Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen =

Bulletin suisse de minéralogie et pétrographie

Band: 76 (1996)

Heft: 2

Artikel: Crystal structure and crystal chemistry of the homeotypes edenharterite

(TIPbAs3S6) and jentschite (TIPbAs2SbS6) from Lengenbach, Binntal

(Switzerland)

Autor: Berlepsch, Peter

DOI: https://doi.org/10.5169/seals-57693

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Mehr erfahren

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. En savoir plus

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. Find out more

Download PDF: 19.11.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

Crystal structure and crystal chemistry of the homeotypes edenharterite (TlPbAs₃S₆) and jentschite (TlPbAs₂SbS₆) from Lengenbach, Binntal (Switzerland)

by Peter Berlepsch1

Abstract

Edenharterite (orthorhombic, Fdd2, a 15.4764(8), b 47.602(3), c 5.8489(4) Å) and jentschite (monoclinic, $P2\sqrt{n}$, a 8.0958(5), b 23.917(2), c 5.8876(5) Å, β 108.063(8)°) belong to a series of recently discovered Tl-sulfosalts that origin from the new quarry at Lengenbach, Binntal (Switzerland). Quantitative electron microprobe analyses on eight jentschite crystals showed seven of them to be inhomogenous. For one crystal the nominal formula TlPb_{1.01(4)} As_{2.47(6)}Sb_{0.54(3)}S_{5.9(1)} was calculated. Jentschite shows much lower contents of Sb than it was expected from the ideal formula.

The structure of edenharterite was anisotropically refined using 1070 reflections with $I > 3\sigma I$ to a final R-value of 0.054. The structure of jentschite was solved with direct methods and anisotropically refined using 1766 reflections with $I > 3\sigma I$ to a final R-value of 0.049. Structure refinements and bond valence estimations revealed an ordered structure of Sb and As. The two minerals are homeotypes, as could be demonstrated by fitting the two structures. Using adequate atomic clusters the transformation matrix between new and old coordinates in crystal system is approximately the unit matrix, and a pseudo-symmetry operator x-0.25, y, z-0.34 (translation) was found.

Edenharterite shows small, jentschite large variations in the As- and Sb-contents. The minerals belong to two different solid solution series. In the literature a similar variation of As and Sb in natural and synthetic rebulites is reported, and for bernardite a comparable As, Sb solid solution behaviour can be expected. At this time it seems as if the amount of Sb incorporated in the structures is not responsible for the formation of either edenharterite or jentschite.

Keywords: edenharterite, jentschite, homeotype, crystal structure, crystal chemistry, Lengenbach (Binntal, Switzerland).

Introduction

The Lengenbach quarry in the valley of Binn, Valais, Switzerland, known for more than 200 years, is one of the the world's classic mineral localities, famous for the wealth of well crystallized lead-arsenic sulfosalts (Hofmann et al., 1993). Within the last hundred years, this locality has provided the systematic mineralogy with a remarkable number of new sulfosalt species (Graeser et al., 1995a). The quarry is beeing operated by the "Arbeitsgemeinschaft Lengenbach" (Lengenbach syndicate) since 1958 solely for the exploitation of mineral specimens (see e.g. Nowacki, 1970; Stalder et al., 1978; Hofmann et al., 1993).

Approximately fifty different sulfides and sulfosalts have been described from the Lengenbach (see e.g. HOFMANN et al., 1993). Among these minerals eleven new sulfosalts with Tl as a major element, briefly Tl-sulfosalts, have been found (cf. Tab. 5 in Graeser et al., 1995a). The classical old site had to be abandoned in 1986 for technical reasons but also for the increasingly unattractive mineral content. Since 1986 minerals of Lengenbach origin from the new quarry adjacent to the old mining site (see e.g. Graeser et al., 1992). In this part of the Triassic dolomite marble a greater variation in the chemical composition of Tl-sulfosalts was observed in comparison to the Tl-sulfosalts from the old quarry. Before 1986 the chemistry of the so far known Tl-sulfosalts from

¹ Mineralogisch-Petrographisches Institut, Universität Basel, Bernoullistrasse 30, CH-4056 Basel, Switzerland. E-mail: berlepsch@ubaclu.unibas.ch.

Tab. 1 Chemical composition (idealized) and cell parameters from single crystal measurements of edenharterite and jentschite.

Mineral	Edenharterite	Jentschite
Formula	TlPbAs ₃ S ₆	TlPbAs ₂ SbS ₆
X-system	orthorhombic	monoclinic
Space gr.	Fdd2	$P 2_1/n$
a (Å)	15.4764(8)	8.0958(5)
b (Å)	47.602(3)	23.917(2)
c (Å)	5.8489(4)	5.8876(5)
β (°)	90.0	108.063(8)
$V(\mathring{A}^3)$	4308.9(5)	1083.8(2)
Z	16	4

Lengenbach was described mainly with the elements Tl, Pb, Cu, Ag, As and S (Graeser and Guggenheim, 1990). However, the recently found Tl-sulfosalts contain additional major elements such as Sn (erniggliite, Graeser, 1988; Graeser et al., 1992); Zn, Fe and Hg (stalderite, Graeser, 1988, Graeser et al., 1995a) or Sb (jentschite, Graeser et al., 1995b). Although Pašava et al. (1989) reported up to 15 wt% of Sb in bernardite (TlAs₅S₈), they did not regard it as a major element in this mineral. As reported in Graeser et al. (1995a), bernardite from Lengenbach contain significant amounts of Sb too.

By comparing edenharterite (TlPbAs₃S₆, GRAESER and SCHWANDER, 1992; BERLEPSCH, 1995) with jentschite (TlPbAs₂SbS₆) some interesting observations could be made (GRAESER et al., 1995b): the two minerals have similar chemical compositions but different symmetries (Tab. 1). It was supposed that a close relationship exists between jentschite and edenharterite (GRAESER and EDENHARTER, oral communication). The aim of the present work is to show the kind of relationship that exists between these two minerals.

For this purpose quantitative chemical analyses were made of both edenharterite and jentschite by means of an electron microprobe (EMP). Furthermore the structure of jentschite was solved and that one of edenharterite refined, since previously obtained structural data of this compound (BERLEPSCH, 1995) were not satisfying.

Chemical investigations

EXPERIMENTAL

Chemical descriptions of edenharterite have been published previously by Graeser and Schwander (1992) as well as Berlepsch (1995). To the pre-existing ten analyses of edenharterite crystal L 20435 fifteen additional analyses were performed to reach a total of 25. For the EMP analy-

ses of jentschite, eight crystals and crystal aggregates were taken from sample L 24428. The single crystals were identified as jentschite by X-ray methods (Gandolfi camera). The crystal aggregates were investigated semi-quantitatively by means of energy-dispersive spectroscopy (EDS) performed on a scanning electron microscope (PHILIPS SEM 515). These foregoing analyses showed the aggregates to be an association of jentschite and wallisite ($Tl(Cu,Ag)PbAs_2S_5$).

