American Mineralogist, Volume 62, pages 296–303, 1977

Infrared evidence of order–disorder in amesites[1]

CARLOS J. SERNA

Department of Agronomy, Purdue University
Lafayette, Indiana 47907

BRUCE D. VELDE

Laboratoire de Petrographie, Faculté des Sciences
9 Quai Saint-Bernard, Paris 5^{eme}, France

AND JOE L. WHITE

Department of Agronomy, Purdue University
Lafayette, Indiana 47907

Abstract

An IR investigation of natural and synthetic amesites has been made. The natural amesite from Chester, Massachusetts, and certain synthetic samples show order in the Al for Si substitution in tetrahedral sheets. Their IR spectra are characterized by sharp absorption bands and vibrations of "isolated" Al tetrahedra. In contrast, the broadening in the absorption bands and the presence of two absorptions around 800 cm^{-1} suggest that amesite from Saranoskoye and some synthetic samples have a random Al for Si substitution.

The IR absorption bands for the hydroxyl groups in amesites appear to arise from the order–disorder nature of the Al for Si substitution in tetrahedral sheets. In ordered amesites the oxygens of the tetrahedral sheets are all coordinated to Al–Si pairs, providing a uniform environment for each of the interacting hydroxyls. By contrast, in amesites with disordered Al for Si substitution the outer hydroxyl groups of the octahedral sheets would experience two different interactions with O–Al and O–Si.

The presence and distribution of Al in tetrahedral sheets appear to account for the hydroxyl vibrations in the trioctahedral series amesite–antigorite.

Introduction

From the first bold suggestion by Barth (1934) that potassium feldspar polymorphs represent different degrees of aluminum–silicon disorder in tetrahedral sites, numerous examples of cation order–disorder have been found in most of the silicate familes (Burnham, 1973). Although Al substitutes for Si in the tetrahedral sites of many silica layers and affects their structural characteristics, the way in which this substitution takes place is difficult to determine because Al and Si appear almost identical by X-ray diffraction, *i.e.* their atomic scattering factors are very similar. However, infrared spectroscopy has proved to be a useful tool in the study of cation distribution (White, 1974). Thus, the ordered Al for Si substitution in the tetrahedral sheets for margarite suggested by Farmer and Velde (1973) on the basis of the absence of Al–O–Al vibrations has been recently confirmed by Guggenheim and Bailey (1975) in the refinement of the margarite structure in subgroup symmetry.

Order–disorder in the stacking of the layers in amesite minerals has been previously reported (Brindley *et al.*, 1951; Steinfink and Brunton, 1956), but no considerations about the cation ordering have been made. Partial refinement with the ideal space group $P6_3$ indicated both tetrahedral and octahedral disorder for Saranoskoye amesite (Steinfink and Brunton, 1956). However, refinement in progress in an amesite from Antarctica (Bailey, 1975; Hall and Bai-

---

[1] Journal Paper 6448, Purdue University Agricultural Experiment Station West Lafayette, Indiana.

ley, 1976) shows indications of both tetrahedral and octahedral cation ordering.

An infrared study of the order–disorder of the cation substitutions in several natural and synthetic amesites is presented here. In addition, a possible explanation for the hydroxyl vibrations in the trioctahedral series amesite–antigorite is given.

Materials and methods

The sources and composition of the natural amesites examined are:

(1) Amesite from Saranoskoye (U.S.S.R.), obtained from the Smithsonian Institution, Washington, D. C. (NMHN 103312). Although no chemical analysis has been given, it was considered to have the ideal composition (Steinfink and Brunton, 1956).

(2) Amesite from Chester, Massachusetts, obtained from the Smithsonian Institution, Washington, D. C. (NMNH 80715). This sample has been described by Gruner (1944). This sample, of chemical composition $(Mg_{1.5}Al_{1.06}Fe^{2+}_{0.41})(Si_{1.01}Al_{0.99})O_5(OH)_4$, was used in a crystal structure determination (Brindley *et al.*, 1951).

In addition, synthetic samples of Mg and Ni amesites of ideal composition and a synthetic aluminous serpentine of low Al content in tetrahedral position were studied. A description of the methods of synthesis can be found in Velde (1973). The characteristics of the synthetic samples are shown in Table 1.

Infrared spectra in the range 4000–300 cm^{-1} were obtained from samples dispersed in KBr discs, or oriented deposits on AgCl windows, using a Perkin-Elmer Model 180 infrared spectrophotometer.

