American Mineralogist, Volume 74, pages 1374–1376, 1989

Wiserite, an occurrence at the Kombat mine in Namibia, and new data

Pete J. Dunn
Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.
Carl A. Francis
Harvard Mineralogical Museum, 24 Oxford Street, Cambridge, Massachusetts 02138, U.S.A.
Robert A. Ramik
Department of Mineralogy, Royal Ontario Museum, Toronto, Ontario M5S 2C6, Canada
Joseph A. Nelen
Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.
John Innes
182 Bielby Road, Kenmore Hills, Brisbane, Queensland, Australia

Abstract

Wiserite, a very rare manganese borate, has been found at the Kombat mine, Namibia, associated with hausmannite, alleghanyite, and pyrobelonite on the hanging-wall side of a 2-m-thick lens of manganese oxide ore. Its formula, derived in part from a crystal-structure analysis by Pertlik and Dunn (1989), is $\{Mn_{14}(B_2O_5)_4(OH)_8\}\{[Si_{1-x}Mg_x][O_{1-x}(OH)_x]_4Cl_{2x}\}$. Wiserite occurs as pinkish brown prismatic crystals up to 1 cm in length. Optically it is uniaxial, negative, with $\omega = 1.751$ and $\epsilon = 1.700$ (both ± 0.003). Its density is 3.54 g/cm^3 (meas.) and 3.57 g/cm^3 (calc.). Wiserite is tetragonal, *P*4/*n*, with $a = 20.192(6)$ and $c = 3.281(2)$ Å, Z = 2.

Introduction

Wiserite is a mineral with a confused history. It was first named by Haidinger (1845) for David Friedrich Wiser (1802–1878), a Swiss mineralogist who had first analyzed it some years before. It was considered by Kenngott (1866) to be a mixture, consisting principally of pyrochroite. Epprecht (1946a, 1946b) found it to be a distinct species with a characteristic X-ray power-diffraction pattern, but the analytical data given were those of a mixture. Epprecht et al. (1959) re-examined wiserite, defined its crystallography, and established the mineral as a manganese borate hydroxide. These studies were all of an impure, fibrous to semiplaty specimen from Gonzen, Switzerland, which was admixed with other phases, chiefly pyrochroite and rhodochrosite. Wiserite was reported from 17 localities in Japan by Kato and Matsubara (1980), but was not chemically analyzed; one specimen, from the Yaei mine, Tsuchiyama, Shiga, Japan, was obtained through the courtesy of Dr. Akira Kato and was analyzed in this study. In spite of the previous studies and the proposal of Gorbov (1973) to regard it as $Mn_3[(OH,Cl)_3(BO_3)]$, the Mn analogue of fluoborite, wiserite has remained a poorly characterized mineral.

Recently, one of the authors (J.I.) obtained excellent crystals of wiserite from the Kombat mine in Namibia, where it occurs with hausmannite and alleghanyite in an assemblage described below. A detailed investigation of this material confirmed that it is indeed wiserite by comparison with type material from Gonzen, Switzerland. The studied specimen is in the Smithsonian Institution under catalogue no. NMNH 163804, and a part of it is in the Harvard Mineralogical Museum under catalogue no. HMM-126918. The type wiserite specimen of Epprecht et al. (1959) was obtained through the courtesy of Dr. H. A. Stalder, but was found to be unsuitable for the detailed crystallographic characterization of the species.

Occurrence

The wiserite described is from the Kombat mine, 49 km south of Tsumeb, Namibia (Innes and Chaplin, 1986). The dominant ores are copper and lead sulfides deposited in unmetamorphosed dolomite. Associated with the sulfide ores, but not in contact with them, are discrete lenses of iron and manganese oxides. These lenses contain a number of rare and unusual minerals (leucophoenicite, glaucochroite, cuspidine, sahlinite, hematophanite, etc.), many of which were previously known only from Långban, Sweden, or Franklin and Sterling Hill, New Jersey. Additionally, these lenses have yielded a number of new species including johninnesite, ribbeite, kombatite, holdawayite, asisite, and other phases under study.

