THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 52 NOVEMBER–DECEMBER, 1967 Nos. 11 and 12

SWITZERITE, $(Mn, Fe)_3(PO_4)_2 \cdot 4H_2O$, A NEW MINERAL

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ABSTRACT

The new mineral switzerite $(Mn_{2.23}, Fe_{0.77})(PO_4)_2 \cdot 4H_2O$, has been found at the Foote Mineral Company Spodumene Mine, Kings Mountain, North Carolina. Switzerite occurs with vivianite in seams in spodumene-rich pegmatite.

Switzerite is pale pink or light golden-brown when fresh, but it is commonly oxidized to various shades of brown. It occurs in bladed crystals or micaceous masses, flattened on {100}. Observed forms include $a\{100\}$, $x\{210\}$, $y\{410\}$, $n\{101\}$, $e\{\bar{1}01\}$, $p\{111\}$, $q\{\bar{1}11\}$. Cleavage is perfect {100} and fair {010}. Switzerite is monoclinic, $P2/a$, $a=17.099$, $b=12.694$, $c=8.282$ Å, $\beta=95°\ 55'$, $Z=8$. Strongest X-ray powder lines are 8.550 (100) (002), 7.128 (40) (012, 110), 6.775 (40) ($\bar{1}11$), 6.346 (30) (020), 3.173 (40) (040), 2.934 (40) ($\bar{1}41$), 2.842 (40) (223), 2.763 (40) (142), 2.585 (60) (143, $\bar{1}35$), 2.371 (20) (242). Optically, switzerite is negative, α(calc) = 1.602, $\beta=1.628$, $\gamma=1.632$, $2V=42°$, $Y=b$, $Z\wedge c=10\frac{1}{2}°$.

Chemical analysis, in weight percent: MnO 36.15, FeO 9.30, Fe_2O_3 3.82, P_2O_5 32.49, H_2O^+17.70, total 99.46. Semi-quantitative spectrographic analysis shows no other element present in amount greater than 0.2%.

The name is for George Switzer, Chairman of the Department of Mineral Sciences, Museum of Natural History, Smithsonian Institution.

INTRODUCTION

Early in 1966 Dr. K. C. Brannock of Kingsport, Tennessee, sent the authors an unknown brown, micaceous mineral from the Foote Spodumene mine at King's Mountain, North Carolina. We collected additional specimens on a field trip to Kings Mountain in June, 1966. X-ray examination revealed that it is a new species, and wet chemical analysis established the probable formula $(Mn,Fe)_3(PO_4)_2 \cdot 4H_2O$.

The name switzerite is proposed for the mineral in honor of George Switzer, Chairman, Department of Mineral Sciences, Museum of Natural History, Smithsonian Institution. The description and name were approved in advance of publication by the Commission on New Minerals and Mineral Names, IMA.

The geology of the Foote mine has been described by Kesler (1961). The local rocks are thin-layered amphibolite and muscovite gneiss and schist, striking roughly NE. The mine, a large open pit, is developed in a

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swarm of pegmatites, which are up to 200′ thick and more than 1000′ long, and which strike roughly parallel to the enclosing country rock and dip steeply east and west. Drilling indicates that many of the bodies are complexly joined at depth. The pegmatites are of uniform composition and texture and contain roughly 32% quartz, 41% feldspars (sodic plagioclase and microcline), 20% spodumene, 6% muscovite, and 1% other minerals.

Numerous fractures and seams cut the pegmatites; many contain quartz and albite crystal druses. Other minerals, including apatite, vivianite, fairfieldite, pyrite, rhodochrosite-siderite, and laumontite are present locally. The minerals of the seams are typical of those formed under hydrothermal conditions. The mineralization of the seams probably took place during the last stages of crystallization of the pegmatite, with manganese, phosphorous, and other elements derived from the pegmatite fluids. Fractures and seams in the country rock do not contain the unusual minerals found in the pegmatites.

Switzerite is found as flat rosettes, as small micaceous masses, and as rare bladed crystals in some of the seams. It is usually associated, and sometimes intergrown, with vivianite. Both switzerite and vivianite are abundant at the Foote mine as very thin films coating fractures. Quartz and albite crystals may be present; the phosphates are later than these species. Veins containing switzerite were observed in place only in a large pegmatite exposed on the east side of the pit. Most of the specimens were collected on the mine dumps or acquired from local collectors.

Physical Properties

Fresh switzerite is pale pink or light golden brown in color, but specimens are commonly oxidized and medium brown to chocolate brown. Fresh specimens are very rare. The mineral occurs in micaceous flakes or bladed crystals, up to 3 mm long, flattened on {100} and elongated [001]. The cleavage is perfect {100} and fair {010}. Crystals are somewhat flexible. Luster is pearly to adamantine on the cleavage. Hardness is about $2\frac{1}{2}$. Specific gravity measured by suspension in heavy liquids is 2.95. This value must be considered a minimum, because even small flakes contain minute lenticular cavities, possibly air-filled, between the cleavages. The calculated specific gravity, assuming $4H_2O$ in the formula, is 3.18.

