

The infra-red spectra of talc, saponite, and hectorite.

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Summary. The absorption spectra of talc, saponite, and hectorite between 4000 and 400 cm^{-1} are closely related, although the bands of the smectites are more diffuse as a result of isomorphous substitutions in the talc structure. Using oriented specimens, vibrations in which the change of dipole moment is perpendicular to the sheets of the minerals are identified, and the results compared with theoretical predictions. Three bands arising from the stretching vibrations of interlayer water molecules in the smectites are distinguished, one of which corresponds to a very weak hydrogen bond. Spectral changes arising from vigorous grinding are discussed.

THE infra-red spectra of the principal clay minerals have now been broadly surveyed by several workers in the frequency range 4000 to 650 cm^{-1} , the principal compilations being those of Adler *et al.* (1951) and Hunt *et al.* (1950). More recently Beutelspacher (1956 *a, b*) has re-examined many of them using improved techniques, and has published well-resolved spectra extending to 400 cm^{-1} . The present situation and some of the outstanding problems awaiting solution have been well summarized by Nahin (1955), and in this paper some of these problems are investigated in the spectra of the trioctahedral minerals based on the talc structure. This group of minerals has received rather less attention than the more common dioctahedral layer minerals based on pyrophyllite. The spectrum of saponite does not appear to have been previously reported. Published spectra of talc and hectorite in the compilations already referred to show some variation, part of which probably arises from the use of oriented specimens by the earlier workers. Variations in the spectra with orientation prove, however, to be of value in correlating a simplified theoretical analysis of the infra-red-active vibrations of talc with its absorption bands. In addition, changes in the spectra associated with the isomorphous substitutions that constitute the difference between talc and the smectites, saponite and hectorite, are discussed, and the influence of the exchangeable ion on the infra-red absorption of the smectites is investigated.

Materials and methods.

The talc used was a pure specimen from Greiner, Tyrol, and the hectorite a type specimen from Hector, California. The saponite, from

Allt Ribhein, Skye, has been characterized by Mackenzie (1957) as of excellent purity, from chemical, thermal, and X-ray data. The spectra were recorded in the region 4000 to 650 cm^{-1} , on a Grubb Parsons S4 double-beam infra-red spectrometer equipped with sodium chloride prism, and in the region 650 to 400 cm^{-1} on a Hilger H800 double-beam spectrometer, using a potassium bromide prism. Calibration was by the usual standards (Downie *et al.*, 1953) and was accurate to within 3 cm^{-1} below 1700 cm^{-1} and to about $\pm 10 \text{ cm}^{-1}$ at 3700 cm^{-1} .

Samples were generally examined in potassium bromide pressed disks, using equipment already described (Farmer, 1956), but oriented films, whose preparation is described below, were also used. Whilst the pressed-disk technique gives excellent spectra of silicates, it is less satisfactory in studying the infra-red absorption of interlayer water in smectites, as the degree of hydration is not easily controlled. Pressed disks generally show bands due to water adsorbed on the potassium bromide particles, but this interference can be reduced to relatively low levels if the grinding time is not too long and if a compensating blank is used. At high humidities some replacement of the exchangeable ion by potassium from the bromide is to be expected, so the two smectites were examined at humidities below 50 % immediately after preparing the disks. Pressed disks are sufficiently porous to permit smectites dispersed in them to be dehydrated by heating the disks to 200° C., so changes in the spectra associated with loss of almost all the interlayer water are readily followed. The process is reversible, and dehydrated smectites in pressed disks rapidly take up water from the atmosphere. This observation may go some way to explain the results of Roy and Roy (1957), who found that clays that had been dehydrated or exposed to D_2O still showed the bands that are generally assigned to interlayer and adsorbed H_2O .

Orientation effects in the preparation of clay samples.

Excellent spectra of clays (e.g. Beutelspacher, 1956 *a, b*) can be obtained by the pressed-disk technique: a small vibratory grinder is used to grind and mix the sample with excess potassium bromide from which a transparent disk is formed under pressure. The spectra show little scattering even at 4000 cm^{-1} , due to the small particle size achieved and to the similar refractive indices of sample and surrounding medium. Before the introduction of this convenient method, good spectra showing little scattering below 1700 cm^{-1} had been obtained by evaporating clays dispersed in *iso*-propyl alcohol on to sodium chloride windows

(Hunt and Turner, 1953) or aqueous suspensions on to silver chloride sheet (Adler and Kerr, 1951; Nahin *et al.*, 1951). It is common practice, however, to obtain partially oriented specimens for X-ray studies by deposition from suspension, and it seemed likely that such deposits would give spectra showing orientation effects, as radiation passing

