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The Effects of Magnesium Fluoride on the Thermal Behavior of Serpentine*

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By means of thermogravimetric, differential thermal, and X-ray diffraction techniques, the thermal behavior of a mixture of serpentine (heated at 730°C for 1 hr.) with 31 per cent magnesium fluoride and or mixtures of serpentine with 10, 15.5, 20, 31, 40, and 62 per cent magnesium fluoride were examined at various temperatures up to 1450°C and for various heating periods. The presence of magnesium fluoride affects the shapes of serpentine thermogravimetric and differential thermal curves, but it hardly affects the starting temperatures of the dehydroxylation of the serpentine (730°C) at all. The thermogravimetric curves showed a gradual weight loss above the dehydroxylation temperature of serpentine. In the differential thermal curves, the height reduction of two serpentine exothermic peaks (830°C and 1100°C), and the appearance of two or three endothermic peaks above 1000°C were observed; moreover, a mixture of the preheated serpentine with 31 per cent magnesium fluoride showed a new exothermic peak at 775°C. These effects of magnesium fluoride were discussed. The main heating products of serpentine in the presence of magnesium fluoride were fluorine norbergite, forsterite, magnesioferrite, and magnesium oxide, whereas those of serpentine alone were forsterite and enstatite.

It is well known that the formation of mullite from kaolinite occurs above 1000°C. Recently Bien and Keyser[1] have shown that mullite can be formed at a temperature as low as 600°C (i. e., immediately after the dehydroxylation of kaolinite) through the action of aluminum fluoride. Locsci[2,3] has also elucidated that aluminum fluoride reacts with kaolinite via an intermediate, topaz $Al_2(F, OH)_2SiO_4$, below 575°C to form $Al_6F_6Si_2O_9$ (veszpremite, metakaolinite fluoride), which decomposes rapidly at 800°C to 900°C to form mullite.

Crystallographically speaking, serpentine is composed of magnesium hydroxylphyllosilicate and is very similar to kaolinite, which is composed of

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[*1] Part XII of "Studies of the Utilization of Serpentine and Olivine."

[1] A. Bien and W. L. Keyser, *Mineral. Mag.*, **4**, 80 (1963).

[2] B. P. Locsci, *Veszpremi Vegyip. Egyet. Kozlemin.*, **6** (3), 217 (1962), *Chem. Abstr.*, **60**, 10250f (1964).

[3] B. P. Locsci, *Keram. Z.*, **16** (6), 350 (1964); *Interceram.*, **1964**, No. 1, 28—29.

aluminum hydroxylphyllosilicate. Therefore, it seems reasonable to assume that magnesium fluoride might contribute to the formation of forsterite and enstatite, which are the stable high-temperature phases of the silica-magnesia system, at a relative lower temperature on the thermal decomposition of serpentine.

Experimental

Materials.—The serpentine used was rock from Kuroishimori (Iwate Prefecture) crushed to powder passable through a 200 mesh sieve with the composition: SiO_2 39.29, Fe_2O_3 7.09, Al_2O_3 2.54, CaO 1.10, MgO 38.02 (ignition loss 12.51, moisture 1.20 per cent). Its thermal behavior was determined by following the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (Figs. 1 and 2 respectively).

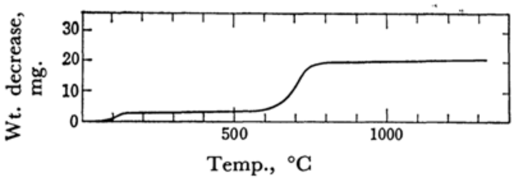

Fig. 1. TGA curve of serpentine.
Sample: 0.3 g.

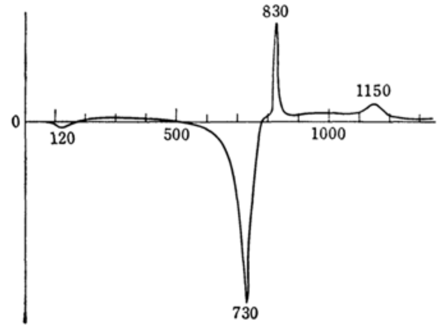

Fig. 2. DTA curve of serpentine.
Sample: 0.890 g.

Figures 1 and 2 indicate that serpentine was endothermally dehydroxylated between 500 and 700°C, and that its original structure was destroyed with a loss in weight and changed exothermally to forsterite and silica at about 800°C without a weight loss.[4-6]

The magnesium fluoride employed was of a G. R. grade of commercial origin (Morita Chemicals Co., Ltd.). Its thermal behavior was shown by TGA and DTA curves (Figs. 3 and 4 respectively), which indicated that the magnesium fluoride hardly changes in weight up to about 790°C, but that it gradually decreases in weight above 790°C and begins to melt at about 1180°C.

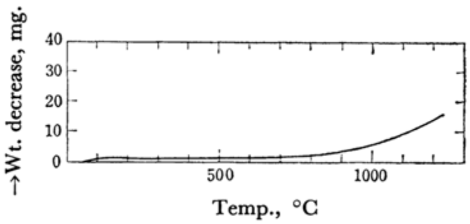

Fig. 3. TGA curve of magnesium fluoride.
Sample: 0.4137 g.

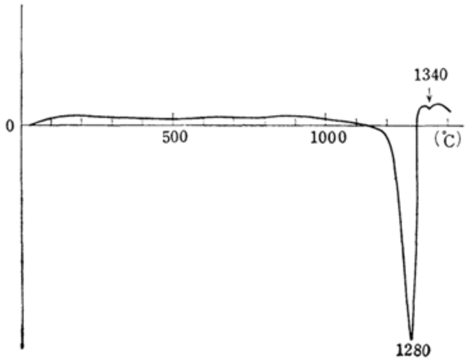

Fig. 4. DTA curve of magnesium fluoride.
Sample: 0.850 g.

Six mixtures of serpentine were prepared, with 10, 15.5, 20, 31, 40, and 62 per cent mangesium fluoride respectively. Moreover, a mixture of the serpentine (heated at 730°C for 1 hr.) was prepared with 31 per cent magnesium fluoride (hereafter referred to as the preheated mixture (31 per cent). These powdered mixtures were homogenized in a dry state. Of these mixtures, those containing 15.5, 31, and 62 per cent magnesium fluoride (hereafter referred to as the 15.5, 31, and 62 per cent mixtures respectively) give materials with the following compositions if it is assumed that serpentine reacts stoichiometrically with magnesium fluoride:

(15.5 per cent) $$2\,Mg_3Si_2O_5(OH)_4 + 2\,MgF_2 \rightarrow 3\,Mg_2SiO_4 + 2\,MgO + SiF_4 + 4\,H_2O$$

(31 per cent) $$Mg_3Si_2O_5(OH)_4 + 2\,MgF_2 \rightarrow Mg_2SiO_4 + 3\,MgO + SiF_4 + 2\,H_2O$$

(62 per cent) $$Mg_3Si_2O_5(OH)_4 + 4\,MgF_2 \rightarrow 7\,MgO + 2\,SiF_4 + 2\,H_2O$$

The ignition losses calculated from these idealized chemical equations are 25.94, 34.87, and 46.38 per cent respectively.

Methods.—A Shimadzu X-ray Diffractometer (GX-A type) with a Geiger Counter was used with Cu$K\alpha$ radiation. The operating conditions were as follows:

Target, Cu; Scatter slit, Not placed;
Filter, Ni; Full scale count, 500 or 1000 c. p. s.;
Voltage, 35 kV.; Scanning speed, 2deg./min.;

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[4] H. Heraldsen, *C. Min. A.*, **1928**, 311; S. Caillire, *Compt. rend.*, **196**, 628 (1933).

[5] R. Kiyoura and Y. Ito, *J. Ceram. Assoc. Japan* (*Yogyo Kyokai Shi*), **16**, 525 (1953).

