Canadian Mineralogist
Vol. 14, pp. 437-441 (1976)

NEW DATA FOR KÖTTIGITE AND PARASYMPLESITE

B. D. STURMAN

Dept. of Mineralogy and Geology, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario, M5S 2C6

Abstract

Microprobe analysis of köttigite from the type locality (Schneeberg, Germany) gave the formula $(Zn_{2.44}Co_{0.42}Ni_{0.14})_{\Sigma=3}(AsO_4)_2 \cdot 8H_2O$. The mineral is light red to carmine red, streak reddish, perfect {010} cleavage, hardness 2-3, D_{calc} 3.24g/cm³. It is biaxial (+), $2V = 85°$, n_α 1.619, n_β 1.645, n_γ 1.681, $X = b$, $Z\Lambda c = +32°$. Pleochroism is weak, absorption $Z < Y = X$. Unit–cell dimensions calculated from powder diffraction data are a 10.240, b 13.401, c 4.752Å, β 105°07', $Z = 2$.

Blue crystals of supposed köttigite from the Ojuela mine, Mexico (Larsen 1921) are parasymplesite. Microprobe analysis gave a formula $(Fe_{1.68}Zn_{1.32})_{\Sigma=3}(AsO_4)_2 \cdot 8H_2O$. Crystals are pale blue, with very pale blue streak, perfect {010} cleavage, hardness 2-3, D_{calc} 3.13g/cm³, D_{meas} 3.12g/cm³. The mineral is biaxial (+), $2V = 86°$, n_α 1.620, n_β 1.648, n_γ 1.685, $X = b$, $Z\Lambda c = +29°$. Pleochroism is weak, absorption $X > Y = Z$. Unit-cell dimensions calculated from the powder pattern are a 10.276, b 13.480, c 4.771Å, β 105°01', space group $C2/m$; $Z = 2$.

Sommaire

La köttigite type de Schneeberg (Allemagne) donne, à la microsonde, la formule $(Zn_{2.44}Co_{0.42}Ni_{0.14})_{\Sigma=3}(AsO_4)_2 \cdot 8H_2O$. De couleur rouge pâle à rouge carmin, rougeâtre dans la rayure, elle possède un clivage parfait {010} et la dureté 2-3. Sa densité calculée est $D_x = 3.24$. Elle est biaxe positive, avec $2V = 85°$, n_α 1.619, n_β 1.645, n_γ 1.681; $X = b$, $Z \Lambda c = +32°$; faiblement pléochroïque, absorption $Z > Y = X$. Les dimensions de la maille, calculées à partir des données de diffraction (méthode des poudres), sont: a 10.240, b 13.401, c 4.752Å, β 105°7', d'où $Z = 2$.

Des cristaux bleus de la mine Ojuela (Mexique), identifiés comme köttigite (Larsen 1921) sont en fait de la parasymplésite. La microsonde donne la formule $(Fe_{1.68}Zn_{1.32})_{\Sigma=3}(AsO_4)_2 \cdot 8H_2O$. De couleur bleu pâle, très pâle dans la rayure, à clivage parfait {010} et de dureté 2–3, cette parasymplésite a pour densité calculée $D_x = 3.13$, mesurée $D_m = 3.12$. Elle est biaxe positive, avec $2V = 86°$, n_α 1.620, n_β 1.648, n_γ 1.685, $X = b$, $Z\Lambda c = +29°$; faiblement pléochroïque, absorption $X > Y = Z$. Les dimensions de la maille, calculées à partir du diagramme de poudre, sont: a 10.276, b 13.480, c 4.771Å, β 105° 01', d'où $Z = 2$; le groupe spatial est $C2/m$.

(Traduit par la Rédaction)

Introduction

The Royal Ontario Museum recently acquired a beautiful specimen of blue crystals, labelled köttigite, from Ojuela mine, Mapimi, Mexico. During routine examination of the crystals, it became evident that data for köttigite, available in the literature, are either incomplete or are not reliable. For example, the two sets of optical data available (Larsen 1921; Wolfe 1940) are not in agreement and both were determined on unanalyzed specimens. Also, the two strong lines characteristic for the vivianite group are missing in the köttigite powder diffraction pattern (JCPDS card #1-744). Consequently, the blue crystals from Mexico, and a Royal Ontario Museum specimen of köttigite from the type locality (Schneeberg, Germany) were analyzed. Microprobe analysis of the crystals from Mexico showed these to be parasymplesite $Fe_3(AsO_4)_2 \cdot 8H_2O$, with large amounts of Fe replaced by Zn. The Museum specimen from Schneeberg is köttigite, $Zn_3(AsO_4)_2 \cdot 8H_2O$, with only a small amount of Co and Ni.