The indices of refraction of fresh switzerite measured in Na light, are α(calc) = 1.602, $\beta = 1.628$, $\gamma = 1.632$, ($\pm .002$), $2V(-) = 42°$, $Y = b$, $Z \wedge c = 10\frac{1}{2}°$. Optic angle and orientation were measured on the universal stage. Cleavage flakes give slightly off-center acute bisectrix figures. Because of the thinness of the crystal blades, α could be measured only ap-

proximately on the spindle stage, and the value given is that calculated from the optic angle and the other two indices. Dispersion is $r<v$, slight. Indices of refraction, pleochroism, and dispersion increase with oxidation. The material analysed for ferrous iron, with about $\frac{1}{4}$ of the total iron trivalent, had $\beta=1.637$, $\gamma=1.641$. Dark chocolate brown material gave $\beta=1.666$, $\gamma=1.670$, pleochroism light to dark red-brown, $r<v$, distinct.

X-ray Study

X-ray precession photographs were made of the 0, 1st, and 2nd levels about all three crystallographic axes of switzerite, using Mo/Zr radiation. These showed that the mineral is monoclinic prismatic, with space group $P2/a$. X-ray diffraction data (Table 1) obtained with Fe/Mn radiation and a 114.59 mm camera and corrected for film shrinkage, were indexed and refined, using a least-squares computer program designed by Evans *et al.* (1963) to yield the unit-cell dimensions. The initial parameters were taken from the precession photographs. The refined cell dimensions are $a=17.099$ Å, $b=12.694$ Å, $c=8.282$ Å, with a standard error of 0.073 Å $\beta=95°\ 55_z$, $a_0:b_0:c_0=1.3470:1:.6524$, cell volume 1788 Å^3.

The fresh pink and oxidized brown varieties give identical powder patterns, with some decrease in the clarity of the pattern with increasing oxidation.

Crystallography

Although euhedrons of switzerite were found on several specimens, measurements of the crystal morphology was very difficult. Most crystals are somewhat bent and are further distorted on being removed from the matrix. Consequently, prism faces tend to give trains of reflections. In addition, terminal faces are frequently undulose. However, the morphology is fairly simple, and with the information derived from X-ray investigations, it proved possible to assign unambiguous indices to the several forms.

Five crystals were measured in detail, and several others examined more briefly. The dominant form on all crystals studied is a $\{100\}$, and x $\{210\}$ is usually well developed. The forms $y\{410\}$, $n\{101\}$, $e\{\bar{1}01\}$, and $p\{111\}$ are generally present on well developed crystals; $q\{\bar{1}11\}$ is somewhat less common.

Figure 1 shows the typical habit of switzerite. Table 2 gives the morphological constants calculated from the X-ray unit-cell data.

Chemistry and Formula

Semiquantitative spectrographic analysis showed that switzerite contains only Mn, Fe, and P in amounts greater than 0.2 percent (Table 3). A sample of switzerite was analyzed

TABLE 1. SWITZERITE—X-RAY POWDER DATA

I_{rel}	d_{obs}	d_{calc}	hkl
100	8.550	8.5039	002
40	7.128	7.0651	012
		6.9104	110
40	6.775	6.6045	$\bar{1}11$
30	6.346	6.3471	020
< 5	5.031	5.0279	120
< 5	4.857	4.9036	$\bar{1}21$
10	4.253	4.2520	004
5	3.950	3.9479	$\bar{1}04$
< 5	3.864	3.8668	$\bar{2}02$
10	3.625	3.6290	104
< 5	3.277	3.2857	015
40	3.173	3.1736	040
< 5	3.035	3.0333	$\bar{2}14$
40	2.934	2.9360	$\bar{1}41$
40	2.842	2.8432	223
40	2.763	2.7650	142
60	2.585	2.5858	143
		2.5850	$\bar{1}35$
10	2.484	2.4885	312
		2.4812	$\bar{3}22$
20	2.371	2.3706	242
< 5	2.125	2.1260	008
		2.1244	$\bar{2}36$
		2.1234	$\bar{3}25$
< 5	2.107	2.1070	037
		2.1067	244
		2.1041	226
5	2.034	2.0346	055
		2.0329	410
		2.0283	161
< 5	1.635	1.5354	363
		1.6343	$\bar{3}38$
< 5	1.603	1.6038	$\bar{4}27$
		1.6031	$\bar{2}66$
		1.6030	308
< 5	1.564	1.5666	435
		1.5619	$\bar{4}08$
< 5	1.521	1.5232	1310
		1.5231	$\bar{2}310$
		1.5230	$\bar{2}67$
		1.5211	347
		1.5192	$\bar{5}33$
< 5	1.476	1.4767	319
		1.4762	258
		1.4758	460

