CORNUBITE, $Cu_5(AsO_4)_2(OH)_4$, FIRST OCCURRENCE OF SINGLE CRYSTALS, MINERALOGICAL DESCRIPTION AND CRYSTAL STRUCTURE

EKKEHART TILLMANNS; WOLFGANG HOFMEISTER and KLAUS PETITJEAN

TILLMANNS, EKKEHART; HOFMEISTER, WOLFGANG and PETITJEAN, KLAUS, 1985: Cornubite, $Cu_5(AsO_4)_2(OH)_4$, first occurrence of single crystals, mineralogical description and crystal structure. *Bull. Geol. Soc. Finland 57, Part* 1—2, 119—127.

The first single crystals of the rare copper arsenate hydroxide cornubite, $Cu_5(AsO_4)_2(OH)_4$, have been found from a silicified barite vein at Reichenbach, Odenwald near Bensheim, Hessen, W.-Germany. Cornubite occurs as apple-green, translucent and mostly tabular crystals, up to 0.3 × 0.3 mm in size and up to 0.05 mm thick. The lustre is vitreous, streak light-green and hardness 4. The indices of refraction are between 1.8 and 1.9 and the optical angle is very large. The results of electron microprobe analysis are As_2O_5 32.01, CuO 58.60, SiO_2 0.34, P_2O_5 0.25, Al_2O_3 0.15, Fe_2O_3 0.32, H_2O (calculated) 5.27 weight %, total 96.94 weight %. The empirical formula is $Cu_{5.03}(As_{1.903}P_{0.024}Fe_{0.027}Al_{0.020}Si_{0.038})_{2.013}O_8(OH)_4$. X-ray single crystal diffraction studies gave triclinic symmetry, space group $P\bar{1}$ with a = 6.121(1), b = 6.251(1), c = 6.790(1) Å, α = 92.93(1)°, β = 111.30(1)° and γ = 107.47(1)°, V = 227.09 Å^3, Z = 1, D_x = 4.85 Mg/m^3. The crystal structure contains sheets of edge-sharing CuO_6-octahedra // $(0\bar{1}1)$ connected by AsO_4 tetrahedra via common corners and by hydrogen bonds.

Key words: cornubite, copper arsenate hydroxide.

Ekkehart Tillmanns and Wolfgang Hofmeister: Institut für Geowissenschaften, Universität Mainz, Saarstr. 21, D-6500 Mainz, Federal Republic of Germany.

Klaus Petitjean: Mainzer Str. 118, 6520 Worms, Federal Republic of Germany.

Introduction

The rare copper arsenate hydroxide cornubite, $Cu_5(AsO_4)_2(OH)_4$, was first described by Claringbull, Hey and Davis (1959) from Wheal Carpenter in Cornwall, U.K., and was named after the Latin name for Cornwall, Cornubia. It is dimorphous with cornwallite. Since the mineral occurred only as botryoidal fibrous masses, crystallographic data could not be determined, and the X-ray powder pattern could not be indexed although the fibre pattern led to the assumption of a triclinic unit cell with a cell volume of 228 Å^3 or an integral multiple of this. Cornubite has since been found at a number of localities together with copper arsenates or copper phosphates, *e.g.* at Neubulach (Walenta 1979) and Oberwolfach (Walenta 1975), Black Forest, W. Germany and at Imsbach, Donnersberg, W. Germany (Dreyer 1973), but the mineral

has always formed crusts or fibrous masses; single crystals or aggregates of crystals have never been found. An X-ray powder investigation of apple-green, translucent, tabular crystals found in 1982 by one of the authors (K.P.) in a silicified barite vein on quartz with other secondary copper minerals near Reichenbach, Odenwald, W. Germany gave a powder pattern identical to that given by Claringbull *et al.* (1959) for cornubite (JCPDS # 12—288). Reported here are the previously unknown data for this mineral.

Occurrence

The silicified barite vein at Reichenbach near Bensheim, Hessen, W. Germany, is the largest of a number of similar silicified veins occurring in the crystalline rocks of the northwestern Odenwald area. Because of its peculiar pseudomorphic structures, the vein material is quarried in some places for use as ornamental stone. The vein strikes WNW and dips vertically to steeply southwards. Locally it reaches thicknesses of more than 10 m and can be traced in the field for about 5 km, where it forms prominent cliffs (Teufelsstein, Borstein, Hohenstein, see Fig. 1).

The wallrocks of the vein are composed of various diorites and gabbros as well as orthogneisses and paragneisses. Owing to its mode of formation by replacement of barite the vein-filling quartz is not massive but displays an irregular pattern of crystallites of different shapes and sizes. According to Baier und Venzlaff (1961), this structure is due to quartz overgrowths on a previously formed framework of thin platy barite crystals. Subsequently barite dissolved and left open spaces. These casts and also the voids remaining between the former