Köttigite

Köttigite crystals on the Schneeberg specimen in the Royal Ontario Museum (ROM specimen No. M15537) are less than 0.3 mm in size. Most of the köttigite is a crust over altered rock; a few small crystals which protrude through the crust in several areas give signals too poor to allow measurements on the optical goniometer. The forms listed in Table 1 were observed, with the universal stage, on three crystals.

Köttigite crystals are elongate parallel to [001] and flattened on {010}. The most common habit is shown in Figure 1a.

TABLE 1. ANGLE TABLE FOR KÖTTIGITE, SCHNEEBERG, GERMANY

monoclinic, a=10.240 b=13.401 c=4.752Å β=105°07'

Form	observed φ	observed ρ	calculated φ	calculated ρ
b 010	0	90°	0°00'	90°00'
m 110	55°	90°	53°35'	90°00'
n $\bar{2}01$	89°	50 1/2°	90°	50°55'
v $\bar{2}21$	-47°	44°	-44°16'	44°43'

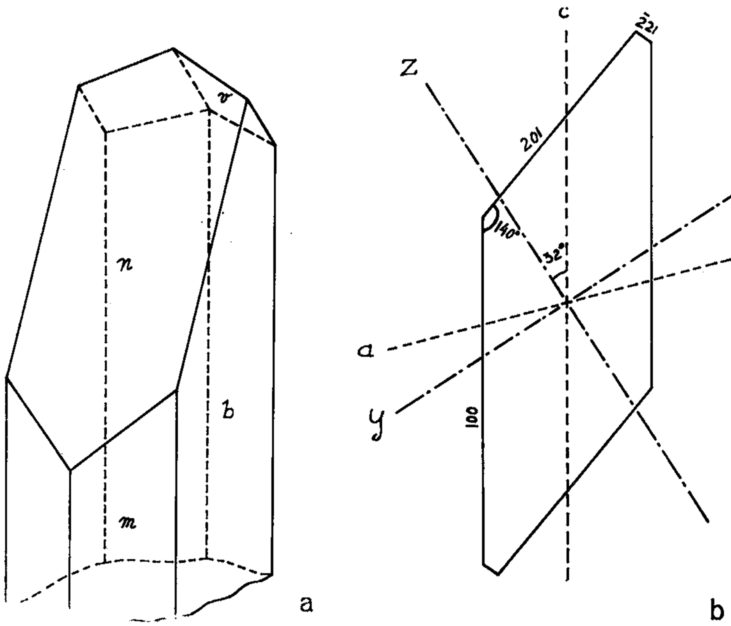

FIG. 1. (a) The common shape of köttigite crystals from Schneeberg, Germany; (b) the orientation of the optical and crystallographic elements for köttigite crystals lying on {010}.

Physical and optical properties

Köttigite is light red to carmine red, with the streak being reddish white. Hardness is 2-3. There is a perfect {010} cleavage. Density was not determined because of the small amount of clean sample available. The calculated density, 3.24 g/cm³, is smaller than the value of 3.32 given by Wolfe (1940) because the unit-cell dimensions, calculated from the powder diffraction pattern, are larger.

Orientation of the principal vibration direc-

TABLE 2. UNIT-CELL DIMENSIONS, OPTICAL AND PHYSICAL CONSTANTS OF KÖTTIGITE FROM SCHNEEBERG, GERMANY

	This study*	Larsen (1921)	Wolfe, (1940)
a	10.240(6)		10.11
b	13.401(8)		13.31
c	4.752(2)		4.70
β	105°07'(2)		103°50'
Space group	C2/m		C2/m
Z	2		2
D_{meas}	---	3.1 g/cm³	3.33 g/cm³
D_{calc}	3.24 g/cm³	---	3.32 g/cm³
H	2-3	2.5-3	2.5-3
n_α	1.619 (1)	1.662	1.622
n_β	1.645 (1)	1.683	1.638
n_γ	1.681 (1)	1.717	1.671
$2V_z$ meas.	85° (1)	---	74°
$2V_z$ calc.	83°	77°	72°
dispersion	$r<v$	$r<v$	imperceptible
pleochroism	weak	nonpleochroic	---
X	colorless	---	---
Y	colorless	---	---
Z	pale red	---	---
absorption	$Y = X$	---	---
orientation of the indicatrix	= b = + 32° (1)	$x = b$ $Z\Lambda c$ = 37°	$x = b$ $Z\Lambda c$ = 37°