Results and discussion

Amesite can be considered as the end member of the serpentine minerals with ideal chemical composition $(Mg_2Al)(SiAl)O_5(OH)_4$, namely a serpentine with the highest substitution of Al for Si. Two different kinds of infrared patterns have been found in the study of several synthetic and natural amesites (Figs. 1–4). Similar infrared spectra of amesites have been previously published (Stubican and Roy, 1961; Shirozu and Momoi, 1972).

The infrared patterns of amesites in Figure 1 resemble those found in chlorites with high Al for Si substitution in tetrahedral sheets (Hayashi and Oinuma, 1967). By comparison with the study made on clinochlore by Serratosa and Vinas (1964), the absorption bands about 3430 and 3570 cm^{-1} can be considered to be due to the outer hydroxyls of the octahedral sheets, which hydrogen-bond to adjacent oxygens in tetrahedral sheets. In the same way, the shoulders at 3615 and 3670 cm^{-1} can be attributed to the inner hydroxyl groups.

Completely different infrared patterns were obtained for the magnesium amesites in Figure 2. These samples show mainly one absorption band for the

TABLE 1. Characteristics of the synthetic samples

Sample	Composition	Starting Material	Pressure (Kbar)	T(°C)	Time	Cell Dimensions		Polytype[***]
						c sin β(Å)	b(Å)	
CH-159	III[*]Mg	gel[1]	2	522°	36 days	7.101	9.210	1M
CH-425	III Mg	gel	14	454°	10 hours	7.115	9.210	1M+1T
CH-466	III Mg	gel+carb.[2]	2	450°	24 days	7.026	9.180	1T+1M minor
CH-476	III Ni	gel+carb.	2	450°	20 days	7.000	9.120	
CH-141	XV[**]Mg	gel	2	408°	62 days	7.260	9.246	1T

[*] $III = (Si_{2.00}Al_{2.00})(Al_{2.00}R^{2+}_{4.00})O_{10}(OH)_8$

[**] $XV = (Si_{3.82}Al_{0.18})(Al_{0.60}Mg_{5.19})O_{10}(OH)_8$

[***] According to Bailey's classification (1969)

[1] gel = oxide mixture

[2] carb. = Mg or Ni carbonate

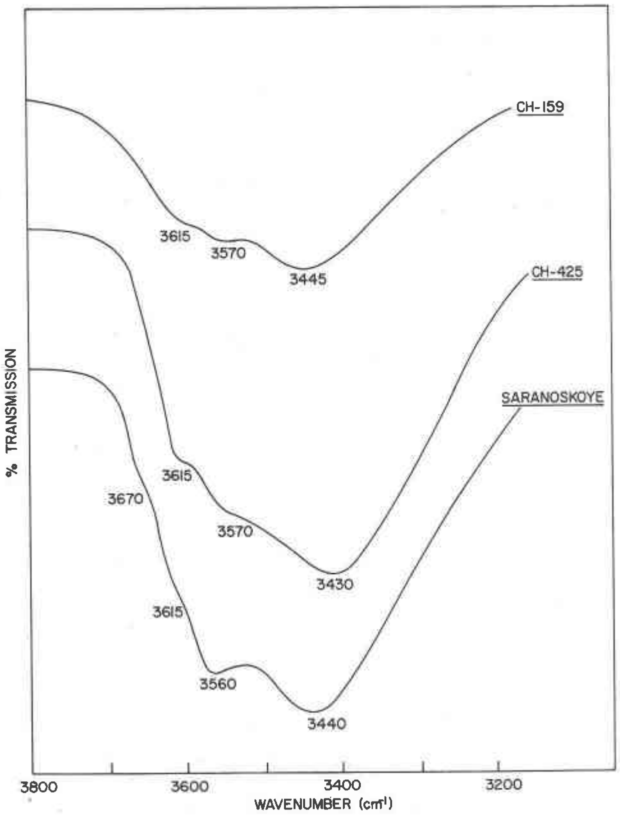

FIG. 1. Hydroxyl stretching absorptions of amesites with random Al for Si substitution.

outer hydroxyls around 3420 cm^{-1}. Although the structure of amesite indicates that the number of outer hydroxyls is three times higher than the number of inner hydroxyls, an extremely high intensity is observed for the outer hydroxyls compared to the inner. This observation can be explained by considering the increase in intensity that takes place when the OH groups form hydrogen bonds (Bellamy *et al.*, 1971). On the other hand, the absorption bands for the hydroxyl groups and lattice vibrations for the Chester amesite and Ch-466 are much sharper than those of the Saranoskoye amesite and CH-159 and CH-425 (Figs. 1–4).

