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MORINITE-APATITE-WHITLOCKITE

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ABSTRACT

New chemical analyses of Black Hills and French morinites confirm the previously published empirical formula of this rare pegmatite fluorophosphate. Thermal experiments of great quantity and diversity on the Black Hills morinite show that it inverts irreversibly to an apatite structure at about 400° C., whether heated in air or vacuum, and to a whitlockite (rhombohedral tri-calcium phosphate) structure if heated in *thin* films in air at a bit under 800°. Since these products are rich in Na, F, and Al, they are here dubbed nafalapatites or nafalwhitlockites, and both of these are thought to show a considerable variation in composition.

In spite (or because) of the great quantity of data assembled, the writer is unable to reach an unequivocal interpretation of what happens during the thermal treatment of morinite. Results postulated, including the existence of a nafalapatite containing over 5% Na, 14% F, and 13% Al, seem so unusual as to be suspect; this research leaves many unanswered questions.

INTRODUCTION

Morinite, a rare hydrothermal hydrous fluorophosphate from the Hugo pegmatite (Black Hills), was recently described by Fisher and Runner. Since then the material has been analyzed chemically, and thermal experiments have been made to study the nature of the contained water. These yielded the surprising results that morinite loses all its water and is converted to an apatite structure in a very narrow temperature range at about 400° C.; this in turn inverts to a whitlockite (rhombohedral) structure at 750°, providing very *thin* layers of the material are heated in air. Morinite is described under that name and also as ježekite.

Table 1 contains recent chemical analyses of Finnish, French, and Black Hills morinite; also three analyses made on samples of Black Hills morinite heated to 550° or higher. The same data in simplified form are given in the first six columns of Table 2. From this table (column VII) it is clear that the formula of morinite is very close to $Ca_4Na_2Al_4(O_2F_6)(PO_4)_4 \cdot 5H_2O$, which may also be written $Ca_4Na_2Al_2(AlOF_3)_2(PO_4)_4 \cdot 5H_2O$. While the existence of $(AlOF_3)$—tetrahedra seems extremely unlikely, writing the formula in this fashion brings out similarities to epidote (see Fisher and Runner) as well as to apatite.

The actual analyses of the Black Hills and French morinites check each other very nicely; the average of these (based on the contents of a single unit cell) yields:

$$Ca_{3.89\pm.06}Na_{1.90\pm.10}Al_{4.16\pm.05}F_{6.95\pm.39}P_{3.96\pm.02}O_{17.50\pm.25} \cdot 5.17 \pm .02H_2O$$

Table 1. Chemical Analyses of Morinite*

	I	II	III	IV	V	VI
CaO	21.14	22.49	23.60	28.37	27.99	28.34
SrO	0.09	—	—	—	—	—
MnO	2.44	0.02	—	—	—	—
Na_2O	6.77	5.85	6.62	7.97	8.08	7.94
Li_2O	0.14	—	—	—	—	—
K_2O	0.18	—	—	—	—	—
Al_2O_3	21.97	22.46	22.33	26.28	24.46	24.97
P_2O_5	29.08	29.31	30.04	36.15	36.01	36.66
BeO	0.28	—	—	—	—	—
SiO_2	0.48	2.40	—	—	—	—
F	11.37	14.58	13.31	3.48	3.34	4.65
H_2O+	9.80	9.80	9.90	—	—	—
H_2O-	0.17	—	0.08	0.04	0.12	0.00
Residue	0.17	0.14	—	—	—	—
Sum	104.08	107.05	105.88	102.29	100.00	102.56
−0 for F	4.79	6.14	5.60	1.46	1.41	1.96
Total	99.29	100.91	100.28	100.83	98.59	100.60
D (det.)	2.957	2.94	2.962	—	—	—

Explanation of Columns

I. Unheated morinite. Viitaniemi, Finland. The fluorine value should be about 1.3% higher.

II. Unheated morinite. Montebras, France. From the Lacroix collections of the Sorbonne.

III. Unheated morinite. Hugo Mine, Black Hills, S. Dakota, U.S.A.

IV. Morinite, S. Dakota. Large sample heated in air to 535° for 46 hrs. and then to 650° for overnight. Apatite structure; probable weight loss of about 18%. (Fig. 1, no. 13; Fig. 2*F*.)

V. Morinite, S. Dakota. Large sample heated in air in unglazed porcelain boat at 930° for 24 hrs. (Fig. 1, no. 32). The powder film made from this heated sample showed an apatite structure, but the (10·0) and (11·1) lines were stronger than with a normal apatite. Also present were the (101) line of low cristobalite and a line with d=4.35A. Corundum lines of moderate strength were also observed. The presence of this small amount of corundum made it difficult to completely dissolve the sample. In an attempt to duplicate this sample, the result was a mixed apatite and whitlockite structure with a weight loss of 17.2% (Fig. 1, no. 26). On the other hand the sample whose analysis is given in Col. IV was duplicated without difficulty; it showed a weight loss of 18.1%.

VI. Morinite, S. Dak. Composite of 10 *thin* samples, each heated in air at 835° for 23 hrs. Whitlockite structure; weight loss 18.93%. (Fig. 1, no. 17; Fig. 2*J*.)

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* A partial analysis of the Black Hills morinite was run at the U. S. Geological Survey. It showed 14.30% F (by S. M. Berthold) and 10.04% total H_2O (by J. J. Fahey). If these figures are used along with the rest of those of the Volborth analyses, one obtains:

$$Ca_{3.92}Na_{1.99}Al_{4.08}F_{7.01}P_{3.94}O_{17.38}\cdot 5.19\ H_2O$$

TABLE 2. ANALYTICAL RESULTS ON MORINITE*

	I	II	III	IV	V	VI	VII	VIII	IX	X
CaO	23.85	22.88	23.55	28.15	28.42	28.37	24.11	28.37	27.79	28.01
Na_2O	7.15	5.95	6.61	7.91	8.21	7.95	6.66	8.02	7.80	7.86
Al_2O_3	22.14	22.83	22.29	26.07	24.84	25.00	21.93	25.03	26.30	26.51
P_2O_5	29.59	29.80	29.98	35.87	36.57	36.71	30.52	36.71	35.38	35.66
F	12.77	14.82	13.28	3.45	3.39	3.40	12.26	3.23		
H_2O+	9.88	9.96	9.88	—	—	—	9.68	—		
Sum	105.38	106.24	105.59	101.45	101.43	101.43	105.16	101.36		
- 0 for F	5.38	6.24	5.59	1.45	1.43	1.43	5.16	1.36		
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00		
D (calc.)	—	—	—	—	—	—	2.91	2.95		

* Analyses taken from Table 1 and summed to 100%; putting SrO and MnO with CaO, Li_2O and K_2O with Na_2O, BeO with P_2O_5; and omitting SiO_2, $H_2O(-)$, and residue. (Also the F-content of analysis I is increased by 1.3).

Explanation of columns

Cols. I–VI, same as the columns of like number in Table 1. In VI the value for F is taken as the same as that in Cols. IV–V; the amount of sample available for the F analysis was too small to yield an accurate result.

VII. Composition calculated for $Ca_4Na_2Al_4(F_6O_2)(PO_4)_4 \cdot 5H_2O$; compare with columns I–III.

VIII. Composition calculated for $Ca_{28}(Ca_{2\cdot 9}Na_{15\cdot 8}Al_{19\cdot 6})(A10_3F)_{10\cdot 4}(PO_4)_{31\cdot 6}$; compare with column VI. Density calculated assuming V=3436 A³. (a=10·32; c=37·24: taken from Guinier film).

IX. First four oxides of analysis III multiplied by 1.1800; compare with column IV; see the text.

X. First four oxides of analysis III multiplied by 1.1893; compare with Col. VI; see the text.

This could be idealized as: $(Ca_4Na_2Al_4O_{3/2}F_7(PO_4)_4 \cdot 5H_2O$. But it seems permissible to take the formula to be that given in the previous or the following paragraph.