*For $(Zn_{2.44}Co_{0.}\ _{0.14})_{\Sigma=3}(AsO_4)_2\cdot 8H_2O$

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR KÖTTIGITE

I_{est}	d_{obs}	d_{calc}	hkl	I_{est}	d_{meas}	d_{calc}	hkl
70	7.87	7.95	110	15	2.078	2.079	350
100	6.66	6.70	020	30	1.956	1.956 1.954	510 $\bar{4}02$
20	4.93	4.94	200				
5	4.59	4.59	001	25	1.914	1.912	132
40	4.385	4.393	$\bar{1}11$	5	1.902	1.900	202
5	4.080	4.071	130	5	1.839		
1	3.983	3.978	220	15	1.689		
30	3.909	3.909	$\bar{2}01$	10	1.677		
15	3.652	3.656	111	10	1.662		
50	3.220	3.221	$\bar{1}31$	15	1.651		
20	3.195	3.200	310	1	1.623		
50	3.006	3.006	$\bar{3}11$	2	1.614		
90	2.994	2.995	201	10	1.601		
1	2.771	2.773	240	20	1.561		
60	2.734	2.734	221	10	1.544		
20	2.706	2.705	041	5	1.531		
30	2.651	2.652	330	2	1.516		
5	2.546	2.544	$\bar{2}41$	30	1.499		
50	2.462	2.460	$\bar{4}01$	1	1.484		
20	2.338	2.338	$\bar{1}12$	5	1.462		
25	2.325	2.325 2.322	$\bar{2}02$ $\bar{1}51$	5 2	1.450 1.423		
10	2.312	2.309	$\bar{4}21$	1	1.418		
1	2.235	2.234 2.233	060 241	1 1	1.391 1.361		
25	2.196	2.196	$\bar{2}22$	1	1.346		
15	2.089	2.090	112	5	1.264		
				1	1.219		
				5	1.188		

Guinier camera Cu$K\alpha$ radiation, intensities estimated visually.

TABLE 4. CHEMICAL COMPOSITION OF KÖTTIGITE FROM SCHNEEBERG, GERMANY

	1	2	3
ZnO	30.52	33.6	32.32
As_2O_5	[37.17]	39.5	37.42
NiO	2.00	1.78	1.70
CoO	6.91	5.39	5.12
H_2O	23.40	n.d.	23.44
	[100.00]		100.00
atomic ratio	Zn:Co:Ni = 2.28:0.56:0.16	Zn:Co:Ni = 2.44:0.42:0.14	Zn:Co:Ni = 2.44:0.42:0.14

1. Köttig (1849) in Palache *et al.* (1951).
2. This study; microprobe analysis by G. Springer.
3. Theoretical $(Zn_{2.44}Co_{0.42}Ni_{0.14})_{\Sigma=3}(AsO_4)_2\cdot 8H_2O$.

TABLE 5. ANGLE TABLE FOR PARASYMPLESITE

monoclinic, a=10.276 b=13.480 c=4.771Å β=105°01'

Form	measured ϕ	measured ρ	calculated ϕ	calculated ρ
b 010	359°40'	89°55'	0°00'	90°00'
a 100	89°10'	90°18'	90°00'	90°00'
m 110	54°19'	90°04'	53°38'	90°00'
w $\bar{2}01$	-90°30'	34°22'	-90°00'	34°44'
v $\bar{2}21$	-44°55'	44°12'	-44°24'	44°44'