Wiserite was found in the West 1150 stope, 10 level, Asis West sector of the Kombat mine, at the 1284-m elevation. Wiserite was associated with hausmannite, jacobsite, calcite, alleghanyite, and pyrochroite (all verified by powder XRD methods) on the hanging-wall side of a thin (2-m-thick) lens of layered manganese ores. The location is indicated by the mine coordinate system at

0003–004X/89/1112–1374$02.00

TABLE 1. X-ray powder-diffraction data for wiserite from the Kombat mine, Namibia

h k l	d_{obs}*	I/I_0	d_{obs}**	I/I_0	d_{calc}
1 1 0	14.4	100	14.5	35	14.278
2 2 0	10.1	30	10.14	30	10.096
2 2 0	7.16	5	7.19	10	7.139
3 1 0	6.42	80	6.40	85	6.385
4 0 0	5.07	10	5.05	35	5.048
3 3 0	4.78	10	4.78	42	4.759
4 2 0	4.51	1	4.52	20	4.515
4 4 0	3.56	5	3.572	20	3.569
5 3 0	3.46	20	3.465	50	3.463
6 0 0	3.36	40	3.365	100	3.365
6 2 0	3.19	5	3.194	20	3.193
2 1 1	3.09	5	3.086	30	3.084
3 1 1	2.92	1	n.o.		2.918
7 1 0	2.86	30	2.854	90	2.856
6 4 0	2.81	5	2.799	25	2.800
4 0 1	2.76	25	2.753	70	2.751
3 3 1	2.70	25	2.702	65	2.701
4 2 1	2.66	80	2.654	80	2.654
5 0 1	n.o.		2.55	25	2.546
5 5 1 8 0 0	2.53	70	2.522	65	2.526 2.524
4 4 1	2.42	25	2.415	30	2.416
6 6 0	2.38	5	2.38	25	2.380
6 0 1 7 5 1	2.35	25	2.349	35	2.349 2.347
6 2 1	2.28	1	n.o.		2.288
9 1 0	2.23	5	n.o.		2.230
7 1 1	2.15	1	2.15	15	2.154
6 4 1 9 3 0	2.13	20	2.13	25	2.130 2.128
7 7 0	2.04	10	2.04	30	2.040
10 0 0	2.02	10	2.02	30	2.019
10 2 0	1.977	1	1.979	25	1.980
9 5 0	1.963	10	1.962	25	1.961
8 4 1	1.865	5	1.861	15	1.860
9 1 1	1.847	20	1.843	30	1.844
9 3 1	1.786	1	n.o.		1.786
11 3 0	1.771	1	n.o.		1.771
9 4 1	1.739	1	n.o.		1.739
10 0 1	1.720	30	1.718	50	1.720
10 2 1	1.697	1	1.694	20	1.695
0 0 2	1.639	5	1.641	30	1.641

Note: n.o. = not observed.

* Film data recorded with Fe$K\alpha$ radiation.

** Diffractometer data recorded with Cu$K\alpha$ radiation and calibrated with NBS Si. Combination of two data sets of differing precision.

TABLE 2. Chemical data for wiserite

	Theo-retical	Kombat mine, Namibia	Gonzen, Switzerland			Yaei mine, Japan
MnO	69.00	64.3	65.13	68.24	61.5	63.8
MgO	1.40	4.9	2.88	3.14	3.1	1.2
CaO		0.3	3.33	0.78	0.3	0.0
FeO		0.2			0.2	0.7
SiO_2	2.09	2.0			1.8	3.5
B_2O_3	19.33	17.5	18.14	17.07		
H_2O	6.28	7.0	8.10	8.37		
Cl	2.46	2.1	3.12	3.09	1.4	1.7
O ≡ Cl	0.56	0.5	0.70	0.69		
Total	100.00	97.8	100.00	100.00		
Source*	1	2	3	3	2	2

* Sources: (1) Theoretical composition from structural formula of Pertlik and Dunn (1989). (2) Present study. (3) From Epprecht et al. (1959); recalculated to 100 wt%.

73 442, 253 524 in Figure 4 of Innes and Chaplin (1986). Fibers and crystals of wiserite are well developed parallel to fold axes in the hinge regions of transpositional folds, and it displays a decussate texture on the fold limbs. The hausmannite is in contact with a khaki-colored argillite in the hanging wall. The argillite contains abundant richterite.

