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NEW DATA ON DEWEYLITE

DAVIS M. LAPHAM,* *Bureau of Topographic and Geologic Survey, Harrisburg, Pennsylvania.*

ABSTRACT

The several sub-varieties of deweylite from Cedar Hill, Pennsylvania, formed from aqueous, possibly colloidal, low temperature solutions by the alteration of pre-existing magnesium silicates in serpentinite. Fluorescent white deweylite, pseudomorphs of deweylite after aragonite, and iron and nickel bearing varieties are described. Molecular water is characteristic of deweylite and is present in varying amounts. The ratio of tetrahedral cations to octahedral cations is approximately 1:1. The structure of deweylite is similar to that of antigorite, containing a superlattice probably in the *a* direction of about $8\frac{1}{2}\ a_0$. Line broadening is extreme and characteristic, and many of the antigorite reflections are weakly diffuse or absent. Analysis of the data suggests that Cedar Hill deweylite may be a dioctahedral modification of antigorite with an undulant character in the *ab* plane and containing crystallites on the order of a few hundred Angstroms. No single crystals or well crystallized samples of deweylite have been discovered.

INTRODUCTION

During the course of a Pennsylvania Geological Survey field mapping project in the serpentinized ultramafics of southeastern Pennsylvania two previously undiscovered minerals were found in a serpentinite fault breccia in the Cedar Hill serpentinite quarry in Lancaster County. One of these is bright emerald green, massive and possesses a conchoidal fracture. The other occurs as small, white radiating crystal groups found in cavities within the breccia matrix. A cursory *x*-ray examination showed that Debye-Scherrer patterns for both of these minerals correspond to previously published diffraction patterns for deweylite. Since the color and crystal form of these specimens differ from other known occurrences, and since the properties and structure of deweylite are not well known, this investigation was undertaken to shed more light on this rather unusual mineral.

Several occurrences and analyses of deweylite have been described in the literature (Rogers, 1918; Ross and Shannon, 1925; Daly, 1935; Selfridge, 1936; Konta, 1951). Rogers (1918) and Daly (1935) report an occurrence in limestone associated with a calcite-brucite rock and spatially related to a nearby quartz monzonite porphyry dike. Rogers (p. 584) states that the sequence of mineral formation, from oldest to youngest, is periclase-brucite-hydromagnesite-deweylite. Daly (p. 651) questions the supergene origin ascribed to this deweylite by Rogers, stating "that the genesis of these silicates (chrysotile and deweylite) can be assigned to the action of solutions emanating from this dike on previously formed

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minerals (epidote or diopside . . .) and thus in this case their origin would be hypogene." However the majority of deweylite occurrences are associated with serpentinites in fractures which post date at least initial serpentinization and are generally believed to be of supergene origin from colloidal suspensions (Konta, 1951, p. 420).

Optical, differential thermal, *x*-ray, and chemical data have been given for deweylite, but only on the specimens described by Konta have all these analyses been performed for each sample. In general, deweylites reported in the literature have the following characteristics: 1) a close resemblance to the serpentine structure but with the absence of many (*hkl*) reflections and a characteristic line broadening; 2) a chemical composition approaching that of serpentine but with a higher Si/Mg ratio and more molecular water, and 3) variable indices of refraction lower than those for chrysotile or antigorite.

Geologic Occurrence

The Cedar Hill Quarry from which these deweylite samples came is located $\frac{1}{2}$ mile east of Pennsylvania Route 222–72 just north of the Pennsylvania-Maryland state line, in Lancaster County. Deweylite may also be found at the old Wood chromite mine about one mile to the east and has been reported on by Selfridge (1936, p. 483, 484, 499).

The Cedar Hill Quarry is composed of serpentinized dunite which has been intruded by siliceous pegmatites, highly fractured, faulted, and deeply weathered along fault and fracture planes. This serpentinite is part of a NE-SW trending belt of ultramafics, mafics, and granitic pegmatites which extend from the Susquehanna River eastward about 15 miles.

There are three distinct occurrences of deweylite at Cedar Hill: 1) reddish brown deweylite associated with limonite in a steeply dipping fault, often slickensided so that it has the appearance of fault gouge; 2) red, yellowish green, and pale yellow in a nearly horizontal fracture and crudely zoned with red along the contact and pale yellow in the center of the fracture, and 3) white pseudomorphs, massive white, and massive green in a vertical fault breccia containing open cavities with small magnesite stalactites, brucite crystals, and deweylite pseudomorphs.

The breccia matrix in the latter occurrence contains blebs of green and white fluorescent deweylite surrounded by a mixture of magnesite and dolomite. Angular fragments of spotted serpentine from a few millimeters to several feet in size are present, often with a narrow rim of chalcedony between the serpentine and the magnesite-dolomite matrix. The spotted appearance of the serpentinite in the breccia is the result of differential weathering of serpentine and olivine.

Assuming that the red-brown deweylite samples in the two unbrecciated fracture systems are contemporaneous, the paragenesis of the deweylite and associated minerals in the above three occurrences may be divided into two groups. (1) In the unbrecciated fractures the red-brown deweylite was followed by both yellow and white fluorescent varieties. A similar paragenetic sequence has been described by Konta (1951, p. 420). This fracture system has been displaced by a later fracture system containing chlorite and vermiculite. (2) In the breccia, the following sequence was observed, from oldest to youngest: chalcedony, dolomite and magnesite, replaced by white fluorescent and green deweylite, brucite, botryoidal and stalactitic magnesite, aragonite, deweylite pseudomorphs, and lastly, opal and hydromagnesite which coat the pseudomorphs (Fig. 1, *b-e*). Sepiolite is associated with some of the deweylite, but its paragenetic relations are not known.