[6] H. Mase, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **60**, 1502 (1957); **62**, 793, 895 (1959).

Current, 15 m amp.; Time constant, 5 sec.;
Divergence slit, 1 mm.;
2θ range measured, 16—70°;
Receiving slit, 0.25 mm.; Chart speed, 20 mm./min.

The TGA and DTA measurements of the mixtures (15.5 and 31 per cent) were carried out at the Shimadzu Analytical Centre. The operating conditions were as follows:

	TGA	DTA
Neutral material	—	α-Al_2O_3
Atmosphere	Air	Air
Sensitivity	200 mg./full scale	100 μV.
Chart speed	2 min./div.	2 min./div.
Heating velocity	12°C/min.	12°C/min.
Sample holder	TB-2S	BHL-2IV.

However, the sample with 62 per cent magnesium fluoride was measured with a Shimadzu Recording Differential Thermal Analysis Apparatus and its attached Thermobalance (DT-2A and TB-2 types, respectively) in our laboratory. The operating conditions were the same as the above except for the following factors:

	TGA	DTA
Sensitivity	100 mg./full scale	—
Chart speed	4 min./div.	4 min./div.
Heating velocity	10°C/min.	10°C/min.

Results and Discussion

Weight Losses During Heating.—Three mixtures (15.5, 31, and 62 per cent) were examined by TGA. The results obtained are shown in Fig. 5, together with that for a preheated mixture (31 per cent). Figure 5 shows that both the mixtures (15.5 and 31 per cent) have two weight losses in the region up to about 800°C—namely, the dehydration of serpentine and magnesium fluoride between 30 and 130°C, and the dehydroxylation of serpentine starting at about 580°C. When these mixtures are heated above 750°C, gradual weight losses are observed up to about 1450°C, whereas pure serpentine shows no weight loss in this temperature region (Fig. 1). These results suggest that magnesium fluoride may affect the starting temperature of the dehydroxylation of serpentine hardly at all, and that a weight loss above 750°C may be closely related to the thermal changes of magnesium fluoride.

Differential Thermal Analysis and X-Ray Diffraction Analysis.—The presence of magnesium fluoride markedly affects the height of the serpentine endothermic and exothermic peaks. This is well shown by the DTA curves in Fig. 6 obtained for the mixtures with magnesium fluoride. These curves and that for serpentine alone (Fig. 2) resemble one another very closely up to 750°C; in this region, endothermic effects due to the dehydration of serpentine and magnesium fluoride and to the dehydroxylation of serpentine were observed. An increase in the amount of magnesium

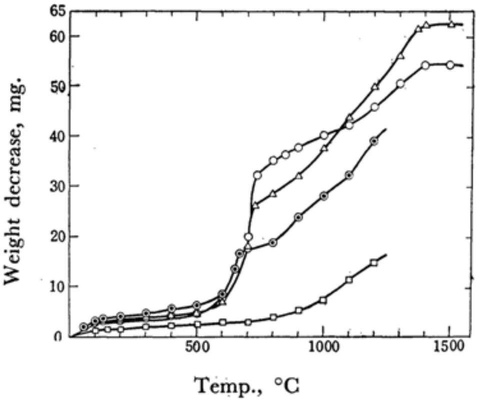

Fig. 5. TGA curves of mixtures of serpentine with magnesium fluoride.

○ 15.5% MgF_2; △ 31% MgF_2;
⊙ 62% MgF_2; □ Preheated mixture (31%)
Sample: 0.3 g.

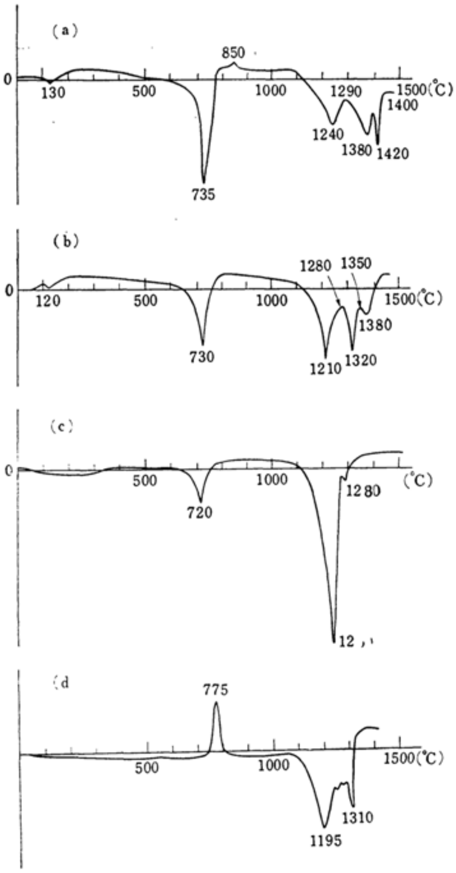

Fig. 6. DTA curves of mixtures of serpentine with magnesium fluoride.

(a) 15.5% MgF_2; Sample: 0.896 g.
(b) 31% MgF_2; Sample: 0.896 g.
(c) 62% MgF_2; Sample: 0.8841 g.
(d) Preheated mixture (31% MgF_2); Sample: 0.805 g.

fluoride markedly reduced the height of the endothermic peak at about 730°C.

With the 15.5 and 31 per cent mixtures, three endothermic peaks appear above 1000°C. Each of these 15.5 per cent mixture peaks was situated at higher temperatures than those of the 31 per cent mixture. On the other hand, the 62 per cent mixture shows a sharp and large endothermic peak near 1250°C and a weak and small endothermic one at 1290°C.

The preheated mixture (31 per cent) shows no endothermic peak below 1000°C, because the serpentine has been completely dehydroxylated, but it does show an exothermic peak at 775°C and two endothermic peaks above 1000°C, which are situated at lower temperatures than those of the 31 per cent mixture. In order to make clear the crystallographic significance of these peaks, each of the

TABLE I. RESULTS OF X-RAY DIFFRACTION ANALYSIS FOR MIXTURES OF SERPENTINE OF PREHEATED SERPENTINE WITH VARIOUS PERCENTAGES OF MAGNESIUM FLUORIDE AND THEIR PRODUCTS HEATED AT VARIOUS TEMPERATURES AND FOR VARIOUS PERIODS*

(1) 10% MgF_2

Raw sample			700°C, 1 hr.			700°C, 2 hr.			800°C, 1 hr.		
19.75°	w	S	19.70°	w	S	17.4°	vw	F	17.4°	w	F
$_{1}$24.65	s	S	$_{1}$24.6	s	S	23.0	vw	F	$_{7}$23.0	m	F
$_{5}$27.4	m	M	$_{4}$27.5	w	M	25.6	vw	F	$_{10}$25.6	w	F
$_{3}$35.75	m	S	$_{2}$36.1	w	S	27.1	vw	M	27.35	vw	M
$_{2}$36.0	m	S	$_{3}$36.9	w	S	$_{5}$32.4	w	F	$_{3}$32.4	m	F
$_{4}$36.8	m	S	40.7	vw	M	$_{1}$35.9	m	F, MF	$_{2}$35.85	m	F, MF
40.6	w	M	53.75	w	M	$_{2}$36.6	m	F	$_{1}$36.65	m	F
53.75	w	M	$_{5}$60.4	w	S	39.9	w	F	$_{6}$39.9	m	F
60.3	w	S	68.3	w	M	$_{3}$40.1	m	M	$_{5}$40.2	m	N
60.7	w	M				40.4	m	M	$_{8}$40.4	m	M
68.35	vw	M				$_{4}$52.6	m	F	41.95	vw	F
						62.1	vw	MF	$_{4}$52.5	m	F
						62.9	w	F	53.65	vw	M
						67.25	vw	F	62.25	w	F
									$_{9}$63.0	w	MF
									67.35	w	F

