

# The crystal structures of lavendulan, sampleite, and a new polymorph of sampleite

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**Abstract:** The crystal structures of lavendulan from the Hilarion mine, Laurion, Greece, and isotypic sampleite from the Northparkes mine, New South Wales, Australia, have been determined from single-crystal diffraction data, resulting in a revision of the symmetry. The structure of lavendulan,  $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$  (space group  $P2_1/n$ ,  $a = 10.011(1)$ ,  $b = 19.478(2)$ ,  $c = 10.056(1)$  Å,  $\beta = 90.37(1)^\circ$ ,  $V = 1960.8(3)$  Å<sup>3</sup>,  $Z = 4$ ) was solved from X-ray data (MoK $\alpha$ , CCD area detector) and refined to  $R1(F) = 5.35$  % for 4179 observed reflections with  $F_o > 4\sigma(F_o)$ . The structure of sampleite,  $\text{NaCaCu}_5(\text{PO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ , was determined from synchrotron data (CCD area detector) obtained from a twinned crystal (space group  $P2_1/n$ ,  $a = 9.676(2)$ ,  $b = 19.284(4)$ ,  $c = 9.766(2)$  Å,  $\beta = 90.07(1)^\circ$ ,  $V = 1822.3(6)$  Å<sup>3</sup>,  $Z = 4$ ) and refined to  $R1(F) = 4.44$  % for 2601 observed reflections with  $F_o > 4\sigma(F_o)$ . The structure type is based on  $\text{Cu}(\text{O},\text{H}_2\text{O},\text{Cl})_5$  pyramids forming  $[\text{Cu}_4\text{O}_{12}\text{Cl}]$  clusters, which are connected by  $\text{XO}_4$  ( $X = \text{As},\text{P}$ ) groups into heteropolyhedral sheets. These sheets ideally have  $p4mm$  symmetry and are aligned parallel to (010), i.e., the plane of the excellent cleavage, and are linked to adjacent parallel sheets via  $\text{NaO}_6$  and  $\text{CaO}_7$  polyhedra as well as by weak hydrogen bonding.

A polymorph of sampleite with the chemical formula  $\text{NaCaCu}_5(\text{PO}_4)_4\text{Cl}\cdot n\text{H}_2\text{O}$  ( $n \sim 4.5$ ) has been found at Lake Boga, Victoria, Australia. The crystal structure (space group  $P2_1/c$ ,  $a = 9.695(2)$ ,  $b = 9.673(2)$ ,  $c = 19.739(4)$  Å,  $\beta = 102.61(3)^\circ$ ,  $V = 1806.5(6)$  Å<sup>3</sup>,  $Z = 4$ ) was determined using single-crystal X-ray diffraction data (MoK $\alpha$ , CCD area detector) and refined to  $R1(F) = 14.67$  % for 3189 observed reflections with  $F_o > 4\sigma(F_o)$ . The heteropolyhedral sheet in the polymorph is topologically identical to that of sampleite (and lavendulan), but the stacking of these sheets is slightly different. Thus, the polymorph may be considered a polytype if the apparently slightly reduced water content of the polymorph is neglected. Some physico-chemical properties of the sampleite polymorph are given.

Sheets identical to those in lavendulan are encountered in zdenekite, the Pb-analogue of lavendulan. Very similar sheets are found in andyrobetsite, calcio-andyrobetsite(-1M), calcio-andyrobetsite-2O, richelsdorffite, and probably bleasdaleite, mahnertite, lemanskiite and the inadequately characterized, lavendulan-related species shubnikovite.

**Key-words:** lavendulan, sampleite, crystal structure, crystal chemistry, polymorphism.

## Introduction

As part of long-term studies on the crystal chemistry and topology of secondary copper minerals, we present the previously unknown crystal structures of the two copper oxysalt minerals lavendulan and sampleite,  $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$  and  $\text{NaCaCu}_5(\text{PO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ , respectively. Crystal structure data for a polymorph of sampleite are also given. For both lavendulan and sampleite, contradictory data on their symmetry have been reported since they were first described.

In the following section, we compile and critically dis-

cuss the previously reported data. Further below, the crystal structures of lavendulan and sampleite are described in detail and it is shown that both are isotypic and that zdenekite,  $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$  (Chiappero & Sarp, 1995; Zubkova *et al.*, 2003) represents the Pb-analogue of lavendulan. The structure type contains heteropolyhedral sheets of  $\text{Cu}(\text{O},\text{H}_2\text{O},\text{Cl})_5$  tetragonal pyramids and  $\text{XO}_4$  ( $X = \text{As},\text{P}$ ) tetrahedra. Very similar sheets occur in andyrobetsite,  $(\text{Cd},\text{Ca},\text{Mn})\text{KCu}_5(\text{AsO}_4)_4[\text{As}(\text{OH})_2\text{O}_2](\text{H}_2\text{O})_2$ , its Ca-analogues calcio-andyrobetsite(-1M) (Cooper *et al.*, 1999; Cooper & Hawthorne, 2000) and calcio-andyrobetsite-2O (Sarp & Černý, 2004), as well as richelsdorffite (Süsse &

Tillmann, 1987), and possibly bleasdaleite (Birch *et al.*, 1999). It will also be suggested that the atomic arrangement in the chemically related mineral lemanskiite,  $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$  (tetragonal dimorph of lavendulan; Ondruš *et al.*, 2006) is based on the same sheets, as are the sheets in mahnertite,  $(\text{Na,Ca})\text{Cu}_3(\text{AsO}_4)_2\text{Cl}\cdot 5\text{H}_2\text{O}$  (Sarp, 1996; Pushcharovsky *et al.*, 2004). Additional comments are provided on the status of the inadequately characterized species shubnikovite, an obviously lavendulan-related, hydrated (K-)Ca-Cu-arsenate-chloride.

## Previous work

### Lavendulan and sampleite

**Lavendulan**,  $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ , is a relatively common supergene arsenate mineral in oxidation zones of Cu- and As-bearing orebodies. Lavendulan was originally described from Jáchymov, Bohemia, Czech Republic, in the late 19<sup>th</sup> century by Breithaupt (*e.g.*, Palache *et al.*, 1951; Gaines *et al.*, 1997, Anthony *et al.*, 2000). It forms bright blue crusts, spherules and thin rectangular platelets which are flexible and have a low Mohs hardness (2.5) and excellent cleavage parallel to the platy face. First X-ray diffraction studies were done by Guillemin (1956a) who proposed a primitive orthorhombic cell with  $a = 9.73$ ,  $b = 41.0$ ,  $c = 9.85$  Å (based on single-crystal studies and indexed X-ray powder diffraction data); on ICDD-PDF 31–1280 the powder data are indexed on a similar cell with  $a = 9.815$ ,  $b = 40.39$ ,  $c = 9.99$  Å. Guillemin (1956a) recognized that lavendulan is isomorphous with sampleite. He also studied the optical properties in some detail and found that they are somewhat variable (crystals showing either straight or oblique extinction, and with  $2V_\alpha$  ranging between 0 and 33°). These observations were tentatively attributed to variable water contents (a 2.8% loss of water between 20 and 70°C was observed). Heating of crystals from Cap Garonne, Var, France, at 90°C for 3 d resulted in a change from oblique extinction (45°) to straight extinction, and a strong decrease of  $2V$  from 33° to lower values. The X-ray powder diffraction pattern was unchanged. Further heating for 5 d at 90°C caused the smallest crystals to become uniaxial negative. Lavendulan is unstable at pH 3–5.5, and disintegrates (hydrolyses) fairly fast in water but much slower at higher pH (Guillemin, 1956a). Observations of one of authors (U.K.) on lavendulan specimens from various localities show that alteration of lavendulan in natural aqueous solutions turns it gradually into pale bluish, earthy and crumbly material with poor crystallinity. SEM-EDS analyses conducted by J. Gröbner (pers. comm., 2001) of partly altered lavendulan crystals from Lavrion, Greece, with reduced transparency, demonstrated that the altered parts (mainly rims) contained much less Na than the fresh and transparent crystals; main reflections in the X-ray powder diffraction pattern were distinctly shifted by comparison to fresh lavendulan.

In any case, the presently available data on lavendulan (and its phosphate analogue sampleite; see below) make it seem probable that strong or prolonged grinding of lavendulan may lead to its partial dehydration. Consequently, care

should be taken when preparing mounts of these minerals for X-ray powder diffraction measurements.

The crystal structure of lavendulan was first solved by one of the authors (G.G.) in 1997 using well-crystallized material from the Hilarion mine, Lavrion, Greece. Based on this information, the X-ray powder diffraction pattern of lavendulan (sample from the same material) was completely revised and reindexed with monoclinic symmetry (space group  $P2_1/n$ ;  $a = 10.009(1)$ ,  $b = 19.467(2)$ ,  $c = 10.059(1)$  Å,  $\beta = 90.31(1)^\circ$ , ICDD-PDF 49–1857). The crystal-structure data of lavendulan presented further below were obtained in 2002 from a second crystal of much better quality which also allowed location of the positions of the hydrogen atoms.

Ondruš *et al.* (1997) provided new X-ray powder diffraction data for lavendulan samples from Jáchymov, Czech Republic. However, their data, which are included in the ICDD-PDF (no. 51–1491), are severely affected by preferred orientation, and are considered unreliable. Moreover, these authors give the primitive orthorhombic unit cell  $a = 9.817$ ,  $b = 40.39$ ,  $c = 9.997$  Å, and index the strongest reflection with 100, which is highly unlikely because the strongest reflection in lavendulan and related minerals always is a reflection on the basal plane (of the pseudotetragonal lattice) which is perpendicular to the long pseudotetragonal axis, and also represents the plane of perfect cleavage.

**Sampleite**,  $\text{NaCaCu}_5(\text{PO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ , was originally described by Hurlbut (1942) from Chuquicamata, Chile, as small platy blue crystals with square to rectangular outline. Sampleite is a hypogene species less abundant than lavendulan, but it has been found in more diverse environments, including occurrence as a cave mineral (Bridge *et al.*, 1978; Onac *et al.*, 2002) and as an anthropogenic compound on ancient copper objects (Fabrizi *et al.*, 1989). Physical properties are similar to those of lavendulan. Single-crystal studies of type sampleite indicated a primitive orthorhombic-pseudotetragonal cell with  $a = 9.70$ ,  $b = 38.40$ ,  $c = 9.65$  Å (Hurlbut, 1942), which would be in accordance with the measured optical properties (biaxial negative,  $2V = 5$  to 20°) and the tabular (010) habit (Hurlbut, 1942). The optical orientation of sampleite from the type locality was later confirmed by Guillemin (1956b). However, a study of sampleite from Western Australia by Bridge *et al.* (1978) conclusively showed that the pleochroic scheme reported by Hurlbut (1942) is erroneous (pleochroism was not addressed by Guillemin, 1956b). Bridge *et al.* (1978) also tried to obtain single-crystal data but found that “Weissenberg films are composed of symmetrically oriented streaks indicating considerable disorder. The respective zero layers could not be identified or indexed.”

Sampleite, as shown by high-temperature X-ray powder diffraction, undergoes a transformation characterized by an irreversible sharp reduction in the layer spacing (040 reflection) between 110 and 112 °C, most likely due to loss of water (Fabrizi *et al.*, 1989; Tarling, 1992). This is in qualitative agreement with earlier experiments by Guillemin (1956b) who observed that sampleite, after being heated at 60°C, showed no change of optics, whereas heating at 90°C for 24 h caused the crystals to become uniaxial or almost uniaxial ( $2V \sim 3^\circ$ ), and heating at 100°C for 48 h induced complete

uniaxiality (compare also the similar behaviour of lavendulan described above).

No fully reliable powder diffraction data for sampleite exist. The published data are incomplete, missing the strongest reflection (Hurlbut, 1942, ICDD-PDF 7–393) and, additionally, containing strongly overestimated intensities of the stronger reflections (Guillemin, 1956b, ICDD-PDF 11–349).

Scarce information is available on the solid solubility and its limits among the members of the lavendulan group. A phosphatian lavendulan with an As:P ratio of 79:21 has been described from South Australia (Kleeman & Milnes, 1973). Members of the solid solution series lavendulan-sampleite with variable As:P ratios are also known from the Santa Catalina Mine, Sierra Gorda, Antofagasta Province, Chile. A lavendulan rich in Zn was found at Tsumeb, Namibia (Strunz, 1959); the exact Cu:Zn ratio is not known although it is reported that the sample was “relatively rich” in Zn. The ‘Strunz Mineralogical Tables’ (Strunz & Nickel, 2001) list the sample of Strunz (1959) as “zinclavendulan”, with a chemical formula equivalent to that of a hypothetical Zn-dominant analogue of lavendulan, but there is no evidence whatsoever for this. A sampleite containing small amounts of Pb has been described from Broken Hill by Birch & van der Heyden (1988, 1997). From Broken Hill, N.S.W., Australia, both cadmian-plumboan and plumboan varieties of sampleite have been identified (Kolitsch *et al.*, unpublished data). The changes in X-ray powder diffraction data and optical properties of these varieties from Broken Hill are in agreement with the observed chemical substitutions (Kolitsch *et al.*, unpublished data).

## Experimental

### Chemical and optical data

The following carefully chosen samples, to be used for the subsequent single-crystal studies, were first characterized by polarized-light microscopy and standard SEM-EDS analyses on carbon-coated crystals.

**Lavendulan** from the Hilarion mine at Lavrion, Greece (Elbin & Wendel, 1996): The sample shows bright blue, transparent, glassy, lath-shaped crystals up to 1.5 mm in length (Fig. 1), which are perched on a brown gossan matrix. Subparallel to radiating intergrowths are common. The laths show a weak striation parallel to their morphological elongation. Optically, the crystals are biaxial negative with an estimated  $2V_\alpha$  of about  $30^\circ$  ( $r > v$ , distinct) and  $\gamma = 1.743(5)$ . Their extinction is diagonal. Four crystals were carbon-coated for standard semiquantitative EDX investigations, performed on a Jeol JSM-6400 scanning electron microscope equipped with a Link EDX unit. Evaluation of nine point analyses showed the laths to contain Na, Ca, Cu, As, and Cl with an average atomic ratio of 1.4 : 0.97 : 5.14 : 4.07 : 0.99. The obtained value for Na is considered to be inaccurate because of severe peak overlap with the  $CuL\alpha$  peak. No further elements were observed within detection limits.

**Sampleite** from the upper oxidation zone of the E26 orebody, Northparkes mine, Goonumbla, New South Wales,

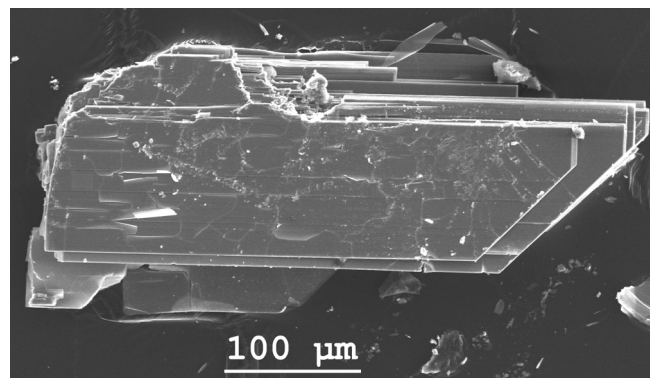


Fig. 1. SEM micrograph of subparallel lath-shaped lavendulan crystals from the Hilarion mine, Lavrion, Greece.

