A NEW VARIETY OF ANTIGORITE (ORTHO-ANTIGORITE) FROM UNST, SHETLAND ISLANDS

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Abstract

Chemical, x-ray and thermal analyses together with petrographical data are given for specimens of antigorite from Unst, Shetland Islands. The x-ray powder diagrams are indexed on the basis of an ortho-hexagonal cell and the mineral is therefore named "ortho-antigorite" to distinguish it from the monoclinic varieties hitherto described. Evidence is obtained for a superlattice similar to that described by Aruja. The unit cell contains two structural layers and their relative orientation is probably similar to that of the kaolin-type layers in amesite. Structural formulae are derived.

Occurrence and General Characters (O. v. K.)

The antigorites described in this investigation were collected during a geological excursion in Unst, the northernmost of the Shetland Islands, in August 1950. The minerals come from the Nikka Vord chromite quarries north of Baltasound. Attention was attracted particularly to two green resinous-looking serpentine minerals forming irregular veinlets in the chromite-bearing serpentine rock, one associated with magnetite, the other with kämmererite (Cr-chlorite).

Antigorite No. 1, is of olive-green color containing scattered well-developed magnetite crystals as striated dodecahedrons. The surrounding rock is an almost black variety of rock-serpentine with chromite.

Antigorite No. 2, is greenish-yellow in color and usually associated with large, perfect crystals of kämmererite, the latter occurring as six-sided, slightly barrel-shaped prisms. Phillips (1927) describes this latter variety "as a pale lemon-yellow serpentine, apparently of secondary origin." The host rock in this case is a yellowish serpentine, with a moderate chromite content.

In hand specimens both minerals have a massive resinous appearance, without any structural features; they are translucent with a conchoidal fracture, and using the old nomenclature could be classed as precious serpentines.

Thin section examination of antigorite No. 1 revealed no significant textural features, the mineral being too fine-grained.

Antigorite No. 2 appeared to be patchy in ordinary light. In thin section the wavy patches are of brownish shade, whereas on a polished surface they are of a lighter color. With crossed nicols an intricate fine

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banded texture could be seen, in places as wavy fibrous bands, as shown in Pl. I, Fig. 1. The birefringence is very low and sometimes thicker sections are almost isotropic.

The axial figure is obtained with difficulty, but where it is seen the sign is always negative.

The relation between the greenish-yellow antigorite and the surrounding chromite-bearing serpentine rock is of some interest. The vein antigorite is separated from the host rock by a margin of graded kämmererite, relatively coarsely crystalline against the antigorite and becoming gradually finer grained towards the country rock. Large crystals of kämmererite, up to 2 cm. in length, are scattered in the middle of the antigorite vein (Pl. I, Fig. 2). In some specimens brucite is developed to a large extent in this marginal zone, partly replacing kämmererite. Chromite, however, is absent in this zone and the nearest chromite grains are in the host rock facing the kämmererite fringe. They are partly or completely replaced by kämmererite (Pl. I, Fig. 3).

The surrounding chromite-serpentine is otherwise of an antigorite type, with outlines of olivine still clearly visible (Pl. I, Fig. 4).

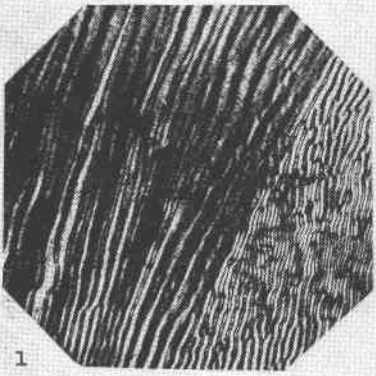
CHEMICAL ANALYSES (O. V. K.)