(2) 15.5% MgF_2

Raw sample			700°C, 1 hr.			800°C, 1 hr.			1070°C, 1 hr.		
19.7°	w	S	19.7°	w	S	17.4°	vw	F	17.4°	w	F
$_{1}$24.6	s	S	$_{1}$24.65	m	S	$_{6}$23.0	w	F	$_{8}$23.0	m	F
$_{2}$27.45	m	M	$_{2}$27.65	w	M	25.75	vw	F	24.0	w	F
$_{4}$36.0	w	S	36.25	w	S	$_{9}$27.35	w	M	$_{10}$29.3	vw	N
36.75	w	S	$_{4}$36.9	w	S	$_{10}$29.3	vw	N	27.0	w	N
$_{3}$40.6	w	M	$_{3}$40.7	m	M	29.9	vw	F	29.85	w	F
43.8	w	M	44.0	w	M	$_{7}$32.4	w	F	30.40	vw	MF
$_{5}$53.75	w	M	$_{5}$53.75	w	M	34.1	vw	N	$_{5}$32.45	m	F
56.5	vw	M	56.5	vw	M	$_{1}$35.85	m	F, MF	$_{1}$35.8	m	F, MF
60.45	w	S	60.5	w	S	$_{2}$36.65	m	F	$_{4}$36.60	m	F
60.8	w	M	60.8	w	M	38.55	vw	N	38.45	vw	N
68.3	w	M	68.3	w	M	39.8	vw	F	39.0	vw	N
						$_{4}$40.15	w	N	$_{9}$39.8	w	F
						$_{3}$40.5	w	M	$_{2}$40.15	m	N
						41.85	vw	F	41.9	vw	F
						43.8	vw	M	$_{7}$52.4	w	F
						$_{5}$52.55	w	F	$_{3}$52.8	m	N
						53.6	w	N	55.1	vw	F
						55.15	vw	F	57.1	vw	N
						$_{8}$63.00	w	MF	57.6	w	MF
						68.25	vw	M	58.95	vw	F, N
						69.75	vw	F	62.05	vw	F
									$_{6}$63.0	w	MF
									67.2	w	F
									69.75	w	F

(TABLE I. continued)

1290°C, 1 hr.			1380°C, 1 hr.			1420°C, 1 hr.		
17.4°	w	F	17.45°	w	F	17.45°	m	F
$_{4}$22.95	w	F	$_{4}$23.0	m	F	$_{5}$22.9	m	F
23.95	w	F	23.95	w	F	$_{9}$23.95	m	F
$_{9}$25.65	w	F	$_{8}$25.6	m	F	$_{8}$25.65	m	F
29.9	w	F	29.9	w	F	29.9	w	F
30.4	vw	MF	30.4	vw	MF	30.4	vw	MF
$_{3}$32.4	m	F	$_{3}$32.45	m	F	$_{3}$32.35	s	F
$_{1}$35.85	s	F, MF	$_{1}$35.8	s	F, MF	$_{1}$35.85	s	F, MF
$_{2}$36.65	s	F	$_{2}$36.65	s	F	$_{2}$36.65	s	F
38.4	vw	N	38.4	vw	N	38.4	w	N
$_{7}$39.8	m	F	$_{7}$39.8	m	F	$_{6}$39.8	m	F
$_{8}$40.15	m	N	$_{6}$40.15	m	N	$_{7}$40.15	m	N
41.9	w	F	41.9	w	F	41.95	w	F
43.5	vw	MF	43.5	vw	MF	43.5	w	MF
$_{5}$52.4	m	F	$_{5}$52.45	m	F	$_{4}$52.45	m	F
55.0	vw	F	55.0	vw	F	55.0	w	F
56.35	vw	F	56.3	w	F	56.35	w	F
57.0	vw	F, N	56.9	w	F, N	56.9	w	F, N
58.9	vw	F, N	58.8	vw	F, N	58.9	w	F, N
$_{10}$62.1	w	F	$_{9}$62.05	w	F	62.1	m	F
$_{6}$63.0	m	MF	$_{10}$62.95	w	MF	$_{10}$63.0	m	MF
67.25	w	F	67.20	w	F	67.2	w	F
69.8	w	F	69.95	w	F	69.65	w	F

(3) 20% MgF_2

Raw sample			700°C, 1 hr.			800°C, 1 hr.		
19.75°	w	S	19.75°	w	S	17.40°	w	F
$_{1}$24.6	s	S	$_{1}$24.6	s	S	$_{10}$23.0	w	F
$_{2}$27.4	m	M	$_{2}$27.4	m	M	24.0	vw	F
$_{4}$35.9	w	S	$_{5}$35.9	w	S	25.5	vw	F
36.8	w	S	36.8	w	S	$_{5}$27.3	m	M
$_{3}$40.6	m	M	$_{3}$40.6	m	M	29.25	w	N
43.8	vw	M	43.8	w	M	29.9	vw	F
$_{5}$53.75	m	M	$_{4}$53.75	m	M	$_{6}$32.4	w	F
56.35	w	M	56.35	vw	M	34.05	vw	N
60.45	w	S	60.45	w	S	$_{3}$35.80	m	F, MF
60.75	w	M	60.75	w	M	$_{2}$36.55	m	F
68.3	w	M	68.3	vw	M	$_{4}$40.15	m	N
						$_{1}$40.50	m	M
						41.80	vw	F
						43.80	vw	M
						$_{7}$52.50	w	F
						$_{8}$53.50	w	M
						56.25	w	M
						57.10	vw	F, N
						60.75	vw	M
						62.10	vw	F
						$_{9}$63.0	w	MF
						68.20	w	M

(Table I. continued)

(4) 31% MgF_2

Raw sample		
19.6°	w	S
$_{2}$24.55	m	S
$_{1}$27.5	s	M
$_{5}$35.75	m	S
36.0	m	S
$_{3}$36.8	w	S
$_{3}$40.6	m	M
43.95	w	M
$_{4}$53.75	m	M
56.5	w	M
60.75	w	M
68.25	w	M

700°C, 1 hr.		
23.1°	vw	F
$_{10}$24.6	w	S
$_{1}$27.4	m	M
32.5	vw	F
$_{4}$35.8	S	S
$_{7}$36.6	w	S
39.8	vw	F
$_{2}$40.5	m	M
$_{5}$43.8	w	M
52.6	vw	F
$_{3}$53.6	w	M
$_{8}$56.5	w	M
$_{9}$60.8	w	M
$_{6}$68.4	w	M

800°C, 1 hr.		
17.4°	w	F
20.4	w	N
21.6	w	N
23.0	w	F
24.0	w	F
24.2	w	F
25.75	w	F
26.9	w	N
$_{6}$27.3	w	M
$_{2}$29.3	m	N
32.4	w	F, N
$_{5}$34.1	w	N
$_{10}$35.75	w	F, MF
$_{8}$36.6	w	F
37.4	w	N
38.6	w	N
$_{4}$40.1	w	N
$_{1}$40.5	m	M
42.0	w	F
43.75	w	M
46.75	w	F, N
49.5	w	N
52.4	w	F
$_{3}$53.2	w	N
$_{7}$53.5	w	N
56.4	w	M
$_{9}$63.2	w	MF
68.2	w	M

1070°C, 1 hr.		
17.25°	vw	N
20.3	vw	N
23.0	vw	F
24.15	vw	F
25.10	vw	F
25.70	vw	F
27.65	w	N
$_{6}$29.25	w	N
$_{8}$29.75	w	F
$_{10}$32.4	w	F, N
$_{9}$33.95	w	N
$_{7}$34.5	w	N
$_{5}$35.8	m	F, MF
36.6	w	F
37.3	vw	N
38.5	vw	N
38.9	w	N
39.25	w	N
$_{1}$40.1	m	N
$_{4}$40.4	m	N
46.8	w	F, N
$_{2}$52.75	m	N
57.15	vw	N
57.65	vw	MF
$_{3}$63.0	w	MF
67.0	w	F