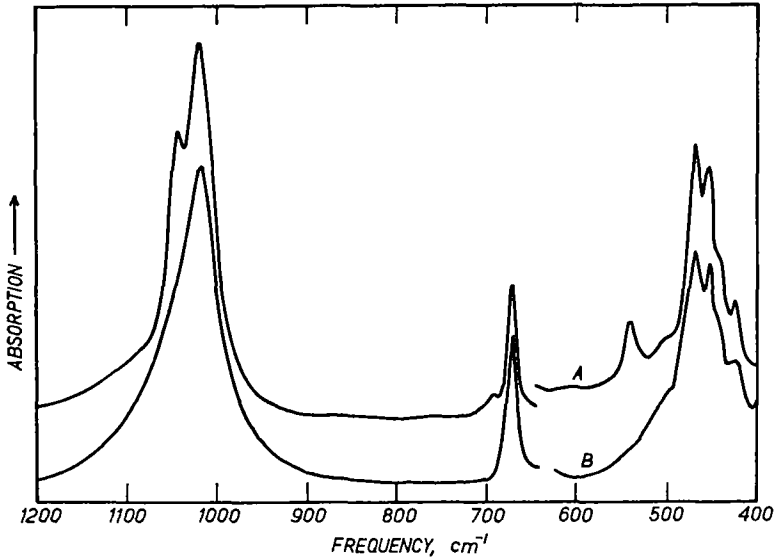


FIG. 1. Infra-red absorption of talc. A, pressed disk, sample concentration about 0.08 mg./cm.²; B, oriented deposit on KBr window.

perpendicularly through clay sheets can only excite dipole moment oscillations with a component parallel to the sheet. A comparison of published spectra proved difficult because of variations in concentration and origin of sample and in the performance of spectrometers. A strict comparison has now been made on one instrument, which leaves little doubt that the effect can occur.

In preparing the oriented specimens, a modification of the technique described by Hunt and Turner (1953) was used. In place of their cyclonic disintegrator, a vibratory grinder of the Ardenne (1941) type was used to reduce particle size. The vibrator, which is developed from a design of Ford, Wilkinson, and Price (1954), has already been described (Farmer, 1956). In preliminary experiments it was noted that after grinding alone for 10 minutes the spectra of talc and saponite were considerably modified (fig. 7). This effect will be discussed more fully later.

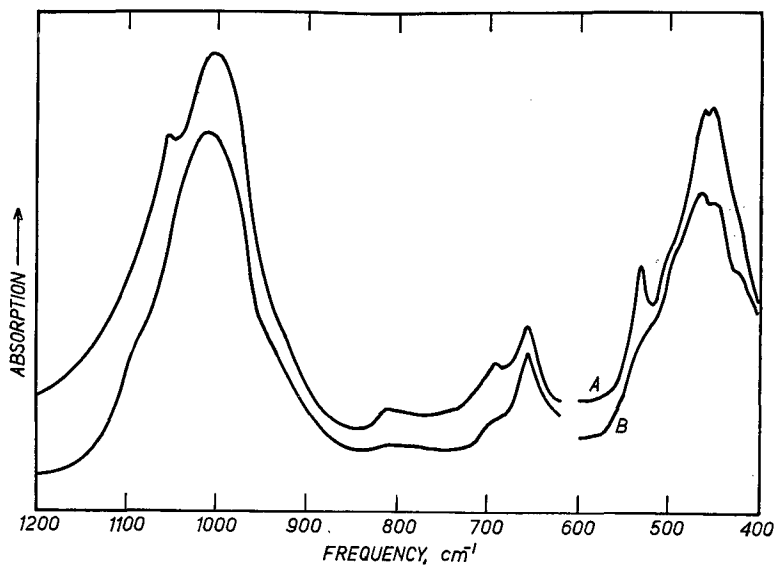


FIG. 2. Infra-red absorption of saponite (Ca^{++} saturated). A, pressed disk, sample concentration about 0.25 mg./cm.^2 ; B, oriented deposit on KBr window.