The two antigorites and the kämmererite were analyzed. The results are shown in Table 1, together with earlier analyses for comparison. The

TABLE 1. CHEMICAL ANALYSES OF ANTIGORITE AND KÄMMERERITE

	1	2	3	4	5
SiO_2	41.65	38.40	41.46	33.23	32.31
TiO_2	none	none	—	—	—
Al_2O_3	0.10	0.10	0.01	10.44	7.50
Fe_2O_3	2.88	3.42	2.42	2.52	—
Cr_2O_3	—	—	—	3.22	7.89
FeO	0.16	none	1.16	—	2.08
MnO	0.05	0.05	0.23	0.02	—
MgO	41.06	41.91	41.76	36.31	32.15
CaO	none	none	tr.	none	3.83
H_2O+	13.10	15.03	12.43	13.40	14.25
H_2O-	1.12	1.26	—	1.22	—
	100.12	100.17	99.47	100.36	100.01

1. Antigorite, No. 1, Nikka Vord quarries, Unst. Analyst, O. v. Knorring.
2. Antigorite, No. 2, same loc. Analyst, O. v. Knorring.
3. Precious serpentine, Niddister, Hillswick Ness. Analyst, M. F. Heddle.
4. Kämmererite, Nikka Vord quarries, Unst. Analyst, O. v. Knorring.
5. Kämmererite, same loc. Analyst, M. F. Heddle.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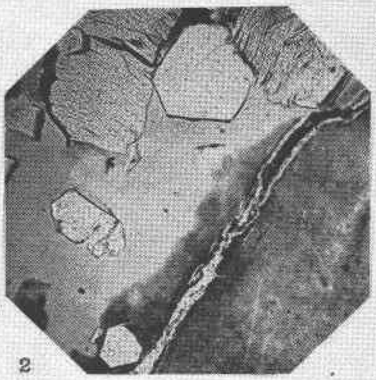
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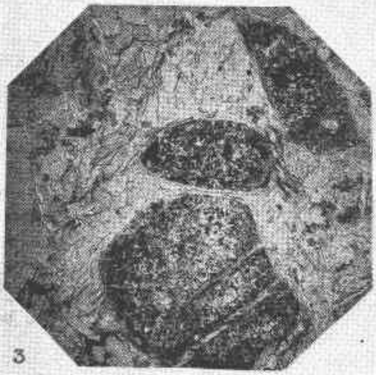
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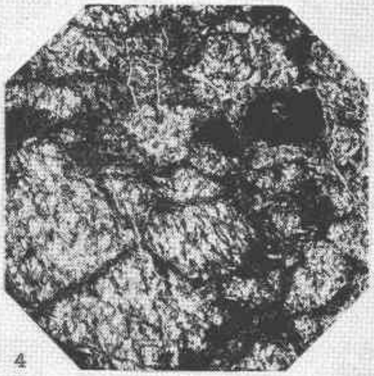
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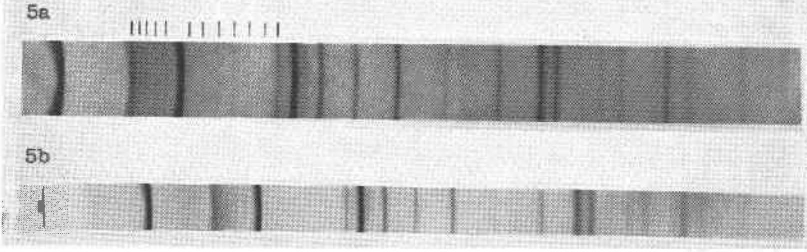

EXPLANATION OF PLATE I

FIG. 1. Wavy thread-like bands of antigorite, No. 2. Crossed nicols. ×33.

FIG. 2. Kämmererite crystals in vein antigorite, No. 2. ×20.

FIG. 3. Chromite crystals replaced by kämmererite. ×33.

FIG. 4. The antigorite rock-serpentine. ×20.