TABLE 6. UNIT-CELL DIMENSIONS, OPTICAL AND PHYSICAL CONSTANTS FOR PARASYMPLESITE

	This study*		Ito *et al.* (1954) $Fe_3(AsO_4)_2 \cdot 8H_2O$
	Ojuela mine, Mexico		Kiuva, Japan
	single crystal	powder data	single crystal
a	10.30 (2)	10.276 (4)	10.25Å
b	13.45 (2)	13.480 (5)	13.48
c	4.78 (2)	4.771 (2)	4.71
β	104°45'(15')	105°01' (3')	103°50'
Space group	$C2/m$	-	$C2/m$
Z	2	2	2
Dmeas.	3.12 g/cm^3		3.07 g/cm^3
Dcalc.	3.13 g/cm^3		3.097 g/cm^3
Hardness	2-3		2
n_α	1.620 (2)		1.628
n_β	1.648 (1)		1.660
n_γ	1.685 (1)		1.705
Optic sign	positive		neg.?
$2V_z$ meas.	86° (1)		-
$2V_z$ calc.	85°		-
Dispersion	$r<v$		-
Pleochroism	weak		weak
	X pale blue		X bluish green
	Y colorless		Y yellowish
	Z colorless		Z brownish yellow
Absorption	$X>Y = Z$		-
Orientation of	$X = b$		$X = b$
the indicatrix	$Z \wedge c$ = + 29° (1)		$Z \wedge c$ = 31°20'

*For $(Fe_{1.68}Zn_{1.32})_{\Sigma=3}(AsO_4)_2 \cdot 8H_2O$

tions and optic axial angle were determined on the universal stage. Refractive indices were determined by the immersion method on crystals lying on (010) and (201) faces in sodium light. Pleochroism is weak, but was easily observed on most grains lying on (010). The absorption is greatest for vibration direction *Z*, as in erythrite. Optical data and some physical properties are listed in Table 2 together with data previously reported by Larsen (1921) and Wolfe (1940). The optical orientation is shown in Figure 1b.

X-ray crystallography

The X-ray powder diffraction pattern of köttigite is similar to those of the vivianite group. The computer program of Evans *et al.* (1963) was used to refine the unit-cell dimensions given in Table 2. The data from the powder diffraction pattern (Table 3) are in agreement with the space group $C2/m$ proposed by Wolfe (1940).

Chemical composition

Dr. G. Springer of the Metallurgical Laboratories, Falconbridge Nickel Mines Ltd., kindly agreed to do a microprobe analysis of the

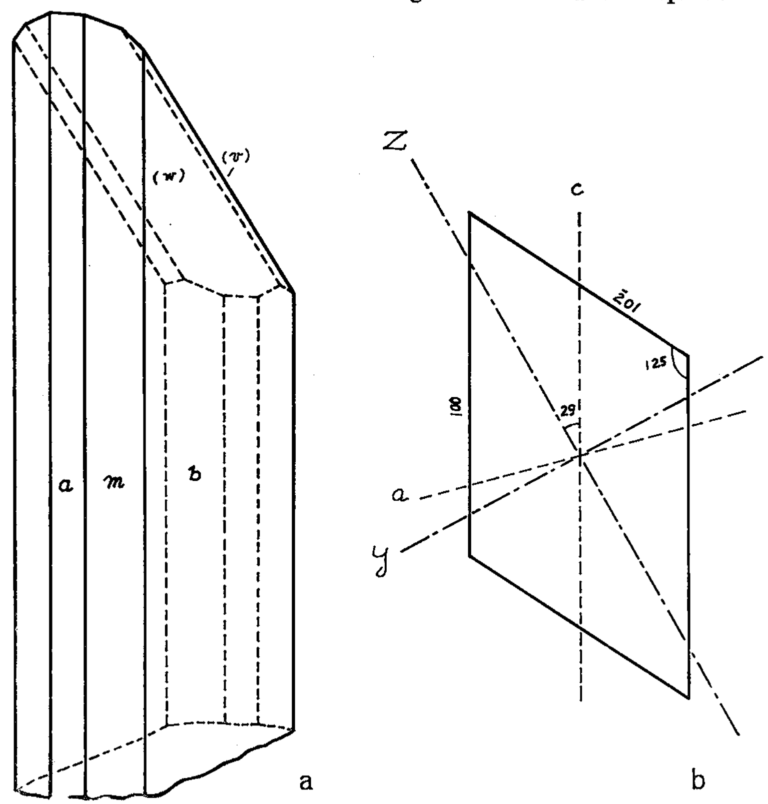

FIG. 2. (a) The common shape of parasymplesite crystals from Ojuela mine, Mexico; (b) the orientation of the optical and crystallographic elements for parasymplesite crystals lying on {010}.