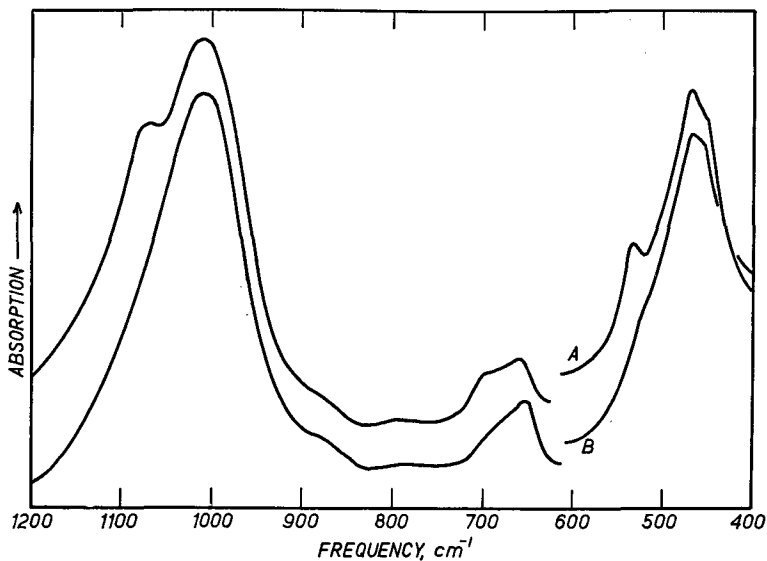


FIG. 3. Infra-red absorption of hectorite (natural). A, pressed disk, sample concentration about 0.3 mg./cm.^2 ; B, oriented deposit on KBr window.

Little change in the spectra occurred during the preparation of potassium bromide disks even after 10 minutes' grinding, but here the excess potassium bromide would be expected to have a cushioning effect.

Similarly, no spectral changes occurred when the minerals were ground in the presence of *iso*-propyl alcohol, and the resulting dispersion gave satisfactory deposits of the smectites. 15 mg. of the mineral (< 200 mesh) together with 0.5 ml. *iso*-propyl alcohol and three ball-bearings were placed in a stainless steel capsule fitted with a polythene stopper, which was then shaken at 100 cycles/sec. in the vibratory grinder for 2 minutes. A few drops of the suspension placed on a potassium bromide plate were then spread and stirred with a fine wire until the suspension gelled. Evaporation then gave a uniform deposit. In preparing deposits of talc, it was found necessary first to grind this mineral alone in the vibratory grinder for 1 minute; *iso*-propyl alcohol was then added and the above procedure followed. An X-ray examination of the hectorite and saponite deposits in the region of their 001 reflections showed them to be well oriented, and it is to be expected that in infra-red absorption measurements refraction of the radiation would improve the effective orientation by bending the beam nearer to the normal to the sheets.

Spectra obtained from such deposits are compared with those from pressed disks for talc (fig. 1), saponite (fig. 2), and hectorite (fig. 3). It will be seen that both types of preparation show strong or very strong absorption near 1010, 660, and 460 cm^{-1} . Bands shown by the pressed disks near 1050, 690, and 530 cm^{-1} , however, are weak or absent in the spectra of the deposits, and so can safely be assigned to vibrations in which the dipole change is perpendicular to the sheets. The frequencies of the absorption bands of these minerals are listed in table I, which includes weaker bands only detectable at higher concentrations than those used for the reproduced spectra. The assignment of those bands that arise from vibrations involving Si-O and Mg-O vibrations (below 1100 cm^{-1}) will be discussed in the following section. The structural hydroxyl group of these minerals and the interlayer water of the smectites have stretching vibrations between 3000 and 3700 cm^{-1} , and these will be treated separately.

Correlation of structure and spectra.

Talc. The spectra of the three trioctahedral minerals reflect the close relationship between them, and it is clear that an interpretation of the better-defined spectrum of talc would lead to an assignment of the

principal bands of the smectites. A full analysis of the normal vibrations of the talc structure is, however, formidable. The mineral consists of magnesium silicate sheets of indefinite extent (Bragg, 1937). The forces within the sheets are largely electrostatic, but between sheets only weak van der Waals forces act. The unit cell, point group C_{2h} , contains two

TABLE I. Frequencies (cm.^{-1}) of infra-red absorption bands of the magnesium silicate sheets of talc, saponite, and hectorite.

Assignment.	Talc.	Saponite.	Hectorite.†
$\nu_4 + (\text{OH})^-$ str.	4330 vvw	4330 vvw	4330 vvw
$\nu_6 + (\text{OH})^-$ str.	4200 vvw		
(OH) ⁻ str.	3670 w	{ 3697 w 3670 w	{ 3670 w 3610 w
summation bands	{ 1919 vvw 1866 vvw 1818 vvw 1770 vvw 1706 vvw		
Si-O $\nu_1 \perp$	1045 vs	1056 vs	1073 vs
Si-O $\nu_3 \parallel$	1018 vs	1005 vs 809 w	1011 vs 799 w
	783 w	784 infl. 737 infl.	
Si-O $\nu_2 \perp$	690 m	692 m	696 m
Si-O $\nu_4 \parallel$	670 s	655 m	655 m
Mg-O $\nu_6 \perp$	539 m	534 m	533 m
	500 infl.	490 infl.	
Mg-O $\nu_7 \parallel$	{ 467 vs 452 vs 444 infl.	{ 464 vs 450 vs	465 vs
Si-O $\nu_5 \parallel$	426 m	420 w	

