THE AMERICAN MINERALOGIST, VOL. 46, JANUARY–FEBRUARY, 1961

ISOMORPHOUS SUBSTITUTION AND INFRA-RED SPECTRA OF THE LAYER LATTICE SILICATES*

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ABSTRACT

Infra-red spectra of series of dioctahedral and trioctahedral synthetic clays in the region 400–5000 cm.$^{-1}$ have been obtained. Characteristic changes in the IR spectra with ionic substitution have been observed with both types. From these results some general conclusions concerning the variations of IR spectra with ionic substitution in both groups of clay minerals can be drawn. In many cases quantitative relationships between frequencies or intensities of the characteristic absorption bands and the extent of ionic substitutions could be established. The same parameters can also be used for the location of substituent ions.

INTRODUCTION

The investigation of solids by the absorption of infra-red rays has attracted considerable interest in recent years. The same technique has also been applied to the study of minerals. Among them the infra-red spectra of the clays have been reported by several workers. For example, Hunt *et al.* (1950, 1951, 1953), Adler (1951), and Keller and Pickett (1949, 1950) surveyed the infra-red spectra of the principal natural clay minerals between 650–5000 cm.$^{-1}$. In the paper of Nahin (1955) the differences between infra-red spectra of some clay minerals as well as the unresolved problems have been pointed out. Further progress in this field was made when Beutelspacher (1956) extended the spectral range of study to 400 cm.$^{-1}$, obtaining well resolved spectra of many clay minerals. An analysis of the literature concerning this subject shows that much remains to be done before the infra-red absorption technique can be successfully applied not only for analytical purposes but also for the study of the crystal chemistry and the structure of clay minerals. To attain this aim it is naturally of the greatest importance to study well defined "pure" specimens, which can rarely be found in nature. On the other hand, synthetic specimens can be prepared in very pure form, and only with such authenticated specimens can one hope to approach more directly the complex relationship between structure or composition and the infra-red spectra of clay minerals. Whereas the first part of our research (Stubičan and Roy, 1959) was concerned with an attempted assignment of the absorption bands to the proper metal-oxygen bonds, in the present investigation an attempt has been made to correlate the nature and extent of ionic substitutions with the changes caused in IR

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spectra. As a matter of fact the results of the latter approach were very helpful in the attempted assignments.

EXPERIMENTAL PROCEDURES

Preparation of the synthetic minerals

The synthetic clays and micas were prepared from mixtures of gels. The gels were obtained as previously described by Roy (1956), by starting with "Ludox" silica sol or ethyl orthosilicate, and solutions of nitrates (Al, Mg). In some cases, to obtain the composition required by the mineral formula, an addition of sodium or potassium hydroxide solution was necessary. The mixtures were evaporated to dryness and then fired to about 500° C. until the nitrates were completely decomposed. The syntheses were carried out in small sealed gold or platinum tubes. A small amount of distilled water was added before the tubes were sealed. The usual equipment (Roy and Tuttle, 1956) was used for the hydrothermal syntheses. The conditions for the syntheses (temperature, pressure) have in general been the same as previously reported from this laboratory, except that in some cases the time of hydrothermal runs was prolonged to obtain better crystallinity of specimens. The crystallinity and the purity of each synthesized specimen were checked by *x*-rays before infra-red spectra were run. A few natural specimens were used, when analyses were available. The specimens investigated are listed in Table I.

Infra-red Spectra

Measurements were made with a Perkin-Elmer model 21 double beam spectrometer in the spectral region between 400–5000 cm.$^{-1}$ using NaCl and KBr prisms. The previously dried specimens (110° C.) were intimately mixed with KBr powder and pressed under vacuum. Usually 0.8–1.5 mg. of the specimens were mixed with 300 mg. KBr. The pressure applied was 75,000 lb/sq. in. Spectra were obtained with scanning speed 3, and with the gain 5–6. It was very convenient to obtain the spectra using different gear combinations which correspond to various scale factors. Generally spectra were obtained with the NaCl prism with the scale factor 2 cm./μ and with the KBr prism with the scale factor 1 cm./μ. For quantitative work scale factors of 4 cm./μ or 2 cm./μ were used. Apparently the faster speed did not adversely affect the resolution for our purposes but much better defined absorption bands were obtained.

RESULTS

In Figs. 1 and 2 are shown the spectra for the end-member minerals representing the dioctahedral and trioctahedral analogues of the 1:1 and 2:1 clays.

