

# The effect of aluminium on the infra-red spectra of 7 Å trioctahedral minerals<sup>1</sup>

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**SUMMARY.** The substitution of  $2\text{Al}^{3+}$  for  $\text{Si}^{4+} + \text{M}^{2+}$  ( $\text{M} = \text{Mg}$  or  $\text{Ni}$ ) has been studied by infra-red spectroscopy in 7 Å trioctahedral minerals over the composition range from  $\text{Al} = 0.00$  to  $\text{Al} = 2.00$ . Significant differences are observed in the infra-red spectra and these make possible an estimation of the amount of Al in tetrahedral coordination. The most striking effect of the substitution is observed in the stretching vibrations of the outer hydroxyl groups and that of the silicate anion.

The aluminous Mg-serpentine can be readily distinguished from their analogues, the aluminous Ni-serpentine, by the absence of the Mg-OH absorption band between 570 and 615  $\text{cm}^{-1}$  in the latter.

ONE mineralogical problem that has attracted considerable attention in recent years concerns the structure and morphology of the serpentines and aluminous serpentines.<sup>3</sup> The misfit between the tetrahedral and octahedral sheets in serpentines ( $b_{\text{oct}} > b_{\text{tet}}$ ) was regarded as the cause of the tubular morphology found in chrysotile (Bates *et al.*, 1950). It was suggested that ionic substitutions like Al or  $\text{Fe}^{3+}$  serve to adjust the dimensions of both tetrahedral and octahedral sheets, resulting in flat-layer structures. However, a recent review (Wicks

and Whittaker, 1975) of the substitution in natural and synthetic chrysotiles and lizardites indicates that there are no compositional differences between curved and flat-layer structures.

The infra-red spectra of the serpentine polymorphs are rather analogous, despite their different morphologies, which must be due to their similarities in chemical composition (Brindley and Zussman, 1959; Yariv and Heller-Kallai, 1975). Antigorite, which has somewhat more distinctive infra-red spectral features than the other polymorphs (Ptak and Pampuch, 1967; Yariv and Heller-Kallai, 1975), was recently considered to have slightly different composition (Wicks and Whittaker, 1975). In addition to the natural and synthetic Mg-serpentine, solid solution series Mg-Ni, Mg-Co, and Ni-Co have been synthesized by several workers (Roy and Roy, 1954; Jasmund *et al.*, 1975). The infra-red spectra published by Jasmund *et al.* (1975) show that the composition of the serpentine produces changes in the shape and position of the infra-red absorption bands.

Significant differences in the infra-red spectra of the serpentine minerals are expected when the substitution  $2\text{Al}$  for  $\text{Si}^{4+} + \text{M}^{2+}$  ( $\text{M} = \text{Mg}$  or  $\text{Ni}$ ) takes place, since not only compositional variations occur but also structural changes (Roy and Roy, 1954; Radoslovich, 1963; Chernosky, 1975). Thus, striking differences are observed in the published infra-red spectra of aluminous serpentines (Tud-denham and Lyon, 1959; Stubican and Roy, 1961a; Shirozu and Monoi, 1972). We have recently shown that the presence and distribution of Al largely dominates the infra-red spectra of amesites (Serna *et al.*, 1977). In this paper, results are presented on the effect of Al on the infra-red spectra of the 7 Å trioctahedral minerals.

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<sup>3</sup> The terms Mg-serpentine and Ni-serpentine are used here as generic names for the polymorphs with two formula units,  $\text{Si}_4\text{M}_6\text{O}_{10}(\text{OH})_8$  ( $\text{M} = \text{Mg}$  or  $\text{Ni}$ ), although some varieties contain one, six, even nine formula units (Wicks and Whittaker, 1975). Aluminous Mg or Ni-serpentine will be considered as those 7 Å trioctahedral minerals in which some aluminium is present ( $\text{Si}_{4-x}\text{Al}_x$ )( $\text{M}_{6-x}\text{Al}_x$ ) $\text{O}_{10}(\text{OH})_8$  ( $2 > x > 0$ ). The end members of the aluminous serpentines,  $x = 2$ , will be referred to as amesite and brindleyite, for the magnesium and nickel series, respectively.

