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Hennomartinite and kornite, two new Mn^{3+} rich silicates from the Wessels Mine, Kalahari, South Africa

by *Thomas Armbruster*[1], *Roland Oberhänsli*[2,3], *Vladimir Bermanec*[1,4] and *Roger Dixon*[5]

Abstract

Hennomartinite, $SrMn_2^{3+}[Si_2O_7](OH)_2 \cdot H_2O$, is an orthorhombic (Cmcm, a = 6.245[1], b = 9.031[2], c = 13.404[2] Å, V = 756.0[1] Å^3, Z = 4) disilicate of the lawsonite structure type which occurs as anhedral poikiloblasts up to 1 mm, strongly intergrown with sugilite and serandite-pectolite. The mineral is translucent in thin section, pleochroic from yellowish brown to dark red-brown and has indices of refraction greater than 1.82. The calculated density is 3.68 g/cm^3. The chemical composition was determined by electron microprobe analyses and IR-spectroscopy. The trivalent character of Mn is derived from stoichiometry and bond lengths obtained from a crystal structure analysis.

Kornite, $(K,Na)(Na,Li)_2(Mg,Mn^{3+},Fe^{3+},Li)_5Si_8O_{22}(OH)_2$, is a monoclinic amphibole (P lattice, a = 9.94[1], b = 17.80[2], c = 5.302[4] Å, β = 105.5[2], V = 904[4] Å^3, Z = 2). The calculated density is 3.15 g/cm^3. The mineral forms bundles of extremely fine fibers (5–20 μ in diameter), often bent, maximum fibre length 0.2 mm. The mineral is dark red to brownish-lilac, biaxial (2 V_x = 88–92°) with indices of refraction α = 1.654(4), β = 1.675 (calc), γ = 1.696(4) determined under white light. The optic orientation is Z = b, Y : c = 60–65° (in obtuse angle β). The mineral is strongly pleochroic: X = pink, Y = dark red, Z = orange-red. The chemical composition was determined by electron and ion microprobe analyses.

Both new minerals occur together with idiomorphic sugilite (70%), serandite-pectolite (25%) as hydrothermal reaction products of primary Mn-ore at the Wessels Mine, Kalahari Manganese Field, Republic of South Africa.

Keywords: hennomartinite, kornite, sugilite, lawsonite, amphibole, new mineral, Mn-silicates, Kalahari Manganese Field, South Africa.

Introduction

CHOICE OF NAMES

In the last two decades, many students starting in geology were fascinated by Henno Martin's book "Wenn es Krieg gibt, gehen wir in die Wüste", an English translation of which was published under the title "The sheltering desert". This book is a biography telling the story of two young German geologists, Henno Martin and Hermann Korn, who emigrated to South West Africa (today Namibia) when Hitler came to power in Germany. "They were not willing to participate in a suicide of civilized nations" (MARTIN, 1970). When the war began they had been hiding for more than two years in the Kuiseb gorges surrounded by the Namib desert. Trained in geological field work, the two young scientists survived the loneliness and dangers of the desert by hunting and sharing water holes with wild animals. They were never intruders into the ecological equilibrium but became part of the system. In their remote hideout they had enough time to think about evolution and the adaptation of life which finally led to human intelligence, now misused (second World War) for the annihilation of mankind. It is this perspective which gives the book a timelessness

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and relevance at the end of the twentieth century, when ecological catastrophes and civil wars have become a major threat to our planet.

After two and a half years hiding in the desert, the two geologists surrendered to the South West African government and later worked as geologists drilling for water in the desert. Hermann Korn died 1946 in a traffic accident. Between 1947–1962 Henno Martin was a member of the Geological Survey of South Africa. In 1963 he became director of the Geologisch-Paläontologisches Institut, Universität Göttingen (Germany). Korn and Martin coauthored several papers on the structural geology of South West Africa. Martin's scientific work deals with Precambrian geology.

