

Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen =
Bulletin suisse de minéralogie et pétrographie

Band: 75 (1995)

Heft: 2

Artikel: Chemical and crystallographical investigations on edenharterite
(TIPbAs₃S₆)

Autor: Berlepsch, Peter

DOI: <https://doi.org/10.5169/seals-57158>

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften. 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. [Siehe Rechtliche Hinweise.](#)

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. [Voir Informations légales.](#)

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. [See Legal notice.](#)

Download PDF: 22.01.2025

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

SHORT COMMUNICATION

Chemical and crystallographical investigations on edenharterite (TlPbAs₃S₆)*

Peter Berlepsch[†]

Abstract

Edenharterite (TlPbAs₃S₆) was analyzed in detail by means of an electron microprobe. The analyses clearly showed that Sb is always present in edenharterite (max. 2.7 wt%), a feature not known until now. A correlation between As and Sb could not be observed.

A structural analysis on the mineral edenharterite was performed. The structure of natural edenharterite is not significantly different from that of the synthetic compound TlPbAs₃S₆. Some structural data for both the mineral and the synthetic compound are compared.

Keywords: edenharterite, Tl-As-sulphosalts, microprobe analyses, crystal structure, Lengenbach (Binntal, Switzerland).

Introduction

The aim of the present work, which is part of the current research project on new minerals from the Lengenbach quarry, Binntal, Switzerland (see e.g. GRAESER et al., 1992), is to show the results of detailed chemical and crystallographical investigations on the mineral edenharterite (TlPbAs₃S₆).

Edenharterite (orthorhombic; $a = 15.465(3)$, $b = 47.507(8)$, $c = 5.843(2)$, space group $Fdd2$) was described as a new mineral by GRAESER and SCHWANDER (1992). It is one of at least eleven Tl-As-sulphosalts that were found in the Lengenbach quarry so far (S. Graeser in HOFMANN et al., 1993). The crystal structure of a new compound synthesized by A. Edenharter (in NOWACKI et al., 1982), with the chemical composition TlPbAs₃S₆ has been published by BALIC-ZUNIC and ENGEL (1983). From comparison of the single-crystal X-ray data of the two compounds GRAESER and SCHWANDER (1992) concluded that both edenharterite and the synthetic compound are identical phases.

The discovery of another new mineral

(jentschite, monoclinic., space group $P2_1/n$; GRAESER and EDENHARTER, in prep; GRAESER, EDENHARTER and BERLEPSCH, 1995) with similar chemical composition (idealized: TlPbAs₂SbS₆) but different symmetry requires a series of detailed chemical and crystallographical investigations. To get the basis for detailed comparison between the two minerals, the chemistry of edenharterite was studied and a structure refinement on the mineral was performed.

Chemical investigations

EXPERIMENTAL

Because limited amounts of material were available, only a few crystals were analyzed. For the chemical analyses with an electron microprobe six crystals were separated from six different rock samples. On these samples edenharterite (associated with various other Tl-sulphosalts) had already been identified by X-ray methods (Gandolfi camera) sometimes ago. All samples originate from the Lengenbach quarry, which is the

* Extended abstract of a contribution presented at the annual meeting of the Swiss Society of Mineralogy and Petrology, Aarau, October, 1994.

[†] Mineralogisch-Petrographisches Institut, Universität Basel, Bernoullistrasse 30, CH-4056 Basel, Switzerland.

Tab. 1 Summarized microprobe analyses (all wt%) of three crystals (above). The standard deviation (σ_{n-1}) and the analytical error (a. e.) are given for the edenharterite phases only. Normalized edenharterite formulae (TI = 1) and charge balances (below).

| | | L 19746 | | | L 20435 | | L 20486 | | | |
|----------|-------|------------------|----------------|----------------|-----------|------------------|----------------|------------------|----------------|----------------|
| | N | Edenharterite 14 | | Baumhauerite 9 | Unknown 8 | Edenharterite 10 | | Edenharterite 25 | | Baumhauerite 5 |
| | a. e. | wt% | σ_{n-1} | wt% | wt% | wt% | σ_{n-1} | wt% | σ_{n-1} | wt% |
| Tl | 0.5 | 24.64 | 0.60 | 4.66 | 4.34 | 24.71 | 0.38 | 24.51 | 0.47 | 5.37 |
| Pb | 0.5 | 23.69 | 0.83 | 44.88 | 42.22 | 23.44 | 0.45 | 23.36 | 0.46 | 45.33 |
| As | 0.2 | 25.69 | 0.49 | 24.62 | 27.48 | 27.03 | 0.30 | 27.14 | 0.35 | 23.86 |
| Sb | 0.03 | 1.60 | 0.45 | 0.98 | 0.84 | 1.32 | 0.22 | 1.00 | 0.14 | 1.67 |
| S | 0.6 | 23.86 | 0.27 | 24.68 | 25.85 | 23.50 | 0.20 | 23.33 | 0.26 | 23.28 |
| Sn | | <0.04 | --- | <0.04 | <0.04 | <0.04 | --- | <0.04 | --- | <0.04 |
| Cu | 0.04* | 0.05 | 0.04 | 0.07 | 0.04 | <0.04 | --- | <0.04 | --- | <0.04 |
| Zn | | <0.05 | 0.02 | <0.05 | <0.05 | --- | --- | <0.05 | --- | <0.04 |
| Σ | | 99.55 | | 99.91 | 100.79 | 100.02 | | 99.35 | | 99.51 |