1240°C, 1 hr.		
17.6°	vw	F
22.9	vw	F
$_{10}$24.2	w	F
25.15	w	F
$_{9}$25.7	w	F
26.3	vw	N
27.8	vw	N
$_{8}$29.75	w	F
30.3	vw	MF
$_{6}$32.45	w	F, N
$_{5}$34.5	m	N
$_{3}$35.8	m	F, MF
36.6	vw	F
38.25	vw	N
39.0	w	N
$_{1}$40.1	m	N
42.1	vw	F
$_{7}$43.0	w	O
45.5	vw	N
46.9	vw	F, N
48.2	vw	F
51.0	vw	N
$_{2}$52.75	m	N
57.6	w	N
62.05	w	F
62.4	w	O
$_{4}$63.0	m	MF

1320°C, 1 hr.		
17.45°	w	F
$_{3}$23.0	m	F
23.95	w	F
25.7	w	F
29.8	w	F, N
$_{4}$32.4	w	F, N
$_{1}$35.8	s	F, MF
$_{2}$36.65	s	F
38.35	vw	N
39.0	vw	N
$_{7}$39.8	m	F
$_{8}$40.1	w	N
41.9	w	F
$_{6}$43.1	m	O
$_{5}$52.45	m	F
55.0	w	F
56.3	w	F
56.9	w	N
58.75	vw	F, N
62.1	w	F
$_{10}$62.5	m	O
$_{9}$62.8	m	MF
67.2	w	F
69.8	w	F

1380°C, 1 hr.		
17.45°	m	F
$_{3}$23.0	m	F
24.0	m	F
25.65	m	F
29.9	m	F
$_{4}$32.5	m	F, N
$_{2}$35.8	s	F, MF
$_{1}$36.65	s	F
38.4	vw	N
39.0	vw	N
$_{7}$39.9	m	F
$_{10}$40.2	m	N
42.0	w	F
$_{5}$43.2	m	O
44.7	vw	N
47.0	vw	F, N
48.6	vw	F
50.5	vw	F
$_{6}$52.5	m	F
55.1	vw	F
56.25	w	F
57.0	w	N
58.8	vw	F, N
62.25	m	F
$_{9}$62.55	m	O
$_{8}$62.85	m	MF
67.2	w	F

(TABLE I. continued)

(5) 40% MgF_2

Raw sample			700°C, 1 hr.			1070°C, 1 hr.			1210°C, 1 hr.		
19.6°	w	S	20.9°	vw	N	20.25°	w	N	17.55°	w	F
${}_{3}$24.6	m	S	23.0	vw	F	26.7	w	N	18.5	w	F
${}_{1}$27.35	s	M	${}_{1}$27.35	s	M	${}_{9}$27.5	w	N	${}_{10}$23.1	w	F
36.0	w	S	32.45	vw	F	${}_{1}$29.2	s	N	24.15	w	F
${}_{2}$40.5	s	M	${}_{8}$35.3	w	M	${}_{10}$29.7	w	N	25.8	w	F
43.95	w	M	${}_{7}$35.8	w	F, MF	${}_{5}$33.9	m	N	26.5	vw	N
${}_{4}$53.7	m	M	${}_{9}$36.7	w	F	${}_{7}$35.8	w	F, MF	30.0	w	F
56.4	w	M	${}_{2}$40.5	s	M	${}_{8}$37.3	w	N	${}_{7}$32.6	w	F
60.75	w	M	${}_{5}$43.8	w	M	38.4	w	N	33.8	w	N
${}_{5}$68.3	w	M	52.45	vw	F	39.2	vw	N	${}_{2}$36.0	m	F, MF
			52.7	vw	N	${}_{4}$40.0	m	N	${}_{6}$36.8	m	F
			53.05	vw	N	${}_{2}$40.4	m	N	37.5	w	N
			${}_{3}$53.7	m	M	43.0	vw	O	39.2	w	N
			${}_{6}$56.35	w	M	${}_{6}$52.75	m	N	${}_{9}$39.9	w	F
			${}_{10}$60.8	w	M	${}_{3}$53.0	m	N	${}_{3}$40.15	m	N
			${}_{4}$68.25	w	M	53.75	w	N	42.2	vw	F
									${}_{1}$43.1	m	O
									52.6	w	N
									${}_{4}$52.9	m	N
									54.5	vw	N
									55.1	vw	F
									${}_{8}$62.55	w	O
									${}_{5}$63.0	w	MF
									69.8	w	F

(6) 62% MgF_2

600°C, 5 hr.			700°C, 1 hr.			1070°C, 1 hr.			1250°C, 1 hr.		
24.5°	w	S	23.0°	vw	F	20.25°	w	N	17.5°	vw	N
${}_{1}$27.3	s	M	${}_{1}$27.3	s	M	20.7	vw	N	20.4	vw	N
35.3	w	M	32.25	vw	N	26.75	w	N	20.8	vw	N
35.9	w	S	${}_{7}$35.25	w	M	${}_{3}$27.2	m	M	26.9	vw	N
36.75	vw	S	${}_{9}$35.75	w	MF, F	${}_{8}$27.8	w	N	${}_{3}$27.3	m	M
${}_{2}$40.5	s	M	${}_{10}$36.7	w	F	${}_{2}$29.2	s	N	27.75	m	N
${}_{5}$43.85	w	M	${}_{2}$40.5	s	M	32.25	vw	N	${}_{2}$29.3	s	N
${}_{3}$53.65	m	M	${}_{5}$43.8	w	M	32.9	vw	N	32.4	vw	N
56.3	w	M	52.5	vw	F	${}_{4}$33.85	m	N	${}_{4}$34.0	m	N
60.8	w	S	${}_{3}$53.65	m	M	35.85	vw	F, MF	35.25	vw	M
63.8	vw	M	${}_{6}$56.3	w	M	36.3	vw	N	35.8	vw	F, MF
${}_{4}$68.3	m	M	${}_{8}$60.75	w	M	${}_{9}$37.3	w	N	36.6	vw	N
			63.7	vw	M	${}_{10}$38.4	w	N	37.5	w	N
			${}_{4}$68.2	w	M	${}_{7}$39.85	w	F	38.7	w	N
						${}_{1}$40.5	s	M	${}_{8}$40.1	m	N
						42.9	vw	O	${}_{1}$40.5	s	M
						43.75	w	M	${}_{9}$43.0	m	O
						46.75	vw	F, N	43.9	w	F, N
						49.5	vw	N	46.9	vw	F, N
						52.8	w	N	52.9	w	N
						${}_{5}$53.0	m	N	${}_{5}$53.25	m	N
						${}_{6}$53.4	m	M	${}_{6}$53.6	m	M
									56.3	vw	M
									57.9	vw	MF
									62.4	w	O
									${}_{7}$63.1	m	MF
									64.2	w	M
									${}_{10}$68.2	w	M

(TABLE I. continued)

(7) Heated Serpentine + MgF_2 (31%)