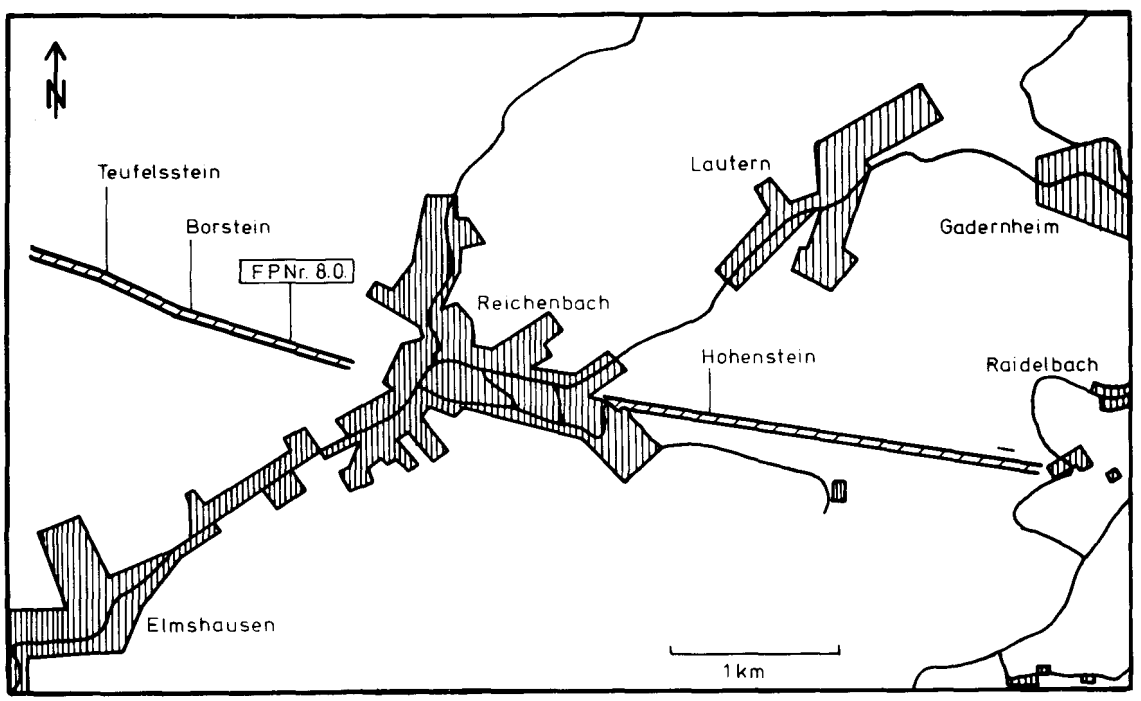

Fig. 1. The silicified barite vein at Reichenbach.

barite crystals were filled w
domorphosed crystals sho
tion perpendicular to the
occur in several generatio
cryptocrystalline quartz.
galena, chalcopyrite and
casionally observed in the
isolated grains of ore mi
within the former barite cr
ing conditions these prim
partially oxidized, leading
of secondary minerals (Ta
phosphates, arsenates an
bution and migration of
oxidation reactions have
formed minerals to occu
adjacent parts of the vei
lized in open joints and

At the site designated
(Borstein, map coordinate

Table 1. Mineral phases of the si
enbach.

Elements	*Carbonates*
copper	azurite
silver	bismutite
	calcite
Sulphides	cerussite
chalcopyrite	malachite
chalcocite	
covellite	*Sulphates, (Chromates, Molybdates, Wolframates,*
enargite	barite
fahlore	beudantite
galena	chalcanthite
luzonite	hinsdalite
	linarite
Halogenides	vauquelinite
chlorargyrite	wulfenite
jodargyrite	
Oxides and Hydroxides	
cuprite	
goethite	
hematite	
lepidocrocite	
pyrolusite	
quartz	
tenorite	

barite crystals were filled with quartz. The pseudomorphosed crystals show a preferred orientation perpendicular to the walls of the vein and occur in several generations separated by dense cryptocrystalline quartz. Small stringers of galena, chalcopyrite and minor fahlores are occasionally observed in the latter, whereas only isolated grains of ore minerals can be found within the former barite crystals. Under weathering conditions these primary ore minerals were partially oxidized, leading to a rich assemblage of secondary minerals (Table 1), predominantly phosphates, arsenates and vanadates. Redistribution and migration of metals during these oxidation reactions have caused secondarily formed minerals to occur as disseminations in adjacent parts of the vein, often well crystallized in open joints and drusy parts.

At the site designated FPNr8.0. in Fig. 1 (Borstein, map coordinates: r3477260 h5508500, topographic map sheet 6218) some minor portions of the vein consist of a dense greyish quartz with abundant younger veinlets of crystalline quartz. Chalcopyrite is a primary mineral but has been largely decomposed into chalcocite and malachite. It was a block of this particular rock that contained the cornubite in clusters of acicular crystals together with goethite as velvet-like coatings on quartz; blue-green crystals of pseudomalachite; light-blue needle-like agardite/mixite crystals; dark-green tabular bayldonite crystals; lightgreen prismatic duftite crystals; colourless to bluish hinsdalite crystals and another not yet identified mineral, probably tsumcorite. The age relationships between the associated minerals are probably quartz — goethite — cornubite + pseudomalachite — agardite/mixite.

Crystals of cornubite are very rare at Reichenbach and only six specimens containing crystals of the mineral have been recovered so far.

Type material is preserved at the Naturhistorisches Museum, Mainz.

Table 1. Mineral phases of the silicified barite vein at Reichenbach.

Elements	*Carbonates*	*Phosphates, (Arsenates, Vanadates)*
copper	azurite	agardite/mixite
silver	bismutite	bayldonite
	calcite	carminite
Sulphides	cerussite	clinobisvanite
chalcopyrite	malachite	cornubite
chalcocite		cornwallite
covellite	*Sulphates, (Chromates, Molybdates, Wolframates)*	descloizite
enargite		duftite
fahlore		mimetite
galena	barite	»mineral TK»
luzonite	beudantite	mottramite
	chalcanthite	olivenite
Halogenides	hinsdalite	pharmacosiderite
chlorargyrite	linarite	pseudomalachite
jodargyrite	vauquelinite	pucherite
	wulfenite	pyromorphite
Oxides and Hydroxides		scorodite
cuprite		vanadinite
goethite		weinschenkite
hematite		
lepidocrocite		
pyrolusite		
quartz		
tenorite		

Appearance and physical properties

Cornubite from Reichenbach crystallizes as apple-green, translucent, mostly tabular crystals //$(2\bar{1}1)$ that are often irregularly intergrown. Individual platelets are up to 0.3 × 0.3 mm in size and up to 0.05 mm thick. The lustre is vitreous, hardness is about 4 on Mohs' hardness scale and the streak is pale green. Two directions of cleavage, both perpendicular to $(2\bar{1}1)$, can be observed: nearly parallel to (011) and $(\bar{1}\bar{1}1)$ intersecting at an angle of about 70°.