Therefore, the characteristics observed in the infrared spectra of the amesites in Figures 2 and 4, such as the sharpness and the reduction in the number of infrared absorption bands, suggest that the isomorphic substitution in these samples is ordered. In contrast, the amesites in Figures 1 and 3 show the characteristics of samples with random isomorphic substitution, even when order is possible. The differences between the infrared spectra of both series of amesites can not be interpreted as being due to grinding effects, since samples of well-ordered amesites (Chester and CH-466) ground for 5 minutes in a mortar did not give the infrared patterns of disordered amesites, but merely a broadening of the absorption bands.

Order–disorder in the Al for Si substitution

The comparison of the infrared spectra of magnesium serpentines (Brindley and Zussman, 1959; Yariv and Heller-Kallai, 1975) with those of amesites indicates that absorption bands between 700–900 cm^{-1} are related to the presence of Al in tetrahedral coordination. According to Tarte (1967) two types of arrangements can be considered for Al in tetrahedral coordination; "isolated" AlO_4 tetrahedra, which have been found to absorb between 650–800 cm^{-1} in some spinels and aluminates and "condensed" AlO_4 tetrahedra that absorb between 700–900 cm^{-1} in numerous aluminates and some transition aluminas.

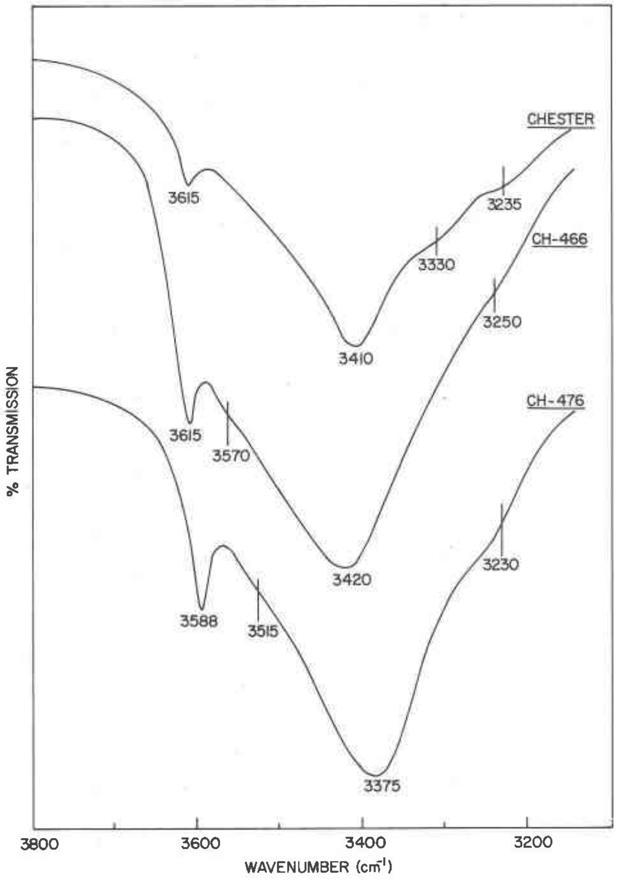

FIG. 2. Hydroxyl stretching absorptions of amesites with ordered Al for Si substitution.

Saranoskoye amesite and synthetic amesites CH-425 and CH-159 show two absorption bands around 800 cm^{-1} (Fig. 3), that would indicate the simultaneous presence of "isolated" and "condensed" AlO_4 tetrahedra in a random distribution in tetrahedral sheets (Fig. 6b). This interpretation would account for the broadening of the infrared absorption bands for these amesites. The refinement of the Saranoskoye amesite within the ideal space group $P6_3$ by Steinfink and Brunton (1956) indicated tetrahedral and octahedral disorder in the cation distribution.

The absorption band around 610 cm^{-1} is characteristic of serpentine minerals, although the position can change with the amount of aluminum ions in octahedral or tetrahedral coordination (Stubican and Roy, 1961). This absorption is very intense for all the amesites studied except for Saranoskoye amesite, in which the absorption is rather small. This could suggest that some chlorite mineral is present as an impurity in the Saranoskoye amesite. As indicated by Farmer (1974), chlorites and serpentines having identical chemical composition are often intergrown in both natural and synthetic minerals.