TABLE I. SPECIMENS USED IN THIS INVESTIGATION

	I. *Trioctahedral 2:1 family*	
1.	Talc	$Mg_3(Si_4O_{10})(OH)_2$
2.	Ni-Mg-Talc	$NiMg_2(Si_4O_{10})(OH)_2$
	Saponites	
3.		$Mg_3(Al_{0.17}Si_{3.83})O_{10}(OH)_2 \cdot Na_{0.17}^+$
4.		$Mg_3(Al_{0.33}Si_{3.67})O_{10}(OH)_2 \cdot Na_{0.33}^+$
5.		$Mg_3(Al_{0.50}Si_{3.50})O_{10}(OH)_2 \cdot Na_{0.50}^+$
6.		$Mg_3(Al_{0.67}Si_{3.33})O_{10}(OH)_2 \cdot Na_{0.67}^+$
	The Phlogopite-Biotite Series	
7.	Phlogopite	$KMg_3(AlSi_3)O_{10}(OH)_2$
8.	Ni-Mg-Phlogopite	$KNiMg_2(AlSi_3)O_{10}(OH)_2$
9.	Al—Phlogopite	$K(Mg_{2.5}Al_{0.5})(Al_{1.5}Si_{2.5})O_{10}(OH)_2$
10.	Al—Biotite I	$K(Mg_{2.0}Al)(Al_{2.0}Si_2)O_{10}(OH)_2$
	II. *Dioctahedral 2:1 family*	
11.	Pyrophyllite	$Al_2(Si_4O_{10})(OH)_2$
	Beidellites	
12.		$Al_2(Al_{0.17}Si_{3.83})O_{10}(OH)_2 \cdot Na_{0.17}^+$
13.		$Al_2(Al_{0.33}Si_{3.67})O_{10}(OH)_2 \cdot Na_{0.33}^+$
14.		$Al_2(Al_{0.50}Si_{3.50})O_{10}(OH)_2 \cdot Na_{0.50}^+$
15.		$Al_2(Al_{0.67}Si_{3.33})O_{10}(OH)_2 \cdot Na_{0.67}^+$
	Montmorillonites	
16.		$(Al_{1.83}Mg_{0.17})Si_4O_{10}(OH)_2 \cdot Na_{0.17}^+$
17.		$(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2 \cdot Na_{0.33}^+$
18.		$(Al_{1.33}Mg_{0.67})Si_4O_{10}(OH)_2 \cdot Na_{0.67}^+$
	The Muscovite-Phengite Series	
19.	Muscovite	$KAl_2(AlSi_3)O_{10}(OH)_2$
20.	½ Muscovite and ½ Phengite	$K(Al_{1.75}Mg_{0.25})(Al_{0.75}Si_{3.25})O_{10}(OH)_2$
21.	Phengite	$K(Al_{1.50}Mg_{0.50})(Al_{0.50}Si_{3.50})O_{10}(OH)_2$
	III. *Trioctahedral 1:1 family*	
22.	Antigorite	$Mg_3(Si_2O_5)(OH)_4$*
23.	Chrysotile	$Mg_3(Si_2O_5)(OH)_4$
	Chlorites	
24.		$(Mg_{2.88}Al_{0.12})(Al_{0.12}Si_{1.88})O_5(OH)_4$
25.		$(Mg_{2.75}Al_{0.25})(Al_{0.25}Si_{1.75})O_5(OH)_4$
26.		$(Mg_{2.50}Al_{0.50})(Al_{0.50}Si_{1.50})O_5(OH)_4$†
27.		$(Mg_{2.36}Al_{0.64})(Al_{0.64}Si_{1.36})O_5(OH)_4$
28.		$(Mg_{2.25}Al_{0.75})(Al_{0.75}Si_{1.25})O_5(OH)_4$†
29.		$(Mg_{2.12}Al_{0.88})(Al_{0.88}Si_{1.12})O_5(OH)_4$
30.		$(Mg_{2.00}Al_{1.00})(Al_{1.00}Si_{1.00})O_5(OH)_4$†
	IV. *Dioctahedral 1:1 family*	
31.	Kaolinite	$Al_2(Si_2O_5)(OH)_4$
32.	Halloysite (Meta-)	$Al_2(Si_2O_5)(OH)_4$

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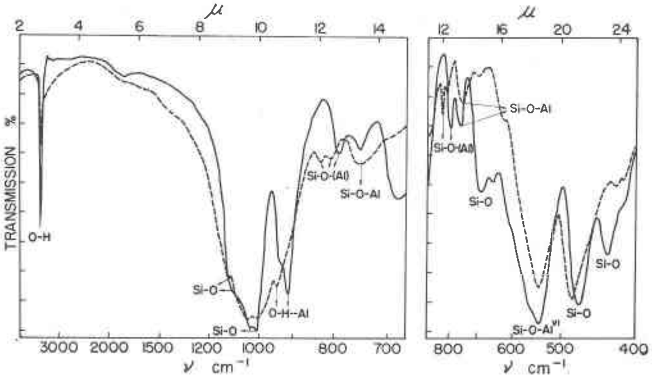
* The natural platy antigorite from Vermlands Taberg, Western Sweden.

† These specimens were investigated both, as the 7 Å and 14 Å polymorphs.



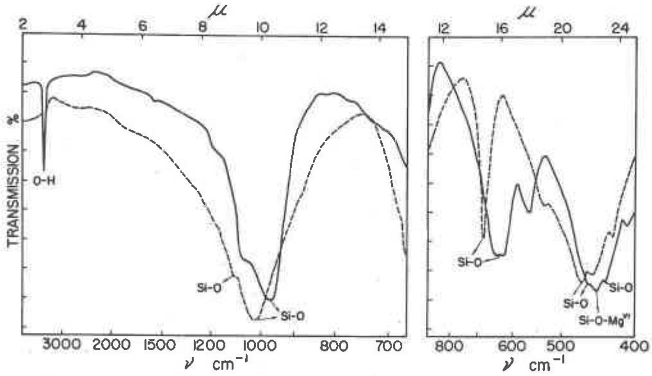


FIG. 1 (above). Infra-red spectra of kaolinite (full line) and pyrohyllite (dashed line).
FIG. 2 (below). Infra-red spectra of antigorite (full line) and talc (dashed line).

Assignments for the main bands are shown on the diagrams themselves and have been discussed by use elsewhere (Stubičan and Roy, 1959).* Starting with each of these end-member spectra one can follow the various types of substitutions common in clays:

I. Trioctahedral 2:1 family

Two types of substitution may be distinguished in this as in most clay mineral families. The first involves a simple ion for ion substitution of Ni^{2+} for Mg^{2+}. Ni^{2+} is used here as a model for the Fe^{2+} common in nature yet relatively difficult to handle in the laboratory. Talc,

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* Assignments for the main absorption bands have been accomplished by studying layer lattice silicates where complete replacement of an ion e.g. Mg^{2+} by Ni^{2+} and Fe^{2+}, Al^{3+} by Ga^{3+} or Fe^{3+}, Ge^{4+} for Si^{4+}. The bands involving various OH-vibrations were located by complete replacement of OH^- by OD^-.

$3MgO \cdot 4SiO_2 \cdot 2H_2O$ may be regarded as the end-member structure here. In this case one can see a distinct shift as follows: the band which appears in talc at 668 cm.$^{-1}$ moves slightly towards higher frequencies (with $\frac{1}{3}$Ni and $\frac{2}{3}$Mg it is at 675 cm.$^{-1}$), and the new poorly resolved band appears at 710 cm.$^{-1}$. (Fig. 3.)

The second type of substitution involves a balanced charge dual substitution. In talc itself experiments in this laboratory have demonstrated that the $2Al^{3+}$ for $(Mg^{2+}+Si^{4})$ substitution is very limited. However, it is of course well known that the replacement of Si^{4+} by ($Al^{3+}+Na^{+}$ in exchange positions) gives rise to the saponite family of the montmorillonoid; and the extent of substitution is very substantial (see Koisumi and Roy, 1959).