FIG. 5. X-ray powder diagrams of ortho-antigorite, No. 2. (*a*) 19 cm. Unicam camera, CoK_α radiation; the positions of the superlattice lines are indicated. (*b*) 20 cm. semi-focusing camera, CuK_α radiation; the imprint of the incident x-ray beam appears on the left-hand side.

most striking feature is that the iron is trivalent in these antigorites. In antigorite No. 2 further hydration has occurred with a consequent higher water content and much smaller silica. This agrees reasonably well with the patches observed in the mineral. The contents of Cr and Ni were not determined, but judging from the rather small Al value obtained by difference the amounts of Cr and Ni must be rather small.

The kämmererite was analyzed mainly to check an old analysis of the mineral from the same locality. The analysis is far from complete but the result already obtained differs considerably from that of Heddle (1924). The Cr content is much smaller and no Ca was found.

As to the origin of these secondary vein minerals it is usual to consider them as late products, belonging to a hydrothermal phase in connection with the serpentinization of former ultra-basic rocks. In this particular case the original rock was a dunite. The vein antigorites, however, are of primary origin, i.e., crystallized from Mg-rich solutions at a late stage, and are not the result of the serpentinization of olivine.

STRUCTURAL FORMULAE FOR ORTHO-ANTIGORITES, NOS. 1 AND 2

From the analyses in Table 1, Columns 1 and 2, structural formulae may be evaluated. The most reasonable basis of calculation is, in the first place, to assume that O and (OH) ions fill completely the 9 positions assigned to them in the ideal structure, and on this basis, the following formula is obtained:

Antigorite No. 1

$$\underbrace{(\mathrm{Mg}_{2.869}\mathrm{Mn}_{0.002}\overset{2+}{\mathrm{Fe}}_{0.006}\overset{3+}{\mathrm{Fe}}_{0.060})}_{2.937\text{ atoms}}\quad\underbrace{(\mathrm{Si}_{1.954}\mathrm{Al}_{0.005}\overset{3+}{\mathrm{Fe}}_{0.041})}_{2\text{ atoms}}\quad\underbrace{\mathrm{O}_{4.898}(\mathrm{OH})_{4.102}}_{9\text{ atoms}}$$

The Si is almost sufficient to fill the tetrahedral positions; the vacancies are filled mainly by Fe^{3+} ions since Al is almost absent. The octahedral ions number almost 3. Alternatively, the Al and Fe^{3+} ions may be placed wholly in octahedral positions, bringing the total still nearer to 3 (actually 2.983), with 0.046 tetrahedral vacancies. It is usual, however, to consider the tetrahedral positions fully occupied. The main points of interest are: (i) the presence of some tetrahedral Fe^{3+} ions, (ii) a slight excess of (OH) above the theoretical value of 4.0.

The evaluation of the formula for antigorite No. 2 is less straightforward. On the basis of $O+(OH)=9$ atoms, we arrive at the formula:

$$\underbrace{(\mathrm{Mg}_{2.905}\mathrm{Mn}_{0.002})}_{2.907\text{ atoms}}\quad\underbrace{(\mathrm{Si}_{1.786}\mathrm{Al}_{0.005}\overset{3+}{\mathrm{Fe}}_{0.120})}_{1.911\text{ atoms}}\quad\underbrace{\mathrm{O}_{4.338}(\mathrm{OH})_{4.662}}_{9\text{ atoms}}$$

The Si content appears very low and there is insufficient Al and Fe^{3+} to fill the tetrahedral positions. The (OH) content is considerably in excess of 4.0 atoms. An alternative approach may be made on the basis of 2 Si atoms per formula unit and the excess Mg and (OH) may be present as an impurity, $Mg(OH)_2$. This leads to the following:

Antigorite No. 2

$$\underbrace{(Mg_{2.716}Mn_{0.002}Al_{0.006}\overset{3+}{Fe}_{0.134})}_{2.858\text{ atoms}}Si_{2.00}(\underbrace{O_{4.857}OH_{4.143}}_{9\text{ atoms}} + 0.537\ Mg(OH)_2.$$

Some justification for this procedure is provided by the presence of brucite associated with the kämmererite, but there is no *x*-ray or thermal evidence for its presence in the antigorite. The O/OH ratio now tends more nearly to the ideal 5/4 ratio. The deficiency of octahedral ions below 3 is not remarkably low. Without further data, this seems to be the most reasonable interpretation of the chemical analysis of the antigorite No. 2.