The chemical analyses were carried out on each crystal of jentschite by means of EMP (JEOL JXA-8600 superprobe, ZAF correction). On all crystals the major elements Tl, Pb, As, Sb, S and the trace elements Cu, Ag, Zn, except two samples, were quantitatively analysed using the lines and spectrometer crystals of standards TlAsS₂ (S K_{α} PET, As L_{α} TAP and Tl M_{α} PET), Sb₂S₃ (Sb L_{α} PET), PbS (Pb M_{α} PET) and CuFeS₂ (Cu K_{α} LiF), Ag₂S (Ag L_{β} PET), ZnS (Zn K_{α} LiF). The conditions of measurement were acceleration voltage 15 kV, beam current 10 nA (20 nA for edenharterite samples), scanned area 15 μ m². The results of the analyses are given in table 2.

CHEMICAL COMPOSITION

The results of the edenharterite analyses (Berlepsch, 1995) may be summarized as follows: all analysed crystals contain significant amounts of Sb (up to 2.7 wt%) but in general no Sn. This is in contradiction to the data of Graeser and Schwander (1992). The detection of Sb in edenharterite is of special interest for comparing the mineral with jentschite.

In case of jentschite the analysed crystals except one are inhomogenous with the standard deviations σ_{n-1} greater than the analytical errors. Here, 1σ refers to the count statistics on jentschite. Attempts to explain these inhomogenities failed. So far in one case, sample G, a zonation could be observed by means of back scattered electron image (BSE image). Yet, both zones (bright: Sb rich, G₁; dark: As rich, G₂) are themselves inhomogenous. So far neither zonations nor topographical effects or operative manipulations could be used as explanation for the inhomogenities. Therefore only minimum/maximum ranges of the EMP data are listed in table 2, except for crystal E. EMP data from crystal E showed minimal variations compared to data from the other seven samples. By accepting a 2 σ analytical error the crystal was found to be apparently homogenous. For these data the average values have been calculated, resulting in a normalized formula given in table 2.

Tab. 2 EMP data of jentschite (N = 25 if not indicated else). Except for sample E, the mean standard deviations are significantly higher than the analytical error (a.e.). Therefore only minimum-maximum ranges are given in wt%. Details are explained in the text. $^{1)}$ N = 24; $^{2)}$ N = 12; $^{3)}$ N = 13.

Jentschite		A	В	С	D	E1)		F	$G_1^{(2)}$	$G_2^{3)}$	Н
	a.e.	range (wt%)	range (wt%)	range (wt%)	range (wt%)	wt%	σ^{-1}	range (wt%)	range (wt%)	range (wt%)	range (wt%)
Tl	0.55	22.28- 24.35	23.32-25.34	22.53-24.42	22.10-24.71	23.94	0.54	22.85-24.77	22.93-24.43	23.21-24.89	23.46-25.53
Pb	0.82	22.65-26.03	22.06-26.54	25.43-28.15	22.19-26.24	24.45	0.78	23.93-26.74	22.16-24.59	23.14-25.48	23.90–27.39
As	0.25	20.37-24.47	20.16-26.03	20.30-23.24	18.21-22.25	21.69	0.20	20.23-21.98	20.79-22.82	23.72-25.59	20.67-25.33
Sb	0.11	4.06- 8.62	3.17-10.50	6.66- 7.73	8.06-10.91	7.68	0.22	8.12- 9.72	6.39- 8.55	2.67- 5.67	3.29- 7.70
S	0.29	20.43-22.26	21.80-23.23	20.73-22.41	21.03-22.84	22.29	0.37	19.98- 22.06	21.08-22.18	21.41-22.52	21.74-23.43
Cu		< 0.04	_	-	< 0.04	< 0.04	-	< 0.04	< 0.04	< 0.04	< 0.04
Ag		< 0.05	-	-	< 0.05	< 0.05	-	< 0.05	< 0.05	< 0.05	< 0.05
Zn		< 0.05	-	-	< 0.05	< 0.05	-	< 0.05	< 0.05	< 0.05	< 0.05
Σ		97.2 –100.3	98.7 -103.5	99.1 –102.8	97.7 –102.7	100.1	1.0	98.4–102.5	95.3-100.2	96.7 -100.1	98.7–102.8
a.e.	= analy	tical error (1σ, v	vt%, from coun	t statistics on je	ntschite)				c. b. = charge b	palance	
Crys	Crystal Normalized jentschite formula (Tl = 1)							Σ As + Sb		c. b.	
Е	E $Tl_1Pb_{101(4)}As_{2,47(6)}Sb_{0,54(3)}S_{5,9(1)}$								3.01(6)		0.02(2)

In the preliminary description of jentschite, Graeser et al. (1995b) presented the ideal formula TlPbAs₂SbS₆ which corresponds to 13.91 wt% of Sb. In our samples the highest Sb value was measured in sample D. It is 10.91 wt% (Tab. 2). This is significantly less than the expected theoretical value, but comparable to the data of GRAESER and EDENHARTER (oral communication). The minimum content of Sb were found to be 2.67 wt% (Sb-poor zone G_2) which is less than the maximum Sb content measured in edenharterite (Berlepsch, 1995). In jentschite As and Sb vary in the range As_{2.25}Sb_{0.83} to As_{2.83}Sb_{0.18}. BALIć-ZUNIĆ et al. (1994) reported a similar variation in synthetic rebulites. The As, Sb solid solution in this mineral extends from Tl₅Sb_{3.6}As_{9.4}S₂₂ to Tl₅Sb₅₃As₇₇S₂₂. Recently jankovicite (Tl₅Sb₉(As, Sb)₄S₂₂), a mineral related to rebulite was described (CVETKOVIĆ et al., 1995). The As, Sb solid solution behaviour in bernardite has not yet been investigated in detail (Pašava et al., 1989).

The variations in chemical composition in both minerals, jentschite and edenharterite, are mainly due to a simple substitution process between the elements As and Sb. The first assumption that these two Tl-sulfosalts belong to the same isomorphic solid solution series had to be rejected because isomorphism is not possible between two phases with different crystal systems (orthorhombic edenharterite, monoclinic jentschite). Furthermore maximum contents of Sb in edenharterite exceeds minimal contents of Sb in jentschite. From these observations it is concluded that the two minerals belong to two different solid solution series. In figure 1 the variable

compositions of edenharterite and jentschite as well as those compositions of some pure compounds are sketched.

