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THE RELATIONSHIP BETWEEN THE I.R. SPECTRA OF SERPENTINES AND THEIR STRUCTURES

S. YARIV and L. HELLER-KALLAI

Department of Geology, Hebrew University, Jerusalem, Israel

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Abstract—Possible assignments are suggested for some of the absorption bands in the 1150–400 cm^{-1} region of the i.r. spectra of serpentines. Polarized light was used to identify the out-of-plane vibrations in antigorites and platy lizardites and the vibrations parallel to the fibre axis in chrysotiles and fibrous lizardites. An attempt is made to correlate some known structural characteristics and the chemical composition of the serpentines with some features of the i.r. spectra.

INTRODUCTION

Criteria for characterizing serpentine minerals by X-ray diffraction were established by Whittaker and Zussman (1956), but these are sometimes inconclusive. Brindley and Zussman (1959) and Luce (1971) pointed out that antigorites can readily be distinguished from chrysotiles and lizardites on the basis of their i.r. spectra, which, however, were merely treated as fingerprints. In this study an attempt is made to correlate some of the observed absorptions bands in the 1150–400 cm^{-1} region with structural features of the serpentines.

EXPERIMENTAL

Materials

Antigorites. F13, F14, F15, USNM70160 (corresponds to F1), USNM47839 (corresponds to F6), USNM80500 (corresponds to F19, a mixture of antigorite and some chrysotile). Samples with the prefix F were described by Faust and Fahey (1962). HU176, Zermatt, Switzerland (Hebrew University mineral collection).

Chrysotiles. HU3261, Pennsylvania, U.S. (Hebrew University mineral collection). 6(2) layered orthoserpentine, Setters Quarry, Unst, Shetland. BPK1 chrysotile, Baie d'Ouie, New Caledonia.

Lizardites. F47 (Faust and Fahey, 1962). HU326 Lizard, Cornwall (Hebrew University mineral collection). HU4050 Cyprus, (Hebrew University mineral collection) SG645 Samaria, Israel.

The specimens were examined with an electron microprobe. The seven antigorite samples are homogeneous within the limits of detection of the instrument (2–3 μmbeam dia.) but most of the other samples are so inhomogeneous and fine-grained as to render microprobe analysis meaningless.

The antigorites were analysed for SiO_2, MgO, Al_2O_3 and FeO (total iron) (Table 1). The results are generally in good agreement with those reported by Faust and Fahey. The differences may be due to the fact that the specimens received were not aliquots of those analysed by Faust and Fahey.

Procedure

Infra-red spectra were recorded on Perkin–Elmer 457 and 237 grating instruments. The specimens were examined in the form of KBr disks and as oriented deposits on AgCl or polythene windows. Analyses were carried out on a JXA5 electron microprobe, 15 kV, sample current on brass 0·05 μA.

Analyses were performed using natural enstatite and samples of synthetic enstatites, with and without

Table 1. Chemical and ionic composition of antigorites

	Chemical composition (%)				Ions in tetrahedral coordination			Ions in octahedral coordination		
	SiO_2	MgO	Al_2O_3	FeO	Si	Al	Fe	Mg	Al	Fe
F1 (USNM70160)	43·07	41·64	0·68	1·09	4·01	—	—	5·76	0·15	0·08
F8 (USNM47839)	42·73	42·95	0·04	0·11	4·00	—	—	5·99	0·01	0·01
F13	41·64	38·85	0·20	2·91	4·04	—	—	5·63	0·04	0·24
F14	43·66	42·10	0·20	0·40	4·05	—	—	5·82	0·04	0·03
F15	40·04	36·51	3·54	5·70	3·85	0·15	—	5·23	0·65	0·45
F19 (USNM80500)	41·37	39·87	0·85	3·78	3·94	0·06	—	5·67	0·13	0·30
HU176	43·10	38·05	1·29	5·27	4·03			5·31	0·03	0·41