Optical investigations were hampered by the high indices of refraction, by the morphology of the crystals and by the rapid reaction of the crystals with the immersion fluids. The refractive indices are between 1.8 and 1.9 ($\bar{n}_{calc}$ = 1.854), the angle of the optical axes is very large, and dispersion has been observed with

Table 2. Observed and calculated powder patterns for cornubite (*: Claringbull *et al.*, 1959; + Debye-Scherrer diagram of a few single crystals from Reichenbach).

d_{calc}	I_{calc}	h k l	d^{*}_{obs}	I^{*}_{obs}	d^{+}_{obs}	I^{+}_{obs}
5.36	17	1 0 0	5.35	60	5.34	30
5.21	1	1 0 $\bar{1}$	5.22	10	5.21	10
4.87	4	1 $\bar{1}$ 0	4.88	10	-	-
4.71	100	0 1 $\bar{1}$	4.72	100	4.69	80
-	-	-	4.53	10	-	-
4.30	7	1 $\bar{1}$ $\bar{1}$	4.31	40	4.27	20
3.93	4	0 1 1	3.93	20	-	-
3.58	20	1 1 $\bar{1}$	3.59	60	3.58	10
3.49	48	1 $\bar{1}$ 1	3.49	80	3.48	40
3.44	3	1 0 1	3.42	10	-	-
3.32	22	1 0 $\bar{2}$	3.33	60	3.34	100
3.11	24	0 0 2	3.10	60	3.10	10
3.05	21	1 $\bar{2}$ 0	3.05	60	3.04	10
2.980	24	0 1 $\bar{2}$	2.98	60	2.98	10
2.933	17	0 2 0	2.932	60	2.927	10
2.917	2	2 0 $\bar{1}$	-	-	-	-
2.868	23	1 1 $\bar{2}$	2.868	70	-	-
2.859	17	0 2 $\bar{1}$	-	-	2.860	30
2.830	1	2 $\bar{1}$ 0	-	-	-	-
2.697	15	1 $\bar{2}$ 1	-	-	-	-
2.679	70	2 0 0	2.688	90	2.673	70
2.624	1	1 1 1	-	-	-	-
2.606	10	2 0 $\bar{2}$	2.616	20	-	-
2.564	12	0 1 2	-	-	-	-
2.561	74	2 $\bar{1}$ $\bar{2}$	2.562	100	2.554	60
-	-	-	2.525	10	-	-
2.486	62	0 2 1	2.489	100	2.478	50
2.452	7	2 $\bar{2}$ $\bar{1}$	-	-	-	-
2.437	16	2 $\bar{2}$ 0	2.443	40	2.440	20
2.402	7	1 $\bar{1}$ 2	-	-	-	-
2.377	11	1 2 $\bar{1}$	2.390	40	2.368	5
2.356	11	0 2 $\bar{2}$	2.358	50	-	-
2.355	6	2 1 $\bar{1}$	-	-	-	-
2.320	11	1 0 2	-	-	-	-
2.304	33	2 $\bar{1}$ 1	2.303	70	2.296	40
2.266	3	1 2 0	2.265	20	-	-
2.260	5	1 0 $\bar{3}$	-	-	-	-
2.235	9	2 1 $\bar{2}$	2.240	40	2.227	10
2.222	2	1 $\bar{2}$ $\bar{2}$	-	-	-	-
2.167	4	2 0 1	2.180	20	-	-
2.152	3	2 $\bar{2}$ $\bar{2}$	-	-	-	-
2.147	4	1 1 $\bar{3}$	2.143	40	-	-
2.137	3	1 $\bar{2}$ 2	-	-	-	-
2.121	2	2 $\bar{2}$ 2	-	-	2.121	10
2.091	25	2 0 $\bar{3}$	2.090	60	2.083	30
2.080	5	1 3 0	-	-	-	-
2.074	8	0 0 3	2.071	50	-	-
2.073	4	1 $\bar{1}$ $\bar{3}$	-	-	-	-
-	-	-	2.027	10B	-	-
1.975	5	1 1 2	1.973	40	-	-
1.969	4	0 3 $\bar{1}$	-	-	1.967	10
1.965	2	0 2 2	-	-	-	-
1.955	22	0 3 0	1.957	60	1.950	20
1.951	4	1 3 $\bar{1}$	-	-	-	-
1.924	7	2 3 0	-	-	-	-
1.918	4	2 1 $\bar{3}$	-	-	-	-
1.914	4	3 $\bar{2}$ $\bar{1}$	1.919	40	-	-
1.911	2	3 0 $\bar{2}$	-	-	1.911	20
1.899	2	3 $\bar{1}$ 0	1.899	10	-	-
1.897	3	2 3 $\bar{1}$	-	-	-	-
1.859	1	0 2 $\bar{3}$	-	-	-	-
1.853	4	0 1 3	1.853	10	-	-
1.829	6	3 $\bar{2}$ 0	1.829	40	-	-
1.822	5	2 2 $\bar{1}$	-	-	-	-
1.814	3	2 $\bar{1}$ 2	-	-	1.813	20
1.809	1	0 3 $\bar{2}$	-	-	-	-
1.792	9	2 2 $\bar{2}$	1.797	40	1.787	10
1.760	1	1 $\bar{3}$ 2	-	-	-	-
1.747	26	2 2 2	1.747	60	1.746	40
1.737	7	3 0 $\bar{3}$	-	-	-	-
1.730	2	1 $\bar{3}$ 1	-	-	-	-
1.722	3	2 $\bar{3}$ $\bar{2}$	-	-	-	-
1.720	5	2 0 2	1.720	20	1.716	10
1.718	1	1 0 $\bar{3}$	-	-	-	-
1.694	3	3 1 $\bar{2}$	1.696	10	-	-
1.662	5	1 3 0	1.662	40B	1.661	10
1.660	4	3 $\bar{3}$ $\bar{1}$	-	-	-	-
1.656	2	3 $\bar{1}$ 1	-	-	-	-
1.629	1	3 $\bar{2}$ 1	1.630	10	-	-
1.608	5	2 $\bar{1}$ $\bar{4}$	1.608	10	-	-
1.591	18	2 1 $\bar{4}$	1.593	50	1.590	10
1.589	3	3 1 $\bar{3}$	-	-	-	-
1.584	2	3 $\bar{3}$ $\bar{2}$	-	-	-	-
1.582	4	1 $\bar{1}$ $\bar{4}$	-	-	-	-
1.576	26	0 1 $\bar{4}$	1.575	70	-	-
1.571	15	0 3 $\bar{3}$	-	-	1.572	10
