

MORINITE FROM THE BLACK HILLS

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ABSTRACT

Unit cell, space group, morphology, optical and other physical properties of the rare pegmatite monoclinic phosphate mineral morinite from the Hugo Mine, Keystone, S. Dakota, are given. Crystallochemical similarities and differences with epidote are described. Associated minerals are montebasite, apatite, augelite, wardite, and probably crandallite, as well as quartz and a clay mineral; paragenetic relations are briefly discussed.

In 1933-34 Runner obtained the samples which form the subject of this study from a mineral stand in Keystone, S. Dakota, run by the daughter of E. E. Hesnard (see Landes, 1929). She was certain that her father had collected them from the Hugo mine, but could supply no other information. Runner was unable to find the mineral suite in place.

Runner identified the minerals on the basis of the data shown in Table 1. Fisher verified the augelite, morinite, and wardite by means of x-ray powder patterns. The "primary" mineral of the suite is hydroxian amblygonite (montebasite), which occurs as coarsely cleavable white masses, part of a typical "nodule." This is embayed and apparently partially replaced by massive cleavable medium-fine grained light gray augelite; vugs in this are lined with the typical tabular subhedra of this mineral (3 by 1 mm.). Crossing the massive augelite in various directions are bundles of nearly parallel crystals of prismatic apatite up to an inch or more in length; these have a coarsely fibrous appearance. Some of this fibrous apatite is a deep violet color, but this grades off (along a single crystal) to light gray material with locally a bluish cast. In Runner's thin-sections he has noted fibrous apatite (frequently violet) cutting amblygonite, and augelite.

In one specimen, outside of the centimeter-wide band of augelite-fibrous apatite (which extends about half way around a projecting knob of amblygonite), there is a somewhat wider zone consisting of faintly pinkish (nearly colorless) morinite crystals in masses of light greenish to light bluish apatite. The morinite is massive, coarsely crystalline, and only locally shows a fair cleavage surface; it has a slightly oily luster, and striated crystal faces up to a centimeter long may be observed. The apatite also has an oily luster, is massive, coarse-grained and shows fair cleavage surfaces up to a centimeter across; it is probably subhedral, but this is not readily evident. No criteria to tell the relative ages of these two minerals were noted. However they are quite possibly younger than the augelite.

One specimen carrying the fibrous apatite has a small vug lined with

TABLE 1. OBSERVED PROPERTIES OF MINERALS

	Apatite	Augelite	Crandallite	Montebrasite	Morinite	Wardite
Color	Blue-grn. to violet	Cols.		White	Cols. to pale pink	Cols.
Habit	Prismatic	Tab. xtals, granular	Tiny prisms	Massive, cleavable	Prismatic, striated	Pyr. xtals, granular
Cleavage	Good, basal	Perfect prismatic	Perfect, \perp to elong.	3; 1 perf., 1 good, 1 dist.	1 good, \parallel elong.	1 good (basal)
H	5	4½	—	6	4½	—
G	—	—	—	2.85	2.962	—
α	1.628	1.573	1.620+	1.613	1.551	1.589
β	—	1.575	—	1.624	1.563+	1.589+
γ	1.632	1.588	1.630—	1.638	1.565	1.599
2V	0°	47°	—	75°+5°	43°	0°-5°
Sign	(-)	(+)	+elong.	(+)	(-)	(+)
Disp.	—	—	—	r < v weak	r < v weak	—
B.B.	Fusibility high	Swells, whitens, barely fusible	—	Fuses easily	Swells, whitens, barely fuses	—
c.t.	H ₂ O	H ₂ O	—	—	H ₂ O	—

NOTE. Optical properties were found with white light using certified immersion liquids, corrected for temperature; 2V determinations based on Mallard's constant.

Qualitative chemical tests were carried out on all minerals except crandallite and wardite. All tests made showed the normal elements to be present. In addition, the morinite gave a weak Li flame and is partially soluble in hot HCl and HNO₃. The apatite yielded a positive test for OH and F, negative ones for Cl and Mn

striated euhedra (1 mm.) of colorless wardite that appears to be dipyr-
amidal. This and other vugs have fine hexagonal needles of white silky
apatite crossing them, obviously a late mineral. Massive semi-milky
quartz occurs in one sample, associated with amblygonite and the mas-
sive greenish apatite. Crandallite (?) and a clay mineral were observed
locally in tiny veinlets in the amblygonite. It is interesting to note the
absence of feldspar, micas, beryl, and columbite in these specimens.