Australia (McLean *et al.*, 2004): The sample consists of large, bright blue spherules, up to 2.5 mm in diameter and composed of subparallel thin rectangular plates. Optically, these plates are biaxial negative with small  $2V_\alpha$ , and a pleochroic scheme very similar to that of the sampleite polymorph from Lake Boga (see below). They show straight extinction, and  $\beta \sim \gamma = 1.675(3)$ , i.e., in good agreement with literature data (Anthony *et al.*, 2000). Standard semiquantitative SEM-EDS analyses showed the presence of Na, Ca, Cu, Cl and P; K or other impurity elements were not detected.

**Sampleite polymorph** from the Lake Boga granite quarry, near Swan Hill, Victoria, Australia: This “sampleite”, which occurs as a late-stage hydrothermal mineral in small miarolitic cavities of a granite, together with several other copper phosphates, is well-characterized (Henry & Birch, 1988). Its chemical formula,  $(Na_{1.06}K_{0.03})CaCu_{4.9}(PO_4)_4Cl_{1.02} \cdot 6H_2O$  (derived from electron microprobe analyses; Henry & Birch, 1988), closely agrees with that of the type material of sampleite (Hurlbut, 1942).

The optical properties of a “sampleite” from Lake Boga (South Australian Museum, collection no. G 15410) have been investigated in some detail. The specimen contains large (up to 1.5 mm in length), lath-shaped crystals with a sharp rectangular outline. All crystals show a faint striation parallel to their elongation and are completely transparent, with glassy lustre. According to semiquantitative SEM-EDS analyses, the crystals are chemically almost pure, with trace amounts of K as the only detectable impurity element. Refractive indices of the crystals, determined in white light, are  $\alpha$  1.630(3),  $\beta$  1.575(2),  $\gamma$  1.576(2), and  $2V_\alpha \sim 10^\circ$ . Pleochroism is strong: X colourless to very pale blue, Y and Z pale blue with greenish tint; absorption  $Z \geq Y \gg X$ , dispersion weak,  $r > v$ . The optical elongation is positive and the optical axis plane is parallel to the crystal elongation. The extinction is straight or nearly so. These properties are generally in good agreement with the literature data for sampleite, except for the pleochroic scheme which disagrees with that given by Hurlbut (1942) for type sampleite, but agrees with the observations of Bridge *et al.* (1978) (see Introduction).

Table 1. Crystal data, data collection information and refinement details for lavendulan from Lavrion, Greece, sampleite from Northparkes, New South Wales, Australia, and the sampleite polymorph from Lake Boga, Victoria, Australia.

	Lavendulan	Sampleite	Sampleite polymorph
<i>Crystal data</i>			
Formula	NaCaCu <sub>5</sub> (AsO <sub>4</sub> ) <sub>4</sub> Cl·5H <sub>2</sub> O	NaCaCu <sub>5</sub> (PO <sub>4</sub> ) <sub>4</sub> Cl·5H <sub>2</sub> O	NaCaCu <sub>5</sub> (PO <sub>4</sub> ) <sub>4</sub> Cl· <i>n</i> H <sub>2</sub> O, <i>n</i> ~ 4.5
Formula weight	1061.98	886.18	868.10
Space group, <i>Z</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i> , 4	<i>P</i> 2 <sub>1</sub> / <i>n</i> , 4	<i>P</i> 2 <sub>1</sub> / <i>c</i> , 4
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.011(1), 19.478(2), 10.056(1)	9.676(2), 19.284(4), 9.766(2)	9.695(2), 9.673(2), 19.739(4)
$\beta$ (°)	90.37(1)	90.07(1)	102.61(3)
<i>V</i> (Å <sup>3</sup> )	1960.8(3)	1822.3(6)	1806.5(6)
<i>F</i> (000), $\rho_{\text{calc}}$ (g · cm <sup>-3</sup> )	2012, 3.597	1724, 3.230	1668, 3.192
$\mu$ (mm <sup>-1</sup> )	12.557	3.471	6.707
Absorption correction	multi-scan* (Otwinowsky <i>et al.</i> , 2003)	none	multi-scan* (Otwinowsky <i>et al.</i> , 2003)
Crystal dimensions (mm)	0.20 x 0.06 x 0.007	0.005 x 0.004 x 0.002	0.53 x 0.08 x 0.02
<i>Data Collection</i>			
Diffractometer	Nonius KappaCCD system	Bruker Kappa Smart 6000CCD system (adapted for synchrotron)	Nonius KappaCCD system
$\lambda$ (Å), <i>T</i> (K)	0.71073, 293	0.5594, 123	0.71073, 293
Crystal-detector dist. (mm)	35	50	48
Rotation axis, width (°)	$\varphi$ , $\omega$ ; 2.0	$\varphi$ , $\omega$ ; 0.3	$\varphi$ , $\omega$ ; 1.0
Total no. of frames	419	1200	727
Collect. time per degree (s)	250	200	200
Collection mode, $2\theta_{\text{max}}$ (°)	sphere, 60	quadrant, 50	sphere, 55
<i>h</i> , <i>k</i> , <i>l</i> ranges	$\bar{1}4/14$ , $\bar{2}7/27$ , $\bar{1}4/14$	$\bar{1}1/11$ , 0/27, 0/13	$\bar{1}2/12$ , $\bar{1}2/12$ , $\bar{2}5/25$
Total reflections measured	11239	4998	6837
Unique reflections	5715 ( $R_{\text{int}}$ 4.26 %)	4894	3834 ( $R_{\text{int}}$ 3.20 %)
<i>Refinement</i>			
Refinement on	$F^2$	$F^2$	$F^2$
$R1(F)$ , $wR2_{\text{all}}(F^2)^{**}$	5.35 %, 13.37 %	4.44 %, 10.80 %	14.67 %, 39.34 %***
'Observed' refls.	4179 [ $F_o > 4\sigma(F_o)$ ]	2601 <sup>#</sup> [ $F_o > 4\sigma(F_o)$ ]	3189 [ $F_o > 4\sigma(F_o)$ ]
Extinct. coefficient	0.00008(10)	0.0064(19)	0.0056(18)
No. of refined parameters	329	135	299
GooF	1.120	1.040	1.736***
$(\Delta/\sigma)_{\text{max}}$	0.0001	0.01	0.414***
$\Delta\rho_{\text{min}}$ , $\Delta\rho_{\text{max}}$ (e/Å <sup>3</sup> )	-1.53, 1.86	-1.12, 1.47	-4.8, 8.8

Note: Unit-cell parameters were refined from *ca.* 5000 (lavendulan), 1022 (sampleite), and 3716 (sampleite polymorph) recorded reflections. Scattering factors for neutral atoms were employed in the refinement.

\* Semiempirical absorption correction based on symmetry-equivalent reflections.

\*\*  $w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 25.00P]$ ;  $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$  (lavendulan)

$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.01P]$ ;  $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$  (sampleite)

$w = 1/[\sigma^2(F_o^2) + (0.20P)^2 + 0.00P]$ ;  $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$  (sampleite polymorph)

\*\*\* These values reflect the low quality (probable stacking disorder) of the crystal fragment studied (see text).

<sup>#</sup> This is the reduced number of reflections used in the final refinement which gave a resolution of 1.0 Å.

## Single crystal X-ray diffraction

### Lavendulan

Several small, rectangular platelets from a well-crystallized lavendulan specimen from Lavrion, Greece, were studied by single-crystal techniques. All platelets showed a primitive cell with monoclinic-pseudotetragonal symmetry ( $a \sim 10.0$ ,  $b \sim 19.5$ ,  $c \sim 10.0$  Å,  $\beta \sim 90^\circ$ ); the long ( $\sim 41$  Å) axis and the orthorhombic symmetry reported by Guillemin (1956a) could not be confirmed. The large majority of the platelets studied showed poor crystal quality and/or twinning, and considerable effort and time were necessary to find a tiny single-crystal plate with a very good crystal quality. We also note that the CCD frames of this plate showed no diffuse streaking or elongated reflections. X-ray intensity

data were collected from a tiny single-crystal plate using a Nonius KappaCCD diffractometer at room temperature (Vienna). Crystal data as well as experimental details are compiled in Table 1. The measured intensities were corrected for Lorentz, background, polarisation and absorption effects. The crystal structure refinement was started with the atomic coordinates of the first lavendulan crystal whose structure had been solved in 1997 by direct methods (SHELXS-97, Sheldrick 1997a) and subsequent Fourier and difference Fourier syntheses. The structure refinement of the new dataset by full-matrix least-squares techniques on  $F^2$  was done with SHELXL-97 (Sheldrick 1997b). The positions of the hydrogen atoms were finally located by difference Fourier maps. Atomic coordinates for all hydrogens could be refined, and the final  $R$ -values were  $R1(F) = 5.35\%$  and

Table 2. Fractional atomic coordinates and displacement parameters (in Å<sup>2</sup>) for lavendulan from Lavrion and sampleite from Northparkes (every second row).

Atom	x	y	z	$U_{eq}/U_{iso}$
Na	0.2902(3)	0.1083(2)	0.6475(3)	0.0309(8)
	0.2865(4)	0.1032(1)	0.6398(4)	0.0112(5)
Ca	0.78303(15)	0.09544(8)	0.13674(16)	0.0207(3)
	0.76999(15)	0.09306(5)	0.14427(16)	0.0043(2)
Cu(1)	0.05806(9)	0.21004(5)	0.13981(9)	0.0175(2)
	0.04881(9)	0.21185(3)	0.14075(10)	0.0032(2)
Cu(2)	0.52395(9)	0.21604(5)	0.14172(9)	0.0178(2)
	0.51567(9)	0.22076(3)	0.14043(10)	0.0033(2)
Cu(3)	0.29061(8)	0.21147(5)	0.36580(9)	0.0172(2)
	0.28372(10)	0.21763(3)	0.36863(8)	0.0029(2)
Cu(4)	0.29423(9)	0.21174(5)	-0.08393(9)	0.0175(2)
	0.28443(12)	0.21228(4)	-0.08722(9)	0.0035(2)
Cu(5)	0.79415(9)	0.09098(5)	0.64051(9)	0.01656(19)
	0.78575(10)	0.09295(3)	0.64142(10)	0.0033(2)
As(1)	-0.00500(7)	0.15757(4)	0.43069(7)	0.01576(17)
P(1)	-0.0109(2)	0.15821(8)	0.4326(2)	0.0029(4)
As(2)	0.00026(7)	0.15848(4)	0.84746(7)	0.01530(16)
P(2)	-0.0086(2)	0.15469(7)	0.8503(2)	0.0025(3)
As(3)	0.58430(7)	0.16290(4)	0.43480(7)	0.01555(16)
P(3)	0.5786(2)	0.16499(8)	0.4328(2)	0.0026(4)
As(4)	0.58955(7)	0.16303(4)	0.84879(7)	0.01553(16)
P(4)	0.5786(2)	0.16071(7)	0.8473(2)	0.0023(3)
O(1)	-0.0729(5)	0.0882(3)	0.4986(5)	0.0216(11)
	-0.0688(7)	0.0928(2)	0.5009(5)	0.0040(8)
O(2)	-0.0455(5)	0.1587(3)	0.2685(5)	0.0207(11)
	-0.0488(8)	0.1578(3)	0.2768(6)	0.0036(9)
O(3)	0.1605(5)	0.1539(3)	0.4595(6)	0.0224(12)
	0.1457(9)	0.1601(3)	0.4592(6)	0.0105(10)
O(4)	-0.0663(5)	0.2307(3)	0.5016(5)	0.0178(10)
	-0.0753(7)	0.2255(3)	0.4961(6)	0.0059(9)
O(5)	-0.0622(5)	0.0883(3)	0.7728(5)	0.0210(11)
	-0.0691(7)	0.0890(3)	0.7827(5)	0.0057(9)
O(6)	0.1646(5)	0.1601(3)	0.8155(6)	0.0221(12)
	0.1466(8)	0.1560(3)	0.8222(5)	0.0056(9)
O(7)	-0.0405(5)	0.1570(3)	1.0086(5)	0.0219(11)
	-0.0460(7)	0.1547(2)	1.0041(5)	0.0041(9)
O(8)	-0.0697(5)	0.2312(3)	0.7804(5)	0.0191(11)
	-0.0751(6)	0.2220(2)	0.7829(5)	0.0028(8)
O(9)	0.6513(5)	0.0936(3)	0.5050(5)	0.0227(11)
	0.6477(8)	0.1018(3)	0.4968(6)	0.0077(9)
O(10)	0.4212(5)	0.1617(3)	0.4674(6)	0.0234(12)
	0.4217(8)	0.1638(3)	0.4620(6)	0.0068(10)
O(11)	0.6239(5)	0.1627(3)	0.2722(5)	0.0201(11)
	0.6133(8)	0.1673(3)	0.2766(6)	0.0050(10)
O(12)	0.6494(5)	0.2361(3)	0.5021(5)	0.0171(10)
	0.6365(6)	0.2332(3)	0.4974(5)	0.0031(8)
O(13)	0.6656(5)	0.0954(3)	0.7840(5)	0.0229(11)
	0.6473(8)	0.0967(3)	0.7855(5)	0.0064(9)
O(14)	0.4250(5)	0.1604(3)	0.8191(5)	0.0201(11)
	0.4233(8)	0.1585(3)	0.8193(6)	0.0061(10)
O(15)	0.6482(5)	0.2374(3)	0.7790(5)	0.0179(10)
	0.6372(7)	0.2293(3)	0.7801(5)	0.0049(9)
O(16)	0.6329(5)	0.1680(3)	1.0119(5)	0.0204(11)
	0.6137(7)	0.1648(3)	1.0037(5)	0.0037(9)
W(1)	0.8525(7)	0.0042(4)	0.2943(7)	0.0320(14)
	0.8509(7)	0.0009(3)	0.2984(6)	0.0077(9)
W(2)	0.2341(10)	0.0227(4)	0.3557(9)	0.046(2)
	0.2394(9)	0.0236(3)	0.3825(6)	0.0175(13)

Atom	x	y	z	$U_{eq}/U_{iso}$
W(3)	0.4415(7)	0.0202(4)	0.6420(7)	0.0361(15)
	0.4579(15)	0.0169(5)	0.6121(11)	0.0340(19)
W(4)	0.8513(8)	0.0069(4)	-0.0096(7)	0.0383(17)
	0.8390(8)	0.0043(3)	-0.0063(7)	0.0113(10)
W(5)	0.5882(9)	0.0224(5)	0.1097(9)	0.054(2)
	0.5576(13)	0.0242(5)	0.1337(15)	0.0354(17)
Cl	0.30063(19)	0.13529(10)	0.1362(2)	0.0244(4)
	0.2911(2)	0.13745(6)	0.1425(2)	0.0053(3)
H(1a)	0.919(11)	-0.019(6)	0.263(11)	0.038*
H(1b)	0.875(11)	0.026(6)	0.363(11)	0.038*
H(2a)	0.270(14)	0.042(8)	0.326(14)	0.055*
H(2b)	0.216(13)	0.051(7)	0.400(13)	0.055*
H(3a)	0.414(11)	-0.008(6)	0.574(11)	0.043*
H(3b)	0.516(11)	0.041(6)	0.619(11)	0.043*
H(4a)	0.757(12)	-0.009(6)	-0.008(11)	0.046*
H(4b)	0.889(13)	0.022(7)	-0.054(12)	0.046*
H(5a)	0.555(15)	0.001(8)	0.068(14)	0.064*
H(5b)	0.562(14)	0.017(7)	0.187(14)	0.064*

Note: Oxygens of H<sub>2</sub>O molecules as W.  $U_{eq}$  as defined by Fischer & Tillmanns (1988).