Admittedly, Henno Martin and Hermann Korn have no association with the Kalahari Manganese Fields (northwestern Cape Province, South Africa) nor did they ever publish anything on the mineralogy of Mn deposits. However, the Kalahari is a giant desert covering parts of Botswana, Namibia and South Africa and the two rare minerals named after Henno Martin and Hermann Korn occur together and even intergrown with each other, which seemed reason enough to us to honor the two geologists by naming the two Mn-silicates after them. The double name hennomartinite was preferred because martinite was previously used for a variety of whitlockite.

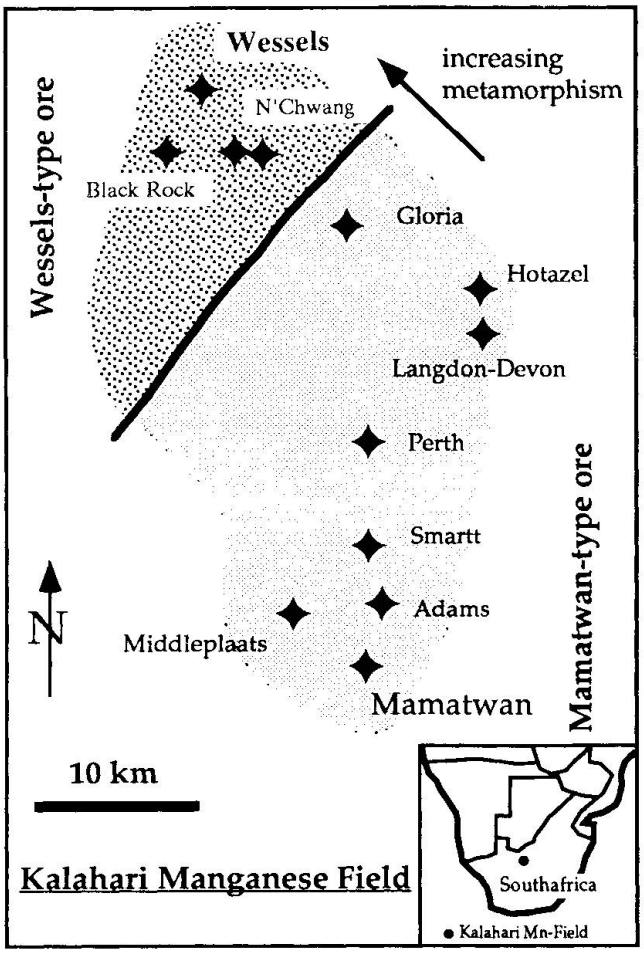

Fig. 1 Sketch map of the Kalahari Manganese Field.

SAMPLE DESCRIPTION AND OCCURRENCE

The sample under investigation comes from the Wessels Mine which is located in the stratabound ore deposits of the Kalahari Manganese Field (Fig. 1). These deposits occur in a mid Proterozoic sequence of volcanogenic sediments. Due to its metamorphic overprint two main ore types are distinguished within the Kalahari Manganese Field, the Mamatwan ores in the southeast and the Wessels-type ores in the northwestern part of the deposit (Fig. 1). The Wessels-type ore was hydrothermally altered and metamorphosed and can be divided in three lateral types within the Wessels Mine: (a) carbonate rich ores with Mn-calcite, kutnahorite and rhodochrosite, (b) B and Li rich ores with sturmanite, gaudefroyite and sugilite, and (c) Ca, Ba, Li ores with andradite, inesite, hydroxylapophyllite, ruizite, barite and celestine (Von Bezing et al., 1991). In a profile from hangingwall to footwall several occurrences of sugilite were distinguished (Dixon, 1985).

Unlike most of the known sugilite samples, which consist mainly of a dense felt of relatively pure sugilite – used as a semiprecious gemstone cut into cabochons – the investigated sample is coarse grained and granular. It has a light purple color with veins (2–10 mm thick) of white serandite-pectolite, often with fine seams of minute dark brown to red needles. From this sample single-crystals of sugilite were separated for structural analysis (Armbruster and Oberhänsli, 1988). At this time we became aware of two further, hitherto unknown minerals.