Morinite was described by Lacroix from Montebras, France in 1891;
its analysis by Carnot was first given in 1908. Ježekite (pronounced
yě' zhě-kīt) was described by Slavik from Greifenstein near Ehren-
friedersdorf, Saxony in 1914. In 1947 Frondel (Pabef, II, 784) established
that a fragment labelled morinite from Montebras supplied to him by
Slavik was identical with ježekite. Volborth in 1954 at Viitaniemi, Fin-
land, found samples of relatively massive morinite which were pen-
etrated by needles of ježekite (see his photo 31). What he called ježekite
was based on scanty data; for instance, he was unable to separate it from
the morinite, thus no x-ray diffraction pattern was obtained. Moreover
the optical properties used by Volborth to distinguish these two min-
erals are too closely similar to be significant of anything except minor
differences in chemical composition; thus ježekite may be regarded as a
sodian hydroxian morinite. X-ray powder patterns taken by the writer
of Volborth's morinite, Greifenstein ježekite and the Black Hills sample,
are identical; see Fig. 1. Spacings and indices are given in Table 2; the

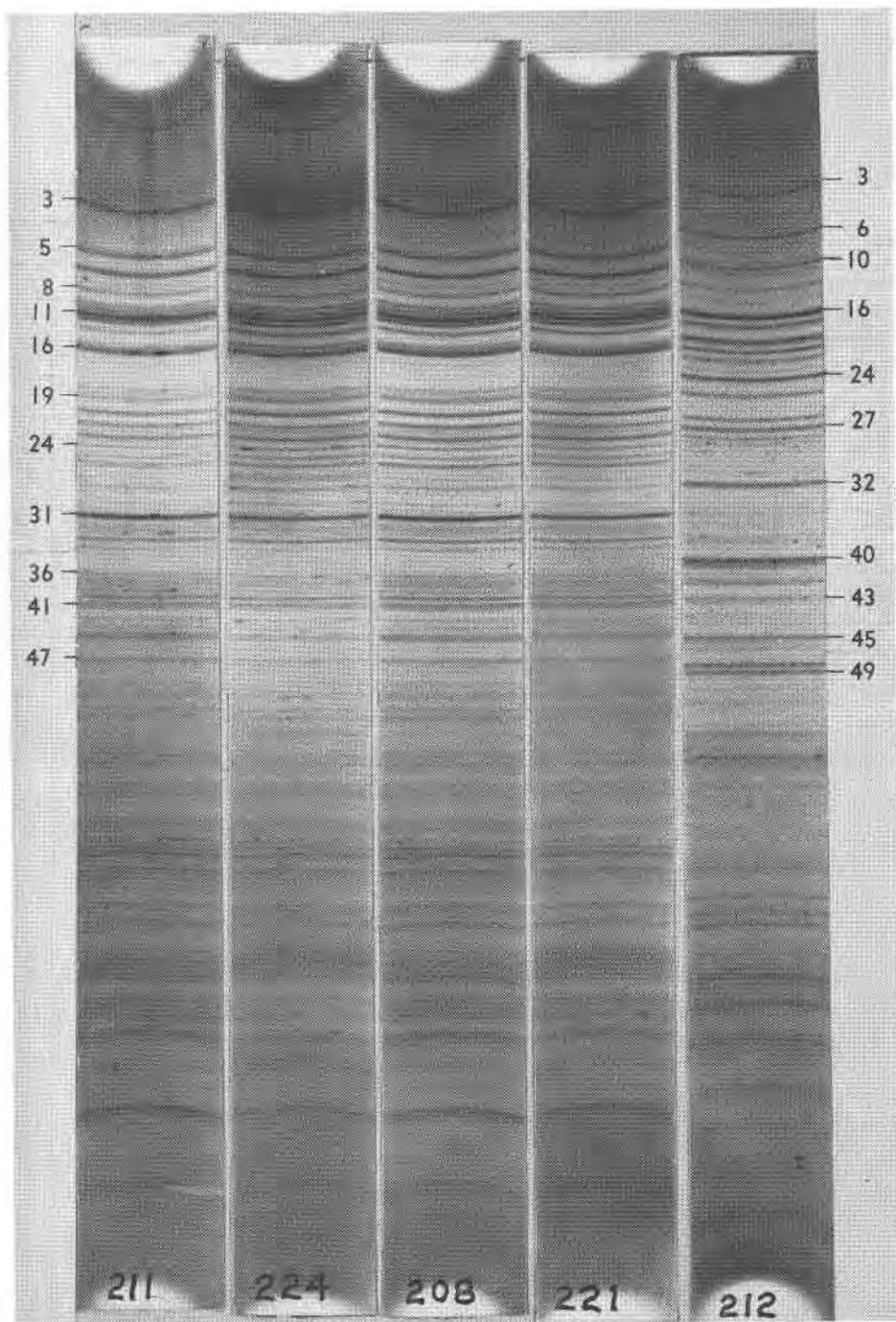


FIG. 1. X-ray powder films of (left to right) Finnish morinite, Saxon ježekite, Black Hills morinite, French morinite and Austrian epidote. All taken with Fe/Mn radiation in a 114 mm. diameter Straumanis-type (Philips) camera. Approximately natural size. See Table 2 for measured data and numbering of lines.

TABLE 2. POWDER FILM DATA

Line No.	Ježekite (Saxony)			Morinite (Black Hills)		Epidote (Untersulzbachtal)		
	Int.	<i>d</i>	Indices	Int.	<i>d</i>	Int.	<i>d</i>	Indices
