

## The crystal structure of the new mineral richelsdorfite, $\text{Ca}_2\text{Cu}_5\text{Sb}(\text{Cl}/(\text{OH})_6/(\text{AsO}_4)_4) \cdot 6 \text{H}_2\text{O}$

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*Dedicated to the memory of Martin J. Buerger*

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### *Richelsdorfite | Antimony | Arsenate | Crystal structure*

**Abstract.** Richelsdorfite, a hydrated arsenate of calcium, copper and antimony, is monoclinic,  $C2/m$ , with  $a = 14.079(5)$ ,  $b = 14.203(6)$ ,  $c = 13.470(5)$  Å,  $\beta = 101.05(7)^\circ$ ,  $V = 2643$  Å<sup>3</sup>,  $D(\text{obs}) = 3.2(1)$  g · cm<sup>-3</sup>,  $Z = 4$ . The crystal structure consists of dense-packed pseudotetragonal layers parallel (001) having a chemical composition  $[\text{Ca}_2\text{Cu}_5\text{Cl}(\text{AsO}_4)_4]^+$ . Penta-valent antimony, octahedrally coordinated by six hydroxyl groups, and water molecules occupy the area between the layers making up an inter-layer composition of  $[\text{Sb}(\text{OH})_6 \cdot 6\text{H}_2\text{O}]^-$ . Both structural parts combined result in a chemical formula  $\text{Ca}_2\text{Cu}_2\text{Sb}[\text{Cl}/(\text{OH})_6/(\text{AsO}_4)_4] \cdot 6\text{H}_2\text{O}$  for richelsdorfite.

### **Introduction**

Richelsdorfite is a new secondary mineral originally found in the Richelsdorfer Gebirge, Hessen, Germany, and later also found at St. Andreasberg in the Harz (Süsse and Schnorrer-Köhler, 1983). Recently, a further occurrence has been reported from the Clara Mine in the Black Forest (Walenta, 1985).

The crystal structure determination was undertaken mainly to establish a reliable chemical formula for the new mineral. This was not possible on

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**Table 1.** Crystal and unit-cell data for richelsdorffite.

Locality of crystal	Iba near Richelsdorf, Hessen, Germany
Shape of crystal	square, platy, twinned parallel (001)
Size of crystal	0.150 × 0.150 × 0.015 mm
Chemical formula	Ca <sub>2</sub> Cu <sub>5</sub> Sb(Cl(OH) <sub>6</sub> (AsO <sub>4</sub> ) <sub>4</sub> ) · 6H <sub>2</sub> O
Laue symmetry	2/m
Extinctions	<i>hkl</i> only $h + k + l = 2n$
Space group	<i>C2/m</i>
Density	$D(\text{obs}) = 3.2(1) \text{ g} \cdot \text{cm}^{-3}$ , $D(\text{calc}) = 3.30 \text{ g} \cdot \text{cm}^{-3}$
Cell dimensions	$a = 14.079(5)$ , $b = 14.203(6)$ , $c = 13.470(5) \text{ \AA}$ , $\beta = 101.05(7)^\circ$
Cell volume	$V = 2643 \text{ \AA}^3$
Cell content	$Z = 4$

the basis of the chemical analysis alone, since neither the valence state of antimony nor the OH<sup>-</sup>/H<sub>2</sub>O relation was known. Crystal chemical considerations on the basis of the determined crystal structure should solve both problems. The knowledge of the crystal structure should also lead to explain the excellent cleavage parallel (001), the twinning parallel to that same plane and the pseudo-tetragonal morphological appearance of the crystals.

The mineral was approved by the I.M.A. Commission on new minerals and mineral names in 1982. Chemical and mineralogical data were published by Süsse and Schnorrer-Köhler, l.c., and preliminary crystal structure results by Tillmann and Süsse, 1982.

### Unit cell and twinning

Richelsdorffite crystallizes in pseudo-tetragonal, small (< 0.5 mm), sky-blue, translucent, platy crystals parallel (001). They show an excellent cleavage parallel to that plane. Single crystal X-ray photographs reveal that they are generally twinned, twinning plane being (001). The twinning causes complete overlapping of reflections of the twin individuals in the reciprocal lattice plane *0kl* and nearly overlapping in *8kl*.

The unit-cell parameters were determined and least-squares refined on the basis of four-circle diffractometer measurements of a crystal of the original locality. The results are compiled in Table 1.

