

DICKINSONITES, FILLOWITE AND ALLUAUDITES

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ABSTRACT

Herein is discussed the crystallography and chemistry of these three Na-Fe-Mn pegmatite phosphates, together with their interrelations. The dickinsonites invert to alluaudites on heating in air to around 500°, to fillowite on heating in vacuum to 850°. Fillowite on heating in air at 885° slowly changes to alluaudite. Alluaudite is stable on heating in air to 1000°, its approximate melting point.

INTRODUCTION

The dickinsonites (dickinsonite *s.s.* and arrojadite), fillowite, and alluaudites are predominantly sodium-manganese-iron phosphates occurring in pegmatites. Fillowite is rhombohedral, and has been found only at Branchville, Connecticut (Shainin, 1946) where it is of hydrothermal origin; the others are monoclinic and are both "primary" and hydrothermal. On heating in air to around 500° C. the dickinsonites change to alluaudites. On heating in a vacuum to 850° C. arrojadite (ferrodickinsonite) inverts to ferrofillowite. On heating in air at 885° fillowite slowly changes to alluaudite. Alluaudites show no important change in their diffraction pattern on heating in air to 1000° C., the approximate melting point.

Analyses of these minerals in substantially all cases show a small water content, always less than 2% when dealing with fresh-appearing material. In Danas' System (Palache *et al.*, 1951) fillowite and dickinsonite (following Brush and Dana, 1879, 1890) are assumed to carry essential water, whereas alluaudites and arrojadite are shown without it. According to Thoreau and Bastien (1954b), alluaudite from Ruanda has an endothermic reaction by DTA at 215° due to loss of water. However their analysis of this material showed 3.55% H₂O (Table 8), a value that seems clearly too high for really fresh material.

INFRARED SPECTRA

In the hope that some knowledge could be obtained regarding the presence or absence of essential H₂O or OH in these phosphates, infrared spectra of alluaudite and arrojadite along with ten other phosphates were run as shown in Fig. 1. All samples were first heated at 105° to drive off adsorbed water. Absorption with peaks in the range 9–10 microns and beyond 15 microns is presumably due to the phosphate ion. Absorption in the 2.75 and 6.1 ranges is attributed to unbonded OH ("water of crystallization" or entrapped liquid molecular water), and in the 3.0 range to bonded OH. None of the samples shows absorption in the 2.75 area (presumably because of the previous heating to 105°), but

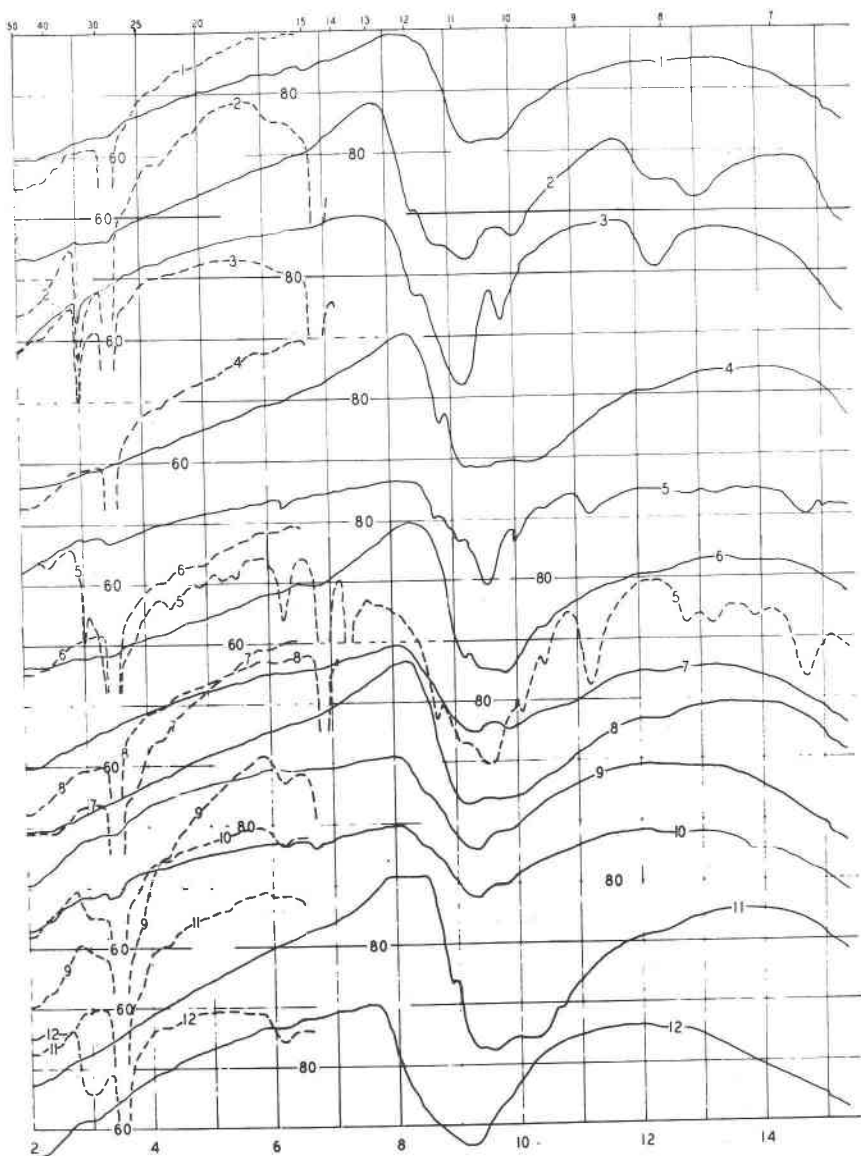


FIG. 1. Infrared spectrum curves for 12 phosphates obtained in 1955 by L. C. Bonham in the laboratory of the California Research Corporation, La Habra, Calif. with a Perkin-Elmer Model 21 equipped with a NaCl prism. Abscissa shows wave length in microns (base) or wave number in $\text{cm}^{-1}/100$ (top); ordinate is % transmittance (lines spaced at 20% intervals). Continuous lines give the results with dry smears on a salt block, and dashed lines (2 to $7\frac{1}{2}$ microns only except in the case of morinite #5) show the results with the

several show absorption near 3.0. These include lazulite (2), montebbrasite (3), morinite (5), sicklerite (10) and wavellite (12). Absorption in the 6.1 region is shown by morinite (5), vivianite (9), sicklerite (10), and wavellite (12). In short, these results confirm the presence of bonded OH in lazulite (2), montebbrasite (3), and wavellite (12), and of unbonded OH in vivianite¹ (9) and wavellite (12). They indicate that morinite (5; Fisher, 1960) and sicklerite (10) contain both kinds of "water" also. None of the other minerals represented in this Fig. 1 is known to carry OH, although this is present in certain varieties of triplite (1) and apatite (6). Sicklerite (10) is a mineral of somewhat doubtful composition which this study perhaps indicates has both of these types of OH. This figure clearly indicates that both alluaudite (7) and arrojadite (8) lack essential OH of either type. Infrared work on mineral phosphates has been published by Adler (1963-64), Anderson *et al.* (1962), Keller *et al.* (1952), Moenke (1962), and Omori (1961, 1964), among others.

CRYSTALLOGRAPHY OF DICKINSONITES

The space group of dickinsonite was given by Wolfe (1941) as #15— $C2/c$. The writer confirms this group, but herewith presents it in the orientation $A 2_1/n$, so that $c < a$. The unit cell values (in Å) in this orientation are shown in Table 1.

The powder data appear in Table 2. Here the calculated d-values (based on the Fisher Branchville unit cell) are shown for "reflections" actually observed (except those marked ?) on single crystal pictures; for any one line these are listed in a rough order of decreasing intensity.

¹ I am indebted to Paul B. Moore of this department for pointing out that H. Mori and T. Ito (*Acta Cryst.* 3, 1-5, 1950) have shown that the "water" in vivianite is bonded to Fe octahedra.

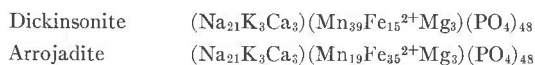
thicker Nujol smears. On these latter the absorption peaks due to the Nujol at 3.5, 6.85, and 7.25 microns are omitted.

- 1—Triplite. Schlaggenwald, Bohemia.
- 2—Lazulite. Death Valley, California.
- 3—Montebbrasite. Custer Mt. Lode, Black Hills, S. Dakota.
- 4—Lithiophilite, Custer Mt. Lode.
- 5—Morinite. Hugo mine, Black Hills.
- 6—Apatite. Buckingham, Quebec.
- 7—Alluaudite. Chanteloube, France.
- 8—Arrojadite. Nickel Plate mine, Black Hills.
- 9—Vivianite. Mullica Hills, New Jersey.
- 10—Sicklerite. Custer Mt. Lode.
- 11—Natrophilite. Branchville, Connecticut.
- 12—Wavellite. Garland County, Arkansas.