Raw sample			775°C, 1 hr.			1075°C, 1 hr.			1195°C, 1 hr.		
17.4°	vw	F	17.4°	vw	F	17.35°	w	F	17.4°	w	F
$_{9}$23.0	w	F	20.5	vw	N	20.5	w	N	18.4	w	N
24.0	vw	F	21.0	vw	N	20.8	w	N	$_{8}$23.05	m	F
25.6	vw	F	23.0	w	F	24.4	vw	F	24.0	w	F
$_{1}$27.4	s	M	24.05	vw	F	26.95	w	N	25.7	w	F
30.0	vw	F	25.65	w	F	27.4	w	M	26.45	vw	N
$_{10}$32.5	w	F	26.85	vw	N	$_{10}$27.8	w	N	29.3	w	N
$_{6}$35.8	w	F, MF	$_{2}$27.35	m	M	$_{1}$29.35	s	N	30.4	w	MF
$_{5}$36.7	w	F	$_{6}$29.3	w	N	32.5	vw	F, N	$_{5}$32.5	m	F, N
39.85	w	F	29.85	w	N	$_{4}$34.1	s	N	33.75	w	N
$_{3}$40.5	s	M	$_{8}$32.5	w	F, N	35.85	w	F, MF	34.85	w	F
41.9	vw	F	34.1	w	N	36.55	w	N	$_{1}$35.85	s	F, MF
$_{7}$43.8	w	M	$_{5}$35.85	w	F, MF	$_{8}$37.5	w	N	$_{4}$36.7	m	F
52.45	w	F	$_{4}$36.7	m	F	$_{9}$38.7	w	N	38.45	vw	N
$_{2}$53.75	s	M	37.6	vw	N	39.35	w	N	39.1	w	N
$_{8}$56.4	w	M	38.6	vw	N	$_{5}$40.15	vw	N	$_{9}$39.8	w	F
60.8	w	M	$_{7}$40.2	w	N	$_{2}$40.6	s	M	$_{2}$40.2	m	N
63.8	vw	MF	$_{1}$40.6	s	M	44.75	vw	N	42.0	w	F
$_{4}$68.25	w	M	41.9	vw	F	46.95	w	N	$_{7}$43.1	m	O
			$_{10}$43.95	w	M	49.75	w	F, N	46.9	vw	F, N
			$_{9}$52.6	w	F	52.6	w	F	48.65	vw	F
			53.3	w	N	$_{7}$53.0	w	N	$_{3}$52.85	m	F
			$_{3}$53.65	m	M	$_{3}$53.3	s	N	55.1	vw	F
			55.15	vw	F	55.8	vw	N	56.35	vw	M
			56.35	w	M	56.3	vw	M	57.1	w	N
			60.8	vw	M	57.95	w	N, F	59.0	vw	N, F
			63.15	w	MF	58.6	w	M	62.15	w	F
			68.25	w	M	60.85	vw	M	$_{10}$62.45	w	O
						$_{6}$63.15	m	F	$_{6}$63.0	m	MF
						68.25	w	M	67.25	w	F
									69.35	w	F

* In this table, the very weak diffraction lines were omitted except when the special need was not seen. Moreover, the figures prefixed in small prints stand for the order in intensity for the main ones. For each specimen:

ffrst column: 2 (°),
second column: intensity of diffraction
(abbr.) s, strong; m, middle; w, weak; vw, very weak
third column: identifiication
(abbr.) S, serpentine; M, magnesium fluoride; F, forsterite;
MF, magnesioferrite; N, fluorine norbergite; O, magnesium oxide

X-ray diffraction data for the raw sample with 62 per cent magnesium fluoride were omitted because those were almost identical with the raw sample with 40 per cent magnesium fluoride.

mixtures was heated at various temperatures and for various heating periods, and then quenched in air. These were then examined by X-ray diffraction analysis. The results are illustrated in Table I.

An Endothermic Effect between 600 and 800°C.—As has been mentioned above, no changes occur below about 600°C except for the dehydration of mixtures occurring below about 200°C. In the case of the 62 per cent mixture, no changes occurred even when it was heated at 600°C for 5 hr. (Table I).

As is generally known, the principal reaction occurring between 600 and 800°C is the dehydroxylation of serpentine; however, in the presence of magnesium fluoride, the following reactions appear to occur successively.

The Formation of Fluorine Norbergite ($Mg_2SiO_4 \cdot MgF_2$).7)—All the mixtures always gave the characteristic diffraction peaks of fluorine norbergite

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7) W. Eitel, "The Physical Chemistry of the Silicates," The University of Chicago Press, Chicago (1952), p. 873.

TABLE II. THE X-RAY DIFFRACTION DATA OF THE PRODUCTS HEATED IMMEDIATELY BELOW AND BEYOND AN EXOTHERMIC PEAK (775°C) OF A MIXTURE OF THE PREHEATED SERPENTINE WITH 31 PER CENT MAGNESIUM FLUORIDE*

700°C			850°C		
17.5°	vw	F	17.4°	vw	F
			20.3	vw	N
			20.7	vw	N
			21.5	vw	N
22.95	vw	F	23.0	w	F
23.85	vw	F	24.0	w	F
25.6	vw	F	25.6	vw	F
			26.8	vw	N
${}_{1}27.3$	s	M	${}_{2}27.3$	m	M
			29.25	w	N
29.9	vw	F			
30.1	vw	MF			
32.3	vw	F	${}_{8}32.4$	w	N, F
			33.25	vw	N
			34.0	vw	N
${}_{9}35.3$	w	M	35.3	vw	M
${}_{6}35.8$	w	F, MF	${}_{5}35.8$	w	F, MF
${}_{4}36.8$	w	F	${}_{4}36.75$	w	F
			37.4	vw	N
			38.5	vw	N
39.75	vw	F			
			${}_{9}40.1$	w	N
${}_{2}40.5$	m	M	${}_{1}40.5$	m	M
			41.8	vw	F
${}_{7}43.85$	w	M, MF	43.85	vw	MF
47.2	vw	M	47.0	vw	M
${}_{10}52.4$	w	F	${}_{6}52.5$	w	F
			${}_{7}53.2$	w	N
${}_{3}53.65$	m	M	${}_{3}53.85$	w	M
54.9	vw	F			
${}_{8}56.3$	w	M	${}_{10}56.3$	w	M
			57.0	vw	F
60.75	w	M			
			62.1	vw	F
			63.05	vw	MF
63.7	vw	M			
${}_{5}68.2$	w	M	68.2	vw	M
69.5	vw	F	69.6	vw	F

* The figures and abbreviations are all the same as those in Table I.

when heated at 700°C or 800°C for 1 hr. The mixtures with higher contents of magnesium fluoride (e. g., 40 or 62 per cent) formed fluorine norbergite at 700°C for 1 hr., while, on the contrary, those with lower contents of magnesium fluoride (10, 15.5, 20, or 31 per cent) formed fluorine norbergite at 800°C for 1 hr. However, even in the latter cases, the serpentine has been dehydroxylated by heating at 700°C and above for 2 hr. Therefore, it is evident that a larger amount of magnesium fluoride facilitates the formation of fluorine norbergite at lower temperatures. As is shown in Table I, the number and intensity of the characteristic peaks of fluorine norbergite decrease with the amount of magnesium fluoride and with the rise in the heating temperatures; namely, its diffraction peaks were intensified as the heating temperature was elevated, showing maximum values at about 1000°C, but being generally reduced above 1070°C. However, the 62 per cent mixture formed a product chiefly consisting of fluorine norbergite when treated even at 1250°C for 1 hr., although the 10 per cent mixture gave a product mainly consisting of forsterite when treated at 800°C for 1 hr.

The preheated mixture (31 per cent) displayed an exothermic peak at 775°C, without any endothermic effect below 1000°C on its DTA curve. The product heated at 775°C for 1 hr. clearly showed the presence of fluorine norbergite; furthermore, the product heated immediately beyond the exothermic peak temperature (850°C) showed the absence of fluorine norbergite (Table II). Therefore, the formation of fluorine norbergite appears to be exothermic.