### Structure determination and refinement

The positions of the heavy atoms Sb, As, Cu and Ca were found through Patterson methods, the positions of the oxygen atoms through subsequent Fourier syntheses. Parameter refinement was carried out with least-squares techniques. The refinement was based on 2618 *hkl* data, excluding the 123

$0kl$  data, because of twin overlapping, and the four innermost reflections, because of obvious measurement errors. Of the remaining 2618  $F_o(hkl)$  365 were  $< 1 \sigma(F_o)$ . They were included in the refinement procedure with assigned values of  $F_o = 1/2 \sqrt{2} \sigma(F_o)$  and unit weights were employed. Atomic scattering curves for  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ , Sb, and As were taken from Table 3.3.1 B and those for Cl and O from Table 3.31 A of Vol. 3 of International Tables for X-ray Crystallography (1962). Details of the X-ray diffraction measurement and the least-squares refinement procedure are compiled in Table 2. The refined positional and isotropic thermal atomic parameters are given in Table 3. Table 4 contains the root-mean-square amplitudes of the principal axes of the ellipsoids of vibration and their orientation with respect to the reciprocal lattice directions. They are given only for the heavy atoms. Their physical meaning should not be overstressed because of the low accuracy of the anisotropic temperature coefficients from which they are derived. However, they seem to indicate a preferential vibration of the Cu and As atoms in the  $c^*$  direction, which is perpendicular to the layers discussed below. On the other hand, Ca and Sb, which are not as strongly attached to those layers, do not show a particular anisotropy of vibration.

Selected interatomic distances and angles are compiled in Table 5<sup>1</sup>.

### Crystal chemistry

One of the main objects of the crystal structure analysis of this mineral was to find the valence state of antimony. This in turn is related to the problem of determining the hydroxyl/water relation in the structure. The fact of antimony being octahedrally coordinated by oxygens strongly favored the assumption of pentavalent antimony in richelsdorffite. Crystal structure investigations of numerous oxydic antimony compounds show that the coordination polyhedra of Sb(III) and Sb(V) are quite different: rather irregular fivefold coordination about Sb(III) and more or less regular octahedral coordination about Sb(V). In  $\alpha\text{-Sb}_2\text{O}_4$  (Thornton, 1977) and pyrochlore (Piffard et al., 1978) both types of antimony coordination may be studied at the same time. In oxydic antimony minerals fivefold coordinated Sb(III) occurs for example in peretaite (Cipriani and Menchetti, 1980) and klebelsbergite (Menchetti and Sabelli, 1980). Mineral examples of crystal structures containing octahedrally coordinated Sb(V) are, among others, mammothite (Effenberger, 1985), bahianite (Moore and Araki, 1976), and manganostibite (Moore, 1970).

<sup>1</sup> Additional material to this paper can be ordered referring to the no. CSD 52287, names of the authors and citation of the paper at the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2.

**Table 2.** X-ray diffraction data measurement and refinement of richelsdorffite.

Crystal	identical with crystal described in Table 1
Instrument	STOE four-circle diffractometer
Radiation	graphite monochromatized MoK $\alpha$
Technique	2 $\omega$ : $\theta$ = 1:1 scan, step width 0.01°, 55 to 65 steps per reflection, 0.5 to 1.5 s per step
Number of data recorded	5472 $hkl$ reflections up to $\sin \theta/\lambda = 0.6200 \text{ \AA}^{-1}$
Independent data	2745 $hkl$ reflections
Range of $h, k, l$	$h$ : -16 to 16, $k$ : 0 to 16, $l$ : -16 to 16
Data used in refinement	2618 $hkl$ reflections, excluding $0kl$ reflections
Corrections	polarisation and Lorentz, absorption ( $\mu = 54 \text{ cm}^{-1}$ )
$R$ values	0.093 for all 2618 reflections and isotropic temperature factors
	0.084 for all 2618 reflections and anisotropic temperature factors
	0.063 for 1721 reflections with $I > 3 \sigma(I)$ and isotropic temperature factors
	0.053 for 1721 reflections with $I > 3 \sigma(i)$ and anisotropic temperature factors

**Table 3.** Positional and isotropic thermal atomic parameters of richelsdorffite. Standard deviations are given in parentheses. Oxygens of hydroxyl groups are designated as Oh, those of water molecules as Ow. Site occupancy factors are 1 for all atoms, except Cl (0.77  $\pm$  0.03).