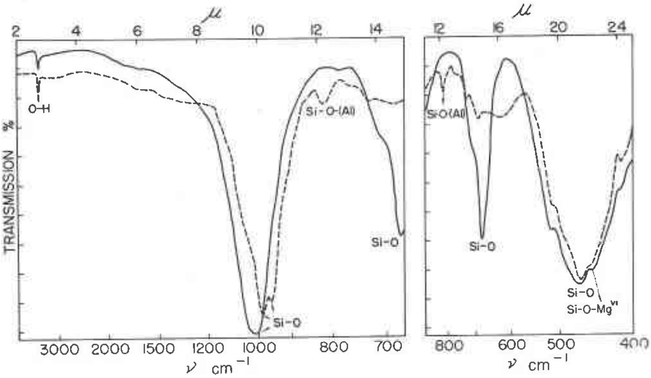


FIG. 3. Infra-red spectra of Ni-Mg-talc No. 2 (full line) and Ni-Mg-phlogopite No. 8 (dashed line).

Saponites

Infra-red spectra of four synthetic specimens (Table I) with increasing amounts of aluminum ions in the tetrahedral sites were obtained. In this case 1 mg. of each specimen was mixed and pressed with 300 mg. KBr.

The spectra obtained (Fig. 4) are comparable to the spectrum of talc. Some differences become more pronounced as the number of aluminum ions in the tetrahedral sites increases. For example, with increasing alumina content there is an increasing intensity of the weak absorption band at 877 cm.$^{-1}$ as well as the gradual appearance of the weak bands between 800–850 cm.$^{-1}$. At the same time the absorption bands at 527, 467, and 427 cm.$^{-1}$ are becoming more diffuse with slight changes in their

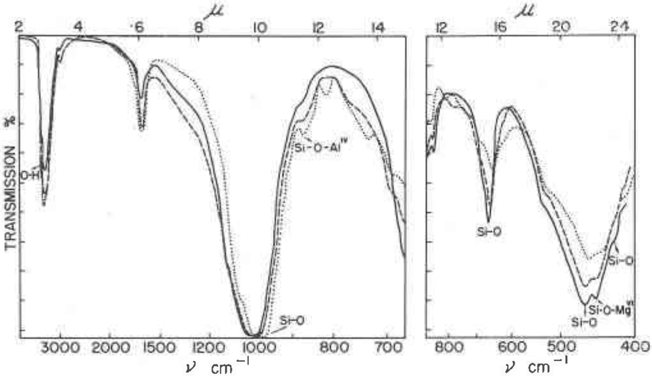


FIG. 4. Infra-red spectra of saponites: No. 3 (full line), No. 4 (dashed line), No. 6 (dotted line).

position. The most radical change can be observed with the Si-O band of talc with the frequency center at 668 cm.$^{-1}$ which decreases in intensity and moves towards lower frequencies. To determine more accurately the position and the intensity of this band for every synthetic saponite, the absorption spectra in the frequency region between 600–740 cm.$^{-1}$ were run using a scale factor of 4 cm./μ (Fig. 5). In Fig. 6 one can see that

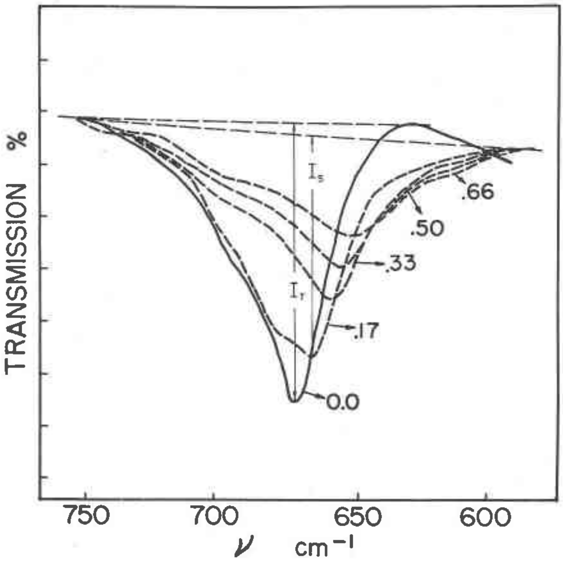
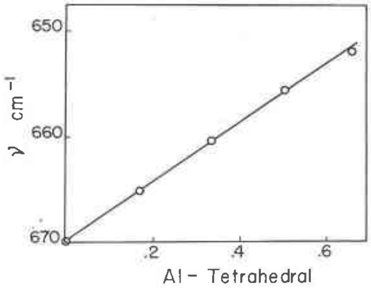


FIG. 5. The Si-O band with talc and saponites. Numbers on the curves refer to the amount of aluminum ions in the tetrahedral coordination.



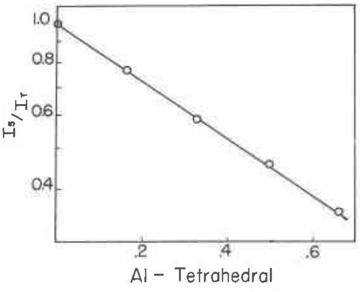


FIG. 6 (left). The relationship between the frequency of the Si-O band in the region 600–750 cm.$^{-1}$ with saponites and the amount of aluminum ions in tetrahedral coordination.

FIG. 7 (right). The ratio of the intensities of the Si-O band with saponites (I_s) to that with talc (I_t) as a function of the amount of aluminum ions in the tetrahedral sites.

there is a simple relationship between the content of aluminum ions in the tetrahedral sites and the frequency at the center of the Si-O vibration, and in Fig. 7 the relative intensities of this band are correlated to the amount of aluminum ions present.