In thin section, the rock consists of fibrous pectolite-serandite intergrown with idiomorphic sugilite crystals up to 0.5 mm in diameter. The serandite-pectolite veins show comb-like structures of large serandite-pectolite fibers. Two additional Mn-minerals, both striking due to their bright colors, were found in this sample. One mineral (hennomartinite) exhibits yellow-brown interference colors and forms poikiloblasts up to 1 mm overgrowing sugilite and serandite-pectolite (Figs 2 and 3). The other mineral (kornite) generally forms a fine grained dark red felt along pectolite veins (Fig. 4). On close inspection, the two new minerals can also be found intergrown with each other (Fig. 3). In general, the minute

dark red fibers of kornite rim the yellow brown poikilitic hennomartinite. These new minerals have now been approved as kornite and hennomartinite by the International Commission on New Minerals and Mineral Names. Holotype material is deposited (NMBE-B5564) at the Museum of Natural History, Bern.

Hennomartinite

Hennomartinite is a rare mineral forming yellow-brown poikiloblast ca. 1 mm in diameter within small veins of serandite-pectolite. It also occurs less commonly in the form of a felty matrix in sugilite-rich parts of the sample.

CHEMICAL AND STRUCTURAL CHARACTERISTICS

The chemical and structural characteristics of hennomartinite have already been published (ARMBRUSTER et al., 1992). The new mineral is orthorhombic (space group Cmcm) and possesses a disilicate structure of the lawsonite type (BAUR, 1978) and nearly end-member composition $SrMn_2^{3+}[Si_2O_7](OH)_2 \cdot H_2O$ with very minor Fe^{3+} substituting for Mn^{3+} and Ba for Sr (Tab. 1). Measurable quantities of Ca could not be expressed in the formula. Li and F were not found by ion microprobe analysis.

The valence of Mn was derived from stoichiometric considerations and from Mn–O distances obtained from a crystal structure refinement (ARMBRUSTER et al., 1992). The $Mn^{3+}O_6$ octahedron in hennomartinite displays the characteristic Jahn-Teller distortion leading to an elongated pseudo-tetragonal octahedron (two long and four short Mn^{3+}–O distances). The fundamental building block of the structure is $Mn_2^{3+}(OH)_2[SiO_4]_2$ which is also observed in orientite, macfallite and ruizite (MOORE et al., 1985), but these minerals have a different stoichiometry.

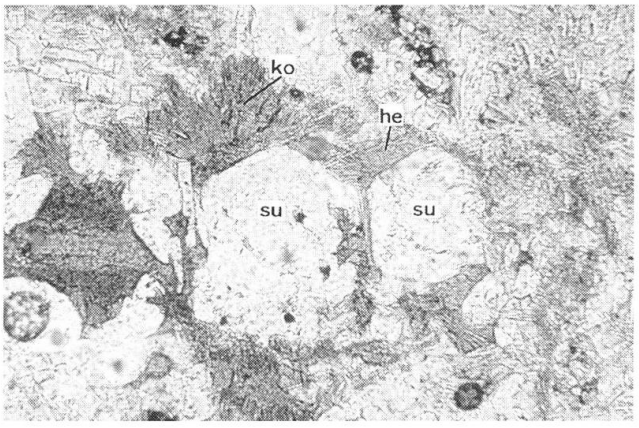

Fig. 2 Photomicrograph of a sugilite serandite-pectolite rock. Hennomartinite overgrows the idiomorphic sugilite crystals (hexagons in the center) and covers a larger area in the left part of the micrograph. Kornite fibers grow on hennomartinite in the upper part of the photograph. Width of the micrograph: 2 mm.

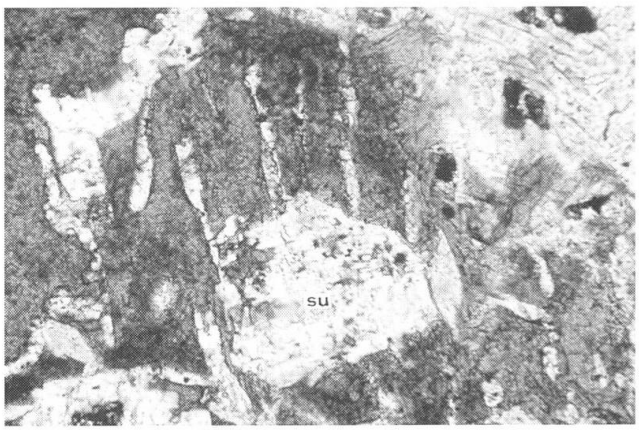

Fig. 3 Photomicrograph of hennomartinite overgrowing idiomorphic sugilite and serandite-pectolite needles. Width of the micrograph: 0.5 mm.