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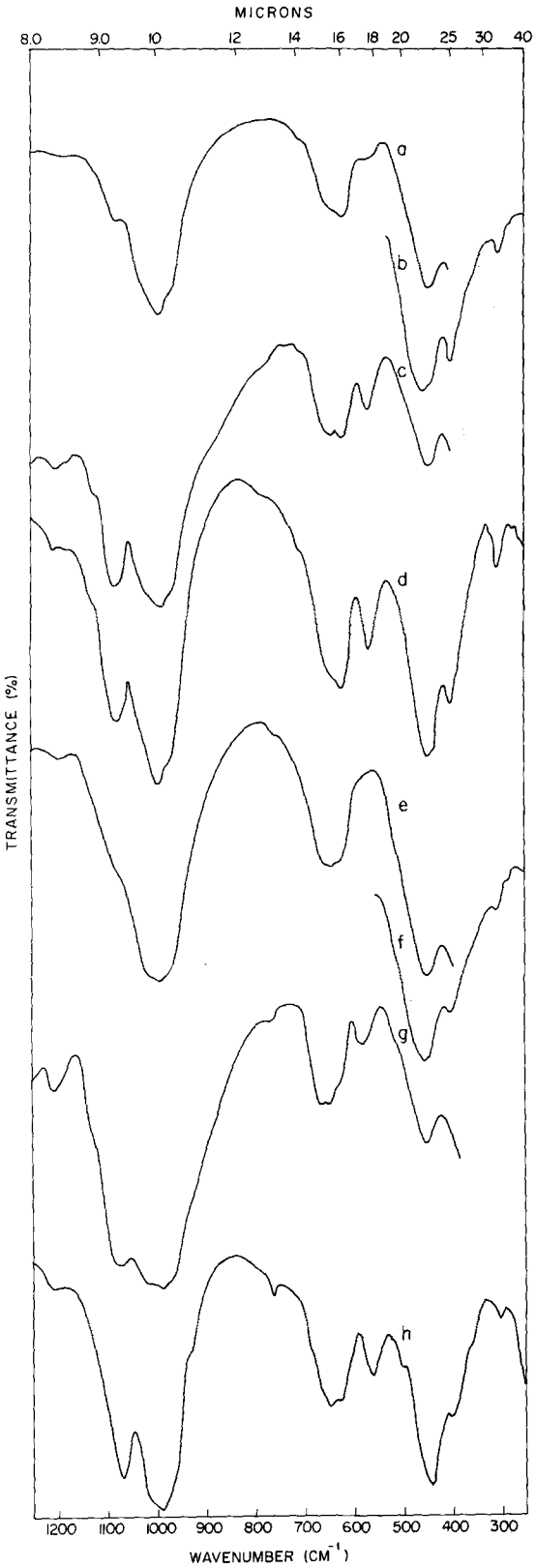

Fig. 1. Infra-red spectra of antigorite F1: (a) oriented on AgCl, normal incidence; (b) oriented on polythene, normal incidence; (c) oriented on AgCl, 45° incidence; and (d) KBr disk. Infra-red spectra of antigorite F15: (e) oriented on AgCl, normal incidence; (f) oriented on polythene, normal incidence; (g) oriented on AgCl, 45° incidence; and (h) KBr disk.

Al, as standards. The results obtained by these independent analyses were in very good agreement, mostly less than ± 1 per cent.

Examination in polarized light

Oriented specimens of layer silicates are commonly used to distinguish between absorption perpendicular to the basal plane (a_1) from absorption in two mutually perpendicular in-plane directions b_1 and b_2 (the nomenclature adopted is that of Farmer and Russell, 1964).