Although the solutions from which deweylite formed are often considered to have contained colloidal suspensions, their source has been variously thought to be both hypogene and supergene. One of the reasons for these two hypotheses lies in its association with both contact metasomatic magnesium silicates and also with supergene magnesium crabonates and hydroxides. The occurrence of the Cedar Hill deweylite in fractures and in a serpentinite breccia indicates that it formed after at least some of the faulting occurred, and that this faulting itself postdates serpentinization. Numerous vertical faults and fractures contain chlorite borders and vermiculite centers. The relation between these and the deweylite is not clear. Although one horizontal fracture containing deweylite ends abruptly at a chlorite-vermiculite fracture filling, another, a horizontal deweylite fracture, appears to continue through the chlorite-vermiculite. The time of the deweylite formation relative to the chlorite-vermiculite crystallization is further obscured by the fact that the vermiculite is probably a supergene alteration product of an earlier hydrothermal mineral assemblage (Klup and Brobst, 1954; Bassett, 1959, p. 293–295).

Several observations bear upon the temperature of deweylite formation. The dolomite-magnesite-deweylite matrix in the fault breccia does not appear to have replaced the angular fragments of serpentine and thus temperatures of formation for this assemblage must have been within the stability range of serpentine, below 500° C. (Bowen and Tuttle, 1949; Gillery 1959, p. 144–146). Numerous cavities in the breccia also indicate that these minerals formed in an open fracture rather than by replacement. Magnesite, brucite, opal, and hydromagnesite, and to a lesser extent deweylite, are found throughout this serpentine belt as a surficial coating on open fracture surfaces and appear to be secondary

minerals of supergene origin. In addition to these data the spotted appearance of the serpentine in the breccia well below the zone of surficial weathering, the presence of limonite associated with the reddish brown deweylite, and also a possibly supergene vermiculite nearly 100 feet below the surface all attest to the activity of supergene ground water solutions migrating along fractures.

Magnesite within the breccia cavities is typically stalactitic and botryoidal, with a glassy appearance and a conchoidal fracture. Deweylite has a similar appearance and is composed of aggregates of colloidal size. Such physical features are characteristic of low temperature mineralization and may represent crystallization from a colloidal gel formed by the alteration of pre-existing magnesium silicates. Likewise, Konta (1951, p. 420) concludes that the very similar Mladotice deweylites in serpentine are of low temperature origin from colloidal suspensions.

Deweylite Pseudomorphs

Representative examples of the deweylite forms are shown in Fig. 1. Sketches (*a*), (*b*), and (*d*) indicate an orthorhombic, or possibly monoclinic, habit; (*c*) is orthorhombic (pseudo-hexagonal); (*e*) is the most common form and consists of a central plate of deweylite coated with hydromagnesite. Pseudomorphs are typically grouped in radial clusters. The associated botryoidal and stalactitic 'pencils' of magnesite are illustrated in (*d*).

A search of the literature was undertaken to determine the original crystal which the pseudomorphs represent. Although positive identification is not possible, the pseudomorphs most closely resemble aragonite (see Goldschmidt, 1913, p. 97, 98, 104) which is relatively common in crystal clusters both at Cedar Hill and the nearby Wood chromite mine.

A survey of the literature and of the excellent collection of serpentine pseudomorphs at the Mineralogical Museum at Columbia University revealed pseudomorphs after pectolite, chrysolite, chlorite, chondrodite, dolomite, calcite, garnet, enstatite, hornblende, tremolite, pyroxene, brucite, apatite, and magnetite. This, however, is believed to be the first report of deweylite after aragonite.

Optical Properties

Indices of refraction (Table 1) were determined in white light with a daylight blue filter. The accuracy of determination is considered to be ± 0.003.

Birefringence is on the order of 0.004 to 0.006. Two types of structures were noted: very fine-grained aggregates, and fibrous bands resembling chalcedony. Where both materials occur together, the banded deweylite

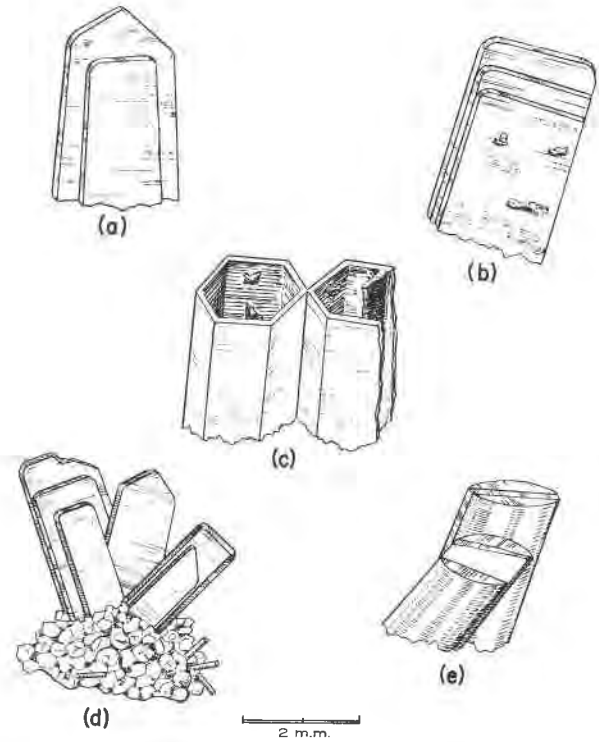

Fig. 1. Pseudomorphs of deweylite after aragonite, Cedar Hill Pennsylvania

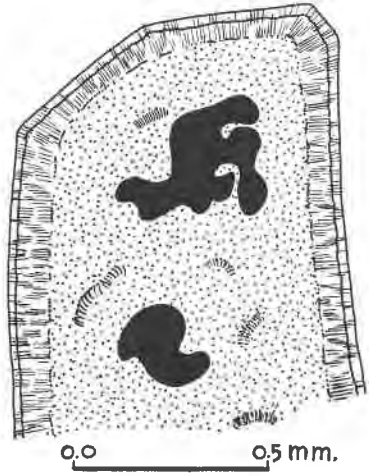

FIG. 2. Pseudomorph of deweylite after aragonite illustrating an earlier aggregated deweylite (center) and a later banded, fibrous deweylite (rim). The black mineral is opal. × nicols.

forms an outer rim (Fig. 2). The white pseudomorphs of deweylite (*#3b* in Table 1) are closely associated with opal (Fig. 2). The reddish brown deweylite (#2 in Table 1) did not exhibit any limonite in either transmitted or reflected light, hence at least some of the reddish brown color is believed to be inherent in the deweylite itself.