Atoms	Wyckoff notation	Point symmetry	$x$	$y$	$z$	$B(\text{\AA}^2)$
Ca	8( $j$ )	1	0.0408(2)	0.2431(1)	0.2320(2)	1.38(5)
Cu(1)	4( $i$ )	$m$	0.2904(2)	0	0.2369(2)	0.70(4)
Cu(2)	8( $j$ )	1	0.1452(1)	0.3852(1)	0.0570(1)	0.82(3)
Cu(3)	8( $j$ )	1	0.3723(1)	0.3867(1)	0.0562(1)	0.80(3)
Sb	4( $f$ )	$\bar{1}$	1/4	1/4	1/2	1.32(2)
As(1)	4( $i$ )	$m$	0.0673(1)	0	0.1319(2)	0.54(3)
As(2)	4( $i$ )	$m$	0.4809(1)	0	0.1322(2)	0.53(3)
As(3)	8( $j$ )	1	0.2735(1)	0.2062(1)	0.1324(1)	0.49(2)
Cl	4( $i$ )	$m$	0.2790(6)	1/2	0.1575(7)	2.06(15)
O(1)	4( $i$ )	$m$	0.1166(9)	0	0.0242(10)	0.52(21)
O(2)	4( $i$ )	$m$	0.1538(9)	0	0.2361(11)	1.12(24)
O(3)	8( $j$ )	1	0.0030(7)	0.1010(8)	0.1296(8)	1.39(17)
O(4)	4( $i$ )	$m$	0.3967(9)	0	0.0227(10)	0.66(21)
O(5)	4( $i$ )	$m$	0.4275(9)	0	0.2320(10)	0.80(22)
O(6)	8( $j$ )	1	0.0453(7)	0.3989(8)	0.1358(8)	1.56(18)
O(7)	8( $j$ )	1	0.2886(7)	0.1386(7)	0.2346(8)	1.24(17)
O(8)	8( $j$ )	1	0.2565(6)	0.1422(7)	0.0247(7)	0.98(16)
O(9)	8( $j$ )	1	0.1680(6)	0.2670(7)	0.1292(8)	1.13(16)
O(10)	8( $j$ )	1	0.3760(6)	0.2691(7)	0.1326(8)	1.47(18)
O(11) $h$	8( $j$ )	1	0.3666(8)	0.1817(9)	0.4805(9)	2.69(23)
O(12) $h$	8( $j$ )	1	0.1839(7)	0.2174(8)	0.3617(8)	1.31(17)
O(13) $h$	8( $j$ )	1	0.3033(9)	0.3633(10)	0.4458(11)	3.84(28)
O(14) $w$	4( $i$ )	$m$	0.3307(12)	0	0.4047(15)	2.93(35)
O(15) $w$	4( $i$ )	$m$	0.1007(11)	0	0.4242(12)	2.21(30)
O(16) $w$	8( $j$ )	1	0.4988(8)	0.1500(9)	0.3513(9)	2.66(23)
O(17) $w$	8( $j$ )	1	0.4715(8)	0.3525(10)	0.3493(10)	2.94(26)

**Table 4.** Parameters of the ellipsoids of thermal vibrations of the heavy atoms in richelsdorfit.

Atoms	Root-mean-square amplitudes along the principal axes (Å)	Angles with the reciprocal lattice vectors (°)		
		a*	b*	c*
Ca	0.14	93	124	145
	0.13	94	34	124
	0.12	6	88	84
Cu(1)	0.08	11	90	90
	0.07	90	0	90
	0.13	79	90	0
Cu(2)	0.09	37	71	110
	0.08	110	21	92
	0.13	61	81	20
Cu(3)	0.13	79	90	158
	0.08	83	7	87
	0.09	13	97	69
Sb	0.14	89	83	167
	0.13	96	8	85
	0.12	6	84	78
As(1)	0.10	82	90	160
	0.06	90	0	90
	0.07	8	90	71
As(2)	0.07	14	90	93
	0.04	90	0	90
	0.12	76	90	3
As(3)	0.07	9	88	88
	0.05	91	2	91
	0.11	81	89	2

The problem of the valence state of antimony being settled in favor of Sb(V), the next question concerned the nature of oxygen atoms surrounding antimony and the other cations. To solve this problem, valence bond strengths for oxygen atoms were calculated after Brown and Wu (1976). The results are compiled in Table 6. The valence bond strength sums for the oxygen atoms in the last column of Table 6 indicate that O(1) to O(10) are of the type of O<sup>2-</sup>, O(11) to O(13) to be hydroxyl oxygen atoms and O(14) to O(17) to be oxygen atoms of water molecules.

