

Edenharterite (TlPbAs₃S₆) : a new mineral from Lengenbach, Binntal (Switzerland)

STEFAN GRAESER^{1,2} and HANS SCHWANDER²

¹ Natural History Museum, Dept. of Mineralogy, CH-4001 Basel, Switzerland

² Mineralogical Institute, University of Basel, CH-4056 Basel, Switzerland

Abstract : The phase TlPbAs₃S₆, synthesized in the course of hydrothermal experiments by A. Edenharter (1982), was found as a natural mineral at the well known occurrence of Pb-Tl-Cu-Ag-As-sulphosalt minerals in Lengenbach, Binntal (Switzerland). It occurs in small cavities in Triassic dolomite, together with a large number of other As sulphosalt minerals such as hutchinsonite, hatchite, wallisite, lorandite, and abundant realgar and orpiment. Edenharterite forms euhedral lathlike crystals (less than 1 mm in size), mostly intergrown to aggregates up to 2 - 3 mm. Electron microprobe analysis yielded (mean of 3 analyses) : Tl 25.51, Pb 25.08, Sn 0.06, As 27.09, S 23.17, total 100.91 wt %. The simplified formula is close to TlPbAs₃S₆. The mineral is bright brown-black. In thin fragments it is red translucent and has a raspberry-red streak. Microhardness is 98 kg/mm² (10 g load), corresponding to a Mohs hardness of about 2 1/2 - 3, $D_{\text{calc}} = 5.09 \text{ g/cm}^3$. Single crystal studies gave an orthorhombic cell with $a = 15.465(3)$, $b = 47.507(8)$, $c = 5.843(2) \text{ \AA}$, $V = 4292 \text{ \AA}^3$, space group $Fdd2$ and $Z = 16$. The strongest lines in the X-ray powder pattern are (d_{obs} , I_{obs} , hkl) : 3.801 (100)(191) ; 3.389 (22)(1.11.1) ; 2.901 (19)(3.11.1) ; 2.767 (43)(4.12.0) ; 2.732 (41)(511) ; 2.656 (24)(3.13.1) ; 1.7905 (15)(8.10.0). The name is for Dr. Andreas EDENHARTER (University of Göttingen) who first synthesized the phase TlPbAs₃S₆ while conducting hydrothermal experiments with Tl-sulphosalts.

Key-words : edenharterite, Tl-Pb-As-sulphosalts, microprobe analyses, single crystal study, formation of Tl-As-sulphosalts at Lengenbach, Binntal (Switzerland).

1. Introduction

Since 1958, a syndicate of Swiss museums and university institutions (« Arbeitsgemeinschaft Lengenbach », AGL) has been working at the famous sulphosalt deposit of Lengenbach, Binntal, with the main goal to extract the special arsenic sulphosalts from the dolomitic rock for scientific study. This activity had become more and more problematic in the early eighties, partly for technical reasons - working in a quarry with steep walls up to 15 meters turned out to be very dangerous - partly, also, because of a change in the mineralisation with increasing depth. The arsenic content of the minerals gradually decreased, and thus the more interesting minerals were mainly absent from this level. These factors

even led to the idea of either shutting down mineral exploitation completely, or of continuing work at a new site.

In 1985, however, a huge loose block from the highest point in the steep dolomitic wall accidentally fell into the old quarry. When this boulder was split, it turned out to be full of most interesting sulphosalt minerals. The scientific study of these minerals led to the discovery of at least three new thallium-arsenic sulphosalts : edenharterite (this paper), stalderite and ernigglite (Graeser *et al.*, in prep.). The discovery of these new minerals led to the decision by the syndicate to continue work at this upper level, but in an easterly direction from the old quarry. The results from the first few years of exploration at this new site proved that this decision was correct.