FeKα radiation, camera diameter = 114.59 mm. Relative intensity measured from Siemens Recording Photometer trace.

for these elements and for water, using classical wet analytical methods, by Joseph Nelen, U. S. National Museum. Iron and manganese were determined on a sample of approximately 26 mg. Iron was reduced with Ag and titrated with potassium dichromate yielding total iron equal to 9.98 weight percent. Manganese was determined spectrophotometrically after periodate oxidation, with repeat, giving total manganese equal to 28.0 weight percent.

Iron was also determined gravimetrically as Fe_2O_3 using a 50 mg sample. This procedure gave total iron equal to 9.78 and the average of the two different determinations, 9.88 weight percent, is the value used for total iron. Phosphorus was determined gravimetrically

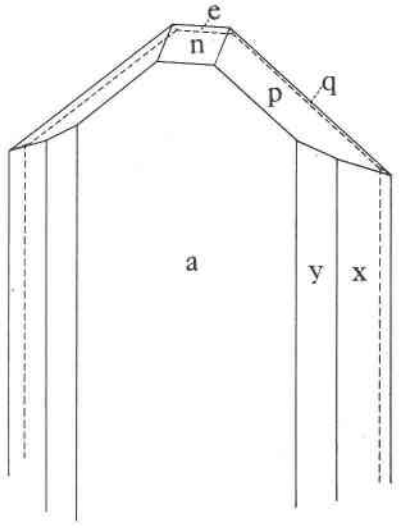

FIG. 1. Crystal habit of switzerite, Foote Spodumene Mine, King's Mountain, North Carolina.

as phosphomolybdate from a 25 mg sample. Repeats gave 14.15 and 14.22 weight percent, and 14.18 weight percent was taken as the average.

At this time another sample of the mineral was sent us by Mr. Jack Eaker, a collector in King's Mountain. The switzerite, in bladed crystals intergrown with Vivianite, was of a lighter color and had considerably lower indices of refraction ($\beta = 1.637$) than the analyzed material. Microprobe analysis of this new material and the material previously wet-analyzed showed that the amounts of Mn, Fe and P were identical in both. Divalent iron was determined on a sample of 25 mg of this material according to the technique of Reichen and Fahey (1962). Total water was determined by the Penfield method on a sample of 57 mg which gave 17.70 weight percent H_2O. (The first material gave H_2O^+13.02 weight percent by Penfield method.) No fluorine was detected.

Table 3 summarizes the analytical results. The difference between total iron of the first analysis and ferrous iron of the second is listed as Fe_2O_3. The sum, 99.46 percent, is satisfactory.

Shortly after the completion of the analysis, we received another specimen of switzerite from Mrs. F. O. Drummond of Kannapolis, North Carolina. This material is flesh-pink in color, and has $\beta = 1.628$, $\gamma = 1.632$, about 0.008 lower than the material analysed for ferric iron. Ferric iron is included with manganese and ferrous iron in calculating molecular proportions. The molecular ratio of total manganese plus iron to phosphorus is precisely 3:2, indicating a formula of the sort $(Mn, Fe)_3(PO_4)_2$

TABLE 2. SWITZERITE—MORPHOLOGICAL DATA FROM UNIT-CELL CONSTANTS
$a:b:c: = 1.3470:1:0.6524$ $\beta = 95°55'$ $p_0:q_0:r_0 = 0.4817:0.6490:1$
$r_2:p_2:q_2 = 1.540:0.7382:1$ $\mu = 84°05'$ $p_0'0.4843$, $q_0'0.6525$, $x_0'0.1036$

Forms:	ϕ	ρ	ϕ_2	ρ_2-B	C	A
*c 001	90°00′	5°55′	84°05′	90°00′	—	84°05′
a 100	90 00	90 00	0 00	90 00	84°05′	—
x 210	56 02	90 00	0 00	56 02	85 06	33 58
y 410	71 23	90 00	0 00	71 23	84 23	18 37
n 101	90 00	26 53	63 07	90 00	20 58	63 07
e $\bar{1}01$	−90 00	24 39	114 39	90 00	30 34	114 39
p 111	36 44	46 52	57 27	54 12	43 32	64 07
q $\bar{1}11$	−36 27	42 53	118 53	56 49	46 12	113 51

* Not observed.

$\cdot XH_2O$, analogous to vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$ and ludlamite, $(Fe, Mg, Mn)_3(PO_4)_2 \cdot 4H_2O$.