Structure refinements

EXPERIMENTAL

Subsequently data are given for jentschite followed by analogous edenharterite data in parenthesis. The X-ray data were collected on a crystal fragment, measuring about $0.035 \times 0.045 \times 0.095 \text{ mm}^3$ ($0.025 \times 0.035 \times 0.115 \text{ mm}^3$), by means of a CAD4 automatic single-crystal diffractometer (ENRAF NONIUS) with Kappa geometry. The lattice parameters were determined and re-

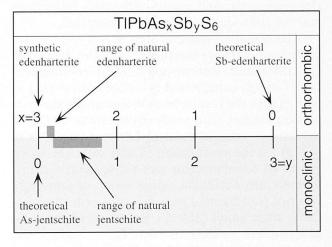


Fig. 1 Sketch with a graphical representation of the variable compositions of edenharterite and jentschite. Details are explained in the text.

150

Tab. 3 Summarized parameters of data collection and reduction and of structure refinement.

	Edenharterite	Jentschite
Crystal data	cf. Tab. 1	cf. Tab. 1
Data collection		
Diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4
Geometry	Kappa	Kappa
Radiation Cu K_{α} (Å)	1.54180	1.54180
Monochromator	Graphite	Graphite
Scan technique	$\omega - 2\Theta$	$\omega - 2\Theta$
Scan width (°)	$0.78 + 0.29 \tan \Theta$	$0.83 + 0.19 \tan \Theta$
Scan speed range (°/min)	0.9-20.1	0.8-20.1
Max. $\sin (\Theta)/\lambda (\mathring{A}^{-1})$	0.6332	0.6332
2 Θ range (°)	4.64-155	4.26-155
Index range	-7 < h < 0, -19 < k < 0, -59 < l < 0	-7 < h < 7, -10 < k < 0, -29 < l < 29
No. of measured reflections	1249	4885
Data reduction		
Lp correction	Yes	Yes
Abs. correction method	Ψ scans	Ψ scans
Abs. coefficient μ (cm ⁻¹)	791.15	950.54
Correction range	3.63-10.08	5.19-16.37
Merging-R	_	5.82
Structure refinement		
No. of used reflections	$1070 [I > 3 \sigma_I]$	$1766 [I > 3\sigma_I]$
No. parameters last circle	101	101
Final R/wR-values	0.054 / 0.060	0.049 / 0.058
Max. final shift/e.s.d.	0.038	0.081
Final delta rho range (e/Å ³)	-4.37 to 2.54	-4.90 to 4.35

fined by the least-squares method, using 25 reflections within the angular range $24.90^{\circ} < \Theta < 45.73^{\circ}$ (8.14 < $\Theta < 46.58^{\circ}$). Diffraction intensities were measured within the 2Θ range $4.26\text{--}155.0^{\circ}$ (4.64–155°), using graphite monochromatized CuK $_{\alpha}$ radiation ($\lambda = 1.54178~\text{Å}$) and operating in the $\omega\text{-}2\Theta$ scan mode. The data reduction included background and Lorentz-polarization corrections. The data were empirically corrected for absorption by using ψ scans. Tables 1 and 3 summarize parameters and results of the data collections and the subsequent structure refinements.

The obtained space groups $P 2_1/n$ (F2dd) and cell parameters are consistent with the data from GRAESER and EDENHARTER (oral communication) and Graeser and Schwander (1992a) as well as with the results from Weissenberg and precession studies (this work; BERLEPSCH, 1995). In agreement with the rules of DONNAY and ONDIK (1973) for the orientation of unit cells, the space group of edenharterite was subsequently transformed into Fdd2. The space group of jentschite was not transformed into $P \frac{2}{1}a$ in order to keep the β angle small (Tab. 1). Based on 1766 (1070) independent reflections with $I_{\rm obs} > 3\sigma[I_{\rm obs}]$, the structures were solved (refined) using direct methods (SIR92, ALTOMARE et al., 1994) and the existing structural model for edenharterite (Berlepsch, 1995). With anisotropic temperature factors and anomalous dispersion terms the refinements converged at R values of 0.049 (0.054).

DISCUSSION AND COMPARISON OF THE STRUCTURES

A detailed description of the structure of synthetic TlPbAs₃S₆ is given by Balić-Žunić and Engel (1983). A short comparison of the crystal structures of natural TlPbAs₃S₆ (edenharterite) and synthetic TlPbAs₃S₆ is given by Berlepsch (1995). It can be concluded that the two structures are very similar.

Site occupancies (occ), final fractional atomic coordinates, and isotropic as well as anisotropic displacement parameters U_{ij} of edenharterite and jentschite are listed in table 4. With one exception only Me–S (Me = Tl, Pb) distances shorter than the smallest Me–As distance were taken into account for the discussion and comparison of the structures. Selected distances and angles are listed in tables 5 and 6. A projection of the crystal structure of jentschite along the c-axis is given in figure 4.

Thallium: In edenharterite Tl is surrounded by seven close S atoms, the Tl–S distances ranging from 3.211 to 3.369 Å (mean 3.309 Å). In

Tab. 4 Site occupancies, final fractional atomic coordinates, isotropic (U_{iso} * 100) and anisotropic displacement parameters (U_{ij} * 100) of edenharterite (TlPbAs₃S₆, above) and jentschite (TlPbAs₂SbS₆, below). $T_{hkl} = exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)].$

