

# THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 44

NOVEMBER-DECEMBER, 1959

Nos. 11 and 12

## YAVAPAIITE, AN ANHYDROUS POTASSIUM, FERRIC SULPHATE FROM JEROME, ARIZONA

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### ABSTRACT

Yavapaiite, a new mineral from Jerome, Arizona, has the composition  $\text{KFe}^{3+}(\text{SO}_4)_2$  with two formula units in the unit cell. The mineral, associated with sulphur, voltaite, and other unidentified sulphates, forms pale pink, brittle, adamantine crystals, elongate parallel to [010], with perfect {100}, {001}, and distinct {110} cleavages, and strong conchoidal fracture. The forms  $c\{001\}$ ,  $d\{101\}$ ,  $f\{201\}$ ,  $a\{100\}$ , and  $m\{110\}$  appear to be most frequently developed.  $H=2\frac{1}{2}-3$ , S.G.=2.88 (meas.), 2.92 (calc.);  $\alpha=1.593$ ,  $\beta=1.684$ ,  $\gamma=1.698$ ,  $\gamma-\alpha=0.105$ ;  $2V_{Na}=30.5^\circ (-)$ ,  $\rho>v$  strong;  $b=Z$ ,  $c\wedge X=6^\circ$ ,  $a=Y$ , or nearly so.  $a_0=8.12 \text{ \AA}$ ,  $\pm 0.01 \text{ \AA}$ ,  $b_0=5.14 \text{ \AA}$ ,  $c_0=7.82 \text{ \AA}$ ,  $\beta=94^\circ 24'$ ;  $a_0:b_0:c_0=1.5797:1:1.5214$ . Measured cell weight =  $936.41 \times 10^{-24}$  gms. Monoclinic, with space group  $C2$ ,  $C2/m$ , or  $Cm$ . Decomposed in boiling water, but readily soluble in HCl to give stable solutions.

The mineral is named for the Indian tribe that inhabits that part of Arizona in which the inactive mining center of Jerome is situated.

### OCCURRENCE

The most complete study of sulphates formed under fumarolic conditions at the United Verde Copper Mine at Jerome, Arizona,\* was made by Lausen (1928), and without exception, all of the sulphates reported in that work are hydrous minerals. Furthermore, most of them appear to have crystallized as the result of the extensive fire that first started in the mine in the fall of 1894, although Lausen (1928, p. 205) points out that many of the sulphates may have crystallized "when water was first used to put out the fires. Conditions, however, must have varied from time to time, as the various sulphates are not mutually intergrown, but rather occur as crystals of one composition resting on those of another."

The mineral described herein was collected by Mr. Scott J. Williams of Scottsdale, Arizona, in 1941. Of very limited occurrence, it formed a cement in rubble that was exposed in the open pit operations of the United

\* For a more comprehensive account of the geology and ore deposits of Jerome in particular, and the region in general, reference may be made to Lindgren, W. (1926), Ore deposits of the Jerome and Bradshaw Mountains Quadrangles, Arizona: *U.S.G.S. Bull.* 782, pp. 1-192.

Verde Extension Mining Co. Operations at the pit ceased very soon after 1941, and all traces of the occurrence are now unhappily lost.

The only specimen that was available for study consisted of an irregularly shaped fragment, 20×25 mm. with saccharoidal texture. Yavapaiite, which makes up 90–95 per cent of the specimen, forms rather equidimensional grains that average about 0.2 mm. in diameter, although here and there, in vugs, short, stumpy crystals with some terminal faces occasionally preserved, may reach 0.6 mm. in length. The mineral in question has formed upon very coarsely crystalline voltaite, and at the same time it is dusted over with very minor quantities of sulphur, jarosite, and at least two other sulphates which have not been satisfactorily diagnosed at this time; alunite may be present but its occurrence here has not been definitely proved.

The mineral has been given the name yavapaiite—Y Ā' V Ā P A I I T<sup>1</sup> or yā' vā pai ite<sup>2</sup>—after the Indian tribe that inhabited that area of Arizona in which Jerome is situated.