\*  $U_{iso}$  values of hydrogen atoms were fixed at 1.2 times  $U_{eq}$  of the respective donor oxygen atoms.

$wR2_{all}(F^2) = 13.37\%$  for 4179 reflections with  $F_o > 4\sigma(F_o)$  (Table 1). We note that various possible twin matrices were also tried, but did not result in any improvement of the model.

The structure parameters of lavendulan are compiled in Tables 2 and 3 (anisotropic displacement parameters), and selected interatomic distances and bond angles including the proposed hydrogen-bonding scheme are given in Table 4. A bond-valence analysis is provided in Table 5. The refined unit-cell parameters of the lavendulan sample,  $a = 10.011(1)$ ,  $b = 19.478(2)$ ,  $c = 10.056(1)$  Å,  $\beta = 90.37(1)^\circ$ ,  $V = 1960.8(3)$  Å<sup>3</sup>, are nearly identical with those given on ICDD-PDF 49–1857 (based on the previous structure solution of a crystal from the same sample, as mentioned above).

For comparative purposes, small crystal fragments of a well-crystallized lavendulan from Chile were also studied by single-crystal methods. The sample is from the El Guanaco gold mine, Taltal, and is associated with excellent dark blue-green lammerite [Cu<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>] crystals and very small amounts of a yellowish globular silver halide (iodargyrite?). Although the crystal quality of the studied lavendulan fragments was fairly low, the studies showed that they have monoclinic symmetry and unit-cell parameters ( $a = 9.976(5)$ ,  $b = 19.433(10)$ ,  $c = 9.991(5)$  Å,  $\beta = 90.23(3)^\circ$ ,  $V = 1936.9(17)$  Å<sup>3</sup> for the fragment with the best crystal quality), which are only slightly lower than those of the lavendulan from Lavrion, and which could indicate either a small P-for-As substitution or a partial dehydration(?). A tentative refinement of an intensity dataset collected with a Nonius KappaCCD single-crystal diffractometer using measurement parameters similar to those applied for the data collection of the sampleite polymorph gave  $R1(F) \sim 18\%$  and a model in good agreement with that of lavendulan from Lavrion. It is interesting to note that the locality providing the lavendulan studied (El Guanaco gold mine, Taltal, Chile) represents the type locality of lemanskiite (tetragonal NaCa-

Table 3. Anisotropic displacement parameters (in Å<sup>2</sup>) for lavendulan from Lavrion.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Na	0.0259(16)	0.042(2)	0.0248(18)	-0.0016(15)	0.0008(14)	0.0036(15)
Ca	0.0172(7)	0.0260(8)	0.0188(7)	0.0001(6)	0.0000(6)	0.0012(6)
Cu(1)	0.0167(4)	0.0253(5)	0.0105(4)	-0.0001(3)	-0.0002(3)	-0.0032(3)
Cu(2)	0.0158(4)	0.0264(5)	0.0113(4)	0.0002(3)	0.0005(3)	0.0025(3)
Cu(3)	0.0113(4)	0.0242(5)	0.0160(5)	0.0027(3)	-0.0006(3)	-0.0001(3)
Cu(4)	0.0116(4)	0.0262(5)	0.0147(4)	-0.0026(3)	0.0003(3)	-0.0002(3)
Cu(5)	0.0130(4)	0.0242(5)	0.0125(4)	-0.0006(3)	0.0002(3)	-0.0001(3)
As(1)	0.0125(3)	0.0236(4)	0.0112(3)	0.0002(3)	0.0009(3)	-0.0005(3)
As(2)	0.0118(3)	0.0230(4)	0.0111(3)	-0.0007(3)	-0.0005(3)	-0.0003(3)
As(3)	0.0123(3)	0.0224(4)	0.0119(3)	0.0004(3)	-0.0006(3)	0.0003(3)
As(4)	0.0119(3)	0.0230(4)	0.0117(3)	-0.0004(3)	0.0012(3)	0.0005(3)
O(1)	0.021(3)	0.027(3)	0.017(3)	0.001(2)	0.008(2)	-0.004(2)
O(2)	0.027(3)	0.025(3)	0.010(2)	0.001(2)	0.001(2)	-0.009(2)
O(3)	0.008(2)	0.032(3)	0.026(3)	0.007(2)	0.001(2)	-0.001(2)
O(4)	0.014(2)	0.026(3)	0.014(3)	-0.002(2)	-0.003(2)	0.001(2)
O(5)	0.017(2)	0.025(3)	0.021(3)	-0.002(2)	-0.004(2)	-0.002(2)
O(6)	0.008(2)	0.036(3)	0.023(3)	-0.009(2)	-0.003(2)	0.002(2)
O(7)	0.018(3)	0.033(3)	0.016(3)	-0.001(2)	-0.001(2)	-0.006(2)
O(8)	0.020(3)	0.026(3)	0.012(3)	0.003(2)	-0.001(2)	-0.001(2)
O(9)	0.023(3)	0.027(3)	0.018(3)	0.003(2)	-0.008(2)	0.001(2)
O(10)	0.013(2)	0.036(3)	0.021(3)	0.010(2)	0.001(2)	0.002(2)
O(11)	0.025(3)	0.028(3)	0.008(2)	0.001(2)	-0.004(2)	0.007(2)
O(12)	0.015(2)	0.025(3)	0.011(2)	-0.0026(19)	0.0036(19)	-0.003(2)
O(13)	0.022(3)	0.029(3)	0.017(3)	-0.002(2)	0.008(2)	0.002(2)
O(14)	0.009(2)	0.031(3)	0.020(3)	-0.007(2)	0.000(2)	0.002(2)
O(15)	0.019(2)	0.022(3)	0.013(3)	0.0044(19)	0.002(2)	0.001(2)
O(16)	0.018(3)	0.032(3)	0.011(2)	-0.002(2)	0.001(2)	0.004(2)
W(1)	0.033(3)	0.038(4)	0.024(3)	-0.006(3)	-0.005(3)	0.002(3)
W(2)	0.070(6)	0.027(4)	0.040(5)	0.002(3)	0.017(4)	-0.002(4)
W(3)	0.032(3)	0.043(4)	0.033(4)	-0.002(3)	0.009(3)	-0.008(3)
W(4)	0.043(4)	0.044(4)	0.028(4)	-0.005(3)	0.006(3)	-0.004(3)
W(5)	0.053(5)	0.065(6)	0.042(5)	0.011(4)	-0.006(4)	-0.030(4)
Cl	0.0246(9)	0.0276(9)	0.0209(9)	0.0018(7)	0.0004(7)	-0.0016(7)

Cu<sub>5</sub>(AsO<sub>4</sub>)<sub>4</sub>Cl·5H<sub>2</sub>O, see Discussion below), and that both lemanskiite and lavendulan occur at this locality, sometimes intergrown with each other (C. Lemanski, pers. comm., 2002).

### Sampleite

Several small, rectangular platelets from an apparently well-crystallized sampleite specimen from the E26 pit, Northparkes mine, Goonumbla, New South Wales, Australia, were studied by single-crystal techniques. As for lavendulan, all platelets showed a primitive cell with monoclinic-pseudotetragonal symmetry ( $a \sim 10.0$ ,  $b \sim 19.5$ ,  $c \sim 10.0$  Å,  $\beta \sim 90^\circ$ ), but twinning was extremely common with only the very smallest crystals appearing to be single. These crystals were too small to provide an acceptable data set from a conventional laboratory diffractometer. X-ray intensity data were thus obtained at the ChemMatCARS facility of the Advanced Photon Source of the Argonne National Laboratory, Argonne, USA. Double diamond (111) reflections were used to obtain monochromated 0.5594 Å radiation from the synchrotron source, and harmonics were eliminated with mirrors. An extremely small single-crystal plate of suitable quality was mounted on a unique Bruker Kappa diffrac-

tometer equipped with a SMART 6000 CCD detector and an Oxford Scientific Cryojet, allowing data to be collected at 123 K. No diffuse streaking or elongated reflections were observed, and there was also no evidence for any phase change from room temperature to 123 K. Crystal data as well as experimental details are compiled in Table 1. The data integration and reduction were undertaken with SAINT and XPREP.6 (Bruker, 1995), but no correction for absorption was made due to the very small size of the crystal. The crystal structure was solved by direct methods (SHELXS-97, Sheldrick 1997a) and subsequent Fourier and difference Fourier syntheses, which revealed the positions of all non-hydrogen atoms and showed that the topology of the structure of sampleite was identical to that of lavendulan from Lavrion. A subsequent isotropic refinement by full-matrix least-squares on  $F^2$  (SHELXL-97, Sheldrick 1997b), and using the atom labeling scheme of the lavendulan from Lavrion, converged and yielded a sensible structure, but only to an  $R$ -value of  $\sim 18\%$  and curiously with anomalously low temperature factors for many atoms, and particularly for phosphorus. At this stage there appeared strong evidence for twinning in this monoclinic structure where with  $\beta \sim 90^\circ$  a tetragonal structure was being emulated. Accordingly, the appropriate twin law (100, 0–10, 00–1) was invoked

Table 4. Selected bond distances (Å) for the coordination polyhedra in lavendulan ( $X = \text{As}$ ) and sampleite ( $X = \text{P}$ ).

	Lavendulan	Sampleite		Lavendulan	Sampleite
Na–W(3)	2.290(8)	2.365(13)	Ca–W(4)	2.371(8)	2.354(6)
–O(6)	2.341(6)	2.460(7)	–O(16)	2.410(5)	2.466(6)
–O(14)	2.407(6)	2.441(8)	–W(5)	2.428(8)	2.449(12)
–O(3)	2.454(6)	2.483(8)	–O(11)	2.478(5)	2.453(6)
–O(10)	2.472(6)	2.470(7)	–W(1)	2.478(7)	2.456(6)
–W(1)	2.683(8)	2.483(7)	–O(2)	2.488(5)	2.511(7)
<Na–O>	2.44	2.45	–O(7)	2.499(5)	2.542(6)
			<Ca–O>	2.45	2.46
Cu(1)–O(2)	1.940(5)	1.936(6)	Cu(2)–O(16)	1.946(5)	1.962(6)
–O(7)	1.941(5)	1.958(6)	–O(11)	1.946(5)	1.929(6)
–O(15)	1.951(5)	1.967(6)	–O(4)	1.965(5)	1.958(6)
–O(12)	1.968(5)	1.950(5)	–O(8)	1.974(5)	1.982(5)
–Cl	2.832(2)	2.749(2)	–Cl	2.734(2)	2.702(2)
<Cu(1)–O>	[4] 1.95	[4] 1.95	<Cu(2)–O>	[4] 1.96	[4] 1.96
	[5] 2.13	[5] 2.11		[5] 2.11	[5] 2.11
Cu(3)–O(10)	1.917(5)	1.920(7)	Cu(4)–O(14)	1.919(5)	1.928(7)
–O(15)	1.942(5)	1.950(6)	–O(6)	1.924(5)	1.933(7)
–O(3)	1.964(5)	1.950(7)	–O(12)	1.975(5)	1.958(6)
–O(8)	1.988(5)	1.981(6)	–O(4)	1.982(5)	1.985(6)
–Cl	2.747(2)	2.697(2)	–Cl	2.668(2)	2.668(2)
<Cu(3)–O>	[4] 1.95	[4] 1.95	<Cu(4)–O>	[4] 1.95	[4] 1.95
	[5] 2.11	[5] 2.10		[5] 2.09	[5] 2.09
Cu(5)–O(13)	1.942(5)	1.946(6)			
–O(5)	1.954(5)	1.969(6)			
–O(1)	1.959(5)	1.968(6)			
–O(9)	1.969(5)	1.951(7)			
–W(2)	2.232(8)	2.273(7)			
<Cu(5)–O>	[4] 1.96	[4] 1.96			
	[5] 2.01	[5] 2.02			
X(1)–O(1)	1.661(5)	1.534(5)	X(2)–O(7)	1.674(5)	1.545(6)
–O(2)	1.679(5)	1.537(9)	–O(6)	1.679(5)	1.527(8)
–O(3)	1.681(5)	1.564(5)	–O(5)	1.679(5)	1.543(5)
–O(4)	1.708(5)	1.569(6)	–O(8)	1.717(5)	1.591(5)
<X(1)–O>	1.68	1.55	<X(3)–O>	1.69	1.55
X(3)–O(9)	1.663(5)	1.524(6)	X(4)–O(13)	1.657(5)	1.526(6)
–O(10)	1.667(5)	1.545(8)	–O(14)	1.673(5)	1.528(8)
–O(11)	1.685(5)	1.563(6)	–O(16)	1.697(5)	1.567(6)
–O(12)	1.705(5)	1.565(5)	–O(15)	1.715(5)	1.581(6)
<X(3)–O>	1.68	1.55	<X(4)–O>	1.69	1.55

## Hydrogen-bonding in lavendulan

D–H	d(D–H)	D–H...A	d(D–A)	$\angle(\text{D–H}\cdots\text{A})$	H–D–H	$\angle(\text{H–D–H})$
W(1)–H(1a)	0.87(11)	W(1)–H(1a)...O(5)	2.850(9)	165.8	H(1a)–W(1)–H(1b)	111(10)
W(1)–H(1b)	0.85(11)	W(1)–H(1b)...O(1)	2.727(9)	170.0		
W(2)–H(2a)	0.62(13)	W(2)–H(2a)...Cl	3.185(8)	149.5	H(2a)–W(2)–H(2b)	91(10)
W(2)–H(2b)	0.74(13)	W(2)–H(2b)...O(3)	2.859(10)	158.3		
W(3)–H(3a)	0.91(11)	W(3)–H(3a)...O(9)	2.819(9)	156.5	H(3a)–W(3)–H(3b)	110(10)
W(3)–H(3b)	0.89(11)	W(3)–H(3b)...O(9)	2.897(9)	160.3		
W(4)–H(4a)	0.98(12)	W(4)–H(4a)...W(5)	2.917(12)	132.6	H(4a)–W(4)–H(4b)	136(10)
W(4)–H(4b)	0.66(12)	W(4)–H(4b)...O(5)	2.842(9)	154.9		
W(5)–H(5a)	0.69(13)	W(5)–H(5a)...W(5)	2.949(17)	151.2	H(5a)–W(5)–H(5b)	110(10)
W(5)–H(5b)	0.83(14)	W(5)–H(5b)...W(3)	2.649(11)	157.1		

Table 4. (Cont.)