1	6	9.115#	100	6	9.11	1—	8.00	$\bar{1}01, 100$
2			$\bar{1}01$	1—	5.22#	$\frac{1}{2}$	7.01	Not indexable
3	8	4.698#	011, $\bar{1}11$	7	4.70	4	5.01	$\bar{1}02$
4			111	1	3.83	$\frac{1}{2}$	4.64	110
5	7	3.742#	211	6	3.73	$\frac{1}{2}$	4.42#	201, ¹
6	9	3.472	220	8	3.47	4	4.00	202, 200
7			130	1	3.32	$\frac{1}{2}$	3.78	111, ²
8	4	3.212#	$\bar{2}21$	2	3.21	1	3.76#	$\bar{1}12$
9	2	3.069	201	2	3.08	1	3.59	(beta for line 12)
10	2	3.006	$\bar{3}01$	2	3.00	3	3.52	21 $\bar{1}$
11	10	2.945	031, $\bar{1}31$	10	2.94	2—	3.40	102, $\bar{1}03$
12	3	2.888	$\bar{3}11$	4	2.88	2	3.24	201, 210
13	3	2.805	230	3	2.81	$\frac{1}{2}$	3.18	203 ³
14			040	2—	2.69	$\frac{1}{2}$	3.06	003
15			$\bar{2}31$	1	2.66	*	2.97	$\bar{3}02, (\bar{3}01)$
16	8	2.631#	$\bar{1}12, 320, 002$	7	2.63	10	2.92	$\bar{1}13, (112)$
17	1	2.553	012	$\frac{1}{2}$	2.56	2	2.815	020, 211
18	2	2.372#	301, 102, $\bar{1}41$	1+	2.37	$\frac{1}{2}$	2.78	213
19	3	2.309#	$\bar{3}02, 311$	2—	2.31	5	2.69	013, 021, 300
20	6	2.230	141, 410, $\bar{2}41$	4	2.23	1	2.66	120, ($\bar{3}03, \bar{1}21$)
21	3	2.163#	321, 122	3	2.16	5	2.62	312, 31 $\bar{1}$
22			$\bar{4}21$	$\frac{3}{4}$	2.13	2	2.53	202, (103)
23	4	2.098	$\bar{2}32, 420$	3	2.10	1	2.46	$\bar{1}22, (121)$
24	3	2.056	202	2	2.055	7	2.40	$\bar{3}13, 022, 22\bar{1}$
25	3	2.017	212, 241	2—	2.015	3	2.30	$\bar{3}04, \bar{2}14, \bar{1}14$
26	4	1.979	$\bar{1}51$	2	1.98	2	2.17	222, 113
27	1	1.920#	222, 430	1	1.925	3	2.13	$\bar{4}01, \bar{1}23$ 122, ($\bar{4}03$) 221, $\bar{2}23, (014)$
28	1	1.886#	$\bar{5}01, \bar{4}22, \bar{2}42$	1+	1.89	2—	2.07	023
29	1	1.830#	500	1—	1.83	$\frac{1}{2}$	2.05	203
30			421, 510	$\frac{1}{2}$	1.80	$\frac{1}{2}$	2.02	400, 104, $\bar{2}05$