1.566	2	0 2 3	-	-	-	-
1.563	1	2 $\bar{3}$ 2	-	-	-	-
1.560	2	3 0 1	-	-	-	-
1.544	3	1 1 3	1.544	10	1.539	30
1.524	7	2 1 2			-	-
1.522	27	4 $\bar{1}$ $\bar{2}$	1.524	70	1.522	10
1.518	1	1 3 $\bar{3}$	-	-	-	-
1.514	27	2 2 1	1.515	60	1.512	20
1.506	1	3 0 $\bar{4}$	-	-	-	-
1.501	3	3 $\bar{1}$ $\bar{4}$	-	-	-	-
1.495	5	2 $\bar{4}$ $\bar{1}$	-	-	-	-
1.493	25	2 $\bar{3}$ $\bar{3}$	1.492	70	-	-
1.492	5	4 $\bar{2}$ $\bar{1}$	-	-	-	-
1.488	15	0 4 $\bar{1}$	-	-	1.488	20
1.484	3	1 $\bar{4}$ $\bar{1}$	-	-	-	-
1.468	22	2 $\bar{4}$ 1	1.467	50	1.465	40
1.459	4	2 2 $\bar{4}$	1.457	10	-	-
1.443	3	2 3 $\bar{1}$	1.442	20B	-	-
1.441	5	3 2 2/0 1 4	-	-	1.439	20
1.421	2	3 2 $\bar{1}$	-	-	-	-
1.415	5	4 $\bar{2}$ 0/4 $\bar{1}$ 0	-	-	1.412	10
1.409	2	4 0 $\bar{3}$	-	-	-	-
1.408	4	1 $\bar{2}$ $\bar{4}$	1.408	20	-	-
1.407	1	3 $\bar{2}$ $\bar{4}$	-	-	-	-
1.399	3	3 $\bar{4}$ $\bar{1}$/1 $\bar{1}$ 4	-	-	-	-
1.394	3	2 0 3	-	-	-	-
1.391	2	2 $\bar{4}$ $\bar{2}$	1.392	10	-	-
1.390	1	4 3 $\bar{1}$	-	-	-	-
1.375	3	4 3 $\bar{2}$	-	-	-	-
1.373	3	0 4 1	-	-	-	-
1.371	20	2 3 0/2 3 $\bar{3}$	1.373	60	1.370	10
1.352	1	1 $\bar{4}$ $\bar{2}$	1.353	10	-	-
1.341	3	3 $\bar{4}$ $\bar{2}$	-	-	-	-
1.340	4	2 $\bar{3}$ 3	1.340	40	-	-
1.339	7	430/400/123	-	-	1.336	40
1.336	2	3 0 2	-	-	-	-
1.324	3	4 $\bar{1}$ $\bar{4}$	1.321	10	-	-
1.319	1	3 $\bar{4}$ 1	-	-	-	-
1.312	2	2 $\bar{1}$ $\bar{5}$	-	-	-	-
1.310	8	0 3 3	1.308	40	1.309	10
1.301	2	4 1 $\bar{3}$	-	-	-	-
1.299	6	4 $\bar{3}$ $\bar{3}$	1.300	50	-	-
1.297	9	4 1 $\bar{1}$	-	-	1.297	5
1.293	1	1 4 3	-	-	-	-
1.282	3	0 2 4	1.281	20	-	-
1.280	3	4 $\bar{2}$ 4/4 $\bar{1}$ 1	-	-	-	-
1.273	2	2 1 3	-	-	-	-
1.269	1	1 $\bar{3}$ 4	1.269	10	-	-
1.268	2	1 2 5	-	-	1.268	10
1.256	1	1 1 4	-	-	1.258	5
1.246	2	4 4 $\bar{1}$	-	-	-	-
1.239	3	2 2 5	1.241	10B	-	-
1.228	2	0 2 $\bar{5}$	1.227	20	1.227	5
1.226	3	4 4 $\bar{2}$	-	-	-	-
1.225	2	4 1 $\bar{4}$	-	-	-	-
1.218	2	3 1 2	-	-	-	-
1.217	2	2 5 $\bar{1}$	1.217	20	-	-
1.216	2	1 4 1	-	-	1.216	5
1.214	1	4 0 1	-	-	-	-
1.208	1	3 $\bar{2}$ $\bar{5}$	-	-	-	-
1.205	7	2 1 $\bar{4}$	1.203	40B	-	-
1.199	3	5 $\bar{2}$ $\bar{1}$/3 3 $\bar{1}$	-	-	1.195	5
1.191	2	1 $\bar{5}$ 2	1.190	10	-	-
1.181	3	4 $\bar{1}$ 5/2 4 $\bar{1}$	1.181	20	-	-
1.178	5	0 4 $\bar{4}$/4 2 $\bar{2}$	-	-	1.178	5
1.175	6	0 1 5	1.172	20	-	-
1.171	1	5 3 $\bar{2}$	-	-	-	-
1.169	1	0 5 2	-	-	-	-
1.165	1	3 3 3	-	-	-	-
1.162	1	1 3 $\bar{5}$	-	-	-	-
1.161	1	5 3 $\bar{1}$	-	-	-	-
1.157	2	1 4 $\bar{4}$	1.158	10	-	-
1.156	2	2 $\bar{5}$ 2	-	-	-	-
1.152	8	4 $\bar{2}$ 2	-	-	1.153	5
1.151	6	4 $\bar{4}$ 1/2 $\bar{3}$ 4	1.151	40	-	-
1.142	1	5 $\bar{1}$ $\bar{4}$	-	-	-	-
1.137	2	1 $\bar{2}$ 5	-	-	-	-
1.134	1	2 2 $\bar{3}$	-	-	-	-
1.130	5	2 0 $\bar{6}$	-	-	-	-
1.124	3	2 3 $\bar{5}$/5 $\bar{1}$ 0	-	-	-	-
1.117	2	0 5 1	-	-	-	-
1.113	1	5 0 $\bar{4}$	-	-	-	-
1.112	1	1 $\bar{5}$ 3	-	-	-	-
1.110	1	0 5 $\bar{3}$	-	-	-	-
1.101	2	2 $\bar{3}$ $\bar{5}$	-	-	-	-
1.099	5	4 $\bar{5}$ $\bar{1}$	-	-	1.097	10

red > blue. For lack of
could not be determined e
calculated density is 4.85
given by Claringbull *et*
crystalline material is 4.6

An analysis by electron
Camebax, MISO progra
with 20kV, 15nA gave
58.60, SiO_2 0.34, P_2O_5 0.
0.32, H_2O(calc) 5.27 we
weight %, as the average
on a single crystal of co
the empirical formula
$Al_{0.020}Si_{0.038})_{2.013}O_8(OH)_4$ o
ative charges (8 O and 4
were $SrCuSi_4O_{10}$, $2Fe_2O_3$
$AlPO_4$ and Fe_3O_4. The i
$(AsO_4)_2(OH)_4$ was used
culations.