The Phlogopite-Biotite Series

A comparison of the saponite with a phlogopite absorption pattern (Fig. 4 and Fig. 8) shows what one would expect; as the substitution of Al for Si is carried further the changes proceed in the same direction as in the saponite series with increasing exchange capacity. Thus a new band appears at about 830 cm.$^{-1}$ and a series of weak maxima between 600 and 780 cm.$^{-1}$ replaces the very sharp band at 668 cm.$^{-1}$. The former is due presumably to a new Si-O-Al^{IV} stretching absorption and the lat-

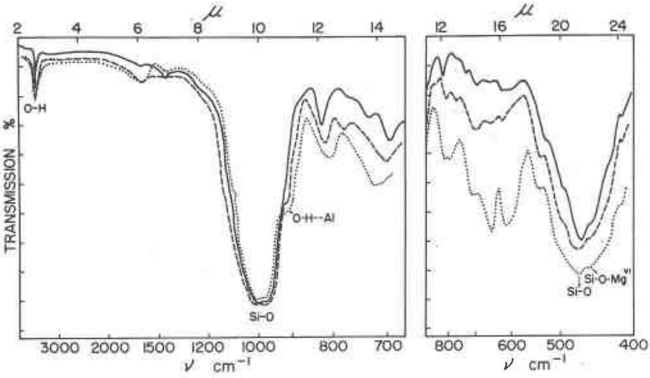


FIG. 8. Infra-red spectra of the members of the phlogopite-Al biotite series: No. 7 (full line), No. 9 (dashed line), No. 10 (dotted line).

ter due to the different Si-O-Si and Si-O-Al combinations made possible. The substitution of Ni^{2+} for Mg^{2+} in phlogopite again shows (Figs. 3 and 8) as in talc, that the substitution of ions with the same charge influences the infra-red spectra much less than the substitution of ions with different charges. This is generally true if the substitution does not exceed a certain value where new bands appear.

Turning to the balanced substitutions one finds that the influence of introducing *octahedral* as well as tetrahedral substitution is most clearly noticed in the increased absorption at about 730 cm.$^{-1}$ which may correspond to the Si-O-Al stretching frequency, and the new sharp bands in the Si-Al, Si-Si, stretching region near 610, 675 cm.$^{-1}$. In addition the pronounced shift in the absorption peak at 830 in pure phlogopite towards 810 in the "Al-biotite" composition may be used as an index of the extent of the balanced substitution in phlogopite.

II. Dioctahedral 2:1 Family

Just as in talc natural pyrophyllite itself shows very little variability in composition. However, when some of the Si^{4+} ions are replaced by Al^{3+} ions and the charge balanced by large cations between the sheets we generate a series of montomorillonoids—the beidellites.

Beidellites

Infra-red spectra of four synthetic beidellites (Table I) were run using 1.5 mg. of each specimen with 300 mg. of KBr. The spectra obtained of 3 specimens are shown in Fig. 9. If we compare these spectra with the spectrum of pyrophyllite, some differences can be observed. It is possible to find in the spectra of beidellites all major Si-O bands as well as

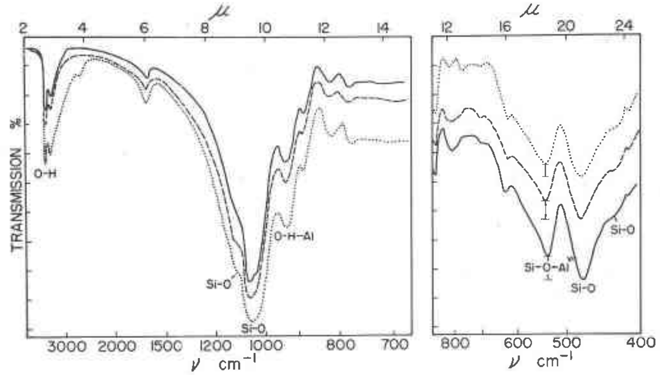


FIG. 9. Infra-red spectra of beidellites: No. 12 (full line), No. 13 (dashed line), No. 15 (dotted line).

the O-H stretching and H-O--Al bands in approximately the same position as in the spectrum of pyrophyllite. Some differences can be observed with the weak bands in the region 700–900 cm.$^{-1}$. With the beidellite of highest alumina content the broad absorption band at 806^{-1} is replaced by two weak bands at 753 and 820 cm.$^{-1}$.

The quantitative relationship between the amount of aluminum ions in the tetrahedral sites and the infra-red spectra can be seen if we consider the intensities of the two strong absorption bands at 535 and 474 cm.$^{-1}$. One can hope to find differences in the intensities of these bands with specimens having the same structures but different relative amounts of octahedral alumina and tetrahedral alumina and tetrahedral silica. With decreasing amount of silica in the tetrahedral sites as the result of replacement with aluminum ions in beidellites, the difference in the intensities of the bands at 473 and 535 cm.$^{-1}$ decreases. These changes in the intensities can be correlated with the amount of aluminum ions in the tetrahedral sites, but the precision here is low.

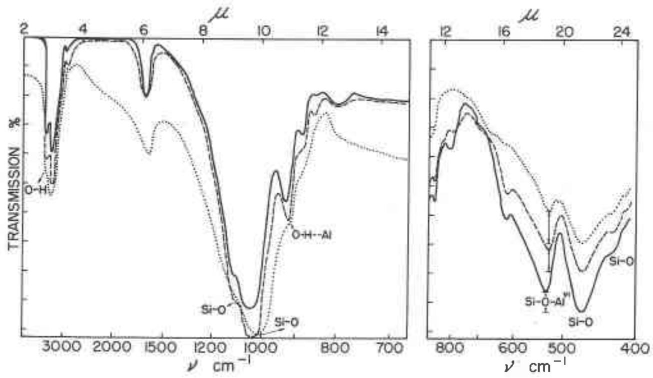


FIG. 10. Infra-red spectra of montmorillonites: No. 16 (full line), No. 17 (dashed line), No. 18 (dotted line).

Another family of montmorillonoids can be generated when Mg^{2+} replaces Al^{3+} in the octahedral layer: this is the montmorillonite family.

Montmorillonites

Infra-red spectra of only three synthetic montmorillonites (Table I) were obtained (Fig. 10). In this case 1.5 mg. of each specimen were pressed with 300 mg. of KBr. The infra-red spectrum of specimen No. 16 which contains only a small amount of magnesia in the octahedral site is essentially identical with the spectra of beidellites. The influence of the increasing amount of magnesia can be observed in two spectral regions which are sensitive to the ionic substitution in the octahedral sites. The absorption band assigned to the H-O--Al at 935 cm.$^{-1}$ becomes more poorly resolved from the main Si-O band and the absorption band at 533 cm.$^{-1}$ shows a small shift towards higher frequencies. The latter band decreases in intensity as the amount of aluminum ions in the octahedral sites decreases, and presumably could be generated by Si-O-AL^{VI} vibrations.