Tentative hydrogen-bonding in sampleite			
	d(D-A)		d(D-A)
W(1)···O(5)	2.85(1)	W(1)···O(1)	2.76(1)
W(2)···Cl	3.25(1)		
W(2)···O(3)	2.88(1)	W(3)···O(9)	2.71(1)
W(3)···O(9)	2.72(1)		
W(4)···W(5)	3.07(2)		
W(5)···W(5)	2.99(2)	W(5)···W(3)	2.61(2)

and this reduced the  $R$  factor to  $\sim 5\%$ , with a refined twin ratio of 44:56, for the 4894 independent reflections in the data set. We note that the presence of an additional twin law cannot be excluded, although it is not considered probable. At this stage, the temperature factors for the four phosphorus atoms were still anomalously low and a significant portion of the data was still calculating very poorly. This suggested that, in addition to the twinning, the crystal might suffer from some kind of stacking disorder for which no retrospective ‘data correction’ could be applied. In order to overcome this problem, the low resolution limit of the reflection data to be used in the final refinement was held at 1 Å and, while the number of data was now reduced to 2601 independent reflections, this allowed the structure to refine smoothly to a most acceptable model and, importantly, with acceptable isotropic thermal parameters for all atoms. We point out that changing the low-resolution limit to 2, 3 and even 4 Å (which of course increases the number of low-angle data in

the refinement) leads only to negligible change in the  $R$  factors for the isotropic model and to no change in the model itself; at 4 Å, the only observable effect is the lowering of all displacement parameters by about 50%.

An attempt to then refine the structure anisotropically was made but then abandoned as this resulted in non-positive definite temperature factors for almost half of the atoms. We note that problems in the anisotropic refinement of displacement parameters using low-temperature synchrotron data are quite common. The positions of about half of the hydrogen atoms were locatable in the final difference Fourier map (at positions that correspond to those in lavendulan), but not reliably so, and hence hydrogens were not included in the final refinement. The final  $R$ -values were  $R1(F) = 4.44\%$  and  $wR2_{\text{all}}(F^2) = 12.08\%$  for 2601 reflections with  $F_o > 4\sigma(F_o)$  (Table 1). For easier comparison with the data obtained for lavendulan, the structure parameters of sampleite are included in Table 2, and selected interatomic distances and bond angles are also given in Table 4.

### Sampleite polymorph

Several small, sharply rectangular platelets from the above-mentioned ‘sampleite’ specimen from Lake Boga, Victoria, were studied by single-crystal techniques. All platelets showed a primitive cell with monoclinic-pseudotetragonal symmetry. Surprisingly, the orientation of the crystal axes ( $a \sim 9.7$ ,  $b \sim 9.7$ ,  $c \sim 19.7$  Å,  $\beta \sim 102.6^\circ$ ) was different from that of lavendulan and sampleite. The following relations of orientation were evident:  $a_{\text{sampl}} = -a_{\text{lav}}$ ,  $b_{\text{sampl}} = c_{\text{lav}}$ ,  $c_{\text{sampl}} = b_{\text{lav}}$ .

Table 5. Bond-valence analysis for lavendulan from Lavrion, Greece.

	Na	Ca	Cu(1)	Cu(2)	Cu(3)	Cu(4)	Cu(5)	As(1)	As(2)	As(3)	As(4)	Sum*
O(1)							0.469	1.332				1.80
O(2)		0.245	0.494					1.269				2.01
O(3)	0.171				0.463			1.262				1.90
O(4)				0.462		0.441		1.173				2.08
O(5)							0.476		1.269			1.75
O(6)	0.232					0.516			1.269			2.02
O(7)		0.237	0.493						1.286			2.02
O(8)				0.451	0.434				1.145			2.03
O(9)							0.457			1.325		1.78
O(10)	0.163				0.526					1.310		2.00
O(11)		0.251		0.486						1.248		1.99
O(12)			0.458			0.449				1.182		2.09
O(13)							0.491				1.346	1.84
O(14)	0.194					0.523					1.289	2.01
O(15)			0.479		0.491						1.151	2.12
O(16)		0.302		0.486							1.208	2.00
W(1)	0.092	0.251										0.34
W(2)							0.224					0.22
W(3)	0.266											0.27
W(4)		0.336										0.34
W(5)		0.288										0.29
Cl			0.106	0.138	0.133	0.164						0.54*
Sum	1.12	1.91	2.03	2.02	2.05	2.09	2.12	5.04	4.97	5.07	4.99	

Note: bond-valence parameters used are from Brese & O’Keeffe (1991). Contributions of hydrogen atoms are not listed.

\* see text for discussion



Table 6. Fractional atomic coordinates and displacement parameters (in Å<sup>2</sup>) for the sampleite polymorph from Lake Boga.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Na	0.1870(8)	0.2080(7)	0.6027(4)	0.0430(19)
Ca	0.3191(3)	0.2770(3)	0.40528(15)	0.0233(8)
Cu(1)	0.73327(16)	0.05287(19)	0.21307(9)	0.0185(5)
Cu(2)	0.26393(17)	0.02044(19)	0.27943(9)	0.0190(6)
Cu(3)	-0.03815(17)	0.28727(15)	0.21499(9)	0.0152(5)
Cu(4)	0.50696(18)	0.28915(16)	0.21511(9)	0.0171(5)
Cu(5)	0.81906(17)	0.28848(17)	0.40553(9)	0.0173(5)
P(1)	0.4195(4)	-0.0036(3)	0.15683(17)	0.0141(8)
P(2)	-0.0013(4)	-0.0080(3)	0.15795(18)	0.0151(8)
P(3)	0.5808(4)	0.0843(3)	0.33693(18)	0.0147(8)
P(4)	-0.0045(4)	0.0824(3)	0.33647(18)	0.0152(8)
O(1)	0.3184(11)	-0.0642(10)	0.0923(5)	0.022(2)
O(2)	0.3939(10)	0.1496(9)	0.1574(5)	0.021(2)
O(3)	0.5725(10)	-0.0420(10)	0.1565(5)	0.024(2)
O(4)	0.3838(11)	-0.0690(10)	0.2242(5)	0.021(2)
O(5)	0.0378(11)	-0.0627(9)	0.0927(5)	0.021(2)
O(6)	-0.1522(9)	-0.0407(10)	0.1579(5)	0.0157(19)
O(7)	0.0255(13)	0.1480(11)	0.1589(6)	0.029(2)
O(8)	0.0971(10)	-0.0708(10)	0.2241(5)	0.020(2)
O(9)	0.6688(11)	0.1537(11)	0.4000(6)	0.027(2)
O(10)	0.4218(9)	0.1165(10)	0.3339(5)	0.0176(19)
O(11)	0.6123(9)	-0.0709(10)	0.3388(6)	0.023(2)
O(12)	0.6183(10)	0.1436(10)	0.2693(5)	0.019(2)
O(13)	-0.0375(11)	0.1497(10)	0.4000(5)	0.022(2)
O(14)	0.1483(11)	0.1139(11)	0.3353(5)	0.022(2)
O(15)	-0.1004(10)	0.1405(10)	0.2697(5)	0.020(2)
O(16)	-0.0315(10)	-0.0694(9)	0.3395(5)	0.019(2)
W(1)	0.2042(13)	0.3515(15)	0.4962(6)	0.042(3)
W(2)	-0.1252(19)	0.2682(16)	0.5214(7)	0.056(4)
W(3)*	0.115(4)	0.045(2)	0.5142(17)	0.059(9)
W(4)	0.5083(13)	0.3408(13)	0.4955(7)	0.040(3)
W(5)	0.356(2)	0.0615(18)	0.4766(10)	0.076(6)
Cl	0.7001(4)	0.2933(3)	0.13837(19)	0.0226(8)

Note: Oxygens of H<sub>2</sub>O molecules are designated as W. *U*<sub>eq</sub> as defined by Fischer & Tillmanns (1988).

\* Refined occupancy of W(3) is 0.56(5).

The reflections of all studied platelets were more or less broadened, and the crystal quality was very poor. Some crystals were apparently twinned, resulting in a “doubled” *c*-axis. In one case, splitting of a twinned crystal along the clearly visible twin plane (parallel to its morphological elongation and perpendicular to its platy face) led to an untwinned fragment, albeit of mediocre quality. Intensity data were collected from this crystal fragment with the same Nonius KappaCCD diffractometer used for the data collection of lavendulan. A full sphere of reciprocal space was measured (see Table 1 for details). The measured intensity data were processed with the Nonius program suite DENZO-SMN and corrected for Lorentz, polarisation, background and absorption effects. Analysis of the measured data indicated the centrosymmetric space group *P*2<sub>1</sub>/*c*. The crystal structure was solved by direct methods (SIR97, Altomare *et al.*, 1999) and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares anisotropic refinements on *F*<sup>2</sup> (SHELXL-97, Sheldrick, 1997b) (Table 1). Because the topology of the structure model obtained was similar (albeit not identical) to that of lavendulan and

sampleite, all atoms were labeled accordingly (as far as possible) to allow easier comparisons of the common and the differing crystal-chemical features. The positions of the hydrogen atoms could not be located, and about four O atoms showed a “non-positive definite” character. The omission of about 40 reflections with a bad fit between calculated and observed structure factors resulted in both a distinct decrease of the *R*-values and a less “non-positive definite” character of the mentioned O atoms. During the last steps of refinement, about 75 further ‘bad’ reflections were omitted, which resulted in the final residuals *R*1(*F*) = 14.67 % and *wR*2<sub>all</sub>(*F*<sup>2</sup>) = 39.34 % for 3189 reflections with *F*<sub>o</sub> > 4σ(*F*<sub>o</sub>) (Table 1). A search for higher symmetry using PLATON (Spek, 2003) was unsuccessful. It should also be noted that the application of various possible twin matrices did not result in any distinct improvement of the model. The fairly high *R*-values are explained by the poor quality of the crystal and probably the additional presence of stacking disorder (all the largest residual peaks in the final electron density map were close to the Cu, Ca and Na atoms). The final positional and displacement parameters are given in Tables 6

Table 7. Anisotropic displacement parameters (in  $\text{\AA}^2$ ) for the sampleite polymorph from Lake Boga.

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Na	0.030(4)	0.035(4)	0.062(5)	0.011(3)	0.005(4)	-0.004(3)
Ca	0.0317(18)	0.0167(15)	0.0204(14)	0.0027(10)	0.0032(12)	-0.0051(12)
Cu(1)	0.0081(9)	0.0171(10)	0.0306(10)	-0.0020(6)	0.0051(7)	-0.0017(6)
Cu(2)	0.0106(9)	0.0182(10)	0.0285(9)	-0.0016(6)	0.0047(7)	0.0006(6)
Cu(3)	0.0141(9)	0.0081(9)	0.0242(10)	-0.0012(6)	0.0057(7)	-0.0022(6)
Cu(4)	0.0134(9)	0.0105(9)	0.0269(10)	0.0012(6)	0.0031(7)	0.0011(6)
Cu(5)	0.0157(9)	0.0108(9)	0.0249(10)	0.0000(6)	0.0035(7)	0.0002(6)
P(1)	0.0103(16)	0.0088(16)	0.0229(16)	-0.0010(12)	0.0030(13)	0.0015(12)
P(2)	0.0117(16)	0.0105(16)	0.0244(17)	0.0004(12)	0.0071(13)	-0.0012(12)
P(3)	0.0120(16)	0.0081(15)	0.0226(16)	0.0005(12)	0.0007(13)	-0.0047(12)
P(4)	0.0119(16)	0.0100(16)	0.0229(16)	-0.0020(12)	0.0016(13)	0.0017(12)
O(1)	0.016(5)	0.021(5)	0.025(5)	-0.005(4)	-0.006(4)	0.007(4)
O(2)	0.017(5)	0.009(4)	0.036(5)	-0.007(4)	0.003(4)	0.009(4)
O(3)	0.011(5)	0.024(5)	0.034(5)	0.006(4)	0.003(4)	0.001(4)
O(4)	0.020(5)	0.019(5)	0.026(5)	0.003(4)	0.006(4)	-0.015(4)
O(5)	0.018(5)	0.011(5)	0.033(5)	0.003(4)	0.006(4)	0.009(4)
O(6)	0.000(4)	0.023(5)	0.023(4)	0.000(4)	0.000(3)	-0.004(3)
O(7)	0.040(7)	0.018(5)	0.033(6)	0.000(4)	0.015(5)	0.003(5)
O(8)	0.011(4)	0.023(5)	0.026(5)	0.001(4)	0.004(4)	0.002(4)
O(9)	0.012(5)	0.028(6)	0.041(6)	-0.010(5)	0.003(4)	-0.020(4)
O(10)	0.005(4)	0.020(5)	0.027(5)	-0.001(4)	0.002(3)	-0.003(4)
O(11)	0.000(4)	0.020(5)	0.049(6)	-0.008(4)	0.003(4)	-0.001(3)
O(12)	0.013(5)	0.017(5)	0.029(5)	0.006(4)	0.012(4)	0.009(4)
O(13)	0.019(5)	0.016(5)	0.034(5)	0.000(4)	0.010(4)	0.002(4)
O(14)	0.020(5)	0.033(6)	0.015(4)	0.000(4)	0.010(4)	0.025(4)
O(15)	0.018(5)	0.014(5)	0.028(5)	-0.006(4)	0.003(4)	0.003(4)
O(16)	0.007(4)	0.011(4)	0.045(6)	-0.011(4)	0.015(4)	-0.008(3)
W(1)	0.024(6)	0.058(8)	0.041(7)	0.001(6)	0.001(5)	-0.003(6)
W(2)	0.078(12)	0.059(9)	0.026(6)	-0.004(6)	0.002(7)	-0.016(8)
W(3)	0.10(3)	0.020(12)	0.08(2)	0.000(13)	0.06(2)	0.010(14)
W(4)	0.030(7)	0.037(7)	0.054(7)	0.007(6)	0.007(6)	-0.009(5)
W(5)	0.090(15)	0.064(11)	0.084(12)	-0.016(10)	0.040(11)	-0.032(10)
Cl	0.0176(16)	0.0204(17)	0.0296(18)	0.0035(13)	0.0048(13)	0.0020(13)

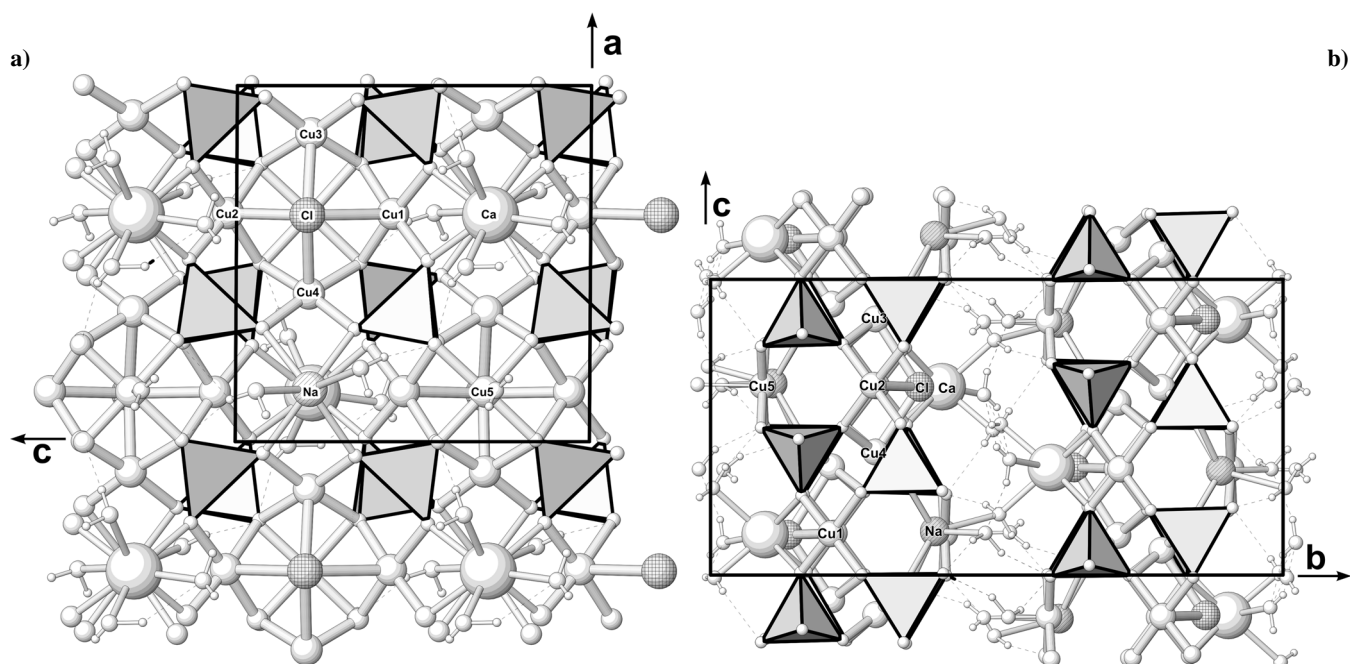


Fig. 2. The heteropolyhedral sheet and the hydrogen-bonding scheme in lavendulan in (a) a view perpendicular to the sheet (along the  $b$  axis; only one sheet shown), and (b) along the sheets (along the  $a^*$  axis). All drawings were done with ATOMS (Shape Software, 2003).