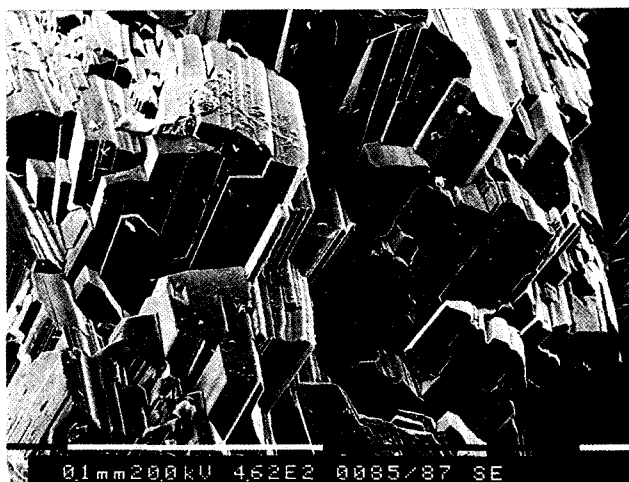


Fig 1. Edenharterite, Lengenbach. The SEM picture shows clearly the elongated lathlike crystals in subparallel intergrowth.

When the single crystal study of the present mineral had been completed, we realised that it was identical to the phase $\text{TlPbAs}_3\text{S}_6$ prepared by A. Edenharter in the course of experimental studies in the system $\text{Tl}_2\text{S}-\text{PbS}-\text{As}_2\text{S}_3$ (Nowacki & Edenharter, 1982). Consequently, the new mineral is named edenharterite in recognition of Dr. Andreas Edenharter's valuable contribution to sulphosalt research.

The mineral and its name were approved by the Commission on New Minerals and Mineral Names, I.M.A., prior to publication.

2. Physical and optical properties

Edenharterite occurs in multiple parallel intergrowth of crystals slightly elongated along the c-axis (Fig. 1). Single crystals are about 0.1 - 0.2 mm and the aggregates up to 2 mm in diameter. The colour of the mineral is brown-black to black, depending on crystal size. Thin fragments are always translucent and dark red in colour. If broken or scratched, the mineral yields a very characteristic raspberry-red powder. It was mainly this remarkable red streak that led us to the conviction that it was a mineral species not yet known from Lengenbach. Edenharterite is quite soft, with Mohs' hardness about 2 1/2 - 3 and thus it is very easily damaged; a cleavage along the length (c-) axis parallel to {100} is evident. The fracture is uneven.

The mineral was studied in polished section with the ore microscope. The colour in reflected light is grayish-white with a particular blue tint. Between crossed polarizers, it displays characteristic internal reflections of a bright red colour. The reflectivity is moderate and very close to other Tl-sulphosalts from Lengenbach, such as hutchinsonite, imhofite, and hatchite. Microhardness, however, is clearly lower for edenharterite than for hutchinsonite, the closest relative of the mineral. Physical and optical data are presented in Table 1.

3. Chemical composition

When it became obvious from the X-ray diffraction data that the mineral was not identical to any other known mineral species, we used SEM techniques (Cambridge Stereoscan Mark 2A, equipped with EDS system) in order to characterize the crystal morphology and, in particular, to obtain preliminary data on the chemical composition. The EDS analysis clearly indicated the elements: Tl, Pb, As, S. From these data, together with the results of the single-crystal X-ray study, it became certain that the mineral was a new species in the sulphosalt family.

Subsequently, a quantitative electron microprobe analysis was carried out on an ARL instrument (SEM-Q, with EDS-system TN 2000, ZAF program). The following materials were used as

Table 1. Physical and optical properties of edenharterite and related minerals from Lengenbach.

	Edenharterite	Hutchinsonite ¹	Imhofite ²
Shape:	isometric	elongated	thin lamellae
Colour:	brown to black	dark red to black	dark red
Streak:	raspberry red	orange	purple
Density:	5.09 g/cm ³ (calc)	4.6 g/cm ³	4.39 g/cm ³
Ore microscope: LEITZ MPV-stat			
Reflectivity: (measured in air) WTiC standard			
480 nm	28.5-30.5		
546	28.5-31.5	30.0-31.0	28.0-31.0
589	27.0-28.5		
656	27.0-29.0		
Microhardness:	95-101 (10g)	170-171 (100g)	71-77 (3g)
Anisotropy:	very weak	distinct	strong

¹ Graeser (1965) - ² Burri et al. (1965)

standards : synthetic TlAsS₂ (Tl, As, S), galena (Pb), metallic Pb, and metallic Sn. The results of three analyses, obtained from individual grains, are shown in Table 2. The calculation of a mineral formula from the analyses unequivocally led to the expression TlPbAs₃S₆ in full agreement with Edenharter's synthetic phase (Nowacki & Edenharter, 1982).