X-RAY POWDER ANALYSIS (G. W. B.)

X-ray powder diagrams were obtained with a 19 cm. diameter Unicam instrument and a 20 cm. diameter semi-focusing camera, using CoK_α and CuK_α radiations. In addition to the two antigoirites already described, a further specimen, antigorite No. 3, from the same locality, was also examined. This had a coarsely columnar appearance and a turquoise green color. The specimens were crushed to a fine powder and mounted either dry or with gum tragacanth.

The powder diagrams of the three materials are closely similar. The lines are moderately sharp but at high angles the K_α doublet is not resolved. Some 50 lines could be accurately measured. Antigorite No. 2 gave the clearest diagrams and most of the detailed *x*-ray analysis has been made on this material; typical diagrams are reproduced in Pl. I, Fig. 5. The measured lattice spacings in Å, referred to a mean CoK_α wavelength 1.79020 Å, are listed with their visually estimated intensities in Table 2. The results show very little agreement with powder data previously published by Selfridge (1936) and by Gruner (1937).

An important feature of the diagram which attracts immediate attention is a series of closely and regularly spaced lines of weak intensity extending from about 4.6 Å down to about 2.7 Å; their positions in Fig. 5*a* are indicated. This series is shown particularly well by specimen No. 2, less clearly by No. 3, and is scarcely visible in the diagram of No. 1. Apart from this series, which will be discussed in detail later, all other features of the diagrams are the same for the three specimens and these will be considered first.

TABLE 2. *X*-RAY POWDER DATA FOR ORTHO-ANTIGORITE

I = intensity, estimated visually; B signifies head of a continuous band of scattering.
d = spacing in Å based on $\lambda(\text{CoK}_\alpha) = 1.79020$ Å.
hkl = indices based on the cell $a = b/\sqrt{3}$, $b = 9.219$, $c = 14.53$ Å.
$N20$ or $02N$ series calculated for superlattice parameter $S = 43.8$ Å.

I	d (Obs.)	d (Calc.)	hkl	$N20$ or $02N$ series	
				d (Calc.)	N
10	7.33	7.265	002		
6 B	4.597	4.610	020	4.610	0
				4.584	1
				4.511	2
1	4.403			4.395	3
1	4.250			4.249	4
1	4.088			4.079	5
½	3.903			3.897	6
10	3.662	3.632	004	3.711	7
½	3.528			3.526	8
½	3.348			3.347	9
½	3.172			3.185	10
½	3.015			3.014	11
½	2.865			2.862	12
½	2.720			2.720	13
3	2.623	2.618	201	2.589	14
10	2.502	2.499	202		
1	2.450			2.467	15
1	2.425	2.422	006		
7	2.335	2.332	203		
6	2.149	2.147	204		
				$\vert\Delta d\vert/d$	
7	1.9629	1.9626	205	0.0002	
½	1.8154	1.8162	008	.0005	
1	1.7905	1.7911	206	.0003	
1 B	1.7392	1.7424	240	.0018	
4	1.6360	1.6368	207	.0005	
8	1.5354	1.5367	060	.0008	
7	1.5013	1.5033	062	.0003	
		1.5002	208		
¼	1.4520	1.4530	00, 10	.0007	
2	1.4148	1.4152	064	.0003	
2	1.3793	1.3803	209	.0007	
1	1.3271	1.3252	401	.0014	
5	1.3092	1.3090	402	.0001	
¼	1.2958	1.2975	066	.0013	
½	1.2832	1.2832	403	.0000	
½	1.2759	1.2752	20, 10	.0006	
1	1.2100	1.2108	00, 12	.0003	
		1.2100	405		
¼	1.1819	1.1832	20, 11	.0011	
½	1.1677	1.1664	406	.0011	
½	1.1207	1.1203	407	.0003	
1	1.0736	1.0734	408	.0002	
1	1.0553	1.0558	06, 10	.0005	
½	1.0277	1.0269	409	.0008	
2	0.9963			Mean $\vert\Delta d\vert/d = 0.0006$	
1	0.9763				
2	0.9511				