**Materials and methods.** Conventional hydrothermal techniques, as reported previously (Velde, 1973), were used to synthesize the specimens. The samples studied were those of 7 Å minerals. No 14 Å reflections were recorded, except for the composition Al = 1.20, which contained a minor amount of 14 Å material. The use of D<sub>2</sub>O in some experiments produced only partially deuterated samples.

The polytypes were determined in samples by reference to the strongest reflections according to Bailey's classification (1969). In the magnesium series members of the group C were found in the range from Al = 0.00 to Al = 1.00, and mainly group A representatives occurred in the composition range from Al = 1.00 to Al = 2.00. However, a variation in polytype was noted depending upon the running time or rate of crystallization for amesite composition minerals (Serna *et al.*, 1977). All the aluminous Ni-serpentine were found in group C except brindleyite (Al = 2.00) which gave patterns of Bailey's A group.

The measurements of the *c* dimensions were obtained from the 002 reflections. Reproducibility measurements indicated a margin of error of about ±0.05 Å. Infra-red spectra in the range 4000–

300 cm<sup>-1</sup> were obtained from samples dispersed in KBr discs, using a Perking-Elmer Model 180 infra-red spectrophotometer.

### Results and discussion

**Hydroxyl stretching vibrations.** In a previous study it was suggested that the lower OH-stretching frequencies (or frequency) in amesites are due to the strong electrostatic forces that appear because of the Al for Si substitution in tetrahedral sheets (Serna *et al.*, 1977). As a result, moderately strong hydrogen bonds between the outer hydroxyls and the adjacent oxygen surfaces occur in amesite, while the OH-stretching frequencies in the serpentine minerals indicate relatively little or no hydrogen bonding.

The effect of the Al for Si substitution on the hydroxyl vibrations in aluminous Mg-serpentine is shown in fig. 1. Even at the low Al content (0.18) a broad absorption band around 3460 cm<sup>-1</sup> is observed. The presence of a low-frequency hydroxyl vibration has been previously noted in natural aluminous serpentine (Heller-Kallai *et al.*, 1975). With increasing Al content this absorption shifts slightly to lower frequencies (3440–3420 in

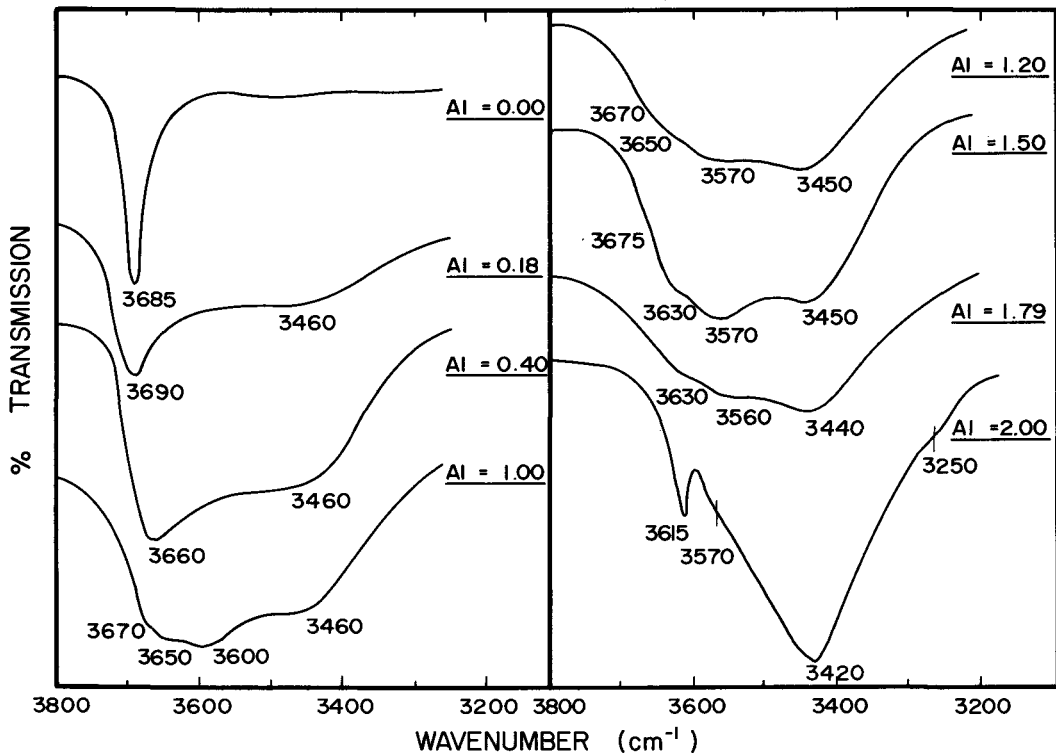


FIG. 1. Hydroxyl-stretching absorption in Mg-serpentine at different aluminium contents.