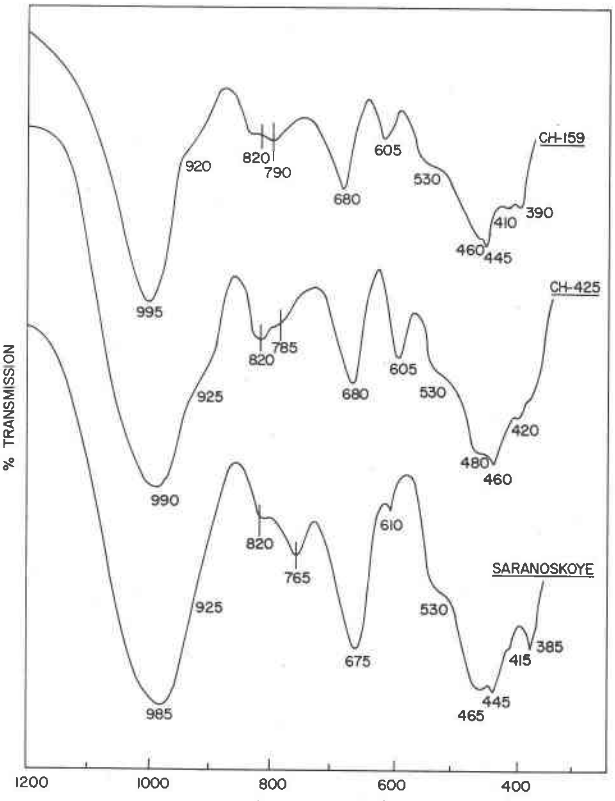

FIG. 3. Infrared absorption spectra of amesites with random Al for Si substitution in the 1200–300 cm^{-1} region.

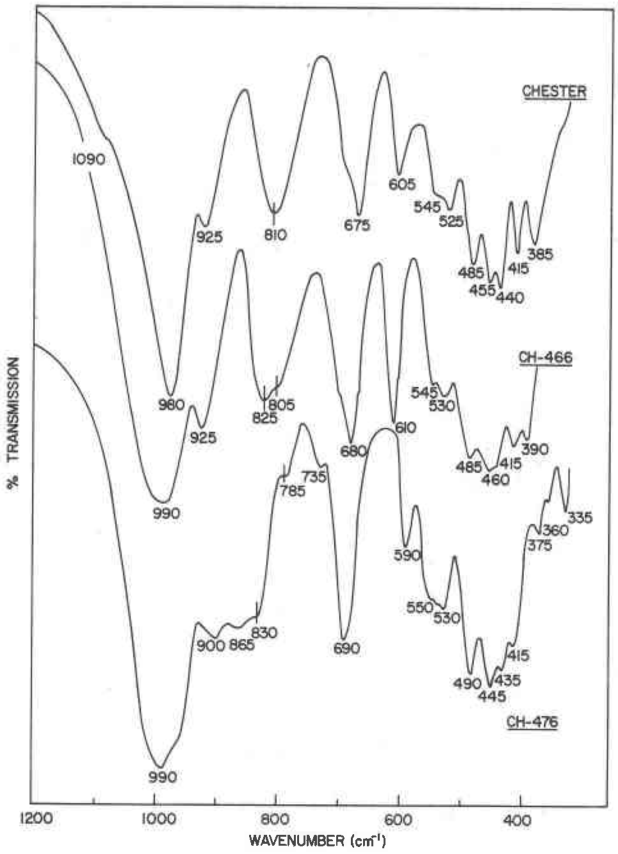

FIG. 4. Infrared absorption spectra of amesites with ordered Al for Si substitution in the 1200–300 cm^{-1} region.

On the other hand, Chester amesite shows only one absorption band at 810 cm^{-1}, presumably due to "isolated" AlO_4 tetrahedra (Fig. 6a). The sharpness of the absorption bands observed in this amesite is in good agreement with an ordered substitution of Al for Si in tetrahedral sheets. Ordering in tetrahedral and octahedral sheets has been suggested by Bailey (1975) and Hall and Bailey (1976) in the structural refinement of an amesite from Antarctica. Although CH-466 synthetic amesite, Figures 2 and 4, can be considered an ordered amesite, some indications of disorder are present, *i.e.*, a shoulder in the hydroxyl stretching vibrations at 3570 cm^{-1} and a small splitting in the absorption around 800 cm^{-1}.

Another striking feature which seems to be associated with the well-ordered amesites is the absorption at 925 cm^{-1} (Fig. 4). This absorption band, unusual for a trioctahedral mineral, was previously found by Stubican and Roy (1961) in the synthetic serpentines richest in Al.