The next step was to find a model of a possible system of hydrogen bonds in this structure. For this purpose all oxygen-oxygen contacts < 3.10 Å outside cation polyhedra were taken into consideration. Starting with O(2), O(5), and O(7), which can serve only as acceptors, a hydrogen

**Table 5.** Selected interatomic distances (Å) and angles (°) in richelsdorffite. Standard deviations are given in parentheses.

Ca—O(3)	2.44(1)	O(3) — Ca—O(6)	116.7(4)
—O(6)	2.57(1)	O(9) — —O(10)	114.3(4)
—O(9)	2.49(1)	O(12) <i>h</i> — —O(16) <i>w</i>	83.6(4)
—O(10)	2.45(1)	O(17) <i>w</i> — —O(3)	80.5(4)
—O(12) <i>h</i>	2.43(1)	O(6) — —O(9)	60.8(4)
—O(16) <i>w</i>	2.37(1)	O(12) <i>h</i> — —O(10)	161.8(9)
—O(17) <i>w</i>	2.43(1)	O(16) <i>w</i> — —O(17) <i>w</i>	74.5(4)
Cu(1)—O(2)	1.92(2)	O(5)—Cu(1)—O(7)	90.5(3) 2 ×
—O(5)	1.94(2)	O(2)— —O(7)	89.4(3) 2 ×
—O(7)	1.97(1) 2 ×	O(5)— —O(14) <i>w</i>	88.5(7)
—O(14) <i>w</i>	2.22(2)	O(2)— —O(14) <i>w</i>	93.8(7)
		O(7)— —O(14) <i>w</i>	90.9(3) 2 ×
Cu(2)—O(4)	1.98(1)	O(4)—Cu(2)—O(6)	92.4(5)
—O(6)	1.93(1)	O(8)— —O(9)	92.5(4)
—O(8)	1.96(1)	O(6)— —O(9)	83.0(5)
—O(9)	1.94(1)	O(8)— —O(4)	91.6(5)
—Cl	2.66(1)	Cl — —O(4)	83.1(4)
		Cl — —O(6)	100.2(4)
		Cl — —O(8)	84.3(4)
		Cl — —O(9)	104.1(4)
Cu(3)—O(1)	1.97(1)	O(3)—Cu(3)—O(10)	83.1(5)
—O(3)	1.92(1)	O(3)— —O(1)	92.3(5)
—O(8)	1.97(1)	O(8)— —O(1)	91.6(5)
—O(10)	1.96(1)	O(8)— —O(10)	92.4(4)
—Cl	2.62(1)	Cl — —O(1)	83.4(4)
		Cl — —O(3)	101.7(4)
		Cl — —O(8)	85.2(4)
		Cl — —O(10)	102.4(3)
Sb—O(11) <i>h</i>	1.97(1) 2 ×	O(11) <i>h</i> —Sb—O(12) <i>h</i>	89.3(5) 2 ×
—O(12) <i>h</i>	1.97(1) 2 ×	O(11) <i>h</i> — —O(13) <i>h</i>	91.9(6) 2 ×
—O(13) <i>h</i>	1.97(1) 2 ×	O(12) <i>h</i> — —O(13) <i>h</i>	90.8(5) 2 ×
As(1)—O(1)	1.72(1)	O(1)—As(1)—O(2)	111.1(8)
—O(2)	1.67(2)	O(3)— —O(3')	115.8(6)
—O(3)	1.69(1) 2 ×	O(1)— —O(3)	106.5(5) 2 ×
		O(2)— —O(3)	108.5(5) 2 ×
As(2)—O(4)	1.71(1)	O(4)—As(2)—O(5)	110.7(8)
—O(5)	1.66(2)	O(6)— —O(6')	115.9(6)
—O(6)	1.69(1) 2 ×	O(6)— —O(4)	107.7(5) 2 ×
		O(6)— —O(5)	107.4(5) 2 ×
As(3)—O(7)	1.66(1)	O(7)—As(3)—O(8)	112.1(5)
—O(8)	1.69(1)	O(8)— —O(9)	105.7(5)
—O(9)	1.71(1)	O(9)— —O(10)	117.9(6)
—O(10)	1.70(1)	O(7)— —O(9)	106.6(5)
		O(7)— —O(10)	109.2(5)
		O(8)— —O(10)	105.4(5)