The spacings and estimated intensities of the stronger lines are 3.05(10), 2.72(9-), 3.22(7-), 2.78(5), 2.85 (5-), 5.93(4), 5.01(4), and 2.55(4-).

CHEMISTRY OF DICKINSONITES

Computations based on the published analyses of dickinsonites (water-free basis) are shown in Table 3. From these it is clear that the approximate formulæ are as follows:



though the latter to provide a better fit with analysis no. 4 can be expressed as $(\text{Na}_{19}\text{K}_3\text{Ca}\cdot) [\text{Ca}_3\text{Mn}_{19}\text{Fe}_{35}(\text{Mn}2/3\text{Mg}7/3)] (\text{PO}_4)_{48}$; (Table 4). The general formula thus becomes $3[\text{W}_9\text{X}_{19}(\text{PO}_4)_{16}]$; or if Ca is put in the X-position, $12[\text{W}_2\text{X}_5(\text{PO}_4)_4]$. The value assumed for the density of the Black Hills arrojadite is less than the 3.55 given by Lindberg

TABLE 1. UNIT CELL DATA ON DICKINSONITES

Name	<i>a</i>	<i>b</i>	<i>c</i>	β	<i>V</i> ₀	Locality	Author
Dickinsonite	24.74	9.97	16.73	104°41'	3992	Poland, Me.	Wolfe
Dickinsonite	24.89	10.11	16.68	105°41'	4041	Branchville, Conn.	Fisher
Arrojadite	24.78	10.05	16.51	105°41'?	3959	Black Hills	Fisher
Arrojadite	24.89	10.02	16.60	105°50'	3983	Black Hills	Lindberg

(1950) or the 3.61 of Headden (1891). If one takes the 3.55 figure, it leads to 196 oxygens in the arrojadite unit cell, a result inconsistent with that obtained for the New England dickinsonites. The 2.66% Al₂O₃ (as well as the 0.80% F) found by Mrs. Lindberg are also neglected (as they are in Danas' System). If these are taken into account and thus the unit cell is assumed to have 188½ oxygens and 3½ fluorines, the computed density is only 3.435. The large amount of Fe₂O₃ in the samples from Serra Branca, Brazil (Guimaraes, 1942) means that the material is highly oxidized; thus the analyses are extremely difficult of interpretation, since the amount of Fe₂O₃ present in the analyzed sample is uncertain.

CRYSTALLOGRAPHY OF FILLOWITE

A decade back I examined a sample of fillowite from Branchville, Conn. (Fisher, 1955a) kindly supplied by Professor Frondel from the Harvard collection. Optically it was found to be biaxial (+) with $2V=30^\circ +$. I therefore assumed that it was monoclinic as stated by Brush and Dana (1879). A second level precession picture (Fig. 2) so

TABLE 2. X-RAY DATA ON DICKINSONITE

Line No.	Powder film data												Reflections observed on single crystal films														
	I			II			III			IV			V			hkl			Calc. d			hkl			Calc. d		
	I	d	I	d	I	d	I	d	I	d	I	d	hkl	Calc. d	hkl	Calc. d	hkl	Calc. d	hkl	Calc. d	hkl	Calc. d	hkl	Calc. d			
1	2	11.822	1	12.08	2	12.14	200	11.980	002	8.080	011*	8.646	111*	8.547	211*	7.618											
2	3	7.623	3	7.65	3	7.62	202	8.000																			
3			1	7.12	1	7.12																					
4	2	6.478	1	6.51	2	6.52	211	6.076	311	6.455																	
5	4	5.931	4	5.93	4	5.93	400	5.990	402	5.794	5.794	311	5.607														
6	3	5.524	4	5.55	4	5.54	411	5.524																			
7	4	4.987	3	5.02	3	5.01	020	5.055	213	4.982	113	5.010															
8	3	4.584	3	4.58	3	4.58	013	4.872	411	4.761	220	4.683	313	4.717	511	4.602	113	4.581									
9			1	4.22	1	4.23	222	4.273	204	4.322	122	4.210	092	4.323	320	4.317	413	4.371									
10			1	3.84	1	3.84	004	4.015	322	4.075	600	3.993	511	4.074	420	3.924	513	3.985	404	4.000	611	3.963					
11																											
12	3	3.410	3	3.42	3	3.42	613	3.609	392	3.631	304	3.667															
13																											
14	1	3.313	1	3.32	1	3.33	031	3.551	522	3.517	520	3.547															
15																											
16	7	3.212	5	3.22	6	3.22	713	3.450	602	3.369	422	3.339	711	3.463	604	3.443											
17																											
18	1	3.118	1	3.13	2	3.14																					
19	10	3.037	10	3.04	10	3.04	421	3.137	415	3.172	231	3.151	331	3.127	331	3.014	811	3.067	515	3.052	015	3.168					
20	5	2.846	2	2.86	4	2.847	115	3.046	522	3.056	800	2.995	404	3.099	524	3.002	124	3.109	513	3.131	711	3.138					
							813	2.859	033	2.862	804	2.807	615	2.903	224	2.968	233	2.899	431	2.981	206	2.88					
											722	2.657	133	3.226	720	2.909	215	3.226									

(Continued on next page)

TABLE 2—X-RAY DATA ON DICKINSONITE (Continued)

Line No.	Powder film data					Reflections observed on single crystal films														
	I	II	III	IV	V	hkl	Calc. d	hkl	Calc. d	hkl	Calc. d	hkl	Calc. d	hkl	Calc. d	hkl	Calc. d	hkl	Calc. d	
21		1	2.843																	
22		1	2.814																	
23	5	2.766	2	2.781	6	2.778		4	2.766	4	2.777									
24		1	2.753																	
25	9	2.703	7	2.719	9	2.715		8	2.712	8	2.723									
26		4	2.676	4	2.676			1	2.680	1	2.68									
27		4	2.650	4	2.650			1	2.594	1	2.59									
28		1	2.603	1	2.603															
29		1	2.567	1	2.567															
30	5	2.553	2	2.552	4	2.56		3	2.554	3	2.56									
31	2	2.505	2	2.517	2	2.52		2	2.518	2	2.518									
32	4	2.415	1	2.429	3	2.44		2	2.421	2	2.424									
33		1	3.413	1	3.413			1	2.385	1	2.391									
34		1	2.382	1	2.380															
35		1	2.342	1	2.342															
36		1	2.313	1	2.313															
37		1	2.283	1	2.283															
38		1	2.279	1	2.257															
39	1	2.218	1	2.222																
40	2	2.194	14	2.200				1	2.214	1	2.226									
41	1	2.148	3	2.132				1	2.192	1	2.202									
42	2	2.119	1	2.115				2	2.115	1	2.150									
43	1	1.982	1	1.981																
44	2	1.955	1	1.961				1	1.976	1	1.989									
45	3	1.914	1	1.922				1	1.93	1	1.955									
46			1	1.910				2	1.915	2	1.92									

I Arrojadite, South Dakota, D.J.F. Fe/Mn radiation, 114 mm Straumanns (Philips) camera
 II Arrojadite, South Dakota, D.J.F. Co/K α radiation, Gunter camera
 III Dickinsonite, Braucheville, Conn., D.J.F. Fe/Mn radiation, 114 mm Straumanns camera
 IV Arrojadite, Brazil, M. L. Lindberg, *Am. Mineral.*, **35** (1950), 72
 V Arrojadite, South Dakota, M. L. Lindberg, *Am. Mineral.*, **35** (1950), 72

TABLE 3. ELEMENTS IN THE UNIT CELLS OF DICKINSONITES CONTAINING 192 OXYGENS

No.	K	Na	Ca	Mn	Fe ²⁺	Mg	Li	P	V ₀	G
1	2.82	20.94	3.34	38.79	16.06	—	1.00	48.57	4041	3.42
2	3.26	20.28	3.17	38.26	15.38	—	1.28	49.11	4041	3.40
3	3.08	20.12	3.02	37.81	14.47	3.48	1.12	48.42	4041	3.39
4	3.20	17.88	3.79	19.25	33.99	2.24	0.50	48.77	3959	3.47
5	3.68	20.86	8.55	18.99	30.22	3.22	1.60	47.18	3959	3.49

1—Dickinsonite, Branchville, Conn. (Wells, 1890, no. 1)

2—Dickinsonite, Branchville, Conn. (Wells, 1890, no. 2)

3—Dickinsonite, Poland, Me. (Gonyer, 1930)

4—Arrojadite, Black Hills, S. Dak. (Lindberg, 1950)

5—Arrojadite, Black Hills, S. Dak. (Headden, 1891)

Above table recomputed to make P=48 and W=24 and X=60

No.	W			X					Sum of cation valences ¹
	K	Na	Ca	Ca	Mn	Fe ²⁺	Mg	Li	
1	2.86	21.14	—	3.44 ^A	39.29	16.26	—	1.01	142.93
2	3.35	20.65	—	3.47 ^B	39.37	15.83	—	1.32	142.44
3	3.12	20.33	0.55	2.50	38.21	14.62	3.52	1.14	143.39
4	3.32	18.58	2.10	1.84	20.00	35.31	2.33	0.51	145.57
5	3.55	20.11	0.34	7.90	18.31	29.14	3.10	1.54	145.78

A includes 0.06 atoms Na

B includes 0.22 atoms Na

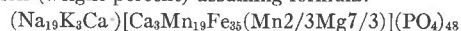
¹ The sum of the cation valences in each row of this lower table is not quite exactly 144, as it theoretically should be.

