ARROJADITE, HÜHNERKOBELITE, AND GRAFTONITE*

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ABSTRACT

Headden's unnamed sodium iron manganese phosphate from the Nickel Plate pegmatite, S. Dak., has been reexamined and its identity with arrojadite from the Serra Branca pegmatite, Brazil, has been established by direct comparison. The optical properties of arrojadite from the Nickel Plate pegmatite are: $\alpha=1.664$, $\beta=1.670$, and $\gamma=1.675$; X colorless, Y pale green, Z pale yellow green, $X=b$, $Z\wedge a=18°$, $2V=86°$, $r<v$ strong. New optical properties of arrojadite from other localities are given. The space group is $C2/m$. (C^3_{2h}) and the unit cell has $a_0=16.60$, $b_0=10.02$, and $c_0=23.99$ Å; $a:b:c=1.656:1:2.389$, $\beta=93°\ 37'$.

Material from Hühnerkobel, Bavaria, and from Norrö, Sweden, originally described as arrojadite is not isostructural with arrojadite from the Nickel Plate pegmatite and from the Serra Branca pegmatite, and the name hühnerkobelite is proposed for this partly oxidized material with formula $(Na_2, Ca)O \cdot 2(Fe, Mn)O \cdot P_2O_5$.

Graftonite $(Fe, Mn, Ca)_3(PO_4)_2$ is associated with arrojadite at the Nickel Plate pegmatite. A new analysis is given, together with a partial analysis of graftonite from the Rice pegmatite, and optical properties are correlated with chemical composition. Optical properties of the graftonite from the Nickel Plate pegmatite are: $\alpha=1.709$, $\beta=1.714$, $\gamma=1.736$, X colorless, Y colorless, Z pink, $X=b$, $Z\wedge c=36°$, $2V=53°$, biaxial+, $r<v$ strong. The space group is $P2_1/c(C^5_{2h})$; the unit cell has $a_0=8.87$, $b_0=11.57$, and $c_0=6.17$ Å; $a:b:c=.766:1:.533$, $\beta=99°12'$. The relationship between the new cell and the Penfield orientation is discussed.

INTRODUCTION

Previous work

In the course of an investigation of phosphate minerals from the Black Hills, it was desired to know whether arrojadite was present. Published descriptions of the mineral were inadequate and appeared to describe

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different minerals. Type arrojadite from the Serra Branca pegmatite,[1] Brazil (Guimarães, 1925) was said to represent the partly oxidized form of the mineral described, but not named by Headden in 1891 (Headden, 1891) from the Nickel Plate mine, Pennington County, S. Dak. Direct comparison of the two had never been made. Quensel (1937) gave the name headdenite to the Nickel Plate mineral. The priority of the name arrojadite was pointed out by both Mason (1941, p. 132) and Guimarães (1942) though neither had access to the Nickel Plate arrojadite. Arrojadite has also been described from the Norrö pegmatite of Sweden (Ericksson, 1946) and from Hühnerkobel, Bavaria (Mason, 1942), but these minerals were called arrojadite primarily on the basis of chemical composition, and not by direct comparison with either the Brazilian or the Black Hills arrojadite. Arrojadite from various localities has quite different chemical analyses, and these should be used with caution as a means of establishing the identity of members of the species, especially when part of the iron is oxidized.

Arrojadite from the Nickel Plate mine and the Serra Branca pegmatite was obtained from the Headden collection of Harvard University and from the U. S. National Museum for direct correlation of physical properties. A sample of varulite from Skrumpetorp, Sweden, and samples of arrojadite from Hühnerkobel, Bavaria, and Norrö, Sweden, were obtained from Professor Brian Mason of Indiana University.

Description of material from the Nickel Plate mine

Headden described a green phosphate from the Nickel Plate mine as being associated with beryl, spodumene, mica, and cassiterite in granite. A dark-green cleavage block about 6 inches long, from the Headden collection of Harvard University, appearing massive and homogeneous on the outside, was found to contain small books of muscovite, granular quartz, graftonite, and cassiterite in the interior.

Thin sections showed that arrojadite and cassiterite were intimately intergrown, with thin seams and some euhedral crystals of cassiterite in the cleavage planes of the arrojadite. Parallel euhderal cassiterite crystals are developed in the cleavage planes of arrojadite and in the associated quartz. The quartz and arrojadite have a curved boundary which suggests replacement of the arrojadite by quartz. Of especial interest are rows of haloes in the cassiterite. As the cassiterite itself is strongly pleochroic, any possible pleochroism of the haloes is marked. The rows of haloes in some thin sections occupy the whole width of the cassiterite

[1] As used in this paper the terms Serra Branca pegmatite, Rice pegmatite, Norrö pegmatite, Etta pegmatite, and Skrumpetorp pegmatite serve only as a convenient means of reference and are not to be considered as analogous to stratigraphic names.

seam in the arrojadite cleavage planes; in other sections, the row of haloes was seen at one side or in the center of the seam. In others several rows occurred. The rows of inclusions are usually parallel to the *b* axis in the arrojadite. A small sample of purified cassiterite was found to be feebly radioactive, but the sample was too small to obtain quantitative results.

At some places the graftonite showed an abrupt contact with the arrojadite; at other places it was surrounded by a rim of material with relief similar to that of the graftonite, but with abnormal blue birefringence. Long, thin stringers of original arrojadite showing parallel extinction lie in the graftonite and suggest that graftonite may have replaced arrojadite along cleavage planes, though definite paragenetic relationships could not be completely determined.

In the arrojadite are occasional shreds of a deep grass green material, which has the appearance of the grass-green varulite from Skrumpetorp, Sweden.