**Table 6.** Valence balance in richelsdorffite, without hydrogen bond and chlorine contributions.

Oxygens	Ca	Cu(1)	Cu(2)	Cu(3)	Sb	As(1)	As(2)	As(3)	Sum
O(1)				0.45		1.08			1.98
O(2)		0.51		0.45		1.30			1.81
O(3)	0.26			0.51		1.20 × 2			1.97
O(4)			0.43	0.43			1.16		2.02
O(5)		0.48					1.35		1.83
O(6)	0.20		0.50				1.29 × 2		1.90
O(7)		0.44 × 2						1.37	1.81
O(8)			0.45	0.44				1.22	2.11
O(9)	0.24		0.49					1.13	1.86
O(10)	0.26			0.46				1.19	1.91
O(11) <i>h</i>					0.84 × 2				0.84
O(12) <i>h</i>	0.27				0.83 × 2				1.10
O(13) <i>h</i>					0.83 × 2				0.83
O(14) <i>w</i>		0.21							0.21
O(15) <i>w</i>									0.00
O(16) <i>w</i>	0.31								0.31
O(17) <i>w</i>	0.28								0.28
Sum	1.82	2.08	1.87	1.86	5.00	4.78	4.91	4.91	

**Table 7.** Valence bond strengths for oxygen atoms in richelsdorffite including contributions of possible hydrogen bonds. Valence bond strengths received and donated are designated by positive and negative signs respectively.

Oxygens	Hydrogen bond to	Oxygen-oxygen distance (Å)	Valence bond strength	Sum from Table 6	Final sum
O(1)				1.98	1.98
O(2)	O(15) <i>w</i>	2.78(2)	+0.17	1.81	1.98
O(3)				1.97	1.97
O(4)				2.02	2.02
O(5)	O(16) <i>w</i>	2.74(2)	+0.19	1.83	2.02
O(6)				1.90	1.90
O(7)	O(12) <i>h</i>	2.71(2)	+0.21	1.81	2.02
O(8)				2.11	2.11
O(9)				1.86	1.86
O(10)				1.91	1.91
O(11) <i>h</i>	O(16) <i>w</i>	2.81(2)	-0.15	0.84	1.08
	O(14) <i>w</i>	2.79(2)	+0.17		
	O(16) <i>w</i>	2.70(2)	+0.22		
O(12) <i>h</i>	O(7)	2.71(2)	-0.21	1.10	0.89
O(13) <i>h</i>	O(15) <i>w</i>	2.79(2)	+0.17 × 1/2	0.83	1.03
	O(17) <i>w</i>	2.92(2)	+0.11		
O(14) <i>w</i>	O(11) <i>h</i>	2.79(2)	-0.17	0.21	-0.13
	O(11) <i>h</i>	2.79(2)	-0.17		
O(15) <i>w</i>	O(2)	2.78(2)	-0.17	0.00	-0.04
	O(13) <i>h</i>	2.79(2)	-0.17		
	O(17) <i>w</i>	2.83(2)	+0.15		
	O(17) <i>w</i>	2.83(2)	+0.15		
O(16) <i>w</i>	O(5)	2.74(2)	-0.19	0.31	0.05
	O(11) <i>h</i>	2.70B(2)	-0.22		
	O(11) <i>h</i>	2.82(2)	+0.15		
O(17) <i>w</i>	O(13) <i>h</i>	2.92(2)	-0.11	0.28	0.02
	O(15) <i>w</i>	2.83(2)	-0.15		

bond system was derived successively as shown in Table 7. A bifurcated hydrogen bond is assumed between the donor O(15)*w*, which is located on the mirror plane, and two O(13)*h* on either side of the mirror plane. The valence strength contributions of the hydrogen bonds were determined after Brown (1976) and added to the sums of Table 7. Thus, the final valence strength sums for the oxygens in the last column of Table 7 nearly match the ideal values of 2.00 for O<sup>2-</sup>, 1.00 for OH<sup>-</sup>, and 0.00 for H<sub>2</sub>O.