It should be pointed out that space group considerations show that the rank of the equipoints in the unit cell is limited to 2 (or 4 in the case of the general position of $P2_1/m$). Thus it is impossible to put $5H_2O$ as such at equipoints, without leaving some of them empty. Therefore a formula such as:

$$Ca_4Na_2Al_4(OH_xF_{5-x})_2(PO_4)_4 \cdot 5 - xH_2O \qquad (\text{where } x = 1 \text{ to } 2)^\dagger$$

may seem more satisfactory. However thermal studies (described later)

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† If $x=3/2$, this formula is a very close fit for the analyses.

TABLE 3. COMPOSITIONS OF THEORETICAL MORINITE PRODUCTS

	I	II	III	IV	V	VI	VII	VIII
Ca	18.67	18.90	19.19	19.83	20.08	20.12	20.88	20.28
Na	5.44	5.54	5.50	5.69	5.63	5.87	5.99	5.90
Al	13.09	13.02	13.51	13.34	13.80	13.80	13.18	13.23
P	14.52	14.60	14.83	15.32	15.51	15.65	15.64	16.02
F	14.74	14.79	10.76	6.95	4.05	3.45	3.40	3.40
O	33.54	33.15	36.21	38.87	40.93	41.11	40.91	41.17
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
D (calc.)	—	2.88	2.90	2.94	2.965	—	2.97	—

Explanation of columns

I. Actual analysis of Black Hills morinite on a water-free basis.

II. Composition of $Ca_4(Ca_{0\cdot3}Na_{2\cdot2}Al_{2\cdot7})(A10F_3)_{1\cdot7}(PO_4)_{4\cdot3}F_2$; this is the assumed formula for 405° nafalapatite.
Densities in II–V calculated assuming $V=525A^3$. (using $a=9.38$ and $c=6.89$ taken from a Guinier film made from a sample of 550° nafalapatite).

III. Composition of $Ca_4(Ca_{0\cdot4}Na_{2\cdot2}Al_{3\cdot0})(A10_2F_2)_{1\cdot6}(PO_4)_{4\cdot4}F_2$; this is the assumed formula for 475°± nafalapatite.

IV. Composition of $Ca_4(Ca_{0\cdot6}Na_{2\cdot3}Al_{3\cdot2})(A10_3F)_{1\cdot4}(PO_4)_{4\cdot6}F_2$; this is the assumed formula for 550°± nafalapatite.

V. Composition of $Ca_4(Ca_{0\cdot7}Na_{2\cdot3}Al_{3\cdot5})(A10_4)_{1\cdot3}(PO_4)_{4\cdot7}F_2$; this is the assumed formula for 650° nafalapatite.

VI. Result obtained by analyzing 650° nafalapatite (Col. IV, Table 2).

VII. Composition of $Ca_{28}(Ca_4Na_{16}Al_{19})(A10_3F)_{11}({}_5PO_4)_{31}$; this is the assumed formula of nafalwhitlockite. Density calculated assuming $V=3436A^3$. A formula fitting the analysis more closely is given in Table 2 (footnote to Col. VIII).

VIII. Result obtained by analyzing nafalwhitlockite (but see Col. VI, Table 2)

make it appear unlikely that there are two kinds of "water" present. Since Stuart and Hellner of this department are engaged in making a structural analysis of this morinite, further speculations regarding its formula are better held in abeyance at this time. Their work has indicated that the material lacks a plane of symmetry. It is possible to derive an orthohexagonal type apatite unit cell whose dimensions are close to those of the morinite cell, but a discussion of this will appear in the morinite structure paper.

Frondel (1941, p. 149) has noted the close relationship of the physical properties of apatite and whitlockite. He compares one unit cell of the latter with six unit cells of the former, instead of seven as in this paper (Table 5). Mackay (1953) has worked on the α-$Ca_3(PO_4)_2$ structure, without however giving a complete solution. Whitlockite [β–$Ca_3(PO_4)_2$] inverts to the higher-temperature α form at 1180°. The α form is monoclinic

TABLE 4. POSSIBLE INTERMEDIATE NAFALAPATITES

Name	Composition				Valence sum	Number of atoms in *B* position
	A_4	$B_{4-6\,1/2}$	$(XO_4)_6$	Z_2		
Morinite	Ca_4	Na_2Al_2	$(Al\ O\ F_3)_2(PO_4)_4$	$5H_2O$	42.0*	4.0
405° Nafalapatite	Ca_4	$Ca_{0\cdot3}Na_{2\cdot2}Al_{2\cdot7}$	$(Al\ O\ F_3)_{1\cdot7}(PO_4)_{4\cdot3}$	F_2	45.2	5.2
475°± Nafalapatite	Ca_4	$Ca_{0\cdot4}Na_{2\cdot2}Al_{3\cdot0}$	$(Al\ O_2\ F_2)_{1\cdot6}(PO_4)_{4\cdot4}$	F_2	46.8	5.6
550°± Nafalapatite	Ca_4	$Ca_{0\cdot6}Na_{2\cdot3}Al_{3\cdot2}$	$(Al\ O_3\ F)_{1\cdot4}(PO_4)_{4\cdot6}$	F_2	48.4	6.1
650° Nafalapatite	Ca_4	$Ca_{0\cdot7}Na_{2\cdot3}Al_{3\cdot5}$	$(Al\ O_4)_{1\cdot3}(PO_4)_{4\cdot7}$	F_2	49.8	6.5
Fluorapatite	Ca_4	Ca_6	$(PO_4)_6$	F_2	50.0	6.0

* Exclusive of H_2O.

TABLE 5. MORINITE-APATITE-WHITLOCKITE DATA

No. of unit cells	Name	Composition				Unit cell volume	G.	Valence sum
		A_4	B_6	$(X\ O_4)_6$	Z_2			
7	Morinite	Ca_{28}	$Na_{14}Al_{14}$	$(Al\ O\ F_3)_{14}(PO_4)_{28}$	$35H_2O$	3710	2.94	294†
7	Nafalapatite	Ca_{28}	$Ca_5Na_{17}Al_{25}$	$(Al\ O_4)_9(PO_4)_{33}$	F_{14}	3675*	3.00	350
7	Fluorapatite	Ca_{28}	Ca_{42}	$(PO_4)_{42}$	F_{14}	3654*	3.20	350
1	Nafalwhitlockite	Ca_{28}	$Ca_4Na_{16}Al_{19}$	$(Al\ O_3\ F)_{11}(PO_4)_{31}$	—	3400*	3.00	325
1	Whitlockite	Ca_{28}	Ca_{35}	$(PO_4)_{42}$	—	3400*	3.17	336

* Hexagonal cell.
† Exclusive of water.

whereas the β form is rhombohedral, a most unusual situation; one wonders if the α form is not a metastable product. Recently it has been found (Nurse *et al*, 1958) that the α form itself inverts at 1430° C. to yield a super-α form (which enters into solid solution with α Ca_2SiO_4), but this new modification does not survive quenching to room temperature. Powder diffraction data for apatite and whitlockite are given in Tables 6 and 7. Jaffe (1951) has compiled abstracts of the papers dealing with the synthesis of apatites. She lists (p. 66) an Al-apatite with 1.88% Al_2O_3. Her literature shows that $Ca_3(PO_4)_2$ is often used as one of the reagents to produce a synthetic apatite, but from my limited experience I would assume that in most if not all cases this was probably actually a hydrated form of $Ca_3(PO_4)_2$. S. Landergren (see Goldschmidt, 1954, p. 455) doubts that aluminum can enter the apatite structure in significant amounts.