Comparison of spectra of oriented and random samples of antigorite (Fig. 1) clearly show that bands at about 1070 and 560 cm^{-1} have perpendicular polarization. The weak band at about 640 cm^{-1} is composite, comprising a perpendicularly polarized component. The fibrous varieties of antigorite examined (F13, F19 and HU176) give rise to less complete polarization of the spectra. In contrast to chrysotiles, this effect is reduced by grinding the samples. The difference between spectra 1(c) (oriented sample at 45° incidence) and 1(d) (KBr disk) may be attributed to the effect of grinding.

The spectra of oriented specimens of chrysotile differ from those of antigorite (Fig. 2). At normal incidence bands marked *P* in Table 2 and Fig. 2 are enhanced in intensity relative to the rest. The difference can be explained in terms of the known crystal structures of chrysotile and antigorite. Antigorite is

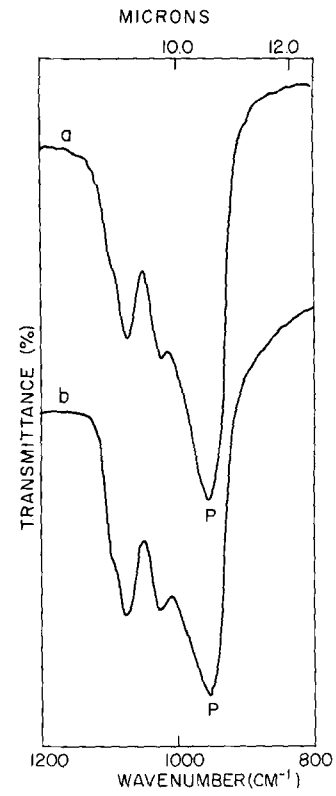

Fig. 2. Infra-red spectrum of oriented deposit of chrysotile (HU3261) on AgCl: (a) normal incidence; (b) 45° incidence.

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Table 2. Frequency of i.r. absorption bands (cm^{-1}) of chrysotiles and lizardites

		Chrysotile HU3261	6(2) Ortho-serpentine	Chrysotile B.P.K. 1	Lizardite HU4050	Lizardite SG645	Lizardite HU11759	Lizardite F47	Lizardite Ch 21-81
Si–O	a_1^1	1071	1075	1080	1083	1080 sh.	1084 sh.	1082	~1072 v.br.
						1045	~1045 sh.		
	$b_1^1 + b_2^2$	1026	1020	~1020 v.br.	~995 sh.	~1015 sh.		~1020 sh.	
		954 (*P*)	950 (*P*)	958 (*P*)	963	962	~955 v.br.	955	~960 v.br.
					~760 w.sh.	800 w.br.			
						~730 w.			
						~698 v.v.w.sh.		~690 v.v.w.sh.	
Si–O	a_1^2		~658 w.sh.	~650 w.sh.					
Si–O	$b_2^4 + b_1^2$ *	610 (*P*)	606 (*P*)	604 (*P*)	610	615 br.	612	617	613
O–H	in-plane								
Mg–O	out-of-plane	545–585 v.v.br.	555–590 v.v.br.	560–600 v.v.br.	~565 sh.	~585 v.br.sh.	560 br.	575 br.	~575 v.v.br.
		485 w.	~490 sh.	~490 sh.				485 v.w.sh.	
		458 v.w.sh.	~460 v.w.sh.	~458 w.sh.	450	458 sh.	455 sh.	458 v.v.w.sh.	~465 sh.
		436 (*P*)	434 (*P*)	438 (*P*)	435	440	440	437	443
		425 w.sh.	~420 v.w.sh.	423 v.w.					410 v.w.
		407 w. (*P*)	405 w. (*P*)	407 w. (*P*)	400 w.	408 w.		408 w.	398 v.w.
		388 w.	385 v.w.	390 v.w.	385 sh.	386 w.		390 v.w.sh.	387 w.
		370 v.w.sh.	355 v.w.sh.	376 v.w.	340 v.w.	360 v.w.sh.		~355 v.v.w.sh.	
		303 m.	303 m.	303 m.	302 w.	304 m.		303	303 w.