The indices of refraction of the Cedar Hill Material are compared with published values in Table I. The indices range in value from very near that of opal at 1.48 to approximately the values for well crystallized antigorite at 1.548. All of the material from Pennsylvania (Table I, 1–8) is in

TABLE I. INDICES OF REFRACTION FOR DEWEYLITE

	(1)	(2)	(3*a*)	(3*b*)	(4)	(5*a*)	(5*b*)	(6)
α	1.504	1.511	1.500	1.511	1.507	1.511	1.522	1.500
γ	1.509	1.516	1.506	1.517	1.512	1.518	1.527	1.509
	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
α	1.500	1.487	1.538	1.505 to	1.528 to	1.532	1.548	1.546
γ		1.510	1.546	1.525	1.555	1.540		

(1) White fluorescent deweylite in fibrous bands; ±.003; Cedar Hill.
(2) Reddish brown deweylite; indices from fibrous bands on edges; no indices determined on inner aggregates; ±.003; Cedar Hill.
(3*a*) White pseudomorphs; outer fibrous bands; ±.003; Cedar Hill.
(3*b*) White pseudomorphs; inner aggregate; ±.003; Cedar Hill.
(4) Yellow green; aggregates; no fibrous bands; ±.003; Cedar Hill.
(5*a*) Emerald green (nickeliferous); outer fibrous bands; ±.003; Cedar Hill.
(5*b*) Pale green; inner aggregates; ±.003; Cedar Hill.
(6) Texas, Pa. (Selfridge, 1936, p. 483).
(7) Lancaster County, Pa. (Selfridge, 1936, p. 483).
(8) Delaware, Pa. (Selfridge, 1936, p. 483).
(9) Pseudomorph after pectolite, Jersey City, N. J. (Selfridge, 1936, p. 483).
(10) Variation of indices; average at 1.510; Webster, N. C. (Ross and Shannon, 1925, p. 445) for a nickeliferous deweylite.
(11) Considered to be a mixture with chrysotile; E. Chino Quarry, Riverside, Calif. (Daly, 1935, p. 651).
(12) Brown; Mladotice, Czech. (Konta, 1951, p. 413).
(13) Green; Mladotice, Czech. (Konta, 1951, p. 413).
(14) White; Mladotice, Czech. (Konta, 1951, p. 413).

lower portion of this range. In addition, where there is a rim of banded fibers, this material has a lower index than the inner, fine-grained aggregates. Within any one sub-variety of deweylite the indices vary: in the Cedar Hill material over a narrow range; in the Webster, N. C. material (Ross and Shannon, 1925, p. 445) and the Riverside, Calif. samples (Daly, 1935, p. 651) over a much wider range.

The influence of molecular water in decreasing the index of refraction may be seen from the data given by Konta (1951, p. 414, 415) and is similar to that observed in the opal-quartz series. It seems highly probable that this wide variation in the indices of deweylite is the result of variable H_2O content and that the conchoidal fracturing observed in deweylite is evidence of hydration. If this is the case, then the outer rims of deweylite either represent a hydration stage in which more water was available, or a rehydration of previous deweylite. The former interpretation is preferred by the author for the Cedar Hill samples. This is based both on the appearance of the rims (Fig. 2) and by analogy with the paragenetic sequence given by Konta (1951, p. 415, 420) which also suggests that the youngest deweylite contains the most molecular water.

With respect to the green deweylite (Table I, 5*a*, *b*), the higher index material contains the deepest green coloration. Since this green variety contains significant amounts of nickel, there may also be a correlation between indices and nickel content, or with the amounts of nickel and H_2O present if the nickel were in a structural position such that an $(OH)^-$-Ni attraction would be significant. As yet, this remains a moot question.

Chemical Composition

Material selected for chemical analysis was examined both optically and with the aid of *x*-ray powder photographs to obtain samples free from impurities. A small amount of magnesite was present in the two samples selected. A negligible amount of opal may also have been present. Because of the difficulty of obtaining sufficient amounts of pure deweylite, only the white, fluorescent (1) and reddish brown (2) deweylites were analyzed (Table II).

The *x*-ray spectrographic methods utilized both external and internal standards. Wet chemical analyses were used as external standards to determine total iron content based on the FeK_α line. For nickel, $NiCO_3$ was used as an internal standard based both on the NiK_α and NiK_β lines. The matrix used was white, fluorescent deweylite. Three runs were averaged at each frequency and the slope of the resulting graph was used to obtain the results listed in Table II. Since the Mn content was quite low and consistently uniform for all the deweylite samples, the amount present was estimated from the slopes of the iron and nickel curves.

The calculation of the chemical formulas (Table II) is based on three tetrahedral cations per unit cell since this yields more nearly whole number octahedral cation values than would two tetrahedral cations per unit cell. The structural formulas are written with $(OH)_4$ plus molecular water to conform to the serpentine structure, rather than expressing all the water as H_2O.

Three steps were performed in obtaining the corrected chemical analyses listed in Table II. Sufficient Mg was subtracted to utilize all of the CO_2 as magnesite, present as an impurity. The iron was recalculated from Fe_2O_3 to FeO on the assumption that all the iron is within the

TABLE II. CHEMICAL ANALYSES, CEDAR HILL DEWEYLITE
Analyses by L. E. Gingerich, Pa. R. R.