Muscovite-Phengite Series

The type dioctahedral mica is moscovite: this mineral

$$KAl_2(AlSi)_3O_{10}(OH)_2$$

represents in reality only an end-member of the phengite family in which Mg^{2+} replaces Al^{3+} in the octahedral layer while some of the Al^{3+} of the tetrahedral layer is replaced by Si^{4+}.

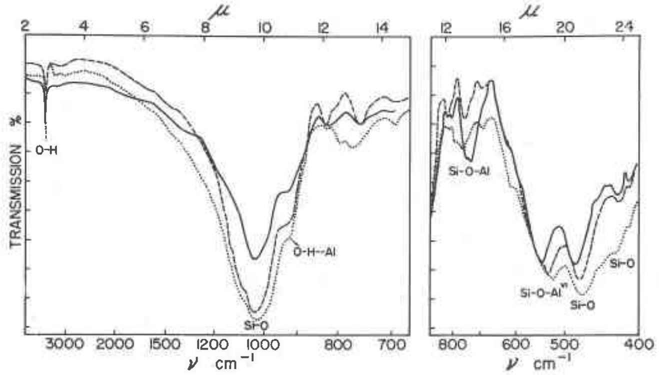


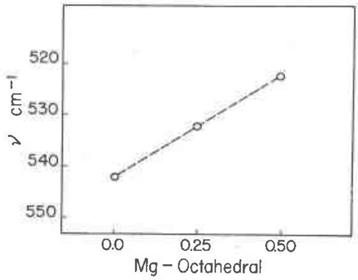
FIG. 11. Infra-red spectra of the members of the muscovite-phengite series: No. No. 19 (full line), No. 20 (dashed line), No. 21 (dotted line).

In Fig. 11 the infra-red spectra of three synthetic specimens (Nos. 19, 20, 21, Table I) which contained increasing amounts of magnesium ions in the octahedral sites are shown. It is evident that, with entry of magnesium into the octahedral sites, the absorption band with the frequency 935 cm.$^{-1}$ becomes more poorly defined, as was also the case with montmorillonites. It seems also that the presence of magnesium ions causes the deactivation of vibrations which give rise to the appearance of the weak absorption bands in the region 600–850 cm.$^{-1}$. The displacement of the absorption band of muscovite at 543 cm.$^{-1}$ towards lower frequencies is very marked and can be correlated with the presence of magnesium ions in the octahedral sites. The quantitative relationship between the amount of magnesia and the frequency center of this band was established (Fig. 12).

III. Trioctahedral 1:1 Minerals

Septechlorites and Chlorites

The chlorites form an extensive isostructural series with extensive ionic substitutions. The natural group comprises mainly magnesium and iron alumino-silicates, but appreciable amounts of chromium, nickel or manganese can also be found in natural specimens.



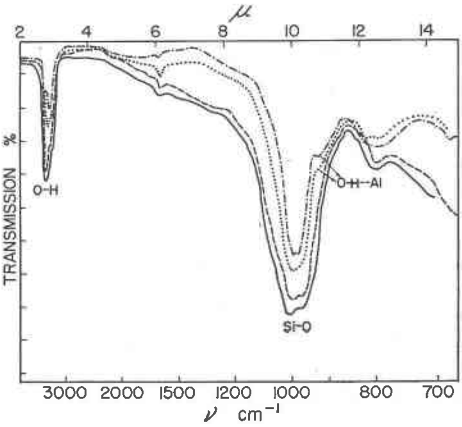


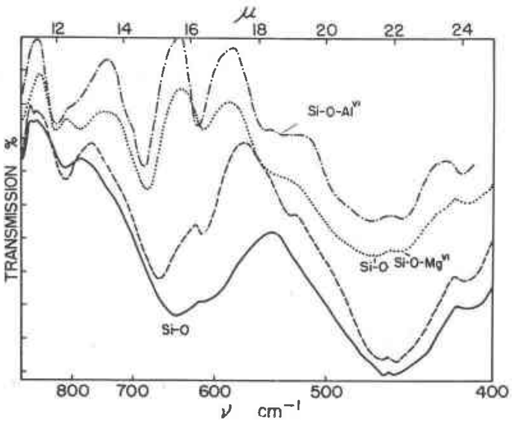
FIG. 12 (left). The relationship between the freuqency of the Si-O-Al^{VI} band with the members of the muscovite-phengite series and the amount of magnesium ions in octahedral coordination.

FIG. 13 (right). Infra-red spectra of 7 Å chlorites (septechlorites) in the region 666–5000 cm.$^{-1}$: No. 25 (full line), No. 26 (dashed line), No. 29 (dotted line), No. 30 (dash-dot line).

Our infra-red studies were concerned only with the magnesium aluminum chlorites and specifically with the 7 Å chlorites (septechlorites) and 14 Å chlorites (normal), the synthesis and stability of which have been reported by Nelson and Roy (1958). According to these authors, chlorites are layer lattice silicates of one of two polymorphic types. The one is a trioctahedral two-layer structure type and the other is a four-layer structure comparable to that of mica with substituted brucite sheets replacing K^+. There is an essentially continuous solid solution in the septechlorites extending between chrysotile and amesite compositions.

Infra-red spectra of 7 specimens of septechlorites (Table I) have been obtained. In this case 1 mg. of the specimen was pressed with 300 mg. of KBr.

With an increasing amount of aluminum ions in the octahedral and tetrahedral sites the most striking change is in the width of the main Si-O bands. Only a weak possible H-O--Al band appears in the richest Al composition at 910 cm.$^{-1}$ (Fig. 13). More sensitive to the amount of aluminum ions present is the Al^{VI}-O-Si band with the frequency center at about 535 cm.$^{-1}$. This band can be resolved with all septechlorites from chlinochlore to amesite (Fig. 14). Neither of the above-mentioned absorption bands is sensitive enough for quantitative treatment of isomorphous substitution in this case. Some other strong absorption bands, *e.g.* the Si-O band at 473 cm.$^{-1}$ as well as the Si-O-Mg^{VI} band at 451 cm.$^{-1}$ are not affected by the presence of aluminum ions in the lattice. However, characteristic changes in the absorption region between 590–750 cm.$^{-1}$ can be correlated in a quantitative way with the amount of aluminum ions in both coordinations.