PHYSICAL AND OPTICAL PROPERTIES

The Kombat wiserite is light pinkish brown, with vitreous luster and no apparent cleavage. The density is 3.54(8) g/cm³, measured using heavy-liquid techniques, compared with the calculated value of 3.57 g/cm³ for the idealized end-member composition. It forms prismatic crystals, up to 1 mm in diameter and 1 cm long, elongate parallel to [001]; the only forms present are {100} and {110}. Most are broken along their length; no terminal forms were observed. Optically, this wiserite is uniaxial, negative, with $\epsilon = 1.700$ and $\omega = 1.751$ (both ±0.003), with no discernible pleochroism. A weak biaxial figure was observed in some crystals and may be due to strain. Calculation of the Gladstone-Dale relationship yields the values $K_C = 0.208$ and $K_P = 0.207$, indicating superior agreement of the chemical and physical data (Mandarino, 1981).

X-RAY CRYSTALLOGRAPHY

Single-crystal X-ray diffraction photography using the precession method and Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å) showed the Kombat wiserite to be tetragonal with approximate unit-cell parameters $a = 20.13$ and $c = 3.28$ Å. There is one systematic extinction condition; reflections of the type $hk0$ are present only when $h + k$ is even. The space group is uniquely determined as $P4/n$.

X-ray powder-diffraction data for unit-cell refinement (Table 1) were collected using a Philips Norelco diffractometer and monochromatized Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The sample was mixed with NBS Si ($a = 5.43088$ Å) for internal calibration of the data. The unit-cell parameters were refined from diffraction maxima in the range 24° to 40° 2θ with the use of the program LCLSQ of Burnham (1962), which yielded values of $a = 20.192(6)$, $c = 3.281(2)$ Å, and $V = 1337.9(9)$ Å³. Kombat wiserite has the same X-ray power-diffraction pattern as the type material.

This unit cell is twice as large as that determined by Epprecht et al. (1959), using rotation methods on fibrous material from the type locality. Their a axis is the [110] zone of the new cell. Miller indices of the old cell may be transformed to those of the new cell using the matrix (110/$\bar{1}$10/001).

CHEMICAL COMPOSITION

The Kombat wiserite was chemically analyzed by several techniques. Elements with atomic number >8 were determined with an ARL-SEMQ electron microprobe, using a 15-kV accelerating voltage, a 0.025-μA sample current measured on brass, a 15-μm beam spot, and a 10-s counting time. A qualitative wavelength-dispersive microprobe scan indicated the absence of elements with atomic number >8, except those reported herein. The standards used were manganite (Mn), hornblende (Si, Fe, Mg, Ca), and scapolite (Cl). Separate analyses using other standards yielded very similar results. The data were corrected with a modified version of the MAGIC-4 program. B was determined by fusion in potassium carbonate, followed by extraction of B and its separation from interfering elements. After careful neutralization of the solutions, the B was titrated with NaOH in the presence of mannitol.

TGA-EGA was performed on 11 mg of hand-picked wiserite. The sample was heated in high vacuum at 10 °C/min with the use of a Mettler TA-1 thermoanalyzer and Inficon IQ-200 quadrupole mass spectrometer system. The decomposition of wiserite is characterized by a continuous loss of volatiles, principally water, between 50 and 1030 °C. The weight loss totaled 9.3 wt%. Evolved gas curves show a very strong water peak and weak peaks for HCl and O_2 at 510 °C. The loss to 530 °C totals 6.8 wt%. An additional 2.5 wt% was lost by 1030 °C and was shown by EGA to be a complex loss, primarily of H_2O, CO_2, HCl, and SO_3.

A water content of 7 ± 1 wt% was determined on the basis of weight loss to 530 °C. The estimated error is high because of the co-evolution of other gases and the fact that H is evolved to some extent as HCl. It is uncertain whether CO_2 and SO_3 originated from the mineral or from impurities, although part of the CO_2 loss is consistent with the decomposition of manganoan or ferroan calcite, and no S was detected in wiserite by electron-microprobe analysis.

A separate water determination by the Penfield method yielded 7.2 (±0.2) wt% H_2O. Chemical analyses of the Kombat wiserite, the type material from Switzerland, and the specimen from Japan, together with those published by Epprecht et al. (1959) are given in Table 2.

The low sum of our analyses of the Kombat wiserite prompted a number of repeat determinations, with similar results. The B_2O_3 value, determined but once, is in good agreement with the values of Epprecht et al. (1959) (17.5 compared with 17.07 and 18.14 wt%); the calculated value for the end-member structural formula presented below is 19.33 wt% B_2O_3. Water determinations by TGA-EGA and the Penfield method are in very close agreement. Although Epprecht et al. (1959) spectrographically analyzed the Gonzen wiserite, they gave no indications of the presence of light elements. An ion-microprobe scan of the Kombat wiserite verified Epprecht et al.'s earlier results; Be and Li were found in only trace amounts.