An ordered Ni–amesite (brindleyite[2])

As we have already shown, the infrared spectrum of an amesite is largely dominated by the order–disorder of the Al for Si substitution in tetrahedral sheets. However, the intrinsic composition of the octahedral sheets must have some influence on the position of the infrared absorption bands. Comparison between Ni–amesite (CH-476) and a Mg–amesite (CH-466), both with similar ordered Al for Si subsitution, is shown in Figures 2 and 4. According to the predicted effect of the substitution of nickel (At. wt. 58.7) for magnesium (At. wt. 24.3), the OH stretching frequencies are shifted to lower values. However, the shift observed for the outer hydroxyls (50 cm^{-1}) is higher than that found for the inner hydroxyls ($\sim$30 cm^{-1}). In chlorites, the space between the 2:1 layer and the interlayer sheet can vary from one specimen to another, independently of the tetrahedral substitution; it was found that the OH–O distance decreased with the increment in heavy cations, *i.e.*, Fe+Cr+Ni+Mn (Bailey, 1972). Thus, a slight decrease in the interlayer space in amesite can be produced when Mg is replaced by Ni, causing an additional shift in the outer hydroxyl groups. The lower d_{001} value found in brindleyite (7.000 A) compared to the magnesian CH-466 (7.026 A) supports this assumption (Table 1).

In the 1200–350 cm^{-1} region the isomorphic substitution of Ni by Mg does not show important changes; mainly a new absorption band for the Ni–amesite is observed at 865 cm^{-1} (Fig. 4), and some absorption bands shift as a consequence of the substitution, *i.e.*, the absorption at 680 cm^{-1} in Mg–amesite is shifted to 690 cm^{-1} in the Ni–amesite. According to Farmer (1974), absorption bands in trioctahedral chlorites between 600–700 cm^{-1} arise from librations of OH groups and appear to be sensitive to octahedral composition.

Interpretation

Hydroxyl vibrations in amesite

In amesites, planes of hydroxyls and oxygens face each other in an arrangement similar to that of kaolinite; but the important difference, in addition to the substitution of half of the Si atoms by Al in tetrahedral sheets in amesites, is that all octahedral positions are occupied by cations. In Figure 5, the infrared spectra for a random (Saranoskoye) and a well-ordered (CH-476) amesite are given for two different angles of incidence. A significant increase in the intensity of the absorptions bands with the increase in the angle of incidence is observed in both amesites. However, it should be pointed out that the observed increase in intensity is smaller than that shown in a flake of clinochlore (chlorite) by Serratosa and Vinas (1964). Since a dichroism effect similar to that of amesites was also observed in some powdery chlorite minerals of apparent good crystallinity (Post and Plummer, 1972), the small dichroism effect observed in amesites (Fig. 5) could be attributed to the fact that only part of the particles are oriented after deposition from suspension on AgCl windows.

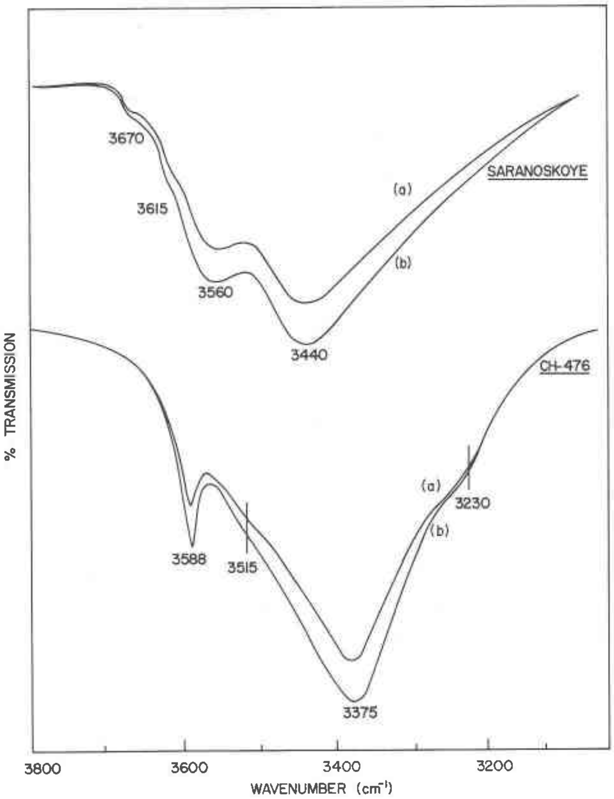

FIG. 5. Hydroxyl stretching absorptions of partially oriented deposits of amesites for two different angles of incidence: (a) 0° (b) 40°.

Despite the order-disorder of the Al for Si substitution, the outer and inner hydroxyl groups appear to have their bond axes essentially perpendicular to the layers. Consequently, the presence of two maxima for the outer hydroxyls in disordered amesites (and therefore two OH—O distances) or one in the well-ordered amesites, must be related to the different locations of the Al for Si substitution. In Saranos-

---

[2] Name recently approved by the I.M.A. Commission.

koye amesite, the absorption bands of the outer hydroxyls at 3570 and 3440 cm^{-1} correspond to hydrogen bond distances of 3.00 and 2.85 A (Nakamoto *et al.*, 1955). Farmer (1974) suggested that the OH–O distance of 2.97 A found by X-ray determinations for Saranoskoye amesite (Steinfink and Brunton, 1956) must represent only an average separation between layers.