amesites) and increases in relative intensity. At Al contents greater than 1.00, a new absorption band between 3600 and 3560  $\text{cm}^{-1}$  appears and one or more shoulders become apparent at higher frequencies, 3670–3630  $\text{cm}^{-1}$ . For the amesite composition, if an ordered Al for Si substitution takes place, only one absorption band is observed for the inner and outer hydroxyl groups at 3615 and 3420  $\text{cm}^{-1}$ , respectively (fig. 1). Similar behaviour is observed in some natural aluminous serpentines (Tuddenham and Lyon, 1959) and in natural and synthetic chlorites (Hayashi and Oinuma, 1967; Shirozu and Monoi, 1972).

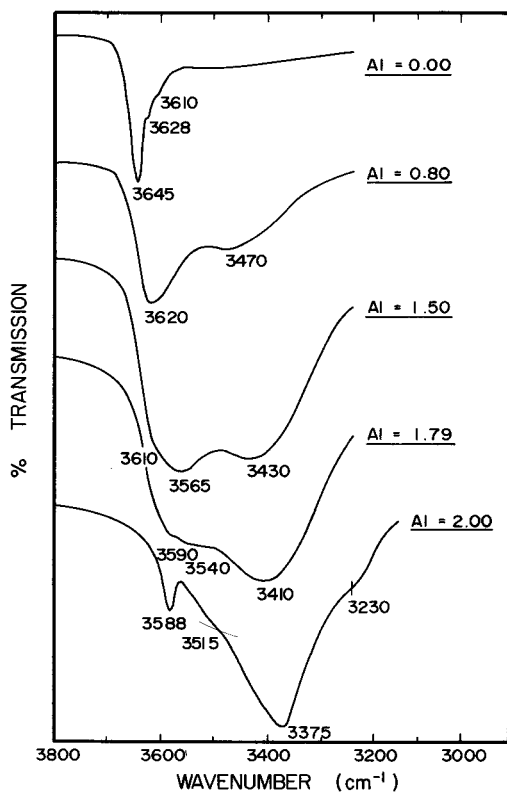


FIG. 2. Hydroxyl-stretching absorption in Ni-serpentines at different aluminium contents.

At the various Al contents the hydroxyl vibrations of the Ni-serpentines show features similar to those observed in the magnesium series (fig. 2), suggesting that the vibrations of the hydroxyl groups in the aluminous serpentines are largely dominated by the amount of Al present. Thus, the infra-red spectra in this region can be used to estimate the composition of the tetrahedral sheets. As expected, at the same Al content, the substitu-

tion of Ni for Mg shifts the absorption bands slightly to lower values.

Samples synthesized at various D/H ratios indicated that the absorptions present in the infra-red spectra of the aluminous serpentines are due to stretching motions of different OH groups, i.e., no coupling or crystal effects are present. Thus, the infra-red spectra of two aluminous serpentines at a D/H ratio of approximately 3 show the same number and relative intensity for the absorption bands in both the OH and OD stretching regions, with  $\nu\text{OH}/\nu\text{OD}$  factors ranging from 1.34 to 1.36 (fig. 3). Therefore, the low frequency vibrations in the infra-red spectra of aluminous serpentine, 3600–3420  $\text{cm}^{-1}$  for magnesium (fig. 1) and 3565–3375  $\text{cm}^{-1}$  for nickel (fig. 2), must be due to a difference in hydrogen bonding between the outer hydroxyl groups of one layer and the neighbouring oxygen surfaces in the next layer. As previously suggested, the lower frequency band can be assigned to interactions of hydroxyl groups with O–Al, and the higher due to interactions with O–Si (Serna *et al.*, 1977).