THERMAL EXPERIMENTS

All samples were prepared by coarse crushing, then picking out the individual crystal grains of morinite under a binocular, then fine grinding

TABLE 6. POWDER DIFFRACTION DATA FOR NAFALAPATITE*

Int.	Obs. *d*	Calc. *d*	Indices	Int.	Obs. *d*	Calc. *d*	Indices
1	8.1	8.11	10·0	2	1.88	1.884	13·2
$\frac{1}{4}$	5.22	5.25	10·1	$\frac{1}{2}$	1.86	1.861	23·0
0	—	4.68	11·0	4	1.836	1.837	12·3
9†	4.08	4.06	20·0	2	1.795	1.797	23·1
1	3.86	3.87	11·1	2	1.767	1.771	14·0
0	—	3.495	20·1	0	—	1.750	30·3
5	3.42	3.442	00·2	2	1.745	1.748	40·2
3	3.17	3.169	10·2	3−	1.720	1.721	00·4
3	3.06	3.067	12·0	0	—	1.715	41·1
10	2.80	2.801	12·1	$\frac{1}{4}$	1.678	1.684	10·4
3	2.76	2.774	11·2	0	—	1.639	22·3
8	2.69	2.705	30·0	2	1.635	1.637	32·2
4	2.61	2.625	20·2	0	—	1.623	50·0
2	2.51	2.517	30·1	0	—	1.615	11·4
$\frac{1}{4}$	2.36	2.342	22·0	2−	1.604	1.607	13·3
1−	2.28	2.290	12·2	$\frac{1}{4}$	1.578	1.584	20·4
3	2.25	2.250	13·0	$\frac{1}{2}$	1.532		
$\frac{1}{4}$	2.21	2.217 2.208	22·1 10·3	$\frac{1}{2}$	1.520		
1	2.14	2.139	13·1	1	1.500		
0	—	2.127	30·2	2+	1.468		
$\frac{1}{2}$	2.08	2.061	11·3	2	1.452		
$\frac{1}{2}$	2.05	2.028	40·0	2	1.446		
$\frac{1}{4}$	1.99	1.997	20·3	2	1.422		
0	—	1.946	40·1	1−	1.400		
3	1.932	1.936	22·2	$\frac{1}{2}$	1.340		
				1	1.309		

* The *x*-ray film from this nafalapatite is shown in Fig. 2*E*. A Guinier film yielded $a=9.369$ and $c=6.884$ (used in the calculations).

† This is the (101) low-cristobalite line.

for two to three hours in a mullite mortar by an electric motor mechanism. The samples so prepared were pure enough to yield an *x*-ray film that showed no extraneous lines; nevertheless they likely contained small amounts of apatite, since the two minerals are very closely associated in the original rock. Such a sample was stored in a vial, and portions taken out of it for the thermal experiments described below.

All samples were heated in electric resistance furnaces. The curves shown in Fig. 1 are based on results obtained on heating for one-day runs (22 to 23 hours) in platinum boats in a furnace with the temperature controlled by a thermocouple and checked by an automatic recorder. The heated samples (which were extremely fine-grained) were air-quenched, weighed, and then studied by means of powder diffraction films such as

TABLE 7. POWDER DIFFRACTION DATA ON PALERMO WHITLOCKITE

(1) No.	(2) Intensity	(3) Measured *d*	(4) Intensity	(5) Measured *d*	(6) Calculated *d*	(7) Indices	(7) Intensity	(9) *d*
1	2	8.03	2	8.005	8.0580	01·2	11	8.15
2	5	6.55	3	6.351	6.4267	10·4	15	6.49
3					6.1667	00·6	5	6.22
4	8	5.24	5−	5.218	5.1600	11·0	20	5.21
5					4.7608	11·3	1	4.80
6				(1)	4.3440	20·2	7	4.39
7					4.1102	01·8	3	4.15
8	4	4.07	3	4.020	4.0225	02·4	15	4.06
9					3.9557	11·6	3	4.00
10	7	3.45	5+	3.407	3.4200	10·10	25	3.45
11					3.3647	21·1	3	3.40
12	1	3.35	1	3.304	3.3245	12·2	9	3.36
13a					3.2165	11·9	7	3.25
13					3.2144	20·8	7	3.25
14	9	3.21	7−	3.160	3.1736	21·4	55	3.21
15					3.0834	00·12	1	3.11
16	1	3.02	1	2.974	2.9791	30·0	15	3.01
17	10	2.88	10	2.837	2.8498	02·10	100	2.880
18	3	2.75	3−	2.719	2.7285	12·8	20	2.757
19	1	2.68	1	2.672	2.6824	30·6	9	2.710
20			½	2.636	2.6469	11·12	7	2.674
21	9	2.60	8	2.572	2.5800	22·0	65	2.607
22	2	2.52	1	2.528	2.5349	01·14	5	2.562
23					2.5253	22·3	7	2.553
24			1	2.491	2.4956	21·10	11	2.520
25					2.4731	13·1	5	2.499
26a					2.3844	12·11	9	2.407
26	2	2.41	2	2.379	2.3804	22·6	9	2.407
27					2.3502	31·5	5	2.375
28	2	2.25	1	2.343	2.2396	10·16	9	2.263

Columns 2–3 from C. Frondel (Cu radiation). *Am. Mineral.*, **28,** (1943) 228.

Columns 4–5: Fisher, Fe/Mn radiation, 114.6 mm. camera. Indexing checked against single-crystal films.

Column 6: results computed assuming $a=10.32$ and $c=37.00$ (values obtained from a precession film; later from a Guinier film I got $a=10.37$ and $c=37.19$).

Columns 8–9 from DeWolff, Cu/Ni radiation, 114.6 mm. camera, intensities by photometer, A.S.T.M. 9–169, heated commercial sample; $a=10.43$, $c=37.38$. Lines (21·5), (21·7), and (32·7) listed by DeWolff are absent or with very weak intensity on my single-crystal films. Line #34 (00·18) is not listed by DeWolff.

TABLE 7 (*Continued*)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
No.	Intensity	Measured *d*	Intensity	Measured *d*	Calculated *d*	Indices	Intensity	*d*
29					2.2257	11·15	3	2.249
30	2	2.19	2	2.230*	2.2183	04·2	1	2.241
31	2	2.16	2	2.171	2.1720	40·4	13	2.195
32			3	2.143	2.1427	30·12	11	2.165
33					2.0820	21·14	3	2.103
34	1	2.07	1	2.078	2.0556	00·18		
34a					2.0542	20·16	7	2.076
35					2.0471	32·1	3	2.068
36	2	2.04	1	2.048*	2.0379	23·2	5	2.061
37	1	2.00	3	2.011	2.0121	04·8	9	2.033
38					2.0016	32·4	5	2.023
39					1.9956	31·11	3	2.017
40			1	1.980	1.9790	22·12	7	2.000
41					1.9505	14·0	1	1.970
42					1.9264	14·3	3	1.946
43a					1.9139	11·18	20	1.933
43	6	1.93	5	1.913	1.9128	40·10	20	1.933
44	5	1.88	3	1.876	1.8744	23·8	15	1.895
45			3	1.860	1.8594	41·6	13	1.879
46	1	1.82	1	1.809	1.8122	01·20	11	1.830
46a					1.8080	13·14	11	1.830
47			2	1.794	1.7934	32·10	5	1.812
48			1	1.780	1.7793	50·2	5	1.798
49					1.7621	41·9	5	1.781
50	3	1.77	2	1.757*	1.7550	05·4	7	1.774
51					1.7200	33·0	3	1.738
52	7	1.72	8	1.701	1.7097	20·20	25	1.728
53	1	1.70	2−	1.692	1.6923	30·18	7	1.711
54	2	1.67	2	1.665*	1.6675	50·8	7	1.685
55					1.6614	24·4	3	1.665
56					1.6585	41·12	5	1.637
57	1	1.63	1	1.622	1.6200	23·14	5	1.625
58	1	1.60	2	1.609	1.6069	40·16	5	1.603
59			1	1.588	1.5868	33·9	3	1.600
60	5	1.55	5	1.537*	1.5366	24·10	11	1.552
61					1.5342	32·16	3	1.532
62			1	1.519			3	1.520
63			1	1.507			3	1.505
64			2	1.493	1.4896	60·0		
65					1.4775	11·24	5	1.465

* Diffuse reflection.

