

## GLAUCONITES: CATION EXCHANGE CAPACITIES AND INFRARED SPECTRA

### Part II. INFRARED ABSORPTION CHARACTERISTICS OF GLAUCONITES

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#### ABSTRACT

Twelve glauconites with increasing percentage of expandable (montmorillonite type) layers, determined by *x*-ray analysis, have been selected for the initial infrared absorption study. The over-all characteristics of the infrared absorption curves are compared to those of other clay minerals, and the major absorption peaks are recognized and assigned to specific bonds.

One of the Si-O bands in the 9- to 11-micron region shows a gradual shift with the increasing percentage of expandable layers. A tentative explanation of this hypsochromic shift (shift to shorter wavelength) is given. The similarity between the absorption curve of a highly expandable glauconite and that of a montmorillonite shows the essential similarity of their structures.

#### INTRODUCTION

The knowledge gained from the infrared absorption studies of many compounds has been helpful in understanding the nature of atomic and molecular bonding, and the modes of the resultant vibrations in these compounds. The infrared absorption spectra which are characteristic of each mineral have been used in the identification of various minerals (Hunt *et al.*, 1950). Further, the absorption spectra have been employed for the quantitative analysis of minerals in some rocks (Hunt *et al.*, 1953). The method is suitable when the interference by the minerals present is minimum.

Recently, various investigators have found and explained some qualitative and quantitative relationships which exist between the structure of a silicate mineral and the number, intensity and position of a particular band or bands of the spectrum. Of these, the study of the shift in the position of a well characterized band or bands has received most attention. Isomorphous substitution has been suggested as one of the main causes of such shift. Lyon and Tuddenham (1960) have shown that the position of the "maxima absorption" in the 9-10 micron region in micas is influenced by the Y-number, that is, the amount of aluminum substituted for silica in the tetrahedral layer (Tuddenham and Lyon, 1959). Milkey (1960) has reported the shift of the major (Si-O) absorption peak toward longer wavelengths with increased aluminum-silicon ratio. In

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their excellent study, Stubičan and Roy (1961) obtained infrared absorption spectra of various synthetic dioctahedral- and trioctahedral-layer silicates and correlated the changes in positions of absorption peaks with the nature and extent of ionic substitutions in the tetrahedral and octahedral positions in layer-lattice silicates.

Another cause of a gradual shifting of the absorption in the infrared spectrum has been shown by various investigators to be the orientation of bond axis. Serratos and Bradley (1958) have recorded the O-H absorption band in the 3.0-micron region of wavelengths in a number of layer silicates and related the differences in the position to the orientation of the O-H vibration bond. Bassett (1960) has similarly shown from infrared studies of single crystals of these minerals how the orientation of the hydroxyl ion (O-H bond) varies in micas such as muscovite (dioctahedral), and phlogopite and biotite (both trioctahedral), and that the position of the O-H absorption band in the infrared curve is related to orientation of the bond which is characteristic for each mica mineral.

The present paper deals with glauconite, a dioctahedral-layer silicate with a large amount of iron in octahedral coordination (Hendricks and Ross, 1941). Burst (1958) has shown that most glauconites belong to the "inter-layered" class. Invariably, there is an interlayering between montmorillonite-type (expandable) and illite-type ( $10 \text{ \AA}$ , non-expandable) layers (Hower, 1961). Because glauconites show variation in chemical composition and in structure, it would be expected that the infrared absorption curves of glauconites would show variations. Twelve glauconites, containing expandable layers in the range of 5-40%, have been selected for this initial study. The authors have qualitatively examined the variations in infrared absorption properties as related to the percentage of montmorillonite (expandable) layers, that is, to the changes in the structure of glauconite.