The variation of the unit cell parameters with composition in aluminous serpentines has been extensively studied (Nelson and Roy, 1958; Shirozu and Monoi, 1972; Velde, 1973; Chernosky, 1975). A reproduction of Chernosky's experimental data on the variation of the *c* parameter with the tetrahedral Al is shown in fig. 4 along with data obtained in this study. A continuous, although not linear, decrease in the *c* parameter as the Al content increases is observed. The principal change in the interlayer spacing occurs for Al contents between zero and 1.00.

Variations in the frequency of the OH-stretching vibrations in the aluminous Mg-serpentines with the Al content are shown in fig. 5. Although the position observed for the outer hydroxyls may vary slightly (the authors have observed slight changes in position and intensity upon grinding), an almost constant relationship is observed for the hydroxyl groups interacting with O–Al (fig. 5, Curve A). In contrast, the frequency of the outer hydroxyls interacting with O–Si decreases with increasing Al content (fig. 5, Curve B). This result suggests that only the hydroxyls interacting with O–Si groups are affected by changes in the interlayer spacing since their behaviour with variation in Al content is similar to that of the *c* parameter. A somewhat analogous relationship is found for the inner hydroxyl groups (fig. 5, Curves C and D). The constant high frequency of the D hydroxyl vibrations indicates an octahedral coordination and tetrahedral environment similar to that present in Mg-serpentines. The inner hydroxyls at lower frequency (fig. 5, Curve C) shift to lower values with

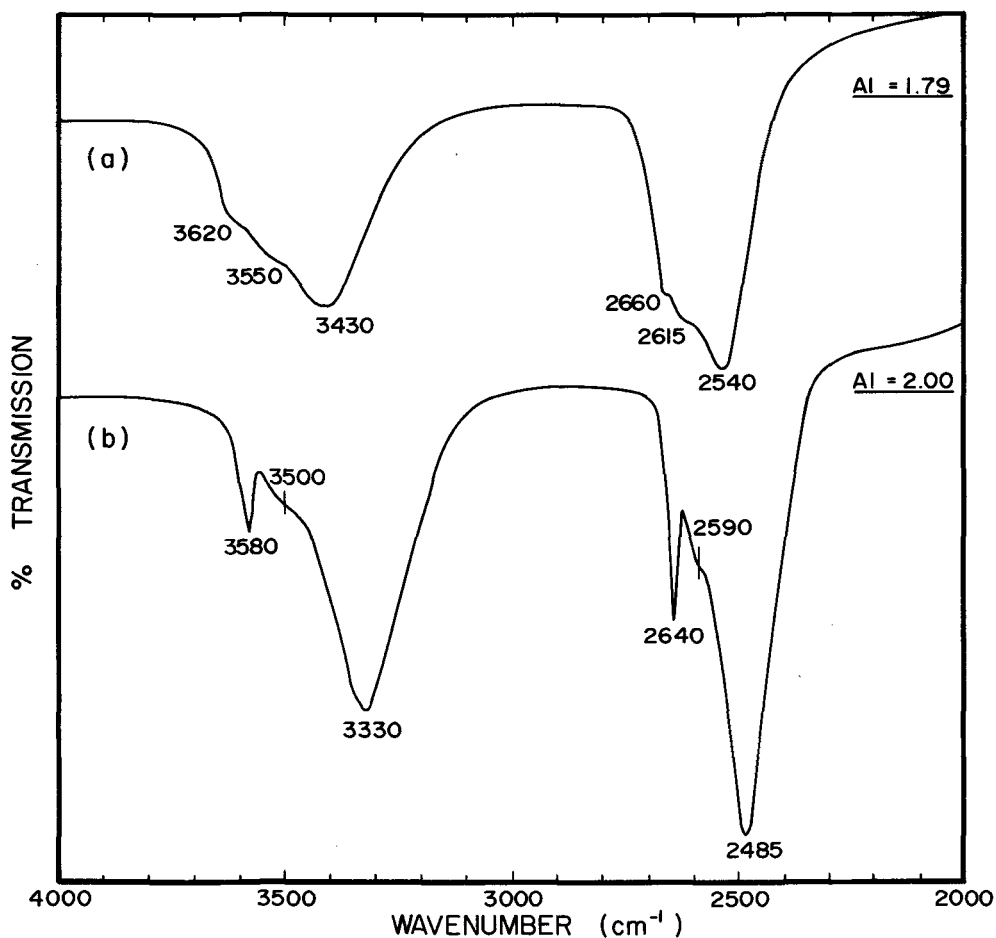
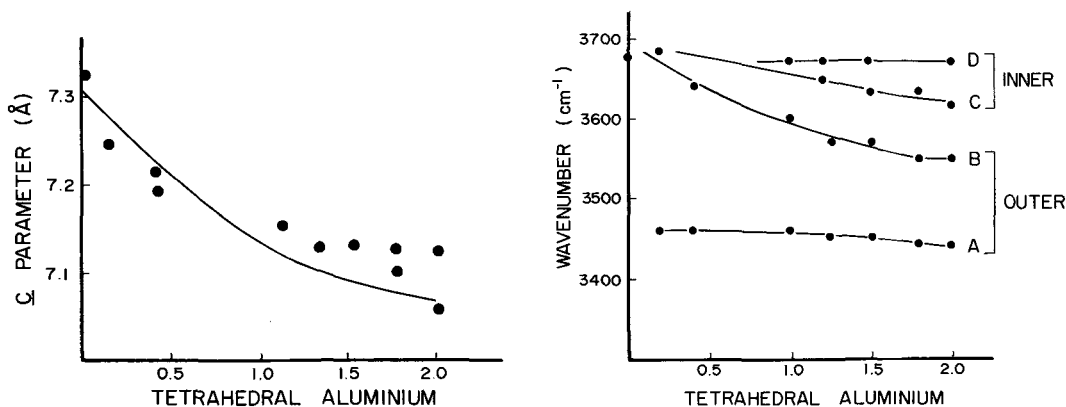