As has been mentioned above, the endothermic peak due to the dehydroxylation of serpentine at about 730°C was reduced with an increase in the amount of magnesium fluoride. This seems to be due not only to the decreased amount of serpentine, but also, at the same time, to the overlapping of the exothermic effect of the formation of fluorine norbergite. In other words, the forsterite formed endothermally on the dehydroxylation of serpentine probably immediately combines with magnesium fluoride under the evolution of heat. The forsterite which is then formed, at the moment of the birth (in statu nascendi), appears to be in a specially active state. From this point of view, the mixtures of serpentine with magnesium fluoride appear to form fluorine norbergite at a temperature lower than 775°C—immediately after the dehydroxylation of serpentine.

$$2\ Mg_3Si_2O_5(OH)_4 \rightarrow 3\ Mg_2SiO_4 + SiO_2 + 4\ H_2O \qquad (1)$$

$$Mg_2SiO_4 + MgF_2 \rightarrow Mg_2SiO_4 \cdot MgF_2 \qquad (2)$$

The Formation of Magnesioferrite ($MgFe_2O_4$).—Magnesioferrite was formed from all the mixtures of serpentine with magnesium fluoride at about 700°C or 800°C for 1 hr., and from serpentine alone at 730°C for 1 hr. The formation temperature of magnesioferrite agreed approximately with those of forsterite and fluorine norbergite. In general, the characteristic X-ray diffraction peaks of magnesioferrite were observed more clearly and more sharply in the presence of magnesium fluoride than those of serpentine alone. It seems likely that magnesium fluoride may accelerate the crystal growth of magnesioferrite.

Magnesioferrite is formed principally according to the following reaction:

$$MgO+Fe_2O_3 \rightarrow MgFe_2O_4 \qquad (3)$$

where magnesium oxide is a component of the intermediate, unstable phase ($Mg_3Si_2O_7$) which had resulted from the dehydroxylation of serpentine,4,6) and where ferric oxide is one of the impurities of serpentine.

Various Reactions between 800 and 1100°C.—As is generally known, serpentine shows two exothermic peaks in this temperature region; the first one, at about 830°C, is attributed to the crystal growth of forsterite, and the second, at about 1100°C, to the formation of enstatite. In the presence of magnesium fluoride, both these exothermic peaks exhibit a tendency to be reduced or to disappear with an increase in the amount of magnesium fluoride.

The disappearance of the first peak is due to Reaction 2—the conversion of forsterite into fluorine norbergite—at about 775°C.

The Hydrolysis of Magnesium Fluoride and Related Phenomena.—A plausible explanation for the disappearance of the second peak is as follows.

The water vapor evolved on the dehydroxylation of serpentine—Reaction 1—appears to react with a part of the magnesium fluoride to produce magnesium oxide, together with hydrogen fluoride, which perhaps successively attacks the serpentine

TABLE III. WEIGHT LOSSES AND X-RAY DIFFRACTION DATA FOR THE HEATED PRODUCTS OF SOME MIXTURES OF RAW AND HEATED SERPENTINE WITH MAGNESIUM FLUORIDE*

(1) 15.5% MgF_2

Heating temp., °C	1000		1290		1400		1450
Weight loss, %	12.20		17.22		18.24		21.95
Difference in weight loss, %		5.02		1.02		3.71	

X-Ray diffraction data

1000°C			1290°C			1400°C			1450°C		
17.4°	w	F	17.4°	w	F	17.4°	w	F	17.4°	m	F
20.6	vw	N				20.7	vw	N	20.7	vw	N
$_{6}$23.0	m	F	$_{3}$22.9	m	F	$_{3}$23.0	m	F	$_{4}$22.95	m	F
23.9	w	F	$_{10}$23.9	w	F	23.9	w	F	23.95	w	F
$_{10}$25.7	w	F	25.6	w	F	$_{9}$25.6	w	F	$_{10}$25.6	w	F
27.3	vw	M									
29.25	vw	N									
29.9	w	F	29.9	w	F	29.85	w	F	29.9	w	F
			30.4	vw	MF	30.4	vw	MF	30.5	vw	MF
$_{3}$32.4	m	F, N	$_{4}$32.3	m	F, N	$_{4}$32.4	m	F, N	$_{3}$32.4	s	F, N
34.0	vw	N									
$_{1}$35.8	m	F, MF	$_{1}$35.75	s	F, MF	$_{2}$35.8	s	F, MF	$_{2}$35.8	s	F, MF
$_{2}$36.7	m	F	$_{2}$36.6	s	F	$_{1}$36.7	s	F	$_{1}$36.65	s	F
38.4	vw	N	38.4	vw	N	38.4	vw	N	38.4	vw	N
39.25	vw	N	38.9	vw	N	39.0	vw	N	38.9	vw	N
$_{7}$39.8	w	F	$_{6}$39.8	m	F	$_{6}$39.8	m	F	$_{6}$39.75	m	F
$_{4}$40.1	m	N	$_{7}$40.15	m	N	$_{7}$40.1	m	N	$_{7}$40.15	m	N
40.5	w	M									
41.9	vw	F	41.8	w	F	41.9	w	F	41.8	w	F
			43.0	vw	O	43.0	vw	O	43.0	vw	O
			43.4	vw	MF	43.4	vw	MF	43.6	vw	MF
44.7	vw	F, N	44.75	vw	F, N	44.6	vw	F, N	44.75	vw	F, N
46.8	vw	F, N	46.7	vw	F, N	46.6	vw	F, N	46.75	vw	F, N
			48.6	vw	F	48.6	vw	F	48.5	vw	F
$_{5}$52.5	m	F	$_{5}$52.4	m	F	$_{5}$52.4	m	F	$_{5}$52.4	m	F
55.1	vw	F	55.1	vw	F	55.1	vw	F	55.1	vw	F
57.0	vw	F, N	57.0	vw	F, N	56.9	vw	F, N	57.0	vw	F, N
						57.5	vw	MF	57.5	vw	MF
58.75	vw	F, N	58.7	vw	F, N	58.75	vw	F, N	58.75	vw	F, N
$_{9}$62.15	vw	F	$_{9}$62.0	w	F	$_{8}$62.0	w	F	$_{9}$62.1	w	F
$_{8}$62.9	vw	MF	$_{8}$62.8	w	MF	$_{10}$63.0	w	MF	$_{8}$62.8	m	MF
64.0	vw	M									
67.2	vw	F	67.2	vw	F	67.2	vw	F	67.2	vw	F
69.75	vw	F	69.8	vw	F	69.6	w	F	69.8	w	F

(TABLE III. continued)

(2) 31% MgF_2

Heating temp., °C	1000		1280		1350		1440
Weight loss, %	12.61		20.19		20.42		20.50
Difference in weight loss, %		7.56		0.32		0.08	