Peak-search and inde
automatic 4-circle X-ra
subsequent precession p
triclinic unit cell, space
6.121(1), b = 6.251(1),
92.93(1)°, β = 111.30(1)
= 227.09 Å^3, Z = 1. Th
re refined from the sett
with 24° ≤ θ ≤ 29° wh

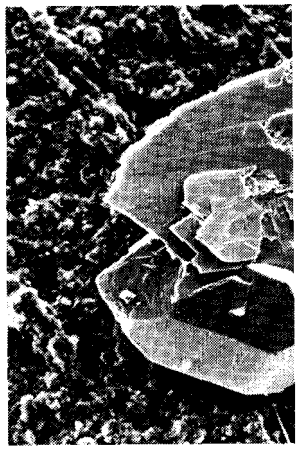

Fig. 2. Cornubite crystal, tabula
(crystal size: 0.

red > blue. For lack of material, the density could not be determined experimentally, but the calculated density is 4.85 Mg/m^3; the density given by Claringbull *et al.* (1959) for cryptocrystalline material is 4.64 Mg/m^3.

An analysis by electron microprobe (Cameca Camebax, MISO program (Abraham 1970)) with 20kV, 15nA gave As_2O_5 32.01, CuO 58.60, SiO_2 0.34, P_2O_5 0.25, Al_2O_3 0.15, Fe_2O_3 0.32, H_2O(calc) 5.27 weight %, total 96.64 weight %, as the average of 20 measurements on a single crystal of cornubite. This leads to the empirical formula $Cu_{5.03}(As_{1.903}P_{0.024}Fe_{0.027}Al_{0.020}Si_{0.038})_{2.013}O_8(OH)_4$ on the basis of 20 negative charges (8 O and 4 OH). The standards were $SrCuSi_4O_{10}$, $2Fe_2O_3 \cdot As_2O_5$, Al_2O_3, SiO_2, $AlPO_4$ and Fe_3O_4. The idealized formula $Cu_5(AsO_4)_2(OH)_4$ was used for all structural calculations.

Peak-search and indexing routines on an automatic 4-circle X-ray diffractometer and subsequent precession photographs yielded a triclinic unit cell, space group $P\bar{1}$ with a = 6.121(1), b = 6.251(1), c = 6.790(1) Å, α = 92.93(1)°, β = 111.30(1)°, γ = 107.47(1)°, V = 227.09 Å^3, Z = 1. The lattice constants were refined from the settings of 25 reflections with $24° \leq \theta \leq 29°$ which had been centred on the diffractometer (MoK_α radiation). Table 2 contains the observed powder patterns of cornubite from Cornwall (Claringbull *et al.* 1959) and from Reichenbach as well as a pattern calculated from the refined atomic coordinates. The differences in the estimated intensity observations may be due to the small number of crystals from Reichenbach available for a Debye-Scherrer diagram.

The scanning electron microscope photograph in Fig. 2 shows a cornubite single crystal of typical shape intergrown with a quartz crystal.

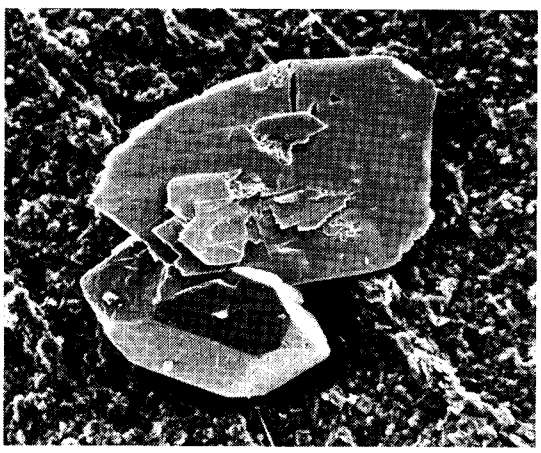

Fig. 2. Cornubite crystal, tabular // $(2\bar{1}1)$ with quartz crystal (crystal size: 0.3 × 0.2 mm).

Determination of the crystal structure

The intensities of 2982 reflections with $\theta < 40°$ were measured on an automatic 4-circle diffractometer (Enraf-Nonius CAD-4) with monochromatized MoK_α radiation, $\omega/2\theta$ step scan mode and a scan width of $\Delta\omega = 0.60 + 0.5\tan\theta$. The intensity and orientation of three standard reflections were monitored regularly. The instability of the measurement (Stout and Jensen 1968) was less than 0.006 for the three reference reflections. The data were corrected for Lorentz polarization and absorption effects. The crystal used for data collection was tabular // $(2\bar{1}1)$ with approximate dimensions of 0.3 × 0.2 × 0.01 mm. The linear absorption coefficient was 18.85 mm^{-1} and the transmission factors were between 0.800 and 0.076. Averaging of equivalent reflections gave 2809 unique reflections, 383 of which were considered to be unobserved ($I < 2\sigma_I$).