m.—medium; w.–weak; sh.—shoulder; br.—broad; v.—very.
For definition of *P* see text.
* See details in text.

built of parallel, slightly corrugated sheets, while chrysotile is composed of curved sheets. Antigorites may assume a platy or a fibrous habit but the fibrous variety differs basically from chrysotile. It consists of elongated narrow laths, while fibres of chrysotile are composed of coaxial tubes. In oriented specimens of chrysotile, therefore, only the fibre axes and not the basal planes are coplanar. It follows that at normal incidence only one of the three mutually perpendicular vibration directions, the *a* crystallographic direction, which is parallel to the fibre axis, is consistently oriented at right angles to the beam, while the other two are random. At normal incidence the relative intensity of absorption in the fibre direction is therefore enhanced. One of the two sets of in-plane vibrations, b_1 or b_2, can thus be differentiated from the other and from the out-of-plane vibrations. The relative intensity of the in-plane vibration at about 1020 cm^{-1} is affected by ultrasonic treatment of the sample: it reaches a maximum and then decreases with concomitant broadening of the band.

By comparing the spectra of antigorite and chrysotile the three sets of mutually perpendicular vibrations can be assigned with some confidence.

In sheet silicates with symmetrical structures, e.g. talc, some of the in-plane vibrations are degenerate. In a curved sheet structure this degeneracy must of necessity be lifted since one of the two perpendicular vibrations is affected by the curvature of the sheets. It is to be expected that some of the bands will be split into two components, the intensity of one of which is enhanced at normal incidence. Such splitting is, indeed, observed in the spectra of chrysotile (Table 2 and Fig. 2).

Polarization effects in sample F47, a fibrous lizardite, are similar to those of chrysotiles, while non-fibrous lizardites resemble antigorites in this respect.

Assignments

Figure 3 shows the 1150–250 cm^{-1} region of spectra of some serpentine minerals. The spectra are in good agreement with those previously published in the literature (Brindley and Zussman, 1959; Veniale and van der Marel, 1963; Luce, 1971). The corresponding frequencies are listed in Tables 2 and 3 together with some of their assignments. These are largely based on comparison with corresponding assignments for other minerals in the literature.

Serpentines are less symmetrical than talc and vibrations b_1^1 and b_2^2, which are degenerate in talc, absorbing at 1018 cm^{-1}, appear as two separate bands in chrysotiles and as a band and shoulder in antigorites. More than two bands sometimes appear in lizardites.

Spectra of serpentines show a sharp band at about 620 cm^{-1} with in-plane polarization. In the antigorite samples examined, except F13, an additional band or shoulder appears at about 640 cm^{-1} which is composite, comprising both parallel and perpendicularly polarized components (Fig. 1). Their relative intensities differ from sample to sample, e.g. in F1 the

