands for each of the above mentioned samples. Here it is shown that the composition of the plagioclase feldspars can be determined by the use of infrared spectroscopy and it is suggested that this method may prove valuable in the study of other isomorphous series.

PROCEDURE

The samples used were obtained from Dr. J. R. Smith (Geophysical Laboratory), Wards Natural Science Establishment and the Mineralogy Department, University of Utah (see Table 1). Identification of the samples, with the exception of four analyzed samples from J. R. Smith, was made by means of the four axis universal stage using the Berek method (1924) and checked by Turner's method (1947). The compositional error is believed to be within 2-3%. The infrared spectra were obtained using a Perkin-Elmer Model 21 double beam recording infrared spectrophotometer. A NaCl prism was used for the spectral region 2 to 15 microns and a KBr prism for the range 15 to 25 microns.

Each sample was prepared for infrared examination in a manner sim-

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TABLE 1. COMPOSITION AND SOURCE OF PLAGIOCLASE SAMPLES

Number	% Anorthite	Host Rock	Source†	Location
13·4·30	5	Granite Pegmatite	U.U.	Unknown
13·4·7	15	Pegmatite	U.U.	Unknown
Wards #11	23	Pegmatite	W.N.S.E.	Bamle, Norway
Wards #5	26	Pegmatite	W.N.S.E.	Tvedestrand, Norway
13·3·5	28	Pegmatite	U.U.	Ontario, Canada
Wards #6	33	Quartz diorite	W.N.S.E.	Transvaal
Wards #2	35	Lava	W.N.S.E.	Japan
Wards #7	43	Anorthosite	W.N.S.E.	Labrador
Wards #12	50	Anorthosite	W.N.S.E.	New York
Wards #8	52	Anorthosite	W.N.S.E.	Lake St. John, Quebec
BV·63*	63	Gabbro	J.R.S.	Bushveld complex, S. Africa
13·1·19	67	Lava	U.U.	Clear Lake, Utah
EB·38*	85	Norite	J.R.S.	Stillwater complex, Montana
2·2·4	85	Anorthosite	U.U.	Stillwater complex, Montana
Wards #3	89	Hornblende Norite	W.N.S.E.	Grass Valley, California
EB·18*	91	Norite	J.R.S.	Stillwater complex, Montana
Wards #4	94	Lava	W.N.S.E.	Miakejima, Japan
HGIF AN 53*	94	Veinlike mass in schist	J.R.S.	Greenland

* Analyzed samples as follows:

Analysts: Samples BV·63, HGIF·AN·53 by Eileen Oslund, Rock Analysis Laboratory, Minnesota (Unpublished to date).

Samples EB·38, EB·18 by A. H. Phillips, Princeton University. (Published by Kracek and Neuvonen, *Am. Jour. Sci.*, Bowen Volume).

Samples BV·63, EB·38, EB·18 were collected by H. H. Hess, Princeton University.

† U.U., Univ. of Utah collection; W.N.S.E., Ward's Nat. Sci. Estab.; J.R.S., J. R. Smith, Geophysical Lab., Wash., D. C.

ilar to the procedure presented by French, et al., (1954) using the pressed pellet technique. A one gram KI plate, 22 mm. in diameter, containing 2 mg. of sample, was found to be most satisfactory in exploring the whole spectral range of 2 to 25 microns. For a detailed study of certain regions of the spectra, 4 mg. of sample were used per plate. The KI used was recrystallized and a one gram plate of pure KI was placed in the reference beam to compensate for any impurities present.

RESULTS AND DISCUSSION

In the preliminary examination, three groups of definitive absorption bands were found at 8.5 to 11 microns, 12 to 15 microns and 15 to 19