#### PHYSICAL PROPERTIES AND CRYSTALLOGRAPHY

Crystals of yavapaiite exhibit perfect transparency, vitreous luster that is almost adamantine in some instances, and very pale pink color with a slight purple hue (close to Ridgway's shell pink—11" f, Plate 28). The streak is white but the color of the finely powdered mineral is very pale yellow; the mineral, however, is perfectly colorless in transmitted light, even for fragments 2–3 mm. in thickness. Hardness is  $2\frac{1}{2}$ –3, and the measured specific gravity, determined by centrifuging in bromoform-diiodomethane-acetone mixtures is 2.88 at 22° C., whereas the calculated value is 2.92. The former value was obtained only after the sample had been finely crushed, dried in air at 110° C. for two hours, and then placed in vacuo; if this procedure is not followed, a value of  $2.81 \pm 0.02$  was obtained for all specimens so measured. The mineral is exceedingly brittle, and those fracture surfaces not determined by cleavage are usually subconchoidal to uneven.

The crystals of yavapaiite do not exceed 0.6 mm. in length, and are usually very much less than this. In some instances, they are singly terminated, but no examples were isolated that would permit accurate and, therefore, worthwhile goniometric treatment. The crystals are short and stumpy in form with the longer dimension parallel to [010]. For one incomplete crystal (Fig. 1) that permitted identification of the faces, {001} is dominant, with {101}, {100}, {201}, and unit prism {110} less

<sup>1</sup> English usage, following the Royal Geographical Society (R.G.S. II) system.

<sup>2</sup> American usage.

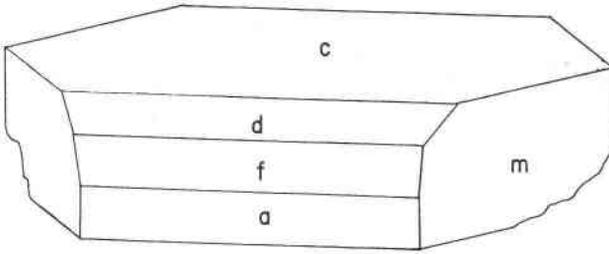


FIG. 1. Incomplete crystal of yavapaiite from Jerome, Arizona, showing development of  $c\{001\}$ ,  $d\{101\}$ ,  $f\{201\}$ ,  $a\{100\}$ , and  $m\{110\}$ .

well developed; other faces are poorly represented as the result of fracture or deep growth pits.

Perfect  $\{001\}$ ,  $\{100\}$ , and distinct  $\{110\}$  cleavages occur, and the dominance of the two former directions leads to the development of slender prismatic fragments with roughly rectangular cross-sections when crystals are crushed.

A very poor choice of crystals was available, but one doubly terminated fragment (Fig. 1) was selected for measurement with a stage goniometer. The interfacial angles thus determined are set out in Table 1, together with the corresponding angles calculated from data determined by the  $x$ -ray study. Most faces exhibit some curvature, and as a result they yielded reflections over a range of as much as  $30'$  in some instances; these data, which should be considered to be within  $\pm 30'$  of the correct values, lead to a linear axial ratio  $a:b:c=1.59:1:1.52$ , and an interaxial angle of  $94^\circ 30'$ .

The calculated elements and standard angles for yavapaiite are listed in Table 2, and these data have been derived from cell dimensions determined by the  $x$ -ray work.

The optical and other physical properties of yavapaiite are given in Table 3, where they may be compared with similar data for the monohydrate, krausite, and the quadrihydrate, goldichite.

TABLE 1. MEASURED AND CALCULATED INTERFACIAL ANGLES FOR YAVAPAIITE

Faces	Measured	Calculated
$100 \wedge 110$	$57^\circ 45'$	$57^\circ 35'$
$001 \wedge 101$	$41^\circ 30'$	$41^\circ 48'$
$001 \wedge 201$	$59^\circ 30'$	$59^\circ 08'$
$201 \wedge 100$	$26^\circ 00'$	$26^\circ 28'$
$001 \wedge 011$	$56^\circ 30'$	$56^\circ 36'$

TABLE 2. ANGLE TABLE FOR YAVAPAIITE

$a:b:c=1.5797:1:1.5214$ ;  $\beta=94^{\circ}24'$ ;  $p_0:q_0:r_0=0.9631:1.5169:1$ ;  $r_2:p_2:q_2=0.6592:0.6349:1$ ;  $\mu=85^{\circ}36'$ ;  $p_0'=0.9658$ ,  $q_0'=1.5214$ ,  $x_0'=0.0769$ .