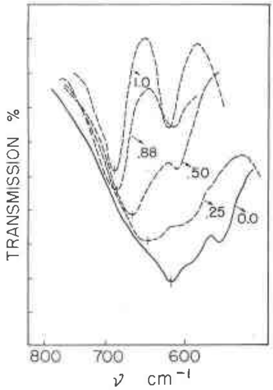


FIG. 14 (left). Infra-red spectra of 7 Å chlorites in the region 450–910 cm.$^{-1}$: No. 25 (full line), No. 26 (dashed line), No. 29 (dotted line), No. 30 (dash-dot line).

Fig. 15 (right). Absorption bands in the region 550–800 cm.$^{-1}$ with 7 Å chlorites. Numbers on the curves refer to the amount of aluminum ions in octahedral or tetrahedral coordination.

Starting from chrysotile (Fig. 15), the strong absorption band at 606 cm.$^{-1}$ is gradually shifted in the direction of higher frequencies as the amount of aluminum ions increases till finally with amesite we find the same band at 685 cm.$^{-1}$. Actually bands which are only poorly resolved in this region with chrysotile can be much better resolved with septechlorites as the result of this shift. It seems very probable that all absorption bands in this spectral region can be assigned to metal-metal stretching vibrations (Stubičan and Roy, 1959). Referring to Fig. 16 it can be noticed that the frequencies of the strongest absorption band in this region can be correlated with the amount of aluminum ions in both coordinations. In this plot the most significant change appears to take in septechlorites between serpentine and chlinochlore, while in septechlorites between clinochlore and amesite the frequency of this Si-O band varies only from 665 to 685 cm.$^{-1}$.

This apparent shape of the curve can easily be seen to be due to the overlapping of two bands which are clearly resolved in amesite but which are affected to different extents by substitution of Si^{4+} by Al^{3+} so that by the time the composition of penninite is reached they are barely resolvable. Rather than attempt to separate the peaks geometrically the plot is simply made using the *apparent* peak position and gives rise to the apparent non-linear variation.

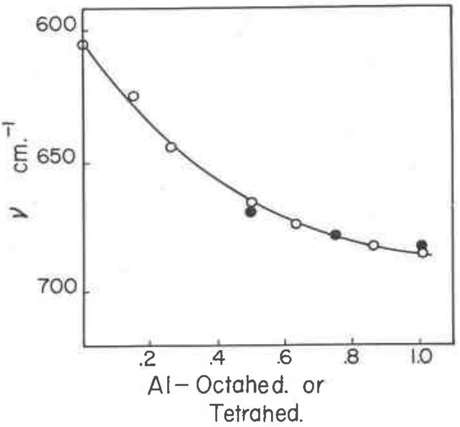


FIG. 16. The relationship between the frequency of the strongest Si-O band in the absorption region 550–800 cm.$^{-1}$ with 7 Å chlorites (open circles) and 14 Å chlorites (solid circles) and the amount of aluminum ions in octahedral or tetrahedral coordination.

A series of normal 14 Å chlorite structures extends continuously between one containing about 10% of alumina and amesite. The similarity of the spectra of 14 Å and 7 Å chlorites is evident (Figs. 12, 13, 17, 18). Nevertheless, several distinctions exist. Regardless of alumina content there is generally no resolved band at 910 cm.$^{-1}$ with 14 Å chlorites (Fig. 13). It is known that this band is much less pronounced with 2:1 type than with 1:1 clay minerals even in the case when all octahedral positions are occupied by aluminum ions. The main difference is in the frequency region 750–850 cm.$^{-1}$ where the two bands are not as well re-

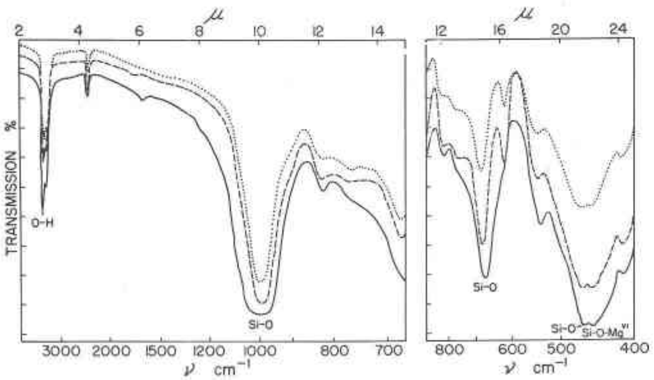


FIG. 17. Infra-red spectra of 14 Å chlorites: No. 26 (full line), No. 28 (dashed line), No. 30 (dotted line).

solved with normal chlorites as with septechlorites. This results in the possibility of using this band also to distinguish between two polymorphs with the same composition. The strongest Si-O band in the frequency region between 665 and 685 cm.$^{-1}$ which was used for quantitative treatment of the amount of octahedral and tetrahedral alumina with 7 Å chlorites (vide supra) is found practically in the same position with the corresponding 14 Å chlorites (Fig. 15). The shifts in this band are also analogous. The relatively small shift in this band from the clinochlore to the amesite composition *may* be related to a disproportionation of the Al^{3+} ions between the two octahedral layers. However, much more precise work will be necessary to establish this. Tuddenham and Lyon have recently (1959) published a paper concerned with the relation of infra-

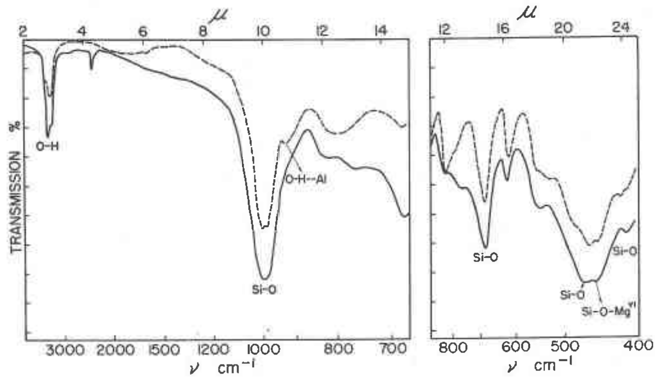


FIG. 18. Infra-red spectra of 7 Å chlorite (dashed line) and 14 Å chlorite (full line) No. 30.

red spectra and chemical composition of some *natural* chlorites. Their spectra extend from 650–5000 cm.$^{-1}$, and they propose the use of the shift in the main Si-O band near 1000 cm.$^{-1}$. The magnitude of the shift is considerably smaller than that shown here, but this shift may be of use to detect Fe^{2+} for Mg^{2+} substitution. Further, it should be noted that in some natural chlorites the band at 1080 cm.$^{-1}$ is completely re-established whereas in synthetic chlorites it is well integrated with the main Si-O band. It is more than likely that this is due to Al-Si disorder in the synthetic specimens, although the synthetic specimens are very well crystallized by *x*-ray diffraction evidence.