FIG. 3. Hydroxyl-stretching absorptions of partially deuterated aluminous serpentines. (a) Mg-serpentine, (b) Ni-serpentine.



FIGS 4 and 5: FIG. 4 (left). Relationship in Mg-serpentines between the  $c$  parameter and the amount of aluminium in tetrahedral sheets. The solid line is from Chernosky's (1975) experimental data. FIG. 5 (right). Relationships in Mg-serpentines between aluminium in tetrahedral sheets and hydroxyl absorption frequencies.

increasing Al content, indicating partial coordination with octahedral Al and the electrostatic effect of the surrounding tetrahedral Al (Farmer and Velde, 1973).

*Stretching vibrations of the silicate anion.* In an undistorted silicate sheet ( $C_{6v}$  symmetry), two stretching vibrations are expected for the silicate anion ( $Si_2O_5$ ) between 1200 and 900  $cm^{-1}$ . These are the  $E_1^1$  and  $A_1^1$  modes, which have dipole moments perpendicular and parallel to the layer silicate, respectively (Farmer, 1974). In the serpentine polymorphs  $b_{oct} > b_{tet}$  so that adjustments in the ideal atomic positions must occur. Although the adjustments depend on the polymorphs, the tetrahedral sheets must be under considerable tension (Wicks and Whittaker, 1975), which may result, if the symmetry is lowered to  $C_s$ , in a greater number of infra-red absorption bands.

The Mg- and Ni-serpentines are not directly comparable since they are different polymorphs. The Mg-serpentine has an antigorite-type spectrum (fig. 6), whereas the Ni-serpentine has a chrysotile-type spectrum (fig. 7). Ptack and Pam-puch (1967) have partially succeeded in relating the symmetry of the tetrahedral sheets to the observed absorption bands in the serpentine polymorphs.

The substitution of Al for Si produces a lowering in the symmetry of the tetrahedral sheets, which may explain the complex pattern observed for the Si-O stretching vibrations until the composition  $(Si_{3.0}Al_{1.0})(Al_{1.0}M_{5.0})O_{10}(OH)_8$  is reached (figs. 6 and 7). Factor group analysis of the lattice vibrations for the  $Si_3Al_4O_{10}$  anion ( $C_s$  symmetry) showed that four vibrations can be infra-red active between 1100 and 950  $cm^{-1}$  (Ishii *et al.*, 1967). However, several other vibrations should also be present between 950 and 800  $cm^{-1}$  as a result of this lower symmetry but they are not observed (figs. 6 and 7).