N = number of analyses; a. e. = analytical error (wt%, from count statistics on edenharterite); * = detection limit

| Sample | Normalised edenharterite formulae (TI = 1) | Σ As+Sb (at%) | c. b. |
|---------|--|----------------------|----------|
| L 19746 | Tl ₁ Pb _{0.95±0.05} (As _{2.85±0.08} Sb _{0.11±0.03})S _{6.18±0.19} | 2.96±0.09 | -0.6±0.2 |
| L 20435 | Tl ₁ Pb _{0.94±0.02} (As _{2.98±0.06} Sb _{0.09±0.02})S _{6.06±0.11} | 3.07±0.06 | -0.0±0.1 |
| L 20486 | Tl ₁ Pb _{0.94±0.03} (As _{3.02±0.08} Sb _{0.07±0.01})S _{6.07±0.17} | 3.09±0.08 | -0.0±0.2 |

c. b. = charge balance

only locality where edenharterite has been found so far. Unfortunately semi-quantitative EDS analyses performed with a PHILIPS SEM 515 (equipped with EDS system) showed that only three of the six crystals had the composition of edenharterite.

CHEMICAL COMPOSITION

Quantitative chemical analyses were carried out on all six crystals by means of an electron microprobe (JEOL JXA-8600 superprobe, ZAF correction). The elements S, As, Sb, Tl, Pb and Cu, Zn, Ag, Sn were quantitatively analyzed using the following standards: TlAsS₂ (S K_α PET, As L_α TAP and Tl M_α PET), Sb₂S₃ (Sb L_α PET) as well as PbS (Pb M_α PET), CuFeS₂ (Cu K_α LiF), ZnS (Zn K_α LiF), Ag₂S (Ag L_β PET) and SnS (Sn L_β PET). The conditions of measurement were: acceleration voltage 15 kV, beam current 20 nA, scanned area 15 μm². The results of the analyses are summarized in table 1.

The crystal L 19746 is inhomogenous (Fig. 1) and composed of three different Sb-bearing phases; edenharterite (TlPbAs₃S₆), baumhauerite (Pb₃As₅S₉) and an unknown phase (Pb₃(As,Sb)₅S₁₁). The crystal L 20435 is homogenous edenharterite. Crystal L 20486 is inhomogenous and consists mainly of edenharterite with minor amounts of baumhauerite. The formulae of edenharterite differ from those given by GRAESER and SCHWANDER (1992) particularly by higher contents of As+Sb and S, but they are similar with respect to Tl and Pb.

The remaining three crystals are wallisite (TlPb(Cu,Ag)As₂S₅, L 24582), an intergrowth of jordanite (Pb₁₄(As,Sb)₆S₂₃, L 18989) with an unidentified Pb-As-sulphosalt and another Pb-As-sulphosalt (L 24626) with extremely small lamellae of probably edenharterite. The latter three samples are not discussed in detail.

In the original description of the chemical composition of edenharterite (GRAESER and SCHWANDER, 1992) very small amounts of Sn but no Sb were reported. In contrast to that, all