TABLE 2—(continued)

Line No.	Ježekite (Saxony)			Morinite (Black Hills)		Epidote (Untersulzbachtal)		
	Int.	<i>d</i>	Indices	Int.	<i>d</i>	Int.	<i>d</i>	Indices
31	9	1.786	060, 113, 232	8	1.783	$\frac{1}{2}$	1.93	213, 215
32				1	1.75#	4	1.88#	224, 123, 124 222, 115, 114 502
33				1—	1.73	$\frac{1}{2}$	1.78	
34	3	1.712		3	1.71	$\frac{1}{2}$	1.75	422?
35	1	1.689		1+	1.687	$\frac{1}{2}$	1.73	231, 032
36				1	1.615	1	1.71	204, 206, 415
37				1—	1.60	1	1.69	
38				1	1.59	$\frac{1}{2}$	1.673	
39	1	1.575		1	1.572	4	1.641	511
40	2	1.559		2	1.56	2	1.63	
41	3	1.542#		1+	1.546	1	1.59	
42				1	1.532	2—	1.58	
43	1	1.507#		$\frac{1}{2}$	1.51	2—	1.548	
44	1	1.492#		$\frac{1}{2}$	1.492	1	1.533	
45	2	1.474#		2	1.476	2	1.461	224, 604
46				2	1.468	$\frac{1}{2}$	1.45	
47	1	1.428#		2—	1.428	1	1.44	
48				$\frac{1}{2}$	1.386#	3	1.412	040
49						3	1.395	

Diffuse line.

* Present with intensity 3 on some synthetic epidote films; not given by the Untersulzbachtal epidote.

¹ Probably a beta reflection for line 6.² Probably a beta reflection for line 11.³ Probably a beta reflection for line 16.

Indices given in parentheses make only minor intensity contributions.

NOTE. The ježekite film was measured accurately by Leon Atlas; the other two measurements were made by Fisher using a Nies scale. The ježekite and French morinite samples were supplied by F. Čech of the Mineralogical Institute of Charles University (Prague) through the kindness of J. Kutina. The Finnish sample was supplied by A. Volborth. Indices were computed graphically by Fisher using the Peacock-Bloss technique (*Am. Mineral.*, **37**, 1952, 588-599). From a number of films the six stronger lines of morinite-ježekite (with intensities) were found to be: 2.94/10; 3.47/9; 2.63/8; 1.79/7+; 4.07/7—; and 3.74/6.

former agree in general with those of Murdoch for ježekite from Brazil, but the spacing for his first line should probably be 9.11 rather than 9.61. Volborth (p. 74) states that a sample of French morinite collected by Lacroix gave him an x -ray powder pattern identical with that he obtained from the Finnish morinite.

Precession and Weissenberg films were made from a single prismatic crystal of Black Hills morinite. The unit cell dimensions are $a_0 = 9.456 \text{ \AA}$, $b_0 = 10.690$, $c_0 = 5.445$. The space group is $P2_1$ or $P2_1/m$, almost certainly the latter when account is taken of the morphology. The b -axis is a screw, since the only systematic extinctions are those for $(0k0)$ where k is odd. β was found to be $105^\circ 27\frac{1}{2}'$. This leads to an axial ratio of 0.8846:1:0.5094. This may be compared to Slavik's determination for ježekite of 0.8959:1:1.0241 with β of $105^\circ 31\frac{1}{2}'$. The agreement is satisfactorily close if Slavik's c -value is halved. Transformation formula, Slavik to Fisher is thus $100/010/00\frac{1}{2}$.

