American Mineralogist, Volume 71, pages 1221–1223, 1986

Switzerite redefined as $Mn_3(PO_4)_2 \cdot 7H_2O$, and metaswitzerite, $Mn_3(PO_4)_2 \cdot 4H_2O$

JOHN S. WHITE, JR.
Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.
PETER B. LEAVENS
Department of Geology, University of Delaware, Newark, Delaware 19711, U.S.A.
PIER F. ZANAZZI
Dipartimento di Scienze della Terra, Università di Perugia, 06100 Perugia, Italy

ABSTRACT

Switzerite, previously defined as $Mn_3(PO_4)_2 \cdot 4H_2O$, is the dehydration product of $Mn_3(PO_4)_2 \cdot 7H_2O$, which is unstable in air. We have proposed that switzerite be redefined as the heptahydrate, and that the tetrahydrate be renamed metaswitzerite. This proposal has been accepted by the New Mineral Names Commission, IMA.

Averages of six microprobe analyses of metaswitzerite gave MnO, 46.05; FeO, 3.60; P_2O_5, 32.94 (all weight percent), with trace amounts of Si, Ca, Mg, and Al. The empirical formula of switzerite is $(Mn_{0.93}Fe_{0.07})_3(PO_4)_2 \cdot 7H_2O$.

The strongest X-ray powder-diffraction lines in ångströms, with intensities and indices, are 11.12(100)(001), 3.37(90)($\bar{1}23$), 6.81(60)($\bar{1}11$,110), 5.08(60)($\bar{1}21$,120), 8.47(50)(011), 2.137(50)(402). Similar data are reported for synthetic $Mn_3(PO_4)_2 \cdot 6H_2O$ (JCPDS 3-0020); the synthetic phase is probably really the heptahydrate. Refinement of the powder data gives a 8.545(2), b 13.164(3), c 11.878(4) Å, β 110.12(3)°, Z = 4. The space group is $P2_1/a$ from single-crystal X-ray study.

Switzerite is transparent to translucent, pink in color, with a vitreous to pearly luster. Crystals are thin tabular on {001} and the cleavage is perfect on {001}. $D_{meas} = 2.535$; $D_{calc} = 2.545$. Switzerite is soft and brittle, unstable in air, and alters irreversibly to metaswitzerite in minutes. Optically, it is biaxial (−), $2V_{meas} = 70°$; $2V_{calc} = 66°$; α 1.560, β 1.574, γ 1.580, (all ±0.001), $Z = \mathbf{b}$, $X \perp (001)$.

Switzerite occurs in the lower levels of the Foote Mineral Company spodumene mine near Kings Mountain, North Carolina, in fissures in quartz–alkali feldspar–spodumene pegmatite. It is found only in freshly exposed rock, but metaswitzerite is widespread throughout the quarry.

INTRODUCTION

"Switzerite" was originally described by Leavens and White (1967). The formula determined was $Mn_3(PO_4)_2 \cdot 4H_2O$. The crystal structure was determined by Fanfani and Zanazzi (1979), who confirmed the formula.

Leavens and White (1967) noted that "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." They stated that the fresh pink and oxidized brown varieties gave identical X-ray powder-diffraction patterns. Subsequently, one of the authors (J.S.W.) collected pale-pink crystals of switzerite in a water-filled pocket and preserved them in the pocket water. X-ray examination of these crystals showed them to be a distinct species, with an X-ray powder pattern substantially different from that of switzerite. Crystal-structure analysis (Zanazzi et al., 1986) showed this species to be the heptahydrate; it dehydrates irreversibly to the tetrahydrate after a few minutes' exposure to the air. We have proposed that switzerite be redefined as the heptahydrate, and that the tetrahydrate, originally called switzerite, be renamed metaswitzerite. This proposal has been accepted by the Commission on New Minerals and Mineral Names, IMA.

Switzerite occurs in fissures in quartz–alkali feldspar–spodumene pegmatite in the lower levels of Foote Mineral Company spodumene mine near Kings Mountain, North Carolina. Its instability necessitates that it be wet, or at least damp, in order to persist, so it is limited in occurrence to freshly exposed rock. Metaswitzerite is widespread throughout the quarry. More details of the occurrence are provided in Leavens and White (1967).

Switzerite is named for George Switzer, retired chairman of the Department of Mineral Sciences, Smithsonian Institution. The name metaswitzerite was chosen to emphasize the close chemical and structural relationship between the two minerals. Type material of both is preserved at the Smithsonian Institution as switzerite (NMNH 120871) and metaswitzerite (NMNH 120230).