The amount of water in the formula is somewhat uncertain. Several percent at least of the 17.70 percent total water is H_2O^-, lost below 100°C; the somewhat oxidized first material gave $H_2O^+ = 13.02$ percent, as noted above. The amount of H_2O^- that is structurally bound cannot be determined from analysis alone. In vivianite half or more of the structural water may be lost below 100°C (Palache, Berman, and Frondel, 1951, p. 744). Many of the iron-manganese phosphate hydrates undergo a concomitant conversion of H_2O to $OH^- + \frac{1}{2}$ H_2 gas during the oxidation of iron from ferrous to ferric. The sample of switzerite analysed for H_2O^+ darkened in color on drying at 100°C, indicating that some of the iron in the structure was oxidized at this temperature. If the oxidation of this iron is balanced by the loss of hydrogen from the structure, then a considerable amount of the H_2O^- may be structural.

The formula calculated from total H_2O contains 4.29 H_2O per 2 P;

this approximates $(Mn, Fe)_{12}(PO_4)_8 \cdot 17H_2O$. However, the much simpler formula $(Mn, Fe)_3(PO_4)_2 \cdot 4H_2O$, with $Z=8$, is preferable in the absence of other data. This is taken as the most probable formula, but it is open to two objections. The calculated gravity, 3.18, is significantly higher than the measured, 2.95, the difficulties in measurement noted under Physical Properties not withstanding. In addition, the Gladstone-Dale law (Larson and Berman, 1934) is not well obeyed; there is more than 10 percent

TABLE 3. CHEMICAL ANALYSIS OF SWITZERITE

	1	2		3
MnO	36.15	26.34	Mn	2.23
FeO	9.30	9.35	Fe	0.56
Fe_2O_3	3.84	3.84	Fe	0.21
P_2O_5	32.49	32.67	P	2.00
H_2O^+	17.70	17.80	H_2O	4.29
	99.46	100.00		
*Si	0.2			
Ca	.15			
Mg	.02			
Cu	.005			
Ni	.005			
Al	.001			
Mo	.001			
Co	.001			
Ba	.0003			
Be	.0001			

1. Oxide percentages 2. Recalculated to 100% 3. Molecules, based on 2P Joseph Nelen, U.S.N.M. analyst.

* Semiquantitative spectroscopic analysis by Joseph L. Harris, U.S.G.S.

discrepancy between the specific refractive energies calculated from the indices of refraction of fresh switzerite and the calculated specific gravity, and that calculated from the formula (Table 4). If the formula $(Mn, Fe)_3(PO_4)_2 \cdot 3H_2O$ is used for switzerite, agreement between measured and calculated specific gravity is much improved, as is internal agreement of the Gladstone-Dale equation (Table 4). However, this formula requires only 13.18 percent H_2O, close to the 13.02 H_2O^+ determined on the first analysed sample, implying that 4.52 percent non-chemical water was found in the analysis. For this reason the formula with $3H_2O$ is tentatively rejected.

Finally, if oxidized iron in the structure is compensated for by reduc-

TABLE 4. CALCULATED SPECIFIC GRAVITIES, d, AND SPECIFIC REFRACTIVE ENERGIES, k, FOR VARIOUS POSSIBLE FORMULAS OF SWITZERITE, $(Mn_{2.23}\ Fe_{.77})(PO_4)_2 \cdot XH_2O$. MEASURED DENSITY = 2.95

X	d	k from d and refractive indices	k from formula
3	3.04	0.204	0.210
4	3.18	0.195	0.215
4.5	3.24	0.192	0.218

tion of water to OH^- with splitting off of hydrogen, the amount of water found in the slightly oxidized sample would be less than the amount expected in completely fresh material. If a number of molecules of hydrogen equal to ferric iron (0.21) is added to water, it brings water to 4.4 H_2O per 2 P or nearly 9 H_2O per 4P. This would suggest the formula $(Mn, Fe)_6(PO_4)_4 \cdot 9H_2O$, with $Z = 4$. However, then the fit between measured and calculated specific gravities, and the internal agreement of the Gladstone-Dale formula become very poor (Table 4).

Structural studies may be necessary to determine the exact amount of water in switzerite.

ACKNOWLEDGMENTS

Mary Mrose, U. S. Geological Survey, Washington, confirmed the unit cell and space group data, and provided helpful advice. Daniel Appleman, U. S. Geological Survey, Washington, ran the computer program for the indexing of the diffraction data and the refinement of the unit cell parameters. Their assistance is gratefully acknowledged. The bulk of this study was made while the senior author was a NAS-NRC post-doctoral research associate at the Smithsonian Institution.

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Manuscript received March 31, 1967; accepted for publication July 26, 1967.