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	U ₁₂ -0.54(6) -0.01(4)
Pb(1) 1.00 0.02544(8) 0.12228(2) -0.0008(3) 2.01 4.02(6) 1.69(4) 1.20(5) -0.01(4) -0.02(5) As(1) \rightarrow 0.93(3) 0.0120(2) 0.03411(6) 0.1156(6) 2.40 4.0(2) 1.7(1) 2.2(2) -0.4(1) -0.4(1)	
Pb(1) 1.00 0.02544(8) 0.12228(2) -0.0008(3) 2.01 4.02(6) 1.69(4) 1.20(5) -0.01(4) -0.02(5) As(1) \ 0.93(3) 0.0120(2) 0.03411(6) 0.1156(6) 2.40 4.0(2) 1.7(1) 2.2(2) -0.4(1) -0.4(1)	
$As(1)$ $\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	
Sb(1) 0.07(3) Sb(2) Sb(3) Sb(4) Sb(4) Sb(5) Sb(6) Sb(6) Sb(7) Sb	-0.1(1)
As(2) 1.00 0.0962(2) 0.07577(6) 0.5656(6) 1.97 3.6(2) 1.5(1) 1.4(2) -0.1(1) 0.2(1)	0.1(1)
As(3) 1.00 0.3029(2) 0.08303(6) 0.7757(5) 1.99 3.5(2) 2.0(1) 1.1(1) 0.1(1) -0.3(1)	0.0(1)
S(1) 1.00 0.3927(4) 0.0045(1) 0.621(1) 2.32 2.8(3) 1.6(3) 2.9(4) -0.1(3) -0.6(3)	-0.2(2)
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	-1.1(3)
S(3) 1.00 0.1425(5) 0.0809(1) 0.204(1) 1.80 3.8(4) 1.9(3) 0.8(3) 0.1(2) 0.1(3)	0.2(3)
S(4) 1.00 0.2068(5) 0.0470(1) 0.682(1) 2.05 3.9(4) 1.3(3) 2.1(3) 0.2(3) -1.1(3)	-0.5(2)
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	0.1(2)
S(6) 1.00 0.2209(5) 0.1213(1) 0.708(1) 2.08 4.1(4) 1.6(3) 1.4(4) -0.2(2) 0.2(3)	-0.2(3)
Jen. occ x/a y/b z/c U_{iso} U_{11} U_{22} U_{33} U_{23} U_{13}	U_{12}
TI(1) 1.00 0.0964(1) 0.06125(5) 0.8597(2) 3.44 3.92(6) 3.04(5) 3.98(6) 0.31(4) 1.64(5)	-0.57(5)
T(1) 1.00 0.0964(1) 0.06125(5) 0.8597(2) 3.44 3.92(6) 3.04(5) 3.98(6) 0.31(4) 1.64(5)	
Tl(1) 1.00 0.0964(1) 0.06125(5) 0.8597(2) 3.44 3.92(6) 3.04(5) 3.98(6) 0.31(4) 1.64(5) Pb(1) 1.00 0.0586(1) 0.25436(3) 0.9145(2) 1.95 2.79(4) 1.30(4) 2.66(4) 0.00(3) 1.49(3)	-0.10(3)
Pb(1) 1.00 0.0586(1) 0.25436(3) 0.9145(2) 1.95 2.79(4) 1.30(4) 2.66(4) 0.00(3) 1.49(3) Sb(1) 0.55(2) 0.4625(2) 0.07058(7) 0.4896(3) 1.95 2.2(1) 1.39(9) 3.0(1) -0.62(7) 0.86(8) 0.45(2)	0.40(6)
Pb(1) 1.00 0.0586(1) 0.25436(3) 0.9145(2) 1.95 2.79(4) 1.30(4) 2.66(4) 0.00(3) 1.49(3) Sb(1) 0.55(2) -0.4625(2) 0.07058(7) 0.4896(3) 1.95 2.2(1) 1.39(9) 3.0(1) -0.62(7) 0.86(8) As(1) 0.45(2) 0.00 -0.3126(3) 0.15277(9) 0.0354(4) 1.50 1.9(1) 1.0(1) 2.4(1) -2.9(8) 1.16(9)	0.40(6)
Pb(1) 1.00 0.0586(1) 0.25436(3) 0.9145(2) 1.95 2.79(4) 1.30(4) 2.66(4) 0.00(3) 1.49(3) Sb(1) 0.55(2) 0.4625(2) 0.07058(7) 0.4896(3) 1.95 2.2(1) 1.39(9) 3.0(1) -0.62(7) 0.86(8) As(1) 0.45(2) 0.00 -0.3126(3) 0.15277(9) 0.0354(4) 1.50 1.9(1) 1.0(1) 2.4(1) -2.9(8) 1.16(9) As(3) 1.00 0.0966(3) 0.16492(9) 1.4450(4) 1.88 2.4(1) 1.5(1) 2.2(1) 0.09(9) 1.2(1)	0.40(6) 0.05(8)
Pb(1) 1.00 0.0586(1) 0.25436(3) 0.9145(2) 1.95 2.79(4) 1.30(4) 2.66(4) 0.00(3) 1.49(3) Sb(1) 0.55(2) -0.4625(2) 0.07058(7) 0.4896(3) 1.95 2.2(1) 1.39(9) 3.0(1) -0.62(7) 0.86(8) As(1) 0.45(2) 0.00 -0.3126(3) 0.15277(9) 0.0354(4) 1.50 1.9(1) 1.0(1) 2.4(1) -2.9(8) 1.16(9) As(3) 1.00 0.0966(3) 0.16492(9) 1.4450(4) 1.88 2.4(1) 1.5(1) 2.2(1) 0.09(9) 1.2(1)	0.40(6) 0.05(8) 0.01(9) -0.2(2) -1.3(2)
Pb(1) 1.00 0.0586(1) 0.25436(3) 0.9145(2) 1.95 2.79(4) 1.30(4) 2.66(4) 0.00(3) 1.49(3) Sb(1) 0.55(2) -0.4625(2) 0.07058(7) 0.4896(3) 1.95 2.2(1) 1.39(9) 3.0(1) -0.62(7) 0.86(8) As(2) 1.00 -0.3126(3) 0.15277(9) 0.0354(4) 1.50 1.9(1) 1.0(1) 2.4(1) -2.9(8) 1.16(9) As(3) 1.00 0.0966(3) 0.16492(9) 1.4450(4) 1.88 2.4(1) 1.5(1) 2.2(1) 0.09(9) 1.2(1) S(1) 1.00 0.2784(7) 0.0122(2) 1.392(1) 2.21 2.2(3) 1.3(2) 3.8(3) -0.0(2) 0.8(2) S(2) 1.00 0.4908(8) 0.0839(2) 0.869(1) 2.44 3.1(3) 2.7(3) 3.2(3) -0.8(2) 2.0(3) S(3) 1.00 -0.2097(7) 0.1637(2) 0.7283(9) 1.82 2.3(3) 1.4(2) 2.6(3) 0.0(2) 1.4(2)	0.40(6) 0.05(8) 0.01(9) -0.2(2)
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	0.40(6) 0.05(8) 0.01(9) -0.2(2) -1.3(2) -0.2(2) 0.1(2)
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	0.40(6) 0.05(8) 0.01(9) -0.2(2) -1.3(2) -0.2(2)

jentschite Tl is surrounded by six close S, the Tl–S distances ranging from 3.222 to 3.419 Å (mean 3.306 Å). A seventh S occurs at a distance a little longer than the shortest Tl–As distance (Tab. 5). However, this S can not be neglected in order to have reasonable Tl–S polyhedra. The S atoms form a distorted trigonal prism defined by six atoms, with one additional atom beyond one prism face (Fig. 2). In both edenharterite an jentschite Tl and S form $^1_\infty[\text{TlS}_5]$ double chains along [001]. In jentschite this double chain is compressed. This leads to a shorter Tl–Tl distance of 3.918 Å compared to 4.354 Å in edenharterite.

Lead: In both minerals Pb is surrounded by seven close S atoms. Six S form a much more regular trigonal prism (compared to S around Tl), with the additional atom beyond one prism face (Fig. 2). The Pb–S distances vary between 2.830 and 3.471 Å (mean 3.075 Å) in edenharterite compared to 2.791–3.408 Å (mean 3.068 Å) in jentschite. Pb and S form ²_∞[PbS₃] planes parallel (010). The Pb–Pb distances are similar in edenharterite (4.144 Å) and jentschite (4.208 Å).