Unit cell dimensions

The powder diagram bears some resemblance to those of amesite and chamosite, and suggests an hexagonal rather than monoclinic or triclinic cell. Preliminary estimates of the lattice parameters were made as follows: Prominent reflections at 7.26 and 3.63 Å and their higher orders were used to obtain the layer thickness. The *b*-parameter was obtained by taking the strong 1.535 Å reflection as the 060. The base of the cell was assumed to be centered and ortho-hexagonal in shape, so that $a=b/\sqrt{3}$. Similarities with the powder diagram of amesite (Brindley, Oughton and Youell, 1951), suggested that the unit cell may contain two layers. With these parameters the observed reflections, apart from the closely spaced series, were indexed in a convincing manner. The full range of experimental data was now used to determine as accurately as possible the lattice parameters, the final values of which are as follows:

$$a = b/\sqrt{3} = 5.322 \text{ Å}$$
$$b = 9.219 \text{ Å}$$
$$c = 2 \times 7.265 = 14.53 \text{ Å}.$$

The calculated spacings, with their *hkl* indices, are compared with the measured spacings in Table 2. The agreement is everywhere close, particularly for spacings below 2 Å where the agreement is of the order of 0.05%. Many reflections are recorded with the *l* index an odd number, thereby confirming that the unit cell has a *c* parameter of 14.53 Å. It must, therefore, contain two structural layers.

The *k* index, with two exceptions, is 0 or 6. When account is taken of the equivalent ortho-hexagonal indices (see footnote to Table 3), it is seen that *k* takes the values 0, 3 or 6. Absence of other values for *k* may be attributed partly to the small structure factors of many of these reflections, but probably arises largely from random layer displacements parallel to *b* of $nb/3$. The "lines" indexed as 020 and 240 appear to be the terminations of *hk* diffraction bands. A few of the closely spaced lines following the 020 could be indexed as 02*l* lines, but their interpretation is dealt with later.

Comparison with amesite

The unit cell of amesite (Brindley, Oughton and Youell, 1951) has $a=b/\sqrt{3}$, $b=9.17$ and $c=13.98$ kX. The similarity of the *x*-ray reflections from the two minerals is shown by the comparison set out in Table 3. The intensities of overlapping lines in the ortho-antigorite diagram are placed in parentheses. The composition of amesite, as indicated by the formula $(Mg_{1.50}Fe_{0.41}{}^{2+}Al_{1.06})(Si_{1.01}Al_{0.99})O_5(OH)_4$, differs somewhat from that of antigorite and in particular it has a higher iron content. When account is taken of these points, the close similarity between the results leaves little doubt that ortho-antigorite and amesite have very similar and probably identical types of structure.

TABLE 3. COMPARISON OF INTENSITIES OF X-RAY POWDER LINES FROM ORTHO-ANTIGORITE, O, AND AMESITE, A

Indices	Intensities		Indices	Intensities	
hkl	*O*	*A*	*hkl*	*O*	*A*
002	10	10	060	8	6
4	10	10	1	0	0
6	1	2*	2	(7)	2
8	$\frac{1}{2}$	1*	3	0	0
10	$\frac{1}{4}$	$3\frac{1}{2}$*	4	2	$2\frac{1}{2}$*
12	(1)	2	5	0	0
			6	$\frac{1}{4}$	0
			7	0	0
			8	0	0
			9	0	0
200	0	0	10	1	2
1	3	2			
2	10	6	400	0	0
3	7	3*	1	1	0
4	(6)	3	2	5	1
5	7	7	3	$\frac{1}{2}$	1
6	1	4*	4	0	0
7	4	6	5	(1)	1
8	(7)	6+	6	$\frac{1}{2}$	0
9	2	5	7	$\frac{1}{2}$	1
10	$\frac{1}{2}$	3	8	1	1
11	$\frac{1}{4}$	2	9	$\frac{1}{2}$	—

Equivalent indices: $20l \equiv 13l$; $06l \equiv 33l$; $40l \equiv 26l$.