† The spectrum given by Beutelspacher (1956) shows absorption bands at 1430 and 880 cm.^{-1} due to a calcite impurity.

w, weak; m, medium; s, strong; v, very; infl., inflexion.

units of empirical formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ from separate sheets, giving 123 normal vibrations, about half of which can be infra-red-active, the remainder being Raman-active. The infra-red-active vibrations fall into two classes, one of symmetry A_u in which the change in dipole moment is along the b -axis, which lies in the plane of the sheets, the other of symmetry B_u in which the dipole moment changes perpendicularly to this axis, so that none need be perpendicular to the plane of the sheets. The presence of perpendicularly polarized bands, together with the relative simplicity of the spectrum, suggests, however, that the spectrum can be interpreted in terms of the marked pseudo-hexagonal

symmetry of talc, arising from the hexagonal symmetry of the silicon-oxygen framework. Qualitative arguments support this.

The problem can be simplified by considering an isolated magnesium-silicate sheet, as the weak forces between sheets have little effect on the vibrations in the region investigated here: it is well known, for example,

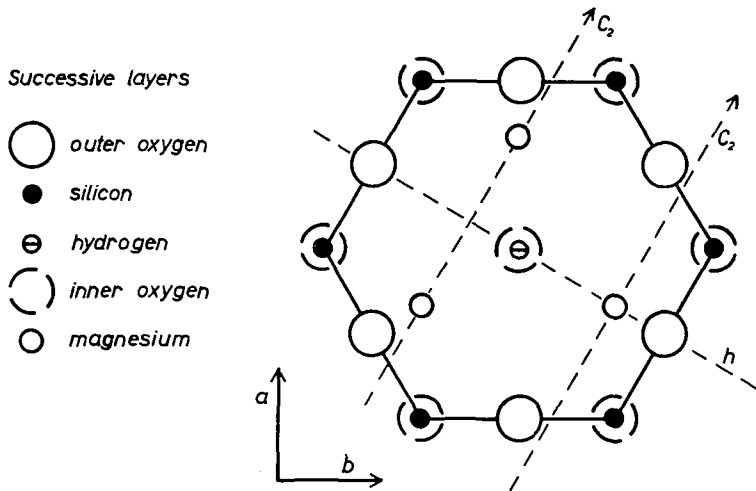


FIG. 4. Single-layer unit cell of talc. Only half of the silicon and oxygen ions are shown, the remainder being obtained by the operation of the twofold axes, C_2 , which pass through the magnesium ions.

that the spectra of rigid non-polar organic molecules in the solid state differ little from their solution spectra. Within a single sheet an effective unit cell of symmetry C_{2h} can be distinguished, as in fig. 4. The magnesium ions lie sandwiched between two silicate layers, which are symmetrically related by twofold axes passing through the magnesium ions. For clarity, only one silicate layer is shown in the figure. The twofold axes, C_2 , and the plane of symmetry, h , of this unit cell are not symmetry elements of the crystal: their orientation alternates in successive sheets by the operation of the glide planes of the space lattice. The centres of symmetry lying at the intersection of the plane with the axes do, however, persist in the crystal.

A further simplification is possible by treating the vibrations of the silicon-oxygen layers separately from the magnesium vibrations. Certainly the higher-frequency vibrations of talc can involve little motion of the magnesium ions: all silicates show strong absorption near

1000 cm^{-1} (Launer, 1952) clearly arising from Si-O stretching frequencies, whereas Mg-O vibrations occur round 450 cm^{-1} in magnesium oxide (Lax and Burstein, 1955). Si-O bending frequencies are less well characterized (Duval and Lecomte, 1954; Matossi and Bronder, 1938) and will certainly vary widely with the particular polysilicate ion involved. Comparison with other XO_4 anions (Hertzberg, 1945) suggests that they probably extend down to at least 400 cm^{-1} , and so are likely to interact with Mg-O vibrations. These considerations make attempts to treat silicate spectra in terms of the vibrations of an isolated SiO_4 tetrahedron unsatisfactory (Weiler, 1932; Matossi and Bronder, 1938).

The silicon-oxygen layers of talc considered as isolated units have hexagonal symmetry (C_{6v}) with the hexagonal axes perpendicular to the sheets. Following the treatment of Mathieu (1945), who gives tables that include some of the special local symmetries that occur in crystals, this structure has only five infra-red active vibrations, two polarized perpendicularly to the sheets (ν_1 and ν_2 , class A_1) and three degenerate vibrations in the plane of the sheets (ν_3 , ν_4 , and ν_5 , class E_1). In addition there is one inactive vibration of class B_1 , three of class B_2 , and three degenerate Raman-active vibrations of class E_2 . When integrated into a crystal of symmetry C_{2h} , however, the degenerate vibrations are split, the previously inactive vibrations can absorb radiation, and the form of the vibrations becomes more or less altered. Nevertheless, in talc the perturbing effect of the environment on the Si-O vibrations appears to be small. This can probably be correlated with the fact that the magnesium ions are linked to the silicon-oxygen layers only through the inner layer of oxygen atoms, each of which has three magnesium ions symmetrically disposed about it, so that the symmetry of the force field is largely preserved.