The positions of Cu and As atoms were determined from the Patterson synthesis. Several cycles of Fourier and difference syntheses gave a model of the structure which could be refined with least-squares methods to a residual of 0.033 for 2436 observed structure factors. The R-value for all 2809 reflections was 0.042. Atomic scattering factors and correction factors for anomalous dispersion were taken from »In-

Table 3. Fractional atomic coordinates with the significant figures of the estimated standard deviations in parentheses and vibrational parameters (in Å²: B(eq) = 8/3 π^a trace U).

atom	X/a	Y/b	Z/c	B(eq)
Cu(1)	0.0	0.0	0.0	0.54(1)
Cu(2)	—0.00406(5)	0.32402(5)	0.33203(5)	0.62(1)
Cu(3)	0.50677(5)	0.32154(5)	0.32393(5)	0.54(1)
As	0.44718(4)	0.17614(4)	0.79809(4)	0.48(1)
O(1)	0.8327(3)	0.6883(3)	0.8602(3)	0.56(5)
O(2)	0.8386(4)	0.9905(3)	0.2147(3)	0.71(5)
O(3)	0.6034(4)	0.0162(3)	0.7386(3)	0.74(5)
O(4)	0.8383(3)	0.3443(3)	0.5329(3)	0.59(5)
O(5)	0.3818(4)	0.3395(3)	0.6067(3)	0.67(5)
O(6)	0.3650(4)	0.6572(3)	0.9623(3)	0.78(5)

ternational Tables for X-ray Crystallography», Vol.IV (1974). A table of observed and calculated structure factors is available upon request. The refined fractional atomic coordinates and thermal parameters are given in Table 3. The computer programs used in the course of the work are the same as given by Tillmanns, Hofmeister and Baur (1983).

Results and discussion

The most prominent feature of the crystal structure of cornubite is the sheet of edge-sharing CuO_6 octahedra parallel to $(0\bar{1}1)$. Individual sheets are linked via common corners by AsO_4 tetrahedra and by hydrogen bonds. Figure 3 shows a polyhedral representation of the crystal structure, and Figure 4 the arrangement of

Table 4. Interatomic distances (Å) and angles (°). The standard deviations of O—O distances are less than 0.005 Å.

Cu(1)	—	O(1)	2x	1.911(2)		Cu(3)	—	O(4)	1.966(1)		
Cu(1)	—	O(2)	2x	2.031(1)		Cu(3)	—	O(1)	1.978(1)		
Cu(1)	—	O(3)	2x	2.467(1)		Cu(3)	—	O(3)	1.984(2)		
O(1)	—	O(1)		3.822	180.0(1)	Cu(3)	—	O(5)	1.994(2)		
O(1)	—	O(2)	2x	2.966	97.5(1)	Cu(3)	—	O(5)	2.320(2)		
O(1)	—	O(2)	2x	2.600	82.5(1)	Cu(3)	—	O(6)	2.342(2)		
O(1)	—	O(3)	2x	2.812	78.8(1)	O(4)	—	O(1)	3.938	173.9(1)	
O(1)	—	O(3)	2x	3.402	101.2(1)	O(4)	—	O(3)	2.843	92.1(1)	
O(2)	—	O(2)		4.062	180.0(1)	O(4)	—	O(5)	2.735	87.4(1)	
O(2)	—	O(3)	2x	3.059	85.1(1)	O(4)	—	O(5)	3.004	88.6(1)	
O(2)	—	O(3)	2x	3.327	94.9(1)	O(4)	—	O(6)	3.131	92.9(1)	
O(3)	—	O(3)		4.935	180.0(1)	O(1)	—	O(3)	2.812	90.4(1)	
						O(1)	—	O(5)	2.808	90.0(1)	
Cu(2)	—	O(4)		1.954(1)		O(1)	—	O(5)	2.930	85.6(1)	
Cu(2)	—	O(1)		1.960(1)		O(1)	—	O(6)	3.136	92.7(1)	
Cu(2)	—	O(2)		1.994(1)		O(3)	—	O(5)	3.978	178.8(1)	
Cu(2)	—	O(4)		2.009(1)		O(3)	—	O(5)	3.192	95.4(1)	
Cu(2)	—	O(5)		2.390(1)		O(3)	—	O(6)	3.076	90.3(1)	
Cu(2)	—	O(6)		2.421(1)		O(5)	—	O(5)	2.881	83.4(1)	
O(4)	—	O(1)		3.914	177.6(1)	O(5)	—	O(6)	3.098	90.9(1)	
O(4)	—	O(2)		3.013	99.5(1)	O(5)	—	O(6)	4.655	174.1(1)	
O(4)	—	O(4)		2.515	78.8(1)						
O(4)	—	O(5)		3.189	93.9(1)	As	—	O(6)	1.674(2)		
O(4)	—	O(6)		3.131	90.8(1)	As	—	O(3)	1.700(1)		
O(1)	—	O(2)		2.600	82.2(1)	As	—	O(5)	1.701(2)		
O(1)	—	O(4)		3.029	99.5(1)	As	—	O(2)	1.714(1)		
O(1)	—	O(5)		2.930	84.1(1)	O(6)	—	O(3)	2.717	107.3(1)	
O(1)	—	O(6)		3.144	91.1(1)	O(6)	—	O(5)	2.765	110.0(1)	
O(2)	—	O(4)		4.001	176.7(1)	O(6)	—	O(2)	2.842	114.0(1)	
O(2)	—	O(5)		3.394	101.1(1)	O(3)	—	O(5)	2.770	109.1(1)	
O(2)	—	O(6)		2.945	83.1(1)	O(3)	—	O(2)	2.824	111.6(1)	
O(4)	—	O(5)		2.735	76.4(1)	O(5)	—	O(2)	2.705	104.8(1)	
O(4)	—	O(6)		3.395	99.6(1)						
O(5)	—	O(6)		4.802	173.1(1)						

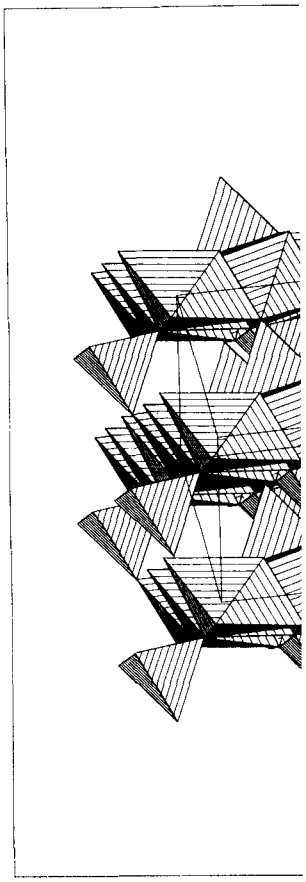

Fig. 3. Crystal struct

Fig. 4. Sheet of CuO_6 octahe $(0\bar{1}1)$ in the crystal structure o nubite.