Table 8. Selected bond distances (Å) for the coordination polyhedra in the sampleite polymorph from Lake Boga.

Na–W(3)*	2.34(3)	Ca–W(4)	2.343(13)
–O(11)	2.428(12)	–W(1)	2.420(13)
–O(16)	2.475(12)	–O(10)	2.449(10)
–O(2)	2.478(12)	–O(14)	2.479(12)
–O(7)	2.525(13)	–O(3)	2.493(11)
–W(1)	2.555(16)	–W(5)	2.497(17)
<Na–O>	2.47	–O(6)	2.530(9)
		<Ca–O>	2.46
Cu(1)–O(3)	1.939(10)	Cu(2)–O(10)	1.908(9)
–O(6)	1.940(10)	–O(8)	1.954(10)
–O(12)	1.945(9)	–O(14)	1.957(9)
–O(15)	1.998(10)	–O(4)	1.960(11)
–Cl	2.735(4)	–Cl	2.708(4)
<Cu(1)–O>	[4] 1.956 [5] 2.111	<Cu(2)–O>	[4] 1.945 [5] 2.097
Cu(3)–O(7)	1.929(11)	Cu(4)–O(11)	1.940(10)
–O(15)	1.957(10)	–O(2)	1.943(10)
–O(16)	1.962(9)	–O(12)	1.946(10)
–O(8)	1.989(10)	–O(4)	1.971(9)
–Cl	2.656(4)	–Cl	2.654(4)
<Cu(3)–O>	[4] 1.959 [5] 2.099	<Cu(4)–O>	[4] 1.950 [5] 2.091
Cu(5)–O(9)	1.940(9)		
–O(13)	1.953(10)		
–O(1)	1.958(11)		
–O(5)	1.995(9)		
–W(2)	2.242(13)		
<Cu(5)–O>	[4] 1.962 [5] 2.018		
P(1)–O(2)	1.503(10)	P(2)–O(6)	1.497(9)
–O(3)	1.529(10)	–O(5)	1.516(10)
–O(1)	1.544(10)	–O(7)	1.530(11)
–O(4)	1.578(10)	–O(8)	1.562(10)
<P(1)–O>	1.539	<P(2)–O>	1.526
P(3)–O(9)	1.505(10)	P(4)–O(16)	1.495(9)
–O(11)	1.532(10)	–O(13)	1.507(10)
–O(10)	1.561(10)	–O(14)	1.518(11)
–O(12)	1.568(10)	–O(15)	1.544(10)
<P(3)–O>	1.542	<P(4)–O>	1.516
Probable hydrogen-bonding in the sampleite polymorph**			
	d(D–A)		d(D–A)
W(1)···O(1)	2.85(2)	W(1)···O(5)	2.73(2)
W(1)···W(4)	2.95(2)		
W(2)···O(7)	2.90(2)	W(2)···Cl	3.20(2)
W(4)···O(1)	2.82(2)		
W(3)*···W(5)	2.61(3)	W(4)···W(4)	3.09(3)
W(3)*···O(13)	2.61(4)	W(3)*···O(13)	2.75(3)
W(3)*···O(14)	3.11(2)		

\* W(3) is half-occupied, with a W(3)–W(3) distance of 2.34(7) Å.

\*\* Only distances < 3.1 Å are listed (except when Cl is acceptor).

and 7 (anisotropic displacement parameters). Selected bond lengths and probable hydrogen bonds are presented in Table 8, and a bond-valence analysis is given in Table 9. A list of

observed and calculated structure factors is available upon request.

### Zdenekite

Several samples of zdenekite,  $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ , were also subjected to X-ray diffraction studies. Only one sample, from the type locality (Cap Garonne, France; collection of South Australian Museum, Adelaide), showed crystal aggregates of sufficient size for any single-crystal studies. These aggregates were composed of very small and thin, tetragonal (001) platelets. Some of the platelets were contact-twinning by rotation of  $45^\circ$  about the pseudotetragonal  $b$ -axis (this twinning is not described in the original publication). Unfortunately, all single crystals were too small and of a too low quality to determine a reliable unit cell or to distinguish between uniaxial and biaxial optics.

## Results and Discussion

### Crystal structure of lavendulan

The asymmetric unit of lavendulan contains one Na atom, one Ca atom, five Cu atoms, four As atoms, 21 O atoms (5 of which represent  $\text{H}_2\text{O}$  molecules) and ten H atoms; all atoms occupy general sites. The previously given formula,  $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ , is therefore confirmed. Lavendulan is characterized by heteropolyhedral sheets parallel to (010) (Fig. 2a), which are composed of  $\text{CuX}_5$  ( $X = \text{O}, \text{Cl}$ ) and  $\text{AsO}_4$  groups, and linked *via*  $\text{NaO}_6$  and  $\text{CaO}_7$  polyhedra as well as by weak hydrogen bonding into a loose framework (Fig. 2b). The Cu atoms are [4+1]-coordinated to form Jahn-Teller distorted tetragonal pyramids: in all cases the square is built by O atoms with Cu–O bond lengths in the range from 1.917(5) to 1.988(5) Å, and the apical ligand is either a Cl atom (for Cu(1) to Cu(4); Cu–Cl = 2.668(2) – 2.832(2) Å) or an  $\text{H}_2\text{O}$  ligand (for Cu(5); Cu(5)–W(2) = 2.232(8) Å). Average  $^{14}\text{Cu}$ -O bond lengths (1.95–1.96 Å, Table 4) in the  $\text{CuX}_5$  groups are in very good agreement with the corresponding grand mean value for the four planar Cu–O bonds in polyhedra centred by [5]-coordinated Cu (1.96 Å, Lambert, 1988).

The four  $\text{CuO}_4\text{Cl}$  polyhedra are linked to each other *via* four common edges of four O atoms and one common Cl atom into a  $[\text{Cu}_4\text{O}_{12}\text{Cl}]$  cluster. These clusters share corners with eight neighbouring  $\text{AsO}_4$  tetrahedra. The  $\text{AsO}_4$  tetrahedra are further bound to the square of the single  $\text{Cu(5)O}_5$  pyramid as illustrated in Fig. 3. Therefore, each arsenate group is linked by common corners to two clusters plus one  $\text{Cu(5)O}_5$  pyramid, which are combined together *via* the arsenate tetrahedra to the sheet, completed by the  $\text{NaO}_6$  and  $\text{CaO}_7$  polyhedra on both sides. The  $\text{NaO}_6$  polyhedron is best described as a distorted trigonal prism, while the  $\text{CaO}_7$  polyhedron may be characterized either as irregular or as a distorted, incomplete cube in which two adjacent corners are merged into a single corner, W(5). The  $\text{NaO}_6$  and  $\text{CaO}_7$  polyhedra both share two opposite edges with  $\text{CuO}_4\text{Cl}$  pyramids; the other ligands are O atoms of  $\text{H}_2\text{O}$  molecules (W(1), W(3), W(4) and W(5)).  $\text{NaO}_6$  and  $\text{CaO}_7$  polyhedra of neighbouring sheets are linked *via* common corners ( $\text{H}_2\text{O}$

Table 9. Bond-valence analysis for the sampleite polymorph from Lake Boga.

	Na	Ca	Cu(1)	Cu(2)	Cu(3)	Cu(4)	Cu(5)	P(1)	P(2)	P(3)	P(4)	Sum
O(1)							0.470	1.176				1.65**
O(2)	0.160					0.490		1.314				1.96
O(3)		0.241	0.495					1.225				1.96
O(4)				0.468		0.454		1.073				2.00
O(5)							0.426		1.269			1.70**
O(6)		0.218	0.494						1.335			2.05
O(7)	0.141				0.509				1.221			1.87
O(8)				0.476	0.433				1.120			2.03
O(9)							0.494			1.307		1.80
O(10)		0.272		0.539						1.123		1.93
O(11)	0.183					0.494				1.215		1.89
O(12)			0.487			0.486				1.102		2.08
O(13)							0.477				1.300	1.78
O(14)		0.251		0.472							1.262	1.99
O(15)			0.422		0.472						1.176	2.07
O(16)	0.161				0.465						1.343	1.97
W(1)	0.130	0.294										0.42
W(2)							0.218					0.22
W(3)*	0.116											0.12
W(4)		0.362										0.36
W(5)		0.239										0.24
Cl			0.137	0.148	0.170	0.171						0.63**
Sum	0.89	1.88	2.04	2.10	2.05	2.10	2.09	4.79	4.95	4.75	5.08	

Note: bond-valence parameters used are from Brese & O'Keeffe (1991).

\* W(3) is half-occupied (see text) and the bond-valence contribution has been halved accordingly.

\*\* see text for discussion

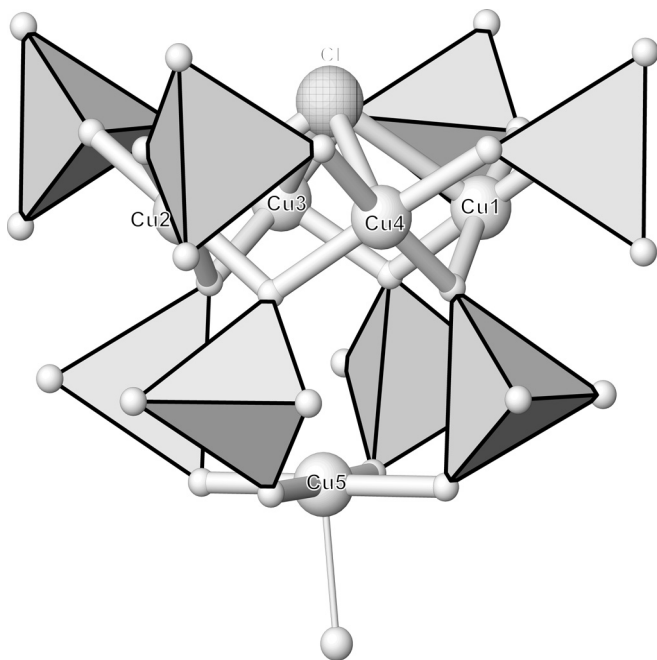


Fig. 3. The main building unit of the heteropolyhedral sheet in lavendulan (shown here), sampleite, and the polymorph of sampleite.

groups) among them as well as by hydrogen bonding (Figs. 2a,b).

The heteropolyhedral sheet in lavendulan would have, in its idealized form, tetragonal  $p4mm$  symmetry (cf. Fig. 2a). The sheet is equivalent to that in the Pb-analogue zdenekite,

$\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$  (Zubkova *et al.*, 2003;  $P2_1/n$ ,  $a = 10.023(7)$ ,  $b = 19.55(1)$ ,  $c = 10.023(6)$  Å,  $\beta = 90.02(1)^\circ$ ). Lavendulan is isotypic to zdenekite; note, however, that in the description of zdenekite the  $a$  and  $c$  axes, which are both identical in length within error limits, are interchanged as compared to lavendulan. The Pb atom in zdenekite is coordinated to seven O atoms, and forms a polyhedron quite similar to the  $\text{CaO}_7$  polyhedron in lavendulan. The  $\text{NaO}_6$  polyhedron in zdenekite, described as a “distorted octahedron” by Zubkova *et al.* (2003), is in fact better described as a slightly distorted trigonal prism completely analogous to the  $\text{NaO}_6$  polyhedron in lavendulan.

The  $[\text{Cu}_4\text{O}_{12}\text{Cl}]$  cluster is topologically equivalent to  $[\text{Cu}_4\text{O}_{13}]$  clusters present in calcio-andyrobartsite (see below) and the synthetic compounds  $\text{BaCu}_4(\text{VO})(\text{PO}_4)_4$  (Meyer & Müller-Buschbaum, 1997) and  $\text{Na}_5\text{ACu}_4(\text{AsO}_4)_4\text{Cl}_2$  ( $A = \text{Rb, Cs}$ ) (Hwu *et al.*, 2002).