4. X-ray diffraction study, structure determination

The first indication that we were dealing with an unknown mineral phase was obtained from the X-ray powder diffraction data. The mineral provided a characteristic diagram with numerous lines, fully identical for several different fragments. The powder data are compiled and compared with the data obtained from Edenharter's synthetic phase in Table 3. The identity of the two substances, however, was recognised only after the single crystal study.

Single crystal work was carried out by means of Weissenberg and Precession techniques on several individual mineral fragments. On the basis of the following systematic extinctions $hkl : h+k, k+l, h+l \neq 2n$; $0kl : k+l \neq 4n, k,l \neq 2n$; $h0l : h+l \neq 4n, h,l \neq 2n$; $hk0 : h,k \neq 2n$, the uncommon space group symmetry *Fdd2* was derived. Unit-cell dimensions of edenharterite were refined from the Guinier-Hägg powder data. The results of the single crystal study of the min-

eral edenharterite and its synthetic equivalent are presented in Table 4.

A crystal structure determination was carried out on Edenharter's synthetic TlPbAs₃S₆ compound by Balic-Zunic & Engel (1983). According to these authors, the Tl atom is coordinated by seven S atoms. The coordination polyhedra form [TlS₇] double chains parallel to the c-axis. The Pb atom is also coordinated by seven S atoms, forming coordination polyhedra of [PbS₇] layers parallel to the {010} crystal face. The As atoms are bonded to three S atoms in the form of a trigonal pyramid with the As atom at the apex.

Table 2. Electron microprobe analyses of edenharterite from Lengenbach, Binntal.

	A	B	C	D	E	
Tl	24.06	25.47	27.01	25.51	24.66	wt%
Pb	25.48	24.70	25.07	25.08	25.01	
Sn	0.06	0.07	0.06	-.-	-.-	
As	26.8	27.92	26.54	27.09	27.12	
S	23.10	23.35	23.06	23.17	23.21	
Total	99.50	101.50	101.75	100.91	100.00	wt%

Structural formula (based on 11 atoms)						
Tl	0.98	1.02	1.10	1.03	1.00	
Pb	1.03	0.98	1.00	1.00	1.00	
As	2.98	3.05	2.94	2.99	3.00	
S	6.01	5.96	5.96	5.98	6.00	

A,B,C analyses of individual crystals						
D mean of 3 analyses						
E theoretical composition for TlPbAs ₃ S ₆						

Table 3. Powder data for edenharterite and synthetic TIPbAs₃S₆.

EDENHARTERITE ¹⁾						synth. TIPbAs ₃ S ₆ ²⁾		
h	k	l	d _(obs)	d _(calc)	I/I ₁	d _(obs)	d _(calc)	I/I ₁
0	4	0	—	—	—	11.8	11.9	30
2	2	0	7.35	7.35	12	7.4	7.4	30
0	8	0	5.934	5.938	3	—	5.95	—
1	1	1	5.425	5.429	10	5.51	5.44	40
1	3	1	5.163	5.166	10	—	5.17	—
2	8	0	4.712	4.710	10	4.74	4.74	40
0	12	0	3.959	3.959	13	3.97	3.97	40
3	1	1	3.855	3.853	13	—	3.86	—
1	9	1	3.801	3.797	100	3.82	3.83	100
3	3	1	3.755	3.755	15	—	3.76	—
2	12	0	—	—	—	—	—	—
1	11	1	3.389	3.389	22	3.534	3.530	30
4	8	0	3.239	3.240	10	3.392	3.394	40
3	9	1	3.121	3.119	15	3.253	3.247	30
4	10	0	2.998	2.999	7	3.126	3.124	40
3	11	1	2.901	2.880	19	3.003	3.005	30
4	12	0	2.767	2.766	43	2.886	2.885	70
5	1	1	2.732	2.729	41	2.774	2.772	80
3	13	1	2.656	2.656	24	2.656	2.650	70
6	7	1	2.536	2.536	7	2.538	2.660	60
0	20	0	2.377	2.375	13	2.538	2.540	20
5	11	1	2.308	2.309	8	2.373	2.372	30
2	12	2	2.249	2.249	11	2.316	2.314	20
5	13	1	2.189	2.189	7	2.254	2.252	20
7	1	1	2.065	2.064	12	—	2.193	—
0	24	0	1.9788	1.9794	8	2.066	2.069	20
7	9	1	1.9239	1.9242	9	—	1.9826	—
4	22	0	1.8848	1.8852	6	1.9245	1.9245	10
7	11	1	1.8619	1.8640	5	—	1.8886	—
8	10	0	1.7915	1.7905	15	—	1.8681	—
7	15	1	1.7224	1.7306	6	1.7945	1.7946	30
3	25	1	1.7079	1.7053	5	—	—	—
			1.6478	—	5	—	—	—
			1.6022	—	5	—	—	—
			1.4396	—	5	—	—	—