Arsenic and Antimony: In both structures, the site occupancy of As versus Sb on the three As

positions were refined keeping the sums of As + Sb = 1. The result for edenharterite might be doubtful because of the small Sb amount (Tab. 4). In jentschite, however, the refinement shows unequivocally one site dominantly being occupied by Sb and two sites being occupied by As. Sb and As, therefore, build up an ordered structure. Both As and Sb form trigonal MeS_3 (Me = As, Sb) pyramids with Me at the apex (Fig. 3). In edenharterite the As(1)S₃ pyramid shows larger As–S distances (mean 2.322 Å) compared to the other two AsS_3 pyramids (mean 2.281 Å and 2.277 Å). This can be regarded as another hint for the location of Sb at the As(1) site. In jentschite SbS₃ exhibits, as expected, distinctly longer Sb-S distances compared to the As-S distances (mean values: 2.428 A versus 2.271 Å and 2.275 Å). Although the Sb(1) position contains large amounts of As the Sb-S distances are in good agreement with the values given by Edenharter (1976).

In edenharterite six AsS_3 form finite $[As_6S_{12}]$ groups whereas in jentschite four AsS_3 and two SbS_3 form $[As_4Sb_2S_{12}]$ groups (Fig. 3). In edenharterite these groups can be described as four-edged As_2S_2 rings with two As_2S_5 molecules in cis posi-

152

Tab. 5 Selected interatomic distances (Å) in edenharterite (left) and jentschite (right). Me–S distances are listed for values less than analogous Me–As distances (Me = Tl, Pb). The arrangement was selected for easy comparison of the data. ¹⁾ Longer than the Tl–As distance. ²⁾ Mean of six (mean of seven: 3.333 Å). ³⁾ Primitive lattice translations are not indicated.

Edenhar	terite			Jentschite				
Tl(1)	30-4	$As(3)_1$	3.463(3)	Tl(1)	-	$As(3)_1$	3.480(3)	
Tl(1)	1/2	$S(1)_1$	3.211(7)	Tl(1)		$S(1)_{1}$	3.240(6)	
	_	$S(1)_{4}$	3.373(7)		_	$S(1)_1$	3.419(5)	
	_	$S(2)_{1}$	3.344(8)		_	$S(2)_1$	3.222(6)	
		$S(3)_{1}^{1}$	3.369(7)		_	$S(3)_1$	3.399(5)	
	_	$S(4)_1$	3.309(9)		-	$S(4)_1$	3.294(5)	
	_	$S(4)_1$	3.337(8)		_	$S(4)_1$	3.495(6) 1)	
	_	$S(5)_1$	3.218(7)		-	$S(5)_1$	3.260(5)	
	mea	n	3.309		me	an	3.306 2)	
Pb(1)		$As(3)_3$	3.518(3)	Pb(1)	-	$As(2)_{-2}$	3.528(2)	
Pb(1)	_	$S(3)_1$	2.931(7)	Pb(1)	_	$S(3)_{-2}$	2.937(5)	
	_	$S(3)_{3}$	3.044(7)		_	$S(3)_{1}$	3.024(5)	
	-	$S(5)_{1}$	2.931(7)			$S(5)_{-2}$	2.980(5)	
	_	$S(5)_{3}$	3.029(7)		-	$S(5)_1$	3.009(5)	
	-	$S(6)_1$	3.471(8)		-	$S(6)_{-2}$	3.327(5)	
	-	$S(6)_3$	2.830(7)		-	$S(6)_1$	2.791(5)	
	_	$S(6)_3$	3.290(7)		_	$S(6)_1$	3.408(6)	
	mea	n	3.075		me	an	3.068	
As(1)	_	$S(1)_1$	2.323(7)	Sb(1)	_	$S(1)_{1}$	2.436(6)	
	_	$S(1)_4$	2.358(7)		-	$S(1)_{-1}$	2.446(6)	
	-	$S(2)_1$	2.284(9)		-	$S(2)_1$	2.401(6)	
	mea		2.322		me	an	2.428	
As(2)	_	$S(2)_1$	2.302(8)	As(2)	_	$S(2)_1$	2.289(6)	
	_	$S(3)_1$	2.247(8)		-	$S(3)_1$	2.228(5)	
		$S(4)_1$	2.295(8)		-	$S(4)_1$	2.297(6)	
	mea	n	2.281		me	an	2.271	
As(3)		$S(4)_1$	2.334(7)	As(3)	-	$S(4)_1$	2.337(6)	
	-	$S(5)_1$	2.244(8)		_	$S(5)_1$	2.230(6)	
	-	$S(6)_1$	2.254(8)		-	$S(6)_1$	2.257(6)	
	mea	n	2.277		me	an	2.275	
Symmeti	ry codes	3)		Symmetry	Symmetry codes 3)			
1 X, Y, Z 2 1/4–X,			/4+X, 1/4-Y, 1/4+Z /2-X, -Y, 1/2+Z	1 X, Y, Z 2 1/2–X,		0.7		

tion. In contradiction to that in jentschite the fouredged ring consists of Sb_2S_2 with two As_2S_5 molecules in trans position (Fig. 3). This explains the different symmetries in edenharterite and jentschite.

Bond valences were estimated (ALTERMATT and BROWN, 1985) and the obtained results are given in table 7. For the estimations the same conditions have been chosen as for the discussion of the structures (see above). The estimated values are in good agreement with the results from the structure refinements. It should be noted that the estimations are influenced (and the results might be even better) by accepting a larger range of Me–S distances. However, this leads to fivefold

coordination in case of As and Sb, which is in contradiction to the described trigonal MeS₃ pyramids.

Two minerals are homeotypes if 1) the form and arrangement of the coordination polyhedra is the same, or similar, and 2) they differ in space group symmetry and crystal chemistry. Edenharterite and jentschite have different space groups and different chemical formulae (Tab. 1) but they exhibit, as described above, very similar Me–S coordination polyhedra (Me = Tl, Pb, As, Sb). This similarity can be quantified by regularization.

Regularizing is a tool, implemented in the program CRYSTALS (WATKIN et al., 1985), that calculates by a least squares fit the similarity between

Tab. 6 Selected interatomic angles (°) in edenharterite (left) and jentschite (right). Details are explained in the text. Cf. table 5 for symmetry codes.