GRAFTONITE

Optical studies

The optical constants for graftonite from the Nickel Plate mine are given in Table 1. The optical orientation is given for the new axial directions as defined by single-crystal *x*-ray studies discussed below. In any

TABLE 1. OPTICAL CONSTANTS FOR GRAFTONITE
Nickel Plate mine, S. Dak.

Indices	Absorption	Orientation
α 1.709	X colorless	X=*b* 2V=53°, sign +
β 1.714	Y colorless	
γ 1.736	Z pink	Z$\wedge c$=36° $r<v$ strong

group of minerals in which isomorphous substitution occurs, it is desirable to correlate the indices of refraction with chemical composition. The chief variables in composition in graftonite are calcium, manganese, and iron. The per cent of each for all known analyzed samples is given in Table 2, together with the indices of refraction, arranged in order of increasing alpha index. It is seen that a high calcium content lowers the indices of refraction and that iron and manganese raise the indices, iron more than manganese. The indices of refraction of graftonite from Olgiasca, Lake Como, Italy, are a little low in comparison with other recorded indices. The low calcium and high ferrous iron content of this mineral indicate that it should have the highest observed indices of refraction. The very

TABLE 2. CORRELATION OF INDICES OF REFRACTION OF GRAFTONITE WITH CALCIUM, MANGANESE, AND IRON CONTENT

	1	2	3	4	5	6
α	1.695	1.700	1.705	1.708	1.709	1.709
β	1.699	1.705	1.708	1.713	1.714	1.714
γ	1.719	1.724	1.722	1.724	1.733	1.736
CaO	12.80	9.23	7.95	4.50	4.71	6.00
MnO	15.96	17.62	15.65	23.32	25.48	21.81
FeO	28.84	30.65	32.58	32.33	27.78	30.70

1. Graftonite, Rice pegmatite, North Groton, N. H., Lindberg, analyst.
2. Graftonite, Melvin Mtn., Grafton Co., N. H., S. L. Penfield, analyst (Penfield, 1900).
3. Graftonite, Valle della Madonna, Brissago, Tessin, Switzerland. (Parker, 1939).
4. Repossite, Olgiasca, Lake Como. Italy. Gallitelli, analyst (Periodico Mineral) (Grill, 1935).
5. Graftonite, Greenwood, Maine, Fahey, analyst (Glass, 1937).
6. Graftonite, Nickel Plate mine, Lindberg, analyst.

similar indices of refraction for the Greenwood, Maine, and the Nickel Plate material show the compensating effect of higher calcium and higher iron and less manganese in the Nickel Plate material. Calcium, manganese, and iron were determined on the graftonite from the Rice pegmatite especially for this study, as the indices of refraction indicated that this had a higher calcium content than any graftonite previously analyzed.

Chemical composition

The graftonite was separated from arrojadite by Clerici solution. Alteration along cleavage cracks on the graftonite produced a material of higher birefringence and lower indices of refraction. This alteration product had a lower specific gravity, and it was possible to float most of the impurity from the graftonite although a complete separation was not obtained.

The analysis of graftonite from the Nickel Plate mine (Table 3) conforms closely to the established formula $(Fe,Mn,Ca)_3(PO_4)_2$. K.J. Murata examined the material spectrographically and reports, in addition, the presence of Sn, Zn, and Cu, in hundredths of 1 per cent, and the absence of Be, B, Ti, Zr, Ag, Tl, Pb, Bi, As, Sb, Ge, In, Cd, Mo, W, Cr, V, Co, Ni, La, Y, Ba, and Sr. The absence of spectrographic amounts of Tl indicates that substitution or base exchange does not occur during the treatment with Clerici solution.

TABLE 3. CHEMICAL COMPOSITION AND FORMULA OF GRAFTONITE FROM THE NICKEL PLATE PEGMATITE

	Analysis	Ratios	Oxygen equivalent	Met. equivalent	Atoms per cell	
P_2O_5	39.66	.2794	1.3968	.5587	7.94 (P)	
Fe_2O_3	none	—				
Al_2O_3	0.20	.0020	.0059	.0039	.06	
FeO	30.70	.4273	.4273	.4273	6.07	
MnO	21.81	.3075	.3075	.3075	4.37	
MgO	0.10	.0025	.0025	.0025	.04	12.24 (R)
Li_2O	0.05	.0017	.0017	.0034	.05	
Na_2O	0.28	.0045	.0045	.0090	.13	
K_2O	none	—	—		—	
CaO	6.00	.1070	.1070	.1070	1.52	
H_2O	0.60					
F	0.20					
Insol.	0.16					
Total	99.76		2.2532 (O)			32.02 (O)
Less F=O	0.08					
	99.68					
Sp. gr.=	3.775					

Atoms per cell found by multiplying oxygen and metal equivalents by 1421×.01.

$$\text{M. Wt.} = \frac{V\ (\text{in Å}^3)\times 10^{-24}\times \text{density}}{1.6604\times 10^{-24}} = \frac{625\times 3.775}{1.6604} = 1421.$$

Formula $R_{12}P_8O_{32} = 4\ R_3(PO_4)_2$.
Lindberg, analyst.

One-half gram graftonite from the Rice pegmatite, North Groton, N. H., was purified to determine the indices of refraction. When these were found to be the lowest observed indices, a partial analysis was made on the remaining portion of the sample: 15.96 per cent MnO, 28.84 per cent FeO, 12.80 per cent CaO, 41.65 per cent P_2O_5; total 99.25 per cent.

Graftonite is completely soluble in dilute HCl, HNO_3, and H_2SO_4, except that of high calcium content, which precipitates gypsum in the presence of sulfuric acid.