X-Ray diffraction data

1000°C			1280°C			1350°C			1440°C		
17.25°	vw	N									
17.4	w	F	17.4°	w	F	17.4°	w	F	17.4°	w	F
20.4	vw	N									
			20.7	vw	N	20.7	vw	N	20.7	vw	N
21.4	vw	N									
22.9	vw	F	$_{8}$22.9	m	F	$_{3}$22.9	m	F	$_{3}$22.95	m	F
23.9	vw	F	24.0	w	F	23.9	w	F	23.95	w	F
25.45	vw	F									
			25.7	w	F	25.6	w	F	25.6	w	F
26.8	vw	N									
27.3	vw	M									
27.7	vw	N									
$_{2}$29.25	m	N									
29.8	vw	F	29.9	w	F	29.9	w	F	29.9	w	F
			30.3	vw	MF	30.3	vw	MF	30.3	vw	MF
$_{10}$32.4	vw	F, N	$_{4}$32.4	m	F, N	$_{4}$32.4	m	F, N	$_{4}$32.4	m	F, N
33.25	vw	N									
$_{6}$34.0	m	N									
$_{8}$35.8	w	F, MF	$_{1}$35.8	s	F, MF	$_{2}$35.75	s	F, MF	$_{1}$35.8	s	F, MF
$_{9}$36.8	vw	F	$_{2}$36.7	s	F	$_{1}$36.6	s	F	$_{2}$36.6	s	F
37.4	vw	N									
38.5	vw	N	38.4	vw	N	38.3	vw	N	38.35	vw	N
			39.0	vw	N	38.9	vw	N	39.05	vw	N
39.25	vw	N									
			$_{7}$39.8	m	F	$_{7}$39.75	m	F	$_{8}$39.8	m	F
$_{3}$40.15	m	N	$_{6}$40.1	m	N	$_{8}$40.1	m	N	$_{9}$40.1	m	N
$_{1}$40.4	m	M, N									
41.9	vw	F	41.9	w	F	41.9	w	F	41.9	w	F
			$_{8}$43.1	m	O	$_{6}$43.0	m	O	$_{6}$43.1	m	O
44.7	vw	N	44.7	vw	N	44.7	vw	N	44.6	vw	N
46.8	vw	F, N	46.75	vw	F, N	46.75	vw	F, N	46.75	vw	F, N
			48.55	vw	F	48.6	vw	F	48.55	vw	F
49.6	vw	M									
									50.6	vw	F
			51.0	vw	N	51.1	vw	N	51.0	vw	N
$_{5}$52.6	m	F	$_{5}$52.5	m	F	$_{5}$52.4	m	F	$_{5}$52.4	m	F
$_{4}$53.2	m	M									
			55.0	vw	F	55.0	vw	F	55.0	vw	F
56.4	vw	F	56.3	w	F	56.2	vw	F	56.25	vw	F
57.1	vw	N	57.0	w	N	56.9	vw	F	56.95	vw	F
									57.6	vw	MF
			58.9	vw	F, N	58.8	vw	F, N	58.9	vw	F, N
62.25	vw	F	62.1	w	F	62.2	w	F	62.25	w	F
			$_{10}$62.5	w	O	$_{10}$62.5	w	O	$_{10}$62.6	m	O
$_{7}$63.0	w	MF	$_{9}$62.9	m	MF	$_{9}$62.8	m	MF	$_{7}$62.85	m	MF
64.0	vw	M									
			67.2	vw	F	67.2	vw	F	67.15	w	F
			69.8	w	F	69.75	w	F	69.8	w	F

(Table III. continued)

(3) 62% MgF_2

Heating temp., °C	1050		1280		1360
Weight loss, %	5.50		18.67		19.50
Difference in weight loss, %		13.17		0.83	

X-Ray diffraction data

1050°C			1280°C			1360°C		
17.3°	vw	N, F	17.3°	w	N, F	17.3°	w	N, F
20.3	vw	N	20.35	vw	N	20.4	vw	N
20.8	vw	N	20.75	vw	N	20.85	vw	N
21.5	vw	N	21.5	vw	N			
						25.7	vw	F
26.8	w	N	26.8	w	N	26.8	vw	N
$_{2}$27.3	s	M, N	27.3	w	N, M	27.3	vw	N, M
$_{8}$27.65	m	N	27.7	w	N	27.7	vw	N
$_{4}$29.3	m	N	$_{2}$29.3	s	N	$_{7}$29.3	m	N
						29.75	vw	F
32.4	vw	N, F	32.35	vw	N, F	32.5	w	F, N
$_{5}$34.0	m	N	$_{6}$34.0	m	N	$_{10}$34.0	w	N
35.25	vw	M						
35.75	vw	F, MF	35.65	w	F, MF	35.85	w	F, MF
36.4	vw	N, F	36.5	vw	N, F	36.6	vw	F, N
			37.0	vw	O	37.1	w	O
37.4	w	N	$_{10}$37.5	w	N	37.4	vw	N
38.5	w	N	38.6	w	N	38.6	vw	N
39.3	vw	N	39.3	vw	N	39.3	vw	N
$_{7}$40.0	w	N	$_{8}$40.1	m	N	$_{6}$40.2	m	N
$_{1}$40.5	s	M	$_{3}$40.5	m	M	$_{2}$40.45	m	M, N
			41.4	vw	N			
			$_{1}$43.05	s	O	$_{1}$43.05	s	O
43.8	w	M	43.8	w	M, MF	43.8	vw	MF, M
44.75	vw	N	44.6	vw	N			
46.7	vw	N	46.75	w	N	46.9	w	N
49.4	vw	N	49.4	vw	N			
52.8	w	N, F	$_{9}$52.95	w	N, F	$_{9}$52.85	m	F, N
$_{6}$53.2	m	M, N	$_{5}$53.3	m	N, M	$_{8}$53.2	m	N, M
$_{3}$53.6	m	N	53.6	m	N	53.6	m	N
						53.9	w	MF
55.7	vw	N, M	55.75	vw	N, M			
56.4	w	M	56.4	vw	M			
57.25	vw	N	57.25	vw	N	57.2	vw	N
58.5	vw	N, F	58.6	vw	N, F	58.5	vw	N, F
60.7	w	M	60.75	vw	M	60.7	vw	M
						$_{4}$62.4	m	F
			$_{4}$62.55	m	O	$_{3}$62.5	m	O
$_{9}$63.1	w	MF	$_{7}$63.15	m	MF	$_{5}$63.05	m	MF
64.1	w	M	64.15	w	M	64.0	vw	M
66.75	vw	M						
			66.9	vw	F	67.0	vw	F
67.8	vw	M	67.8	vw	M			
$_{10}$68.2	vw	M	68.3	vw	M	68.3	vw	M
			69.4	vw	F	69.4	vw	F

(TABLE III. continued)

(4) Heated serpentine with 31% MgF_2

Heating temp., °C	1000		1280		1350
Weight loss, %	4.24		7.67		7.90
Difference in weight loss, %		3.43		0.23	

X-Ray diffraction data

1000°C			1280°C			1350°C		
17.3°	vw	F, N	17.4°	w	F	17.4°	w	F
20.35	vw	N						
22.95	vw	F	$_{3}$22.9	m	F	$_{3}$23.0	m	F
23.9	vw	F	23.95	w	F	24.0	w	F
25.7	vw	F	25.65	w	F	25.7	w	F
27.1	w	M						
27.7	vw	N						
$_{2}$29.25	m	N						
			29.85	w	F	29.9	w	F
30.3	vw	MF	30.4	vw	MF			
32.4	vw	N, F	$_{4}$32.4	m	F, N	$_{4}$32.4	w	F, N
33.25	vw	N						
$_{7}$34.0	m	N						
$_{8}$35.8	w	F, MF	$_{1}$35.8	s	F, MF	$_{2}$35.8	s	F, MF
$_{9}$36.6	w	F	$_{2}$36.65	s	F	$_{1}$36.7	s	F
37.4	vw	N						
38.5	vw	N	38.35	vw	N	38.4	vw	N
			39.0	vw	N	39.0	vw	N
			$_{9}$39.8	w	F	$_{7}$39.8	m	F
$_{4}$40.15	m	N	$_{7}$40.15	m	N	$_{8}$40.15	m	N
$_{1}$40.5	m	M						
41.85	vw	F	41.9	vw	F	41.9	w	F
			$_{6}$43.15	m	O	$_{6}$43.1	m	O
43.85	vw	M						
44.7	vw	N	44.9	vw	N	44.75	vw	N
46.75	vw	N	46.8	vw	N	46.75	vw	N
						48.5	vw	F
49.7	vw	N						
						50.4	vw	F
$_{5}$52.5	m	F	$_{5}$52.5	m	F	$_{5}$52.4	m	F
$_{3}$52.85	m	N						
$_{10}$53.15	m	N						
53.5	w	N						
55.0	vw	F	55.2	vw	F	55.0	w	F
			56.4	vw	F	56.3	w	F
57.2	vw	N	57.0	vw	F	57.0	w	F
			57.6	vw	MF, N	57.6	vw	MF, N
58.4	vw	N						
			58.75	vw	F	58.9	vw	F
59.65	vw	N						
60.75	vw	M						
			62.1	w	F	62.25	w	F
			$_{10}$62.5	w	O	$_{10}$62.5	m	O
$_{6}$63.1	m	MF	$_{8}$62.95	m	MF	$_{9}$62.8	m	MF
67.1	vw	F	67.2	vw	F	67.15	w	F
69.7	vw	F	69.85	w	F	69.8	w	F