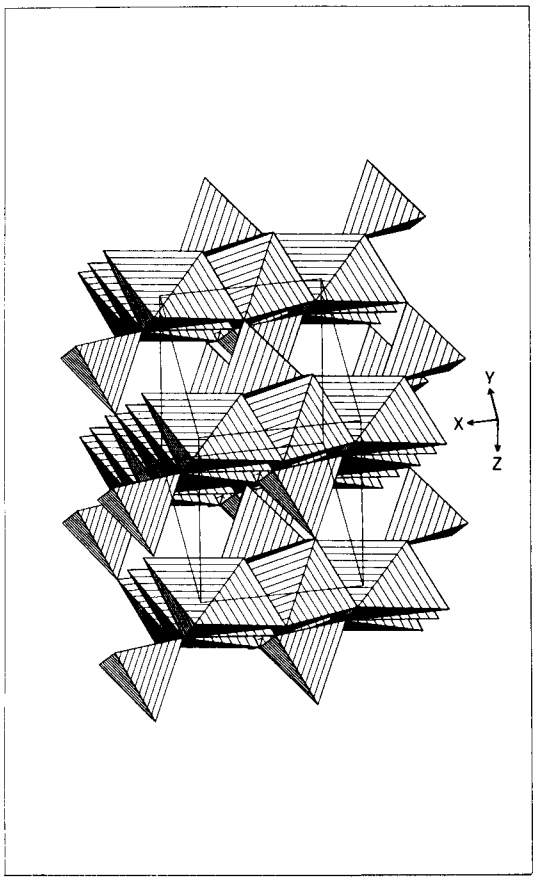

Fig. 3. Crystal structure of cornubite.

CuO_6 octahedra within one sheet. Interatomic distances and angles are listed in Table 4.

All three crystallographically different copper atoms have a distorted octahedral or tetragonal bipyramidal coordination of 4 + 2 oxygen atoms, as it is often found for coordination of oxygen atoms around copper (Zemann 1972). The arrangement of the four closer oxygen atoms is almost planar with values of 360°, 359.91° and 359.89° for the sums of the four O—Cu—O angles around Cu(1), Cu(2) and Cu(3). The average Cu—O distances in the plane are 1.971, 1.979 and 1.981 Å respectively.

The AsO_4 tetrahedra share all four corners with CuO_6 octahedra, three in the same octahedral sheet and the fourth in an adjacent one. The spread of individual As—O distances is small, as are the deviations of tetrahedral angles from the ideal value of 109.47°.

An inspection of the bond strength sums received by each oxygen atom from the surrounding cations (Table 5) reveals that O(1) and O(4), which are coordinated by three Cu with a bond strength sum of 1.0 v.u., are the most likely (OH)-sites. Hydrogen bonds are probably formed from O(1) to an oxygen atom O(6), which is not in the same CuO_6 octahedron as O(1), at a

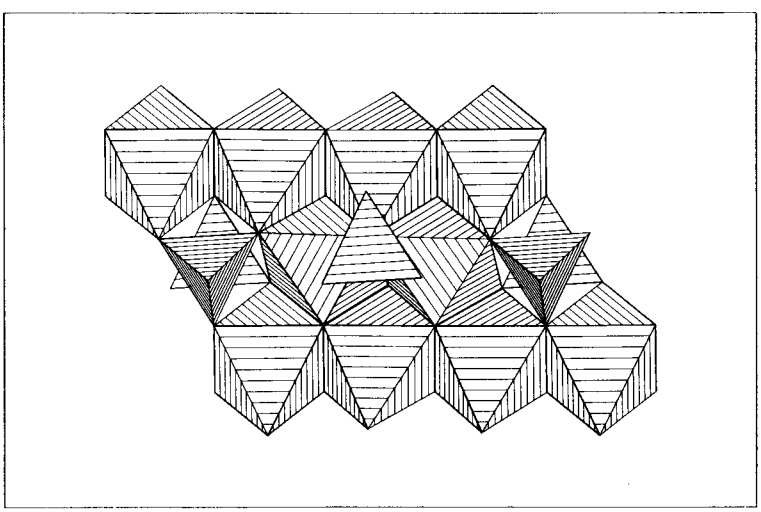

Fig. 4. Sheet of CuO_6 octahedra // $(0\bar{1}1)$ in the crystal structure of cornubite.

Table 5. Electrostatic bond strength sums (Baur 1970, Pauling 1960).

atom	Cu(1)	Cu(2)	Cu(3)	As	H(D)	H(A)	Σ
O(1)	0.33	0.33	0.33	—	0.83	—	1.83
O(2)	0.33	0.33	—	1.25	—	—	1.92
O(3)	0.33	—	0.33	1.25	—	0.17	2.09
O(4)	—	2×0.33	0.33	—	0.83	—	1.83
O(5)	—	0.33	2×0.33	1.25	—	—	2.25
O(6)	—	0.33	0.33	1.25	—	0.17	2.09

distance of 2.709 Å, and from O(4) to O(3) at a distance of 2.865 Å.

$Cu_5(AsO_4)_2(OH)_4$ has been found in nature in two polymorphic forms, triclinic cornubite and monoclinic cornwallite. Three polymorphs are known for the analogous phosphate compound: the mineral pseudomalachite (Shoemaker, Anderson and Kostiner 1977) and two synthetic polymorphs: »PPM» (Anderson, Shoemaker, Kostiner and Ruszala 1977) and »QPM» (Shoemaker, Anderson and Kostiner 1981), which have also been found in nature (Shoemaker and Kostiner 1981). Two of these, pseudomalachite and the natural analog of »PPM», have also been identified in samples from Reichenbach.