#### *Bond valences and hydrogen bonding in lavendulan*

The bond-valence analysis of the structure model (Table 5) yields bond-valence sums (BVSs) in good agreement with formal valencies, except for the Cl atom, with only 0.54 v.u. (valence units). However, the reported bond-valence parameters for Cu-Cl bonds seem to be insufficient; in sampleite and the sampleite polymorph (see below), equally ‘low’ BVSs are found for the Cl atoms. Furthermore, in clinocatacamite, the monoclinic polymorph of  $\text{Cu}_2(\text{OH})_3\text{Cl}$  (Grice *et al.*, 1996), the BVS for the Cl atom is also only 0.37 v.u., but this atom receives additional hydrogen-bonds from three O atoms. This is not the case for lavendulan: the proposed hydrogen bonding scheme for lavendulan (Table 4, Figs. 2a,b)

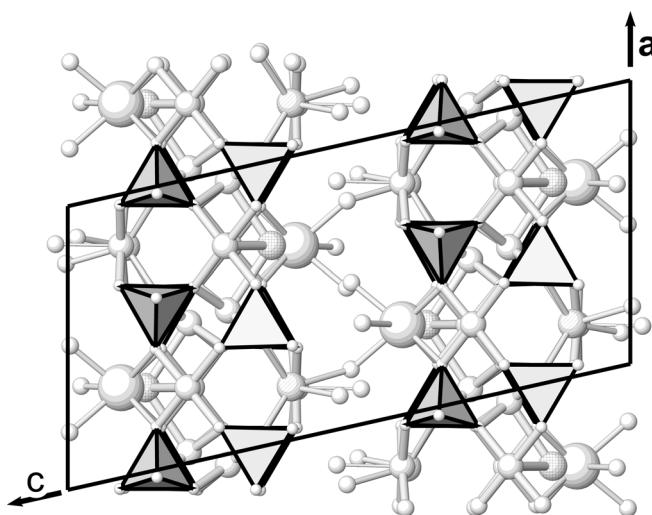


Fig. 4. The crystal structure of the polymorph of sampleite in a view along the heteropolyhedral sheets (compare Fig. 2b).

shows that the D...A donor-acceptor distances are in the range between 2.65 and 2.95 Å for those bonds with O ligands as acceptor atoms; in the case of H2a the acceptor is a Cl atom ( $W(2)-Cl = 3.185(8)$  Å) which thereby slightly improves its bond-valence requirements. In the tabulated bond-valence analysis of zdenekite,  $NaPbCu_5(AsO_4)_4Cl \cdot 5H_2O$  (Zubkova *et al.*, 2003; Table 3), no bond-valence contribution is listed for the Cl atom because it is stated to be “overestimated”. A recalculation gave a BVS of 0.55 v.u., *i.e.*, a value nearly identical with that of the Cl atom in lavendulan.

### Crystal structure of sampleite

The structures of sampleite and lavendulan have identical topology, as described above, with negligible differences being found in the bond distances and the geometry of the coordination polyhedra for the corresponding Cu, Ca and Na atoms (see Table 4), despite the distinct difference between the respective  $X-O$  ( $X = P$  or  $As$ ) distances ( $P-O \sim 1.55$  Å;  $As-O \sim 1.685$  Å). We note that these average distances are all close to commonly observed metal-oxygen distances (Baur, 1981).

The hydrogen bonding scheme in sampleite, tentatively given in Table 4 on the basis of probable donor-acceptor distances, appears fairly similar to that in lavendulan.

### Crystal structure of the polymorph of sampleite

The heteropolyhedral sheet in the sampleite polymorph from Lake Boga is topologically identical to that of sampleite (and lavendulan), as demonstrated by Fig. 4. However, the stacking of these sheets in the polymorph is slightly different, thus leading to a different space-group orientation. The  $NaO_6$  polyhedron is a slightly distorted trigonal prism, very similar to that in lavendulan/sampleite. The  $CaO_7$  poly-

hedron is equally similar. As in lavendulan/sampleite, each  $NaO_6$  and  $CaO_7$  polyhedron shares two opposite edges with  $CuO_4Cl$  pyramids, and the  $H_2O$  ligand  $W(1)$  connects Na and Ca in all three structures. In contrast to lavendulan and sampleite,  $W(3)$ , one of the four interlayer  $H_2O$  molecules, which represent ligands of the Na and Ca atoms, is only half-occupied (refined occupancy 0.56(5)), in agreement with an unrealistically close  $W(3)-W(3)$  distance of 2.34(7) Å. Thus, the chemical formula of the polymorph,  $NaCa-Cu_5(PO_4)_4Cl \cdot nH_2O$ ,  $n \sim 4.5$ , appears to be slightly different from that of sampleite.

The slightly different arrangement of the interlayer atoms, especially that of the  $H_2O$  ligands (Fig. 4), is believed to cause the somewhat different stacking and the change in space-group orientation as compared to sampleite (and lavendulan). The sampleite polymorph may be considered a polytype, if these slight topological differences and the apparently decreased water content are neglected. The unit-cell volume of the sampleite polymorph ( $1806.5(6)$  Å<sup>3</sup>; at 293 K) is smaller than that of sampleite ( $1822.3(6)$  Å<sup>3</sup>; at 123 K), in agreement with a formula seemingly containing 2  $H_2O$  less per unit cell.

Calculated BVSs (Table 9) show good agreement with formal valencies. As in lavendulan and sampleite, the Cl atom has an anomalously low BVS, 0.63 v.u. (see above for discussion). The rather low values calculated for O(1) and O(5), 1.65 and 1.70 v.u., respectively, indicate that these atoms will be acceptors of various hydrogen bonds, in agreement with the hydrogen bonding scheme discussed below.

Because no H atoms could be located during the refinement, the hydrogen bonding scheme in the polymorph can be discussed only on the basis of the probable donor-acceptor distances (Table 8). These range between about 2.6 and 3.2 Å, indicating strong to very weak hydrogen bonds. The two shortest donor-acceptor distances both involve the partially occupied  $W(3)$  site. The strongest and the third-strongest hydrogen bonds ( $W(3)-O(13)$  at 2.61(3) Å and  $W(1)-O(5)$  at 2.73(2) Å, respectively) strengthen the bonding between the sheets, whereas the second-strongest bond ( $W(3)-W(5)$  at 2.61(3) Å) extends roughly within the sheet. The strongly underbonded atoms O(1) and O(5) each receive hydrogen bonds from at least one  $H_2O$  molecule, very similar to the situation for the equivalent oxygen ligands in lavendulan and sampleite. The hydrogen bond involving the Cl atom as an acceptor,  $W(2)-Cl = 3.20(2)$  Å, is of a length very similar to the corresponding bond in lavendulan.

We prefer to consider the polymorph of sampleite from Lake Boga only as a stacking variant instead of a new mineral species. We point out the similar relation between calcio-andyrobobersite-1*M* and calcio-andyrobobersite-2*O*, which are both characterized by different stacking of a lavendulan-like sheet (see below). Calculated X-ray powder diffraction patterns of sampleite and the sampleite polymorph are similar, although a careful comparison shows small, but distinct differences in the range around  $d = 3.0$  Å.

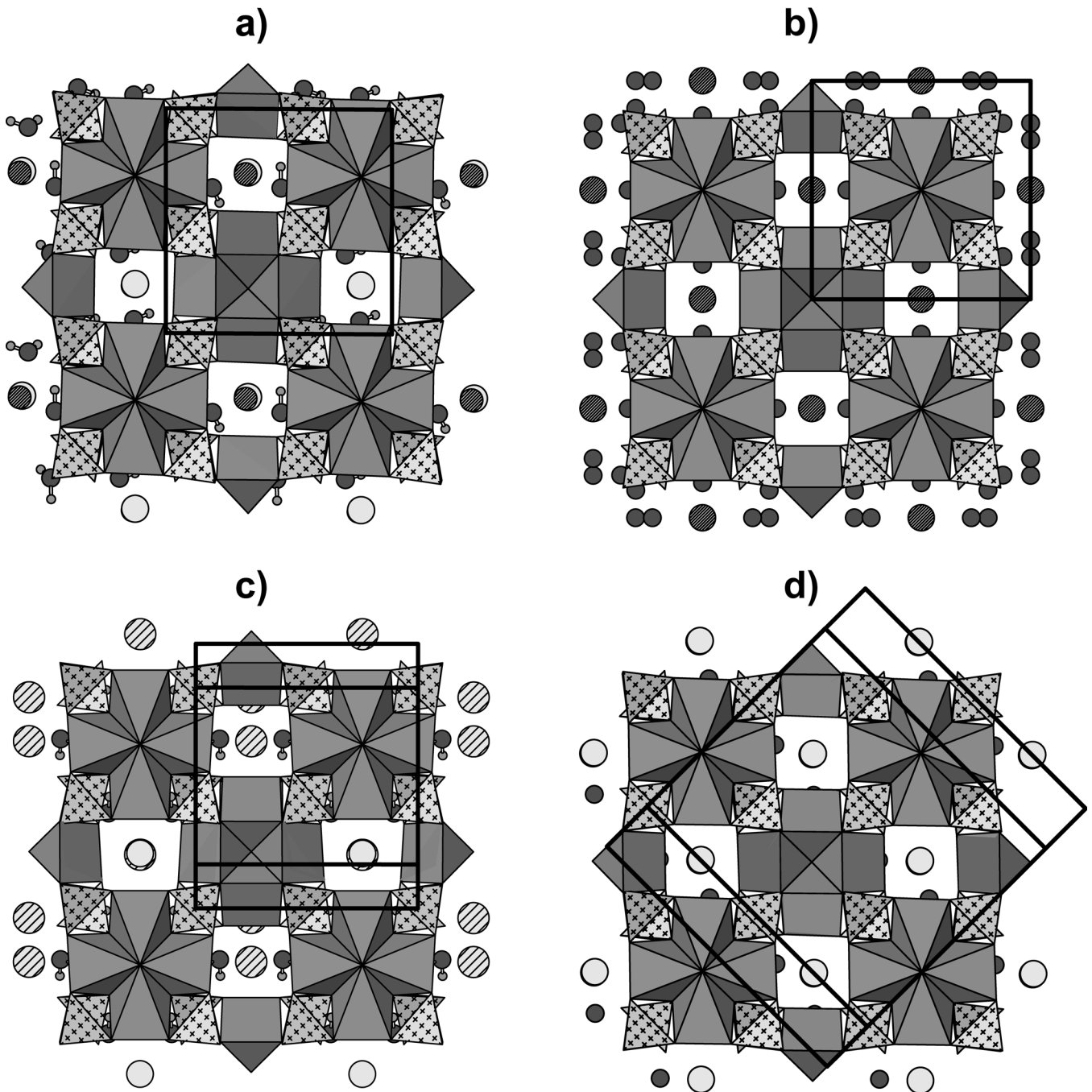


Fig. 5. Comparative views perpendicular to the heteropolyhedral sheets of the crystal structures of (a) lavendulan [representative also of sampleite and the sampleite polymorph], (b) mahnertite, (c) andyrobertsite-1M [representative also of calcio-andyrobertsite-1M and -2O], and (d) richelsdorfitite [probably also representative of bleasdaleite]. Alkali atoms are shown as large hatched circles, Ca atoms as large circles, O atoms of water molecules as small dark grey circles, and H atoms as very small grey circles. Note the different orientations of the respective unit cells. The presently unknown crystal structures of lemanskiite and shubnikovite are thought to be based on more or less identical heteropolyhedral sheets (see text).

### Related species and a re-classification of the lavendulan group

Lavendulan, sampleite and its polymorph belong to a group of visually similar, predominantly blue to turquoise-blue secondary arsenate and phosphate minerals, all of which

form small, soft, platy crystals with apparent tetragonal or pseudotetragonal symmetry, and perfect cleavage parallel to the platy face (a result of the distinct features of the sheet-based crystal structure). We propose a re-classification of the lavendulan group, and suggest that this group should also include zdenekite, lemanskiite, mahnertite and shubniko-

Table 10. Comparison of lavendulan, sampleite, the sampleite polymorph, zdenekite, mahnertite and lemanskiite.

Locality	Lavendulan Lavrion, Greece	Sampleite Northparkes, Australia	Sampleite polymorph Lake Boga, Australia	Zdenekite Cap Garonne, France	Mahnertite Cap Garonne, France	Lemanskiite El Guanaco, Chile
Ref.	<i>This work</i>	<i>This work</i>	<i>This work</i>	Zubkova <i>et al.</i> (2003)	Pushcharovsky <i>et al.</i> (2004)	Ondruš <i>et al.</i> (2006)
Ideal formula	NaCaCu <sub>5</sub> (AsO <sub>4</sub> ) <sub>4</sub> Cl·5H <sub>2</sub> O	NaCaCu <sub>5</sub> (PO <sub>4</sub> ) <sub>4</sub> Cl·5H <sub>2</sub> O	NaCaCu <sub>5</sub> (PO <sub>4</sub> ) <sub>4</sub> Cl· <i>n</i> H <sub>2</sub> O, <i>n</i> ~ 4.5	NaPbCu <sub>5</sub> (AsO <sub>4</sub> ) <sub>4</sub> Cl·5H <sub>2</sub> O	(Na,Ca)Cu <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> Cl·5H <sub>2</sub> O	NaCaCu <sub>5</sub> (AsO <sub>4</sub> ) <sub>4</sub> Cl·5H <sub>2</sub> O
Symmetry	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal	tetragonal
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>I</i> 4/ <i>mmm</i> <sup>d)</sup>	<i>P</i> 4 <sub>1</sub> 22 or <i>P</i> 4 <sub>3</sub> 22
<i>a</i> (Å)	10.011(1)	9.676(2)	9.695(2)	10.023(7)	10.037(1)	9.9758
<i>b</i> (Å)	19.478(2)	19.284(4)	9.673(2)	19.55(1)	–	–
<i>c</i> (Å)	10.056(1)	9.766(2)	19.739(4)	10.023(6)	23.739(1)	36.714
β (°)	90.37(1)	90.07(1)	102.61(3)	90.02(1)	–	–
<i>V</i> (Å <sup>3</sup> )	1960.8(3)	1822.3(6)	1806.5(6)	1964.0	2391.5(4)	3653.6
<i>Z</i>	4	4	4	4	8	8
Strongest lines in the X-ray powder pattern <sup>a)</sup>	9.74 (100), 6.981 (6), 4.870 (11), 4.452 (8), 4.379 (7), 3.121 (15), 3.079 (9), 2.978 (13), 2.968 (10), 2.861 (9), 2.724 (8), 2.628 (8)	9.64 (100), 4.315 (13), 3.032 (21), 3.029 (15), 2.904 (7), 2.883 (6), 2.797 (7), 2.567 (7)	9.63 (100), 6.764 (7), 4.311 (11), 3.046 (15), 2.996 (16), 2.584 (6)	9.78 (100), 6.998 (52), 4.888 (21), 4.460 (26), 4.393 (43), 3.973 (26), 3.114 (44), 3.113 (32), 3.083 (20), 2.973 (20), 2.732 (24)	11.90 (100), 9.29 (60), 7.132 (50), 5.043 (60), 3.098 (80), 3.061 (70)	9.60 (9), 9.18 (100), 4.59 (32), 4.17 (10), 3.06 (15), 2.924 (5), 2.606 (6)
D <sub>meas.</sub> ; D <sub>calc.</sub>	3.64; 3.60	3.26; 3.23	n.d.; 3.19	4.1(1); 4.16	3.33; 3.14	3.78; 3.86
Mohs hardness	2.5–3	~4	n.d.	“soft”	2–3	~2.5
α or ε	1.645	1.625	1.630(3)	1.710(5)	1.635(2)	1.647
β	(–)	1.674	1.675(2)	(–)	(–)	(–)
γ or ω	1.748	1.674	1.676(2)	1.770(5)	1.686(2)	1.749
Birefringence	0.080	0.049	0.046	0.060	0.051	0.102
Opt. character	biax. neg. <sup>b)</sup>	biax. neg. <sup>b)</sup>	biax. neg. <sup>b)</sup>	uniax. neg.	uniax. neg.	uniax. neg.
2 <i>V</i> (meas.); (calc.)	variable: 0–30° <sup>b)</sup> 30° (this work)	5–10°; 22.5° <sup>b)</sup>	~10°; 16.6° <sup>b)</sup>	(–)	(–)	(–)
Dispersion	<i>r</i> > <i>v</i> (this work)	<i>r</i> > <i>v</i>	<i>r</i> > <i>v</i>	(–)	(–)	(–)
Orientation	variable; <i>Z</i> partly inclined to fiber axis (?)	XYZ = bac (pseudo-orthorhombic)	XYZ = cab (pseudo-orthorhombic)	(–)	(–)	(–)
Elongation	variable?	pos.	pos.	pos.	pos.	pos.
X or O (colour)	blue to greenish blue	turquoise-green to light blue green	colourless to very pale blue	intense turquoise-blue	blue to intense green-blue	dark green-blue
Y (colour)	pale blue	benzol-green	pale blue with greenish tint	(–)	(–)	(–)
Z or E (colour)	blue to greenish blue	benzol-green	pale blue with greenish tint	pale blue to light green	clear blue to clear green	light blue-green
Absorption	X,Z>Y	Y,Z>X	Z ≥ Y >> X	O>E	O>E	O>E
Habit	elongate, rectangular plates {010}, fibrous	elongate [001], rectangular plates {010}	elongate [100](?), rectangular plates {001}	thin tabular {001}	thin tabular {001}	thin tabular {001}
Twinning	none observed	indicated by single-crystal study	indicated by single-crystal study	none observed <sup>c)</sup>	none observed	not given
Cleavage	{010}, perfect; {100} and {001}, distinct	{010}, perfect; {100} and {001}, good	{001}, perfect; {100}, {010}	{001}, perfect	{001}, perfect	{001}, perfect