(1) The (20·2) line ($d=4.34$) shows up very well on some of the synthetic whitlockites.

TABLE 7 (*Continued*)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
No.	Intensity	Measured *d*	Intensity	Measured *d*	Calculated *d*	Indices	Intensity	*d*
66	1	1.46	2	1.452	1.4511	43·4	3	1.440
67	1	1.43	2	1.431	1.4253	04·20	3	1.429
68			1	1.418			3	1.414
69	1	1.40	2	1.403	1.4003	34·8	5	1.409
70	1	1.38	3	1.396	1.3939	52·6	3	1.387
71			1	1.374	1.3738	23·20		
72			1	1.367	1.3695	03·24		
73			1	1.324	1.3620	16·1		
74			2−	1.311	1.3193	33·18?		
75			1	1.300	1.3118	12·26		
76			2	1.292	1.2900	44·0		
77					1.2842	34·14		
78			2	1.278	1.2760	35·1		
79	2	1.25	4	1.250	1.2475	42·20		
80			1	1.242	1.2379	25·15		
81	2	1.24	4	1.225*	1.2333	00·30		
82			2	1.211	1.2283	62·4		
				Two faint lines omitted				
85	1	1.18	3	1.178	1.1745	52·18		
86			1	1.171	1.1693	23·26		
87			1	1.153	1.1507	34·20		
88	1	1.15	2	1.141*	1.1398	03·30		
89			2	1.121	1.1131	22·30		
90	3	1.11	6	1.116*				
				One faint line omitted				
92	1	1.09	2	1.097	1.0933	54·10		
93			3	1.088	1.0843	27·4		
				Three faint lines omitted				
97	1	1.05	3−	1.053	1.0490	52·24		
98	1	1.03	2	1.033	1.0320	55·0		
99			3	1.029	1.0298	26·20		
100			2	1.026	1.0256	54·16		
101			1	1.023				
102			1	1.020	1.0225	34·26		
103			2	1.010				
104			1	1.002				
105			1	0.9913	0.9881	46·10		
106			2	0.9858				
107			1	0.9839				
108			1	0.9821	0.9828	37·8		
109			1	0.9742*	0.9785	55·12		

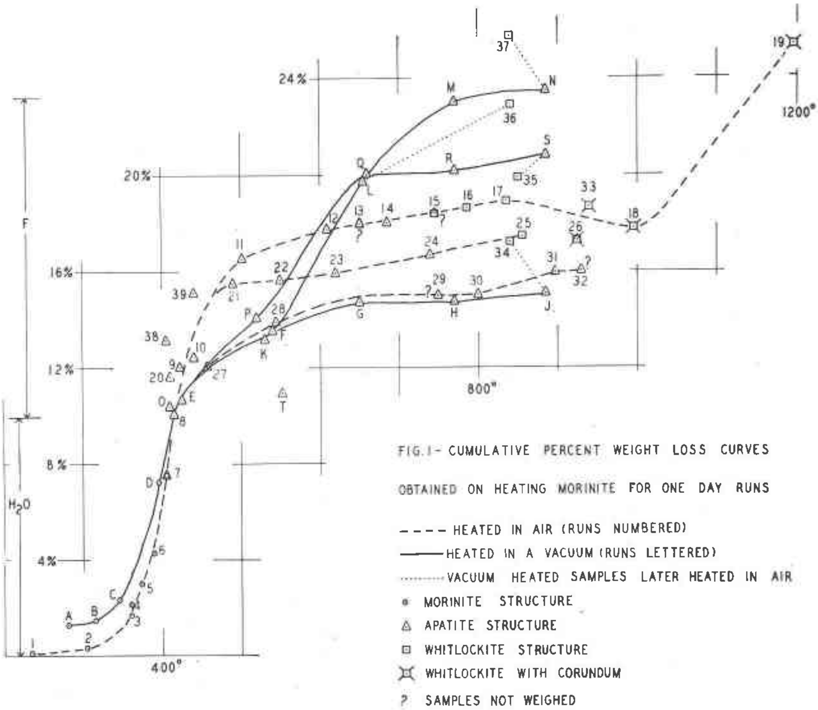


Fig. 1. Cumulative per cent weight-loss curves obtained on heating morinite for one day runs.

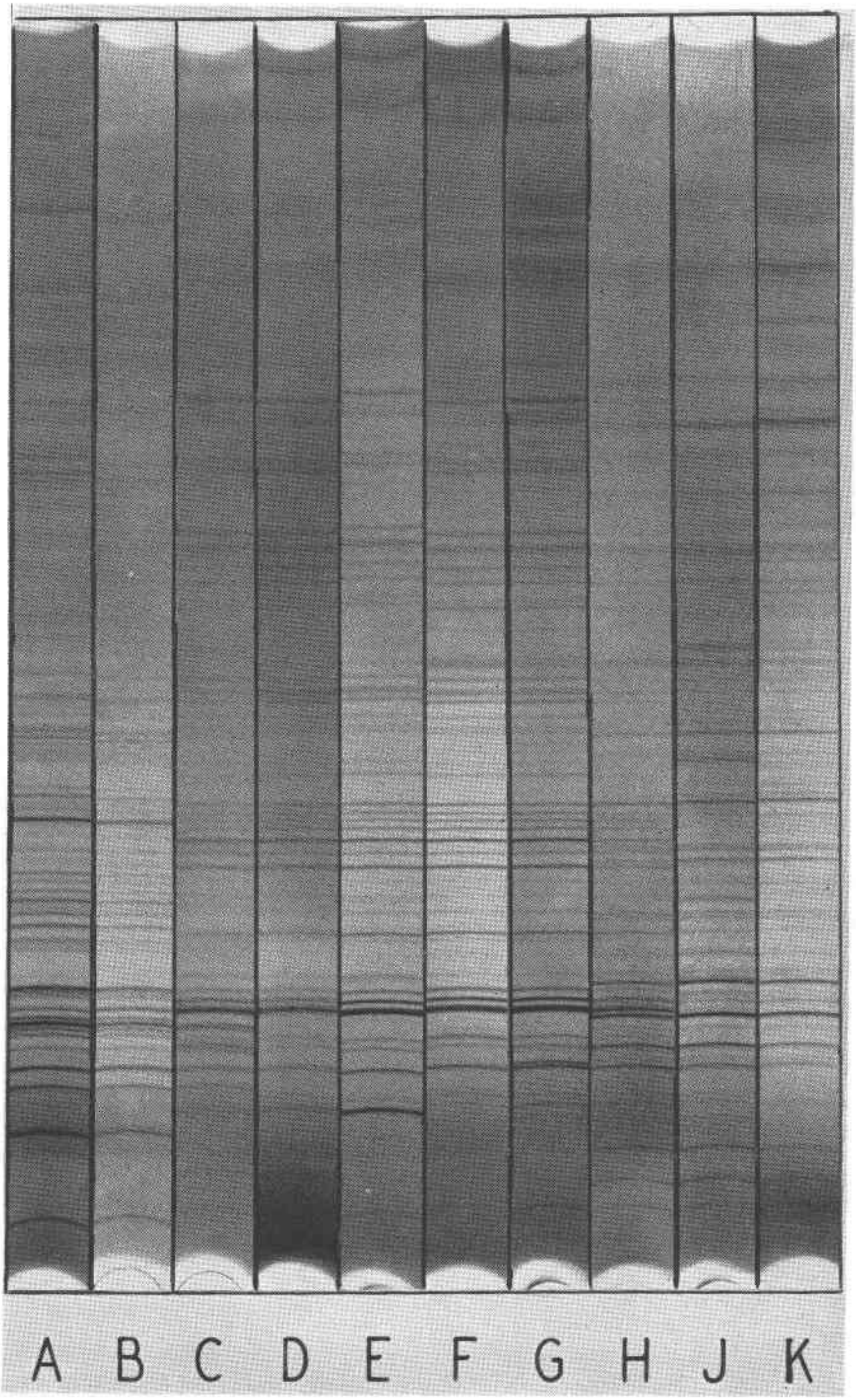
those illustrated in Fig. 2. After heating some samples in air it was decided to try heating in a constantly-pumping vacuum mainly in hopes of finding out what was happening to the fluorine.