TABLE 4. BLACK HILLS ARROJADITE

	1	2	Percent difference
K ₂ O	1.82	1.69	7.1
CaO	2.57	2.68	4.3
Na ₂ O	6.69	7.04	5.2
MnO	16.50	16.68	1.1
FeO	29.51	30.06	1.9
MgO	1.09	1.12	2.7
P ₂ O ₅	41.82	40.73	2.6
	100.00	100.00	

1. Analysis by Lindberg (1950) omitting Li, Al, F, and H₂O.

2. Composition (weight percent) assuming formula:



with G=3.51. The fit is very good, especially if one assumes that a little of the Na is replaced by K. The dot after the Ca indicates one vacant lattice position.

intrigued me that I sent it out as my 1954 Christmas card to about 100 of my crystallographer friends stating that in the picture the b -axis was horizontal and that precession was in the direction $[101]$. While many told me they admired the card, only one, Professor J. D. H. Donnay of Johns Hopkins, informed me it was not monoclinic but rhombohedral. I thereupon checked back on the pictures of the other levels and concluded Professor Donnay was right. From Fig. 2 (a_{hex} . axis horizontal, c_{hex} . the precessing direction) it almost looks as though

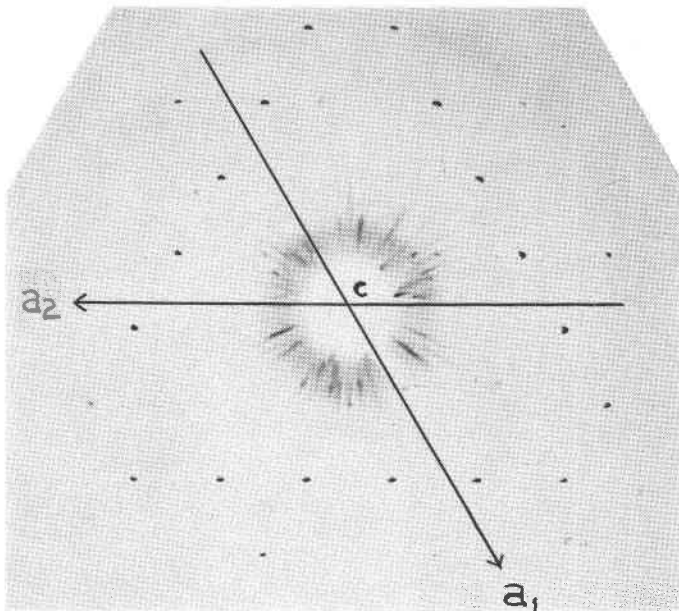


FIG. 2. Second level precession photo of fillowite from Branchville, Conn. Fe $K\alpha$, 45 kv., 10 ma., 31 hrs.

there were three vertical symmetry planes, but from the 0- and 1-level pictures in the same orientation it is clear that there are no such planes; thus the 0-level picture shows (+) or obverse hexagonal clino-prisms $\{41\bar{5}0\}$ and $\{52\bar{7}0\}$, but lacks the (-) or reverse forms $\{14\bar{5}0\}$ and $\{25\bar{7}0\}$. Similarly the 1-level photograph has the (+) or obverse right clino-rhombohedral $\{32\bar{5}1\}$, but lacks $\{23\bar{5}1\}$, $\{35\bar{2}1\}$, and $\{25\bar{3}1\}$. It also has the (-) or reverse right clino-rhombohedral $\{24\bar{6}1\}$, and the left form $\{64\bar{2}1\}$, but lacks the (+) forms $\{42\bar{6}1\}$ and $\{62\bar{4}1\}$. The 2-level pattern (Fig. 2) shows an equilateral triangle of spots for the (+) right and left clino-rhombohedral $\{314\bar{2}\}$ and $\{413\bar{2}\}$ and the (-) right and left forms $\{235\bar{2}\}$ and $\{532\bar{2}\}$; also $\{156\bar{2}\}$ and $\{651\bar{2}\}$; the latter

(near the corners) are of lesser intensity. The six "outside spots" are the (+) right and left clinorhombohedral {4262} (medium strong) and {6242} (weak). Since the 0-level photo also shows the absence of two-fold axes normal to $[c]$, and the "reflections" all fit $-h+k+l=3n$, the space group must be $R3$ (#146) or $R\bar{3}$ (#148). Until some test is made to indicate the presence or absence of a center of symmetry, it is not possible to make a certain choice between these two space groups. However preference is given to the latter on a morphological basis, since Brush and Dana (1879) state that "rarely a nearly complete crystal" is observed; since this is taken to have a rhombohedron (rather than two trigonal pyramids) with small basal pinacoid, fillowite may be assumed for the time being to have a center of symmetry and belong to the dolomite class. The Brush and Dana forms p (201) and d ($\bar{1}11$) thus become e (01 $\bar{1}2$). Fillowite has $a_{\text{hex.}}=15.25^4 \text{ \AA}$ and $c=43.32 \text{ \AA}$ with unit cell volume of 8730 \AA^3 (Fisher, 1955a). The rhombohedral unit cell has $a=16.91^4 \text{ \AA}$ and $\alpha=53^\circ 36'$ with volume of 2910 \AA^3 . ρ (0112) = $58^\circ 37'$, (01 $\bar{1}2$) \wedge (1 $\bar{1}02$) = $95^\circ 21'$, $a:c=1:2.84$, $p_0:r_0=3.28$, and $\lambda=111^\circ 52'$. The writer measured a single crystal on the reflection goniometer and in addition to three faces of e {01 $\bar{1}2$ } found a poor face with the approximate indices of (4 $\bar{1}$ $\bar{3}$ \cdot $\bar{1}\bar{3}$). The Branchville fillowite is (+) with $\omega=1.671 \pm .002$ and $\epsilon=1.676 \pm .002$ (Fron del, 1941). The synthetic ferrofillowite (see below) has $\omega=1.682 \pm .002$. Data obtained from the powder pictures of Branchville fillowite are given in Table 5. The spacings and estimated intensities of the stronger lines are 2.80(10), 3.01(7), 3.62(6+), 2.54(6), 1.89(4), 3.79(4-), and 11.3(3+).

CHEMISTRY OF FILLOWITE

The results from the study of fillowite analyses are shown in Table 6. From columns I & II of this table it seems highly probable that the hexagonal unit cell carries 412 oxygens. Assuming the formula



the hypothetical composition would be that shown in column III if the specific gravity is taken as 3.42 (one of the values given by Brush and Dana, 1879); the figures given here are in satisfactory agreement with those of columns I and II. While the data shown in column IV are not out-of-line with those of columns I and II, the formula on which they are based is rather unsatisfactory, since it carries only 408 oxygens; moreover the assumed specific gravity of 3.38 is definitely too low to fit the observed values, and the 100. figure for Mn is also too low. However it does have the advantage that the number of PO_4 -ions (=102) is divisible by three, thus allowing for a rhombohedral cell containing