The approximate form of the infra-red-active vibrations for C_{6v} symmetry are shown in fig. 5 in so far as they affect a single silicon-oxygen tetrahedron. Examination of these shows that ν_1 is a pure stretching frequency and so is correlated with the highest-frequency perpendicular vibration at 1045 cm^{-1} . The parallel vibration ν_3 is largely a stretching frequency but necessarily includes a small bending component which agrees well with the slightly lower frequency of the band at 1018 cm^{-1} . Both ν_2 and ν_4 combine stretching and bending motions, and are assigned to the bands at 690 and 670 cm^{-1} respectively. Vibration ν_5 , largely a bending vibration, should be of lowest frequency and so may contribute to the complex absorption band centred on 450 cm^{-1} .

Turning now to the motions of the magnesium ions, it may be noted that the position of these ions in talc, sandwiched between sheets of close-packed oxygens, is similar to their position in brucite, where the oxygens belong to hydroxyl groups (Bragg, 1937). The brucite structure is of higher symmetry, however (D_{3d} with both Mg and OH on threefold

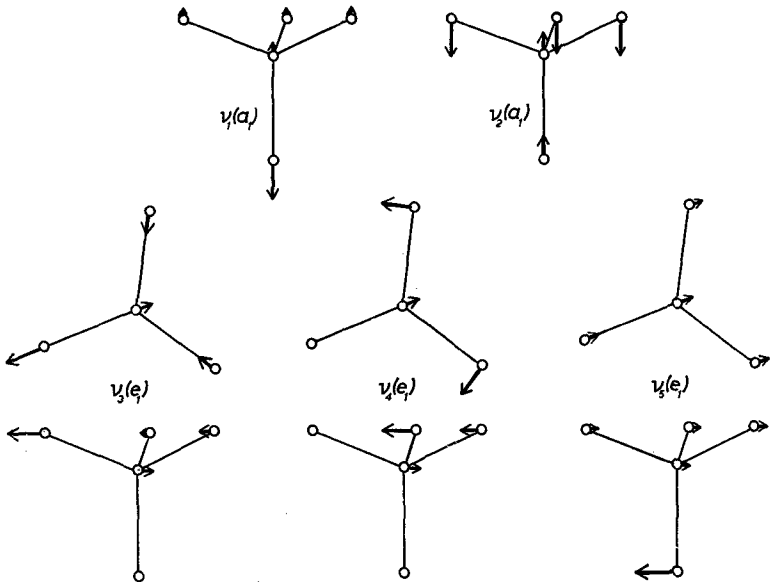


FIG. 5. Approximate form of the infra-red vibrations of silicon-oxygen tetrahedra, when linked in a sheet of symmetry C_{6v} .

axes), for which elementary theory predicts only two infra-red-active vibrations involving magnesium ions, one in which they move perpendicularly to the oxygen sheets, and the other a degenerate vibration parallel to the sheets. Brucite absorbs at 560 and 458 cm^{-1} (Beutelspacher, 1956a) and our own observations indicate that the weaker higher-frequency band corresponds to the perpendicular mode, as it is absent from the spectrum of an oriented film. The only other perpendicular vibration of brucite is an O-H stretching frequency near 3700 cm^{-1} . The band at 458 cm^{-1} is probably largely due to the degenerate in-plane Mg-O vibrations although the bending frequency of the hydroxyl groups has been predicted to lie near 400 cm^{-1} , and is of the same symmetry type (Hexter and Dows, 1956).

It seems likely that the magnesium ions of talc perform vibrations

similar in type to those of brucite. It is only if the magnesium ions all move in phase, and if their motions are restricted to being either perpendicular or parallel to the sheets, that they can couple with the silicon-oxygen vibrations, already discussed, without perturbing their form markedly and splitting the degeneracy of the E_1 vibrations. It seems reasonable, then, to assign the band of talc at 539 cm^{-1} to the perpendicular magnesium vibration, its frequency being rather lower than that of brucite owing to an increase in the effective mass of the oxygen atoms of talc. Similarly the strong doublet at 452 and 467 cm^{-1} is taken to correspond to the in-plane vibration of brucite at 458 cm^{-1} , with its degeneracy lifted. This vibration should couple strongly with the vibration ν_5 of the silicate layer, which may be at 426 cm^{-1} .