For compositions between Al = 1.00 to Al = 2.00 a simple pattern is observed for the Si-O stretching vibrations (figs. 6 and 7). The principal feature is a broad absorption band at around 1000  $cm^{-1}$  with a shoulder at 925  $cm^{-1}$ . This shoulder only becomes a separate band at the amesite composition, and is clearest when an ordered Al for Si substitution takes place (Serna *et al.*, 1977). The differences in the Si-O stretching vibrations between amesite and brindleyite are more apparent than real, since deuterated brindleyite samples show only two absorption bands at 990 and 910  $cm^{-1}$ . This simple pattern observed for the Si-O

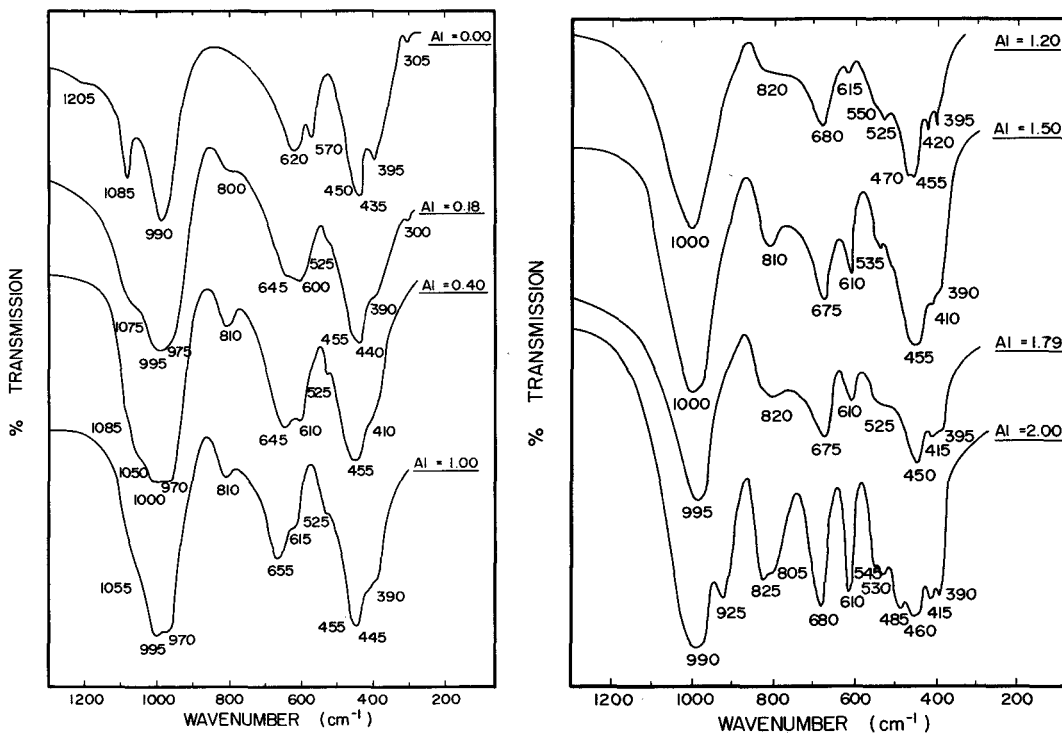


FIG. 6. Infra-red absorption spectra of Mg-serpentines at different aluminium contents in the 1200–300  $cm^{-1}$  region.