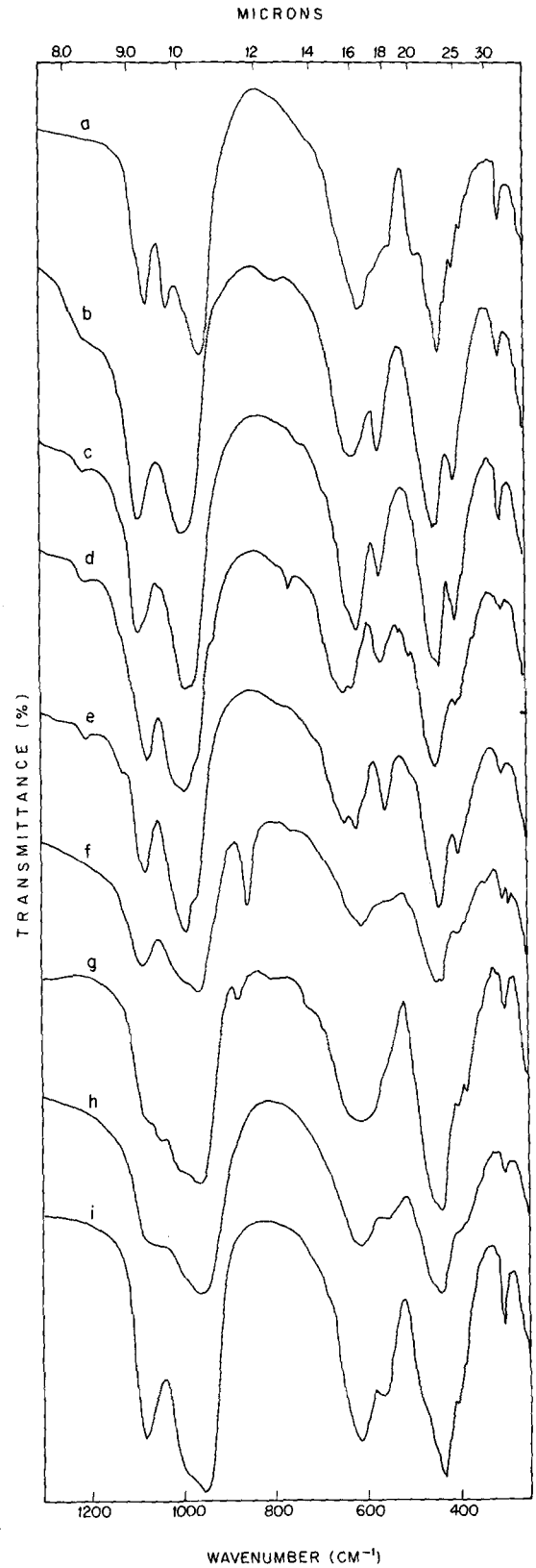

Fig. 3. Infra-red spectra of KBr disks of serpentines: (a) chrysotile HU3261; (b) antigorite F13; (c) antigorite F14; (d) antigorite F15; (e) antigorite HU176; (f) lizardite HU4050; (g) lizardite SG645; (h) lizardite HU11759; and (i) lizardite F47.

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Table 3. Frequency of i.r. absorption bands (cm^{-1}) of antigorites

Sample number		Fl	F8	F13	F14	F15	F19	HU176
Tetrahedral composition		$Si_{4.01}$	$Si_{4.00}$	$Si_{4.04}$	$Si_{4.05}$	$Si_{3.85}Al_{0.15}$	$Si_{3.94}Al_{0.06}$	$Si_{4.03}$
Octahedral composition		$Mg_{5.76}Al_{0.15}Fe_{0.08}$	$Mg_{5.99}Al_{0.01}Fe_{0.01}$	$Mg_{5.63}Fe_{0.24}$	$Mg_{5.82}Al_{0.02}Fe_{0.13}$	$Mg_{5.23}Al_{0.65}Fe_{0.45}$	$Mg_{5.67}Al_{0.13}Fe_{0.30}$	$Mg_{5.31}Fe_{0.41}Al_{0.03}$
Si–O	a_1^1	1078	1077	1081	1081	1062	1078	1076
						1010 sh.	1000 v.w.sh.	
	$b_1^1 + b_2^2$	990	990	987*	987	981	995	986
		~970 sh.	~970 sh.		~969 sh.	~958 w.sh.	~971	~968 sh.
		785 v.w.		785 v.w.br.	740 v.w.br.	760 w.	780 v.w.	~780 w.sh.
		710 v.w.	715 sh.		688 v.w.sh.	685 v.w.sh.	710 v.w.	
Si–O	a_1^2					665 v.w.sh.		
	$b_2^4 + b_1^2$ †	642	640		635 sh.	646	653	645
O–H	in-plane	623	620	620	614	626	620	618
						585 sh.		
Mg–O	out-of-plane	570	570	574	574	573	570	572
						520		
						500		
		455	455	455	457 sh.	450	452	450
		440 sh.	442 sh.	445 sh.	443	440 sh.	442 sh.	443 v.w.sh.
		400 m.	398 w.br.	401 m.	400 m.	399 w.	396 m.	398 w.
		300 m.	300 w.br.	300 m.	300 m.	300 m.	303 m.	300 w.