A stricter analysis shows that the magnesium ions in talc, unlike those of brucite, are not all symmetrically related, one ion in each unit cell being at a site of symmetry C_{2h} , the other two having symmetry C_2 . As a result they contribute six degrees of freedom to the infra-red-active vibrations of talc. If three of these have been correctly characterized above, then the other three would involve out-of-phase motion of the two types of magnesium atom, giving rise to weak absorption. It seems probable, too, that these vibrations would tend to couple only with the 'inactive' vibrations of the silicon-oxygen sheets, in which alternate oxygens of the inner layer (fig. 4) are 180° out of phase.

Finally, it may be noted that the rocking frequency of the structural hydroxyl groups has not been identified, nor have the bands which should arise from vibrations of the hydroxyl groups as a whole, out of phase with the other oxygen atoms of the inner layer in which they lie (fig. 4). These must be low-frequency vibrations, and in general it may be concluded that whilst the identification of the origin of the higher-frequency bands is probably satisfactory, the assignments in the low-frequency region must be regarded as tentative. It would be desirable to extend the spectra to lower frequencies and also to study a talc in which deuterium has been substituted for hydrogen.

Saponite and hectorite. The structures of saponite and hectorite are derived from that of talc by isomorphous substitution: in saponite the substitution is mainly aluminium for silicon, while in hectorite substitution of lithium for magnesium and fluorine for hydroxyl occurs. In both minerals the result is to give the layers of the clay minerals a negative charge, which is compensated by exchangeable cations that lie between the layers. With the exchangeable cations is associated a water layer of variable thickness, which gives the characteristic swelling properties

of these smectites. Corresponding to their structural similarities, the analogy between the spectra of talc and saponite is close, and the hectorite spectrum is clearly related, so that there is no difficulty in correlating the principal features of their spectra, as has been done in table I.

The shape and position of the magnesium silicate absorption bands of the smectites is insensitive to changes in either the water content or the exchangeable ions, so that the broadening of their bands compared with those of talc must be due principally to the damping effect of isomorphous substitution within the layers. That the broadening is more pronounced in hectorite can perhaps be correlated with the great change in valency and mass when lithium is substituted for magnesium. The change is proportionally less in both respects when aluminium is substituted for silicon, as in saponite.

It may be noted that it is the symmetrical distribution of magnesium ions with respect to the silicon-oxygen tetrahedra that largely preserves the hexagonal symmetry of the silicon-oxygen framework in talc. In its aluminium analogue, pyrophyllite, there are aluminium ions in only two of the three positions occupied by magnesium in talc. Because of the lower effective symmetry, pyrophyllite has a more complex spectrum (Beutelspacher, 1956*b*), in which none of the absorption bands in the region 650 to 1100 cm.^{-1} appear, from the spectra of oriented films, to be polarized perpendicularly to the silicate sheets. In hectorite the replacement of some of the magnesium atoms of talc by lithium must disturb the vibrations of the silicate sheet in a similar but less regular manner, and it may be for this reason that its perpendicularly polarized bands are poorly defined. In saponite the aluminium-for-silicon substitution lies on threefold axes, and so has a more symmetrical effect on the surrounding structure. This agrees with its well-defined perpendicular bands.

The general broadening of the bands resulting from isomorphous substitution in talc is readily understood. In the infra-red- and Raman-active vibrations of a homogeneous crystal, the unit cells over a considerable area are in phase. Indeed, in talc the individual tetrahedra of a silicon-oxygen layer are either in phase or else alternate tetrahedra are 180° out of phase. The presence of a foreign atom in some of the tetrahedra, for example, will distort both the structure of neighbouring tetrahedra and also the form and natural frequency of their vibrations through shared oxygen atoms. In saponite, where the substitution is one in eight (Mackenzie, 1957), nearly half the silicon tetrahedra have an

aluminium-containing tetrahedron as a first neighbour. In consequence, the sharp absorption band of talc is replaced by a broader band corresponding to the coupling of out-of-resonance vibrations. Even as it is no longer possible for the tetrahedra to be in phase, similarly it becomes impossible for them exactly to cancel each other. As a consequence the inactive vibrations of talc can become active, and in saponite and hectorite this may account for some of the weaker bands that are found in their spectra.