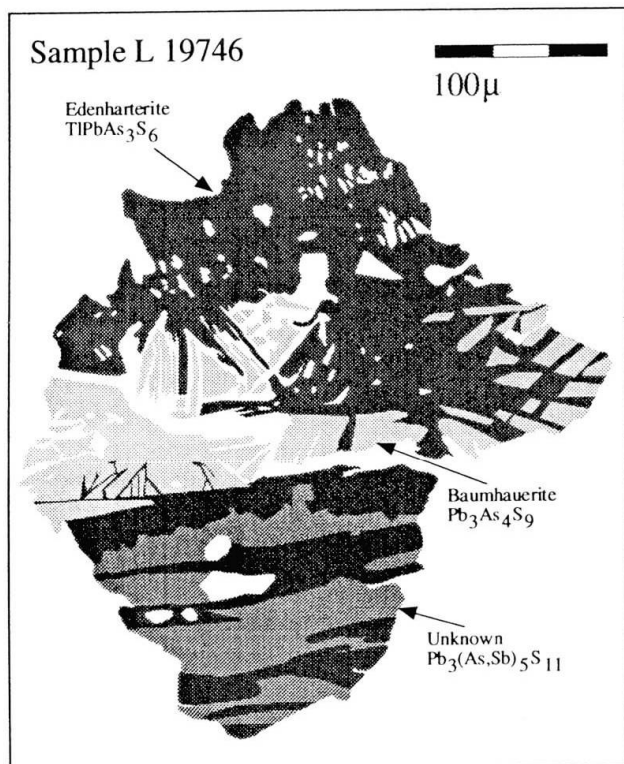


Fig. 1 The inhomogeneous crystal L 19746: schematic presentation of the three different phases (all Sb bearing) edenharterite (TIPbAs₃S₆), baumhauerite (Pb₃As₄S₉) and an unknown sulphosalt (Pb₃(As,Sb)₅S₁₁).

recently analyzed crystals of edenharterite contain significant amounts of Sb (max. 2.7 wt%) like the associated baumhauerite. Traces of Sn, Cu and Zn but no Ag were also found in some cases.

The variations in the chemical composition of edenharterite are small (Fig. 2). With the given analytical error (Tab. 1) the three crystals of edenharterite exhibit almost homogeneous composition. A distinct correlation between As and Sb could not be observed (Fig. 3).

From these observations it can be seen that a limited substitution of As by Sb exists in edenharterite. Compared to the synthetic compound, which is a pure As-edenharterite, natural edenharterite contains up to 2.7 wt% of Sb (= 0.19 mol%).

Structure refinement

EXPERIMENTAL

A structure determination of the mineral edenharterite has not been performed so far. According to the X-ray data and chemical composition it was suggested that both the natural and the syn-

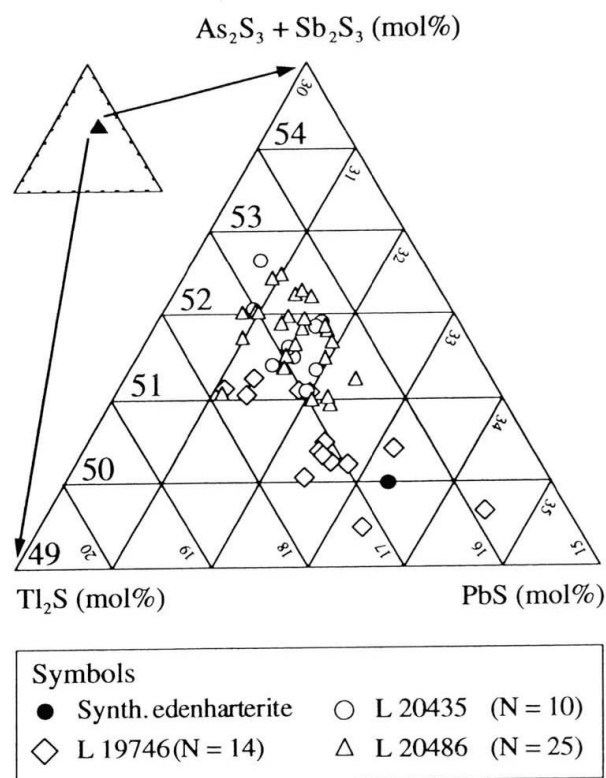


Fig. 2 Triangular plot with Tl₂S (mol%), PbS (mol%) and As₂S₃+Sb₂S₃ (mol%) which shows almost no variations in the chemical composition of edenharterite within the analytical error.

thetic compound represent identical structures. To verify this and to check whether or not the substitution of As by Sb has an influence on the crystal structure of edenharterite, a structure refinement was executed.