TABLE 5. POWDER DATA FOR FILLWITE

Line No.	d_c	d_m	I_p	hk·l	I_s	hk·l	I_s	hk·l	I_s	hk·l	I_s	hk·l	I_s
1	11.280	11.438	3+	01.2	4+								
2	8.400	8.492	2	01.4	6								
3	7.220	7.352	$\frac{1}{2}$	00.6	4								
	6.744	—	—	11.3	5								
4	6.318	6.365	$\frac{1}{2}$	20.2	2								
5	5.640	5.690	1	02.4	7								
6	5.242	5.288	1	11.6	—								
7	4.963	5.158	$\frac{1}{2}$	21.1	$\frac{1}{2}$								
	4.874	—	—	12.2	1								
8	4.541	4.565	1	32.4	10								
9	4.35-.40	4.367	$\frac{1}{2}$	30.0	4	20.1	—						
10	4.21	4.252	$\frac{1}{2}$	03.3	6	02.8	4						
11	3.76-.81	3.789	4-	03.6	8	22.0	2						
12	3.66-.69	3.716	$\frac{1}{2}$	22.3	6	13.1	2						
13	3.61-.62	3.640	6+	00.12	10	31.2	8						
14	3.475	3.492	1	13.4	5								
15	3.372	3.397	1	22.6	1								
16	3.27-.29	3.293	$\frac{1}{2}$	40.2	1	12.10	5	40.1	$\frac{1}{2}$				
17		3.234	1										
18	3.159	3.172	$\frac{1}{2}$	01.4	4								
19	3.025	3.029	1	32.1	4								
20	2.99-3.01	3.017	7	23.2	9	01.14	8	42.9	6				
21	2.9204	2.935	1	52.4	1								
22	2.8880	2.896	1	00.15	1								
23	2.86-.88	2.873	$\frac{1}{2}$	41.0	6	53.5	4						
24	2.827	2.843	1	41.3	9	04.8	—						
25	2.79-.80	2.814	10	03.12	10	02.14	10	31.10	6	30.12	—		
26	2.680	2.692	1	14.6	7	14.11	7						
27	2.62-.64	2.647	1	05.1	4	52.8	5	31.14	6	50.2	0	22.12	—
28	2.5423	2.552	6	33.0	10								
29	2.48-.50	2.500	$\frac{1}{2}$	24.1	9	42.2	4	33.3	$\frac{1}{2}$				
30		2.442	$\frac{1}{2}$										
31	2.40-.41	2.408	1	33.6	8	00.18	2						
32	2.3811	2.390	$\frac{1}{2}$	13.16	7								
33	2.36-.37	2.367	1	15.2	7	11.14	6	51.1	—				
34	2.25-.26	2.25	$\frac{1}{2}$	63.9	4	05.10	—						
	2.2017	—	—	60.0	7								
35	2.16-.18	2.16	2	60.3	4	62.10	5	20.19	4	43.1	—		
36	2.09-.12	2.10	$\frac{1}{2}$	06.6	6	52.0	7	01.16	5	31.17	4	25.3	1
	2.06-.08	—	—	00.21	5	63.12	6	20.20	4				
37	2.0353	2.04	$\frac{1}{2}$	22.18	5								
38	2.01	2.01	$\frac{1}{2}$	05.14	5	16.1	—	61.2	—				
39	1.94-.95	1.94	$\frac{1}{2}$	25.9	1	01.22	7	31.19	5				
40	1.88-.91	1.888	4	06.12	10	51.14	9	63.15	6	05.16	5		
41	1.8474	1.853	$\frac{1}{2}$	15.18	7								
42	1.83	1.831	1	16.10	8	25.12	1	26.2	—	62.1	—		
43	1.8050	1.81	$\frac{1}{2}$	00.24	9								
44	1.73-.75	1.7404	1	51.17	8	13.22	7	17.0	—	71.3	—		

Explanation of columns d_c =calculated spacing d_m =measured places (Guinier camera, Co radiation, except for lines whose spacing is given to only two decimal places; these based on 114 mm Straumanis (Philips) camera with Fe radiation) I_p =Uncorrected visual intensities from powder film I_s =Uncorrected visual intensities from single-crystal films

hk·l=Bravais-Miller indices

Possible planes contributing to line #40 also include 70.1, 35.1, 07.2, 53.2, and 44.3.

TABLE 5—(Continued)

Line No.	d_e	d_{in}	I_p	hk·l	I_s	hk·l	I_s	hk·l	I_s	hk·l	I_s	hk·l	I_s
45	1.68-70	1.69	$\frac{1}{2}$	41.21	7	25.15	4	54.1	—	50.20	—	45.2	
46	1.65-.66	1.66	$\frac{1}{2}$	01.26	8	36.0	—						
47	1.64-65	1.64	$\frac{1}{2}$	17.9	7	08.1	—	80.2	—				
48	1.60-.61	1.61	$\frac{1}{2}$	07.14	8	00.27	1	27.1	—				
49	1.5889	1.59	$\frac{1}{2}$	52.18	2								
50		1.57	$\frac{1}{2}$										
53		1.51	1										
56	1.46-.47	1.46	1	09.0	9	90.3	—						
	1.4440	—	—	00.30	$\frac{1}{2}$								
59	1.4100	1.41	$\frac{1}{2}$	08.16	—								
60		1.39	$\frac{1}{2}$										
73		1.16	1+										
74		1.12	1										

TABLE 6. RESULTS FROM FILLOWITE ANALYSES ON A H₂O-FREE BASIS

	I		II		III		IV	
	Wt. %	Cations per U.C.	Wt. %	Cations per U.C.	Wt. %	Cations per U.C.	Wt. %	Cations per U.C.
CaO	4.17	13.40 ⁵	3.70	11.89	3.75	12	3.79	12
Na ₂ O	5.87	34.14	5.54	32.22	5.69	33	5.76	33
MnO	40.35	102.55	40.36	102.57 ⁵	40.27	102	39.92	100
FeO	9.55	23.96	9.88	24.79	9.60	24	9.71	24
Li ₂ O	0.06	0.72	0.07	0.84	—	—	0.08	1
P ₂ O ₅	40.00	101.60	40.45	102.74	40.69	103	40.74	102
Total	100.00	411.34 ¹	100.00	412.64 ¹	100.00	412 ¹	100.00	408 ¹
Water	1.66		1.58		0.00		0.00	

¹ Anions per unit cell

I. Average of two analyses by Penfield (1879); G=3.43

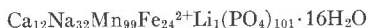
II. Analysis by Wells (1890); G=3.43

III. Composition assuming a formula of Ca₁₂Na₃₃Mn₁₀₂Fe₂₄²⁺(PO₄)₁₀₃ with G=3.42IV. Composition assuming a formula of Ca₁₂Na₃₃Mn₁₀₀Fe₂₄²⁺Li(PO₄)₁₀₂ with G=3.38



with $\frac{1}{3}$ of a Mn missing and another $\frac{1}{3}$ Mn replaced by $\frac{1}{3}$ Li.

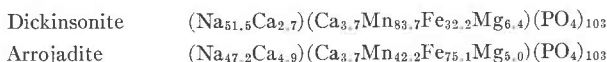
In Danas' System (Palache *et al.*, 1951) fillowite is assumed to have an essential water content. Taken this way, the unit cell contents are approximately:



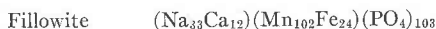
if an average analysis is computed with density of 3.435. However if one attempts to integrate the water into the formula not as "water of crystallization," it is seen that there is a hopelessly large deficiency of P in the analysis for this purpose, requiring 105 (PO₄). About five of the oxygen tetrahedra in the average unit cell would need to have a central cation other than P under these conditions.

DICKINSONITE AND FILLOWITE

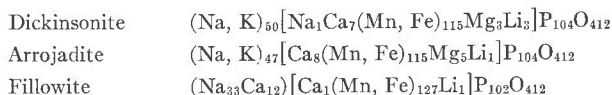
Are dickinsonite and fillowite dimorphous? In the thermal experiments described ahead it is shown that when arrojadite (ferro-dickinsonite) is heated in an evacuated Vycor tube, fillowite is formed at a temperature between 750 and 850 or higher. However since at these temperatures low cristobalite is also produced, it is not safe to conclude from these experiments that the two substances have the same composition. If the formulas of dickinsonites are multiplied by 103/48, one gets (putting K with the Na):



which may be compared with



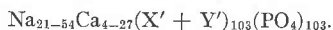
The major difference in composition (allowing for vicarious elements) thus seems to be that fillowite carries less Na. Looked at another way, taking the dickinsonites to be $\text{W}_{24}\text{X}_{60}(\text{PO}_4)_{48}$, one can multiply this by 412/192 yielding approximately $\text{W}_{51}\text{X}_{129}(\text{PO}_4)_{103}$. On this basis, comparing the actual analytical results (using the averages of the analyses) for a block containing 412 oxygen atoms, the result is (to a close approximation):



It will be noted that the dickinsonite analyses are one atom too high in P, the fillowite one a single atom of P too low. Considering the large numbers of atoms involved, and taking into account possible analytical and sampling errors, it seems the presumption of dimorphism is not unwarranted. But the final answer to this question can better wait until

structures are determined, so that one can have a clearer idea of possible unoccupied sites.