Schneeberg köttigite. The result is compared in Table 4 to that given in Palache *et al.* (1951) and to the composition calculated for the same Zn:Ni:Co atomic ratio as determined with the microprobe.

PARASYMPLESITE

Radiating sprays of light blue crystals of parasymplesite up to 5x1x0.2 mm are present on altered rock from the Ojuela mine, Mapimi, Mexico (ROM specimen M 34013). A drawing of a typical crystal is shown in Figure 2a. Most parasymplesite crystals are elongate parallel to [001] and flattened on {010}. The following forms were observed with the optical goniometer on two crystals: {010}, {100}, {110}, {$\bar{2}$01} and {$\bar{2}$21}. Measured and calculated values of Φ and ρ for these forms are given in Table 5.

Physical and optical properties

The crystals are pale blue, with a very pale blue streak. The {010} cleavage is perfect, and crystals can be bent easily. Hardness is about 2-3. The density determined with a Berman microbalance is 3.12 g/cm³, which compares well with D_{calc}=3.13 g/cm³.

TABLE 7. X-RAY POWDER DIFFRACTION DATA FOR PARASYMPLESITE

Ojuela mine, Mexico*				Kiuva, Japan Ito *et al.* 1954		Ojuela mine, Mexico				Kiuva, Japan	
I_{est}	d_{obs}	d_{calc}	*hkl*	I_{est}	d_{obs}	I_{est}	d_{obs}	d_{calc}	*hkl*	I_{est}	d_{obs}
-	-	-	-	18	9.006	25	2.205	2.205	$\bar{2}22$	-	-
70	7.91	7.99	110	12	8.119			2.202	$\bar{1}51$	-	-
-	-	-	-	17	7.499	1	2.107	2.107	$\bar{1}32$	-	-
-	-	-	-	38	7.063	10	2.092	2.090	350	8	2.099
100	6.68	6.74	020	100	6.830	-	-	-	-	6	2.059
20	4.95	4.96	200	9	5.051	5	1.964	1.964	510	-	-
5	4.59	4.61	001	-	-	5	1.961	-	-	-	-
40	4.407	4.410	$\bar{1}11$	7	4.429	10	1.925	-	-	-	-
5	4.092	4.093	130	8	4.051	1	1.914	-	-	-	-
1	3.992	3.996	220	9	3.991	5	1.847	-	-	-	-
30	3.914	3.921	$\bar{2}01$	-	-	10	1.694	-	-	8	1.694
15	3.675	3.675	111	10	3.723					8	1.690
-	-	-	-	9	3.423					8	1.688
				10	3.395	5	1.673	-	-	-	-
50	3.237	3.237	$\bar{1}31$	10	3.250	5	1.662	-	-	-	-
20	3.218	3.213	310	-	-	1	1.627	-	-	-	-
-	-	-	-	10	3.177	1	1.620	-	-		
90	3.013	3.011	$\bar{2}01$	9	3.038	5	1.610	-	-		
		3.015	$\bar{3}11$	-	-	15	1.569	-	-		
-	-	-	-	11	2.845	10	1.549	-	-		
1	2.787	2.788	240	-	-	1	1.538	-	-		
50	2.749	2.749	221	-	-	5	1.521	-	-		
15	2.718	2.720	041	9	2.693	20	1.507	-	-		
25	2.664	2.664	330	-	-	1	1.491	-	-		
5	2.559	2.556	$\bar{2}41$	9	2.572	5	1.469	-	-		
40	2.469	2.468	$\bar{4}01$	7	2.496	5	1.455	-	-		
-	-	-	-	6	2.411	2	1.439	-	-		
10	2.349	2.348	$\bar{1}12$	-	-	1	1.422	-	-		
20	2.338	2.334	$\bar{1}51$	9	2.335	1	1.394	-	-		
		2.333	$\bar{2}02$	9	2.330	1	1.367	-	-		
10	2.317	2.317	$\bar{4}21$	6	2.306	1	1.352	-	-		
1	2.246	2.247	060	6	2.264	5	1.271	-	-		
		2.245	241	6	2.252						

* Guinier camera, CuKα radiation, intensities estimated visually.