	$\phi$	$\rho$	$\phi_2$	$p_2=B$	C	A
<i>c</i> 001	90°00'	4°24'	85°36'	90°00'	0°00'	85°36'
<i>a</i> 100	90 00	90 00	0 00	90 00	85 36	0 00
<i>m</i> 110	32 25	90 00	0 00	32 25	87 38½	57 35
<i>w</i> 011	2 53½	56 43	85 36	33 23	56 37	87 35
<i>d</i> 101	90 00	46 12	43 48	90 00	41 48	43 48
<i>f</i> 201	90 00	63 32	26 28	90 00	59 08	26 28

When mounted in refractive index media, and due to development of perfect {001} and {100} cleavages, the crushed powder provides a large number of fragments with approximately maximum birefringence, and about an equal number that yield nearly centered, negative, acute bisectrix figures (Fig. 2); the latter orientation, however, is the more obvious one owing to striking anomalous interference tints displayed therein.

#### X-RAY WORK

Rotation and Weissenberg photographs about the *a*, *b*, and *c* axes were taken with a 57.29 mm. diameter camera; nickel-filtered copper radiation ( $\text{CuK}\alpha=1.5418 \text{ \AA}$ ) was employed, and although some degree of fluorescence resulted thereby, it did not prevent satisfactory study and measurement of films.

Appropriate measurement of zero layer Weissenberg films, calibrated with quartz, gave unit cell dimensions as follows:

$$a_0=8.12 \text{ \AA}, \pm 0.01 \text{ \AA}, b_0=5.14; c_0=7.82; \beta=94^{\circ} 24'.$$

These data lead to a linear axial ratio of 1.5797:1:1.5214, compared with the figures derived from crystal measurement, *viz.*  $a:b:c=1.59:1:1.52$ .

Indexing of Weissenberg films and a study of the systematic extinctions therein indicates that the space group is *C*2, *C*2/*m*, or *C**m*. Unfortunately this ambiguity could not be resolved further at this time.

The x-ray diffraction powder pattern is set out in Table 4, column 1, and the lines therein have been indexed on the basis of the unit cell constants determined for yavapaiite by single crystal work, and the reflections recognized on Weissenberg films. Indexing is not complete in the sense that each reflection observed on single crystal Weissenberg photographs has had a corresponding *d*-value calculated for it, since, at angles greater than about  $79^{\circ} 2\theta$ , most of the lines are weak and many are quite

TABLE 3. COMPARISON OF YAVAPAIITE WITH THE MONOHYDRATE AND QUADRIHYDRATE

	Yavapaiite $K Fe^{3+}(SO_4)_2$ (This study)	Krausite $K Fe^{3+}(SO_4)_2 \cdot H_2O$ (Foshag, 1931)	Goldichite $K Fe^{3+}(SO_4)_2 \cdot 4H_2O$ (Rosenzweig and Gross, 1955)
$\alpha$	$1.593 \pm 0.002$	1.588	1.582
$\beta$	1.684	1.650	1.602
$\gamma$	1.698	1.722	1.629
$\gamma - \alpha$	0.105	0.134	0.047
$2V$ { 5500 Å 5890 Å 7200 Å.	29.5° 30.5° 33.0°	} large	82° (calc.)
Optic sign	(-)		(+)
Dispersion	horizontal with $p > v$ , strong	—	$p < v$ , strong <sup>1</sup>
$b$	Z	Z	X
Extinction	$c \wedge X = 6^\circ$ $a = Y$ , or nearly so.	$c \wedge X^2 = 35^\circ$	$c \wedge Z = 11^\circ$
Color	colorless in section; otherwise very pale pink.	colorless in section; pale yellow and weakly pleochroic in thick grains.	colorless in section; greenish-yellow and lavender in artificial light.
Cleavage	{001}, {100} perfect; {110} distinct.	{001} perfect, {100} good.	{100} excellent.
Symmetry	monoclinic	monoclinic	monoclinic
Space group	$C2, C2/m$ , or $Cm$	—	$P 2_1/c$

<sup>1</sup> Determined by the present writer upon material from the type locality—Dexter No. 7 Mine, Calf Mesa, San Rafael Swell, Utah.

<sup>2</sup> Palache, Berman and Frondel (1951, p. 463) incorrectly state that the angle  $Y \wedge c = -35^\circ$ .