Alluaudite formulas multiplied by 103/12 yield:



Here the major difference seems to be in the smaller number of (X' + Y') atoms, as compared to X atoms in the dickinsonites and fillowites.

CHEMISTRY OF THE ALLUAUDITES

The unit cell data on the alluaudites (space group 15-I₂/a) are given in Table 7 (Fisher, 1955b, 1957). The results of computations on the chemical analyses of alluaudites on a H₂O-free basis from 11 locali-

TABLE 7. UNIT CELL DATA ON ALLUAUDITES

Locality	<i>a</i>	<i>b</i>	<i>c</i>	β	<i>V</i> ₀	<i>G</i>	<i>M</i> ₀	Weight % P ₂ O ₅	
								By analysis	Theory
Varuträsk (varu- lite)	11.00	12.64	6.51	97°54'	897	3.58	1935	44.69	44.02
Hagendorf	10.93	12.59	6.52	97°59'	888	3.77 ¹	2020	42.07	42.16
Varuträsk (alluaudite)	11.04	12.62	6.48	97°51'	894	3.58	1926	44.12	44.21
Sukula	11.05	12.59	6.49	97°40'	894	3.58	1927	43.39	44.20
Chanteloube	11.03	12.52	6.44	97°30'	882	3.58 ¹	1902	42.80	44.78
Buranga	11.03	12.53	6.40	97°34'	878	3.45 ¹	1820	44.08	46.80

¹ G-values by D. J. Fisher; others from the literature.

Weight % P₂O₅ on a H₂O-free basis; total summed to 100.

Theoretical weight % P₂O₅ = (600 × 141.95) / M₀, where the unit cell is assumed to carry 6(P₂O₅).

The unit cell data for the Sukula and two Varuträsk samples are taken from Guinier camera powder films, the others are from single crystal precession measurements.

ties are shown in Table 8. From this using the figures in column W* it is clear that the alluaudite formula can be written W₄₋₈(X + Y)₁₂(PO₄)₁₂, where W = Na + Ca (+K) + (in some cases) a little Mn; X = Mn + Fe²⁺ + Mg (+Li) + (in some cases) a little Na or Ca; Y = Fe³⁺; and water is regarded as non-essential. Except for the limitation on the W-value, this is the same formula as given earlier (Fisher, 1957). The formula of caryinite (Boström, 1957) is in agreement with this if most of the Ca (or Na) is assumed to be in the X-position, although Strunz (1960) has given a different interpretation. All alluaudites probably fall in the range of Na₂₋₇ and Ca₀₋₃ in the unit cell; in only one known sample is Ca in excess of Na. In Table 9 are shown some idealized formulas for various alluaudites (based on the data of Table 8). From this it is also clear that

TABLE 8. ELEMENTS IN THE UNIT CELLS OF ALLVAUDITES CONTAINING 48 OXYGENS
(In Order of Increasing $Fe^{2+} = Y$)

Locality	W			X					Weight per cent										
	K	Na	Ca	Sum W	Mn	Fe ²⁺	Mg	Li	Sum X	Y = Fe ³⁺	Fe ²⁺ + Fe ³⁺	X+Y	W*	P	G	M ₀	Fe/Mn	H ₂ O ⁺	H ₂ O ⁻
Skrumpetorp	tr	6.33	1.29 ⁸	7.62	5.99	3.37	0.04 ⁶	—	9.41	1.63	5.00	11.03	6.65	12.68	3.61	2017	0.85	1.52	0.14
Varuträsk (varulite)	0.03	5.41	0.90	6.34	7.09	2.80	0.05	1.18	11.11	1.86	4.66	12.97	7.31	12.43	3.58	1974	0.67	0.80	0.13
Lernås	0.18	5.93	1.67	7.79	8.04	0.55	0.27	0.03	8.88	3.27	3.81 ⁵	12.15	7.93	11.80	3.58	2046	0.48	1.48	0.13
Hägendorf	0.07	5.47	0.60	6.14	5.22	4.30	0.33	—	9.84	3.33	7.63	13.18	7.32	11.91	3.77	2010	1.49	—	—
Norrå	0.03	6.26	0.48	6.77	2.77	5.07	1.27	0.34	9.43	3.63	8.70	13.08	7.85	11.86	3.55	2007	3.20	0.85	0.20
Varuträsk (allvaudite)	0.05	4.53	0.78	5.31	7.48	0.56	—	0.38	8.42	4.16	4.72	12.58	5.89	12.18	3.58	1960	0.64	1.60	0.88
Sukula	—	5.28	0.96	6.24	5.81	0.89	0.05	0.09	6.85	5.14	6.03	11.98 ⁸	6.22 ⁸	11.96	3.58	1956	1.06	0.96	0.17
Chanteloube	—	2.54	0.58	3.11 ⁶	6.88	—	—	—	6.88	6.51 ⁸	6.51 ⁸	13.39	4.50 ⁸	11.80	3.58	1956	0.96	2.65	—
Hühnerköbel	0.02	2.47	3.55	6.04 ⁵	1.86 ⁵	2.03	0.35	0.49	4.73	6.81	8.84	11.54	5.58 ⁸	11.40	—	2053	4.82	4.49	0.24
Pringle	0.01	2.78	1.41	4.20	3.56	0.44	0.19	—	4.19	7.57	8.01	11.76 ⁵	3.96 ⁵	11.86	3.52	1957	2.29	1.9	0.05
Buranga	—	2.51	0.50	3.01	4.54	—	0.23	0.12	4.89	7.86 ⁵	7.86 ⁵	12.75	3.76	11.83	3.45	1908	1.76	3.55	—

Chanteloube analysis with 1.6% CaO (in place of part of Na₂O) determined spectroscopically; also Mn₂O₃ converted to MnO in this and the Buranga analysis. Varuträsk (varulite) analysis is average of three (1940-41)

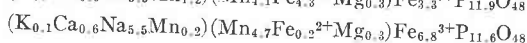
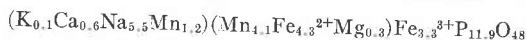
Results based on the assumption that water is not essential

M₀ value is that used to calculate exactly 48 oxygens in the unit cell; only the Buranga value (and to a lesser extent that for Chanteloube) is seriously high.

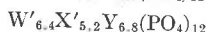
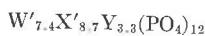
* Value of $WH (X+Y)$ is made equal to 12, and in doing this some Ca (or Na) is added to X or some Mn is added to W.

there is a pronounced tendency towards an inverse relation between Na and Fe^{3+} ; the less Na, the more Fe^{3+} . In some cases this would indicate that oxidation also involves the concomitant leaching of Na. The four lowest analyses in Tables 8 and 9 are of those with less than 3 atoms Na per unit cell; these four are also highest in water (except for the Varuträsk alluaudite, which is also relatively low in Na). This indicates the possibility that "Na holes" in the structure may be occupied by OH or H_2O .

A sample of the Hagendorf alluaudite (Strunz, 1954) was heated in air for 48 hours at 890°C .; it was then analyzed by Oiva Joensuu who found no change in its Na content, but FeO was reduced to approximately 1% and Fe_2O_3 increased to 32.3%. The formulas of the unheated (above) and heated (below) samples may be written as follows:



or



The lower density of the ferri-alluaudites (the bottom three of the

TABLE 9. IDEALIZED FORMULAS OF ALLUAUDITES
(Listed in order of increasing values of $\text{Fe}^{3+} = Y$)

Ideal formula	Na	Ca*	Na+Ca*	X'	Y	Locality
$\text{Na}_6\text{Ca}_2(\text{X}_{10}'\text{Y}_2)(\text{PO}_4)_{12}$	6.3	0.3	6.7	10.4	1.6	Skrumpetorp
$\text{Na}_6\text{Ca}_2(\text{X}_{10}'\text{Y}_2)(\text{PO}_4)_{12}$	5.4	1.9	7.3	10.1	1.9	Varuträsk (varulite)
$\text{Na}_5\text{Ca}_2(\text{X}_9'\text{Y}_3)(\text{PO}_4)_{12}$	5.9	1.8	7.8	8.7	3.3	Lemnäs
$\text{Na}_5\text{Ca}_2(\text{X}_9'\text{Y}_3)(\text{PO}_4)_{12}$	5.5	1.8	7.3	8.7	3.3	Hagendorf
$\text{Na}_6\text{Ca}(\text{X}_8'\text{Y}_4)(\text{PO}_4)_{12}$	6.3	1.6	7.8	8.4	3.6	Norrö
$\text{Na}_5\text{Ca}(\text{X}_7'\text{Y}_5)(\text{PO}_4)_{12}$	4.5	1.4	5.9	7.8	4.2	Varuträsk (alluaudite)
$\text{Na}_5\text{Ca}(\text{X}_7'\text{Y}_5)(\text{PO}_4)_{12}$	5.3	1.0	6.2	6.9	5.1	Sukula
$\text{Na}_2\text{Ca}(\text{X}_6'\text{Y}_6)(\text{PO}_4)_{12}$	2.5	2.0	4.5	5.5	6.5	Chanteloube
$\text{NaCa}_2(\text{X}_5'\text{Y}_7)(\text{PO}_4)_{12}$	2.5	3.1	5.6	5.2	6.8	Hühnerkobel
$\text{Na}_2\text{Ca}(\text{X}_4'\text{Y}_8)(\text{PO}_4)_{12}$	2.8	1.2	4.0	4.4	7.6	Pringle
$\text{Na}_2\text{Ca}(\text{X}_4'\text{Y}_8)(\text{PO}_4)_{12}$	2.5	1.3	3.8	4.1	7.9	Buranga

* Value for Ca if some is added to X (or some Mn is subtracted from X and added to Ca) so that $(X'+Y)=12.00$.