IV. Dioctahedral 1:1 Minerals

The type dioctahedral mineral is kaolinite and no appreciable substitutions for Al or Si are known in nature. In the laboratory we have failed to introduce large amounts of Ga^{3+}, Fe^{3+} or Ge^{4+}, and the $3Mg^{2+}$ for $2Al^{3+}$ substitution has not been achieved.

THE INFLUENCE OF POLYTYPISM

While gross spectral differences did not appear to exist between clays which differed only slightly in composition it may be anticipated from theory that perhaps more important differences will be found with minor structural variants. It has already been pointed out elsewhere (Stubičan and Roy, 1959) that the use of space group selection rules in such complex structures is very difficult if at all possible. However it seemed worthwhile to record infra-red spectra of several clay minerals which have essentially the same chemical composition but slightly different structure. Of special interest are the polytypic phases with different symmetry. Several polytypes exist in the serpentine group of minerals. Recently Brindley and Zussman (1959) published infra-red absorption data for serpentine minerals in the region 650–5000 cm.$^{-1}$. However, it could be anticipated that better distinction between spectra of these minerals can be obtained in the absorption region between 400–900 cm.$^{-1}$ where bending movements are involved since these would be most affected by stacking differences. It can be observed from Figs. 19, 20 that this is, indeed, the case. The platy antigorite (Vermlands, Taberg) and the fibrous antigorite (picrolite, Shipton, Quebec) with approximately the same composition but different morphology* have very similar absorption curves though some important differences can be observed. This can be seen in the different positions of the strong absorption bands in the ab-

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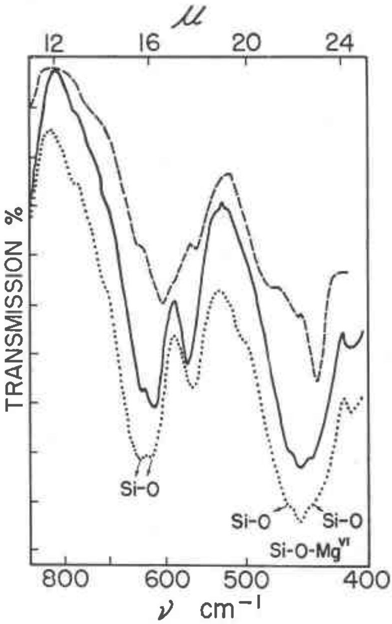
* For the data concerning morphology and unit cell parameters, see: Zussman, J., Brindley, G. W., and Comer, J. J. (1957), "Electron Diffraction Studies of Serpentine Minerals," *Am. Mineral.* **42,** 133–153.



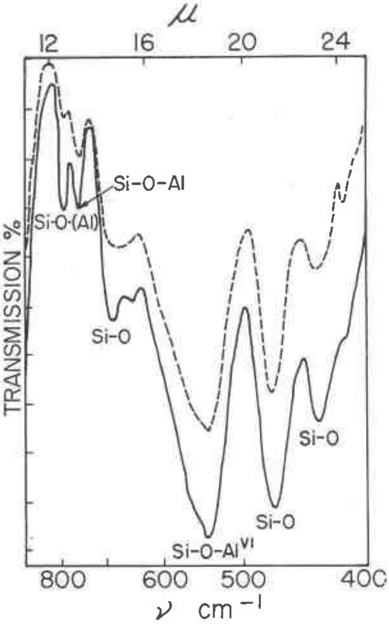


FIG. 19 (left). Infra-red spectra in the 450–910 cm.$^{-1}$ of the fibrous antigorite, Quebec (full line), chrysotile, Quebec (dashed line), and the platy antigorite, Taberg, Western Sweden (dotted line).

FIG. 20 (right). Infra-red spectra of synthetic kaolinite (full line) and metahalloysite, Eureka (dashed line).

sorption region near 700 cm.$^{-1}$ as well as in the relative intensities of the bands at about 645 and 625 cm.$^{-1}$.

Chrysotile, (Clinochrysotile, Thelfas, Quebec) with a different structure, shows an apparently different absorption spectrum because the relative intensities of the absorption bands are very much different from those of antigorite. However all absorption bands present in the infrared spectra of antigorites can be found in the spectrum of chrysotile slightly shifted in position, or more poorly resolved, or with different relative intensities. Since the question of composition of these phases raises questions about interpretation, our attempt was made to work with synthetic phases with *nearly* identical composition. In the infra-red spectra of three synthetic polytypes of muscovite, 1M, 2M, and 3T (the composition of the 3T phase was $K_{0.7}Al_2(Al_{0.7}Si_{3.33})O_{10}(OH)_2$) small differences were obtained (Fig. 21). The most important of these are the presence of a much stronger absorption band at 760 cm.$^{-1}$ in the triclinic phase than in the monoclinic forms. Conversely the absence of the shoulder at 640 cm.$^{-1}$ in the 3T phase distinguishes it from the 1M and 2M

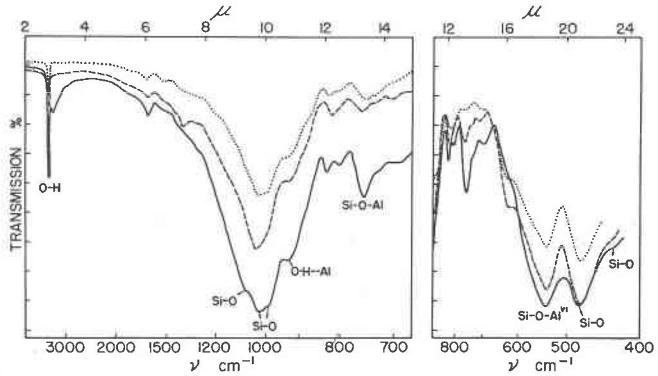


FIG. 21. Infra-red spectra of three polytypes of muscovite: 3T (full line), 2M (dashed line), 1M (dotted line).

phases. Similar effects can be observed if one compares the absorption bands in the same region with pyrophyllite and beidellites (Figs. 1 and 9), as well as in the spectra of kaolinite and halloysite (Fig. 20), which reflect the influence of rather extensive stacking disorder in the latter phases as compared with reasonable order in pyrophyllite and kaolinite.