Edenharterite	2				Jentschite				
$S(1)_1 -$	Tl(1)	_	$S(1)_4$	107.6(2)	$S(1)_1 -$	Tl(1)	-	$S(1)_{-1}$	108.0(1)
$S(1)_1 -$		-	$S(2)_{1}$	82.6(2)	$S(1)_1 -$		-	$S(2)_1$	83.8(2)
$S(1)_1 -$		-	$S(3)_{1}$	125.3(2)	$S(1)_1 -$		-	$S(3)_1$	124.2(1)
$S(1)_{1}$ -		_	$S(4)_{1}$	65.7(2)	$S(1)_1 -$		-	$S(4)_1$	64.8(1)
$S(1)_{1}$ -		_	$S(4)_{1}$	169.5(2)	$S(1)_1 -$		-	$S(4)_1$	171.7(1)
$S(1)_{1}^{1}$ -		-	$S(5)_{1}$	72.2(2)	$S(1)_{1}$ -		-	$S(5)_1$	70.5(1)
$S(1)_{4}^{1}$ -		_	$S(2)_{1}$	147.3(2)	$S(1)_{-1}$ -		_	$S(2)_1$	146.6(1)
$S(1)_4$ -		_	$S(3)_{1}$	75.6(2)	$S(1)_{-1}^{-1}$ -		_	$S(3)_1$	77.6(1)
$S(1)_4$ -		-	$S(4)_{1}$	70.4(2)	$S(1)_{-1}$ -			$S(4)_{1}$	67.6(1)
$S(1)_4$ -		_	$S(4)_1$	81.9(2)	$S(1)_{-1}$ -		-	$S(4)_1$	82.9(1)
$S(1)_4 - S(1)_4 -$		_	$S(5)_1$	142.9(2)	$S(1)_{-1}$ -		-	$S(5)_1$	144.9(1
$S(1)_4 - S(2)_1 -$		_	$S(3)_1$		$S(2)_1$ -		-	$S(3)_1$	
			$S(4)_1$	93.8(2)			_	$S(4)_1$	96.4(1)
$S(2)_1 - S(2)_1$		-					3	$S(4)_1$ $S(4)_1$	129.5(1)
$S(2)_1 -$		_	$S(4)_1$	129.6(2)	$S(2)_1 -$			S(4) ₁	68.3(1
$S(2)_1 -$		-	$S(5)_1$	69.7(2)	$S(2)_1 -$			$S(5)_1$	
$S(3)_1 -$		-	$S(4)_1$	60.8(2)	$S(3)_1 - S(3)_1 -$		-	$S(4)_1$	60.9(1
$S(3)_1 -$		-	$S(4)_1$	64.8(2)	$S(3)_1 -$		-	$S(4)_1$	62.6(1
$S(3)_1 -$		-	$S(5)_1$	75.3(2)	$S(3)_1 -$		-	$S(5)_1$	75.5(1
$S(4)_1 -$		-	$S(4)_1$	123.3(2)	$S(4)_1 -$		-	$S(4)_1$	120.2(2
$S(4)_1$ -		-	$S(5)_1$	64.0(2)	$S(4)_1 - S(4)_1 -$		-	$S(5)_1$	64.4(1
$S(4)_1 -$		-	$S(5)_1$	115.9(2)	$S(4)_1$ -		-	$S(5)_1$	117.3(1
$S(3)_1 -$	Pb(1)	_	$S(3)_3$	160.9(3)	$S(3)_{-2}$ -	Pb(1)	-	$S(3)_1$	162.5(2
$S(3)_{1}^{1}$ -		_	$S(5)_1$	92.8(2)	$S(3)_{-2}$ -		_	$S(5)_{-2}$	94.0(1
$S(3)_1 -$		_	$S(5)_{3}$	88.8(2)	$S(3)_{-2}$ -		_	$S(5)_1$	88.2(1
$S(3)_1 -$		_	$S(6)_1$	69.7(2)	$S(3)_{-2}^{-2}$ -			$S(6)_{-2}$	69.9(1
$S(3)_1 -$			$S(6)_3$	82.5(2)	$S(3)_{-2}$ -		_	$S(6)_1$	
$S(3)_1$ -		-		127.9(2)	$S(3)_{-2}$ -		_	S(6).	129.3(1
				88.5(2)					87.1(1
$S(3)_3 - S(3)_3 -$			$S(5)_{3}$	83.1(2)	$S(3)_1 -$		_	$S(5)_{-2}$ $S(5)_{1}$	85.1(1
				123.8(2)	$S(3)_1 -$		_	$S(6)_{-2}$	
$S(3)_3 -$			$S(0)_1$					$S(6)_{-2}$ $S(6)_{1}$	80.4(1
$S(3)_3 -$		-		78.5(2)					67.8(1
$S(3)_3 -$		-	$S(6)_3$	71.0(2)	$S(3)_1 -$			$S(6)_1$	
$S(5)_1 -$		-	$S(5)_3$	158.1(3)	$S(5)_{-2}$ -		-	$S(5)_1$	160.5(2
$S(5)_1 -$		-	$S(6)_1$	126.9(2)	$S(5)_{-2}$ -		-	$S(6)_{-2}$	124.4(1
$S(5)_1 -$		-	$S(6)_3$	85.8(2)	$S(5)_{-2}$ -		-	$S(6)_1$	87.6(2
$S(5)_1 -$		-	$S(6)_3$	78.0(2)	$S(5)_{-2}$ -		-	$S(6)_1$	
$S(5)_3$ -		-	$S(6)_1$	74.0(2)	$S(5)_1 -$		-	$S(6)_{-2}$	74.4(1
$S(5)_3$ -		- "	$S(6)_3$	72.8(2)	$S(5)_1$ -		-	$S(6)_1$	73.5(1
$S(5)_3 -$		-	$S(6)_3$	117.6(2)	$S(5)_1 -$		-	$S(6)_1$	119.4(1
$S(6)_1 -$		_	$S(6)_3$	75.7(2)	$S(6)_{-2}$ -		-	$S(6)_1$	77.5(1
$S(6)_1 -$		_	$S(6)_3$	136.6(3)	$S(6)_{-2}$ -		_	$S(6)_1$	137.6(2
$S(6)_3$ -		-	$S(6)_3$	145.6(3)	$S(6)_1$ -		-	$S(6)_1$	143.4(2
$S(1)_1 -$	As(1)		$S(1)_4$	91.4(3)	$S(1)_1 -$	Sb(1)	_	$S(1)_{-1}$	90.4(2
$S(1)_{1}$ -		_	$S(2)_{1}^{4}$	89.4(3)	$S(1)_1$ -		_	$S(2)_1$	85.6(2
$S(1)_4$ -		-	$S(2)_{1}$	98.7(3)	$S(1)_{-1}$ -		-	$S(2)_1$	95.7(2
	As(2)		$S(3)_1$	97.9(3)	0(0)	As(2)	_	S(3) ₁	97.1(2
$S(2)_1 - S(2)_1$	AS(2)	_		2 /		173(2)		$S(4)_1$	96.3(2
$S(2)_1 - S(3)$		-	$S(4)_1$	96.3(3)	$S(2)_1 - S(3)$				97.2(2
$S(3)_1 -$		-	$S(4)_{1}$	96.2(3)	S(3) ₁ -			S(4) ₁	
$S(4)_1 -$	As(3)	-	$S(5)_1$	98.1(3)	$S(4)_1 -$	As(3)	-	$S(5)_1$	99.7(2
$S(4)_1 -$		-	$S(6)_1$	101.1(3)	$S(4)_1$ -		-	$S(6)_1$	101.6(2
$S(5)_1 -$		_	$S(6)_1$	101.4(3)	$S(5)_1 -$		-	$S(6)_1$	101.4(2

two crystal structure fragments (clusters). One cluster of 11 atoms with the composition TlPbAs₂SbS₆ and the geometry of jentschite has

been fitted to an adequate cluster of 11 atoms with the composition TlPbAs₃S₆ and the geometry of edenharterite (Fig. 5). Table 8 summarizes the de-