#### PREVIOUS INVESTIGATION

A considerable amount of research has gone into the study of the infrared absorption characteristics of silicates. A few papers pertinent to this study will be discussed briefly. Keller (1948 and 1950) and Keller *et al.* (1949) have examined the absorption bands of silica and silicate minerals in the infrared region of the spectrum. Launer (1952) obtained infrared absorption spectra of various silicate minerals and correlated his observations with the silicon-oxygen groups present in minerals. His findings in the case of the layer-lattice Si-O minerals include: strong absorption peaks in the 9.4- to 10.4-micron region; a relation between the ratio of silicon to oxygen and the wavelength of the maximum absorption peak; and the position of the strong Si-O band in the 9.4- to 10.4-micron region

as related to the substitution of magnesium for aluminum in the octahedral layer. In general, the strong absorption of all Si-O minerals, which also include clay minerals, in the region approximately between 9.0 and 11.0 microns is due to Si-O bonds.

Nahin (1955) has pointed out various problems in the study of the infrared absorption curves of the principal clay minerals. Previously, he recorded similarities as well as differences in the infrared spectra of these minerals (1951). Although different clay minerals having major structural differences can be distinguished from their absorption curves, those

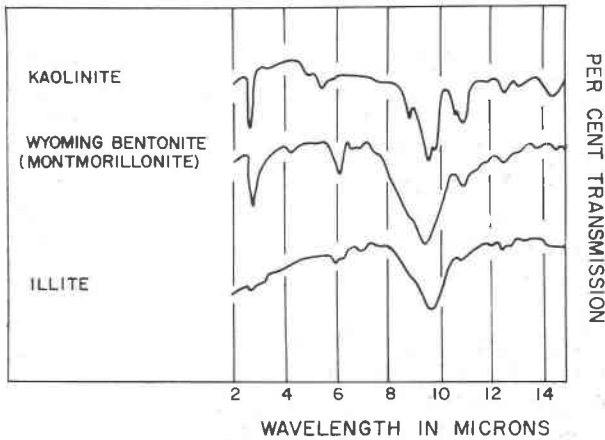


FIG. 1. Infrared absorption curves of kaolinite, montmorillonite, and illite (Nahin, 1951).

with similar structure cannot be identified so easily. This can be seen from Fig. 1, adapted from Nahin's paper, showing the absorption curves of kaolinite, montmorillonite, and illite. The infrared absorption curve of kaolinite is characterized by more absorption bands in the 9- to 11.0-micron region than in the two other cases. Hunt and others have shown that kaolinite absorbs strongly at wavelengths of 9.8 and 10.7, and weakly at 12.6 and 14.5 microns; this property is not observed in other clay minerals. It is somewhat difficult to distinguish the infrared spectrum of montmorillonite from that of illite. There are differences between the absorption bands of the two minerals in the regions of 3.0 and 6.0 (O-H vibrations) and at about 10.0 microns (Si-O vibration), as shown by Hunt *et al.* (1950). The Si-O band, which accounts for a strong peak in the case of both minerals, occurs at 9.6 and 9.7 microns in montmorillonite and illite, respectively.

Stubičan and Roy (1961a), and Stubičan (1963) have recently presented a most authoritative discussion of the infrared spectra of the layer silicates including the clay minerals.

#### EXPERIMENTAL METHODS

The infrared absorption spectra of the glauconites were recorded by use of a Beckman IR5 infrared spectrophotometer. This spectrophotometer is an automatic recording, double-beam instrument which has a wavelength range between 2.0 and 16.0 microns. Parameters such as scale expansion, slit program, and time constant are fixed in this instrument.

*Sample preparation.* Samples of twelve glauconites, having a percentage of expandable layers in the range of 5 to 40 (*cf.* Manghnani and Hower, 1964), were obtained by carefully hand-picking the clean pellets under a microscope to insure the purity desired in the infrared absorption analysis. The potassium bromide pellet technique, in which a mixture of known weights of KBr and glauconite are pressed into a pellet, was used for sample preparation. The following procedures were involved in recording the infrared absorption curves of glauconite.

*Pellet Pressing.* Potassium bromide and samples were dried in a vacuum at a temperature of 320° C. ( $\pm 5^\circ$ ) for about 6 hours. Four hundred mgm of KBr and 1.5 mgm of glauconite sample were weighed and ground together to allow thorough mixing. The glauconite was completely dispersed in the KBr matrix by triturating the ground mixture in a "Wig-L-Bug" amalgamator for 30 seconds. The mixture was pressed in vacuum between the two polished optical surfaces of the die in a metal ring under a pressure of about 10 tons applied on the 2" diameter ram of the hydraulic press. Pellets prepared in this way were sufficiently transparent. If the pellets were cloudy, possibly because of insufficient grinding or unequal pressure, they were rejected and others prepared. The advantage of the pellet-pressing technique is that there is a minimum scattering of beam because of the very small size of the particle, and thus the spectra obtained are excellent.