( ) Indicate overlapping ortho-antigorite reflections.

* Overlapping amesite reflections, the observed intensities being shared in the ratio of the calculated intensities.

The closely spaced series of lines

The appearance of this series suggests a long spacing or superlattice such as Aruja (1945) found in his study of single crystals of antigorite. Since the series proceeds from the 020 position, the lines may be of the general type $H20$ or $02L$, the indices H and L corresponding to superlattice parameters along the a and c axes respectively. Both groups of reflections are calculated from an expression of the type

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

where N stands for H or L, and S is the super-spacing along a or c. Close agreement is obtained with the observed spacings with $S = 43.8$ Å and acceptable agreement is obtained with

$$43.5 < S < 44.0.$$

Table 2 gives the calculated $N20$ or $02N$ spacings for $S=43.8$, with N ranging from 0 to 15.

The nature of the superlattice

Aruja (1945) gave for the a parameter of an antigorite from New Zealand the value $a=43.39=8\times5.42$. Since his measurements were made on single crystals, it was clear that the superlattice parameter was in the direction of the a-axis and equal to $8a$. The present value for S, 43.8, is so close to Aruja's value that there is little doubt that it arises in a similar way. However, the present value of a is 5.322 Å and the 8-fold value, 42.58 Å, lies outside the acceptable limits of S. Onsager (1952) suggested an undulating structure with a superlattice parameter of $8\frac{1}{2}a$, in which the additional $\frac{1}{2}a$ is a necessary feature of the undulations. With $a=5.322$ Å, $8\frac{1}{2}a=45.24$ Å which is also well outside the limits for S. For the present ortho-antigorite, the ratio $S/a=8.23$ which is near to $8\frac{1}{4}$. Onsager's model is then applicable if we take $S=16\frac{1}{2}a$ and use even values only for the index H.

An alternative hypothesis is that the superlattice is related to the c parameter, a possible interpretation being

$$S = 3c = 3 \times 14.53 = 43.59 \text{ Å}.$$

A superlattice parameter of $3c$ corresponds to a 6-layer structure, a result which recalls the 6-layer structure of nacrite and the 6-layer mica structures. On this basis, it is evident that superlattice reflections with N a multiple of 3 could be indexed as $02l$ reflections with respect to the small cell.

The available data provided by x-ray powder analysis are insufficient to distinguish between these alternative interpretations of the superlattice parameter S. From a purely numerical standpoint $S=3c$ is the simpler interpretation, but in the light of the unambiguous single-crystal data of Aruja it seems very probable that we have observed a similar superlattice with $S=8\frac{1}{4}a$ or $16\frac{1}{2}a$.

A COMPARISON OF ANTIGORITE STRUCTURES

Four closely related structures have now been suggested for antigorite, namely by Aruja (1945), by Ito (1950), by Midgley (1951), and in the present work. Their principal features are compared in Table 4. While the present structure may be referred to hexagonal axes, it seems preferable to retain the ortho-hexagonal cell and indices to facilitate compari-

TABLE 4. STRUCTURE DATA* FOR ANTIGORITE

	1	2	3	4
a	43.39=8×5.42 kX	5.32 Å	5.29 kX	5.322 Å
b	9.238	9.50	9.18	9.219
c	7.265	14.90	7.45	14.53
β	91.40°	101.9°	91.4°	90.0°
Layer thickness	7.262	7.29	7.45	7.265
Space group	—	*Cm*	*C*2/*m*, *Cm*, *C*2	*C*6$_3$*cm* (?)
Supperlattice parameter	43.39	—	—	43.8
Texture	*b*=fibre axis	*b*=fibre axis	Platy	Massive

* The lattice parameters are given in kX and in Å units; values in kX are converted to Å units by multiplying by 1.002.