The molecular weight of Nickel Plate graftonite is 353.

X-ray studies

Two sets of rotation and Weissenberg photographs were taken on a small cleavage fragment so oriented that (1) the *X*-optical direction = *b* was the axis of rotation, and (2) {010} and {100} were in a zone parallel

to the axis of rotation $=c$, $Z\wedge c=36°$ in acute angle (new cell). Two cleavages were observed: {010} good and {100} fair. The unit-cell dimensions are a_0 8.87, b_0 11.57, and c_0 6.17 Å, with $\beta=99°12'\pm15'$. The volume of the unit cell is 625 Å^3. Four molecules per unit cell were computed from the observed gravity 3.775. Examinations of projections of Weissenberg photographs showed (hkl) all orders present; ($h0l$) present when $l=2n$; and ($0k0$) present when $k=2n$. The space group is $P2_1/c(C^5_{2h})$.

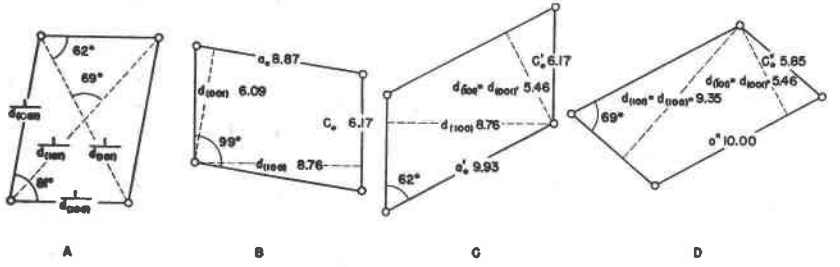

FIG. 1. ORIENTATION OF GRAFTONITE

The directions of a and c were chosen, according to x-ray convention, so as to give the unit cell with the most orthogonal β. The ratio $a:b:c=0.766:1:0.533$, $\beta=99°12'$. This is a different orientation of the unit cell from that chosen by Penfield (Penfield, 1900) $a:b:c=.886:1:.582$, $\beta=66°$. Penfield considered his measurements made with a contact goniometer on large crystals intergrown with triphylite as approximate only: "The fundamental measurements are not very reliable, and the axial ratios therefore can only be appriximately correct." The zero layer about the b axis of rotation was examined to see what directions made angles approximately at 66°. Two sets of directions, one with a β^* of 62° and the other with a β^* of 69° were found. Figure 1 shows the reciprocal cell (A) and the corresponding direct lattice cell (B), patterned after Buerger (1942). If the direction for c remains unchanged, and the short diagonal of the unit cell becomes a, (C) shows a possible orientation corresponding to that of Penfield. If the directions of both a and c are changed to become the long and short diagonals of the unit cell projection, a second orientation (D) is also possible. Reference to Fig. 1 shows that cell (b) is most nearly orthogonal. Table 4 shows the relationship between d values calculated from measurements made from the zero level of Weissenberg films around the b axis of rotation, cell edges, axial ratios, and β.

The x-ray powder-diffraction spacing data from graftonite from the Nickel Plate mine are given in Table 5. For comparison, spacing data are given for graftonite from Greenwood, Me. (U. S. Nat. Museum No. 103008; analyzed by J. J. Fahey (Glass, 1937), and graftonite from the Rice pegmatite, North Groton, N. H.

TABLE 4. ORIENTATION OF GRAFTONITE

	New orientation Å	Possible old orientation		Penfield orientation
		1st choice Å	2nd choice Å	
$d_{(100)}$	8.76	8.76	9.35	
$d_{(001)}$	6.09	5.46	5.46	
β^*	80°48′	62°	69°	66°
a_0	8.87	9.93	10.00	
b_0	11.57	11.57	11.57	
c_0	6.17	6.17	5.85	
β	99°12′	118°	111°	114°
$a:b:c$	0.766:1:0.533	0.858:1:0.533	0.866:1:0.506	0.886:1:0.582

TABLE 5. *X*-RAY POWDER SPACING DATA FOR GRAFTONITE—IRON RADIATION, MANGANESE FILTER (Å)

Nickel Plate, S. D.		Rice Pegmatite, N. H.		Greenwood, Me.	
I	*d*	*I*	*d*	*I*	*d*
2	4.31	3	4.31	3	4.30
1	3.61				
9	3.50	9	3.52	9	3.50
1	3.36				
1	3.17	1	3.14		
1	3.08				
4	3.02	4	3.01	4	3.01
4	2.956	4	2.966	3	2.953
2	2.902			1	2.906
10	2.860	10 (Broad)	2.899	10	2.867
		4	2.860		
1	2.810				
7	2.715	8	2.706	7	2.715
1	2.550				
1	2.510	1	2.510	1	2.52
		1	2.464		
3	2.412	3	2.405	2	2.410
2	2.377			1	2.377
1	2.311	1	2.323	1	2.311
1	2.271	1	2.271	1	2.276
1	2.230			1	2.226
2	2.133	1	2.126		
		1	2.082		
2	2.067	1	2.052	1	2.058
2	2.042			1	2.037
1	1.970	1	1.972		

TABLE 5—(*continued*)