*Scanning.* Besides keeping the absorption of water by KBr in the pellet to a minimum value, it was also necessary to test the purity of the KBr sample. To do this, two KBr pressed pellets were respectively introduced in the paths of analytical and compensating beams, and a spectrum was obtained. If the spectrum was without any superfluous absorption peak, except that of low intensity in the 3.0- and 6.0-micron regions (O-H vibrations), it indicated the reliability of the KBr sample (Fig. 2).

To obtain the infrared absorption curve of a glauconite, the pellet prepared from a mixture of KBr and glauconite sample was introduced in the analytical beam and a blank KBr pellet was placed in another beam path. The spread of scanning was from 2.0 to 16.0 microns. The automatic recording point moved at the rate of 1.0 micron in 1 minute.

*X-ray analysis.* The percentage of expandable (montmorillonite type) layers in the same glauconite samples was determined by *x*-ray diffraction analysis, using an American Philips *x*-ray apparatus. Nickel-filtered  $\text{Cu}\alpha$  radiation was employed. The analysis was done by studying the diffraction patterns obtained from clay-size glauconite grains with their (001) planes oriented parallel to the surface of a porous porcelain plate.

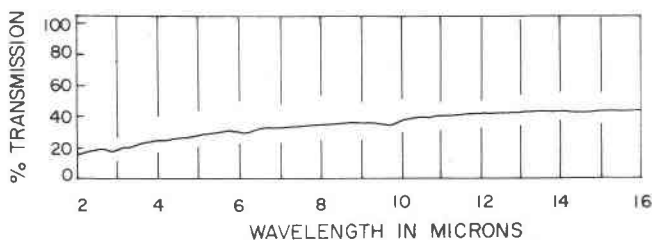


FIG. 2. Infrared absorption curve of pure KBr.

The method employed for preparing the oriented samples is described by Kinter and Diamond (1956). Diffraction patterns were obtained for untreated, potassium-treated, and glycol-solvated specimens of each of the samples. The percentage of expandable layers in glauconites was estimated from the curves of Brown and MacEwan (1951), and Weaver (1956), using the positions of the resultant 001/001 ( $17 \text{ \AA}/10 \text{ \AA}$ ) peaks following the ethylene glycol and potassium (1*N* KCl) treatments. This has already been shown in Part I of this paper (Manghnani and Hower, 1964).

#### EXPERIMENTAL DATA AND INTERPRETATION

Figures 3 and 4 present the infrared absorption curves of twelve glauconite samples with increasing amounts of expandable layers from 5 to 40 per cent. The over-all patterns of the infrared absorption curves of glauconites more or less resemble those of 2:1 dioctahedral layer-lattice silicates such as montmorillonite and illite (compare Figs. 1, 3 and 4). Like most of the Si-O clay minerals, glauconites absorb strongly in the region of 9 to 11 microns, and this is due to the Si-O (stretching) bond vibration (Launer, 1952; Stubičan and Roy, 1961a).