Samples heated in air (dashed-line curves of Fig. 1).

In the early work (1957) samples were heated in air on platinum foil in porcelain boats without weighing. Such samples were obtained on which two of the chemical analyses given in Tables 1 and 2 (those listed in columns IV and V) were made. Beginning in January 1958 samples were weighed before and after heating. Because of the inconsistent results obtained, it was soon realized that interaction with air played an important part in the reactions occurring when the temperatures exceeded 400° C. Thereafter, in general, such samples were heated only as very *thin* layers (not over a few tenths of a mm. in thickness) spread out evenly along the bottoms of the boats. It was also observed that (when heated above 400°) the result depended in part on whether the sample was put in a hot furnace, or in a cool furnace and slowly raised to the temperature of heating. The dashed-line curves of Fig. 1 show the results thus obtained. Above 400° these split into a triple set, the bottom one (nos. 27–32) giving the results when thick samples were used (some of these were heated over 100 hours); the other two were secured by working with thin samples. The top one (nos. 9–19) fits the case when the samples were put in a hot furnace, the middle one (nos. 20–25) when they went into a cool furnace. In the range 500–900° these three curves are roughly parallel to each other and the top and bottom ones are nearly two weight per cent from the middle one. Presumably the top layer of the samples used to plot the bottom curve underwent the same reaction as did the samples that yielded the top curve; thus an idealized position for the bottom curve (had the surficial parts of the samples suffered no action from air) would presumably be very close to the lowest solid-line (vacuum heated) curve. When heating thick samples in air, the conversion from the apatite structure to the whitlockite structure (except presumably for a thin layer at the top of the sample) did not take place, even on material heated to 1000°, although a little corundum separated out above 800° or so.

The conversion of the morinite to the apatite structure takes place at around 400°. This occurs whether the sample is thick or thin, but the per cent weight loss at a given temperature is somewhat greater for a thin sample than for a thick one on one-day runs. At 405° (Fig. 1, no. 7) the lines for the two structures are equally strong on the *x*-ray film; at 373° (Fig. 1, no. 5 and 6; see Fig. 2*B*) just a trace of apatite appears; at 422° (Fig. 1, no. 9) no morinite lines are left, but the apatite (20.0) line appears to be heavy. Actually this heavy line is largely due to the (101) reflection from low cristobalite ($d=4.04$). This conversion is closely related to the driving off of all the water present. A sample (Fig. 1, no. 8) weighing 0.86 grams was heated in an unglazed porcelain boat during some of the early work. Held at 105° for 19 hours the weight loss was .03%; at 410° for six days the additional weight loss was 9.94%. This sample was then analyzed by Volborth who found it contained 13.65% F. (Note that "water-free morinite" carries 14.74% F.) An *x*-ray film (Fig. 2*D*) showed it to have a good apatite structure, with a heavy (101) cristobalite line, but with no other extraneous lines. Since an ordinary fluorapatite is not supposed to contain more than 3.76% F, this is a most unusual specimen. However, the air-heated apatite-structure (Fig. 1, no. 13) produced at 650° on which a complete chemical analysis was made (Table 1, col. IV), which carried but 3.45% F, gave a perfectly normal apatite film (Fig. 2*F*).

A few of the air-heated samples shown in Fig. 1 do not lie on any of the curves. Thus No. 26 represents a large (0.4 gr.) sample heated at 925° for


A
B
C
D
E
F
G
H
J
K

a day on Pt foil in an unglazed porcelain boat in an attempt to duplicate No. 32, the analyzed sample; the resulting powder yielded quite a different *x*-ray film from that obtained from No. 32 (which was heated in an unglazed porcelain boat without Pt foil). No. 33 represents a half-gram sample heated in a Pt crucible by Volborth for a day at 550° (wt. loss of 15.6%), two days at 650° (additional wt. loss of 1.7%), and then several days at 940° (total wt. loss of 18.65%). Nos. 38 and 39 represent samples heated respectively for eight days at 405° and for nine days at 440°. On

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FIG. 2. *X*-ray powder diffraction patterns of heated morinite samples (except K). All taken with Fe/Mn radiation in a 114-mm. diameter Straumanis-type (Philips) camera. Approximately natural size.

A. Vacuum-heated at 325° for 25 hours; at *C* in Fig. 1. This is a normal morinite pattern.

B. Thin layer heated in air at 375° for 23 hours; Fig. 1, no. 6. This is a normal morinite pattern with but a faint trace of apatite structure.

C. Heated at 550° under an aspirator vacuum in a Vycor glass tube for 88 hours; weight loss 10.9% at *T* in Fig. 1. This is an apatite pattern with some extraneous lines; the sample carries 14.11% fluorine.

D. Large sample heated in air at 415° for six days; Fig. 1, no. 8. This is an apatite pattern with a (101) low cristobalite line at $d=4.04$; the sample carries 13.65% fluorine. The lines are somewhat fuzzy; presumably the sample is not very well crystallized.

E. Small samples vacuum-heated at 885° for 23 hours with an apparent weight loss of 36.80%. These samples were put into a hot furnace, and some of the apparent loss in weight resulted from sputtering. Part of this weight loss is material which condensed as a ring deposit of cryolite near the cool end of the silica glass tube. This is an excellent apatite pattern, with a heavy (101) cristobalite line. This experiment was later repeated putting the samples in a cool furnace; results were the same, but with a weight loss of only 23.5% (*N* of Fig. 1).

F. Large sample heated in air at 535° for 46 hours and then overnight at 650°; Fig. 1, no. 13. This sample was subjected to a complete chemical analysis (Table 1, col. IV). The *x*-ray pattern is that of an ordinary apatite with $a=9.38$ and $c=6.89$.

G. Vacuum-heated at 665° for 21 hours; at *L* in Fig. 1. This is an apatite pattern with an additional line at $d=3.37$, very close to the (00.2) line of $d=3.44$. A deposit of chiolite formed in the silica tube where it became cool.

H. Thin layer heated in air at 745° for 23 hours; Fig. 1, no. 15. This pattern represents about half apatite and half whitlockite.

J. Thin layer heated in air at 835° for 23 hours; Fig. 1, no. 17. Ten such samples were combined and subjected to a complete chemical analysis (Table 1, col. VI). The pattern is typical of whitlockite with the addition of two weak corundum lines. These latter appear if the sample is put in a hot furnace, but are absent if it is put in a cool furnace. Therefore the chemical analysis represents a possible "pure" whitlockite.