* The figures and abbreviations used in X-ray diffraction data are all the same as those in Table I.

or amorphous silica and forsterite resulting from Reaction 1:

$$MgF_2+H_2O \rightarrow MgO+2\ HF \tag{4}$$

$$SiO_2+4\ HF \rightarrow SiF_4+2\ H_2O \tag{5}$$

$$Mg_2SiO_4+8\ HF \rightarrow 2\ MgF_2+SiF_4+4\ H_2O \tag{6}$$

$$Mg_3Si_2O_5(OH)_4+14\ HF \rightarrow 3\ MgF_2+2\ SiF_4+4\ H_2O \tag{7}$$

The following reaction also appears to occur at that time:

$$2\ MgO+SiO_2 \rightarrow Mg_2SiO_4 \tag{8}$$

This reaction is a combination of magnesium oxide and silica in the amorphous state, and it appears to be accelerated by the hydrogen fluoride and silicon tetrafluoride resulting from Reactions 4—7.8) The product, forsterite, successively reacts with magnesium fluoride to form fluorine norbergite —Reaction 2, or with hydrogen fluoride—Reaction 6.

According to Sychev,8) pure magnesium fluoride does not show any volatilization between 800 and 1300°C, but water vapor present in the furnace atmosphere hydrolyzes it rapidly, forming magnesium oxide. Therefore, Reaction 4—the hydrolysis of magnesium fluoride—was expected to progress rapidly, but magnesium fluoride remained in the free state when heated up to 1070°C for 1 hr. In addition, the preheated mixture (31 per cent) also contained the free magnesium fluoride, even when heated at 1075°C for 1 hr., because the constitutional water of serpentine had almost all been lost.

The X-ray diffraction data of the heated mixtures (Table I) showed that magnesium fluoride exists partly in the form of fluorine norbergite and partly in the free state. However, the free magnesium fluoride disappeared entirely at about 1070°C, except for the 62 per cent mixture. It is worth noticing that the X-ray diffraction peaks of magnesium oxide distinctly appeared immediately after the magnesium fluoride had disappeared. This indicates that the hydrolysis of magnesium fluoride—Reaction 4—progresses completely in practice at 1070°C for 1 hr., and that the thermal change of magnesium fluoride is very closely related to the formation of magnesium oxide. However, this reaction seems to progress gradually to a slight degree in the region between about 730 and 1070°C, as is shown by the gradual weight decrease above 730°C on the TGA curves (Fig. 5).

The Formation of Magnesium Oxide and Forsterite. —The mixtures with comparatively large amounts of magnesium fluoride formed magnesium oxide above about 1070°C. The X-ray diffraction peaks of magnesium oxide were especially clearly confirmed in the mixtures with 31 per cent and more magnesium fluoride; on the contrary, its formation was not clear in the mixtures with 20 per cent and less magnesium fluoride. In the case of serpentine alone, no formation of magnesium oxide was observed in this temperature region. Thus magnesium oxide results from the hydrolysis of magnesium fluoride according to Reaction 4, and a part of it successively reacts with the amorphous silica formed on the dehydroxylation of serpentine —Reaction 1 — to produce forsterite according to Reaction 8.

The disappearance of the second exothermic peak of serpentine at 1100°C seems to be caused by the interaction of amorphous silica with magnesium oxide or hydrogen fluoride—Reaction 8 or 5, because the amorphous silica plays an important role in the formation of enstatite ($SiO_2+Mg_2SiO_4 \rightarrow 2\ MgSiO_3$).

Two or Three Endothermic Effects above 1000°C.—In order to elucidate these effects, the 15.5, 31, and 62 per cent mixture and the preheated mixture (31 per cent) were heated just below and beyond these peak temperatures. They were then examined in term of their weight losses (and fluorine contents in the case of the 31 per cent mixture only), and by X-ray diffraction. The results are summarized in Table III.

Table III shows that the first endothermic peak in the temperature region above 1000°C is most closely related to the remarkable decrease in weight (and the fluorine contents*). Moreover, just beyond these peak temperatures, none of the mixtures contained magnesium fluoride except for the 62 per cent mixture, and none formed magnesium oxide except for the 15.5 per cent mixture.** Therefore, it can be concluded that these first endothermic effects are to be attributed to the hydrolysis of magnesium fluoride by the water vapor according to Reaction 4, which leads to the evolution of hydrogen fluoride and silicon tetrafluoride. It should be noted that, besides the constitutional water of serpentine and the moisture of the furnace atmosphere, the water vapor resulting from Reactions 5—7 participates in Reaction 4.

The second endothermic effect may perhaps be attributed to the melting of magnesium fluoride (m. p. 1265°C). This is deduced from the fact

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8) M. M. Sychev, *Trudy Leningrad Tekhnol. Inst. im Lensoveta,* **1955**, No. 34, 29—31; *Chem. Abstr.*, **50**, 12434d.

* When the 31 per cent mixture was heated for 1 hr. at the following temperatures, the fluorine contents of the products were as follows:

	1075°C	1210°C	1280°C	1320°C	1350°C
F, %	7.84	5.59	0.65	0.46	0.33

were 1210°C and 1320°C correspond to the first and second peaks respectively.

** In the 15.5 per cent mixture, the characteristic peaks of magnesium oxide were too weak for its presence to be concluded.

that the product heated immediately beyond the peak temperature was sintered. However, at about 1250°C (its first peak) and above, the 62 per cent mixture gave the sintered mass, which was shrunked and cracked. Furthermore, the intensities of the first and second peaks of both the 15.5 and 31 per cent mixtures exhibit a tendency to increase and to approach nearer toward each other with an increase in the amount of magnesium fluoride. These appear to indicate that its first endothermic peak between 1060 and 1280°C is to be attributed to the melting of magnesium fluoride in addition to its hydrolysis; namely, in this temperature region, the melting of magnesium fluoride occurs simultaneously with its hydrolysis. From this point of view, the second endothermic peak of a mixture (62 per cent) probably corresponds to the third ones for both the mixtures (15.5 and 31 per cent). Moreover, in this mixture, the existence of the free magnesium fluoride in the temperature region above the first endothermic peak is also probably caused by the melting of magnesium fluoride, which results from a decrease in the contact area between the magnesium fluoride and the water vapor.

The third endothermic peak of the preheated mixture (31 per cent) was not found in the region above the second one. Moreover, the intensity of the third endothermic peak decreases with an increase in the amount of magnesium fluoride. The reason for these results is not yet evident. Further work is required to explain fully the second and third effects.

Furthermore, the weight losses during heating were by far smaller than the calculated values (Table III). This is probably due to the formation of fluorine norbergite, which is more thermally stable than magnesium fluoride.

The Mineral Composition of the Heated Products.—The color of the heated products of all the mixtures generally vary from brownish white to dark brown as the temperature is raised. This is mainly caused by the formation and the crystal growth of magnesioferrite, and of the ferric oxide resulting from the oxidation of ferrous oxide, which is one of the impurities of serpentine.

Independent of the amount of magnesium fluoride, the products heated above the first endothermic peak temperature mainly consist of similar components—forsterite, magnesioferrite, fluorine norbergite, and magnesium oxide. The amount of the latter two increases with an increase in the amount of magnesium fluoride; especially in the case of the mixture with 62 per cent magnesium fluoride, its product when it is heated at 1250°C for 1 hr. is composed chiefly of magnesium oxide and fluorine norbergite, accompanied by a small amount of magnesioferrite—it contains almost no forsterite (Table I). On the other hand, forsterite is the principal component of the heated products with a decrease in the amount of magnesium fluoride. Moreover, among these components, the amount of fluorine norbergite tends to decrease in the temperature region above 1070°C; on the contrary, the three others are thermally stable.

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