Nickel Plate, S. D.		Rice Pegmatite, N. H.		Greenwood, Me.	
I	*d*	*I*	*d*	*I*	*d*
2	1.927	2	1.927	2	1.927
1	1.892	1	1.886	1	1.887
1	1.875			1	1.875
1	1.836	2	1.850	2	1.831
1	1.802			1	1.806
1	1.788	1	1.774	1	1.778
2	1.757	2	1.769	1	1.760
1	1.733	1	1.735	1	1.728
1	1.711	1	1.715	1	1.717
2	1.687	1	1.693	1	1.687
1	1.658	1	1.659	1	1.657
2	1.617	1	1.619	2	1.619
1	1.600	1	1.600	1	1.600
1	1.577	1	1.584		
1	1.549	1	1.539		
1	1.543				
2	1.516	1	1.524	2	1.501
2	1.495	2	1.495	2	1.481
1	1.453			1	1.455
1	1.424			1	1.436
1	1.411	1	1.414	1	1.414
1	1.386			1	1.397
1	1.371	1	1.366		
1	1.351	1	1.351	1	1.356
1	1.337			1	1.327
2	1.315	2	1.319		
1	1.306	2	1.314	1	1.301
1	1.287				
2	1.251	1	1.248		
1	1.231	1	1.213	1	1.236
1	1.205	1	1.205		
1	1.200				
1	1.160	1	1.170		
1	1.156	1	1.157		
1	1.103	1	1.102		
1	1.083				
1	1.061				
1	1.057				
1	1.047				
1	1.012				
1	0.9882				
1	0.9864				
1	0.9735				

Arrojadite

Optical properties

The optical properties and the chemical composition of arrojadite from the Nickel Plate mine, S. Dak., are listed in Table 6, together with newly determined indices of refraction of arrojadite from the Serra Branca pegmatite, Brazil, and from the Etta pegmatite, S. Dak. In addition, the published optical properties and chemical composition of varulite and oxidized related minerals are given. The indices of refraction of the Nickel Plate arrojadite are found to be almost identical with those of arrojadite from the Etta mine, and slightly higher than the newly determined indices of arrojadite from the Serra Branca pegmatite (U.S.N.M. 96111). Guimarães (1942) obtained lower indices, but his low indices are a correction of his earlier reported higher indices ($\gamma=1.70$; $\gamma-\alpha=.007$) (Guimarães 1925). Guimarães' optical orientation is incorrect, possibly due to misidentification of directions and planes which are here identified by taking single-crystal x-ray pictures about certain directions previously oriented optically. In a monoclinic mineral, the optic plane cannot coincide with {110}. The new optical orientation is $X=b$; $Z\wedge a=18°$. The best cleavage is {001}; {201} is a fairly well developed cleavage; the angle between the two is 68°. Z lies in the acute angle.

In any group of minerals in which substitution occurs, it is desirable to correlate chemical composition with indices of refraction. Despite wide differences in chemical composition between the arrojadite from the Nickel Plate and Serra Branca mines, the indices of refraction differ by no more than 0.003, and it is very likely that an analysis made upon a pure sample of the latter might show less oxidation of the iron. Samples of so-called arrojadite from Europe have much higher indices of refraction, and if they are considered in a separate series, which excludes the Serra Branca arrojadite, they show increasing indices with increasing ferric iron, decreasing phosphate, and decreasing manganese. The substitution of large amounts of calcium for sodium in the Hühnerkobel, Bavaria, arrojadite probably also contributes to its higher indices. Increasing birefringence may accompany this change in indices, but enough optic data for the series are not yet known.

The absorption is so weak in the Nickel Plate and Serra Branca arrojadite, that pleochroism can be observed only in thick pieces. In the European material, with the exception of the type varulite from Varuträsk, the absorption is very strong grass green. The arrojadite from Hühnerkobel and Norrö occurs in dense, very fine grained masses, whereas the arrojadite from the Nickel Plate and Serra Branca pegmatites is coarsely crystalline, cleavage pieces 6 inches in length being known.

TABLE 6. OPTICAL PROPERTIES AND CHEMICAL COMPOSITION OF ARROJADITE AND OXIDIZED RELATED MINERALS

Indices	1	2	3	4	5	6	7	8
α	1.649	1.662	1.665	1.664	1.708	1.718	1.720	1.754
β	1.654	1.668	1.670	1.670				
γ	1.657	1.672	1.675	1.675	1.722	1.731	1.732	>1.770 probably 1.785
Absorption	weak	weak	weak	weak	strong	strong	colorless	strong
X	colorless			colorless		green yellow		gray green
Y	colorless			pale green				
Z	pale green			pale yellow green		grass green		dark green
Orientation								
X	$c=3\frac{1}{2}°$			$=b$				
Z plane	(110)			(001) = 18°				
2V	82°	80°	90°	86°	Large		70°	
Sign	−	−	(±)	−	+			
Dispersion				$r<v$			$r>v$	
X-ray		true arrojadite	true arrojadite	true arrojadite	different	different		different
Composition								
P_2O_5	34.32			40.00	44.60	41.93	42.80	39.40
Fe_2O_3	12.39			none	6.44	14.45	8.35	26.49
Al_2O_3				2.66			0.36	
FeO	19.84			28.22	12.01	8.15	7.52	7.09
MnO	12.33			15.78	21.06	9.79	25.30	6.44
CaO	5.69			2.46	3.60	1.35	4.86	9.70
MgO	1.85			1.04	0.09	2.55	0.00	0.68
Na_2O	4.67			6.40	9.72	9.67	7.12	3.73
K_2O	1.45			1.74	trace	0.06	0.12	0.05
Li_2O	trace			0.09		0.25	0.88	0.36
H_2O+	4.96			0.91	1.52	0.85	0.75	4.49
H_2O^-	0.44			none	0.14	0.20	0.14	0.24
F				0.80	0.08	0.00	0.06	
Insol.	0.66			0.11	0.44	0.50	1.80	1.88
SnO_2	1.52							
Total	100.12			99.87	99.70	99.75	100.06	100.55
Sp. gr.				3.553		3.55		3.45