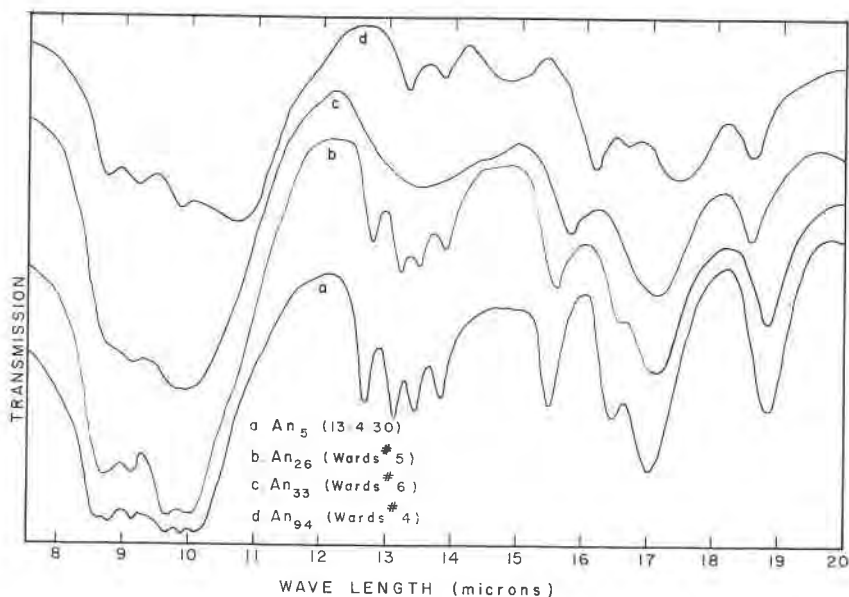


Fig. 1. Infrared spectra of plagioclase feldspars of various composition in the wave length region 8-20 microns.

microns, Fig. 1. These groups were examined more closely by expanding the spectral scale of the instrument. In each of the three groups, changes in number or position of the absorption bands were noted, corresponding to the changes in the composition of the sample. Two gross structural changes in the plagioclase series appear in the composition ranges An_{28} - An_{33} and An_{67} - An_{85} . This is evident from the curves of Fig. 1 and the tabulated data of Table 2.

One band (15.4-16.2 microns) was observed to shift consistently toward the longer wave lengths as the sample composition increased in anorthite content. Figure 2 is a plot of the measured wave length of this band versus composition. The extrapolated intersection of the two regions of this curve more closely fixes the composition of the structural shift indicated between An_{28} and An_{33} according to the gross variations of the spectra of Fig. 1. It appears that the lower limit of this shift is approximately An_{31} . Such a break may be interpreted as a structural shift resulting in an abrupt variation of some of the lattice frequencies. The data used to plot Fig. 2 was recalculated and presented in Fig. 3.

The solid curve of Fig. 3 represents the increment ($\Delta\lambda$) in wavelength between the 15.4 to 16.2 micron feldspar band and the 14.99μ CO_2 band versus the silicon to aluminum molar ratio. This shift is useful because

TABLE 2. POSITIONS OF ABSORPTION BANDS

Number	% Anorthite	8.5 to 11 Micron Region					12.5 to 15 Micron Region					15 to 19 Micron Region				
		8.78M	9.16S	9.65S	9.85S	10.06S	12.73S	13.16S	13.46S	13.86S	15.44S	16.46S	16.98S	18.82S		
13·4·30	5	8.77M	9.12S	9.68S	9.95S		12.75S	13.20S	13.50S	13.80S	15.50S	16.48M	17.06S	18.74S		
13·4·7	15	8.77S	9.13S	9.67S	9.91M		12.75S	13.20S	13.50S	13.85S	15.52S	16.52W	17.02S	18.77S		
Wards #11	23	8.75M	9.11S	9.67S	9.91S		12.72S	13.15S	13.48S	13.80S	15.54S	16.44W	17.06S	18.74S		
Wards #5	26	8.81M	9.12S	9.67S	9.91S		12.75S	13.20S	13.50S	13.80S	15.54S	Weak	17.06S	18.74S		
13·3·5	28		9.13S	9.88S							15.78S		17.06S	18.58S		
Wards #6	33		9.18S	9.85S		12.52W					15.89S		17.18S	18.46S		
Wards #2	35		9.09S	9.99S			12.90W				15.98S		17.28S	18.50S		
Wards #7	43		9.19S	10.00S				13.40S		14.86W	15.98S		17.26S	18.58S		
Wards #12	50	8.75W	9.07S	10.03S			12.85W	13.40S			16.00S		17.28S	18.50S		
Wards #8	52		9.17S	10.08S			12.90W	13.36M			16.06S		17.26S	18.58S		
BV·63*	63		9.14S	10.03S				13.50S			16.08S		17.24S	18.52S		
13·1·19	67	8.75W	9.18S	9.88S	10.12S			13.28S	13.74S		16.08S	16.57W	17.40S	18.60S		
EB·38*	85	8.76S	9.17S	9.90S	10.09S			13.25S	13.70S	14.65M	16.12S	Weak	17.50S	18.56S		
2·2·4	85	8.75S	9.21S	9.83S	10.12M			13.25S	13.75S	14.70M	16.12S	16.62M	17.52S	18.56S		
Wards #3	89	8.73S	9.17S	9.82S	10.12M			13.25S	13.72S	14.67M	16.14S	17.40S	18.60S			
EB·18*	91	8.76S	9.24S	9.88S	10.14S			13.30S	13.80S	14.75M	16.14S	17.34S	18.54S			
Wards #4	94	8.79S	9.25S	9.85S	10.08M			13.25S	13.76S	14.65M	16.16S	16.61M	17.34S	18.54S		
HGIF·AN·53*	94	8.76S	9.25S	9.85S	10.08M			13.25S	13.76S	14.65M	16.16S	16.60M	17.40S	18.62S		