Note that the last three formulas of the above table have W^* values (see Table 8) of only 3; this is because the "ideal formula" given above is based primarily on the $(X_m'Y_n)$ figures.

Note that the Na & Ca* are a poor fit in the Hühnerkobel specimen, and the "fit" is very bad in the case of Ca* in the Skrumpetorp analysis. But one can be suspicious of the latter, since it has $X+Y$ (Table 8) equal to only 11.03 (the lowest value) and P of 12.68 (the highest value).

table) is because of the relatively small amount of Na present. The Chanteloube (also the Sukula) samples are mangan-alluaudites, but close to the ferri-alluaudite boundary (Fisher, 1957); the Norrö specimen is the only ferro-alluaudite.

THERMAL EXPERIMENTS ON THESE MINERALS

Powdered samples of alluaudite from six localities were heated while resting on platinum foil in air in an electric furnace for various intervals (generally 24 hours) at various temperatures, after which powder *x*-ray pictures were made. These specimens and some of the results from their study are shown in Table 10.

All the samples listed except the two heated above 1000° C. yielded excellent alluaudite patterns; in fact heating this mineral to around 800° serves to prepare a specimen that will give the best *x*-ray powder picture.

TABLE 10. RESULTS FROM HEATING POWDERED ALLUAUDITE IN AIR

No.	Locality	Temperature	Time (hours)	Result
1	Black Hills (Pringle, South Dakota)	a) 910	23	no sintering
		b) 940	22	strongly sintered; no glass
		c) 975	23	in part a very dark brown glass; very weak "glass bands"
2	Buranga (Ruanda, Africa)	a) 910	23	no sintering
		b) 940	22	slightly sintered
		c) 990	22	very strongly sintered
3	Chanteloube (France)	a) 995	20	very strongly sintered; "glass bands"
		b) 1010	24	completely melted; few very weak alluaudite lines left; "glass bands"
4	Hagendorf (Bavarian "hagendorfite")	a) 985	24	apparently partially melted; no "glass bands"
		b) 1015	43	completely melted; almost none of alluaudite pattern left; pronounced "glass bands"
5	Skrumpetorp (Swedish "varulite")	a) 985	18	nically sintered. Excellent alluaudite pattern including strong back reflection lines at $d=0.9726$ and 0.9748
6	Varuträsk (Swedish "varulite")	a) 800	18	no sign of sintering
		b) 910	1	very strongly sintered; shows same pattern (including back reflection pair) as no. 5

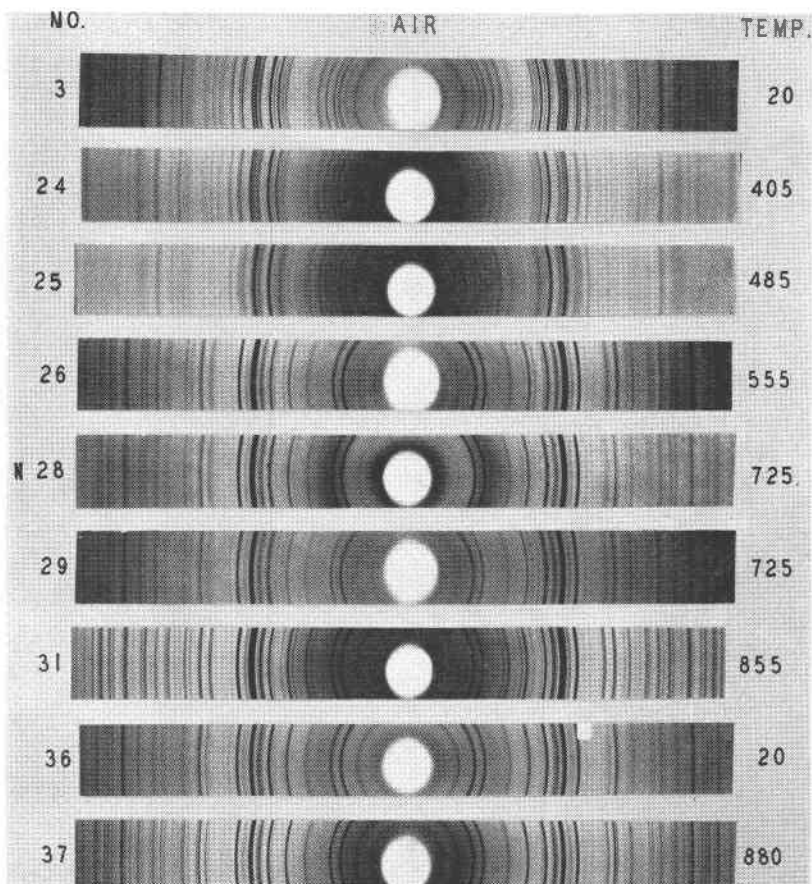


FIG. 3. X-ray powder pictures of Black Hills arrojadite (ferrodickinsonite) at room temperature (3) and after heating in air for 24 hours at the temperatures shown. The two basal pictures are of Chanteloube alluaudite at room temperature (36) and after heating for 24 hours at 880° (37). See caption for figure 6 to explain numbers 28 and 29. Fe/Mn radiation, 114 mm. Straumanis-type camera.

The "glass bands" referred to in the table are broad zones of darkening centered near $d=16$ and 5.3 . It is clear that the melting point of alluaudite is very close to 1000° C.

Powdered samples of the Headden arrojadite from the Nickel Plate Mine, S. Dakota, supplied by Professor Frondel of Harvard were heated for approximately 24 hours in an electric furnace. Some of these were done in Pt boats in air, others were first put in sealed and exhausted Vycor glass capsules. X-ray powder pictures were made from the heated samples with results as shown in Fig. 3 (heated in air) and Fig. 4 (heated in evacuated tubes). In Fig. 3 the two basal pictures are of Chanteloube,

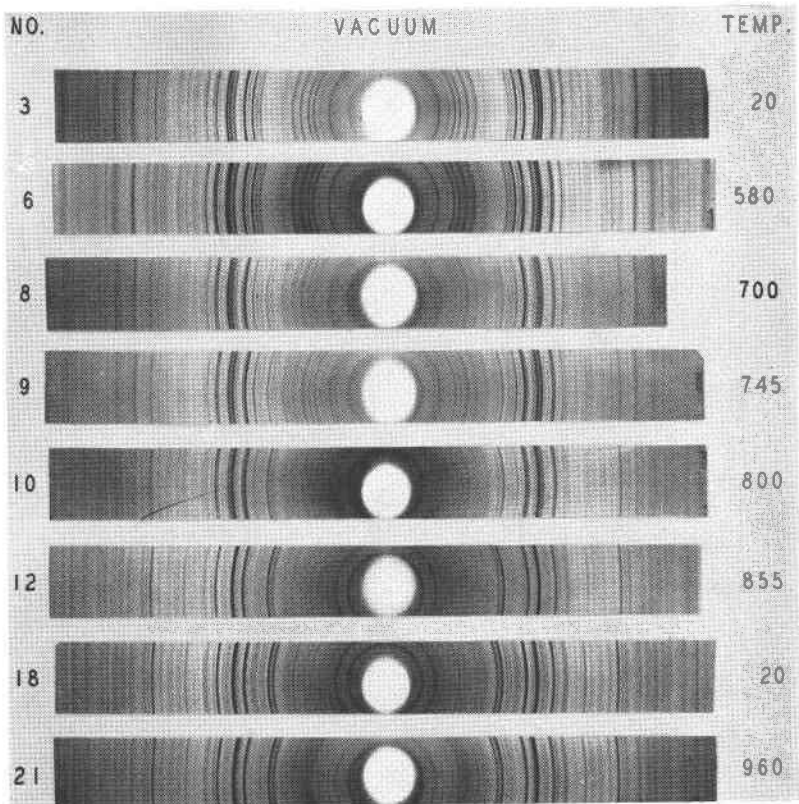


Fig. 4. Same as Fig. 3 except samples heated in evacuated and sealed Vycor glass tubes. The two basal pictures are of Branchville, Conn. fillowite (at room temperature and after heating for 24 hours at 960°).