### Structure topology

A main feature of the richelsdorffite atomic framework is its layer structure parallel (001), as may be seen in Figure 1. There are dense-packed layers

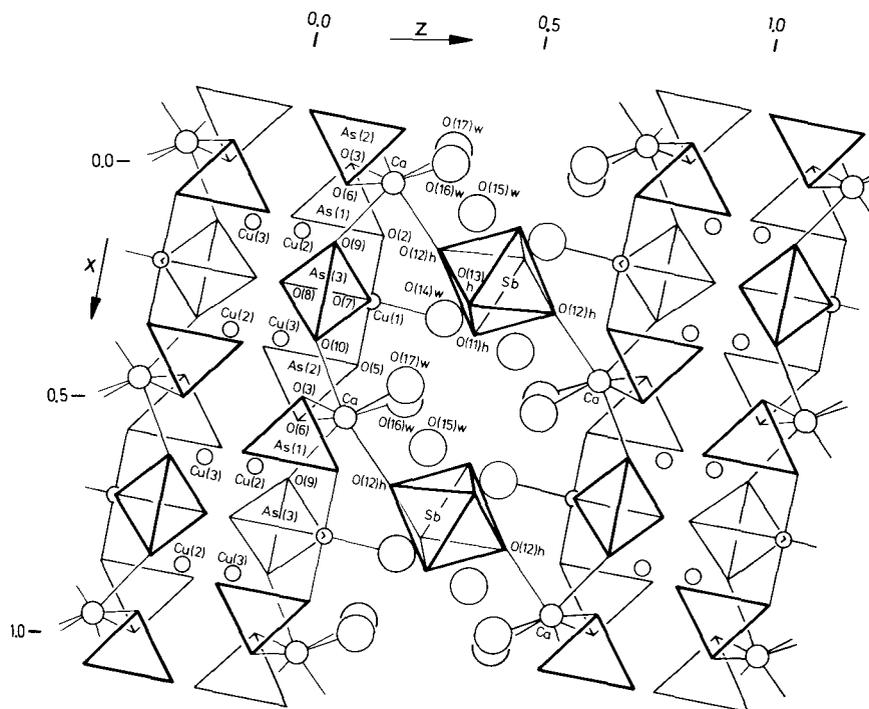
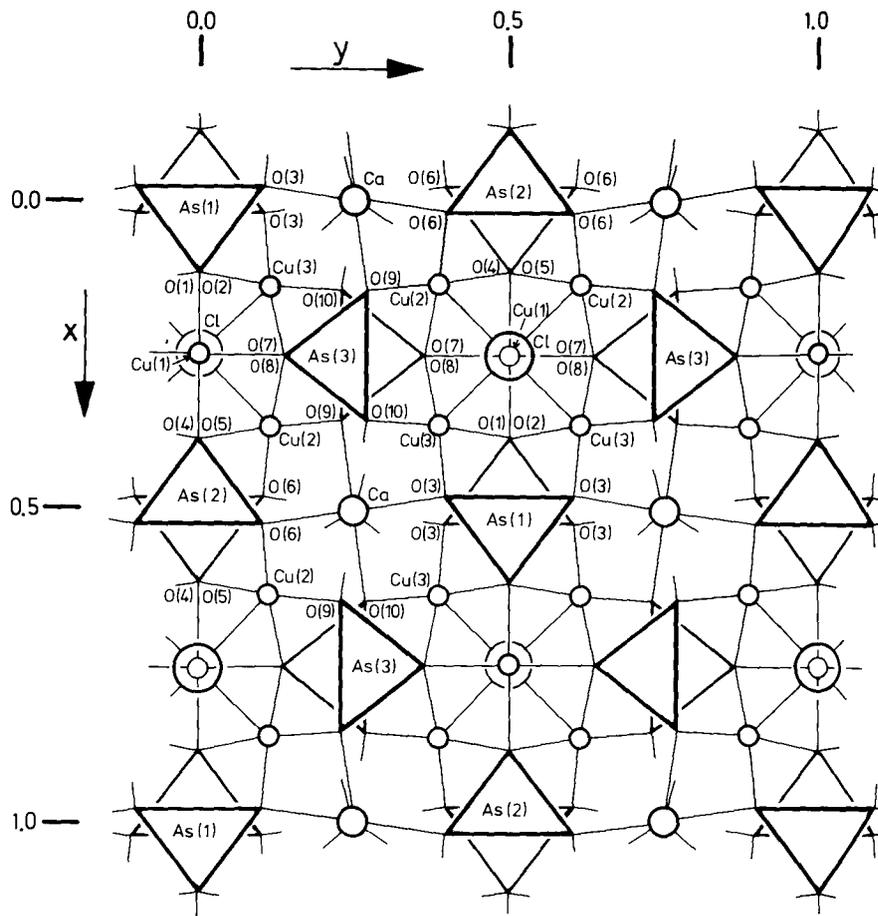