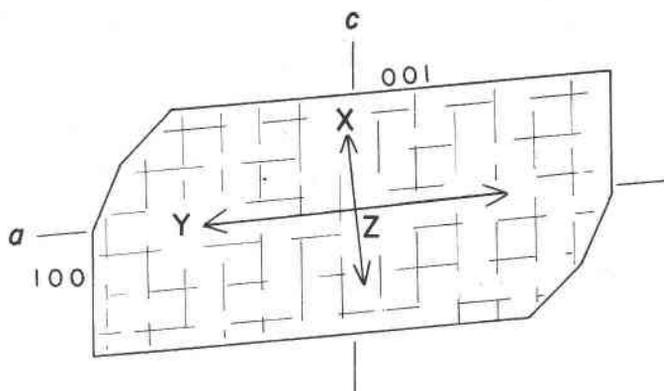


FIG. 2. Optical orientation of yavapaiite.

diffuse; under these circumstances indexing is uncertain. It should be realized, however, that many reflections, additional to those observed in the powder patterns, have been recognized on single crystal films; for in-

TABLE 4. POWDER PATTERNS OF YAVAPAIITE, AND ARTIFICIAL  $KFe^{3+}(SO_4)_2$ .

Camera diameter: 114.59 mm.

Radiation:  $CuK\alpha = 1.5418 \text{ \AA}$ .

hkl	1		2		3		I	hkl	1		2		3		I
	d meas.	d calc.	d meas.	d meas.	d meas.	d meas.			d meas.	d calc.	d meas.	d meas.	d meas.	d meas.	
001	7.85	7.79	7.88	7.82	90	204	1.706	1.706	1.707	1.710	5				
110	4.35	4.35	4.35	4.33	5	313	—	1.703	—	—	—				
200	4.05	4.05	4.06	4.05	40	223	1.700	1.700	1.700	1.701	1				
002	3.90	3.90	—	—	2	130	1.6775	1.676	1.6775	1.6775	1				
$\bar{1}11$	3.87	3.86	3.88	3.86	80	403	—	1.654	—	—	—				
111	3.73	3.73	3.74	3.73	75	131	1.647	1.644	—	1.647	5				
201	—	3.71	—	—	—	131	1.636	1.634	—	—	<1				
201	3.49	3.49	3.49	3.49	60	223	—	1.633	—	—	—				
$\bar{1}12$	2.97	2.96	2.98	2.97	100	420	—	1.590	—	—	—				
202	2.92	2.92	2.92	—	<1	421	1.576	1.580	—	—	8				
112	2.842	2.843	2.846	2.842	75	314	1.560	1.564	—	—	1				
202	2.705	2.708	2.703	2.702	2	005	—	1.560	—	—	—				
003	2.603	2.600	2.602	2.606	5	024	1.553	1.554	1.552	1.553	15B				
020	2.572	2.570	2.577	2.570	35	132	—	1.549	—	—	—				
021	2.441	2.441	—	2.441	<1	510	—	1.545	—	—	—				
310	2.394	2.391	2.396	2.394	80	403	—	1.544	—	—	—				
311	2.330	2.330	2.330	—	<1	205	1.534	1.540	1.534	—	1				
$\bar{1}13$	2.283	2.270	2.285	2.282	20	421, 511	—	1.537	—	—	—				
203	2.260	2.266	—	—	<1	132	—	1.531	—	—	—				
311	—	2.241	—	—	—	511	1.515	1.519	1.514	1.510	20				
113	2.200	2.191	2.192	2.191	<1	422	—	1.505	—	—	—				
220	—	2.170	—	—	—	—	1.493	—	1.492	1.490	15B				
022	2.151	2.147	2.152	2.152	25	115	—	1.487	—	—	—				
203	—	2.115	—	—	—	224	—	1.481	—	—	—				
221	2.116	2.113	2.116	—	30	512	—	1.473	—	—	—				
312	—	2.102	—	—	—	314	1.466	1.463	1.466	1.466	10				
221	2.065	2.068	2.069	—	<1	404	—	1.461	—	—	—				
400	2.027	2.024	2.027	2.027	5	115	—	1.449	—	—	—				
401	1.996	1.996	—	—	<1	—	1.447	—	1.448	1.446	30B				
312	—	1.972	—	—	—	330	—	1.447	—	—	—				
004	1.951	1.950	1.952	1.953	<1B	422	—	1.443	—	—	—				
222	1.933	1.930	1.934	1.934	20	331	—	1.433	—	—	—				
401	—	1.925	—	—	—	—	1.425	—	1.426	1.425	<1				
222	1.867	1.865	1.865	1.867	25	224	—	1.422	—	—	—				
402	—	1.856	—	—	—	205	—	1.420	—	—	—				
023	—	1.828	—	—	—	133	—	1.419	—	—	—				
313	1.824	1.822	1.824	1.824	35B	331	—	1.412	—	—	—				
204	—	1.812	—	—	—	512	1.402	1.402	1.403	1.402	10				
$\bar{1}14$	—	1.806	—	—	—	133	—	1.399	—	—	—				
114	1.757	1.752	1.759	1.759	10	423	—	1.395	—	—	—				
402	1.742	1.743	1.742	1.741	25	332	—	1.375	—	—	—				

(Continued on facing page)

1. Yavapaiite, Jerome, Arizona.
2. Powder pattern yielded by R. C. Corey's material (author's own diffraction pattern).
3. Artificial  $KFe^{3+}(SO_4)_2$  compound prepared by the Dow Chemical Company, Midland, Michigan, and  $\alpha$ -ray work by the present writer.