¹⁾Guinier-Hagg-camera, CuK_{α1}-radiation, intensities determined densitometrically

²⁾Debye-Scherrer-camera, 90mm, FeK_α-radiation, intensities determined visually.

The pyramids are connected to form [As₆S₁₂] groups which contain a two membered ring.

5. Occurrence, mode of formation

The new mineral occurs as aggregates (up to 2x1x1 mm) of euhedral individual crystals in

Table 4. Crystallographic data of edenharterite and synthetic TIPbAs₃S₆.

	Edenharterite	synth. TIPbAs ₃ S ₆
Space group :	Fdd2	Fdd2
Unit-cell dimensions:		
a (Å)	15.465 (3) ¹	15.476 (7) ²
b (Å)	47.507 (8)	47.453 (2)
c (Å)	5.843 (2)	5.847 (2)
V (Å ³)	4292	4294
Cell content:	16	16

¹refined from Guinier-Hagg powder diagram

²CAD4 diffractometer (Balic-Zunic & Engel, 1983)

small, rounded cavities in the characteristic white Lengenbach dolomite of Triassic age. The formation of these cavities is undoubtedly a product of the circulation of hydrothermal solutions by which Tl and As were introduced into the dolomite. The reaction between Tl-Cu-As-S-solutions and galena (of synsedimentary origin) in the dolomite led to the formation of the various sulphosalt minerals (Graeser 1965, 1975). Edenharterite is always closely associated with As-rich minerals (realgar, orpiment) and, in particular, with various other Tl-sulphosalts such as hutchinsonite, hatchite, wallisite, lorandite, and a Tl-bearing sartorite. Its occurrence is strictly confined to the higher level of the new location of the quarry. In contrast to the apparently very rare new Tl-sulphosalts stalderte and ernigglite (Graeser *et al.*, in prep.), edenharterite turned out to be a rather common mineral in this assemblage. More than 100 unequivocally determined samples have been found so far.

From Edenharter's hydrothermal experiments,

in which he studied the systems $Tl_2S - As_2S_3$ and $Tl-Pb-As-S$, it was possible to derive the p-T-conditions for the formation of Tl-sulphosalts in Lengenbach (Edenharter & Peters, 1979 ; Nowacki & Edenharter, 1982). During Edenharter's investigation he synthesized the phases $TlPbAs_5S_9$ (hutchinsonite) and $TlPbAs_3S_6$ (at that time not yet found in nature) at pressures of 1500 bars and in a temperature gradient of $340^\circ - 225^\circ C$. These results are in full agreement with the mineralogical evidence that Lengenbach sulphosalt minerals formed by hydrothermal processes, and that the Tl-sulphosalts, in particular, represent the latest phases in the sulphosalt mineralisation in Lengenbach (Graeser, 1965, 1975).

6. Geochemical considerations

Some major geochemical differences exist between the old location of the quarry (which has been exploited for its unusual sulphosalts for more than 150 years) and the new working level (in operation since 1988). It is strange but true that in the whole Lengenbach locality (appr. 50 x 30 m, and about 20 m deep) geochemical characteristics change rapidly within a few meters, especially with respect to the elements arsenic and thallium. Besides the technical problems of working in a quarry with steep walls up to 20 meters high, the main reason for abandoning the old workings after 1985/86 was the fact that, with increasing depth, the contents of As and Tl in the minerals rapidly decreased, a result that could have been predicted from previous core drilling (Graeser, 1968).