It can be observed that all the glauconites show either one or two

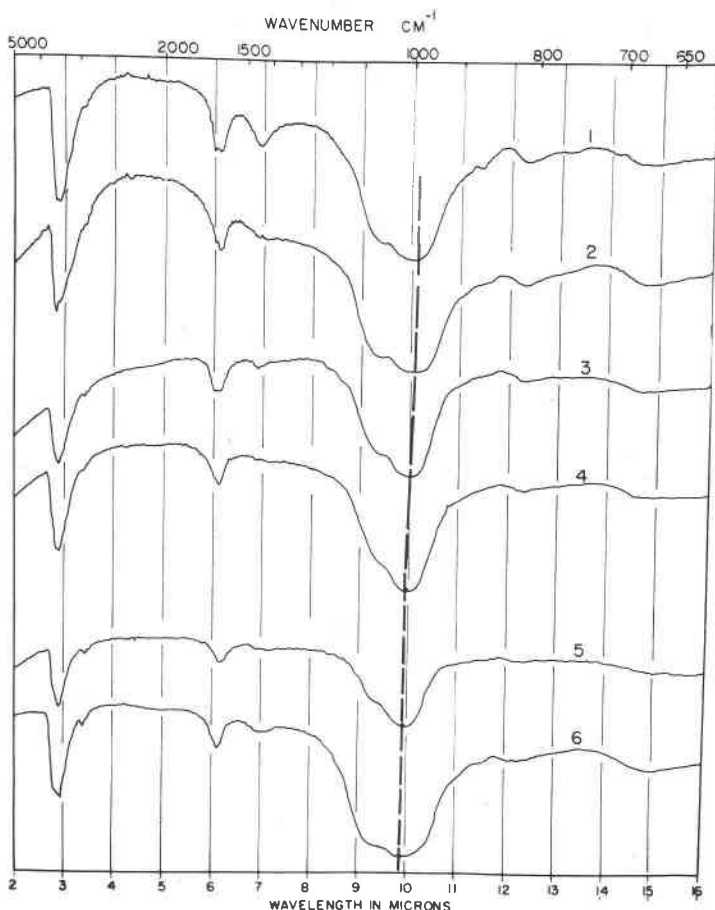


FIG. 3. Infrared absorption curves of glauconites having expandable layers from 5 to 15 per cent.

peaks of moderate absorption intensity in the region of 2.8 to 3.0 microns. These peaks are due to the unbonded and hydrogen-bonded hydroxyl (O-H stretching) groups, respectively, in the lattice (Hunt and Turner, 1953). Another O-H bending absorption peak occurs at a wavelength of a little more than 6.0 microns, and this is invariably present in all the curves. No correlation exists between the O-H absorption bands and the structural variation of glauconites.

The weak absorption band in the region of about 7.0 microns in the curve numbered 1 (Fig. 3) is probably caused by a carbonate bond. Calcite was detected by  $x$ -ray analysis in this sample, but no attempt was

made to remove this impurity and then to observe the infrared spectrum.

The most interesting features are observed in the region of maximum absorption, that is between 9 and 11 microns. There are two distinct Si-O peaks recorded in the curves of samples 1 to 7 (Figs. 3 and 4). These glauconites are less expanding, relatively speaking, and contain from 5 to 15 per cent expandable layers—increasing in that order. In these curves, one of the Si-O peaks occurs at 9.3 to 9.4 microns and another on the higher wavelength side. The inactivation of one of the Si-O stretching vibrations may be due to the interference of other vibrations caused by isomorphous substitution in the tetrahedral and octahedral layers (Farmer, 1958). Lyon and Tuddenham (1960) have attributed such diffusion of the absorption peaks in the 9–10 micron region in chlorites to the