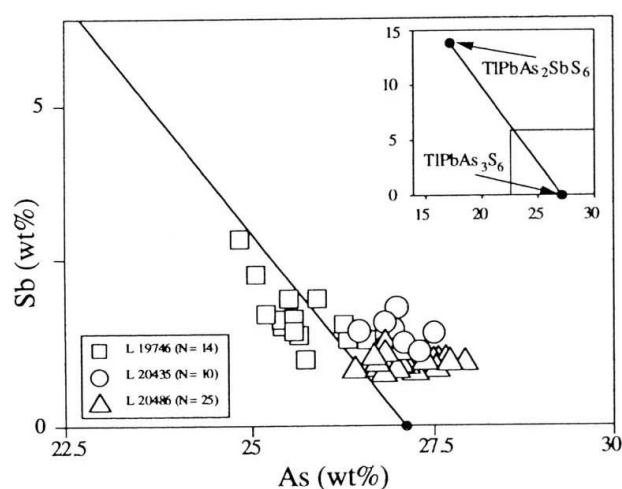


Fig. 3 Variation diagram with Sb (wt%) against As (wt%). Poor correlation between As and Sb can be observed. The line indicates the theoretical correlation curve for perfect substitution of As by Sb between TIPbAs₃S₆ and TIPbAs₂SbS₆.

The X-ray data collection was performed on a platy crystal, measuring about $0.045 \times 0.19 \times 0.26$ mm, by means of an ENRAF NONIUS FR 590 CAD4 automatic single-crystal diffractometer with Kappa geometry. The lattice parameters were determined and refined, using 25 reflections within the angular range $26.76^\circ < \vartheta < 52.16^\circ$. Diffraction intensities were measured within the range $5.4^\circ < 2\vartheta < 155^\circ$, using graphite monochromatized Cu K_α radiation ($\lambda = 1.54178 \text{ \AA}$) and operating in the ω - 2ϑ scan mode. Data reduction included background and Lorentz-polarization corrections. The data were empirically corrected for absorption by using ψ scans.

The obtained space group ($F2dd$) and cell parameters (orthorhombic; $a = 5.848(1)$, $b = 15.478(2)$, $c = 47.600(9)$) are in agreement with the data from GRAESER and SCHWANDER (1992) as well as with own results from Weissenberg and precession investigations. Based on 1155 independent reflections ($I_{\text{obs}} > 3\sigma[I_{\text{obs}}]$), the structure was solved using the model by BALIC-ZUNIC and ENGEL (1983) and refined anisotropically to a R-value = 13.8%. In agreement with the rules of DONNAY and ONDIK (1973) for orientation of unit cells, the space group was subsequently transformed into $Fdd2$.

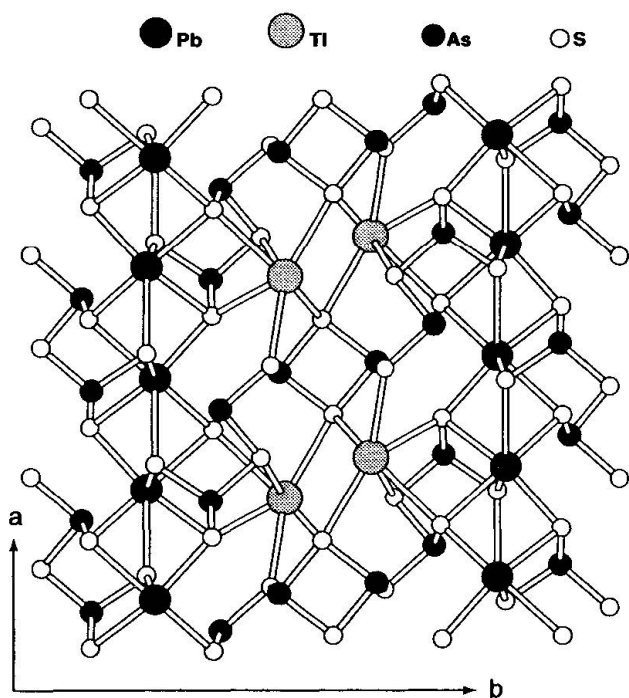


Fig. 4 Central projection of the edenharterite structure (only part of the unit cell) along the c -axis. The structure consists of $\infty[TlS_5]$ double chains along $[001]$ and $\infty[PbS_3]$ planes parallel to (010) which are themselves interconnected by $[As_6S_{12}]$ clusters.

DISCUSSION

The structure by BALIC-ZUNIC and ENGEL (1983) for the synthetic compound $(TlPbAs_3S_6)$ and the structure of edenharterite (this paper) can easily be converted into each other. The poor value of R does not permit detailed conclusions.

Thallium: Tl is surrounded by one As- and nine S-atoms in a distance ranging from 3.17 \AA to 3.87 \AA . For the graphical presentation (Fig. 4) some restrictions were made. Bonds between Tl and S are drawn only for atoms closer than the nearest As atom. In this case seven Tl-S bonds are drawn in a range from 3.17 \AA to 3.42 \AA . Tl forms $\infty[TlS_5]$ double chains along $[001]$. For the synthetic compound BALIC-ZUNIC and ENGEL (1983) indicate a seven plus two coordination of S-atoms around Tl, seven S-atoms in a range from 3.17 \AA to 3.39 \AA , and two more distant S-atoms (3.67 \AA and 3.88 \AA).