(1) Massive, white, fluorescent deweylite (*a*)

	Analysis	Corrected	Atomic Ratio	Atoms/unit cell
% SiO_2	49.64	52.43	.8748	3.000
% Al_2O_3	0.00			
% Fe_2O_3	2.40			
% FeO		2.16	.0301	0.1036
% MgO	32.07	31.62	.7841	2.6997
% NiO	tr	0.16*	.0021	0.0072
% CO_2	2.34			
% H_2O	12.90	13.62	3.0238	10.4109
Total	99.35	99.99		

Formulas: 1. $(Mg_{2.70}Fe_{.10}Ni_{.01})_{2.81}Si_{3.0}O_7 \cdot (OH)_{4.0} \cdot 3.2H_2O$
2. $(Mg, Fe, Ni)_3Si_3O_7 \cdot (OH)_4 \cdot 3H_2O$

(2) Reddish brown deweylite (*b*)

	Analysis	Corrected	Atomic Ratio	Atoms/unit cell
% SiO_2	44.82	48.69	.8124	3.000
% Al_2O_3	0.67	0.73	.0286	
% Fe_2O_3	3.29			
% FeO		3.23	.04495	0.1600
% MgO	33.38	32.72	.81099	2.893
% NiO	tr	0.11*	.00147	0.005
% CO_2	3.56			
% H_2O	13.36	14.51	3.22176	11.492
Total	99.08	99.99		

Formulas: 1. $(Mg_{2.9}Fe_{0.16})_{3.1}(Si_{2.9}Al_{0.1})_{3.0} \cdot (OH)_{4.0} \cdot 3.75H_2O$
2. $(Mg, Fe)_3(Si, Al)_3O_7 \cdot (OH)_4 \cdot 4H_2O$

* Analyses by *x*-ray spectrograph.

deweylite and not present as limonite, since optical observations did not reveal any limonite or hematite. However, small amounts are probably present and hence the iron content listed in Tables II and III is a maximum value. The resulting values were then recalculated to total 100 per cent.

An interesting feature is the high nickel content of the emerald green deweylite (Table III, #5). The intensity of the green coloration is directly proportional to the amount of nickel present. The analyzed sample was selected from material which was largely emerald green. However, since small amounts of pale green and white deweylite could not be completely separated, the value of 4.53% NiO is not the maximum nickel content, although the maximum probably does not exceed 5%. Previously Ross and Shannon (1925, p. 445) have reported a green deweylite from Webster, N. C., containing 4.2% NiO.

Perhaps the most interesting result from the chemical analyses is the

TABLE III. *X*-RAY SPECTROGRAPHIC ANALYSES OF DEWEYLITE

	% Cr_2O_3	% NiO	% FeO	% MnO
(1) White fluorescent	nil	0.16±.03	2.16	.03±.01
(2) Reddish brown	nil	0.11±.03	3.23	.02±.01
(4) Yellow-green	nil	0.11±.03	2.38	.02±.01
(5) Emerald green	nil	4.53±.04	2.13	.03±.01

Ni Analyses: $NiCO_3$ internal standard on NiK_α and NiK_β.
Fe Analyses: Wet chemical external standard FeK_α.
Mn Analyses: Estimate based on slope of Ni and Fe curves.

high Si:(Mg+Fe+Ni) ratio. In most chrysotiles and antigorites this ratio is approximately 2:3, representing a trioctahedral structure. The Cedar Hill deweylites in Table II have a ratio very close to 1:1. Analyses given by Ross and Shannon (1925, p. 445), Daly (1935, p. 650), Selfridge (1936, p. 449), and Konta (1951, p. 414) for deweylite generally fall between these ratios. One consequence of this ratio will be discussed under the differential thermal analysis data in reference to the formation of clinoenstatite (1:1 ratio) as opposed to forsterite (1:2 ratio). Another consequence lies in the speculation that octahedral cation holes may exist in deweylite. In the case of the two analyzed Cedar Hill deweylites, a 1:1 tetrahedral to octahedral cation ratio would represent a dioctahedral serpentine, while the values reported by other analysts would be more trioctrahedral in character. Bates (1959, p. 95) has discussed the possibility of cation deficiencies as it relates to serpentine morphology, but did not note a completely dioctahedral serpentine.

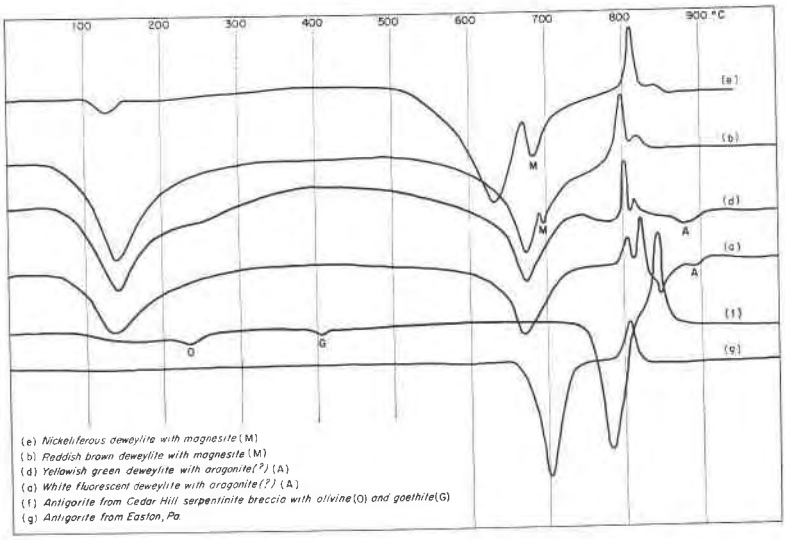

FIG. 3. Differential thermal curves of deweylite and antigorite.

No chemical explanation has been found for the fluorescence of the white deweylite. Neither manganese (Table III) nor chromium (not present) is responsible.

DIFFERENTIAL THERMAL ANALYSIS

The DTA curves reproduced in Fig. 3 were run on a commercial instrument, the Deltatherm, at 10° C/min. The sample head accommodates four samples. Both quartz and kaolinite were used as standards. The accuracy is $\pm 10°$ C. One deweylite and one Cedar Hill serpentine from the breccia were also kindly rerun by Robert C. Bolger to serve as a further check.

In Fig. 3 several deweylite curves are compared with two antigorite curves. There is a general correspondence between them, although the transformation temperatures serve to differentiate them. The endothermic reaction at 125°–140° C. represents the loss of molecular water. The endothermic reaction at 625°–675° for deweylite and at 700° and 775° C. for antigorite represents the loss of structural water. Magnesite tends to lower the peak temperature of this endothermic reaction. Between this endothermic and the following exothermic reactions, *x*-ray powder photographs do not exhibit diffraction lines, indicating that the short range order of a crystal structure has disappeared. The exothermic reactions at 800° to 850° C. represent the crystallization of anhydrous magnesium silicates.