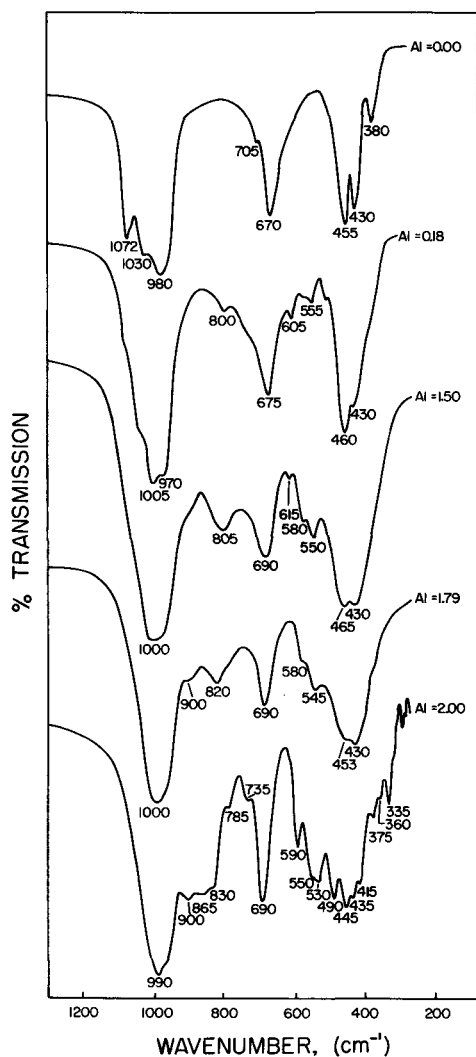


FIG. 7. Infra-red absorption spectra of Ni-serpentine at different aluminium contents in the 1200–300  $\text{cm}^{-1}$  region.

vibrations is in agreement with the fact that within this compositional range the tetrahedral sheets go towards a higher symmetry; a regular 1:1 Al for Si substitution (amesite composition) is consistent with  $C_{3v}$  symmetry and, consequently, only two Si–O absorption bands must be infra-red active between 900 and 1200  $\text{cm}^{-1}$ .

On the other hand, with an increase in the Al for Si substitution the greatest effect is observed in the absorption band at 1085  $\text{cm}^{-1}$  and at 1072  $\text{cm}^{-1}$  for the Mg- and Ni-serpentine respectively (figs. 6 and 7). These absorption bands, created by the

dipole changes in the vibration of the apical oxygen against the silicon, decrease in intensity and energy with the increase in Al content until they are obscured by the absorption around 1000–900  $\text{cm}^{-1}$ . Similar observations were first reported by Stubican and Roy (1961*b*) for several aluminosilicates and more recently by Velde (1978) for the muscovite-celadonite system. The increase in the Si–O<sup>-</sup> bond length from lizardite ( $1.56 \pm 0.05$ ) to amesite ( $1.71 \pm 0.03$ ) may account for most of the decrease in frequency of the Si–O<sup>-</sup> vibration. In addition there are differences in the tetrahedral bond angles between serpentine and amesite, which theoretical calculations have shown to lower the frequency of the Si–O<sup>-</sup> vibration (Ptak and Pam-puch, 1967). However, this would only account for a small portion ( $c.20 \text{ cm}^{-1}$ ) of the decrease in the Si–O<sup>-</sup> vibration frequency.

*The Al–O tetrahedral vibrations.* The most distinctive feature in the infra-red spectra of the aluminous serpentines is the presence of an absorption band around 800  $\text{cm}^{-1}$  (figs. 6 and 7). Although an absorption band around this position is expected for a distorted silicate anion, it would seem more likely to be due to Al in tetrahedral coordination. This is supported by the absence of this absorption band in the infra-red spectra of cronstedtite, a 7 Å trioctahedral mineral analogous to amesite with formula  $(\text{Si}_2\text{Fe}_2^{3+})(\text{Fe}_4^{2+}\text{Fe}_3^{3+})\text{O}_{10}(\text{OH})_8$  (Van der Marel and Beutelspacher, 1976). The absorption band at around 800  $\text{cm}^{-1}$  remains unaffected by the nature of the octahedral sheets, although it shifts slightly to higher frequencies with increase in Al content. Since only one absorption band is observed, the Al for Si substitution may take place in such a way that only 'isolated'  $\text{AlO}_4$  tetrahedra are present. Al–O–Al linkages must be avoided whenever possible since electrostatic aluminium repulsion tends to favour alternating rather than continuous aluminium distribution (Loewenstein, 1954). However, Al–O–Al linkages must be responsible for the features in the infra-red spectra of some disordered amesites (Serna *et al.*, 1977).