1. Arrojadite, Serra Branca, Brazil. (Guimarães, 1942.)
2. Arrojadite, Serra Branca, Brazil. U.S.N.M. No. 96111, optics by Lindberg.
3. Arrojadite, Etta pegmatite, South Dakota. Harvard No. 523, optics by Lindberg.
4. Arrojadite, Nickel Plate mine, South Dakota. Harvard No. 543, optics and analyses by Lindberg.
5. Varulite, Skrumpetorp, Sweden. (Mason, 1940.)
6. Arrojadite, Norrö pegmatite, Sweden. (Eriksson, 1936.)
7. Varulite, Varuträsk, Sweden. Type material. (Quensel, 1937.)
8. Arrojadite, Hühnerkobel, Bavaria. (Mason, 1942.)

Chemical composition

A piece an inch wide was cleaved from the end of a large block of the Nickel Plate sample, and a fresh unoxidized sample of arrojadite was prepared from the interior. Impurities were removed by the use of methylene iodide and Clerici solution; the sample was washed until the washings gave no test for thallium. A small portion of the sample was then dissolved and gave no test for thallium. The sample so obtained for chemical analysis is at least 99.5 per cent pure.

The new chemical analyses and ratios are given in Table 7 together with Headden's old analysis. Although the author analyzed material from the Headden collection of Harvard University, certain discrepancies were found to exist between the two analyses. The greater purity of

TABLE 7. CHEMICAL ANALYSIS AND FORMULA OF ARROJADITE, NICKEL PLATE MINE, S. DAK.

	1	2	Ratios	Calculations of Analysis		
				Oxygen equivalent	Met. equivalent	Atoms per cell
P_2O_5	38.64	40.00	.2818	1.4090	.5636	48.02
Fe_2O_3	none	none				
Al_2O_3		2.66	.0261	.0783	.0522	4.45
FeO	25.05	28.22	.3928	.3928	.3928	33.47
MnO	15.54	15.78	.2226	.2226	.2226	18.97
MgO	1.50	1.04	.0258	.0258	.0258	2.20
CaO	5.53	2.46	.0439	.0439	.0439	3.74
Li_2O	0.28	0.09	.0030	.0030	.0060	.51
Na_2O	7.46	6.40	.1032	.1032	.2065	17.60
K_2O	2.00	1.74	.0185	.0185	.0369	3.14
H_2O	0.73	0.91	.0505	.0505	.1010	8.61
F	0.69	0.80	.0421	−.0211		3.59
Insol.	2.47	0.11				
Total	99.89	100.21	Total O	2.3265		198.24 (O)
Less O=F	.23	0.34				
	99.66	99.87				
Sp. gr.		3.553				

Atoms per cell found by multiplying oxygen and metal equivalents by 8521×.01.

$$\text{M Wt.} = \frac{\text{Vol.} \times \text{density}}{1.6604} = \frac{3982 \times 3.553}{1.6604} = 8521.$$

1. Headden, analyst.
2. Lindberg, analyst.

the author's sample is indicated by the smaller amount of insoluble material (2.47 per cent in Headden's analysis, 0.11 per cent in the new analysis). In addition to insoluble impurity it is very likely that small amounts of graftonite or other soluble impurities existed in his sample.

The number of atoms of each kind per unit cell is given in the last column of Table 7. In deriving a formula for arrojadite, it must be considered (1) whether calcium occupies a position equivalent to other divalent ions, or whether on the basis of ionic radius it should be grouped with sodium and potassium; and (2) whether water present occurs in the mineral as water of crystallization or as hydroxyl. Previous authors (Mason 1941 and Headden 1891) have calculated the formula of arrojadite on a dry basis. Formulas based on the above considerations are:

$(Na, K)_{5.15}(Fe, Mn, Mg, Ca, Al, Li)_{15.84}(PO_4)_{12}(F, OH)$, 1.05 H_2O, Z=4.
$(Na, K, Ca)_{2.04}(Fe, Mn, Mg, Al, Li)_{4.97}(PO_4)_4$, Z=12 (dry basis).
$(Na, K, Ca)_{2.04}(Fe, Mn, Mg, Al, Li)_{4.97}(PO_4)_3 \cdot (PO_{4-x})(OH, F)_{2x}$, $x=.51$, Z=12

The ratios were obtained by grouping the number of atoms per cell (last column Table 7), and by dividing through by Z, the number of molecules per unit cell. The space group imposes the requirement that Z be an even number of molecules. The simplified formula for (1) can be written

$$(Na, K)_5(Fe, Mn, Ca)_{16}(PO_4)_{12}(F, OH) \cdot H_2O$$

and for (2) and (3)

$$(Na, K, Ca)_2(Fe, Mn)_5(PO_4)_4.$$

Arrojadite is completely soluble in dilute HCl, HNO_3, and H_2SO_4.

X-ray studies

Two sets of rotation and Weissenberg photographs were taken on a small cleavage fragment so mounted that (1) the x-optical direction ($=b$) was the axis of rotation, and (2) {001} and {010} were in a zone parallel to the axis of rotation=[100]. The a and c directions were so chosen as to make a c-centered cell with $\beta=93°\ 37' \pm 15'$. The best cleavage is {001}; {201} is a fairly well developed cleavage; the angle between the two cleavages is 68°. The unit-cell dimensions are a_0 16.60, b_0 10.02, and c_0 23.99 Å; $a:b:c=1.656:1:2.389$. The volume of the unit cell is 3982 Å^3. Examinations of projections of Weissenberg photographs show (hkl) present when $h+k$ even, ($h0l$) present when h even and ($0k0$) present when k even. Three possible space groups are $C\ 2/m$, C_2 and C_m (C_{3h}^3, C_2^3, C_s^3). Since arrojadite is apparently not piezoelectric,*

* C. Frondel, private communication.