Several features are of interest. The lower temperature for the second endotherm of deweylite, as contrasted with a higher temperature for antigorite, is probably in part a consequence of its greater degree of disorder. Nickel also appears to lower this peak temperature as has been noted by Caillere and Henin (1957, p. 221–224). If, as Caillere and Henin believe (1948, p. 114–118), this peak temperature is related to the composition of the octahedral layer, nickel may be the cause of this lower decomposition temperature. It may also be related to the extent to which the cation octahedral sites are filled.

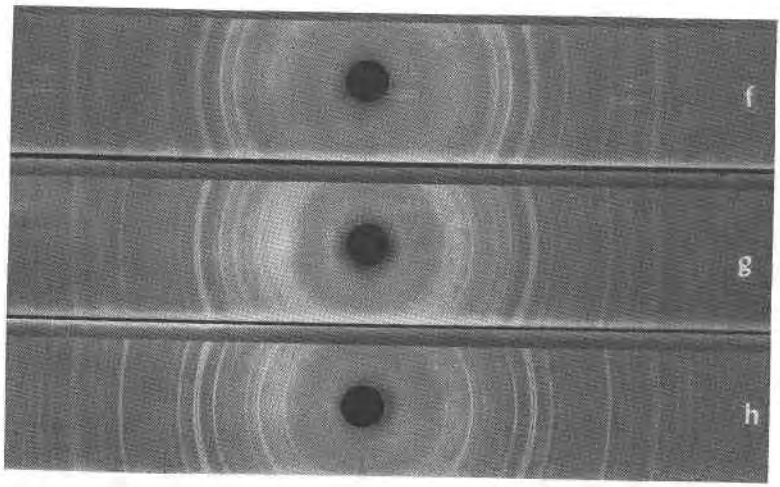

FIG. 4. *X*-ray powder patterns of (f) clinoenstatite with minor forsterite, (g) forsterite with clinoenstatite and (h) forsterite from differential thermal treatment of samples (b), (a), and (f) (brown deweylite, white fluorescent deweylite, and antigorite respectively) in Fig. 3.

Another interesting feature is the occurrence of two exothermic peaks for deweylite, at about 800° and 820° C., while antigorite exhibits only a single exothermic reaction between 805° and 840° C. Post DTA *x*-ray powder patterns of the antigorite samples contain only forsterite. Similarly Aruja (1945, p. 72) notes that only forsterite is produced by heating antigorite until a run of 25 hours at 1000° C. exhibited a faint line at the position of the strongest line of enstatite. From this, he was not able to differentiate between enstatite and clinoenstatite. Konta (1951, p. 416) reporting on the differential thermal analysis of deweylites presents curves with a single exothermic reaction at about 800° C., noting that "the crystallization of the orthosilicate Mg_2SiO_4" predominates but that $MgSiO_3$ is also shown to be present in the *x*-ray powder photographs. Post DTA *x*-ray photographs corresponding to DTA curves of deweylites (*b*) and (*a*), and of antigorite (*f*) in Fig. 3 are reproduced in Fig. 4,

labelled (*f*), (*g*) and (*h*) respectively. The DTA curves show an increase in the area under the curve for the higher temperature exotherm, and the *x*-ray photographs show a corresponding change from predominantly clinoenstatite in (*f*) to predominantly forsterite in (*h*). This correspondence is taken to mean that the lower exotherm represents forsterite formation dominantly from antigorite, and the higher temperature that of clinoenstatite from deweylite.

The formation of forsterite at a temperature below that of clinoenstatite is quite interesting. From the points of view both of mineral structures and paragenetic field evidence, forsterite is often considered to be the higher temperature mineral. In the case of the deweylite and antigorite thermal products it is believed by the author that initial chemical composition is the controlling factor. Clinoenstatite has a Si: Mg ratio of 1:1, whereas the ratio in forsterite is 1:2. The former ratio corresponds almost exactly to that of the two Cedar Hill deweylites (Table II), while the latter corresponds more closely to the 2:3 ratio of serpentines. There is, however, an even closer correlation within the deweylites themselves. The white fluorescent deweylite contains more silica than the reddish brown deweylite (Table II). This correlates very well with the greater area under the higher temperature endotherm for clinoenstatite from the white deweylite as compared to that from the reddish brown deweylite. It also correlates with the relative amounts of clinoenstatite in the *x*-ray patterns (Fig. 4). Further support is lent to the supposition that chemical composition controls the decomposition products by the apparently amorphous nature of the deweylite preceding the exothermic reactions. Thus structural control does not seem to be significant.

Structural Data and Interpretations

General Discussion

Several *x*-ray powder techniques were utilized in an attempt to determine the structural characteristics of deweylite. Two or more powder photographs were taken for each sample using Cu K_α radiation, a Ni filter, approximately a 3-hour exposure time, and Duco Cement as the bonding medium. As a result of the extreme line broadening (Fig. 5) measurements of 2θ are accurate only in the first decimal place, despite the fact that they have been checked by diffractometer runs calibrated by a Si standard. Intensities listed in Table IV were estimated visually, and modified somewhat by diffractometer runs between 5° and 60° 2θ. The (N20) or (02N) series listed in Table IV are all weak reflections.