K. Whitlockite, Palermo, N. H. Sample heated in air at 890° for 23 hours; same pattern as is given by the unheated material. A Guinier film of the unheated material yielded $a=10.37$, $c=37.19$.

the other hand long heating (10 days) effected no change in sample No. 25 as regards weight-loss or diffraction film; incidentally the whitlockite-structure films from these two samples (No. 25) showed a strong $d=17.5$ line whose origin is unknown; certainly it does not belong to the whitlockite structure. A series of eight one-day runs made on *thin* samples at temperatures between 713 and 800° showed (Fig. 1, No. 15) that the whitlockite and apatite diffraction lines (Fig. 2*H*) are about equally strong at a temperature of 745°. The analyzed nafalwhitlockite (Fig. 1, No. 17; Tables 1–2, col. VI) gave an *x*-ray film (Fig. 2*J*) identical with that of the Palermo whitlockite (Fig. 2*K*; Table 7) except for the presence of a couple of weak corundum lines. These lines do not appear if the sample is put in a cool furnance and raised to 835°, but they are present when the sample is put directly into a hot furnace.

Samples heated in a vacuum (solid-line curves of Fig. 1).

The morinite powder was put in platinum boats placed in a continuously-evacuated silica-glass tube.* Here too the single curve obtained at lower temperatures (Fig. 1) split into three branches (above about 500°) depending on whether a single sample was heated repeatedly at successively higher temperatures (bottom solid-line curve, if a small sample; middle solid-line curve, if a large sample), or new (small) samples were used for each heat (top solid-line curve).

Samples *E-F-G-H-J* (bottom solid-line curve of Fig. 1) were placed as single *small* samples (.05 to .06 gr.) in each of two platinum microboats in the silica tube and were heated for one day each at successive increases in temperature. These all have apatite structures, though *F* is a bit peculiar (like *K* it shows a number of extra lines), and *J* shows a trace of whitlockite structure. On heating *J* in air at 860° for a day it gave a whitlockite structure (Fig. 1, No. 34). *E* has a (101) cristobalite line.

Samples *K-L-M-N* (top solid line of Fig. 1) were handled just like the last series, except that a new pair of samples was introduced at each temperature; however, each sample was put in a cool furnace. Note that *K* duplicated the structure of *F*, but that at a higher temperature chiolite (*L*) or cryolite (*M* and *N*) condensed as a ring deposit on the silica tube where it became cool at the furnace entrance.† The chiolite ($Na_5Al_3F_{14}$) and cryolite ($Na_3Al\ F_6$) patterns are well marked, but *x*-ray films of both

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* Using a fairly new Welch no. 1405*H* two-stage duo-seal vacuum pump (guaranteed vacuum of 0.05 micron Hg).

† For this reason the percentage weight losses shown by curves *L-M-N* and *Q-R-S* are fictitious in the sense that at least part of this is represented by these two minerals (which were not weighed).

have extra (unidentified) lines. The apatite structures of *L* (see Fig. 2*G*) and *M* are unusual in that they show an additional line at $d=3.37$, very close to the (00.2) apatite line of $d=3.44$, that is fairly strong, and a weaker extraneous line at $d=4.28$. *N* shows a (101) cristobalite line. A whitlockite structure forms when a *thin* sample of either *L* (see No. 36) or *N* (see No. 37) is heated in air at 860° for a day. Since the heating of *thin* films of *J*, *L*, or *N* in air at 860° for a day yields whitlockite structures (nos. 34, 36, or 37 respectively) with a further *loss* in weight of 2.4% (2.1, 2.9, and 2.2 respectively), it would seem that this phenomenon is not simply a replacing of fluorine by oxygen. It is also to be noted that these three whitlockite structures apparently have quite different compositions, since they represent percentage weight losses from the original morinite of 17.2, 22.9, or 25.7 respectively.

Samples *O-P-Q-R-S* (middle solid line of Fig. 1) were made from a single *large* sample (0.3 gr.) which was heated in a large platinum boat (7 by 26 mm.) for one day each at successively higher temperatures (*cf.* *E–J* incl.). Here *O* and *P* practically duplicate *E* and *F* (though near 550° it was difficult to get consistent results), and *P* and *Q* (the latter with a ring deposit of chiolite) duplicate *K* and *L*. But just as *G* showed practically no change on heating to higher temperatures (see *H*, *J*), so also did *Q* (see *R*, *S*). In short, whatever product is formed at 670° seems to be relatively stable at higher temperatures; i.e., it is "locked in." Chiolite is produced at 670° with a fresh small sample (*L*), or with a large sample (*Q*) heated at successively higher temperatures; but does not appear from a small sample (*G*) heated at successively higher temperatures. It is not surprising that Na-Al-F can be removed from a heated morinite (which has been converted to apatite) and still leave apatite; this final product should be much closer to a "normal" fluorapatite than the first one. The apatite-structure films of *Q-R-S* are quite standard, though the (10.0) line is a bit more pronounced than is usual; *O* and *P* are like *E* and *F*, *K* respectively. On converting *S* to a whitlockite structure by heating a thin layer in air at 860° for a day (see No. 35), there was a weight-gain of 0.9%; all other such conversions involved a weight-loss of over 2%.

Under vacuum heating morinite converts to an apatite structure at about 400°. The conversion takes place at a weight loss of about 10%. At 385° with a 7.2% weight loss (*D*, Fig. 1) the material is still morinite; *cf.* Fig. 2*A*. An early sample obtained by heating at 550° for 88 hours in a Vycor glass tube connected to an aspirator, which had lost 10.9%* by weight (*T*, Fig. 1), was analyzed by Volborth and yielded 13.91, 14.30 (average 14.11) % F; this is to be compared with the original morinite

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* Contrast this with *F* and *K* done later (see Fig. 1) under better vacuum conditions with a weight loss of 13.3%.

which contains (on a H_2O-free basis) 14.74% F. An *x*-ray film of this material (Fig. 2*C*) showed an apatite structure with a fuzzy (20.0) line and weak extraneous lines at $d=2.94$, 3.21, and 3.72. These appear to be residual lines from morinite (but note the heavy 9.11 and 4.70 lines of morinite are absent), with an additional weak line at $d=5.90$ which is unaccounted for.† Two samples scraped from the tube (at 13 and 21 cms. from its hot end, where the tube cooled as a result of entering the insulating plug of the furnace, and of leaving this plug for the outside air) which apparently formed from the vapor state, showed patterns (13 cms.) identical with that of Fig. 2*C* and (21 cms.) of a pure apatite [but with a (101) cristobalite line]. It is thus evident that the change in structure morinite to apatite at 400° is identified with substantially complete dehydration. This is not to say that the apatite produced at this temperature contains 14.1% F (but see the results described earlier on heating in air); some part of the latter may be in the residual morinite, or in a possible decomposition product represented by the unidentified diffraction lines. It thus seems established that on heating morinite all the water comes off at a single temperature, indicating a single kind of water-bonding in the morinite.

The apatite structure thus produced holds through 885° under the conditions of experimentation, though one film (from sample *J*) shows the development of a trace of whitlockite structure at this temperature. Since the apatites formed represent a weight loss from the original morinite of 10.4 to 23.5%, it is reasonable to assume that they show a considerable variation in composition.

Additional thermal experiments.

A few tiny subhedrons of morinite were put in a Pt boat and heated in air at 420° for one day. The crystals were visibly unchanged except for minor milky areas. An *x*-ray powder film showed the material to be morinite. Another such batch was heated under identical conditions, but for 29 days. The crystals appeared like white opal, but otherwise there was no visible change. However an *x*-ray rotation picture of one of them showed it to be a pseudomorph consisting of tiny apatite crystals of various orientations, with only slight evidence of a preferred orientation; in

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† Samples were removed from the Vycor tube after 23, 40, and 64 hours also (after % weight losses of 8.9, 9.6, and 10.1 respectively) and x-ray patterns were made of each sample. The film from the 23 hr. heat is identical with Fig. 2*E*, except for the presence of a few weak (none with intensity >1) morinite lines; note it has the very heavy cristobalite (101) line, much more pronounced than in Fig. 2*C*, and it is a better crystallized apatite than that represented in Fig. 2*C*.

short it gave a powder-type pattern with somewhat fuzzy lines and with weak extraneous lines at *d* of 6.15, 4.12, and 3.60.