* Tailing off towards lower frequencies.
† For details see text.
m.—medium; w.—weak; sh.—shoulder; br.—broad; v.—very.

out-of-plane vibration predominates while in F15 the in-plane contribution is more intense. Disks, or oriented samples of F13 at 45° incidence, show an unresolved broad band with a maximum at about 620 cm^{-1}. At normal incidence this band is considerably sharper and the maximum is shifted to 615 cm^{-1}, i.e. the sharp in-plane mode appears at 615 cm^{-1} and the composite band, which here is predominantly perpendicularly polarized, occurs at about 620–630 cm^{-1}. Sample F15 shows a weak shoulder at about 660 cm^{-1}, which, by comparison of oriented spectra at 45° and normal incidence, is seen to be perpendicularly polarized.

The main absorption of chrysotile in the 610 cm^{-1} region is in the direction of the fibre axis. A weak broad shoulder appears at higher frequency.

Farmer attributed a band at 687 cm^{-1} in talc to the a_1^2 out-of-plane vibration and a band at 669 cm^{-1} to the degenerate in-plane pair b_2^4 and b_1^2 (Farmer, 1958). Russell *et al.* (1970) showed that the 669 cm^{-1} band is affected by deuteration and suggested OH libration as an alternative assignment. Pampuch and Ptak (1970) present i.r. spectra of samples of chrysotile, antigorite and lizardite before and after deuteration. Absorption in the 600–650 cm^{-1} region disappears completely on deuteration of chrysotile and is considerably weakened with lizardite and antigorite. This confirms that the effect of the OH libration is dominant in this region. Stubičan and Roy (1961) reported a strong absorption band at 663 cm^{-1} with a shoulder at 622 cm^{-1} in Ni chrysotile. They attributed these bands to Si–O vibrations, but it seems more reasonable to assign the strong bands at 663 and 610 cm^{-1} to OH librations of Ni and Mg chrysotile respectively. The perpendicular component in the 630–650 cm^{-1} region in serpentines may be ascribed to the contribution of the Si–O mode a_1^2. It overlies bands with in-plane polarization, possibly including b_1^2 and b_2^4, which are expected to occur in this region, combination bands or OH librations.

The perpendicularly polarized band near 560 cm^{-1} is sharp in spectra of antigorites, diffuse in those of chrysotiles and absent in the spectra of Ni chrysotile reported by Stubičan and Roy (1961). According to Pampuch and Ptak (1970) this band is almost unaffected by deuteration. By analogy with talc it is assigned to Mg–O out-of-plane vibrations.

In all serpentine spectra a band and shoulder appear at about 445 cm^{-1}. With some samples the peak occurs at the higher and the shoulder at the lower frequency and vice versa. Stubičan and Roy (1961) assigned a band of antigorite at about 450 cm^{-1} and a shoulder in the vicinity to Si–O–Mg and Si–O vibrations respectively. Russell *et al.* (1970) showed that absorption at 465 cm^{-1} in talc is affected by deuteration and attributed the bands at 465 and 450 cm^{-1} in talc to in-plane vibrations of OH and Mg ions respectively. In the absence of deuterated samples of serpentines the bands in the 460–430 cm^{-1} region cannot be definitely assigned. It seems reasonably certain, however, that absorption in this region is at least partly due to Mg–O in-plane vibrations, which are perhaps modified by the neighbouring silicate sheets.

Bands below 450 cm^{-1} in serpentines cannot be assigned with any confidence at this stage.

Effect of chemical composition

Attempts to correlate the polymorphic form of serpentines with their chemical composition (Page, 1968) have been severely criticized (Whittaker, 1970). Moreover, our electron microprobe analyses indicate that some serpentines are so inhomogeneous that it is questionable whether the average chemical composition has any real significance.