0003–004X/86/0910–1221$02.00

Table 1. X-ray powder-diffraction data for switzerite

I/I_0	d_{obs}	d_{calc}	*hkl*	I/I_0	d_{obs}	d_{calc}	*hkl*
100	11.12	11.153	001			2.352	243
						2.353	203
50	8.47	8.510	011	40	2.353	2.353	114
						2.349	234
		6.796	111			2.353	034
		6.851	110				
				50	2.137	2.136	402
		5.066	121				
		5.088	120	25	1.914	1.914	243
90	3.37	3.373	123			1.847	045
						1.847	411
30	2.94	2.943	232				
				5	1.678	1.678	073
15	2.82	2.828	202				
						1.614	364
		2.697	231	30	1.612	1.611	181
		2.707	124			1.612	180
		2.598	222	5	1.580	1.580	182
		2.601	321				
				15	1.504		—
		2.562	224				
15	2.57	2.562	051	14	1.462		—
		2.568	024				
				20	1.413		—
		2.454	323				
		2.459	134	5	1.353		—
				5	1.184		—

Note: Ni-filtered Cu*Kα* radiation (λ = 1.5418 Å), 114.59-mm-diameter Gandolfi camera. Intensities estimated visually. Diffraction maxima were indexed taking into account intensities measured from single crystals.

Table 2. X-ray powder-diffraction data for synthetic Mn phosphate and for metaswitzerite

d*	I/I_0*	d**	I/I_0**
8.30	32	8.55	100
7.00	48	7.128	40
		6.775	40
6.00	40	6.346	30
3.35	100	3.173	40
3.01	80	2.934	40
		2.842	40
		2.763	40
2.60	100	2.585	60

* Synthetic manganese phosphate tri-hydrate (JCPDS card 3-0426).

** Metaswitzerite (Leavens and White, 1967).

CHEMISTRY

Six chemical analyses were made on fragments of switzerite (NMNH 120871), which dehydrated to metaswitzerite during sample preparation. Analyses were performed using an ARL-SEMQ electron microprobe with an operating voltage of 15 kV, a beam current of 0.15 μA, and a beam diameter of 1–2 μm. The data were corrected using Bence-Albee factors; standards were Durango apatite (NMNH 104021) for P, manganite (NMNH 80387) for Mn, Kakanui hornblende (NMNH 143965) for all other elements. Spectroscopic analysis showed no other elements to be present in significant amounts besides those determined with the microprobe.

The analytical results are (ranges and averages, in weight percent): MnO 43.8–47.8, 46.05; FeO 2.8–4.8, 3.60; MgO 0.07–0.19, 0.15; CaO 0.14–0.24, 0.20; Al_2O_3 0.15–0.57, 0.27; SiO_2 0.00–0.11, 0.06; P_2O_5 32.4–33.5, 32.94; average total 83.27. The average empirical formula for switzerite, discounting the trace amounts of Si, Al, Mg, and Ca, and correcting for water loss, is $(Mn_{0.93}Fe_{0.07})_3(PO_4)_2 \cdot 7H_2O$. The water content of $7H_2O$ was determined through crystal-structure analysis, reported in the accompanying paper (Zanazzi et al., 1986).

X-RAY DIFFRACTION STUDY

A small quantity of switzerite, from the sample chemically analyzed, was ground under water to produce a suspension of minute grains. This suspension was sealed in a Lindemann capillary, and powder photographs were obtained using a Gandolfi camera, 114.59-mm diameter, with Cu*Kα* radiation (Ni filter). The diffraction data are listed in Table 1. The reflections were indexed using the single-crystal intensities as a guide. A least-squares refinement of the powder data yielded the following lattice parameters: $a = 8.545(2)$ Å, $b = 13.164(3)$ Å, $c = 11.878(4)$ Å, and $\beta = 110.12(3)°$. The X-ray powder-diffraction pattern for switzerite is very similar to that reported on JCPDS card 3-0020 for synthetic $Mn_3(PO_4)_2 \cdot 6H_2O$; this compound is most probably synthetic switzerite and thus the heptahydrate, as shown below.

Single-crystal study (Zanazzi et al., 1986) shows that switzerite is monoclinic. Systematic absences uniquely determine the space group as $P2_1/a$. Least-squares refinement of 25 reflections gave lattice parameters $a = 8.528(4)$ Å, $b = 13.166(5)$ Å, $c = 11.812(4)$ Å, $\beta = 110.05(3)°$, in good agreement with the parameters from the powder data.