*Absorption bands of the structural hydroxyl groups
and of interlayer water.*

The stretching frequencies of the structural hydroxyl groups in talc, saponite, and hectorite all give rise to weak sharp bands at 3670 cm.^{-1} , which is 20 cm.^{-1} lower than the corresponding band of brucite. These bands are very much weaker than the corresponding absorption bands of the dioctahedral minerals, pyrophyllite and montmorillonite. Saponite has an additional weaker sharp band at 3697 cm.^{-1} , and so resembles the magnesium mica, phlogopite, which also has doublet absorption at these frequencies. The higher-frequency component of the mica doublet is, however, the stronger. Hectorite, too, has an additional weaker but broader band at 3610 cm.^{-1} , which was detectable only after removing most of the interlayer water. In this it resembles the mica biotite, which absorbs at 3670 and 3600 cm.^{-1} . In talc and saponite the hydroxyl groups are linked only to three magnesiums, and in hectorite the majority are also so linked, although there lithium is substituted for some of the magnesiums. The appearance of an absorption band common to all three minerals is therefore easily understood, but further work is necessary to identify the origin of the additional bands of the smectites.

Whilst talc has a broad weak band due to the stretching modes of adsorbed water at 3413 cm.^{-1} , the smectites show strong absorption in this region arising mainly from interlayer water. The broad diffuse bands consist of at least three components, as can be particularly clearly seen in the spectrum of sodium-saturated saponite (fig. 6A). In calcium- and magnesium-saturated saponite, the outlying absorption bands are little affected in position and intensity, but the central peak increases and shifts to lower frequencies (table II). In caesium-saturated saponite all three absorption bands are weak at room temperature (fig. 6B). That these bands are due to interlayer water is established by their disappearance from a spectrum of caesium-saturated saponite, recorded after heating a pressed disk containing the saponite to 80° C. for 16 hours

(fig. 6c). The water-absorption bands of calcium-saturated hectorite are identical with those of the corresponding saponite, but in calcium-saturated montmorillonite the absorption band of the structural hydroxyl group, at 3630 cm.^{-1} , overlies the highest-frequency water-absorption band. There is little doubt, however, that this water absorption is also present in montmorillonites, leading to marked changes with water content in the apparent intensity of the structural hydroxyl absorption, which is always an outstanding feature of montmorillonite spectra in this region (Beutelspacher, 1956 *a, b*; Buswell and Dudenbostel, 1941). In contrast, the structural hydroxyl group absorption of trioctahedral minerals can scarcely be resolved from the adjacent water absorption at room humidity. Similar three-banded water absorption is found in vermiculite, whose interlayer-water structure is probably very similar to that of smectites.

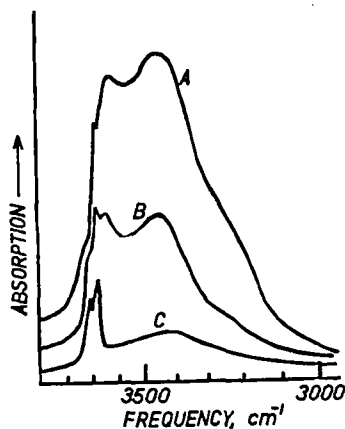


FIG. 6. Absorption of saponite (1.6 mg./cm.^2 in pressed disks) due to the O-H stretching vibrations of the structural hydroxyl group and of inter-layer water. A, Na^+ -saturated; B, Cs^+ -saturated; c, Cs^+ -saturated, dried 16 hours at 80° C.

One type of water molecule can give rise to at most two O-H stretching frequencies. More commonly, adsorbed water such as is found in pressed alkali-halide disks, gives only one asymmetric band. Accordingly,

TABLE II. Frequencies (cm.^{-1}) of O-H stretching frequencies of interlayer water in saponite.

Exchangeable ion.			
Mg^{++}	Ca^{++}	Na^+	Cs^+
3610	3610	3620	3630
3400	3420	3440	3460
3260	3260	3260	3250

we must postulate at least two types of water molecule in these smectites. Using the empirical relationship derived by Glemser and Hartet (1955), we find that the higher-frequency absorption near 3620 cm.^{-1} corresponds to a weak hydrogen bond with an $\text{H}_2\text{O}-\text{O}$ distance exceeding 3 \AA . The central maximum corresponds to an $\text{H}_2\text{O}-\text{O}$ distance increasing from 2.75 \AA . in Mg^{++} -saturated saponite to 2.85 \AA . in Cs^+ -saturated saponite,

and the low-frequency shoulder to an $\text{H}_2\text{O}-\text{O}$ distance of 2.63 \AA . The empirical relationship, however, applies strictly only when crystal water is bonded to an oxygen atom of an oxy-anion, and is not wholly applicable to saponite, where bonds between water molecules will also occur. Nevertheless, the evidence for three very different types of hydrogen bonding is strong. Mathieson and Walker (1954; see also Walker, 1956) have derived a detailed picture of the interlayer-water structure of a vermiculite phase with a 001 spacing of 14.36 \AA , from which it is concluded that in the vicinity of a cation site the water molecules are coordinated around the magnesium atoms in an octahedron, in which each water molecule forms a strong hydrogen bond with a neighbouring oxygen of the silicate sheet ($\text{H}_2\text{O}-\text{O}$ distance 2.90 \AA), and a very weak bond with adjacent water molecules. The presence of such a weak bond is in agreement with the infra-red measurement, but Mathieson and Walker's structure does not include a short enough hydrogen bond to account for the lowest-frequency absorption band at 3260 cm.^{-1} . A detailed comparison of infra-red measurements with the postulated structure must, however, be based on more closely controlled humidity conditions than has been possible here, and a better understanding of the infra-red absorption of water molecules in crystalline hydrates and in the adsorbed state.