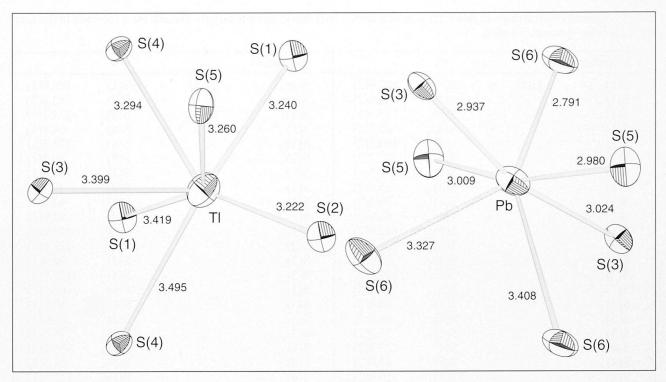


Fig. 2 TlS₇ (left) and PbS₇ (right) polyhedra in jentschite. The Me atoms are surrounded by six S atoms forming more or less distorted trigonal prisms, with one additional atom beyond one of the prism faces. See text for details.

viations in best plane system after fitting. The transformation matrix between new and old coordinates in crystal system is approximately the unit

matrix. This result may be expected since adequate clusters were used. A pseudo-symmetry operator x–0.25, y, z–0.34 (translation) was found.

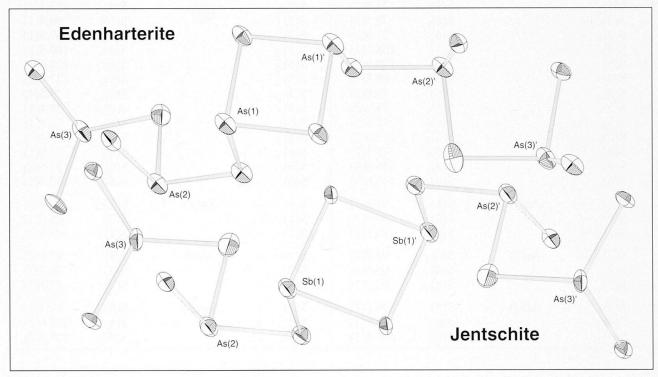


Fig. 3 [As₆S₁₂] group in edenharterite: a four-edged As₂S₂ ring and two As₂S₅ molecules in cis position. In jentschite the four-edged ring consists of Sb₂S₂ with two As₂S₅ molecules in trans position. This explains the reduced symmetry in jentschite compared to edenharterite.

Eden.	S_1	S_2	S_3	S_4	S_5	S_6	Σ	Jen.	S_1	S_2	S_3	S_4	S_5	S ₆	Σ
Tl_1	0.17 0.11	0.12	0.11	0.13 0.12	0.16		0.92	Tl_1	0.15	0.16	0.10	0.13 0.08	0.14		0.85
Pb ₁	0.11		0.35 0.26	0.12	0.35 0.27	0.46 0.13	1.90	Pb ₁	0.09		0.34 0.27	0.00	0.31 0.28		1.93
			0.20		0.27	0.13					0.27		0.28	0.12	
As_1	0.91 0.83	1.02					2.76	Sb ₁	0.87 0.84	0.96					2.67
As_2		0.93	1.08	0.94	1.00	1.01	2.95	As_2		0.96	1.13	0.94	1.10	1.01	3.03
As_3	2.01	2.07	1.80	0.84	1.06	1.04	2.94	As_3		2.08	1.84	0.84	1.12	1.04	3.00

Tab. 7 Estimated bond valences for edenharterite (left) and jentschite (right). They are in good agreement with the results from structure refinements. See text for details.

Significantly higher deviations in distances and angles were only found for As(1) and S(1). This is explained by the fact that the As(1) position in edenharterite is mainly occupied by the larger Sb(1) in jentschite (see above).

Conclusions

Edenharterite incorporates a certain amount of Sb (Berlepsch, 1995) without being influenced in its formation. However, Sb is not needed for

the formation of edenharterite (Balić-Žunić and Engel, 1983). Edenharterite shows small, jentschite large variations in their amounts of As and Sb. The minerals belong to two different solid solution series. Balić-Žunić et al. (1994) reported a similar variation of As and Sb in synthetic rebulites. In bernardite a comparable As, Sb solid solution behaviour can be expected. More investigations are needed to understand the role of Sb.

The crystal structures of edenharterite and jentschite were discussed. It was shown that eden-

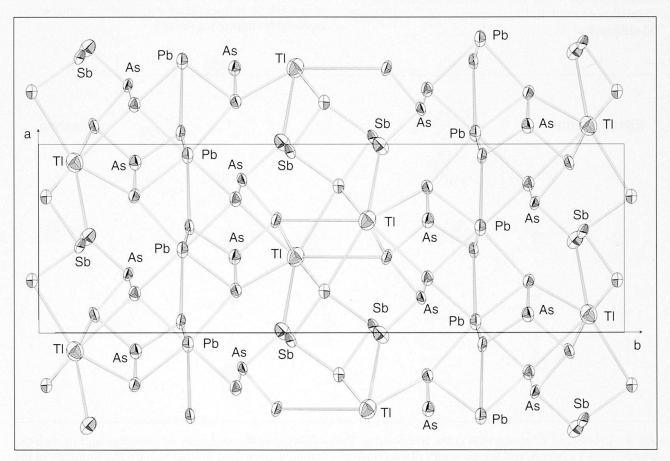


Fig. 4 Projection of the crystal structure of jentschite along the c-axis with the unit cell indicated.

<i>Tab.</i> 8	Regularization of the crystal structures of edenharterite and jentschite. Deviations in best plane system
after fit	ting (RMS = root mean square). See also figure 5. Details are explained in the text.

Туре	Serial	d(x)	d(y)	d(z)	Distance/Å	Angle/°
Tl ↔ Tl	1	-0.008	-0.023	0.009	0.026	0.452
Pb ↔ Pb	1	-0.010	-0.047	0.044	0.066	0.974
$As \leftrightarrow Sb$	1	-0.027	0.073	-0.104	0.130	1.833
$As \leftrightarrow As$	2	0.008	-0.004	-0.009	0.012	0.269
$As \leftrightarrow As$	3	0.006	0.020	-0.002	0.021	0.360
$S \leftrightarrow S$	1	-0.080	0.052	0.076	0.122	1.599
$S \leftrightarrow S$	2	0.020	-0.004	-0.027	0.034	0.513
$S \leftrightarrow S$	3	-0.002	-0.048	-0.005	0.048	1.095
$S \leftrightarrow S$	4	0.005	-0.008	0.004	0.011	0.257
$S \leftrightarrow S$	5	0.042	-0.007	-0.011	0.044	0.712
$S \leftrightarrow S$	6	0.047	-0.003	0.024	0.053	0.804
Total squared	deviations	0.012	0.014	0.020	→ Total	0.046
RMS deviation		0.033	0.035	0.043	→ Mean	0.064

harterite and jentschite are homeotypes. At this time it seems as if the amount of Sb incorporated in the structures is not responsible for the formation of either edenharterite or jentschite. It can be imagined that pure Sb-edenharterite and/or pure As-jentschite exist (Fig. 1) as well as any other mixed compound. It would be of interest to verify this by doing hydrothermal synthesis. Probably other reasons than the Sb contents may be responsible to explain the formation of the different Tl-sulfosalts.