DISCUSSION

For many years it has been well known that the absorption frequencies in crystalline solutions* vary with the concentration of components. Infra-red spectra of solid solutions of alkali halides contain only one absorption maximum and not two, as could be expected in the case of a true mixture (Krüger *et al.*, 1928). The same result was obtained with solid solutions of $NaNO_3$ and KNO_3 (Raju, 1945). Likewise in the Raman spectrum only one line appeared with the solid solution for every line of each of its components, the frequency being intermediate. The theoretical approach to the interpretation of the vibration spectra of solid solutions was taken by Matossi (1951). An averaging effect is obtained at least at low concentrations of solute due to the influence of each cation (or anion) upon neighboring cation-anion bonds. In other words, one does not have individual dipoles vibrating independently and giving rise to frequencies corresponding to each cation-anion pair. In one way this is a pity, since other properties such as lattice spacings also reflect this averaging effect; on the other hand, where ionic sizes are similar the infra-red shifts are much more sensitive than lattice shifts. In crystalline solutions with high concentrations of solute separate ab-

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* More commonly, though less accurately, referred to as solid solutions.

sorption bands do appear, even though *x*-ray diffraction properties vary continuously in this region.

In the light of this earlier knowledge one can consider the variation in the spectra caused by crystalline solubility in the layer silicates. As the first example of isomorphous substitution in the clays one can consider the substitution in tetrahedral coordination of Al^{3+} for Si^{4+}.

Quite different responses were obtained with the two families, di- and trioctahedral. This different response arises mainly from the fact that vibrations of ions in the crystal lattice are not independent of the rest of the crystal. Up to now no specific band in the spectra of either family could be assigned to the Al-O vibrations with Al^{3+} in tetrahedral coordination.* Hence, only indirect evidence of the presence of aluminum ions in the tetrahedral sites can be observed.

The best examples of this case are found with saponites and beidellites. Farmer (1958) discussed the infra-red spectra of talc, a saponite and a hectorite, and he pointed out only the general broadening of the absorption bands of "smectites" as the result of the isomorphous subsitution in the talc structure. According to this author the broadening of bands is the result of the coupling of out-of-resonance vibration. However, more fundamental changes in the spectra of saponites with increasing amount of aluminum ions in the tetrahedral sites can be found. The gradual decreasing of the frequency and intensity of the Si-O band of talc at 668 cm.$^{-1}$ reflects the disturbing influence of the presence of the tetrahedral aluminum ions on their Si^{4+}-O neighbors (Fig. 5). With dioctahedral clay minerals, *e.g.* with beidellites, the absorption spectrum in this region is modified due to the presence of trivalent ions in the octahedral sites (Fig. 9). The absorption spectra in this latter case offers less possibility for quantitative treatment of ionic substitution. The presence of aluminum ions in the tetrahedral sites in this case can be correlated only to the decreasing of intensity of the Si-O band at 473 cm.$^{-1}$ relative to the bands at 535 cm.$^{-1}$.

Quite a different response can be observed when the substitution takes place in the octahedral sites. Probably the most radical changes are observed when the substitution of ions *with different charge* takes place. Consider first the substitution in dioctahedral clay minerals. The effect of this kind of substitution on the infra-red spectra of montmorillonites and the members of the muscovite-phengite series can be easily observed (Figs. 10 and 11). In this case two spectral regions are very sensitive to substitutions. First, with increasing amount of magnesia in the octa-

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* The position of such a band calculated by the method of Dachille and Roy (1959) would indicate a value of 10.5 μ. The band may be slightly shifted due to the environment and obscured by the neighboring bands.

hedral sites, the H-O--Al absorption band at 935 cm.$^{-1}$ decreases in intensity and is more poorly resolved. Second, the frequency and the intensity of the Si-O-Al^{VI} band at 535 cm.$^{-1}$ decreases as the result of this substitution. Both parameters can be useful for the estimation of the amount of magnesium ions in the octahedral sites with dioctahedral clays (Fig. 12). No bands for Mg-O absorption appear clearly in this range of concentration of Mg^{2+}.

With trioctahedral clays both above-mentioned bands are absent, though with increasing amount of aluminum ions in the octahedral sites one could expect their gradual appearance. These bands do indeed become visible in the spectra but only in specimens containing large amounts of alumina. With trioctahedral clays the shifts in these regions are not sensitive enough for more quantitative determination of the amount of aluminum ions in the octahedral sites. Nevertheless, even with trioctahedral clays the typical changes of spectra can be correlated with the amount of aluminum ions in the octahedral sites (Fig. 8). Certainly in these cases we have to consider also the combined influence of the octahedral and tetrahedral substitution.

In summary, it can be said that:

1. The ions involved in the vibrations responsible for most of the major absorption bands in the 400–500 cm.$^{-1}$ infra-red region are now fairly well-established.
2. Shifts in the absorption frequency and/or intensity can be used to indicate the amount and location of substituent ions, providing a sensitive method for the study of layer lattice silicates.
3. Structural changes in the clays in various reactions, *e.g.* heating (Stubičan, 1959) or chemical leaching, may also be followed by changes in infra-red spectra.

ACKNOWLEDGMENT

This research was supported by the American Petroleum Institute Project 55. It appeared as Technical Report Number 4 of the same Project, dated 20 July, 1959.

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Manuscript received March 19, 1960.