A general structural correspondence between the serpentine minerals and deweylite may be seen from Fig. 5 and Table IV. The assigned indices are based on those of antigorite as given by Brindley and von Knor-

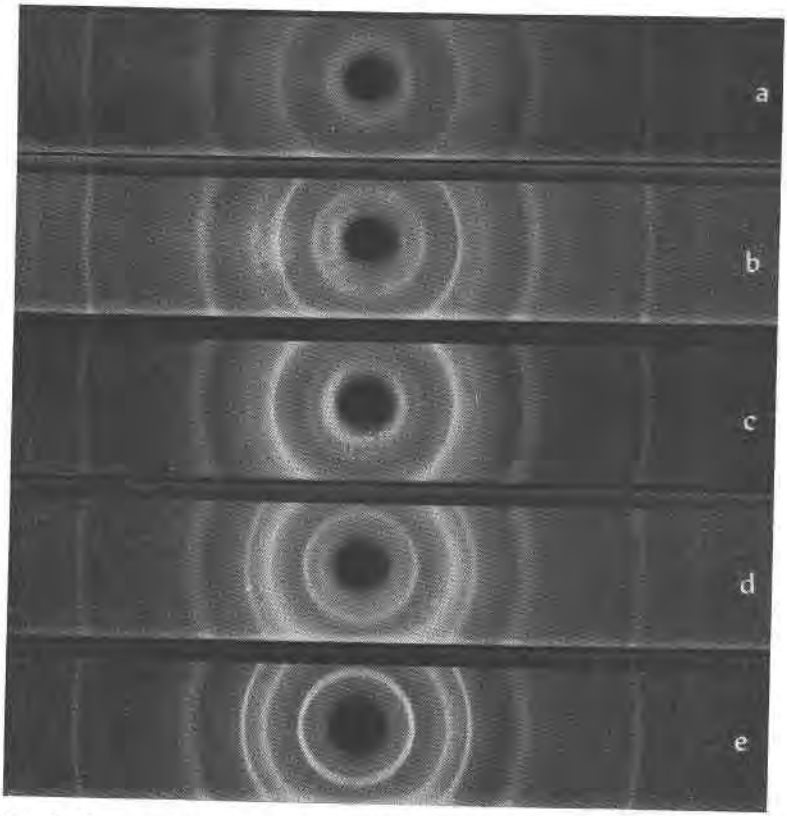

FIG. 5. *X*-ray powder patterns of deweylite: (a) white fluorescent; (b) reddish brown; (c) pseudomorphs after aragonite; (d) yellowish green, and (e) nickeliferous. Letters correspond to Table IV.

ring (1954, p. 799) and will be discussed later. The reflections which are present in deweylite are also present in the serpentine minerals. However many of the serpentine reflections are absent in deweylite, notably among the (20*l*) series. Those present are all broad and diffuse in character. In comparison with the serpentines, all of the deweylite samples in Table IV exhibit lattice expansion in the *c* direction and a small contraction along the *b* axis. Such a contraction as that of the (060) may be another indication of a tendency toward dioctahedral character for deweylite as suggested by an M^{+2} cation deficiency calculated from the chemical analyses. As may be seen from Fig. 5 and Table IV there are significant variations in intensity within the deweylites themselves, notably between the (00*l*) and (0*k*0) series of reflections. These differences between serpentine and deweylite in *x*-ray characteristics appear to be consistent

TABLE IV. X-RAY POWDER REFLECTIONS FOR DEWEYLITE

(*a*) = White, fluorescent; Cedar Hill
(*b*) = Reddish brown; Cedar Hill
(*c*) = Pseudomorphs; Cedar Hill
(*d*) = Yellowish green; Cedar Hill
(*e*) = Nickeliferous; Cedar Hill
N = index in (N20) or (02N) series
B = very broad, diffuse reflection
* = includes some sepiolite
† = probably magnesite

Powder Photographs										Diffractometer		(hkl)
(*a*)		(*b*)		(*c*)		(*d*)		(*e*)		Selfridge (1936)				
d Å	I/I$_o$	d Å	I/I$_o$	d Å	I/I$_o$	d Å	I/I$_o$	d Å	I/I$_o$	d Å	I/I$_o$	d Å	N	
7.37	20	7.46	55	7.45	55	7.42	85	7.35	100	7.37	50			(002)
4.562*	100	4.552	100	4.552*	100	4.550	100	4.538	50	4.594	85	4.560	1	(020)
												4.510	2	
												4.27	4	
												4.07	5	
												3.92	6	
3.660	10	3.666	40	3.660	40	3.668	60	3.659	80	3.668	50	3.66	7	(004)
												2.88?	12	
														(201)
2.599	65	2.597	35	2.592	25	2.601	30	2.595	30					(202)
2.500*	50B	2.500	65B	2.500*	50B	2.500	50B	2.510	35					
2.470	40B	2.450	50B	2.460	40B	2.473	50B	2.452	30B	2.457	80	2.448	15	(006)
										2.127	10			
						1.753	5	1.753	5					(240)
										1.717†	50			
1.532	100	1.533	85	1.533	60	1.535	90	1.533	50	1.520	100			(060)
												1.507		(062)(208)
1.315	15	1.320	20	1.312	10	1.318	8	1.311	10	1.306	70			(401)(402)
										1.040	3			
0.994	?	0.993	1	0.994	2	0.997	?	0.995	2	0.990	40			
		0.884	1	0.887	1	0.889	1	0.888	2	0.878	30			
										0.761	10			
										0.728	10			

and should serve to differentiate deweylite from both antigorite and chrysotile whose characteristics recently have been summarized by Eitel (1958, p. 131–138).

The 10 Å reflections visible in Fig. 5 are believed to represent the presence of sepiolite and are most noticeable in patterns (*a*) and (*c*), white fluorescent and white pseudomorphic deweylite respectively. Those reflections which may in part be a combination of sepiolite and deweylite are denoted in Table IV. Magnesite is nearly always present in small amounts, and it seems probable that at least one of the reflections (1.717 Å) listed by Selfridge (1936, p. 469) and Konta (1951, p. 419) for deweylite belongs to magnesite.

Influence of M^{+2} Cations

The deweylite *x*-ray powder photographs in Fig. 5 and Table IV have been arranged to show a progressive increase in intensity of (002)/(020). A possible explanation may exist in a correlation between M^{+2} cation substitution and the effect of this substitution on the absolute structure factor, $|F|$. If it is assumed that substitutional changes in either the octahedral or a possible interlayer site will not affect the (020) intensity, and this seems probable, then semi-quantitative F calculations based on a modification of the basic units of the chlorite structure show that increasing degree of substitution, or the substitution of heavier atoms, will increase the (00*l*) intensity for at least the first four orders. Such a calculation also shows that the effective increase in intensity will be greater for octahedral than for interlayer substitution. The evidence for such a cause and effect is slight, but worth noting.