France, alluaudite; and in Fig. 4 the two basal pictures are of Branchville, Conn., fillowite.

From Fig. 3 (air heated) it is clear that only a slight change has taken place at 405° (#24), but more extensive changes have occurred by 485° (#25). However, the big break is between this temperature and 555° (#26) at which temperature the sample has the typical alluaudite structure shown in all the lower pictures of this figure, though sample #31 (heated to 855°) contains a number of additional lines. Samples nos. 28 and 29 are further discussed below. Patterns from material heated to 910° and 965° were also taken, but they were essentially the same as no. 31 of Fig. 3. The 910° sample was sintered, and the 965° sample was a near black fused mass.

Figure 4 (heated in a vacuum) shows practically no difference between the first two pictures (#3 and 6), but transitional changes appear in the

next three films, so that at 855° (no. 12) the structure is substantially the same as that of fillowite at 960° (no. 21), which differs only in minor detail from the fillowite at 20° (no. 18). Of course no. 12 represents a ferro-fillowite, whereas nos. 18 and 21 are of a manganofillowite.

Fig. 5 is a Guinier film showing the results from heating ferrodickinsonite in a vacuum for 24 hours. The top line is unheated material, the second on heating to 600°, the third on heating to 885°, and the bottom line is unheated fillowite. This shows that the inversion takes place between 600° and 885°. From Fig. 4 it is clear that at 745° the changes are very minor, most of them occurring between 745° and 855°. All samples heated to 800° or above also contained the white powder of low cristobalite produced from the Vycor glass. Also all samples heated above 800° were sintered. Two samples heated to 885° and 905° still gave nice

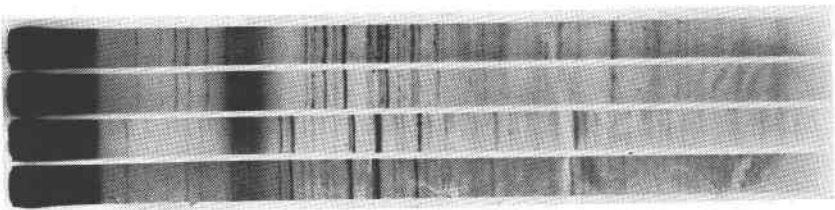


FIG. 5. Guinier film showing unheated arrojadite (Black Hills) in the top row, the same heated for 24 hours in a vacuum at 600° on the second row, to 885° on the third row, and unheated fillowite (Branchville) in the bottom row. Co $K\alpha_{1-2}$ radiation, film protected by Al foil, 52 Kv, 10 ma, 76 hrs in a vacuum.

fillowite patterns; they appeared to be material recrystallized from a gray-black glass, though when fillowite itself was heated to 960° (Fig. 4, no. 21) the material seemed to be only very strongly sintered.

Powdered samples of the Branchville fillowite were heated in air at 885° for 24 hours and for 46 hours respectively. The diffraction films from the resulting powders yielded mixed fillowite and alluaudite patterns. Judging from line intensities, the 24-hour sample was less than half converted to alluaudite, and the 46-hour one was possibly slightly more than 50% converted.

Fragments of single crystals of arrojadite were heated to see if they could be converted as single crystals, but the result was polycrystalline material. One sample heated in a vacuum at 855° for 22 hours yielded a lump which gave the ferrofillowite *powder* pattern on the Weissenberg. Another sample heated in air at 700° for 25 hours yielded a lump which gave the alluaudite *powder* pattern.

Figure 6 shows the results of three DTA runs made in July 1954 on the Headden arrojadite by D. L. Graf at the Illinois State Geological Survey. The upper two were made in a nitrogen atmosphere, the lower

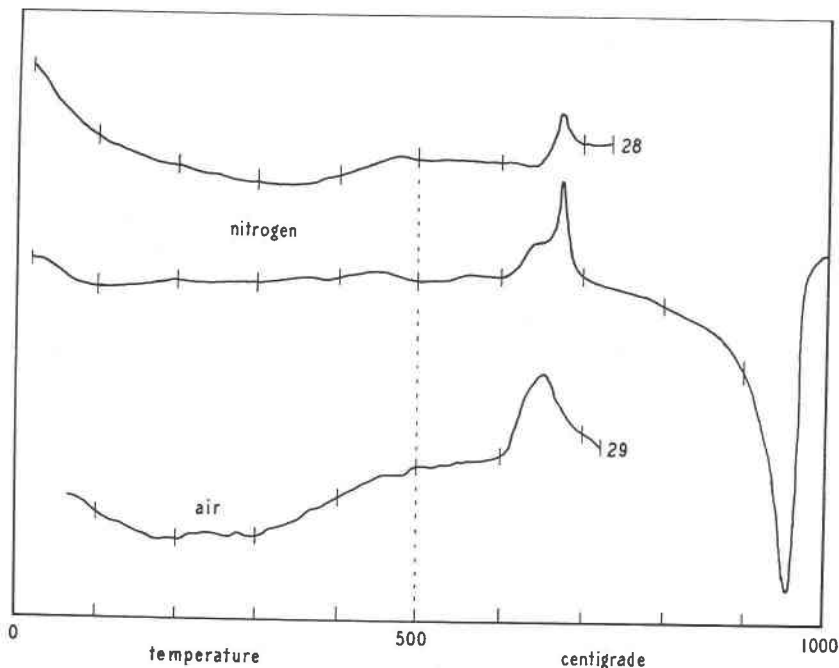


FIG. 6. DTA runs on Black Hills arrojadite. The upper two were made in a nitrogen atmosphere, the lowest one in air. Samples yielding *x*-ray films nos. 28 and 29 of Fig. 3 were taken from the end points of the top and bottom curves respectively. Runs made in July 1954 by Donald L. Graf at the Illinois State Geological Survey using a small sample block, -200 mesh powder, with 50 ohms resistance (100 ohms for the top curve below 290° C.; the drift of the baseline here indicates that the thermocouple centering was imperfect). Heating rate approximately 10° per minute.

one in air. Samples that gave the top and bottom curves were removed after heating to 725° and *x*-ray powder pictures were run on them (see nos. 28 and 29 of Fig. 3). These gave essentially the same pattern—that of alluaudite. At first glance a possible explanation of this is that (at least in the N-heated sample no. 28) the small amount of water present (0.73 to 0.91%) occurs distributed in molecular-size cavities throughout the structure, and on heating this breaks down to OH, which serves to oxidize the iron to the ferric state, and protons, which escape. However, if this is a true explanation, one might expect the material when heated in a vacuum to show a similar conversion, which it does not. Thus a more likely explanation is that some oxygen (or air) was present. The exothermic break is at about 650° in the air-heated sample and 675° in the N-heated samples, though the middle curve of the figure shows some evidence of a minor 650° break also. The pronounced endothermic break at slightly under 1000° shown by the middle curve is presumably con-

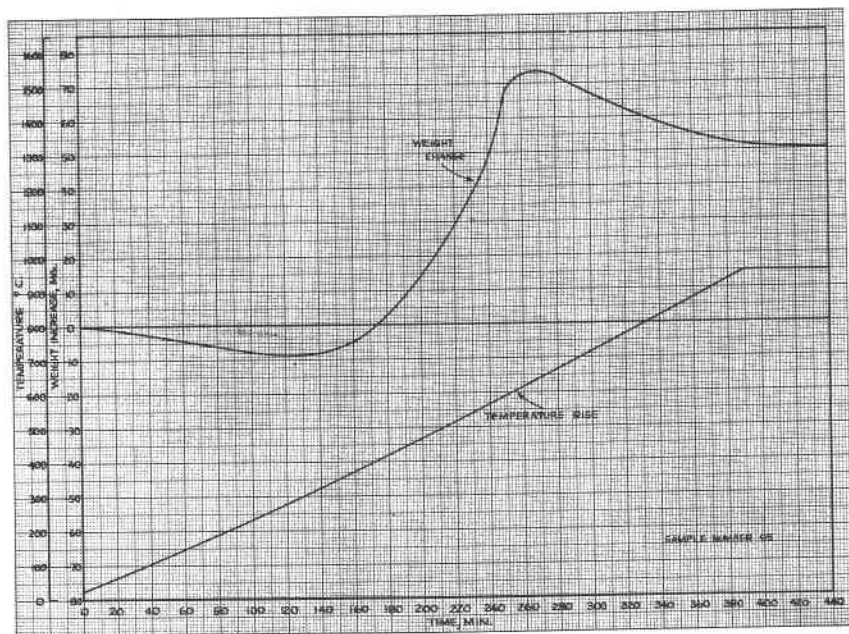


FIG. 7. Thermogravimetric analysis of the Black Hills arrojadite. Run in March 1956 on a sample weighing initially 5.0016 grams by M. J. Spendlove of the College Park, Maryland laboratory of the U. S. Bureau of Mines.

nected with the melting phenomena. Additional publications giving the results of DTA work on mineral phosphates include Heystek and Schmidt (1953), Manly (1950), Thoreau and Bastien (1954, a and b), as well as others.