Powdered samples of morinite were sealed into evacuated Vycor tubes and heated for one day at (1) 420°, (2) 465°, (3) 510°, and (4) 705°. The first remained morinite, the other three were converted to apatite with some extraneous lines. On removing the tubes from the furnace there was no sign of water; but this condensed as the tubes were cooled. In the case of (1) and (2) there was no visible etching of the glass, though this occurred in tubes (3) and (4). It would thus appear that little or no F was driven off up to 465° under these conditions.

To make certain that the apatite structure was the stable one at higher temperatures, *x*-ray powder patterns were taken with a heating camera (the 19 cm. Unicam in C.S. Barrett's laboratory). A sample of morinite was heated in a porcelain boat in air for 25 hours at 775°; this was then placed in a Vycor capillary and pictures were taken of it at room temperature (20°) and at 740° C. Both films showed the apatite structure, but at the higher temperature the value of a_0 had increased by 0.106 A. and that of c_0 by 0.124 A.

D.T.A. experiments.

The results of some differential thermal analyses are shown in Figs. 3 and 4. The two runs (*A* and *B*) given in the former roughly duplicate each other (except in the case of *B* in which heating stopped at 800°), but they were made four months apart on different samples in different furnaces and by different operators. They clearly show a broad endothermic trough from 460° to 550° that undoubtedly corresponds to the loss of water that occurs at about 400° on prolonged heating. They also agree on the presence of two sharp endothermic reactions at 640° and 705°. In addition in *B* there is a minor sharp endothermic break at 600°; this last is broader and much less obvious in *A*. It seems possible that these three sharp breaks are associated with the loss of fluorine, as is discussed later.

In Fig. 4 are shown three DTA curves made on morinite samples which had previously been heated in air. Curve *C* is a re-run made the next day on the cooled sample of *B*. All four breaks (including the water one) are still apparent, but it and the "last fluorine" one are greatly subdued. In *D* a run made on a thick sample pre-heated in air at 700° for 28 hours shows the "last fluorine" break as still very pronounced; in addition there is a sharp exothermic reaction at 650°. A run made on a large sample preheated in air at 800° for five days is given in *E* and shows the substantial elimination of all breaks. All DTA residues (including those from *A* and *E* heated to 1000°) still had the apatite structure as shown by *x*-ray diffraction films, though above 800° some corundum separated out.

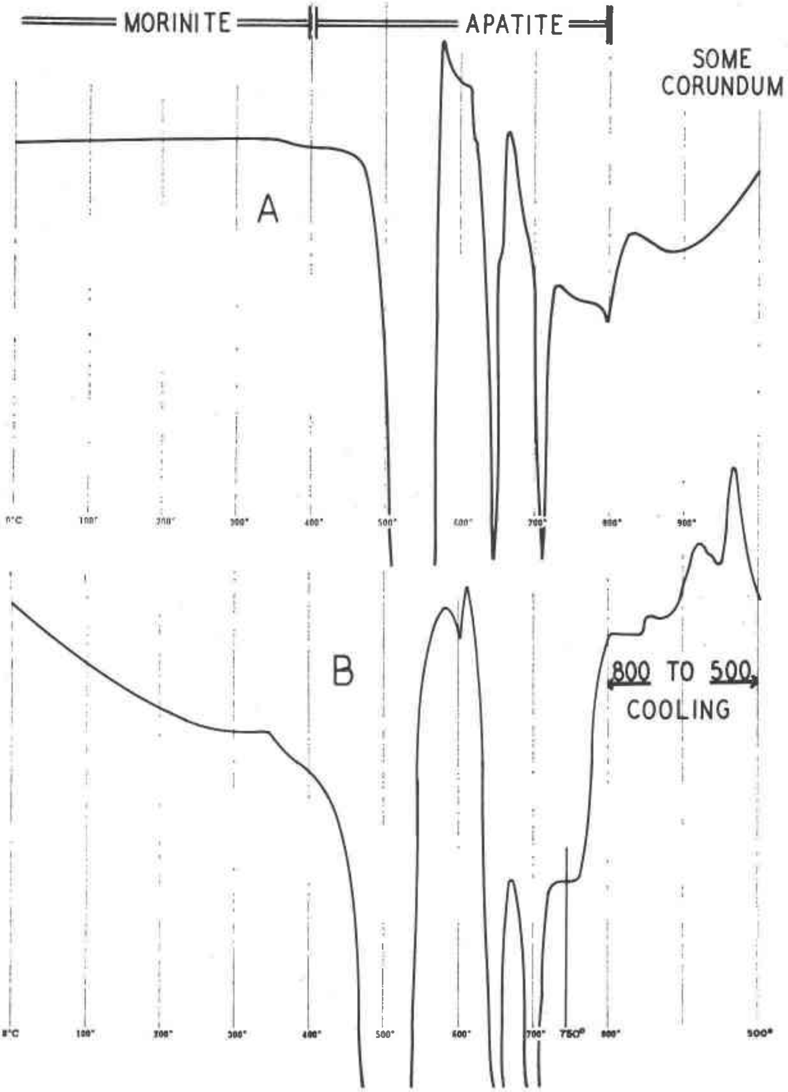

FIG. 3. DTA curves from morinite. Resistance 100 ohms; temperature raised 100° every eight minutes (after reaching 200°).

A. Normal run to 1000°. Done in furnace no. 2 by W. A. White on Sept. 19, 1957.

B. Normal run to 800°; then cooled to 500. Done in furnace no. 3 by W. E. Parham on Jan. 27, 1958.

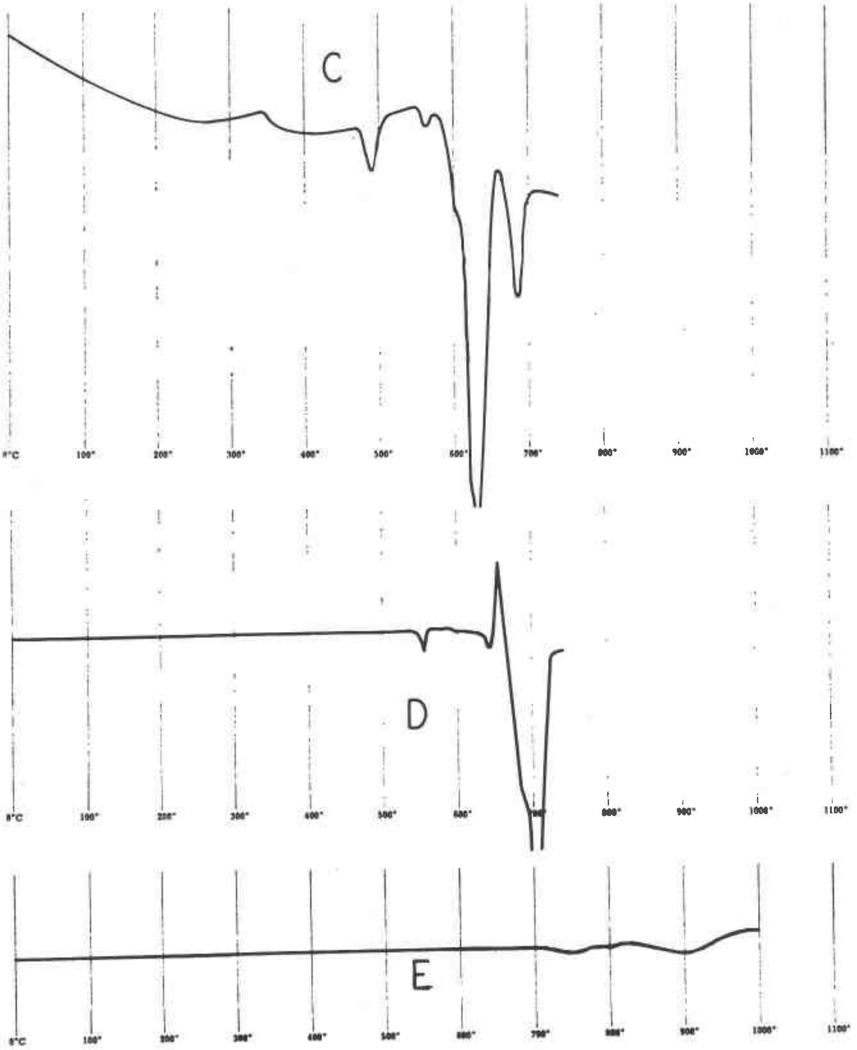

FIG. 4. DTA curves on heated morinite (data as for Fig. 3).