S—Strong. M—Medium. W—Weak.

* Analyzed samples (see Table 1).

of the close proximity of the CO_2 band which acts as a calibration for the measured shift and tends to normalize results without extreme care in terms of absolute wavelength. The dotted curve of Fig. 3 represents the relationship between the Si/Al molar ratio and the weight per cent of anorthite. This plot also suggests the possibility that the structural change in the region, An_{28} – An_{33} gives rise to a skeletal frequency due to

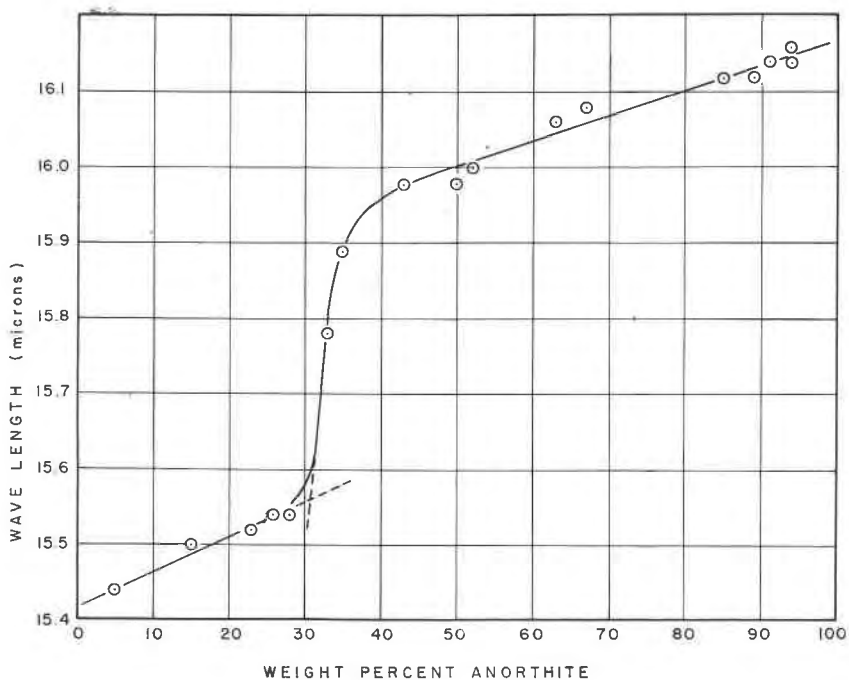


FIG. 2. Correlation of the wave length of the infrared band in the 15.4–16.2 micron region with per cent anorthite for plagioclase feldspars of various composition.

an ordered structure at a Si/Al ratio of 2:1, halfway between the albite ratio of 3:1 and the anorthite ratio of 1:1. The existence of structural changes was demonstrated by Chao and Taylor (1940) within the ranges of An_{22} – An_{57} and An_{67} – An_{80} ; also Cole, Sorum and Taylor (1951) stated that plagioclases up to the composition An_{30} are isomorphous with the albite structure but that the exact limit of isomorphism is obscure. They also state that the composition An_{72} is the lower limit for plagioclases which are isomorphous with the anorthite structure. There is no evidence of a structural shift in the region An_{67} – An_{85} in the infrared data presented in Fig. 2. It is conceivable, however, that a structural shift may occur

without affecting the frequency mode corresponding to the absorption band in the 15.4–16.2 micron region.