The interlayer bonding of the 1:1 structures is known to involve long hydrogen bonds between the hydroxyls which form one of the surfaces of the 1:1 layer and the oxygens which form the adjacent surface of the next layer (Cruz *et al.*, 1972; Giese, 1973). Theoretical calculations indicate that the long range interaction between an hydroxyl group and an oxygen is predominantly electrostatic (Coulson and Danielsson, 1954). Thus, the strength of the interaction of the hydroxyl hydrogen with the aluminum-coordinated oxygen in the tetrahedral sheet will be greater than with the silicon-coordinated oxygen, because of the greater electron donor effect of the aluminum cation (Farmer, 1974). In ordered amesites the oxygens of the tetrahedral sheets are all coordinated to Al–Si pairs (Fig. 6a), providing a similar environment for each of the interacting hydroxyls. In contrast, in amesites with disordered Al for Si substitution (Fig. 6b) the outer hydroxyl groups of the octahedral sheets would experience two different interactions with O–Al and O–Si. Another effect produced by the Al for Si substitution is in the thickness of the tetrahedral sheet. It is known that the average (Si,Al)–O distance varies nearly linearly with the tetrahedral Si–Al composition and standard values of Si–O = 1.62 A and Al–O = 1.77 A have been suggested for layer silicates (Smith and Bailey, 1963). In accordance with this, the oxygens bound to Al atoms in the tetrahedral sheets would be in a closer position to interact with the hydroxyl groups by hydrogen bonding, reinforcing the electron donor effect of the aluminum. The exponential relationship between the O–H—O distances and the frequency of the O–H bonds in the range considered would cause a shift of about 150 cm^{-1} for a change of 0.15 A in the O–H—O distance (Nakamoto *et al.*, 1955).

Therefore, the Al for Si substitution will produce both a decrease in the hydrogen bond distance and an increase in the electronegativity of the oxygens. These two effects and the order–disorder due to the aluminum cation in the tetrahedral sheets are responsible for the observed hydroxyl absorption bands in amesites.

Hydroxyl stretching frequencies in 7 A trioctahedral minerals

In the 1: magnesium serpentine minerals no cation disorder can be present due to the lack of substitution in octahedral and tetrahedral sheets. Although, structurally speaking, there are differences between the various members of the magnesium ser-

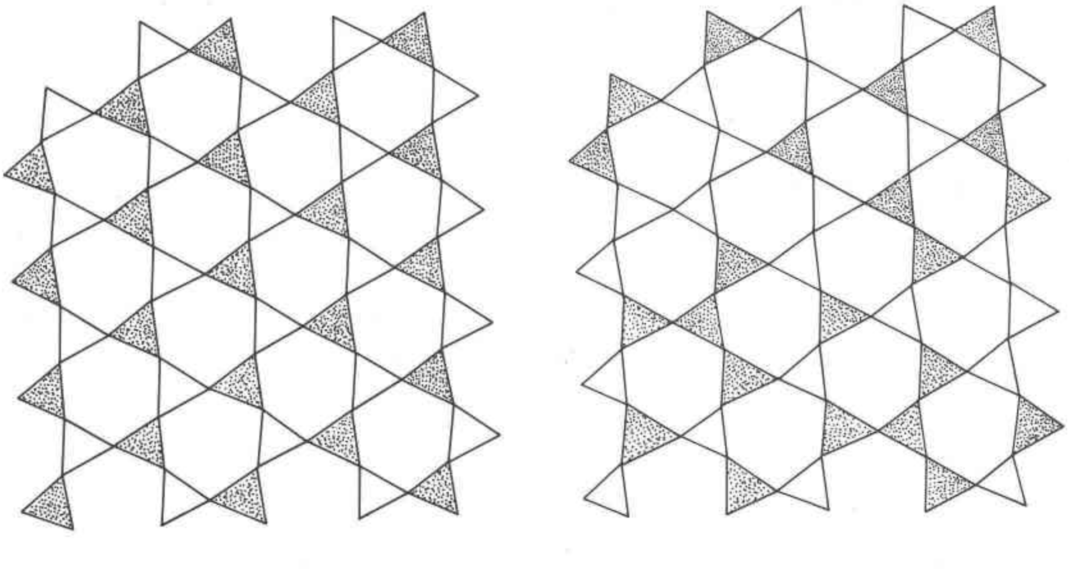
(a) (b)

FIG. 6. Substitution of Al for Si in the tetrahedral sheets of amesites, (a) ordered substitution, (b) random substitution.