Re-analysis of the Epprecht et al. (1959) sample demonstrates that CaO is 0.3 wt%, rather than the larger value they reported (see Table 2). Similarly, Epprecht et al. (1959) did not report silica; it probably was in their insoluble residue of 1.2 wt%. The approach of taking the new CaO and SiO_2 values as 0.3 and 1.2 wt%, respectively, and normalizing their first analysis to 100 wt%, yields a ratio of M^{2+} cations to B of 29.83:16.00. This value is only slightly higher than the theoretical value (28.50:16.00) expected for a wiserite with this silica content, as discussed below.

The crystal structure of the Kombat wiserite recently determined by Pertlik and Dunn (1989) confirms the unit cell and space group, and the general formula $\{Mn_{14}(B_2O_5)_4(OH)_8\}\{[Si_{1-x}Mg_x][O_{1-x}(OH)_x]_4Cl_{2x}\}$, with x approximately 0.5 and Z = 2 in the studied material. Calculation of unit-cell contents for the analysis of the Kombat wiserite (Table 2), yields $Mn_{12.98}Mg_{1.74}Fe_{0.04}Ca_{0.08}Si_{0.48}Cl_{0.85}H_{11.08}B_{7.17}O_{32.52}$, with Z = 2. This composition is in agreement with the general formula, except for a shortfall of 0.83B and a slight excess of octahedral cations and H, all of which we attribute to analytical error. As noted above, some carbonate was found, likely as an impurity, but perhaps in substitution for borate. We call attention to the variable Si, Mg, and Cl contents.

ACKNOWLEDGMENTS

We thank the management of the Tsumeb Corporation Ltd., and Mr. R. C. Chaplin, the geological superintendent, for facilitating the collection and transport of samples from the Kombat mine. We are grateful to Professor Dr. H. A. Stalder of the Natural History Museum in Bern, Switzerland, for a portion of the type wiserite of Epprecht et al., and to Dr. Akira Kato for the Japanese specimen and a partial translation of Kato and Matsubara's study. We are grateful to Dr. Dale Newbury of the National Bureau of Standards for analytical assistance with the ion microprobe. P.J.D. expresses his gratitude to Mrs. E. Hadley Stuart, Jr., for research assistance. We thank Drs. Paul B. Moore, Donald R. Peacor, and Franklin Foit for critical readings.

REFERENCES CITED

Burnham, C.W. (1962) Lattice constant refinement. Carnegie Institution of Washington Yearbook 61, 132–135.

Epprecht, W. (1946a) Die Eisen- und Manganerze des Gonzen. Beitrage für Geologie der Schweiz, Geotechnische Serie, 24.

——— (1946b) Die Manganmineralien vom Gonzen und ihre Paragenese. Schweizerische Mineralogische und Petrographische Mitteilungen, 26, 19–27.

Epprecht, W., Schaller, W.T., and Vlisidis, A.C. (1959) Ueber Wiserit, Sussexit, und ein weiteres Mineral aus den Manganerzen vom Gonzen (bei Sargans). Schweizerische Mineralogische und Petrographische Mitteilungen, 39, 85–104.

Gorbov, A.F. (1973) The composition of wiserite and mineral-X, two manganese borates. Trudy Vsesoiuznogo Nauchno-Issledova-Tel'skogo Instituta Galurgii, 64, 54–56.

Haidinger, W. von. (1845) Handbuch der bestimmenden Mineralogie. Vienna, Austria, 8 volumes.

Innes, J., and Chaplin, R.C. (1986) Ore bodies of the Kombat Mine, South West Africa–Namibia. In C.R. Anhaesser and S. Maske, Eds., Mineral deposits of southern Africa, 1789–1805. Geological Society of South Africa, Johannesburg, Republic of South Africa.

Kato, A., and Matsubara, S. (1980) Manganese borate minerals from Japan. Journal of the Mineralogical Society of Japan, 14, Special Publication 3, 86–97.

Kenngott, G.A. (1866) Die Minerale der Schweiz, 460 p. Leipzig, G.D.R.

Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. Canadian Mineralogist, 19, 441–450.

Pertlik, F., and Dunn, P.J. (1989) Crystal structure of wiserite. American Mineralogist, 74, 1351–1354.

MANUSCRIPT RECEIVED DECEMBER 22, 1988
MANUSCRIPT ACCEPTED JULY 26, 1989