Acknowledgements

The measurements on the CAD4 were carried out at the Laboratory for Crystallography, Department of Chemistry, those on the SEM were made at the SEM-Laboratory, both University of Basel. I am greatly obliged to S. Graeser, M. Zehnder, R. Guggenheim, A. Edenharter, M. Neuburger, D. Mathys, S. Th. Schmidt, J. Brugger and M. Krzemnicki as well as to many others for their help and constructive discussions in connection with the present work. St. Hafner (Marburg) provided valuable suggestions for improving the text.

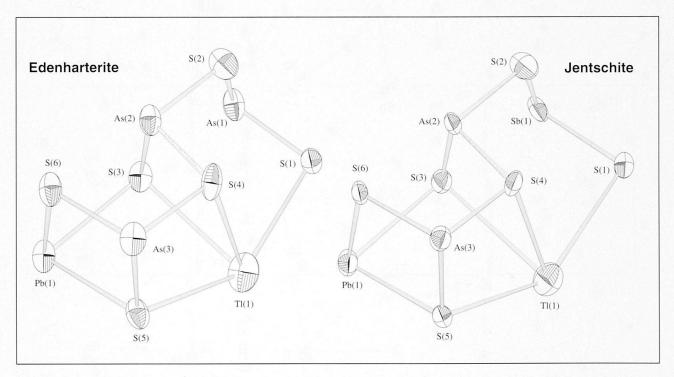


Fig. 5 Clusters of 11 atoms with i) the composition $TlPbAs_2SbS_6$ and the geometry of jentschite and ii) with the composition $TlPbAs_3S_6$ and the geometry of edenharterite that have been used for a fit to show the similarity of the two structures (see text for details). Note that the fractional coordinates in table 4 do not represent these clusters.

References

ALTERMATT, D. and Brown, I.D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. Acta Cryst., B41, 244-248.

Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M.C., Polidori, G. and CAMALLI, M. (1994): SIR92 - a program for automatic solution of crystal structures by direct methods, J. Appl. Crystallogr., 27, 435

BALIĆ-ŽUNIĆ, T. and ENGEL, P. (1983): Crystal structure of synthetic TlPbAs₃S₆. Z. Krist., 165, 261–269.

BALIĆ-ŽUNIĆ, T., MAKOVICKY, E. and MOËLO, Y. (1994): The experimental study of the As/Sb solid solution behaviour in Tl sulphosalts. Int. Mineral. Assoc., 16th Gen. Meet., Pisa, Abstracts, p. 26.

BERLEPSCH, P. (1995): Chemical and crystallographical investigations on edenharterite (TlPbAs₃S₆). Schweiz. Mineral. Petrogr. Mitt., 75, 277–281.

Cvetković, L., Boronikhin, V.A., Pavićević, M.K., Krajnović, D., Gržetić, I., Libowitzky, E., Gie-STER, G., TILLMANNS, E. (1995): Jankovicite, Tl₅Sb₉ (As, Sb)₄S₂₂, a new Tl-sulfosalt from Allchar, Macedonia. Mineral. Petrol., 53, 125-131

DONNAY, J.D.H. and ONDIK, H.M. (1973): Crystal data determinative tables. 3rd ed. Vol. 2. U. S. Department of Commerce, National Bureau of Standards and the Joint Committee on Powder Diffraction Standards,

EDENHARTER, A. (1976): Fortschritte auf dem Gebiete der Kristallchemie der Sulfosalze. Schweiz. Mineral. Petrogr. Mitt., 56, 195-217.

GRAESER, S. (1988): Drei neue Mineralien aus dem Binn-

tal. Uni Nova – Mitt. aus der Univ. Basel, 48, 17–19. Graeser, S. and Guggenheim, R. (1990): Brannerite from Lengenbach, Binntal (Switzerland). Schweiz. Mineral. Petrogr. Mitt., 70, 325–331.

GRAESER, S. and SCHWANDER, H. (1992): Edenharterite (TlPbAs₃S₆): a new mineral from Lengenbach, Binntal (Switzerland). Eur. J. Mineral., 4, 1265–1270.

Graeser, S., Schwander, H., Wulf, R. and Edenharter, A. (1992): Erniggliite (Tl₂SnAs₂S₆), a new mineral from Lengenbach, Binntal (Switzerland): description and crystal structure determination based on data from synchrotron radiation. Schweiz. Mineral. Petrogr. Mitt., 72, 293-305.

GRAESER, S., SCHWANDER, H., WULF, R. and EDENHAR-TER, A. (1995a): Stalderite TlCu(Zn,Fe,Hg)₂As₂S₆ a new mineral related to routhierite: description, and structure determination. Schweiz. Mineral. Petrogr.

Mitt., 75, 337-345.

GRAESER, S., EDENHARTER, A. and BERLEPSCH, P. (1995b): Jentschite (TIPbAs₂SbS₆): Description and structure refinement of a new mineral from the Lengenbach quarry, Binntal, Canton Valais, Switzerland. Terra Abstr., 7, 290.

HOFMANN, B., GRAESER, S., IMHOF, T., SICHER, V. and STALDER, H.A. (1993): Mineralogie der Grube Lengenbach, Binntal, Wallis. Jb. Nathist. Mus. Bern,

11, 3-90.

Nowacki, W. (1970): Über einige Mineralien der Grube Lengenbach. Urner Mineralienfreund, 3-60.

PAŠAVA, J., PERTLIK, F., STUMPFL, E.F. and ZEMANN, J. (1989): Bernardite, a new thallium arsenic sulphosalt from Allchar, Macedonia, with a determination of the crystal structure. Min. Mag., 53, 531–538.

STALDER, H.A., EMBREY, P., GRAESER, S. and Nowacki, W. (1978): Die Mineralien des Binntales. Jb. Nathist.

Mus. Bern, 6, 5–143.

WATKIN, D.J., CARRUTHERS, R.J. and BETTERIDGE, P. (1985): Computer Program CRYSTALS. Chemical Crystallography Laboratory, Oxford, UK.

Manuscript received November 13, 1995; revision accepted February 26, 1996.