The Black Hills crystal (0.2805 mm. thick along the b -axis, and 0.2020 mm. thick along the a^* -axis and about 3 mm. along c) has $b(010)$, $a(100)$, $m(110)$, $n(120)$, $l(210)$, $f(011)$, $r(\bar{1}01)$, $u(201)$ and $p(\bar{2}11)$. Forms $e(021)$, $t(102)$, and $s(101)$ found by Slavik on the Greifenstein ježekite are not present on the Black Hills crystal. Note that all these indices are given in terms of Fisher's axial ratio, but Slavik's letters are retained. The Black Hills crystal has only one "line" face ($\bar{1}20$) and ($\bar{2}10$) showing for n and l , and only ($\bar{2}11$) of the p -form is present on the crystal, but it is the largest face found; the crystal is terminated only at one end.

The Black Hills crystal is $(-)$ with $\gamma \rightsquigarrow b$ and $\beta \wedge c$ of $-60\frac{1}{2}^\circ$ (that is, the β direction lies in obtuse angle β). This was determined on the same crystal on the same goniometer head (no remounting) used for the x -ray work, by placing it on the universal microscope-goniometer (Fisher, 1952). Using the technique described for alluaudite (Fisher, 1955) the birefringence for Na light was found to be $\gamma - \alpha = 0.01400$ and $\beta - \alpha = 0.01234$. This leaves by difference that $\gamma - \beta = 0.00166$. Using these values and assuming $\alpha = 1.55100$ (approximate measurement by Runner) $2V$ is calculated at $39^\circ 42'$. For the Greifenstein ježekite Slavik gives extinction on (010) in obtuse angle β as $\alpha \wedge c = 29^\circ$ and $b = \beta$; Larsen and Berman state $\alpha \wedge a = 29^\circ$, $b = \beta$. For the French morinite Lacroix notes that the acute bisectrix $(-)$ makes an angle of about 30° in obtuse β , and that the optic plane is (010) ; Larsen and Berman give $b = \beta$, extinction at 30° in obtuse angle β , and $2V = 38^\circ \pm$. These results are very different from those found for the Black Hills morinite.¹ For the Viitaniemi mor-

¹ It is difficult to understand how both Lacroix and Slavik found the optic plane to be (010) . That they put direction α in obtuse angle β (rather than in acute angle β) at an angle of 30° to the c -axis is perhaps explicable since $\rho_{(001)} = 15^\circ 27\frac{1}{2}'$ and $\rho_{(\bar{1}01)} = 17^\circ 47'$. In short an alternative orientation for morinite is to reverse the direction of the $(+)$ a -axis making

inite Volborth has $b? = \gamma$ with $(001)? \wedge \alpha = 44^\circ$, but he is not certain as regards his morphology. Fisher's findings show $(001) \wedge \alpha = 45^\circ$; thus check Volborth's results almost perfectly, confirming his choice of indices.

TABLE 3. ANALYSES OF MORINITE AND JEŽEKITE

	I	II	III	IV	V	VI	VII	VIII
CaO	24.11	23.92 ¹	18.16	19.05	17.27	11.63	12.84	13.50
Na ₂ O	6.66	7.16 ²	3.35	5.13	6.36	25.72	25.74	27.07
Al ₂ O ₃	21.92	22.20	22.01	17.56	20.93	21.15	20.84	21.92
P ₂ O ₅	30.52	30.16 ³	30.65	33.05	29.14	29.45	28.81	30.30
F	12.26	11.49	14.36	13.02	13.65	7.88	7.75	8.15
H ₂ O	9.68	9.90	17.51	17.66	18.40	7.48	7.31	7.69
Total	105.15	104.83 ⁴	106.04	105.47	105.75	103.31	103.29	108.63
-O for F	5.16	4.84	6.04	5.48	5.75	3.32	3.26	3.46
Total	99.99	99.99	100.00	99.99	100.00	99.99	100.03	105.17
D	2.911	2.957	2.90	2.94	3.06	3.02	2.94	2.94