Although similarities in X-ray diffraction patterns and lattice constants of cornwallite and pseudomalachite lead to the assumption that both minerals are isostructural, this is not true for cornubite and »QPM» even though both minerals crystallize in space group $P\bar{1}$, have similar X-ray diffraction patterns and comparable unit cell volumes of 219.6 $Å^3$ and 227.1 $Å^3$, respectively. The unit cell dimensions of »QPM» are a = 4.445, b = 5.873, c = 8.668 Å, $\alpha = 103.62$, $\beta = 90.35$, $\gamma = 93.02°$. Transformation of the unit cell of cornubite so that the CuO_6 octahedral sheets are oriented the same way in both cells gives a = 9.46 (2×4.73), b = 6.12, c = 8.99 Å and $\alpha = 119$, $\beta = 85$, $\gamma = 93°$ (transformation matrix: $0\bar{1}1/\ 1\ 0\ 0/\ 0\ 1\ 1$). It is to this B-centred cell that the layer-line spacings derived by Claringbull *et al.* (1959) from a fibre photograph correspond.

Topological analyses of the crystal structures (Baur, Tillmanns and Hofmeister 1983) show that, while CuO_6 octahedra are topologically identical in both structures, their connection is not. This results in a different arrangement of edge-sharing CuO_6 octahedra within one sheet. A difference also exists in the way in which two octahedral sheets are linked by XO_4 tetrahedra: in cornubite, the AsO_4 tetrahedra share three corners with one sheet and the fourth with an adjacent one; in »QPM» the PO_4 tetrahedra share two corners each with neighbouring sheets.

The structures can be expressed formally as close-packed arrangements of oxygen atoms with Cu in octahedral and P or As in tetrahedral voids. This arrangement, however, is appreciably distorted in the phosphate polymorphs, probably because of the smaller dimensions of the PO_4 tetrahedron. Thus the pseudohexagonal angle in »QPM» is reduced to 104° from its ideal value of 120°, whereas in cornubite it is 119°.

These distortions are also reflected in the shape of the coordination octahedra around Cu, which are much more irregular in »QPM» than in cornubite.

Acknowledgements. The authors are indebted to Dr. K. Abraham and Dr. B. Schulz-Dobrick for the microprobe analyses and to N. Sieber, Dr. R. Krupp and Dr. O. Medenbach for useful discussions. Computing time was provided by the Computing Center of the University of Mainz.

References

Abraham, K., 1970. MISO. Univ
Anderson, J. B.; Shoemaker, G. . la, F. A., 1977. The crystal st $(PO_4)_2(OH)_4$, a polymorph c Mineral. 62, 115—121.
Baier, E. & Venzlaff, V., 1961. Ü Barytgängen. Notizbl. hess. I 365—379.
Baur, W. H., 1970. Bond lengtl coordination polyhedra in ir Amer. Cryst. Assoc. 6, 129—
Baur, W. H.; Tillmanns, E. & Ho logical analysis of crystal stru 669—674.
Claringbull, G. F.; Hey, M. H. & nubite, a new mineral dimo Min. Mag. 32, 1—6.
Dreyer, G., 1973. Neue Mineral Pollichia III. Reihe, 20, 113–
International Tables for X-ray Cr vised and supplementary table Hamilton, W. C., *eds.)*. Birm

References

Abraham, K., 1970. MISO. University of Bochum, FRG.

Anderson, J. B.; Shoemaker, G. L.; Kostiner, E. & Ruszala, F. A., 1977. The crystal structure of synthetic $Cu_5(PO_4)_2(OH)_4$, a polymorph of pseudomalachite. Am. Mineral. 62, 115—121.

Baier, E. & Venzlaff, V., 1961. Über die Verquarzung von Barytgängen. Notizbl. hess. L.-Amt Bodenforsch. 89, 365—379.

Baur, W. H., 1970. Bond length variation and distorted coordination polyhedra in inorganic crystals. Trans. Amer. Cryst. Assoc. 6, 129—155.

Baur, W. H.; Tillmanns, E. & Hofmeister, W., 1983. Topological analysis of crystal structures. Acta Cryst. B 39, 669—674.

Claringbull, G. F.; Hey, M. H. & Davis, R. J., 1959. Cornubite, a new mineral dimorphous with cornwallite. Min. Mag. 32, 1—6.

Dreyer, G., 1973. Neue Mineralien der Rheinpfalz. Mitt. Pollichia III. Reihe, 20, 113—136.

International Tables for X-ray Crystallography, Vol IV. Revised and supplementary tables, 1974. (Ibers, I. A. and Hamilton, W. C., *eds.)*. Birmingham, Kynoch Press.

Pauling, L., 1960. The Nature of the Chemical Bond. 3rd ed. Ithaca: Cornell Univ. Press.

Shoemaker, G. L.; Anderson, J. B. & Kostiner, E., 1977. Refinement of the crystal structure of pseudomalachite. Am. Mineral. 62, 1042—1048.

Shoemaker, G. L.; Anderson, J. B. & Kostiner, E., 1981. The crystal structure of a third polymorph of $Cu_5(PO_4)_2(OH)_4$. Am. Mineral. 66, 169—175.

Shoemaker, G. L. and Kostiner, E., 1981. Polymorphism in $Cu_5(PO_4)_2(OH)_4$. Am. Mineral. 66, 176—181.

Stout, G. H. & Jensen, L. H., 1968. X-ray Structure Determination. A Practical Guide. 1st printing. New York: The Macmillan Company.

Tillmanns, E.; Hofmeister, W. & Baur, W. H., 1983. Crystal Structure of the Microwave Dielectric Resonator $Ba_2Ti_9O_{20}$. J. Am. Ceram. Soc. 66, 268—271.

Walenta, K., 1975. Die Sekundärmineralien des Schwerspatganges der Grube Clara bei Oberwolfach im mittleren Schwarzwald. Der Aufschluß 26, 369—411.

Walenta, K., 1979. Die Sekundärmineralien der Erzgänge von Neubulach im nördlichen Schwarzwald. Der Aufschluß 30, 213—252.

Zemann, J., 1972. Copper. Crystal Chemistry. Handbook of Geochemistry, Vol. II, (Wedepohl, K. H. *ed.*). Berlin: Springer-Verlag.