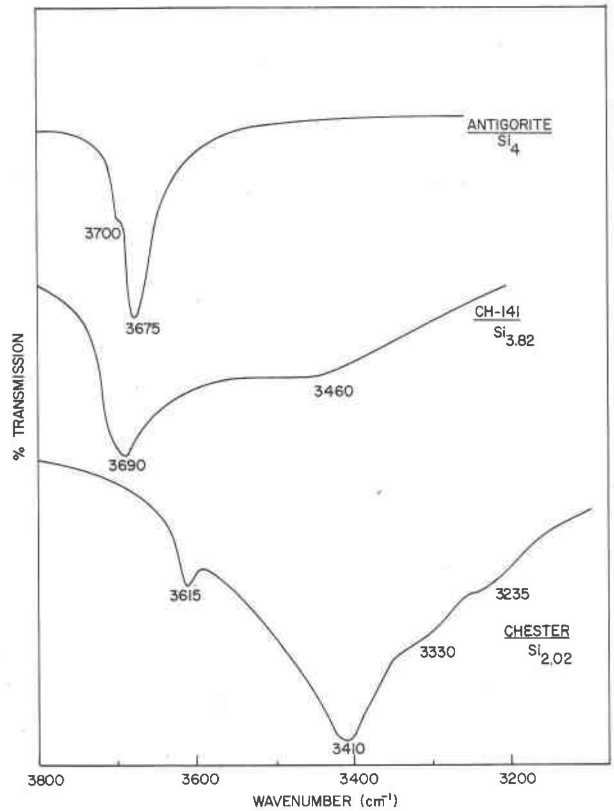

FIG. 7. Hydroxyl stretching absorptions in the 7 A series antigorite–amesite.

pentines, their infrared spectra have been found to be rather similar (Yariv and Heller-Kallai, 1975). For comparison the infrared spectrum of an antigorite (Farmer, 1974) has been included along with a well-ordered amesite (Chester) and a synthetic serpentine with low Al content in the tetrahedral sheets (Fig. 7).

The forces which bind successive amesite layers are the net ionic charges on the tetrahedral and octahedral sheets resulting from the isomorphic substitutions. As a result of these electrostatic forces, the layers in amesite are sufficiently close so that the outer hydroxyls can form hydrogen bonds with the adjacent oxygens. In the infrared spectra this effect results in a good resolution between the absorption bands for the inner and outer hydroxyls in amesite (Fig. 7). However, due to the lack of substitutions, and therefore the absence of this electrostatic attraction between layers, the absorption bands due to the inner and outer hydroxyls in magnesium serpentine minerals cannot be distinguished (Farmer, 1974). In general, the fact that the d_{001} spacing in amesite is smaller than those of magnesium–serpentine minerals (7.00–7.11 A compared to 7.28–7.31 A) can explain the less intense hydrogen bonding for the hydroxyl groups in the latter. According to this interpretation the broad absorption band observed at 3460 cm^{-1} in the serpentine CH-141 may be due to the substitution of small amounts of Al for Si in tetrahedral sheets (Fig. 7). The presence of an absorption band at 3400 cm^{-1} in natural serpentines has been recently suggested to be a consequence of the Al in tetrahedral sheets (Heller-Kallai *et al.*, 1975).

On the other hand, the structure and composition of the tetrahedral sheets may also affect the vibrations of the inner hydroxyl groups, since the OH stretching frequencies are affected by the charge on and the distance from the neighboring oxygens and cations. Thus, in clintonites an increase in the substitution of Si by Al produces a shift to lower frequencies in the inner hydroxyl groups (Farmer and Velde, 1973). This is consistent with the lower frequency for the inner hydroxyls found in amesite (3615 cm^{-1}) compared to antigorite (shoulder at 3700 cm^{-1}). The sharpness of the inner hydroxyls in amesite corroborates the assumption made for clintonites that the interaction is almost entirely electrostatic (Farmer and Velde, 1973).

Acknowledgments

One of us (C. Serna) gratefully acknowledges the support of the Commission for Cultural Exchange between the United States and Spain. Appreciation is also expressed to Dr. S. W. Bailey for his suggestions and criticisms of the manuscript.

References

Bailey, S. W. (1969) Polytypism of trioctahedral 1:1 layer silicates: *Clays Clay Minerals.*, *19*, 355–371.

——— (1972) Determination of chlorite composition by x-ray spacings and intensities. *Clays Clay Minerals.*, *20*, 381–388.