I = Intensities determined visually and referring specifically to yavapaiite in column 1.

B = Broad and usually diffuse line.

TABLE 4 (Continued)

1	2	3		1	2	3	
<i>d</i> meas.	<i>d</i> meas.	<i>d</i> meas.	I	<i>d</i> meas.	<i>d</i> meas.	<i>d</i> meas.	I
1.350	—	1.350	1	1.098	1.098	1.098	1
1.322	1.323	1.322	5	1.042	1.041	1.042	10B
1.306	1.307	1.306	1	.993	.993	.993	1B
1.286	1.288	1.286	15	.961	.961	.961	1
1.268	1.268	1.266	45	.947	.948	.947	1B
1.215	1.214	1.214	10	.920	.919	.920	1
1.198	1.198	—	15	.911	.911	.910	<1
1.171	1.171	1.170	10	.884	.884	.884	1
1.158	1.158	1.158	10	.811	.810	.810	<1B
1.145	1.144	1.145	1	.796	.796	.796	<1B
1.111	—	1.111	1	.781	.781	.781	<1

stance, between 0.884 and 0.811, 41 reflections have been observed whose *d*-spacings were calculated, but are not reported here.

In the first instance, the nature of this mineral was suspected on account of the similarity of its powder pattern with that recorded on ASTM card No. 3-0617 for artificial  $K Fe^{3+}(SO_4)_2$  supplied to the Dow Chemical Company by R. C. Corey of the Combustion Engineering Corporation. Through the generosity of Dr. H. W. Rinn of the Dow Chemical Company of Midland, Michigan, the present author obtained a sample of Corey's material; furthermore, a second sample of  $K Fe^{3+}(SO_4)_2$  was generously made available, and this had been prepared by Dow Company officers by vacuum crystallization of a solution containing  $K_2SO_4$  and  $Fe^{3+}_2(SO_4)_3$  in 1:1 mol ratio and subsequent heat-treatment of the crystallized product at 400° C. The x-ray powder patterns yielded by these two artificially prepared samples (Table 4, columns 2 and 3) are closely similar to that obtained with Jerome, Arizona material of natural origin.

At angles greater than about 65°  $2\theta$ , many of the reflections in the powder photographs become rather broad and diffuse, especially so at angles greater than 79°  $2\theta$ , so that precise measurement thereof is not always possible; nor is there any distinct resolution of  $\alpha_1$ , and  $\alpha_2$  lines. This difficulty was not resolved by careful heating of the mineral, because the patterns yielded by yavapaiite heated in air to 280° C. and 400° C. for periods of 17 and 8 hours respectively, were in no sense distinct from the pattern recorded for the unheated material.

#### CHEMICAL PROPERTIES

When finely powdered yavapaiite is added to hot water, the mineral decomposes immediately with concomitant precipitation of ferric hydroxide, and production of a weakly acid solution. In cold water, on the

other hand, solution is extremely slow and precipitation of the hydroxide is not evident for several days. The mineral is readily soluble in warm 2N HCl to give a pale yellow solution that appears to be quite stable. When yavapaiite is heated in air to about 500° C. the mineral turns pale brown, and slightly stronger heating results in a deep red-brown powder. In a closed tube, the mineral decrepitates slightly, and a strongly acidic water is evolved.

TABLE 5. ANALYSIS AND EMPIRICAL UNIT CELL CONTENTS OF YAVAPAIITE

	1	2	3	4	5	6
SiO <sub>2</sub> +insol.	0.26					
Al <sub>2</sub> O <sub>3</sub>	0.11	0.11	.0014			
TiO <sub>2</sub>	nil					
Fe <sub>2</sub> O <sub>3</sub>	27.69	27.82	1.9944	2.01	27.89	1.9980 2.0
FeO	0.07	0.07	.0051			
CaO	tr.					
MgO	0.08	0.08	.0108			
K <sub>2</sub> O	15.39	15.46	1.8788	1.99	15.50	1.8836
Na <sub>2</sub> O	0.62	0.62	.1145		0.62	.1144
SO <sub>3</sub>	55.58	55.84	3.9928	3.99	55.99	4.0012 4.0
H <sub>2</sub> O at 105°C.	tr.					
H <sub>2</sub> O—	0.14					
	99.94					