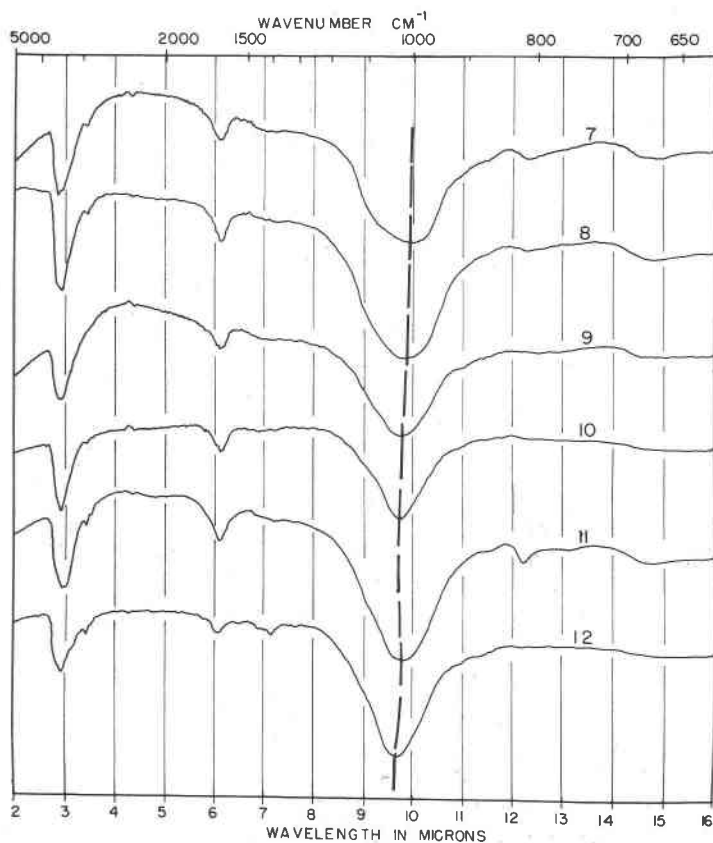


FIG. 4. Infrared absorption curves of glauconite having expandable layers from 15 to 40 per cent.

increasing amount of substitution in the tetrahedral layer. Additional cause of this phenomenon of diffuse absorption band may be due to the disordered structure of glauconite, as explained by Milkey (1960) in his study of the infrared absorption spectra of various tectosilicates. Milkey has shown that the patterns of the spectra of the tectosilicates are related to the degree of disorder of aluminum and silicon in their structures. Glauconites with 10–20 per cent expandable layers have “disordered” structure (Hower, 1961), and one would expect perturbation of the natural frequency of the said Si-O vibration and therefore diffusion band (9–10 microns) in the spectra of these glauconites and those containing higher per cent expandable layers. This point is indicated in Figs. 3 and 4.

While two Si-O absorption bands, though somewhat diffused, are observed in the curves of a low expandable glauconite (less than 15 per cent expandable layers), as shown in Fig. 3, only one band is observed in highly expandable glauconites (more than 15 per cent expandable layers). Also, in the case of glauconite containing a few per cent expandable layers, the region of maximum absorption is broad (9–11 microns) and this gradually narrows down as the percentage of expandable layers increases (Fig. 4). This effect may also be related to structure. In a glauconite which contains fewer expandable layers, there exists a high excess negative charge on its lattice (Hower, 1961a). The structure of such glauconite is tighter and approaches that of a mica. The probability of resonance between the two Si-O frequencies is therefore reduced, yielding a broad absorption region consisting of two resolved Si-O bands. Such a broadening of an absorption band caused by isomorphous substitution was also noted by Farmer (1958) in the study of saponite.

In addition to the characteristics mentioned above, a shift occurs in the position of the Si-O absorption band. This phenomenon is quite apparent in samples 8 to 12 (Fig. 4). The position of the Si-O absorption peak shifts from about 10.1 microns in the Tonto Fm. sample having 5 per cent expandable layers to about 9.7 microns in the Byram Fm. sample having 40 per cent expandable layers. The shift is very regular, as is shown by the dashed lines in Figs. 3 and 4. The position of one of the Si-O absorption bands and the per cent expandable layers in the twelve glauconites are listed in Table I. Figure 5 is the plot of the relationship between the per cent expandable layers, as determined by *x*-ray analysis, and the position of the Si-O absorption band. The wavelength of the band decreases with an increase in the amount of expandable layers. The gradational change in the position of the Si-O band is probably related to the substitution in both the octahedral layers and the tetrahedral layers in glauconites. Hower (1961a) has pointed out that the location of the major ionic substitution in glauconites is in the octahedral layers and the minor amount



TABLE 1. LIST OF GLAUCONITE SAMPLES WITH GEOLOGICAL AGE, THE PER CENT EXPANDABLE LAYERS, AND THE WAVELENGTH VALUES OF THE Si-O PEAK