It is to be expected that the chemical composition of serpentines affects their i.r. spectra. Inhomogeneity of the sample will result in broadening of the bands, because each band corresponds to a range of energy values. The observed broadening of some of the absorption bands of lizardite and chrysotile may perhaps be partially attributed to this effect. It is significant that the spectrum of sample F47, which is chemically more homogeneous than the other lizardites examined, is sharper than the rest.

The seven samples of antigorite are homogeneous within the limits of detection of the electron microprobe and are therefore suitable for a study of the effects of chemical substitution on the i.r. spectra.

It is evident from Table 3 that the spectrum of F15 differs in several respects from the spectra of the other antigorites. Bands a_1^1 and $b_1^1 + b_2^2$ occur at lower frequencies and additional shoulders appear at 1010 and 660 cm^{-1}, with parallel and perpendicular polarization respectively. It seems reasonable to attribute these features to the presence of tetrahedral Al. The only other specimen which contains tetrahedral Al, F19, is contaminated with chrysotile and is therefore not strictly comparable. F15 contains less Mg than the other samples, but in this respect it does not differ greatly from HU176, which, however, does not show any of these features.

Stubičan and Roy (1961) reported that the frequency of the band at about 610 cm^{-1} increases with increasing Al content of diphormic minerals. This does not apply to the samples under investigation: no correlation was found between the chemical composition and the frequency of the composite bands in the 610–650 cm^{-1} region. Moreover, no correlation could be established between the frequency of the Mg-O out-of-plane absorption at about 570 cm^{-1} and the chemical composition. The band at 450–457 cm^{-1}, on the other hand, occurs at a lower frequency in samples F15 and HU176, which contain less Mg in the octahedral layer. This may be regarded as confirmatory evidence for assigning the band to a vibration principally involving this layer.

Comparison of antigorite, chrysotile and lizardite

The most striking feature of the antigorite spectra, which differentiates them from those of other serpen-

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tines, is the sharp band at 570 cm^{-1} assigned to Mg–O out-of-plane vibrations. Chrysotile has a broad absorption band in this region. The spectrum of lizardite varies from sample to sample, but the band at about 570 cm^{-1} is never as sharp as that of antigorite.

Absorption in the 1030–950 cm^{-1} region, which has been attributed to Si–O stretching, also differs in the various serpentines. In antigorite, bands b_1^1 and b_2^2 either do not occur as two distinguishable maxima (Fig. 3b; Luce, 1971) or appear as a band with a shoulder at a distance of 20–35 cm^{-1} from the maximum (Figs. 3(c), (d), (e); Luce, 1971; Brindley and Zussman, 1959; Veniale and van der Marel, 1963). The separation between bands b_1^1 and b_2^2 in chrysotile is 60–70 cm^{-1} (Fig. 3(a); Luce, 1971; Brindley and Zussman, 1959). In this region the spectra of lizardites resemble those of chrysotile rather than those of antigorite, though different specimens vary considerably.

Differences also arise between the bands in the 460–430 cm^{-1} region. According to Luce (1971) chrysotiles and lizardites absorb at 440 and antigorites at 455 cm^{-1}. Our spectra suggest that the main difference does not lie in the position of the bands but in their appearance. With chrysotile the band at about 440 cm^{-1} is relatively sharp and a shoulder occurs at higher frequencies, at a distance of 20–25 cm^{-1} from the maximum (Fig. 3(a)). The separation between the bands in antigorite is smaller, with a maximum ranging from 440 to 457 cm^{-1} (Table 3). The shoulder appears on either the low or high frequency side of the maximum, at a distance of 7–13 cm^{-1}. A single band is observed in the 400 cm^{-1} region of antigorites but two bands appear in chrysotiles and lizardites.