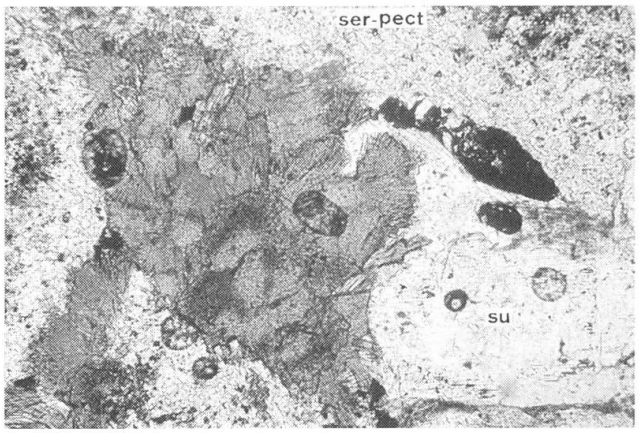

Fig. 4 Photomicrograph of a fine grained kornite felt with serandite-pectolite. To the right a sugilite crystal is visible. Width of the photomicrograph: 0.5 mm.

PHYSICAL AND OPTICAL PROPERTIES

Intergrowth with other minerals from the paragenesis (especially serandite-pectolite and sugilite) complicated the measurements of physical properties, such as hardness, cleavage, density etc. Hennomartinite has a Mohs hardness of ca. 4. With a 100 g load, the Vickers hardness varies between 200 and 400. Parting and cleavage were not observed. Hennomartinite is yellow-brown,

Tab. 1 Chemical composition of hennomartinite and lawsonite.

	hennomartinite	lawsonite (BAUR, 1978)
	wt%	wt%
CaO	0.02	17.18
BaO	0.46	
SrO	24.32	
Mn_2O_3	37.82	
Fe_2O_3	0.53	0.90
SiO_2	28.22	37.75
Al_2O_3	0.00	31.09
TiO_2	0.00	0.33
H_2O	8.62	4.00
Total	99.99	98.54
number of ions on the basis of ten O		
Ca	0.00	0.98
Ba	0.01	
Sr	0.98	
Mn^{3+}	2.01	
Fe^{3+}	0.03	0.04
Si	1.97	2.01
Al	0.00	1.95
Ti	0.00	0.01
O	7.00	7.00
OH	2.00	2.00
H_2O	1.00	1.00

Note: H_2O of hennomartinite was determined by difference to 100 wt%.

has a vitreous luster and is translucent; fluorescence was not observed under short- and long-wave UV radiation. The density was not measured (because of the intimate intergrowth) but calculated from cell dimensions and chemical composition, yielding 3.68 g/cm³.

In spite of the very close crystallochemical connection between hennomartinite and lawsonite the refractive indices of hennomartinite are much higher (>1.82) than lawsonite (1.665–1.685), due to the heavier metals (Mn, Sr) in hennomartinite. The new mineral shows strong pleochroism from yellowish-brown to dark red-brown. These intense colors and the very high refractive indices did not allow the determination of the optical parameters more precisely. Spindle stage measurement under white light gave an optical axial angle of 63(1)° (Tab. 2). It remains unclear, however, whether the optical character is positive or negative.

X-RAY DIFFRACTION

An X-ray powder diffraction pattern was recorded with a Guinier camera at room temperature using Si as internal standard. The pattern shows the presence of minor sugilite, with which hennomartinite is closely intergrown. In the calculation of the unit cell dimensions (program GITTER, HUMMEL pers. comm.) all lines which overlapped with sugilite reflections were omitted (Tab. 3).

INFRARED SPECTRUM

By careful separation under a binocular microscope it was possible to extract enough material for the preparation of a KBr-pellet. The IR spectrum (ARMBRUSTER et al., 1992) shows absorptions near 3500 and 1600 cm^{-1} characteristic for H_2O and/or OH vibrations. Bands between 1200 and 850 and 600 and 350 cm^{-1} resemble those of lawsonite (LABOTKA and ROSSMAN, 1974; MOENKE, 1961).