Fig. 1. Richelsdorffite projected on (010) illustrating the layer structure. The chlorine atoms, coinciding with the As(3) tetrahedra in this view, were omitted here. For their location and bonding see Fig. 2.

containing all the heavy atoms (except antimony) as well as chlorine and the greater part of the oxygens, making up a chemical composition of  $(\text{Ca}_2\text{Cu}_5\text{Cl}(\text{AsO}_4)_4)^+$ . These layers occupy half of the unit cell from  $z = 1/4$  to  $z = -1/4$ , while the area between  $z = 1/4$  and  $z = 3/4$  contains only  $(\text{Sb}(\text{OH})_6 \cdot 6\text{H}_2\text{O})^-$ . Thus, the density of the two half cells is remarkably different, three quarters of the atomic matter being concentrated within the layers (calculated density  $4.86 \text{ g} \cdot \text{cm}^{-3}$ ), one quarter in the area between the layers (calculated density  $1.62 \text{ g} \cdot \text{cm}^{-3}$ ).

The area between the layers is occupied by four non-equivalent  $\text{O}_w$  and by antimony being octahedrally coordinated by six  $\text{O}_h$ . Two of the four  $\text{O}_w$  are bound to Ca, one to Cu(1) and one to no cation at all. There is one connection between the layers via  $\text{Ca}-\text{O}(12)h-\text{Sb}-\text{O}(12)h-\text{Ca}$ . Aside from this only hydrogen bonding takes place between the layers.



**Fig. 2.** The richelsdorffite structure projected along  $c^*$  on (001). Shown are only the atoms along  $c^*$  within one layer between  $z = -1/4$  and  $z = 1/4$ .

The atomic arrangement within the dense-packed layers is shown in Figure 2. Three non-equivalent  $\text{AsO}_4$  tetrahedra are connected by three non-equivalent Cu and one Ca to form a two-dimensional network. Cu(2) and Cu(3) are coordinated by four oxygen atoms plus one chlorine, Cu(1) is bound to four oxygen neighbours within the layer and to one  $\text{O}_w$  between the layers. Calcium is bound to four oxygens within the layer plus two  $\text{O}_w$  and one  $\text{O}_h$  outside the layer. Chlorine in turn is surrounded by four Cu atoms.

It is very striking to notice the almost perfect tetragonal symmetry of one individual layer. However, the way the layers are stacked along [001]

makes the structure as a whole only monoclinic. Besides, the atoms between the layers do not follow tetragonal symmetry.

## Conclusions

By means of the crystal structure analysis a fairly reliable chemical formula could be established for richelsdorffite. It should be mentioned though, that the occupancy factor of the chlorine site is only 0.77(3). This corresponds to a scattering power of 13 electrons and may be interpreted as a site statistically occupied by 55%  $\text{Cl}^-$  and 45%  $\text{OH}^-$ . This is in accordance with the chemical analysis (Süsse and Schnorrer-Köhler, l.c.), which also states a slight deficiency of chlorine. Indeed, it seems that in other richelsdorffites chlorine may be entirely replaced by hydroxyl, since the Black Forest richelsdorffite (Walenta l.c.) does not contain chlorine at all.

Although no more diffracting matter could be detected in the inter-layer area of this particular crystal structure, the richelsdorffite structure is possibly capable of accommodating more water molecules between the layers. This may cause varying water contents of richelsdorffites of different origin and history.

The layer structure of richelsdorffite is responsible for the excellent cleavage parallel (001). The pseudo-tetragonal habit of the crystals and the twinning may be explained through the almost exact tetragonal symmetry of dense-packed layers held together by relatively weak bonding in the inter-layer area.

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