$C\ 2/m$ is favored. Additional absences are: $(h00)$ with h not divisible by 4, $(00l)$, l not divisible by 2, and $(h0l)$, $h/2+l$ odd.

In Table 8 are given the x-ray powder spacing data for arrojadite and related minerals. The arrojadite from the Nickel Plate mine, Pennington County, S. Dak. represents the pure analyzed sample. It has the same powder pattern as arrojadite from the Serra Branca pegmatite, Brazil (U.S.N.M. No. 96111), and the identity of the two is thus established by direct comparison of the two minerals. Also included for comparison are new x-ray data for so-called arrojadite from the Norrö pegmatite, Sweden, and from Hühnerkobel, Bavaria, and varulite from Skrumpetorp, Sweden, and from Varuträsk, Sweden. Microscopic examination shows that the material from the Norrö pegmatite contained a small amount (under 10 per cent) triphylite. The sample from Hühnerkobel was part of the analyzed sample (Mason, 1942) and contained a small amount of alluaudite. The varulite from Varuträsk, supplied through the courtesy of Professor Quensel corresponds to the yellow green phosphate described by him as representing beginning alteration to alluaudite (Quensel, 1937, p. 94). No mineral, colorless under the microscope, with indices α 1.720 and γ 1.732 was noted. These latter four are remarkably similar, though some differences, in part due to the purity of the samples, occur. All four are more alike than they are similar to true arrojadite. True arrojadite shows many lines, some relatively intense, that are not present in the material from Varuträsk, Skrumpetorp, Norrö, and Hühnerkobel, as is illustrated in Fig. 2. It is here proposed to consider arrojadite from the Serra Branca pegmatite and the Nickel Plate mine as isostructural, and to consider the minerals from the Norrö pegmatite and from Hühnerkobel as isostructural with the varulite from Skrumpetorp, and Varuträsk, but to consider the two groups as no longer isostructural with each other. Truly they are separate but related minerals. Mason (1941) in computing formulas for varulite and arrojadite, recognized the partial oxidation of his samples as being different from the Nickel Plate analysis, but did not have type material, and could not foresee the small differences in pattern between the two types.

In addition, the x-ray spacing data for a triplite sample, Serra Branca pegmatite, obtained through the courtesy of the National Museum, Departmento Nacional da Produção Mineral, Rio de Janeiro, Brazil, is given. Two other samples from this museum (Nos. 3618 and 3619) were also triplite. These samples are probably similar to the source material for the paper by Fornaseri (1943), as Fornaseri concludes that data obtained from rotation and Weissenberg photographs prove the identity of arrojadite and triplite, and publishes unit-cell dimensions and an analysis not of arrojadite but of triplite. His values for the unit cell are: a_0 5.99, b_0

TABLE 8. *X*-RAY POWDER SPACING DATA
Iron radiation, manganese filter (Å)