Some of these observations can be tentatively related to the known crystal structures of the minerals. The misfit between the tetrahedral and octahedral sheets of the serpentines is relieved by curving of the chrysotile layers, corrugation of the layers of antigorite and probably by the small crystal size and random layer stacking of lizardites.

The tetrahedra of all the serpentines, like those of other layer silicates, are distorted. The greater splitting of the Si–O in-plane stretching frequencies in chrysotile and lizardite suggest that the tetrahedral layers of these minerals are more distorted than those of antigorite. Several weak bands and shoulders which appear in the 300–500 cm^{-1} region of spectra of chrysotiles and lizardites but not in those of antigorites may be due to these distortions.

The broad, indistinct Mg–O band at about 560 cm^{-1} in chrysotile indicates that absorption occurs over a range of frequencies. This is in agreement with the structure proposed by Whittaker (1956) in which Mg is surrounded by 6(OH + O) groups of which four are structurally independent. One 'plane' contains two structurally related oxygens and one hydroxyl group, which, however, are not entirely coplanar. The other 'plane' contains two symmetry related and one independent hydroxyl. The Mg ions occupy positions which are not mid-way between the sheets. The layers are randomly stacked and the entire structure is curved. A wide range of Mg–O bond energies is therefore to be expected.

The relatively sharp absorption band of antigorite in this region is compatible with the contention of Kunze (1961) that in the wavy structure of antigorite the symmetry of the Mg–O octahedra is relatively well preserved.

The perpendicular modes designated a_1^1 are very sensitive to the physical state and structural order of some layer silicates (Farmer, 1964). Grinding of samples of serpentine affects this band more than any other. Its width varies considerably in different lizardites. This may be partly due to the small particle size of the minerals but may also be related to structural disorder.

Small but significant differences occur between spectra of antigorites of very similar chemical composition, e.g. F8 and F14, which are almost pure Mg silicates. Such differences must be due to some features of the crystal structure. Antigorites differ from each other mainly in the length of the superlattice parameter a which is known to range from about 18 to 100 Å in various specimens. It has been suggested that the most commonly occurring form, with an a parameter of 33–45 Å, may correspond to a rectified waveform and the larger a parameter to an alternating waveform (Brindley *et al.*, 1958) or that the former represents a single wavestructure ~ and the latter a double wavestructure ~ ~ (Kunze, 1961). In either case the pitch of the waves of samples with a large a parameter is similar to that of common antigorites, obviating the necessity of compensating for internal strain by greater distortion of the polyhedra. F14, the well-known Yu-Yen stone, has an a parameter of about 100 Å (Brindley *et al.*, 1957). The small splitting of the Si–O stretching vibrations and the sharpness of the Mg–O out-of-plane absorption suggest that despite the large a parameter, the polyhedra are no more distorted than those of the other antigorites studied. Although the evidence is certainly not conclusive, it is at least compatible with the concept of a different nature of the waveform of this sample.

F13 has a strongly platy habit, like that of a serpentine sample from the same locality previously described by Aumento (1967), who concluded that it is either a unique mineral or a mixture of antigorite and chrysotile. The i.r. spectrum of F13 precludes the presence of chrysotile but shows some specific features which differentiate it from spectra of other antigorites. In particular an unresolved broad band is observed at 990 cm^{-1} where other antigorites show split bands. The X-ray pattern of sample F13, which differs from that given by Aumento, resembles the pattern of splintery, poorly ordered antigorite described by Whittaker and Zussman (1956). This is compatible with the relatively low thermal stability of this compound observed by Faust and Fahey

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(1962). Grinding or ultrasonic treatment merely reduces the crystallinity and does not produce the chrysotile-like properties found by Aumento. It thus appears that this antigorite has distinctive properties, some of which may differ from sample to sample.

It seems that comparison of a larger number of serpentines with known structure and chemical composition may lead to acceptable criteria for correlating i.r. patterns with specific structural features.

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