Notes: Lavendulan non-crystallographic data from Guillemin (1956a), Gaines *et al.* (1997) and Anthony *et al.* (2000). Sampleite non-crystallographic data from Gaines *et al.* (1997); Hurlbut (1942) gives cell parameters *a* = 9.70, *b* = 38.40, *c* = 9.65 Å, and refractive indices α 1.629, β 1.677, γ 1.679; Guillemin (1956a) gives refractive indices α 1.627, β 1.677, γ 1.679, 2*V* 22°. Zdenekite non-crystallographic data from Chiappero & Sarp (1995). Closely related species are andyrobtsite, calcio-andyrobtsite(-1*M*), calcio-andyrobtsite-2*O*, richelsdorfite, bleasdaleite and the inadequately characterized, lavendulan-related mineral shubnikovite (see text). n.d. = not determined.

<sup>a)</sup> Powder diffraction data listed for lavendulan, sampleite, the sampleite polymorph and zdenekite are calculated from the respective structure models, in order to avoid the considerable effects of preferred orientation on measured reflection intensities. Note that the lavendulan powder diffraction data of ICDD-PDF 49–1857 (based on the earlier structure model of the first author) are in good agreement with calculated intensities.

<sup>b)</sup> Optics of lavendulan and sampleite are influenced by heating (see text). <sup>c)</sup> On a zdenekite sample from the type locality, we observed some {001} platelets contact-twinning by rotation of 45° about the pseudotetragonal *b*-axis (see text). <sup>d)</sup> Originally reported space group is *P*4<sub>2</sub>2 (Sarp, 1996).

vite, as well as richelsdorffite, bleasdaleite, andyrobartsite, calcio-andyrobartsite(-1*M*) and calcio-andyrobartsite-2*O*. Figure 5 compares the heteropolyhedral sheets in selected lavendulan group minerals with known crystal structures. Table 10 gives a detailed comparison of the relevant physico-chemical properties of the six chemically most closely related minerals. The remaining species, which show more different chemical compositions, are briefly addressed below.

We point out that the lengths of the (pseudo-)tetragonal *a*-axes are similar in (nearly) all species; they range from about 9.6 to 10.1 Å. To facilitate the understanding of the close relation to lavendulan and sampleite, a very brief, chronological description of the minerals is given here and the relations are discussed.

**Zdenekite**, NaPbCu<sub>5</sub>(AsO<sub>4</sub>)<sub>4</sub>Cl·5H<sub>2</sub>O, was described as the Pb analogue of lavendulan by Chiappero & Sarp (1995) from the Cap Garonne mine, Var, France. It was reported as tetragonal, *a* = 10.066, *c* = 39.39 Å, with possible space groups *P*4<sub>1</sub>22 or *P*4<sub>3</sub>22. By contrast with the optically biaxial members lavendulan and sampleite, zdenekite is optically uniaxial negative (Chiappero & Sarp, 1995). A very recent crystal-structure determination of zdenekite by Zubkova *et al.* (2003) demonstrated, however, that zdenekite is monoclinic-pseudotetragonal, with space group *P*2<sub>1</sub>/*n* and *a* = 10.023(7), *b* = 19.55(1), *c* = 10.023(6) Å, β = 90.02(1)°. The atomic arrangement was found to be isotypic to that of lavendulan. The crystal studied was twinned and of relatively poor quality, such that *R*1(*F*) = 9.6%. Only the Pb atom could be modelled anisotropically, and the isotropic displacement parameters of all O atoms and some of their positions had to be fixed.

Zdenekite from the type locality contains some Ca replacing Pb (Pb:Ca ≅ 88:12), and the probable presence of a restricted solid solution range between tetragonal zdenekite and pseudo-tetragonal lavendulan has been postulated by Chiappero & Sarp (1995). Subsequently, the mineral has also been found at Broken Hill, NSW, Australia (Birch, 1999), and Lavrion, Greece (Möckel, 2001; Gröbner & Kolitsch, 2002). From Broken Hill, N.S.W., Australia, calcian, calcian-phosphatian and cadmian varieties of zdenekite have been identified (Kolitsch *et al.*, unpublished data; see also Birch, 1999). The changes in X-ray powder diffraction data and optical properties of these varieties are in agreement with the observed chemical substitutions (Kolitsch *et al.*, unpublished data).

**Lemanskiite**, NaCaCu<sub>5</sub>(AsO<sub>4</sub>)<sub>4</sub>Cl·5H<sub>2</sub>O, is dimorphous with lavendulan, and thought to represent the Ca-analogue of zdenekite (Ondruš *et al.*, 2006; type locality: Abundancia mine, El Guanaco mining district, Chile). Lemanskiite is tetragonal (space group *P*4<sub>1</sub>22 or *P*4<sub>3</sub>22), with *a* = 9.9758, *c* = 36.714 Å, and uniaxial negative. Because zdenekite was very recently shown to be monoclinic-pseudotetragonal (Zubkova *et al.*, 2003; see above), lemanskiite may in fact also be pseudotetragonal. Ondruš *et al.* (2006) comment that they did not use the structure model of zdenekite (Zubkova *et al.*, 2003) for their whole-pattern fitting of the powder X-ray diffraction data of lemanskiite as they found “large discrepancies in bond-valence data derived from that refinement”; it is not mentioned, however, that the refinement had

to use data that were collected using synchrotron radiation from a tiny platelet of poor quality and severely affected by twinning; we also note that the BVS calculated by Ondruš *et al.* (2006) as 7.9 v.u. for the As<sub>4</sub> atom in zdenekite is incorrect (it should read 5.2 v.u.). Apparently, Ondruš *et al.* (2006) did not try a Rietveld refinement based on the model of Zubkova *et al.* (2003).

The strongest reflections in the X-ray powder diffraction pattern of lemanskiite are distinctly different from those of lavendulan (cf. Table 10). We note that the X-ray powder diffraction data listed in Ondruš *et al.* (2006) are affected by a (small, but distinct) systematic error: for all first 24 *hkl* *d*<sub>calc</sub> > *d*<sub>meas</sub> (the remaining *hkl* are not indexed). Ondruš *et al.* (2006) report that grinding of lavendulan from Lavrion led, after several days, to a phase change from lavendulan to lemanskiite, whereas pulverized lavendulan from Jáchyrov remained stable. This observation appears to be in agreement with the results of the temperature-dependent optical studies on lavendulan by Guillemin (1956a), mentioned in the section ‘Previous work’. Although lemanskiite may be considered as a partly dehydrated (*V*<sub>lav</sub> = 1961 Å<sup>3</sup> vs. ½*V*<sub>lem</sub> = 1827 Å<sup>3</sup>) and therefore tetragonal or nearly tetragonal “lavendulan”, the empirical formula of lemanskiite determined by Ondruš *et al.* (2006) is fairly close to NaCaCu<sub>5</sub>(AsO<sub>4</sub>)<sub>4</sub>Cl·5H<sub>2</sub>O (water determined by CHN analyser).

**Mahnertite**, (Na,Ca)Cu<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>Cl·5H<sub>2</sub>O, is a mineral chemically closely related to lavendulan. It has been originally described by Sarp (1996) from the Cap Garonne mine, Var, France as tiny, thin square platelets which are uniaxial negative. Another occurrence at Lavrion, Greece, is briefly described by Rieck (1999). Mahnertite was reported as tetragonal (space group *P*4<sub>2</sub>2<sub>1</sub>2), with *a* = 10.085, *c* = 23.836 Å, and *Z* = 8 (Sarp, 1996). The X-ray powder diffraction pattern of mahnerite (Sarp, 1996) is distinctly different from that of lavendulan (cf. Table 10). The crystal structure of mahnerite was solved very recently by Pushcharovsky *et al.* (2004) using single-crystal synchrotron diffraction data. These authors revised the space group to *I*4/*mmm* (*a* = 10.037(1), *c* = 23.739(1) Å, *V* = 2391.5(4) Å<sup>3</sup>), and showed that the atomic arrangement in mahnerite is based on sheets very similar to those in lavendulan. The formula of mahnerite was suggested to be (Na,Ca)Cu<sub>2.75</sub>(AsO<sub>4</sub>)<sub>2</sub>Cl<sub>0.62</sub>·3.63H<sub>2</sub>O (Pushcharovsky *et al.*, 2004). The increase of the length of the *c*-axis by about 4 Å is caused by more ‘interlayer’ (Na, Ca) and Cl atoms per formula unit, and also because of a different interlayer connectivity. The mahnerite sheet can be considered a prototype motif of the newly defined lavendulan group, because this sheet shows the highest symmetry among all sheets (compare Fig. 5).

**Shubnikovite** is a hydrated (K-)Ca-Cu-arsenate-chloride originally described and named by Nefedov (1953, 1955) using samples from the oxidation zone of an unstat- ed locality (according to Pekov (1998) it is the Northern Area of the Khovu-Aksy Ni-Co-deposit, Tuva, Siberia). This species, with a formula currently given as Ca<sub>2</sub>Cu<sup>2+</sup><sub>8</sub>(AsO<sub>4</sub>)<sub>6</sub>Cl(OH)·7H<sub>2</sub>O (?), is considered an inadequately described mineral (*e.g.*, Gaines *et al.*, 1997, Pekov, 1998, Anthony *et al.*, 2000; Mandarino & Back, 2004). In fact, no published X-ray powder data exist for shubnikovite.



te and, as shown below, it might be identical with or closely related to lavendulan.

In the original description of the species, Nefedov (1953) briefly reports on light blue, platy, translucent crystals found in the oxidation zone of an unstated locality. Their Mohs hardness is 2. Chemically, the mineral is reported to be a hydrous chloro-arsenate of Cu, Ca and K. Chemical analyses gave CuO 37.32, CaO 7.33, Cl 2.7, As<sub>2</sub>O<sub>5</sub> 41.43; insol. 1.66 % [note that no data are given for K<sub>2</sub>O(!) or Na<sub>2</sub>O]. Optically, shubnikovite was reported to be biaxial negative, with a small optical angle and dispersion  $r < v$ . Refractive indices are  $\alpha = 1.640$ ,  $\beta = 1.690$ ,  $\gamma = 1.690$ , and absorption is X light blue, Y,Z greenish blue. The mineral was assumed to be orthorhombic(?) but no X-ray data are given. Later, Nefedov (1955) reports a monoclinic-pseudorthorhombic unit cell with  $a = 14.08$ ,  $b = 14.11$ , and  $c = 30.1$  Å [note: recalculated from originally reported kX units], specific gravity 3.38 g/cm<sup>3</sup>, and the orientation  $X // c$  and  $Y // b$ . This reported cell is close to the cell of lavendulan if it is assumed that the  $\sim 14$  Å dimension is the diagonal of the pseudotetragonal  $ac$  plane in lavendulan ( $a, c \sim 10.0$  Å); however, two  $\sim 14$  Å axes are also encountered in the structurally related mineral richelsdorfite (see below). No further confirmed occurrences are known. A "shubnikovite" reported from Lavrion, Greece, by Wendel (2000) was found to be lavendulan instead (Gröbner & Kolitsch, 2002).

In conclusion, the data reported for shubnikovite are clearly related to those of lavendulan (and possibly mahnerite), although the unit cell may have different dimensions. A re-investigation of the type specimen of shubnikovite is clearly warranted. Unfortunately, attempts to locate the type specimen have been unsuccessful.

**Richelsdorfite**, Ca<sub>2</sub>Cu<sup>2+</sup><sub>5</sub>Sb<sup>5+</sup>[Cl(OH)<sub>6</sub>(AsO<sub>4</sub>)<sub>4</sub>].6H<sub>2</sub>O (Süsse & Schnorrer-Köhler, 1983; Süsse & Tillmann, 1987; Sarp *et al.*, 1994) is chemically similar to lavendulan, and also pseudotetragonal. The crystal structure solution (Süsse & Tillmann, 1987) demonstrated that the mineral is monoclinic (space group  $C2/m$ ,  $a = 14.079$ ,  $b = 14.203$ ,  $c = 13.470$  Å,  $\beta = 101.05^\circ$ ,  $V = 2643$  Å<sup>3</sup>,  $Z = 4$ ). There seem to be several structural and chemical 'varieties' (possibly new species) of richelsdorfite: (i) Süsse & Tillmann (1987) state that richelsdorfite can exist also without any chlorine; the structure is still stable because the Cl<sup>-</sup> anion is replaced by an OH<sup>-</sup> group; (ii) a structural investigation of a 'carbonate richelsdorfite', in which a CO<sub>3</sub> group substitutes for one specific AsO<sub>4</sub> group, was briefly reported by Drescher & Susse (1997); (iii) at least four different minerals similar to richelsdorfite have been briefly described from the Black Forest (Walenta, 2000); some of these do not contain Sb, others contain no Cl (Walenta & Dunn, 1988; Walenta, 2000).

**Bleasdaleite**, (Ca,Fe<sup>3+</sup>)<sub>2</sub>Cu<sub>5</sub>(Bi,Cu)(PO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O,OH,Cl)<sub>13</sub> (Birch *et al.*, 1999), has been shown to be closely related to richelsdorfite, and, although the crystal structure could not be determined, the probable space group and unit-cell parameters ( $C2/m$ ,  $a = 14.200$ ,  $b = 13.832$ ,  $c = 14.971$  Å,  $\beta = 102.08^\circ$ ,  $V = 2875$  Å<sup>3</sup>,  $Z = 4$ ) are quite similar to those of richelsdorfite. It was suggested that the interlayer [Sb(OH)<sub>6</sub>.6H<sub>2</sub>O]<sup>-</sup> complex in richelsdorfite is replaced by a [Bi(OH)<sub>4</sub>.8H<sub>2</sub>O]<sup>-</sup> complex in bleasdaleite (Birch *et al.*, 1999). Thus, bleasdaleite probably also shows a close structural relation to lavendulan.