Figure 7 shows the results of a thermogravimetric analysis on the Headden arrojadite made in March 1956 using the apparatus described in U. S. Bureau of Mines Report of Investigation No. 5181 (1955). On a sample initially weighing 5.0016 grams there is a loss in weight of 9 mg. (about 0.18%) up to a temperature of about 300°, and then a gain in weight of some 83 mg. (or 1.66%) by the time the temperature reached 650°. Presumably the small loss represents extraneous water, the large gain being connected with oxidation as the material goes over to alluaudite.

The thermogravimetric study of Fig. 8 was run in December 1955 on two samples of alluaudite. The lower curve (sample #48) was made on the dense, fine-grained Pringle, South Dakota material (1.9% H₂O) and the upper curve (sample #151) on the coarsely-crystalline Buranga, Ruanda specimen (3.55% H₂O). The probable interpretation of these curves is that they indicate a rather regular loss in weight due to loss of

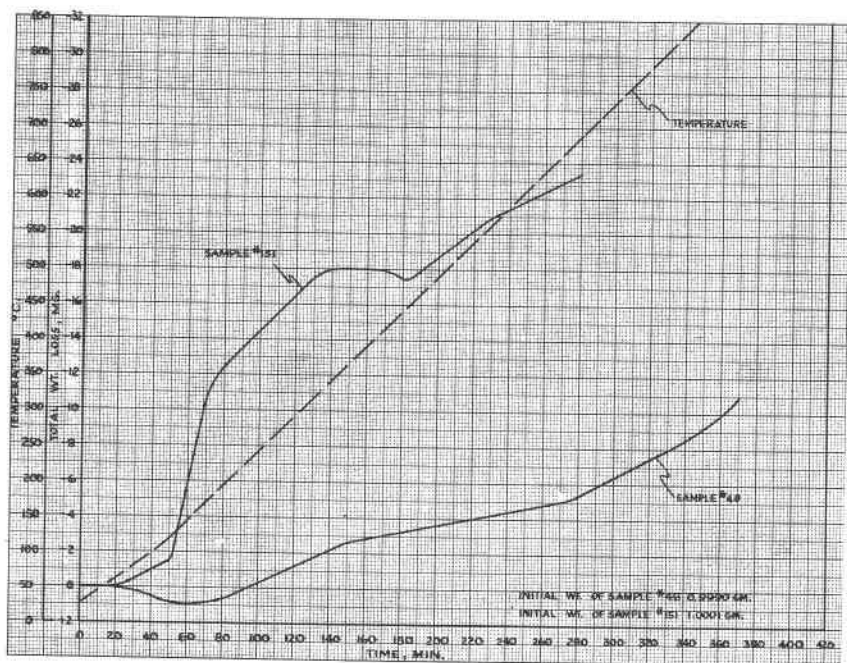


Fig. 8. Thermogravimetric study of alluaudite made in December 1955 by M. J. Spendlove. Lower curve (#48) on Pringle, South Dakota sample weighing 0.9990 grams (after pre-heating), upper curve (#151) on Buranga, Ruanda specimen weighing 1.0001 grams. No. 48 was held at 105° for 24 hours (losing 0.0010 gram) before starting the TGA run; the other two samples (#95 of Fig. 7 and #151) were not pre-heated. The final weight of sample no. 48 was 0.9960 grams.

extraneous water as the temperature is raised, the African material having the steeper curve because it contains more such water. In this figure a weight-loss of 10 mg corresponds to approximately 1%.

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REFERENCES

- ADLER, H. H. (1963) Some basic considerations in the application of infrared spectroscopy to mineral analysis. *Econ. Geol.* **58**, 558-568.
- (1964) Infrared spectra of phosphate minerals. *Am. Mineral.* **49**, 1002-1015.
- ANDERSON, W. R., B. STRINGHAM AND J. A. WHELAN (1962) Secondary phosphates from Bingham, Utah. *Am. Mineral.* **47**, 1303-1309.
- BOSTRÖM, K. (1957) The chemical composition and symmetry of caryinite. *Ark. Mineral.* **2**, 333-336.
- BRUSH, G. J. AND E. S. DANA (1879) On the mineral locality of Fairfield County, Connecticut (Fillowite). *Am. Jour. Sci.* **17**, 359-368.
- (1890) On the mineral locality at Branchville, Connecticut (Dickinsonite). *Am. Jour. Sci.* **39**, 201-216. Also see *ibid.* **16**, 1878, 114-123.
- FISHER, D. J. (1954) Arrojadite is a ferro-dickinsonite. *Am. Mineral.* **39**, 676-680.
- (1955a) Soda Fe-Mn pegmatite phosphates. *Science* **121**, 312.
- (1955b) Alluaudite. *Am. Mineral.* **40**, 1100-1109.
- (1957) Alluaudites and varulites. *Am. Mineral.* **42**, 661-664.
- (1960) Morinite-apatite-whitlockite. *Am. Mineral.* **45**, 645-667.
- (1962) Alluaudite and caryinite. *Am. Mineral.* **47**, 163-165.
- FRONDEL, C. (1941) Whitlockite: a new calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$. *Am. Mineral.* **26**, 148-149.
- GUIMARÃES, D. (1942) Arrojadite, um novo mineral do grupo da wagnerita. *Bol. Fac. Fil. Ciên. Let., Univ. S. Paulo*, **30** (*Mineralogia* **5**, 1-14).
- HEADEN, W. P. (1891) A new phosphate from the Black Hills of South Dakota (arrojadite). *Am. Jour. Sci.* **41**, 415-417.
- HEYTEK, H. AND E. R. SCHMIDT (1953) The technique of DTA and its application to some South African minerals. *Geol. Soc. S. Africa, Trans. and Proc.* **56**, 149-176.
- KELLER, W. D., J. H. SPOTTS AND D. L. BIGGS (1952) Infrared spectra of some rock-forming minerals. *Am. Jour. Sci.* **250**, 453-471.
- LINDBERG, M. L. (1950) Arrojadite, hühnerkobelite, and graftonite. *Am. Mineral.* **35**, 59-76.
- MANLY, R. L. (1950) The differential thermal analysis of certain phosphates. *Am. Mineral.* **35**, 108-115.
- MOENKE, H. (1962) *Mineralspektren*. Akademie-Verlag, Berlin.
- OMORI, K. (1961) Infrared absorption spectra of some essential minerals. *Sci. Repts. Tohoku Univ.* **7**, 101-130.
- (1964) Infrared studies of essential minerals from 11 to 25 microns. *Sci. Repts. Tohoku Univ.* **9**, 65-97.
- PALACHE, C., H. BERMAN AND C. FRONDEL (1951) *The System of Mineralogy of the Danas*, Vol. II.
- SHAININ, V. E. (1946) The Branchville, Connecticut, pegmatite. *Am. Mineral.* **31**, 329-345.
- STRUNZ, H. (1954) Hagendorfit, ein neues Mineral der Varulith-hühnerkobelitreihe. *Neues Jb. Mineral., Mh.*, 252-255.
- (1960) Karyinit, ein Arsenat vom Strukturtypus der Phosphate Hagendorfit und Alluaudit. *Neues Jb. Mineral., Mh.*, 7-15.
- THOREAU, J. AND G. BASTIEN (1954a) Lazulite et scorzalite de pegmatites du Congo belge et du Ruanda. *Acad. Roy. d. Belgique, Bull. Cl. Sci.* **40**, 600-607 (DTA graphs).
- (1954b) Les phosphates des pegmatites du Ruanda occidentale. *Acad. Roy. Sci. Colon., Bull. Sci.* **25**, 1595-1603.
- WOLFE, C. W. (1941) The unit cell of dickinsonite. *Am. Mineral.* **26**, 338-342.