Table 2 gives the positions of all the absorption bands which occur in the three regions under consideration. In light of the data available at present, infrared spectra do not appear to distinguish between high and low temperature plagioclases. The data for both high and low tempera-

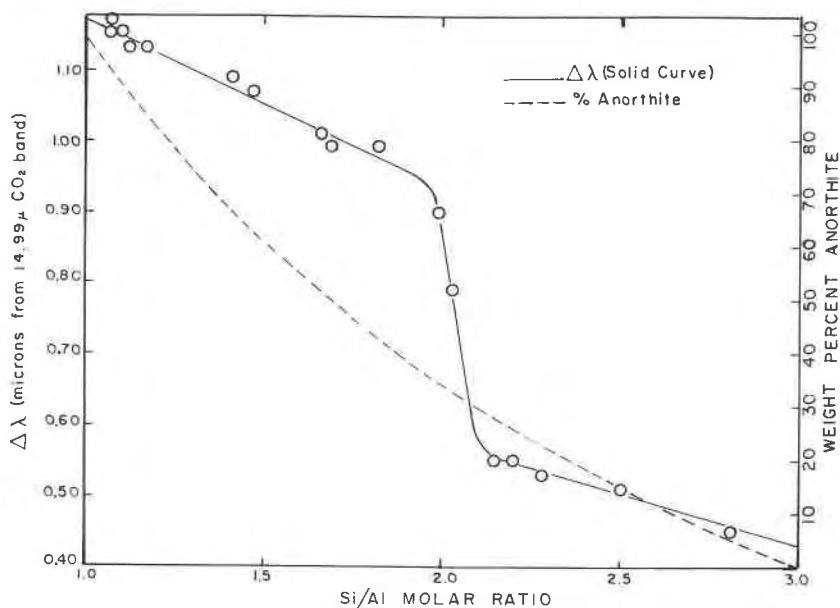


FIG. 3. Correlation of the position of the infrared band in the 15.4–16.2 region (relative to the CO₂ band at 14.99 μ) with the Si/Al molar ratio and with the weight per cent anorthite.

ture forms (Table 1—inferred by host rock) are well correlated as is evident by the curve of Fig. 2. Therefore, it is suggested that this method may be more useful than other methods which are hampered by this problem.

Some attempt has been made to correlate the vibrational frequencies of the plagioclase feldspars with those of alpha quartz as presented by B. D. Saksena (1940). Alpha quartz exhibits three absorption bands (8.63 microns, 8.7 microns and 9.40 microns) which seem to correspond approximately with the plagioclase bands in the 8.5–11 micron region. Saksena has assigned the following symmetry modes to the above mentioned bands: 8.63 microns, deformational oscillation of oxygen atoms in the basal planes; 8.71 microns, valence oscillation of oxygen atoms;

9.40 microns, oscillation of oxygen and silicon atoms along the optic axis. There are also four alpha quartz absorption bands in the 12–15 micron region with symmetry modes assigned as follows: 12.04 microns and 12.58 microns, oscillation of oxygen atoms along the optic axis; 12.86 microns, radial motion of oxygen atoms; 14.55 microns, translational oscillation of oxygen atoms against each other in the basal planes.

There appears, therefore, to be a general similarity between the infrared spectra of quartz and the plagioclase feldspars, particularly in the 8–15 micron region. In the 15–19 micron region several additional bands appear which are not present in the quartz spectrum. The 15.4–16.2 micron band which has been shown to vary systematically through the entire plagioclase series is among the latter group. Consequently, it is not possible to describe the character of this particular symmetry mode by comparison with the quartz spectrum. The closest quartz band is the 14.55 micron translational oscillation band. The increased complexity of the plagioclase spectra compared to quartz is expected because of the lower order of symmetry of the triclinic system and because of the substitution of aluminum for silicon atoms in the tetrahedral positions.

CONCLUSIONS

It appears from the results of this study that the positions of the symmetry mode in the plagioclase feldspars giving rise to an absorption band in the 15.4–16.2 micron region of the infrared spectrum is a direct indication of composition. Also the position of this particular band does not appear to be influenced by the high or low temperature history of the sample. A definite structural shift is indicated at a composition of approximately An_{31} – An_{33} , and a gross examination of several spectra indicates a second structural shift in the An_{67} – An_{85} region.

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ADDENDUM

Since the writing of this paper, an article has come to our attention by George W. DeVore (*Zeits. Krist.*, **107**, 247-264, 1956) which concludes, on the basis of bond energy changes, that the mineral An·33.3 represents a high degree of ordering in the Si-Al positions, and that "An·33.3 and anorthite are interpreted as unique compounds in the plagioclase series."

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