Arrojadite Serra Branca Pegmatite, Brazil; U.S.N.M. 96111		Arrojadite Nickel Plate mine, Pennington County, South Dakota; Harvard 543 Pure		Varulite Skrumpetorp, Sweden		Varulite Varuträsk, Sweden		So-called Arrojadite, Norrö pegmatite, Sweden; 90% pure, 10% triphyllite		So-called Arrojadite, Hühnerkobel Bavaria; Analyzed sample; contains alluaudite		Triplite, Serra Branca Pegmatite, Brazil		Natrophilite, Branchville, Connecticut; Harvard 95263	
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*
1	12.08	2	12.14							1	16.06				
3	7.65	3	7.62			1	8.30			6	8.76				
1	7.12	1	7.12							1	8.30				
1	6.51	2	6.52	5	6.33	3	6.35	5	6.26	5	6.30				
4	5.93	4	5.93							1	5.58				
4	5.55	4	5.54	2	5.47	3	5.46	3	5.44	2	5.44			1	5.25
4	5.02	3	5.01					1	5.27						
3	4.58	3	4.58			1	4.30							5	4.51
1	4.22	1	4.23			1	4.14	2	4.28	1	4.36	1	4.27	6	4.04
1	3.84	1	3.84					1	3.92			4	3.62	1	3.92
3	3.42	3	3.42	4	3.50	4	3.498	5	3.48	3	3.49	2	3.41	4	3.66
1	3.32	1	3.33							3	3.33	6	3.23		
										2	3.21				
6	3.22	6	3.22	3	3.11	3	3.12	3	3.12	2	3.08	8	3.03		
1	3.13	2	3.13	1	3.08	1	3.08	1	3.01	1	3.02	10	2.86	8	3.15
10	3.04	10	3.04	1	2.95	1	2.96	1	2.942	1	2.913	1	2.83		
4	2.487	4	2.85	2	2.90	3	2.909	2	2.880	1	2.853	1	2.73	10	2.867
4	2.766	4	2.77	1	2.79	2	2.792	1	2.766	1	2.772	1	2.69		
8	2.712	8	2.72	10	2.73	10	2.737	10	2.712	10	2.718	2	2.60		
1	2.680	1	2.68	1	2.62	1	2.635	1	2.672			1	2.53		
1	2.594	1	2.59							1	2.580	1	2.471	8	2.608
3	2.554	3	2.56	4	2.547	4	2.556	6	2.531	3	2.526	1	2.377	8	2.586
2	2.518	2	2.518	1	2.508	1	2.506	1	2.500			1	2.316	1	2.494
2	2.421	2	2.424			1	2.432					1	2.290	3	2.420
1	2.385	1	2.391			1	2.359					2	2.218		
		1	2.309									1	2.179	3	2.377
		1	2.305			1	2.212					2	2.148	3	2.318
1	2.214	1	2.226	1	2.145	2	2.152	1	2.137	1	2.175	3	2.108	3	2.262
1	2.192	1	2.202	2	2.117	2	2.215	1	2.101	1	2.148	3	2.012		
1	2.115	1	2.156	1	2.074	2	2.070	1	2.060	1	2.087	1	1.975		
1	1.976	1	1.989	1	1.993	1	1.999	1	1.982	1	2.060	1	1.917		
1	1.955	1	1.964	1	1.961	1	1.967	1	1.952	1	1.949	1	1.833	1	1.911
2	1.915	2	1.92	1	1.935	1	1.937	1	1.859			1	1.825	1	1.851
1	1.875	1	1.888	1	1.831	1	1.832	1	1.815	1	1.824	1	1.815	5	1.836
1	1.857	1	1.865	1	1.795	1	1.796			1	1.795	1	1.788	1	1.818
3	1.757	3	1.767	1	1.757	2	1.750	1	1.750			1	1.765	3	1.744
1	1.715	1	1.719	1	1.738	1	1.742			1	1.739	1	1.744		
1	1.687	1	1.687	1	1.687			1	1.671			1	1.672	5	1.695
		3	1.664	1	1.656	1	1.666	1	1.652			2	1.638		
1	1.650	2	1.654									2	1.627	3	1.648
2	1.610	2	1.616	1	1.606	1	1.613	1	1.623	1	1.618	2	1.600	1	1.606
1	1.590	1	1.597					1	1.600					2	1.587
1	1.572	1	1.58	1	1.575	1	1.577							2	1.580
1	1.566	1	1.562					1	1.565	1	1.568	1	1.565		
1	1.553	1	1.539	1	1.544	1	1.548	1	1.534					2	1.535
		1	1.529	1	1.524	1	1.528					1	1.524		
1	1.501	1	1.506									1	1.520		
1	1.485	2	1.492			1	1.499								
1	1.478	1	1.478			1	1.484								
		1	1.463	1	1.459	1	1.462					1	1.471	1	1.460
1	1.456	1	1.448									3	1.453	1	1.443
		1	1.432	1	1.435	1	1.437					1	1.435	1	1.419
1	1.424	1	1.421					1	1.419			1	1.414	1	1.401
1	1.389	1	1.388			1	1.401					1	1.394	1	1.387
		1	1.378	1	1.368	1	1.375							1	1.375
1	1.353	1	1.360												
		1	1.338	1	1.340	1	1.341							1	1.349
		1	1.330			1	1.315					1	1.330	1	1.336
		1	1.255			1	1.299					1	1.242	1	1.308
1	1.240	1	1.243									1	1.299	1	1.227
		1	1.205									1	1.196	1	1.206
		1	1.195											1	1.158
		1	1.183											1	1.135
		1	1.161	1	1.147			1	1.139			1	1.090	1	1.090
		1	1.108									1	1.085	2	1.072
		1	1.094											1	1.065
		1	1.052											1	1.038
		1	1.040									1	1.041	3	1.027
		1	1.013									1	1.017	1	.981

6.80, and c_0 5.01 Å, $\beta = 73° 42'$. X-ray powder spacing data of natrophilite (Harvard No. 95263) show a more complete structural difference from arrojadite than is suggested by statements by Brian Mason that natrophilite is distinguished from varulite and arrojadite by the presence of calcium in the latter:

"The essential feature which distinguishes varulite and arrojadite from natrophilite is the presence of calcium. The question thus arises as to what part this calcium plays in the structure of varulite and arrojadite.

"Thus three names are current for the iron-rich members of the arrojadite varulite group—soda triphylite, arrojadite, and headdenite. Application of the law of priority