Cell contents: (K, Na)<sub>1.99</sub>(Al, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Mg)<sub>2.01</sub>[SO<sub>4</sub>]<sub>3.99</sub> or (K, Na)<sub>2</sub>Fe<sup>3+</sup><sub>2</sub>[SO<sub>4</sub>]<sub>4</sub>

1. Analysis of yavapaiite (analyst: C. Osborne Hutton).
2. Analysis of yavapaiite with SiO<sub>2</sub> removed; total recalculated to 100.
3. Cations on the basis of 16 oxygen atoms per unit cell.
4. Analysis of yavapaiite with SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, MgO removed; total recalculated to 100.
5. Cations for analysis in column 4 on the basis of 16 oxygen atoms to the unit cell.
6. Theoretical composition of K Fe<sup>3+</sup>(SO<sub>4</sub>)<sub>2</sub> in weights per cent.

A complete chemical analysis was made of a sample composed of crystal fragments that had been concentrated by hand-picking, and any particles that appeared to be contaminated with sulphur, voltaite, jarosite, or any other extraneous material were rejected. Accordingly, it is believed that the analysis (Table 5) is representative of very nearly pure yavapaiite. Small amounts of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, and MgO were found to be present, and SiO<sub>2</sub>, at least, is possibly an impurity; this oxide has been set aside from the analysis reported in column 2, whereas the other three oxides have been omitted in column 4. In both cases (columns 2 and 4, Table 5) the empirical unit cell contents have been

calculated on the basis of 16 oxygen atoms. The total quantities of ions other than  $\text{Fe}^{3+}$ , K, Na, and S are very small, and the results of calculations set out in column 3 do not differ significantly from those listed in column 5. It is not clear, therefore, whether the small amounts of Al,  $\text{Fe}^{2+}$ , and Mg represent contamination of the sample of yavapaiite by minute amounts of other compounds, or not, but the results of a spectrographic analysis (Table 6) of very carefully selected water-clear crystal fragments of this mineral tends to support the conclusion that small amounts of Al and Mg are present in the pure mineral; and the same may be true for  $\text{SiO}_2$  as well.

TABLE 6. SPECTROGRAPHIC ANALYSIS OF YAVAPAIITE

## MAJOR ELEMENTS:

Fe &gt; 10 per cent.

K &gt; 5 per cent.

## MINOR ELEMENTS:

Na &lt; 0.3 per cent.

Si = 0.1 - 0.2

Ca = 0.1 - 0.15

Al = 0.05 - 0.1

Mg = 0.01 - 0.05

B = 0.01

Ti = 0.01 - 0.03

Mn = 0.005 - 0.01

Mo = 0.005 - 0.01

Cu = 0.001 - 0.005 (part of this could come from electric motors in operation nearby).

Ag = 0.001 ±

Ba = 0.001 ±

Rb seems to be present, but lines are obscured by CN lines.

## ELEMENTS UNDETECTED:

Li, Sr, V, Cr, Co, Ni, Au, Zn, Cd, Hg, Sn, Pb, Bi, Sb, As, Te, P, Be, Ga, Ge, Th, U, Zr, In, W, Cs, rare earths, and platinum.

Attempts were made to prepare yavapaiite by careful dehydration of krausite, goldichite, and potassium iron alums, but these experiments failed in every case; none of the products obtained yielded x-ray diffraction patterns that were in any way comparable to that typical of yavapaiite.

## ACKNOWLEDGMENTS

I wish to acknowledge gratefully the kindness of Dr. H. W. Rinn, Spectroscopy Laboratory, The Dow Chemical Company, Midland, Michigan, for his gift of two samples of artificial  $\text{K Fe}^{3+}(\text{SO}_4)_2$ , and for his helpfulness in allowing me to record data secured from my study of these samples. It is a pleasure to acknowledge Dr. John Stone's assistance in connection with the spectrographic analysis of yavapaiite, Dr. Michael Fleischer's courtesy in offering an opinion as to the suitability of the name given to the mineral, Mr. Scott J. Williams' donation of ma-

terial that formed the basis of this study, and finally Dr. F. G. Tickell's assistance in the laboratory in many ways.

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*Manuscript received January 30, 1959.*