Explanation of columns

- I. Composition calculated for formula $\text{Ca}_4\text{Na}_2\text{Al}_4\text{F}_6\text{OH}_4(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$.
- II. Finnish morinite (Volborth, p. 77). Footnotes:
 - ¹ Including .09 SrO and 2.47 MnO; this is $\frac{1}{3}$ ion of Mn per unit cell.
 - ² Including .14 Li₂O and .18K₂O.
 - ³ Including .28 BeO and .49 SiO₂.
 - ⁴ This omits .17 H₂O(-) and .17 insoluble residue.
- III. Composition calculated for formula $\text{Ca}_3\text{NaAl}_4\text{F}_7(\text{PO}_4)_4 \cdot 9\text{H}_2\text{O}$.
- IV. French morinite (Carnot & Lacroix, 1908) summed to 100% (after eliminating 1.50 SiO₂ and 0.20 H₂O-).
- V. Composition calculated for formula $\text{Ca}_3\text{Na}_2\text{Al}_4\text{F}_7\text{OH}(\text{PO}_4)_4 \cdot 9\text{H}_2\text{O}$.
- VI. Composition calculated for formula $\text{Ca}_2\text{Na}_3\text{Al}_4\text{F}_4(\text{OH})_3(\text{PO}_4)_4$.
- VII. Composition in Column VIII made to sum to 100%.
- VIII. Saxon Ježekite (Skarnitzl, in Slavik, 1914) with 1.85% Li₂O included with Na₂O. Skarnitzl lists 18.71 Na, 0.86 Li, 7.26 OH, and trace of Fe₂O₃. He sums to 100.70. In the above, his values for Na, Li, & OH are converted to oxides.

The Black Hills specimen is suitable material to furnish a good chemical analysis, but at the moment no chemist is available. If we take Volborth's analysis (see col. II of Table 3) of the Finnish morinite and assume the unit cell volume is 530.5 \AA^3 and the specific gravity is 2.96, the unit cell contents (allocating the minor elements as follows: Li and K with Na; Mn and Sr with Ca; Be and Si with P) are calculated to be:

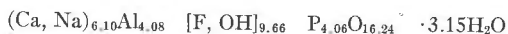


$\beta = 107^\circ 47'$ with direction α lying in obtuse angle β . Volborth has the cleavage as $(010)?$ and $(001)?$, whereas Lacroix and Slavik both make it (100) ; Slavik also lists (001) as an imperfect cleavage.

This can be recalculated to:



which can be written:



Volborth notes that the F-content should be about 1.3% higher than shown in the analysis; thus the ideal unit cell contents would seem to be very close to:



Actually all of the "water" in this analysis came off at +105°. Thus writing the analysis with 3H₂O and 4 OH is really a purely artificial technique which permits one to balance the analysis in convenient fashion. Thermogravimetric and perhaps infra-red studies are needed to tell more about the nature of the "water" as it actually occurs in the crystal.

At first glance it appears as if morinite might bear some crystallochemical relationship to epidote, since unit cell dimensions and chemical composition seen to have resemblances; thus:

	<i>S.G</i>	<i>a</i>	<i>b</i>	<i>c</i>	β	<i>Z</i>	<i>V</i>	<i>D</i>
Epidote ¹	<i>P</i> 2 ₁ / <i>m</i>	8.905 Å	5.636	10.145	115°23'	2	460	3.47
Morinite	<i>P</i> 2 ₁ / <i>m</i>	9.456 Å	2(5.345)	$\frac{1}{2}$ (10.890)	105°28'		530	2.96
Epidote	Ca ₂	(Al, Fe) ₃	(OH)	Si ₃ O ₁₂				
Morinite ²	(Ca, Na) ₄₋₈	Al ₃	(F, OH, O) ₅₋₉	P ₃ O ₁₂			0-2 H ₂ O	

This apparent similarity is enhanced when one plots (on a projection normal to the *b*-axis) the 0-level planes of the lattices of these two minerals, providing the *a*-axis of epidote is made to coincide with the \bar{c} -axis of morinite. In this case it is clear that there are a number of lattice points substantially in common; such common points form a pseudo-hexagonal network. Since the (100) spacing for morinite is only 0.57% less than the (001) spacing for epidote² (*a** is .1097 for morinite and *c** is .1091 for epidote), if the 0-levels (normal to the *b*-axis) of the reciprocal lattices for the two are plotted, not only do the (*h*00)* nodes of morinite practically coincide with the (00*l*)* nodes of epidote, but the nodes of the morinite third row (parallel *a**) nearly coincide with those of the epidote

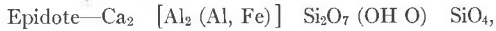
¹ New determination on an Untersulzbachtal crystal by Fisher; values $\pm .003\text{Å}$. This crystal is (-) with $2V=73^\circ00'$ and $\alpha \wedge [c] = -5^\circ17'$ (Na light).