*Vibrations in the 750–350  $\text{cm}^{-1}$  region.* In the region between 750 and 570  $\text{cm}^{-1}$  the Mg-serpentine minerals present at least three types of vibrations. Two are associated with the octahedral sheets, the OH libration and the Mg–OH out-of-plane vibration. The third is a Si–O stretching vibration,  $A_1^2$  mode. Yariv and Heller-Kallai (1975) have shown that the absorption band around 570  $\text{cm}^{-1}$  is the Mg–OH out-of-plane vibration, so the broad absorption band for the Mg-serpentine at 620  $\text{cm}^{-1}$  must be a combination of the Si–O stretching and the OH libration (fig. 6). The Mg–OH vibration is absent in the infra-red spectrum of

the Ni-serpentine (fig. 7). The analogous Ni-OH vibration must lie around  $430\text{ cm}^{-1}$  since this absorption disappears progressively in Ni-serpentes with the increasing substitution of Mg for Ni (Jasmund *et al.*, 1975). This is also supported by the presence of a vibration in Ni-talc at  $455\text{ cm}^{-1}$  and assigned to out-of-plane Ni-OH (Russell *et al.*, 1970).

Partially deuterated Ni- and Mg-serpentes with different Al contents showed an appreciable decrease in the intensity of the absorption bands between  $620$  and  $690\text{ cm}^{-1}$  (figs. 6 and 7); this confirms the character of this vibration, which is due in part to librational OH modes. With an increase in the Al for Si substitution the OH librational mode in the nickel and magnesium series moves to higher frequencies and it is observed at  $680\text{ cm}^{-1}$  in amesite and at  $690\text{ cm}^{-1}$  in brindleyite (figs. 6 and 7). In 14 Å chlorites an absorption band between  $600$  and  $700\text{ cm}^{-1}$ , assigned to OH libration, was correlated with the nature of the octahedral sheets (Hayashi and Oinuma, 1967). However, this shift to higher frequencies seems more likely to be due to an increase in hydrogen bonding in the outer hydroxyl groups.

It is interesting to note that the absorption band in brindleyite at  $865\text{ cm}^{-1}$  is also due to OH vibrations, since this absorption is absent in the spectra of deuterated samples and a new absorption band is observed at  $630\text{ cm}^{-1}$ . The ratio  $\nu\text{OH}/\nu\text{OD}$  is 1.37, which is the value expected for a purely librational mode. The reason for the observed OH librational mode at such a high value is unknown.

In the magnesium series, the Mg-OH vibration moves to higher frequencies with an increase in Al content (fig. 6) and may be correlated with the contraction in the octahedral sheets due to the Al for Mg substitution. Thus, the average Mg-O distance in antigorite is  $2.17\text{ \AA}$  while in amesite  $M\text{-O}$  (where  $M = \text{Mg}_2\text{Al}$ ) distances were found to be  $2.04\text{ \AA}$  (Wicks and Whittaker, 1975). The absence of this absorption band in the aluminous Ni-serpentes is the most striking difference between these series.

The presence of Al in the serpentine minerals produces several absorption bands between  $550$  and  $500\text{ cm}^{-1}$  in the magnesium series and between  $590$  and  $500\text{ cm}^{-1}$  in the nickel series (figs. 6 and 7). Absorption bands in this region have been assigned to vibrations involving Al in octahedral coordination (Stubican and Roy, 1961a). Absorption bands below  $500\text{ cm}^{-1}$  are difficult to assign since vibrations of the tetrahedral sheets (Si-O bending) are strongly coupled with vibrations of the octahedral cations and with translatory vibrations of hydroxyl

groups (Farmer, 1974). The infra-red spectra of the solid solution Ni-Mg serpentes (Jasmund *et al.*, 1975) suggest that the absorption band at  $450\text{ cm}^{-1}$  in Mg-serpentine may be due mainly to a Si-O bending vibration since it remains unaffected by the Ni for Mg substitution. The frequency of this absorption changes with an increase in the Al content and is observed at  $460\text{ cm}^{-1}$  at the amesite composition (fig. 6). Similar features are observed in the nickel series, in which the Si-O bending vibration is present at  $455\text{ cm}^{-1}$  (fig. 7). The absorption bands at  $395\text{ cm}^{-1}$  and  $380\text{ cm}^{-1}$  in the Mg- and Ni-serpentine, respectively, have been assigned to hydroxyl bending vibrations (Jasmund *et al.*, 1975). These absorptions are obscured, due to the disorder introduced by the presence of Al in tetrahedral and octahedral sheets, until the composition  $\text{Al} = 2.00$  is reached, when several absorption bands appear in this region (figs. 6 and 7).

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