C. A rerun on the cooled sample from Fig. 3B. Done in furnace no. 3 by W. E. Parham on Jan. 28, 1958.

D. Run made on a sample preheated at Urbana in air at 700° for 28 hours. Done in furnace no. 2 by W. E. Parham on Feb. 26, 1958.

E. Run made on a sample preheated in air at 800° for five days. Done in furnace no. 2 by W. E. Parham on March 11, 1958. *X*-ray powder diffraction films made on this material both before and after the DTA run are substantially identical, showing excellent apatite structures with the addition of weak corundum lines.

INTERPRETATION

In attempting to interpret the previously described results on heating morinite, the writer first arrived at the following conclusions. Because the apatite and whitlockite structures produced are rich in Na, F, and Al as compared to the standard minerals, they are here referred to as nafalapatites or nafalwhitlockites. Since the first apatite structure formed seems to have the same composition as morinite except for the loss of the water (Table 3, col I), its formula is assumed to be that shown in Table 4 for 405° nafalapatite (cf. Table 3, col. II). Since the 650° nafalapatite was analyzed (Tables 1–2, col. IV; Table 3, col. VI), its formula was calculated to be that shown in Table 4 (cf. Table 3, col. V). Assuming the DTA breaks previously suggested as being due to loss of fluorine to be correct, then the two intermediate stages might be designated 475°± and 550°± nafalapatites and their formulas derived to be those shown in Table 4; compositions of these two hypothetical phases are given in Table 3 (cols. III and IV). Finally the nafalwhitlockite was analyzed (Tables 1–2, cols. V–VI) and its formula calculated to be that shown in Table 5 (cf. Table 3, cols. VII and VIII). In Table 5, seven unit cells of morinite and apatite are compared with one unit cell of whitlockite.

In columns IX and X of Table 2 are shown the partial compositions of hypothetical samples of morinite air-heated to 650° and to 835° (*thin* sample), assuming that this resulted only in the loss of water and part of the fluorine. The multiplication factors are based on actual measured percentage weight losses when heated in the manner described. The values thus obtained are so close to the actual analytical results that it seems reasonable to assume that on heating under these conditions, after the water is driven off from the morinite, nothing else is lost in any significant amount except fluorine. However, contrary to this view is the fact (shown by Fig. 1) that in going from 405° nafalapatite (weight loss of 10%) to 650° nafalapatite (weight loss of 18%) there has been a considerable weight loss. The formulas shown in Table 4 would presume a loss of 5.1 fluorines and a gain of 5.1 oxygens (plus minor amounts of various cations to retain electrical neutrality); these changes would account for less than a 2% loss in weight.

Although the samples were too fine to carry out satisfactory optical checking, the writer considers that the formulas given for the 650° nafalapatite and for the nafalwhitlockite are substantially correct. The evidence for the formula given for the 405° nafalapatite is based on the assumption that it has essentially the same composition as morinite without its water, and that the analyzed samples (Fig. 1, no. 8 and *T*) showing 13.65 and 14.11% fluorine consisted of single phases. As already noted the film (Fig. 2 *D*) for the former of these showed no extraneous (non-apatite) lines except for the (101) line of cristobalite, but the film of the latter had several extra lines. However did it not seem that postulating the presence of ($AlOF_3$) tetrahedra is so hazardous, the evidence for the existence of the 405° nafalapatite with the formula given would be regarded as very good. If the formula for this substance is wrong, then there is little evidence for assuming 475°± and 550°± nafalapatites; in fact the DTA results constitute about the only reason for postulating these two substances.

There are other reasons why some of the postulated compounds must be regarded as suspect. Clearly as shown in Table 4, the changes assumed from 405° to 650° nafalapatite are (chemically speaking) step by step substitution of oxygen for fluorine. And yet the thermal experiments indicated that no outside oxygen (or water) was needed to produce a nafalapatite that represented a 14% weight loss from the original morinite. Is it possible that the oxygen came from the morinite water, releasing H to form HF? Another enigma appears in comparing the formulas of nafalwhitlockite and 650° nafalapatite in Table 5. The nafalapatite is shown with (AlO_4) tetrahedra; i.e., all the fluorine presumed present at lower temperatures has been "cooked out" of these, the only fluorine left being in the Z position. And yet on further heating of this material (in *thin* films in the presence of air) nafalwhitlockite is produced and this is assumed to have (AlO_3F) tetrahedra!

Now why is any oxygen or water from the air needed to convert 650° nafalapatite to nafalwhitlockite? Note from Table 3 (cols. VI and VIII) that these two have essentially the same composition. In fact looking at their formulas (Table 5) it is seen that multiplying the numbers in the nafalwhitlockite formula by about 1.1 yields the numbers of the 7-unit cell 650° nafalapatite formula. This is about the ratio of the cell volumes, and the specific gravities appear to be the same.

According to the formulas given in Table 4, no additional oxygen is needed to produce 405° nafalapatite from morinite at 405°. Thus this conversion takes place on a thin or thick sample, in air or a vacuum; apparently it requires simply the removal of the water from the morinite. On the other hand from the formulas given it would appear that substitution of oxygen for fluorine is required to produce the "higher" nafalapatites. Should one assume that the necessary oxygen came from some residual morinite water, releasing the F as HF? This seems reasonable assuming the apatites represented by the lower vacuum curve (*F–J* of Fig. 1) are higher nafalapatites of some sort. Such possibilities make clear why what happens on heating morinite up to 500–650° shows considerable variation, depending on rate of heating, size of sample, whether exposed to air or not, etc.

ACKNOWLEDGMENTS

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ADDENDUM

While the manuscript of this paper was awaiting publication, a note on a synthetic apatite by W. Johnson appeared in the *Mineralogical Magazine* (March 1960, 408–411). By heating a 10:3 mixture of CaO and Cr_2O_3 in ordinary (moist) air at 900°C. for 24 hours, he obtained an apatite structure product of composition $Ca_4Ca_6\ (Cr^{+6}O_4)_4(Cr^{+3}O_4)_2\cdot(OH)_2$. It should be noted that Glasser and Osborn (*Journ. Amer. Cer. Soc.*, 41, 1958, 365–6) produced a whitlockite structure compound by heating a mixture of composition $3CaO\cdot Cr_2O_3$ in air between 900 and 1000° C. for 24 hours or longer. Johnson (and others) thought this was $Ca_9\ (Cr^{+6}O_4)_4(Cr^{+3}O_4)_2$, but Glasser and Osborn considered it to be $Ca_3(Cr^{+5}O_4)_2$. On crystallo-chemical grounds the presence of the relative large Cr^{+3} ion in these structures seems somewhat doubtful. However, Johnson found a cell volume of 568 A^3. (7.6% larger than the cell volume of a normal hydroxyapatite.) Taking the d values given by Glasser and Osborn for (22.0) and (30.6) yields $a=10.8$ and $c=38.2$ with a cell volume of 3850A.,^{3} over 13% larger than the value given in Table 5.

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