An anomaly was discovered when we compared the diffraction patterns of switzerite and metaswitzerite with those of the Dow Chemical Company's synthetic "hexahydrate" (JCPDS card 3-0020) and tri-hydrate (JCPDS card 3-0426). In order to make direct comparisons of the patterns, samples of the "hexahydrate" were obtained from Dow. Switzerite and this synthetic phase gave virtually identical diffraction patterns. When the synthetic phase was heated slightly, a partially dehydrated phase was produced, which gave the tri-hydrate pattern Dow reported on JCPDS card 3-0426. This pattern does not, however, match that of metaswitzerite; in fact there is practically no similarity between the two. Most of the major lines of the two patterns are shown in Table 2. Thus, while the synthetic "hexahydrate" appears to be identical with switzerite, it does not become metaswitzerite upon partial dehydration. As switzerite differs from the synthetic hexahydrate only in that it contains several percent of Fe^{2+} and metaswitzerite contains both Fe^{2+} and Fe^{3+} (Leavens and White, 1967), it may be that oxidation of some of the Fe during dehydration is responsible for these quite different phases. If a synthetic hexahydrate could be grown with a Mn^{2+}/Fe^{2+} ratio of about 3:1, then it is possible that it would become metaswitzerite upon partial dehydration.

MORPHOLOGY

Switzerite occurs exclusively in crystals, which are tabular on {001} or bladed and elongated on {100}. The largest crystals observed are less than 5 mm in maximum dimension. The morphology of switzerite was described by Leavens and White (1967). Their measurements of the angles of crystal faces were of poor quality because, as they noted, "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." They assigned Miller indices with the aid of information derived from the single-crystal study of metaswitzerite, since they did not then recognize that the crystals they studied were actually dehydration pseudomorphs of metaswitzerite after switzerite.

In their work on switzerite—now metaswitzerite—Fanfani and Zanazzi (1979) interchanged the *a* and *c* axes of metaswitzerite in their description of its crystal structure. In the present orientation, *c* of switzerite is almost exactly ⅔ *c* of metaswitzerite; *a* and *b* are the same, but β differs by 14°. The simplest transformation of the indices of Leavens and White (1967) into the new orientation, taking into account the actual *c* of switzerite, is 003/030/200. This transformation gives rise to somewhat cumbersome Miller indices; the common prism {210} becomes {034}, for example. However, the original morphological measurements of Leavens and White (1967) were not reported because of their poor quality, and a new study, hampered by the rapid dehydration and easy deformability of switzerite crystals, would be necessary before a different indexing could be proposed.

PHYSICAL PROPERITES

Switzerite crystals are transparent to translucent and pale pink in color. Cleavage is perfect and micaceous on {001}. Crystals are soft and somewhat flexible. The specific gravity is 2.535 (measured) and 2.545 (calculated). The luster is pearly on (001), but otherwise vitreous. Switzerite is not stable in air and will in minutes alter irreversibly to metaswitzerite. The alteration may be violent, the crystals bursting into fragments when exposed to the light and heat of the sun.

Optically, switzerite is biaxial negative, $2V_{\text{meas}} = 70°$; $2V_{\text{calc}} = 66°$. The refractive indices are $\alpha = 1.560$, $\beta = 1.574$, $\gamma = 1.580$, all ± 0.001, $Z = b$, $X \perp (001)$. Indices were measured in Na light using a spindle stage; indices of the immersion oils were measured on an Abbe refractometer.

REFERENCES

Fanfani, L., and Zanazzi, P.F. (1979) Switzerite: Its chemical formula and crystal structure. Tschermaks Mineralogische und Petrographische Mitteilungen, 26, 255–269.

Leavens, P.B., and White, J.S., Jr. (1967) Switzerite, $(Mn,Fe)_3(PO_4)_2 \cdot 4H_2O$, a new mineral. American Mineralogist, 52, 1595–1602.

Zanazzi, P.F., Leavens, P.B., and White, J.S., Jr. (1986) The crystal structure of switzerite, $Mn_3(PO_4)_2 \cdot 7H_2O$, and its relationship to metaswitzerite, $Mn_3(PO_4)_2 \cdot 4H_2O$. American Mineralogist, 71, p. 1224–1228.

MANUSCRIPT RECEIVED MAY 2, 1985
MANUSCRIPT ACCEPTED MAY 16, 1986