The chemical analyses of the white (*a*) and reddish brown (*b*) deweylites in Table II show that the latter contains more M^{+2} cations. Similarly, there is a noticeable increase in the (002)/(020) intensity ratio. The nickeliferous deweylite (*e*) yields the highest intensity ratio of those analyzed. This may be explained easily either by degree of octahedral (or interlayer) substitution or by the substitution of Ni which has a greater atomic weight than Mg. Since this intensity ratio cannot be explained for the non-nickeliferous, iron deweylites (*a–d*) solely on the basis of total Fe content, it seems logical to assume that the unit cell quantity of all the M^{+2} cations is as important as the substitution of a heavier cation for Mg. It is also interesting to note that most serpentine minerals have a high (002/020) intensity ratio and also have significantly more M^{+2} cations than deweylite, suggesting that the observed intensity changes in deweylite may be the result of octahedral substitutions which approach that of serpentine in the degree to which the octahedral sites are filled.

There is also a noticeable increase in most of the deweylite lattice spac-

ings as compared with those of antigorite and chrysotile. This may well be the result, in part, of interlayer molecular water, which helps to explain the variability of the (00*l*) spacings. It is also possible that a correlation may exist with the M^{+2} cations. For example the nickeliferous deweylite appears to have the smallest c_0 value. However, the diffuse character of the reflections does not allow a sufficient accuracy of measurement to draw conclusions in this regard.

Line Broadening and Crystallite Size

Measurements of line broadening for comparison among the deweylite samples and for crystallite size calculations were made at one half the peak height ($\beta_{\frac{1}{2}}$) from diffractometer traces. This is often inaccurate because of pronounced peak asymmetry and because the establishment of a background base-line is difficult as a result of the extreme broadening. In addition, superlattice reflections (to be discussed below) often are superimposed upon the flanks of major peaks. As a consequence of these limitations quantitative calculations are highly inaccurate as far as absolute numerical values are concerned. It is hoped, however, that relative comparisons are useful if used with caution.

Line broadening in deweylite could be, and probably is, the result of several factors, rather than any single one. Limited randomness in the packing of the layers (stacking disorder resulting in crystallites) may be a significant factor. The colloidal size and aggregated optical character of the deweylites may be a large scale consequence of such a disorder. Aruja (1945, p. 71) in connection with antigorite also mentions the possibility of variation in the structure factor from one unit cell to the next as a result of two different types of octahedral cavities. However, the deweylite line broadening is much greater than that in antigorite and hence this cannot be the major factor. Extreme warping of atomic planes will also result in line broadening. A double half wave structure, such as that proposed by Kunze (1957, p. 104) for antigorite, may be contributory but again seems unlikely as an explanation for the more pronounced broadening of deweylite. However, warping of atomic planes might also be caused by incomplete lattice substitution or by "stuffing." Evidence has been presented previously that incomplete octahedral substitution may exist. The extent to which this may be a cause of deweylite line broadening is not known.

Calculations of crystallite size were carried out for all five deweylite samples (*a*–*e*) assuming all line broadening to be the result of the presence of crystallites. The values thus obtained are minimal values. The formula used was

$$D_{hkl} = \frac{K\lambda}{\beta_{1/2} \operatorname{Cos} \theta} \quad \text{where} \quad K = 0.9$$

on the assumption that the crystallites sufficiently approach sphericity so that no significant errors are introduced in the shape factor. Data are presented in Table V only for the nickeliferous (*e*) and yellowish green (*d*) deweylite samples since all others yield values similar to that for yellowish green deweylite. Useful determinations in the *c* direction were not obtainable.

From Table V it can be seen that the minimal crystallite size is on the order of 100 Å. It also can be seen that the *k* dimension is somewhat greater than the *l* for all except the nickeliferous deweylite where the situation is reversed. If, as Aruja suggests for antigorite (1945, p. 66), the *b* axis is the fiber axis, then the longer dimension of the majority of the deweylite crystallites parallels this direction. That this is not the case for the nickeliferous deweylite suggests that crystallite dimensions may be compositionally or structurally controlled by the presence of Ni ions in the lattice.

TABLE V. CRYSTALLITE SIZE (*D*) DETERMINATIONS FOR DEWEYLITE

(d) Yellowish green (similar for white and reddish brown)					
	$D_{(006)}$	$D_{(020)}$	$D_{(0.0.12)}$	$D_{(060)}$	$D_{(206)}$
	80 Å	115 Å	82 Å	98 Å	
	$k>l$				
(e) Nickeliferous					
	106 Å	81 Å	105 Å	77 Å	56 Å
	$l>k(>h)$				

Superlattice Structure

Diffractometer traces of the Cedar Hill deweylite samples contain numerous small peaks belonging to an ($h20$) or ($02l$) series of reflections (Table IV). This series suggests a superlattice for deweylite similar to the superlattice structures of antigorite. Aruja (1945) proposed a superlattice in the *a* axis direction for antigorite, while Brindley and von Knorring (1954, p. 801–802) also discuss the possibility of a *c* axis superlattice.

Since *x*-ray powder analysis cannot distinguish between a superlattice in the ($h20$) planes from one in the ($02l$) series, calculations of the superlattice dimension (*S*) were carried out for comparison with a_0 and c_0 according to the expression

$$(1/d)^2 = (2/b)^2 + (N/S)^2$$

for both the yellowish green (*d*) and nickeliferous (*e*) deweylite samples. For (*d*), the value of b_0 used was 9.18 Å, and for (*e*), 9.15 Å. Calculations of *S* were made for $N = 2$, 4, 5, 6, 12, and 15 (Table IV) with their corre-

sponding d spacings. These values are compared with $3c_0$, $8a_0$, $8\frac{1}{2}a_0$, and $8\frac{3}{4}a_0$ for both yellowish green (d) and nickeliferous (e) deweylites (Table VI). The a_0 values were calculated and averaged from the (201) and (202) planes for each sample according to the expression.

$$a_0 = \frac{hd_{(h0l)}}{\mathrm{Cos}\left(89° - \mathrm{Cos}^{-1}\dfrac{d_{(h0l)}}{1/lc_0}\right)}$$

where β has been assumed to have a value of 91°. This assumption probably falls within the limits of error of the d spacing measurements, and hence within the average value of c_0.