Kornite

In a detailed study on sugilite and associated metamorphic silicate minerals from the Wessels Mine, Kalahari Manganese Field, DIXON (1989) distinguished two groups of amphiboles on the basis of their color. One group (group A), dark red through red and pink to blue, was strongly pleochroic. Group B comprised pale green am-

Tab. 2 Cell dimensions, strongest X-ray powder diffraction lines (XRD), and refractive indices of hennomartinite and lawsonite (BAUR, 1978).

	hennomartinite	lawsonite
formula	$SrMn_2(Si_2O_7)(OH)_2 \cdot H_2O$	$CaAl_2(Si_2O_7)(OH)_2 \cdot H_2O$
space group	Cmcm	Cmcm
cell dimensions [Å]	6.255(1), 9.034(1), 13.397(2)	5.847(1), 8.795(3), 13.142(6)
strongest XRD lines [Å]	2.83, 2.69, 4.80, 2.40	2.72, 2.62, 2.13, 6.56
refractive indices	> 1.82	1.665, 1.675, 1.685

Tab. 3 Room temperature XRD powder pattern of hennomartinite from the Wessels Mine.

I_{calc}	d_{meas}	d_{calc}	h	k	l
10		6.70	0	0	2
30	5.149	5.136	1	1	0
86	4.804	4.796	1	1	1
42	sug	4.516	0	2	0
56	4.287	4.279	0	2	1
26	3.752	3.745	0	2	2
66	3.373	3.371	1	1	3
22	3.347	3.3510	0	0	4
100	2.833	2.8304	2	0	2
82	2.807	2.8066	1	1	4
58	2.715	2.7117	1	3	0
98	2.695	2.6910	0	2	4
24	2.666	2.6579	1	3	1
26	sug	2.5683	2	2	0
48	2.518	2.5138	1	3	2
68	2.401	2.3982	2	2	2
26	2.379	2.3766	1	1	5
54	2.231	2.2266	2	2	3
20	2.113	2.1080	1	3	4
20	2.018	2.0151	0	4	3
20	2.009	2.0050	3	1	1
11		1.8724	0	4	4
40	1.819	1.8169	2	0	6
14	1.795	1.7942	1	1	7
30		1.7650	2	4	2
14		1.7629	0	2	7
11		1.7353	3	1	4
14		1.7269	0	4	5
27		1.7122	3	3	0
30		1.6931	2	4	3
38	1.687	1.6856	2	2	6

Hennomartinite is closely intergrown with sugilite, thus the powder pattern always shows the presence of sugilite lines which are indicated by sug and omitted in the observed pattern. Intensities are calculated (LAZY-PULVERIX: YVON et al., 1977) from refined coordinates (ARMBRUSTER et al., 1992) for Guinier symmetry and $FeK\alpha_1$ radiation.

Tab. 4 Chemical composition of kornite and related minerals.

	kornite	leakeite (HAWTHORNE et al., 1992)
	wt%	wt%
K_2O	3.56	1.12
Na_2O	7.61	9.69
Li_2O	1.96	1.42
MgO	10.03	10.96
Mn_2O_3	13.17	3.86
Fe_2O_3	4.93	12.23
SiO_2	56.06	55.80
Al_2O_3	0.00	1.27
TiO_2	n.d.	0.03
CaO	0.00	0.50
H_2O	2.68*	1.63
F	n.d.	1.08
TOTAL	100.00	99.11
number of ions on the basis of ten O and two OH		
K	0.65	0.20
Na	2.10	0.75
Li	1.12	0.81
Mg	2.13	2.32
Mn^{3+}	1.43	0.42
Fe^{3+}	0.52	1.31
Si	8.00	7.93
Al	0.00	0.07
Ti	n.d.	0.00
Ca	0.00	0.08
OH	2.00	1.51
F	n.d.	0.49

* – calculated as difference to 100%

phiboles. The brightly colored amphiboles were less common than the pale green type. Electron microprobe analyses of group A amphiboles revealed deficiencies of C site cations (Mn^{3+}, Fe^{3+}, Al, Mg), in extreme cases down to 4.5 a.p.f.u. DIXON (1989) had no access to an ion probe but admitted that Li can be an important constituent of alkali amphiboles where it is ordered on the C site. Furthermore he noticed that the reddish amphiboles (group A) were enriched in Mn^{3+} while the pale-green ones were Fe^{3+} rich. The electron microprobe analyses of group A amphiboles by DIXON (1989) are extremely similar and probably identical to the kornite defined in this study.