The new working level (in a NE continuation of the dolomite schists and about 25 meters above the bottom of the old quarry, on the right-hand bank of the Lengenbach stream) is characterised by an unexpectedly high content of As and Tl in the sulphosalts. This fact leads to an extraordinarily high abundance of rare and unique Tl-sulphides. Within a few years, more specimens of the Tl-Pb-Ag-As-sulphosalt hatchite were collected here than in the period since its discovery in 1902. In several common Pb-As sulfides, Tl substitutes partly for Pb, thereby changing the normally black colour of the minerals into a dark red (e.g. sartorite, $PbAs_2S_4$, may contain more than 4 wt. % Tl). Besides these two elements, some « exotic » elements like Hg and Sn have been identified as the

main constituents in the two new minerals staldarite, $TlCu(Zn,Fe,Hg)_2As_2S_6$, and ernigliite, $Tl_2SnAs_2S_6$ (Graeser *et al.*, in prep.). It may be assumed that Hg and Sn occur exclusively at this higher level, and that they were absent in the old Lengenbach quarry where the Hg- and Sn-bearing horizon long ago had been eroded away by the Lengenbach stream. It is unlikely that these unusual minerals would have escaped the keen attention of the old mineralogists.

The differences between the mineralogy at the original, « historical » quarry and at the new operation may be summarised as follows :

At the old quarry, the sulphosalts occur as discrete, individual crystals. In any one hand specimen, all crystals tend to have similar chemical compositions ; for example, arsenic-bearing minerals, such as realgar, do not coexist with sulphides such as galena. Consequently, although visual identification of a given species may remain problematic, it is a simple matter to separate homogeneous material for identification by X-ray techniques.

At the new site, by contrast, several compositionally different minerals may be intimately and minutely intergrown. Intergrowths of realgar with lengenbachite (one of the sulphosalts with the lowest arsenic content) and with galena are quite common. Hence, without careful pre-preparation and examination it is difficult to obtain pure, single-phase material for X-ray identification.

A possible explanation for these differences, and for the small-scale variation in composition noted at the new operation, may be found in the relatively higher position of the latter, *i.e.*, faster cooling rates led to less complete separation of elements during crystallisation, and to the development of smaller and more intimately intergrown crystals because of faster crystal growth.

Acknowledgements : We are greatly obliged to R. Guggenheim and M. Düggelin (SEM laboratory, University of Basel) who provided SEM pictures and the preliminary qualitative analyses. The « Arbeitsgemeinschaft Lengenbach », the syndicate exploiting the Lengenbach minerals, put the material at our disposal. A. Edenharter (Göttingen) kindly provided us with his synthetic material for study. J.G. Saunders, Natural History Museum Basel, discussed and corrected the English version of the text. Two referees, A. Criddle (London) and Y. Moëlo (Orléans), provided valuable suggestions for improving the text.

References

- Balic-Zunic, T. & Engel, P. (1983) : Crystal structure of synthetic $PbTlAs_3S_6$. *Z. Krist.*, **165**, 261.
- Burri, G., Graeser, S., Marumo, F., Nowacki, W. (1965) : Imhofit, ein neues Thallium-Arsensulfosalz aus dem Lengenbach (Binntal, Kt.Wallis). *Chimia*, **19**, 499-500.
- Edenharter, A. & Peters, T. (1979) : Hydrothermalsynthese von Tl-haltigen Sulfosalzen. *Z. Krist.*, **150**, 169-180.
- Graeser, S. (1965) : Die Mineralfundstellen im Dolomit des Binnatales. *Schweiz. Mineralog. Petrogr. Mitt.*, **45/2**, 597-795.
- (1968) : Die Sulfosalz-Mineralien des Binntales - Geochemie und Genese. *In* : Stalder, H.A. *et al.* : Die Mineralfundstelle Lengenbach im Binntal. *Jahrb. Nathist. Mus. Bern.*, 1966-1968.
- (1975) : Die Mineralfundstelle Lengenbach, Binntal. *Schweiz. Mineralog. Petrogr. Mitt.*, **55/1**, 143-149.
- Nowacki, W. & Edenharter, A. (1982) : The crystal chemistry of some thallium sulphides and sulphosalts. *In* : Ore Genesis - The State of the Art ; edited by Amstutz, G.C. *et al.*, Springer Verlag Berlin, Heidelberg, New York, 1982.

Received 19 July 1991

Accepted 3 February 1992