TABLE 8. CHEMICAL COMPOSITION OF PARASYMPLESITE, OJUELA MINE, MEXICO

	microprobe	Ideal $(Fe_{1.68}Zn_{1.32})_{\Sigma=3}(AsO_4)_2 \cdot 8H_2O$
ZnO	16.86	17.84
FeO	18.98	20.55
As_2O_5	38.12	38.18
H_2O	n.d.	23.43
		100.00
atomic ratio	Fe:Zn = 1.68:1.32	Fe:Zn = 1.68:1.32

The optical properties are listed in Table 6 and are compared to those given by Ito *et al.* (1954). Indices of refraction were determined by the immersion method, and the orientation of the principal vibration directions (Figure 2b) and optic axial angle were determined on the universal stage. The crystals are pale blue to colorless under the microscope. Pleochroism is weak, with absorption being strongest for *X*.

X-ray crystallography

Powder diffraction data are given in Table 7. The pattern reported by Ito *et al.* (1954) has more lines because some are Cu$K\beta$ lines, and because some symplesite is present. All lines observed in this study are in agreement with powder data for other minerals of the vivianite group, except for differences in the intensities of the strong lines.

Refined unit-cell dimensions (Table 6) were calculated from the powder diffraction pattern with the computer program of Evans *et al.* (1963). Single-crystal study with Weisenberg and precession cameras gave the possible space groups *C*2, *Cm*, *C*2/*m*. Because the crystals bend easily, unit-cell values from the single-crystal study are inferior to those calculated from the powder pattern.

Chemical composition

D. R. Owens, Mineralogy Section, CANMET, Ottawa, kindly performed a microprobe analysis of parasymplesite (Table 8). The Zn/Fe ratio varies slightly from spot to spot over the surface of the crystals, indicating weak zoning. Ni Co, Sb or P were not detected.

It is impossible to calculate the exact formula from the microprobe analysis, since the water content was not determined. The values for ZnO and FeO probably represent the true Fe/Zn ratio in the crystals, and give an atomic ratio of 1.27 for Fe/Zn so that the formula may be written as $(Fe_{1.68}Zn_{1.33})_{\Sigma=3}(AsO_4)_2 \cdot 8H_2O$. The calculated chemical composition for a mineral with this Fe/Zn ratio is given in Table 8.

CONCLUSIONS

The new data for köttigite, determined on the analyzed crystals from Schneeberg, Germany, are in good agreement with the results obtained by Wolfe (1940) from Schneeberg material which he analyzed with a blow-pipe test. Small differences are probably attributable to minor variations in chemical composition. Larsen (1921) obtained optical properties for köttigite on material which was not analyzed, and it may be speculated that his data were determined on some other mineral.

The blue crystals from the Ojuela mine, Mexico, are intermediate members in the parasymplesite-köttigite series. For the crystals on the Royal Ontario Museum specimen, the ratio between Fe and Zn varies slightly, but is clearly on the parasymplesite side of the series.

There are small but distinct differences in the refractive indices and unit-cell dimensions among köttigite from Germany, parasymplesite from Japan, and parasymplesite from Mexico. The differences do not seem to be linearly related to changes in chemical composition. Intermediate members of the series should be examined to establish the relationships among chemical composition, optics, and crystallography.

Acknowledgements

The author would like to thank Dr. G. Springer for the microprobe analysis of the köttigite, and D. R. Owens for the microprobe analysis of parasymplesite. Mrs. Cynthia Peat prepared films with the Guinier camera, and Miss Helen Driver typed the manuscript. Special thanks are due to Dr. J. A. Mandarino for his help in the preparation of this manuscript.

References

Evans, H. T. jr., Appleman, D. E. & Handwerker, D. S. (1963): The least-squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method. *Program Abst. Amer. Cryst. Assoc. Ann. Meet.*, Cambridge, Mass., 42-43.

Palache, C., Berman, H. & Frondel, C. (1951): The System of Mineralogy 2, 7th ed., John Wiley & Sons, New York.

Ito, T., Minato, H. & Sakurai, K. (1954): Parasymplesite, a new mineral polymorphous with symplesite. *Proc. Jap. Acad.* **30**, 318-324.

Larsen, E. S. (1921): Microscopic determination of the nonopaque minerals. *U. S. Geol. Surv. Bull.* **679**.

Wolfe, C. W. (1970): Classification of the minerals of the type $A_3(XO_4)_2 \cdot nH_2O$. *Amer. Mineral.* **40**, 787-809.

Manuscript received April 1976, emended June 1976.