The crystal structures of **andyrobertsite**, (Cd,Ca,Mn)KCu<sub>5</sub>(AsO<sub>4</sub>)<sub>4</sub>[As(OH)<sub>2</sub>O<sub>2</sub>](H<sub>2</sub>O)<sub>2</sub> and its Ca-dominant analogue **calcio-andyrobertsite(-1M)** (space group  $P2_1/m$ ,  $a = 9.8102(9)$ ,  $b = 10.0424(6)$ ,  $c = 9.9788(7)$  Å,  $\beta = 101.686(7)^\circ$ ; Cooper *et al.*, 1999, Cooper & Hawthorne, 2000), as well as the polytype **calcio-andyrobertsite-2O** (space group  $Pnma$ ,  $a = 19.647(2)$ ,  $b = 10.087(1)$ ,  $c = 9.963(1)$  Å; Sarp & Černý, 2004) are closely related to those of lavendulan and the other minerals described above, as already indicated by the similarity in the length of the crystal axes. In fact, the structures are characterized by topologically very similar sheets. However, they differ from that of lavendulan in that they do not contain Cl, i.e., they feature Cu(O,H<sub>2</sub>O)<sub>5</sub> and [Cu<sub>4</sub>O<sub>13</sub>] clusters instead of Cu(O,H<sub>2</sub>O,Cl)<sub>5</sub> and [Cu<sub>4</sub>O<sub>12</sub>Cl] clusters. Furthermore, the sheets are directly connected to each other by an As(OH)<sub>2</sub>O<sub>2</sub> group. Voids in the resulting framework are occupied by  $M$  ( $M = \text{Cd, Ca, Mn}$ ) and K atoms.

We conclude that the mutual arrangement and interconnection of the common heteropolyhedral sheet in the minerals discussed above are fairly flexible, and the occurrence of further polymorphs/polytypes (stacking variants) and structural analogues can be assumed. It is planned to explore the crystal-chemistry of this mineral group in more detail by hydrothermal syntheses.

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## References

- Altomare, A., Burla, M.C., Camalli, M., Cascarano, G.L., Giacovazzo, C., Guagliardi, A., Moliterni, A.G.G., Polidori, G., Spagna, R. (1999): SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Crystallogr.*, **32**, 115–119.
- Anthony, J.W., Bideaux, R.A., Bladh, K.W., Nichols, M.C. (2000): Handbook of Mineralogy. Vol. IV: Arsenates, phosphates, vanadates. Mineral Data Publishing, Tucson, Arizona, USA, 680 pp.
- Baur, W.H. (1981): Interatomic distance predictions for computer simulation of crystal structures. in "Structure and bonding in crystals", O'Keeffe, M. and Navrotsky, A., eds. Vol. II. Academic Press, New York, Chapter 15, 31–52.
- Birch, B. (1999): The minerals. in "The minerals of Broken Hill", Birch, W.D., ed. Broken Hill City Council and Museum of Victoria, Broken Hill, Australia, pp. 88–262.
- Birch, W.D. & van der Heyden, A. (1988): Minerals from the Kintore Opencut, Broken Hill, New South Wales. *Mineral. Rec.*, **19**, 425–436.
- , – (1997): Minerals of the Kintore and Block 14 open cuts at Broken Hill, New South Wales. *Austral. J. Mineral.*, **3**, 23–71.
- Birch, B., Pring, A., Kolitsch, U. (1999): Bleasdaleite,  $(\text{Ca}, \text{Fe}^{3+})_2\text{Cu}_5(\text{Bi}, \text{Cu})(\text{PO}_4)_4(\text{H}_2\text{O}, \text{OH}, \text{Cl})_{13}$ , a new mineral from Lake Boga, Victoria, Australia. *Australian J. Mineral.*, **5**, 69–75.
- Breese, N.E. & O'Keeffe, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.*, **B47**, 192–197.
- Bridge, P.J., Pryce, M.W., Clarke, R.M., Costello, M.B. (1978): Sampleite from Jingemba Cave, Western Australia. *Mineral. Mag.*, **42**, 369–371.
- Bruker (1995): SMART, SAINT+ and XPREP.6. Area Detector Control, Data Integration and Reduction Software. Bruker Analytical X-Ray Instruments Inc., Madison, Wisconsin, USA.
- Chiappero, P.-J. & Sarp, H. (1995): Zdenekite,  $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}_5\text{H}_2\text{O}$ , a new mineral from the Cap Garonne mine, Var, France. *Eur. J. Mineral.*, **7**, 553–557.
- Cooper, M.A. & Hawthorne, F.C. (2000): Highly undersaturated anions in the crystal structure of andyrobertsite – calcio-andyrobertsite, a doubly acid arsenate of the form  $\text{K}(\text{Cd}, \text{Ca})[\text{Cu}^{2+}_5(\text{AsO}_4)_4\{\text{As}(\text{OH})_2\text{O}_2\}](\text{H}_2\text{O})_2$ . *Can. Mineral.*, **38**, 817–830.
- Cooper, M.A., Hawthorne, F.C., Pinch, W.W., Grice, J.D. (1999): Andyrobertsite and calcioandyrobertsite, two new minerals from the Tsumeb mine, Tsumeb, Namibia. *Mineral. Rec.*, **30**, 181–186.
- Drescher, I. & Susse, P. (1997): Crystal structural investigation of a carbonate richelsdorffite. *Eur. J. Mineral.*, **9**, Beih. No. 1, 81.
- Elbin, K. & Wendel, W. (1996): Lavendulan aus Laurion. *Lapis*, **21** (11), 42–43. (in German)
- Fabrizi, M., Ganiaris, H., Tarling, S.E., Scott, D.A. (1989): The occurrence of sampleite, a complex copper phosphate, as a corrosion product on copper alloy objects from Memphis, Egypt. *Studies in Conservation*, **34**, 45–51.
- Fischer, R.X. & Tillmanns, E. (1988): The equivalent isotropic displacement factor. *Acta Crystallogr.*, **C44**, 775–776.
- Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. (1997): "Dana's New Mineralogy". The System of Mineralogy of James Dwight & Edward Salisbury, rewritten and enlarged 8<sup>th</sup> ed., John Wiley & Sons, Inc., New York, NY, 1819 pp.
- Grice, J.D., Szymański, J.T., Jambor, J.L. (1996): The crystal structure of clinoatacamite, a new polymorph of  $\text{Cu}_2(\text{OH})_3\text{Cl}$ . *Can. Mineral.*, **34**, 73–78.
- Gröbner, J. & Kolitsch, U. (2002): Neufunde von Laurion aus den Jahren 2001 und 2002. *Aufschluss*, **53**, 363–371. (in German)
- Guillemin, G. (1956a): Contribution à la minéralogie des arsénates, phosphates et vanadates de cuivre. I. Arsénates. *Bull. Soc. franç. Minéral. Cristallogr.*, **79**, 7–95.
- (1956b): Contribution à la minéralogie des arsénates, phosphates et vanadates de cuivre. II. Phosphates et vanadates. *Bull. Soc. franç. Minéral. Cristallogr.*, **79**, 219–75.
- Henry, D.A. & Birch, W.D. (1988): Sampleite and associated minerals from the Lake Boga granite quarry, Victoria, Australia. *Austral. Mineral.*, **3**, 135–148.
- Hurlbut, C.S., Jr. (1942): Sampleite, a new mineral from Chuquicamata, Chile. *Am. Mineral.*, **27**, 586–589.
- Hwu, S.-J., Ulutagay-Kartin, M., Clayhold, J.A., Mackay, R., Wardojo, T.A., O'Connor, C.J., Krawiec, M. (2002): A new class of hybrid materials via salt inclusion: novel copper(II) arsenates  $\text{Na}_5\text{ACu}_4(\text{AsO}_4)_4\text{Cl}_2$  (A = Rb, Cs) composed of alternating covalent and ionic lattices. *J. Am. Chem. Soc.*, **124**, 12404–12405.
- Kleeman, A.W. & Milnes, A.R. (1973): Phosphorian lavendulan from Dome Rock mine, South Australia. *Trans. Royal Soc. South Austral.*, **97**, 135–137.
- Lambert, U. (1988): Kristallchemie von Cu(I) und Cu(II) in oxidischer Bindung. *Heidelberger Geowissenschaftliche Abhandlungen*, **18**, 1–222. (in German)
- Mandarino, J.A. & Back, M.E. (2004): Fleischer's Glossary of Mineral Species 2004. The Mineralogical Record Inc., Tucson, USA, 309 pp.
- McLean, A.L., Chapman, J., Sharpe, J.L., Williams, P.A. (2004): The mineralogy of the oxidized zone of the E26 orebody at Northparkes, New South Wales. *Austral. J. Mineral.*, **10**, 53–57.
- Meyer, S. & Müller-Buschbaum, H. (1997):  $\text{Cu}_4\text{O}_{12}$  groups built of square planar  $\text{CuO}_4$  polygons in the barium vanadyl oxocuprate(II) phosphate  $\text{Ba}(\text{VO})\text{Cu}_4(\text{PO}_4)_4$ . *Z. Anorg. Allg. Chemie*, **623**, 1693–1698. (in German)
- Möckel, S. (2001): Wallkilldellit und weitere acht Neubestimmungen aus Lavrion, Griechenland. *Lapis*, **26** (11), 43. (in German)
- Nefedov, E.I. (1953): Report on new minerals discovered by him. P. 317 in V. A. Mokievsky. The scientific session of the Federov Institute together with the All-Union Mineralogical Society. *Zap. Vses. Mineral. Obshch.*, **82**, 311–317.
- , – (1955): Neue Minerale. *Geologie, Geol. Zeits.*, **4**, 526–528. (in German)
- Onac, B.P., Breban, R., Kearns, J., Tamas, T. (2002): Unusual minerals related to phosphate deposits in Cioclovina Cave, Şureanu Mts. (Romania). *Theoretical and Applied Karstology*, **15**, 27–34.
- Ondruš, P., Veselovský, F., Hloušek, J., Skála, R., Vavřín, I., Frýda, J., Cejka, J., Gabašová, A. (1997): Secondary minerals of the Jáchymov (Joachimsthal) ore district. *J. Czech Geol. Soc.*, **42**, 3–76.
- Ondruš, P., Veselovský, F., Sejkora, J., Skála, R., Paflout, R., Frýda, J., Gabašová, A., Vajdak, J. (2006): Lemanskiite,  $\text{NaCaCu}_5(\text{AsO}_4)_4\text{Cl}_5\text{H}_2\text{O}$ , a new mineral species from the Abundancia mine, Chile. *Can. Mineral.*, **44**, 523–531.
- Otwinowski, Z., Borek, D., Majewski, W., Minor, W. (2003): Multi-parametric scaling of diffraction intensities. *Acta Crystallogr.*, **A59**, 228–234.
- Palache, C., Berman, C., Frondel, C. (1951): Dana's System of Mineralogy. 7th ed., Vol. II. John Wiley, New York, 1124 pp.
- Pekov, I.V. (1998): Minerals first discovered on the territory of the former Soviet Union. Ocean Pictures Ltd., Moscow, 369 pp.
- Pushcharovsky, D. Yu., Zubkova, N. V., Teat, S. J., Maclean, E. J., Sarp, H. (2004): Crystal structure of mahnertite. *Eur. J. Mineral.*, **16**, 687–692.

- Rieck, B. (1999): Seltene Arsenate aus der Kamariza und weitere Neufunde aus Lavrion. *Lapis*, **24** (7–8), 68–76; 90. (in German)
- Sarp, H. (1996): Mahnertite,  $(\text{Na,Ca})\text{Cu}_3(\text{AsO}_4)_2\text{Cl}\cdot 5\text{H}_2\text{O}$ , a new mineral from the Cap Garonne mine, Var, France. *Archs. Sci. Genève*, **49** (2), 119–124. (in French)
- Sarp, H. & Černý, R. (2004): Calcio-andyrobertsite-2O,  $\text{KCaCu}_5(\text{AsO}_4)_4[\text{AsO}_2(\text{OH})_2]\cdot 2\text{H}_2\text{O}$ : its description, crystal structure and relation with calcio-andyrobertsite-1M. *Eur. J. Mineral.*, **16**, 163–169.
- Sarp, H., Dominik, B., Chiappero, P.-J. (1994): Nouveau gisement (Triembach-Le Val, Vosges, France): nouvelles propriétés optiques et diagramme de poudre de la richelsdorffite,  $\text{Ca}_2\text{Cu}_5\text{Sb}[\text{Cl}(\text{OH})_6(\text{AsO}_4)_4]\cdot 6\text{H}_2\text{O}$ . *Schweiz. Mineral. Petrogr. Mitt.*, **74**, 273–277. (in French)
- Shape Software (2003): ATOMS for Windows and Macintosh V6.1. Kingsport, TN 37663, U.S.A.
- Sheldrick, G.M. (1997a): SHELXS-97, a program for the solution of crystal structures. University of Göttingen, Germany.
- (1997b): SHELXL-97, a program for crystal structure refinement. University of Göttingen, Germany.
- Spek, A.L. (2003): Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.*, **36**, 7–13.
- Strunz, H. (1959): Tsumeb, seine Erze und Sekundärminerale, insbesondere der neu aufgeschlossenen zweiten Oxydations-Zone. *Fortschr. Mineral.*, **37**, 87–90. (in German)
- Strunz, H. & Nickel, E.H. (2001): Strunz Mineralogical Tables. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, Germany, 870 pp.
- Süsse, P. & Schnorrer-Köhler, G. (1983): Richelsdorffite,  $\text{Ca}_2\text{Cu}_5\text{Sb}[\text{Cl}(\text{OH})_6(\text{AsO}_4)_4]\cdot 6\text{H}_2\text{O}$ , ein neues Mineral. *N. Jahrb. Mineral. Monatsh.*, **1983**, 145–150. (in German)
- Süsse, P. & Tillmann, B. (1987): The crystal structure of the new mineral richelsdorffite,  $\text{Ca}_2\text{Cu}_5\text{Sb}[\text{Cl}(\text{OH})_6(\text{AsO}_4)_4]\cdot 6\text{H}_2\text{O}$ . *Z. Kristallogr.*, **179**, 323–334.
- Tarling, S.E. (1992): Laboratory high-temperature X-ray powder diffraction. *Phase Transitions*, **39**, 199–213.
- Walenta, K. (2000): Richelsdorffitähnliche Mineralien aus dem Schwarzwald. *Erzgräber*, **14**, 1–9. (in German)
- Walenta, K. & Dunn, P.J. (1988): Ein richelsdorffitähnliches Mineral von der Grube Clara. *Erzgräber*, **2** (2), 97–103. (in German)
- Wendel, W. (2000): Laurion-News 2000. *Lapis*, **25** (10), 45–47. (in German)
- Zubkova, N.V., Pushcharovsky, D.Yu., Sarp, H., Teat, S.J., MacLellan, E.J. (2003): Crystal structure of zdenekite  $\text{NaPbCu}_5(\text{AsO}_4)_4\text{Cl}\cdot 5\text{H}_2\text{O}$ . *Crystallogr. Reports*, **48**, 939–943.

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