Glaucouite sample	Geological Age	Expandable layers	Wavelength (microns)
1. Tonto Fm.	Cambrian	5	10.10
2. Birkmose Fm.	Cambrian	5	10.05
3. Reno Mem., Franconia Fm.	Cambrian	10	10.00
4. Bashi Fm.	Eocene	10	9.98
5. Park Shale	Middle Cambrian	10-15	9.95
6. Folkstone Fm.	Jurassic	15	9.93
7. Gros Ventre Fm.	Cambrian	15	9.93
8. New Zealand glauconite	Tertiary	20	9.80
9. Sundance Fm.	Jurassic	30	9.75
10. Moody's Branch Fm.	Eocene	30	9.70
11. Brown Bear	Recent	30	9.75
12. Byram Fm.	Oligocene	40	9.65

of substitution occurs in the tetrahedral layers. The nature and extent of such substitution and its effect on the pattern of infrared absorption curves would be better understood from the chemical analyses of these glauconites; this is being followed up.

It would be of interest to predict the position of the Si-O absorption band of a glauconite having 100 per cent expandable layers. If such a glauconite exists, it should be similar in structure to a montmorillonoid. On extrapolating the relationship shown in Fig. 5, it is found that the probable position of the Si-O peak in a 100 per cent expandable glauco-

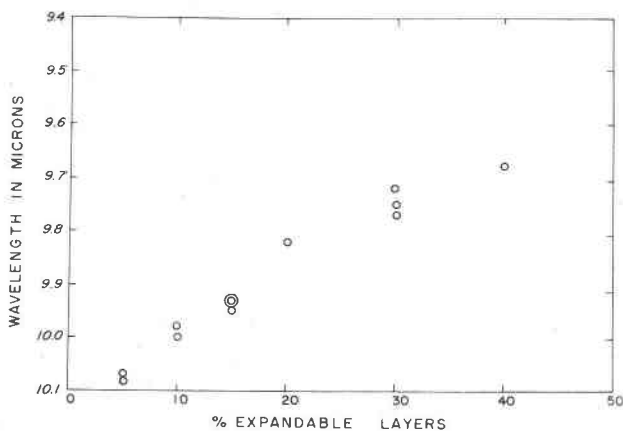


FIG. 5. Plot wavelength value of the Si-O absorption peak vs. per cent expandable layers in glauconite.

nite is about 9.5 microns. In montmorillonite, this peak occurs at 9.5 microns (Hunt and Turner, 1953) to 9.6 microns (Nahin, 1955). (See also Stubičan and Roy, 1961.) Thus, in the present investigation, the predicted value of the wavelength of a Si-O band in a 100 per cent expandable glauconite is quite in agreement with the value of a similar band present in montmorillonite.

The patterns of the infrared curves in the region of 11 to 16 microns are simple. The Si-O band which occurs in the region of 12 microns in saponites, montmorillonites, and chlorites as reported by Stubičan and Roy (1961), is also found in the glauconite samples (numbers 1 to 8, Figs. 3 and 4). This weak absorption band, however, diminishes in intensity in higher per cent expandable glauconites, except in curve 11 where it is quite prominent.

Another Si-O band which has been recognized by Stubičan and Roy (1961) in chlorite at about 14.8 microns is also found in the absorption curves of glauconite samples. The absorption peak due to this band is rather asymmetrical and tends to flatten out in highly expandable material, with the exception of the peak in curve 11.

#### CONCLUSION

Summing up, it is seen that the spectra of glauconites vary significantly according to the expandability of the glauconite, which property is related to the amount of charge, that is, the amount of ionic substitution, on the tetrahedral and octahedral units in the crystal structure of glauconite. On the basis of the 9.6- to 10.2-micron absorption peak, the per cent expandable layers can be estimated in a glauconite. The pattern of an infrared absorption curve can suggest the expandability of a glauconite which is related to the degree of glauconitization as shown by Hower. True 1M mica structure glauconites, with low per cent expandable layers, have characteristic absorption patterns having well-defined peaks, such as for number 1 (Tonto formation) and 2 (Birkmose formation). On the other hand, highly expandable glauconites, showing high degree of disorder of octahedral sites or of layer-stacking show patterns such as in number 12 (Byram formation). Intermediate types exhibit gradational features in their absorption curves.

Further study of the chemical and structural composition, and infrared absorption properties of these glauconites in the region of 16-25 microns would be of interest in order to substantiate or modify the explanations put forward.

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