——— (1975) Cation ordering and pseudosymmetry in layer silicates. *Am. Mineral.*, *60*, 175–187.

Barth, T. F. W. (1934) Polymorphic phenomena and crystal structure. *Am. J. Sci.*, *27*, 273–286.

Bellamy, L. J., M. J. Blandamer, M. C. R. Symons and D. Waddington (1971) Infrared spectra of salt hydrates. *Trans. Faraday Soc.*, *67*, 3435–3440.

Brindley, G. W., B. M. Oughton and R. F. Youell (1951) The crystal structure of amesite and its thermal decomposition. *Acta Crystallogr.*, *4*, 552–557.

——— and J. Zussman (1959) Infrared absorption data for serpentine minerals. *Am. Mineral.*, *44*, 185–188.

Burnham, C. W. (1973) Order-disorder relationships in some rock-forming silicate minerals. *Annual Rev. Earth Planet Sci.*, *1*, 313–338.

Coulson, C. A. and W. Danielsson (1954) Ionic and covalent contributions to the hydrogen bond. *Arkiv Fysik*, *9*, 239–244.

Cruz, M., H. Jacobs and J. J. Fripiat (1972) The nature of the interlayer bonding in kaolin minerals. *Proc. Int. Clay Cònf. Madrid,* 35–46.

Farmer, V. C. (1974) The layer silicates. In V. C. Farmer, Ed. *The Infrared Spectra of Minerals*. Mineral. Soc., London, p. 331–364.

——— and B. Velde (1973) Effects of structural order and disorder on the infrared spectra of brittle micas. *Mineral. Mag., 39,* 282–288.

Giese, R. F. (1973) Interlayer bonding in kaolinite, dickite and nacrite. *Clays Clay Minerals, 21,* 145–149.

Gruner, J. W. (1944) The kaolinite structure of amesite, $(OH)_8$ $(MgFe)_4Al_2(Si_2Al_2)$ O_{10} and additional data on chlorites. *Am. Mineral., 29,* 422–430.

Guggenheim, S. and S. W. Bailey (1975) Refinement of the margarite structure in subgroup symmetry. *Am. Mineral., 60,* 1023–1029.

Hall, S. H. and S. W. Bailey (1976) Amesite from Antarctica. *Am. Mineral., 61,* 497–499.

Hayashi, H. and K. Oinuma (1967) Si-O absorption bands of chlorite. *Am. Mineral., 42,* 1206–1210.

Heller-Kallai, L., S. M. Yariv and S. Gross (1975) Hydroxyl stretching frequencies of serpentine minerals. *Mineral. Mag., 40,* 197–200.

Nakamoto, K., M. Margoshes and R. E. Rundle (1955) Stretching frequencies as a function of distances in hydrogen bonds. *J. Am. Chem. Soc., 77,* 6480–6486.

Post, J. L. and C. C. Plummer (1972) The chlorite series of Flagstaff Hill area, California: a preliminary investigation. *Clays Clay Minerals, 20,* 271–283.

Serratosa, J. M. and J. M. Vinas (1964) Infrared investigations of the OH bonds in chlorites. *Nature, 202,* 999.

Shirozu, H. and H. Momoi (1972) Synthetic Mg-chlorite in relation to natural chlorite. *Mineral. J., 6,* 464–476.

Smith, J. V. and S. W. Bailey (1963) Second review of Al–O and Si–O tetrahedral distances. *Acta Crystallogr., 11,* 191–195.

Steinfink, H. and G. Brunton (1956) The crystal structure of amesites. *Acta Crystallogr., 9,* 487–492.

Stubican, V. and R. Roy (1961) Isomorphous substitution and infrared spectra of the layer lattice silicates. *Am. Mineral., 46,* 32–51.

Tarte, P. (1967) Infra-red spectra of inorganic aluminates and characteristic vibrational frequencies of AlO_4 tetrahedra and AlO_6 octahedra. *Spectrochim. Acta, 23A,* 2127–2143.

Velde, B. (1973) Phase equilibria in the system $MgO–Al_2O_3–SiO_2–H_2O$ chlorites and associated minerals. *Mineral. Mag., 39,* 297–312.

White, B. (1974) Order–disorder effect. In, V. C. Farmer, Ed., *The Infrared Spectra of Minerals*, Mineral. Soc., London, p. 87–110.

Yariv, S. and L. Heller-Kallai (1975) The relationships between the infrared spectra of serpentines and their structures. *Clays Clay Minerals, 23,* 145–152.

Manuscript received, September 23, 1976; accepted for publication, November 1, 1976.