Lead: For the Pb-atoms the situation is similar. In general, the distances between Pb and S are smaller than those between Tl and S, which actually permits to distinguish these two atoms within the same structure (EDENHARTER, 1976). In the range up to 3.73 \AA Pb, like Tl, is surrounded by ten atoms. In contrast to Tl, Pb is surrounded by seven S- and three As-atoms. The restriction used for drawing Tl-S bonds can be neglected for Pb, because all seven S-atoms are closer than the nearest As-atom. Seven Pb-S bonds were drawn in a range from 2.74 \AA to 3.51 \AA . Pb forms $\infty[PbS_3]$ planes parallel to (010) (Fig. 4). For the synthetic compound, BALIC-ZUNIC and ENGEL (1983) indicate a five plus two coordination of S-atoms around Pb. Five close S-atoms in a range from 2.80 \AA to 3.06 \AA and two more distant S-atoms (3.33 \AA and 3.48 \AA).

Arsenic: As forms the apex of a trigonal pyramid with S-atoms at the base. Six AsS_3 pyramids are connected to form $[As_6S_{12}]$ clusters which themselves are connected to the $\infty[TlS_5]$ double chains and the $\infty[PbS_3]$ planes, thus forming the full crystal structure of edenharterite (Fig. 4). The As-S distances range from 2.23 \AA to 2.32 \AA identical with the data from BALIC-ZUNIC and ENGEL (1983).

Conclusions

In contrast to the original description of GRAESER and SCHWANDER (1992), Sb could be identified in all measured edenharterite crystals. Sb-contents vary from approximately 1 to 2.7 wt% (0.06 to 0.19 mol%). The presence of Sb in edenharterite was not known until now; it is of

special interest for the comparison of edenharterite and jentschite.

The structure refinement of edenharterite revealed, as expected, very similar crystal structures for both the synthetic compound and the mineral. Due to the poor R-value, no detailed conclusions can be made. The incorporation of Sb up to 2.7 wt% into the lattice of edenharterite has no influence to the formation of the mineral.

The next step in the current work will be a detailed study of jentschite to describe its chemistry, its chemical variations and its structure. This study may give the informations for understanding the structural change from orthorhombic to monoclinic symmetry.

Acknowledgements

The measurements on the ENRAF NONIUS FR 590 CAD4 were carried out at the Laboratory for Crystallography, Department of Chemistry, those on the PHILIPS SEM 515 were made at the SEM-Laboratory, both at the University of Basel. I am greatly obliged to S. Graeser, M. Zehnder, R. Guggenheim, A. Edenharter, M. Neuburger, D. Mathys, J. Brugger and R. Gieré as well as to many others for their help and constructive discussions in connection with the present work. Th. Armbruster (Bern) provided valuable suggestions for improving the text.

References

BALIC-ZUNIC, T. and ENGEL, P. (1983): Crystal structure of synthetic TlPbAs₃S₆. *Z. Krist.*, 165, 261–269.
DONNAY, J.D.H. and ONDIK, H.M. (1973): Crystal data determinative tables – Vol. II. 3rd edition. U. S. De-

partment of Commerce, National Bureau of Standards and the Joint Committee on Powder Diffraction Standards. U.S.A.

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

GRAESER, S. and EDENHARTER, A. (in. prep): Jentschite (TlPbAs₂SbS₆): a new mineral from Lengenbach, Binntal (Switzerland). *Min. Mag.*

GRAESER, S., EDENHARTER, A. and BERLEPSCH, P. (1995): Jentschite (TlPbAs₂SbS₆): Description and structure refinement of a new mineral from the Lengenbach quarry, Binntal, Canton Valais, Switzerland. Abstract supplement No. 1 to *Terra Nova*, 7, 290.

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.

HOFMANN, B., GRAESER, S., IMHOF, T., SICHER, V. and STALDER, H.A. (1993): Mineralogie der Grube Lengenbach, Binntal, Wallis. *Jahrb. Naturhist. Mus. Bern*, 11, 3–90.

NOWACKI, W., EDENHARTER, A., ENGEL, P., GOSTOJIC, M. and NAGL, A. (1982): On the Chemistry of Some Thallium Sulphides and Sulphosalts. In: AMSTUTZ, G.C. et al. (eds): *Ore Genesis – The State of the Art*. Springer-Verlag Berlin, Heidelberg, New York, 689–704.

Manuscript received April 19, 1995; major revision accepted May 15, 1995.