² Approximate average of the two morinite and one jezekite formulae given in Volborth.

³ This does not show up well on the powder films (see Fig. 1), since the only moderately strong "front pinacoid" line of morinite is (100) [though (500) makes an important contribution to a weak line], while the only "basal pinacoid" line for epidote is the weak (003). The powder films of the two minerals are on the whole rather dissimilar (see Fig. 1); though each has its strongest line at $2.93 \pm .01$, this seems not to be due to any common structural condition.

fifth row (parallel c^*); the reciprocal spacing for this row in morinite is 0.551 and in epidote it is only about 0.011 greater.

However, when the formula for epidote is written to fit the structure determined by Belov and Rumanova or by Ito *et al.*:



since $Z=2$, it is seen that there are six silicate tetrahedra (4 double, 2

TABLE 4. UNIT CELL CONTENTS
(Omitting $3\text{H}_2\text{O}$ of morinite)

Cation	Morinite	Epidote	Anion	Morinite	Epidote
Ca	4	4			
Na	2	—	F	6	—
Al	4	4	OH	4	2
Fe'''	—	2	O	16	24
P	4	—			
Si	—	6			
Total	14	16		26	26
Unit cell volume	530	460	Vol. per anion	20.4	17.7
Σ valencies	42	50	D	2.91	3.47

single) in the unit cell, as opposed to only four phosphate tetrahedra in the morinite unit cell. The data as regards the unit cell contents (omitting the $3\text{H}_2\text{O}$ of morinite) are summarized in Table 4.

The greater density (D) of the epidote may be attributed largely to the presence in the unit cell of 2Fe (rather than 2Na), of two more Si (than P); and of only 2% H_2O . The difference in unit cell volume is of little significance in this connection, since the extra volume of the morinite cell is necessary to pack in the larger Na (than the smaller Fe), and especially to hold the $3\text{H}_2\text{O}$. If the latter be assumed to add the volume of 3 anions to the unit cell, the volume per anion is reduced from 20.4 (see Table 4) to 18.3, a figure not significantly different from the 17.7 of epidote. But this comparison is not very rigorous, since the morinite unit cell contains two large cations (sodium) absent in epidote.

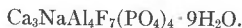
The unit cell contents clearly indicate that morinite is a nesophosphate (unless some of its aluminum is in 4-coordination), whereas epidote was found to be a combination neso- and sorosilicate. Thus the two structures would seem to be quite different, even though geometrically and chemically they have much in common. The concept that morinite has sort of a "stuffed" epidote structure seems very doubtful. This is borne out by the differences in the powder diffraction patterns; see Fig. 1.

Analyses of the French morinite (IV) and Saxon ježekite (VII) also

appear in Table 3. The formula for the latter as given in Pabef (II, 785) seems unsatisfactory because of the lack of agreement between analyzed and theoretical OH. The actual unit cell contents of the French morinite are computed to be:



This may be idealized as:



or as:



The actual unit cell contents of the Saxon ježekite are computed to be:



This may be idealized as:



The analyses on which these formulae are based were made long ago. It was with considerable difficulty that enough material was obtained. It is not surprising that they show disagreements. The presence of 1.1 ion of Li in the ježekite unit cell seems very doubtful; more probably there was some amblygonite contamination. In both of these analyses an attempt was made to balance fluorine (or F+OH) against calcium (France) or the alkalis (Saxony) as was customary in those days. In the former case there was insufficient calcium, in the latter excess alkalis. If the ježekite analysis is recast from the partly-elementary form as given (see Pabef) into the oxide form (col. VIII of Table 3) it is seen that it sums to 105%, indicating serious errors somewhere.

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