CHEMICAL CHARACTERISTICS

A polished thin section mount, one inch in diameter, was used for electron and ion-microprobe analyses. Seven analyses were carried out by mean of an electron microprobe using the following standards: albite (Na,Si), $MnSiO_3$ (Mn), olivine (Fe,Mg), sanidine (K) and anorthite (Al,Ca). Sugilite was used as Li standard for the ion-probe. H_2O could not be determined due to scarcity of the material so it was calculated from stoichiometry. Mean analytical results are given in Tab. 4. Additional experimental details are given in ARMBRUSTER and OBERHÄNSLI (1988) and ARMBRUSTER et al. (1992). Following HAWTHORNE (1983), the amphibole formula was normalized on 46 negative charges (22 O + 2 OH^-) leading to the empirical formula $(K_{0.65}Na_{0.31})_{\Sigma 0.96}(Na_{1.79}Li_{0.21})_{\Sigma 2.00}$-$(Mg_{2.12}Mn^{3+}_{1.43}Fe^{3+}_{0.52}Li_{0.91})_{\Sigma 5.00}Si_8O_{22}(OH)_2$. The simplified formula is $(K,Na)(Na,Li)_2(Mg,Mn^{3+},Fe^{3+},Li)_5[Si_8O_{22}](OH)_2$.

Tab. 5 The main crystallographic and optical data of kornite compared with related minerals.

	kornite	eckermannite	leakeite
formula	$KNa_2(Mg_2Mn^{3+}_2Li)[Si_8O_{22}](OH)_2$	$Na_3(Mg,Fe)_4Al[Si_8O_{22}](OH)_2$	$NaNa_2(Mg_2Fe^{3+}_2Li)[Si_8O_{22}](OH)_2$
space group	P-lattice	C2/m	C2/m
cell dimensions [Å]	a 9.94(1)	a 9.762	a 9.822(3)
	b 17.80(2)	b 17.892	b 17.836(6)
	c 5.302(4)	c 5.284	c 5.286(2)
	β 105.5(2)°	β 103.17°	β 104.37(3)°
refractive indices	n_x 1.654 pink	1.614–1.636 blue-green	1.667 dark mauve-red
	n_y 1.675(calc) dark red	1.625–1.644 pale blue-green	1.675 dark mauve-red
	n_z 1.696 orange-red	1.630–1.649 yellow-green	1.691 light pink-red
	$2V_x$ 88–92°	74°	59–71°

Note: Refractive indices of eckermannite from TRÖGER (1982).

This idealized formula is comparable with eckermannite (end member $Na_3(Mg,Fe)_4Al[Si_8O_{22}](OH)_2$) and especially with leakeite (end-member formula is $Na_3(Mg_2Fe^{3+}_2Li)[Si_8O_{22}](OH)_2$) (HAWTHORNE et al., 1992). Kornite has no Al in octahedral position, as eckermannite has, but all three-valent cations are mostly Mn^{3+} with lesser Fe^{3+} (in the C position). For the distinction between leakeite and kornite the Mn^{3+}/Fe^{3+} ratio is decisive. The C position in kornite is predominantly occupied by Mn^{3+} while in leakeite Fe^{3+} is dominant. Less important is the fact that in kornite K is dominant on the A position, while Na is dominant in leakeite. Kornite with Li > 0.50, Mn > 1.00 and K > 0.50 p.f.u. would be named lithian potassium manganese magnesio-arfvedsonite under the IMA amphibole scheme (HAWTHORNE, 1983) as there is no Fe^{2+} and no ^{VI}Al. It is not emphasized that K > Na on the A position of kornite, because it would logically loom with an enormous increase in names for the amphiboles (LEAKE, pers. comm.).