(1) Aruja (1945), *Mineral. Mag.*, **27**, 65–74.
(2) Ito (1950), "*X*-ray Studies on Polymorphism" (Tokyo), 160–167.
(3) Midgley (1951), *Mineral. Mag.*, **29**, 526–530.
(4) Present paper.

son between these structures. The probable space group for the ortho-antigorite is that determined for amesite, namely *C*6$_3$*cm*.

THERMAL ANALYSIS (G. W. B.)

Differential thermal analysis curves of antigorites, Nos. 1, 2, and 3, are shown in Fig. 6 together with a comparison curve for kaolinite from Cornwall. Specimens No. 1 and No. 2 give closely similar curves with endothermic peaks at 685° and 690° C. and exothermic peaks at 825° and 840°C. respectively. Specimen No. 3 gives a somewhat different curve with peaks at 720° C. and 845° C., with a marked arrest in the curve at about 790° C. The results are broadly in agreement with data by Caillère and Hénin (1947) for their α-antigorite, by Kauffman and Dilling (1950), by Kiefer (1951), and by Midgley (1951). Kiefer has shown that the exothermic peak tends to be suppressed in unground materials (the so-called β-antigorite of Caillère and Hénin) and to appear prominently after grinding. The materials used in the present work were lightly ground.

The products obtained after heating in the thermal analysis unit to 1000° C. followed by slow cooling in the furnace have been identified by *x*-ray analysis as principally olivine. Additional lines in the powder diagram of the product from specimen No. 3 may be due to enstatite. The agreement with the data for enstatite in the *A.S.T.M.* Index is not exact and rests on three lines only.

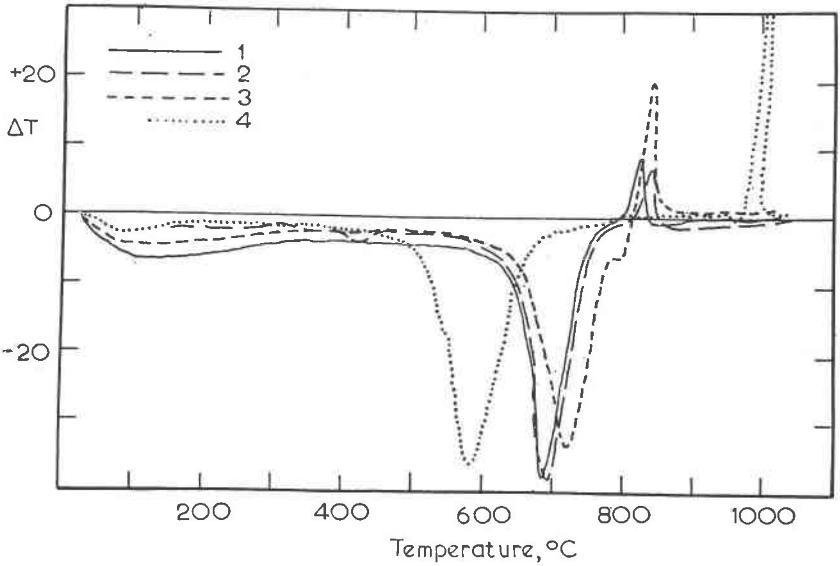

FIG. 6. Differential thermal analysis curves for ortho-antigorites and kaolinite.
——— ortho-antigorite, No. 1; 1.01 gm. specimen.
— — — ortho-antigorite, No. 2; 1.08 gm. specimen.
- - - - - ortho-antigorite, No. 3; 0.89 gm. specimen.
.... kaolinite (Cornwall); 0.36 gm. specimen.

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