TABLE VI. COMPARATIVE SUPERLATTICE CALCULATION FOR DEWEYLITE

Yellowish Green (d)	Nickeliferous (e)
$S_{(d)}=45.0\pm1.0$	$S_{(e)}=45.5\pm1.0$
$3c_0=44.0$	$3c_0=44.10$
$8a_0=42.16$	$8a_0=42.24$
$8\frac{1}{2}a_0=44.80$	$8\frac{1}{2}a_0=44.88$
$8\frac{3}{4}a_0=46.11$	$8\frac{3}{4}a_0=46.20$

The best fit for the data is between a superlattice in h (a_0) and the S dimension for both deweylite samples. Both also correlate best with an $8\frac{1}{2}a_0$ superlattice dimension. This fractional correlation of a_0 suggests that undulations may be a necessary part of the deweylite structure as proposed by Onsager (1952) for serpentine. Such undulations, or warping of atomic planes, have been mentioned as a possible contributor to line broadening and would conform to the suggestions of Kunze (1957) regarding possible types of wave structures in antigorite. However, as Brindley and von Knorring have noted (1954, p. 802), analysis of the data from x-ray powder analysis cannot conclusively distinguish between an a_0 and a c_0 superlattice, nor is the accuracy of the data sufficient to confirm an undulating structure in deweylite.

High Temperature X-Ray Diffraction Data

High temperature powder x-ray diffractometer scans and oscillations were run on several deweylite samples using the instrument and techniques described by Bassett and Lapham (1957). The purposes of this method of analysis were to determine 1) if line broadening is a function of mechanical or structural strain, 2) the relative persistence in maintaining crystallinity of the various (hkl) planes under heat treatment, 3) if the deweylite structure might exercise a control over the formation of an-

hydrous magnesium silicates and 4) if any significant difference exists among the Mg-Fe deweylites.

In general, there are no *d* spacing shifts, intensity changes, or changes in the amount of line broadening for any of the major reflections previous to the collapse of any one atomic plane. The lack of peak sharpening upon heating indicates that line broadening is not a function of mechanical strain. Aruja (1945, p. 72–73) arrived at a similar conclusion from single crystal studies of antigorite.

The thermal stability of various (*hkl*) planes varies considerably. Planes with even *h* and *l* indices are most stable, (*hk*0) planes slightly less stable, while (00*l*) planes are the least stable. The latter collapse at about 500° C., while the other atomic planes persist to approximately 600° C. This suggests that linkages in the *ab* plane are strongest and again coincides with the conclusion of Aruja (1945, p. 73) for antigorite. The superlattice reflections begin to disappear at a lower temperature, between 400° C. and 500° C., indicating the relative instability of the superlattice structure. Also, the (201), (202), and (15.2.0) planes merge into one reflection approximately coinciding with the position of the (202) reflection.

Although all the deweylite samples behaved in similar fashion, small differences were noted for the Ni deweylite. It must be borne in mind, however, that the magnitude of these differences is so small that they may be more apparent than real. A slight tendency was noted toward greater stability of the (00*l*) planes in the Ni deweylite than in the other samples. There also appeared to be a small increase in line broadening upon heating which was not noted for other deweylite samples. These data are much too indefinite to draw any conclusions.

As noted previously, there were no reflections present at scans higher than 650° C. and hence the influence of the deweylite structure on the formation of clinoenstatite relative to forsterite is probably not significant.

Conclusions

Several methods of investigation have been combined in an attempt to elucidate the nature of deweylite based upon samples from Cedar Hill, Pa. All of the methods confirm that deweylite is a member of the serpentine group of minerals closely related to antigorite. It is suggested that both indices of refraction and c_0 are related to molecular water content. Deweylite with at least 4.5% NiO is reported. The onset of the 660° C. endotherm is probably lowered slightly by the presence of this nickel. The nickel is believed to be present in the octahedral site although the evidence from chemical, differential thermal, and *x*-ray powder analyses is far from conclusive. The high ratio of tetrahedral to octahedral cations is offered as an explanation for the predominance of clinoenstatite relative

to forsterite at about 820° C., which is slightly higher than the temperature of forsterite crystallization.

The deweylite structure is similar to that of antigorite with a superlattice probably in the a direction of $8\frac{1}{2}a_0$ although a $3c_0$ superlattice is a plausible alternative. Line broadening is taken to be indicative of the presence of crystallites 100 Å or 200 Å in size. An undulant structure in the ab plane and distortion of atomic linkages associated with octahedral cation holes may be a contributing factor. Analysis of differential thermal, chemical, and x-ray data suggest that the Cedar Hill deweylite may be a dioctahedral variety of antigorite. The alternative explanations of cation stuffing or tetrahedral cation deficiencies to explain the nearly 1:1 ratio of M^{+4} to M^{+2} cations seems less plausible.

Geological evidence indicates that deweylite is of low temperature origin and at Cedar Hill has formed by the alteration of pre-existing serpentine minerals. Physical characteristics suggest formation from a colloidal suspension concomitant with a gradual decrease in the amount of available water.

Pseudomorphs of deweylite after aragonite are discussed and are believed to be the first report of such an occurrence.

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Note added in press: A reddish brown deweylite from Cedar Hill has the following *x*-ray characteristics indicative of a greater dioctahedral character than any previously found:

$$\frac{(002)}{(020)} = \frac{15}{100}, \text{ and } (060) = 1.525 \text{ Å}.$$

A tan deweylite from the Sparvetta quarries one mile west of Nottingham, Pa., associated with serpentinite cut by a feldspar pegmatite, is relatively trioctahedral:

$$\frac{(002)}{(020)} = \frac{85}{100}, \text{ and } (060) = 1.536 \text{ Å}.$$

The indices are $n_\alpha = 1.517 \pm 0.003$ and $n_\beta = 1.523 \pm 0.003$.