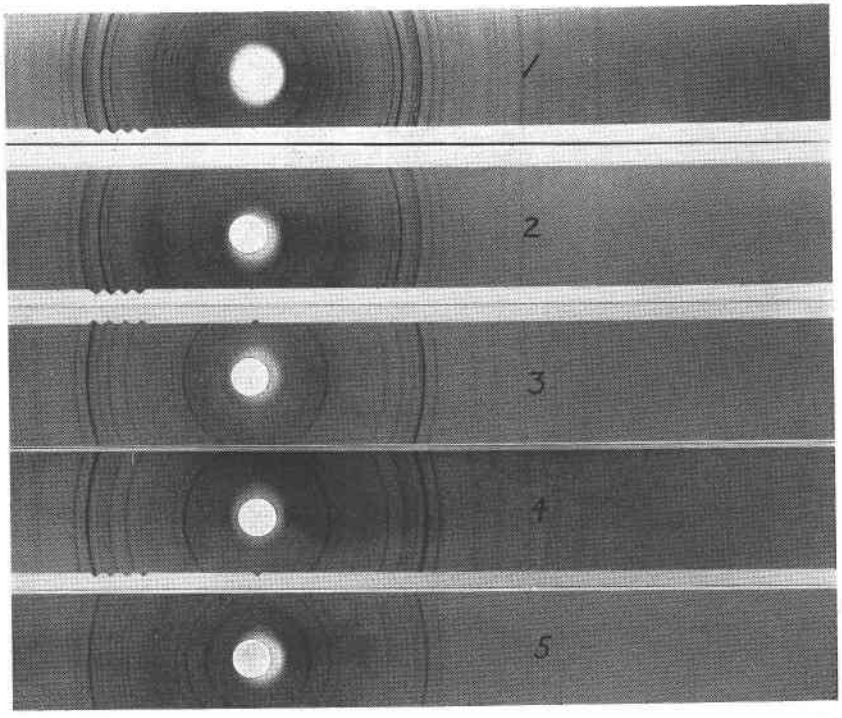

FIG. 2. *X*-ray powder diffraction photographs of arrojadite and related minerals. 1. Arrojadite from the Nickel Plate mine, South Dakota. Pure. 2. Arrojadite from the Serra Branca pegmatite, Brazil. Pure. 3. Varulite from the Skrumpetorp pegmatite, Sweden. Pure. 4. Hühnerkobelite (previously called arrojadite) from the Norrö pegmatite, Sweden. Contains triphylite as impurity. 5. Hühnerkobelite (previously called arrojadite) from Hühnerkobel, Bavaria. Contains alluaudite as impurity.

would assign the name soda-triphylite to these iron-rich minerals. That is all that can be said in favor of Ziegler's name. In other respects it is thoroughly a bad name. The name soda-triphylite, if it suggests anything, suggests a mineral in which the lithium of triphylite has been replaced by sodium; this mineral is already known and has been named natrophilite. Headden's phosphate differs from natrophilite in its calcium content, and this calcium is its distinguishing feature."

Definition of arrojadite

Arrojadite from the Nickel Plate pegmatite and from the Serra Branca pegmatite are isostructural. The material from Hühnerkobel, Bavaria, and from Norrö, Sweden, are isostructural with varulite from Skrumpetorp. The relationship of the varulite from Skrumpetorp and type varulite from Varuträsk is not clear. Quensel's (1937) original description of varulite states:

"Most grains are intimately interwoven with a yellowish green phosphate, without doubt alluaudite, representing beginning alteration to that mineral."

Samples of varulite supplied through the courtesy of Professor Quensel appear to be the yellowish green phosphate and are isostructural with the Skrumpetorp varulite.

The varulite from Skrumpetorp as well as the arrojadite from Hühnerkobel and Norrö are fine-grained green minerals which could correspond either to the varulite or alluaudite of Quensel's original description of varulite. However, Mason (1942) describes arrojadite from Hühnerkobel to be associated with alluaudite; therefore, if his mineral is not arrojadite it also is not alluaudite. His description of the two minerals follows:

"The arrojadite was first identified by *x*-ray powder photographs, which showed its structural identity with the varulite from Varuträsk; the predominantly iron-rich nature of the phosphate minerals at Hühnerkobel suggested that in this specimen the mineral was the iron-rich member of the isomorphous series, arrojadite, rather than the manganese-rich member, varulite. This was later confirmed by chemical analysis.

"Thin sections showed that, besides being associated with triphylite and eosphorite the arrojadite was intimately mixed with about 10–20% of alluaudite, evidently the oxidation product of the arrojadite; one section also showed a small amount of a mineral wine-red in section, almost certainly heterosite formed by the further oxidation of the alluaudite. A small amount of a black mineral, probably a mixture of iron and manganese oxides, occurred along the cracks in the other minerals. The arrojadite was fine-grained, pleochroic in shades of green, and showed no cleavage; the alluaudite was also fine-grained and pleochroic in yellow and brown. As far as the paragenesis of the minerals can be read from the sections of one small specimen, it appears to be as follows: the arrojadite has been formed from and replaces triphylite, the triphylite being a crystallographic unit, the scattered remnants of which extinguish uniformly over large areas. The first stage in the replacement appears to be the changing of the triphylite to a clear mineral with a slightly yellow tinge, faintly pleochroic and with birefringence about 0.01. There is very little of this mineral in the sections as it is apparently rapidly changed to the green arrojadite, and the arrojadite is in turn further changed to the yellow alluaudite. The black opaque mineral is latest of all, and is probably not derived from the arrojadite and alluaudite of the section, but is rather a late infiltration. None of the sections showed the relationship between eosphorite and the surrounding arrojadite, but the general features of the specimen suggest that the eosphorite is later. The refractive indices of the arrojadite are: $\alpha = 1.754 \pm 0.003$, $\gamma > 1.770$, probably about 1.785. The pleochroism is strong, X = pale gray-green, Z = dark green. All the indices of the alluaudite are greater than 1.770; the pleochroism is X = dark yellow, Y = yellow brown, Z = brown."

Mason's description of arrojadite is that of a mineral altered from triphylite. The arrojadite from the Norrö pegmatite is also a mineral associated with triphylite. The arrojadite from the Nickel Plate is a primary unaltered mineral with a distinctive x-ray pattern. It is here proposed to give the name hühnerkobelite to the material from Hühnerkobel and from Norrö, not isostructural with true arrojadite.

The varulite from Skrumpetorp is isostructural with hühnerkobelite and with the yellowish green material of the varulite samples from Varuträsk. These may be considered the manganese equivalent of hühnerkobelite. A manganese equivalent to arrojadite has not yet been verified, but the possibility is suggested that the colorless mineral of Quensel's original description of varulite may be equivalent to arrojadite.

Summary

Optical, chemical, and x-ray studies were made upon graftonite and arrojadite from the Nickel Plate mine, Pennington County, South Dakota. The arrojadite from the Nickel Plate pegmatite was found to be isostructural and identical with arrojadite from the Serra Branca pegmatite. Arrojadite from the Nickel Plate mine was found to be structurally different from arrojadite from Hühnerkobel, Bavaria, and Norrö, Sweden, and are designated hühnerkobelite to differentiate them from true arrojadite.

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