In addition to the stretching vibrations discussed above, and to the broad $\text{H}-\text{O}-\text{H}$ angle deformation frequency at 1640 cm.^{-1} , the interlayer water was found to give rise to diffuse unspecific absorption throughout the 900 to 600 cm.^{-1} region, corresponding to the hindered rotation found in liquid water at 710 cm.^{-1} (Giguere and Harvey, 1956). The corresponding band in crystalline hydrates can move up to 800 cm.^{-1} , where it now represents a rocking of water molecules coordinated round cations.

Effects of grinding on the infra-red spectra of layer minerals.

As previously noted, grinding these layer minerals in the vibratory-ball mill caused marked changes in their spectra, which occurred most rapidly when small quantities were ground. Changes in infra-red spectra, and in other physical and chemical properties of clays (Perkin *et al.*, 1955) and micas (Mackenzie, Meldau, and Farmer, 1956) have been noted after grinding in an agate mortar or rotary ball-mill for periods varying from 8 hours to 6 weeks: these changes indicate the formation of an amorphous product. It is clear, however, from arguments used in discussing the broadening due to isomorphous substitution, that very

small particle size must also lead to broadening of the absorption bands, due to the effects of the disrupted structure at the particle edges, but it is not clear at what particle size it will first produce striking changes in the spectra. It may be, however, that this stage is reached when talc is

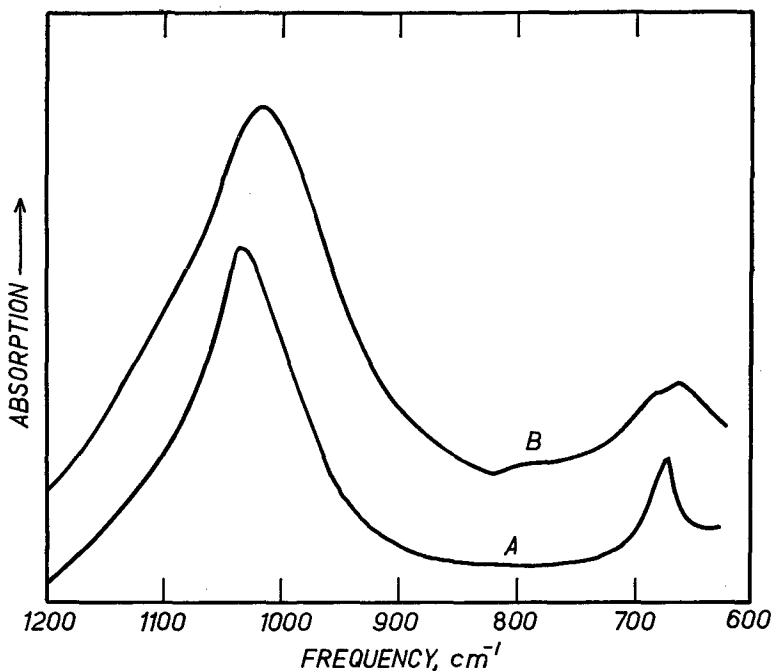


FIG. 7. Effect of grinding on the infra-red absorption of talc (A) and saponite (B). The spectra were obtained from pressed disks, 15 mg. of the minerals having been previously ground alone for 10 minutes in the vibratory grinder.

ground in the vibratory ball-mill (fig. 7). The persistence of the absorption band at 670 cm.^{-1} indicates that the talc structure persists to some degree, since this absorption band does not occur in amorphous silica or magnesium oxide. Unlike the Si-O vibrations, the O-H stretching vibrations should not be greatly affected by particle size, since coupling between adjacent hydroxyl groups can only be weak. This absorption does, in fact, remain sharp and well defined after the Si-O vibrations have markedly broadened. The spectral changes are therefore consistent with a small particle size, or with numerous dislocations in the structure of larger particles, perpendicular to the plane of the sheets. Separation

of the mineral into individual sheets should have little effect on the spectra, since mechanical coupling between vibrations in different sheets is slight.

Grinding of saponite under similar conditions also leads to a broadening of its Si-O absorption bands. In addition, a broad diffuse band appears near 1430 cm.^{-1} , which probably arises from carbonate formation, and so indicates some breakdown in the saponite structure.

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