PHYSICAL AND OPTICAL PROPERTIES

Kornite occurs in bundles of fine fibers (5–20 μ in diameter), often bent, with a maximum fibre length of less than 200 μ. The mineral is dark red to brownish-lilac, transparent with a vitreous luster and does not fluorescence under long-wave or short-wave ultraviolet light. The [001] fibers are brittle with a cleavage parallel to [001] but the plane was not determined. The calculated density is 3.15 g/cm³, the observed density and hardness could not be measured because the fibers are too small and intergrown. Hardness, streak, twinning and IR absorptions were not determined because

Tab. 6 Room temperature XRD data of kornite.

I/I_o	d_{meas}	d_{calc}	h	k	l	flag
medium	8.890	8.901	0	2	0	*+
medium	8.427	8.436	1	1	0	+
medium	5.077	5.044	1	3	0	+
weak	4.756	4.790	2	0	0	*+
medium	4.442	4.450	0	4	0	*+
medium	3.357	3.360	1	3	1	o
strong	3.257	3.260	2	4	0	+
strong	3.132	3.143	3	1	0	+
weak	2.938	2.921	0	5	1	*
strong	2.812	2.812	3	3	0	+
medium	2.680	2.682	1	5	1	o
strong	2.553	2.554	0	0	2	*
medium	2.391	2.395	4	0	0	*
medium	2.372	2.377	3	5	0	+
weak	2.272	2.277	0	7	1	*
weak	2.213	2.215	0	4	2	*
medium	2.038	2.041	4	0	–2	*
medium	2.038	2.039	2	0	2	*
medium	1.900	1.9049	5	1	0	*
weak	1.852	1.8445	0	9	1	*
weak	1.812	1.8232	5	3	0	+
weak	1.689	1.6778	0	8	2	*
weak	1.594	1.5966	6	0	0	*
medium	1.558	1.5537	6	0	–2	*
medium	1.558	1.5520	4	0	2	*
weak	1.480	1.4835	0	12	0	*
weak	1.283	1.2828	0	12	2	*
weak	1.276	1.2771	0	0	4	*

The flags for each reflection indicate the method which was applied for its determination:
* Precession photograph MoKα-radiation
+ Weissenberg photograph hk0, FeKα-radiation
o Rotation photograph of the crystal mounted parallel to c, FeKα-radiation. Intensities were estimated by eye.

of low quantity and small grain sizes of the mineral.

A spindle stage equipped polarizing microscope was used to determine 2 V_x = 88–92° and to orient the crystal for the determination of pleochroism, optic orientation and refractive indices. Refractive indices were measured with white light for maximum intensity, yielding α = 1.654(4), β = 1.675 (calc), γ = 1.696(4). Dispersion was not determined. The optic orientation measured relative to the morphology is: Z = b, Y : c = 60–65° (in obtuse angle β). Pleochroism: X = pink, Y = dark red, Z = orange-red (Tab. 5).

X-RAY DIFFRACTION

Only a few individual crystals could be separated from the hand specimen. The maximum size of the separated fibers was 0.005 × 0.020 × 0.1 mm. Gandolfi-photographs of bundles of such small fibers did not lead to measurable films, thus the diffraction pattern was obtained from various long exposure (up to 14 days) single-crystal photographs which are much more sensitive for this purpose because the crystal is oriented in the diffraction position. Three different techniques were applied: (1) precession photographs 0kl, k0l with Zr filtered MoKα-radiation, (2) Weissenberg hk0 photograph with Mn filtered FeKα-radiation, (3) rotation photograph, crystal mounted parallel to c (FeKα-radiation). In general, X-ray reflections were diffuse due to the bending and cleavage of the fibers. The measured reflections (Tab. 6) suggest a primitive lattice. The observed systematic extinctions are in agreement with space groups $P2_1/m$ and P2/a which have already been described for amphiboles (HAWTHORNE, 1981). Refinement of cell dimensions using the program GITTER (HUMMEL pers. comm.) with the data in Tab. 6 yielded a = 9.94(1), b = 17.80(2), c = 5.302(4) Å, β = 105.5(2)°.

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