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Quadratite $Ag(Cd,Pb)(As,Sb)S_3$ – a new sulfide mineral from Lengenbach, Binntal (Switzerland)

by *Stefan Graeser*[1,2], *Wim Lustenhouwer*[3] and *Peter Berlepsch*[2]

Abstract

With the mineral quadratite another new sulfide phase has been identified in the famous Lengenbach locality (Binntal, Switzerland). Like the numerous other, mainly As-sulfide minerals at this locality, quadratite occurs in small vugs in a white dolomitic rock of presumably Triassic age. Different from the new minerals discovered within the last few years, which all belong to the very special group of thallium sulfosalts and therefore always occur in close association with As-rich phases, quadratite exclusively occurs together with minerals poor in arsenic. Therefore it is closely associated with minerals like jordanite and galena, whereas realgar is clearly absent. In general, quadratite forms crystals of characteristic quadratic, sometimes octogonal shape; always tabular along the basis (001). The size is normally about 0.1 mm across, crystals with a diameter of more than 1 mm are extremely rare. With few exceptions the mineral is untwinned, one or two samples show an oriented intergrowth which may be interpreted as contact twins along (016). Small crystals are brown-red translucent, larger specimens are opaque with grey metallic luster, streak is reddish-brown. Single-crystal X-ray diffraction yielded a tetragonal cell with $a = 5.499$ (5) and $c = 33.91$ (4) Å, $V = 1025$ (2) Å^3, space group *I4/amd*, $Z = 8$. The strongest lines in the powder diagram are (d_{obs} in Å, I_{obs}, hkl): 2.77 (100) (200), 1.960 (80) (2.0.12), 1.679 (70) (2.0.16), 1.598 (70) (2.2.12;3.0.11), 1.274 (60) (4.0.10), 3.19 (50) (116). Chemical composition (electron microprobe, mean of 6 analyses, wt%) is: Ag 26.30, Cu 0.05, Tl 0.49, Cd 21.42, Pb 10.17, As 18.06, Sb 0.27, S 23.61, total 100.37 wt%. The simplified formula is close to $AgCdAsS_3$. The calculated density $D_{calc} = 5.31$ g/cm^3. From the microhardness VHN (load 10 g) of 57–72 kg/mm^2 a Mohs hardness of ≤ 3 may be derived. Quadratite has a perfect cleavage along {001} and distinct along {110}.

The name is derived from the conspicous quadratic shape of the mineral, unique among Lengenbach sulfosalts, so far.

Keywords: quadratite, new Ag–Cd–As-sulfide mineral, single-crystal data, microprobe analyses, Lengenbach, Switzerland.

1. Introduction

The Lengenbach quarry in Binntal (Ct. Valais, Switzerland) is well known for its very uncommon sulfosalt minerals, mainly Pb–Cu–Ag–Tl–(As,Sb)-sulfides occurring in small cavities in the white dolomitic rock. With exception of some periods during the two world wars, the sulfosalt mineralisation has been mined for minerals almost professionally since more than 150 years. It was purely the scientific interest to study these minerals that was responsable for their exploitation. Starting with 1958, a Swiss syndicate consisting of several scientific institutions (Museums, Mineralogical Institutes but also private people) has been active in Lengenbach and organized the mineral extraction until 1998. From 1958 to 1986, the works were carried out in the old classical quarry, which was abandoned in 1987 due to lack of attractive material. Since the new site was opened in 1987, a remarkable number of new mineral species has been discovered, which mainly belong to the special family of thallium sulfosalts (see e.g. GRAESER and EDENHARTER, 1997).

In contrast to the mostly longprismatic Tl–As-sulfosalts, quadratite, with Cd, Ag, As, besides sul-

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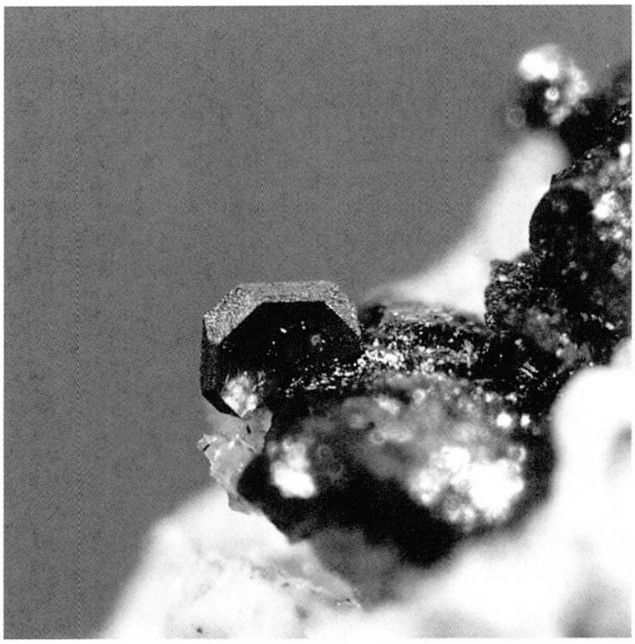

Fig. 1 Quadratite crystal (0.45 mm Ø), grown on jordanite. Sample M. Siegel, photograph by W. Gabriel.

fur as main constituents, represents a completely new type of sulfide minerals in Lengenbach, a fact which is documented by the special morphology of the mineral, too. First specimens of the mineral were discovered by the mineral collectors Monika and Walter Gabriel (Basel) on the dump of the quarry in 1989. These crystals reached about 0.1 mm in diameter, a size that was suitable to establish a new species but did not allow to derive all the data necessary for the submission of a proposal to the Commission on New Minerals and Mineral Names, I.M.A. Additional material was found in 1993, with crystals of more than 1 mm (e.g. Markus Ecker, Spiesen, Germany). These crystals enabled derivation of a complete set of data for the new mineral. Subsequently, the proposal for the new mineral was submitted to the I.M.A. commission, which accepted name and description of the new species (I.M.A. No. 94-038). Type material is preserved at the Natural History Museum Basel, and at the Mineralogical Institute, University of Basel.

2. Description

2.1. PHYSICAL AND OPTICAL PROPERTIES

It was the very uncommon morphology – thin tabular crystals of unmistakable quadratic shape, unlike any other Lengenbach mineral – that drew the attention to the unknown mineral. The thin platy crystals occur always as octogonal tablets, the smaller edge clearly corresponding to (hhl)-faces (Fig. 1). One of the small crystals could be measured on an optical goniometer from which the following faces were calculated: a large pinacoid (001), two bipyramids of second order (103) and (104), which are always dominant over the two additional small bipyramids of first order (111) and (116). One unique sample (found by the German collector Ralph Cannon) displayed a very conspicous twinning law. Though the twinned crystals could not be measured goniometrically, an interpretation as penetration twins along (016) is obvious. Viewed with the naked eye, the two crystals cross at (nearly) 90°, therefore the angle ρ for the twinning-plane must be about 45°, and

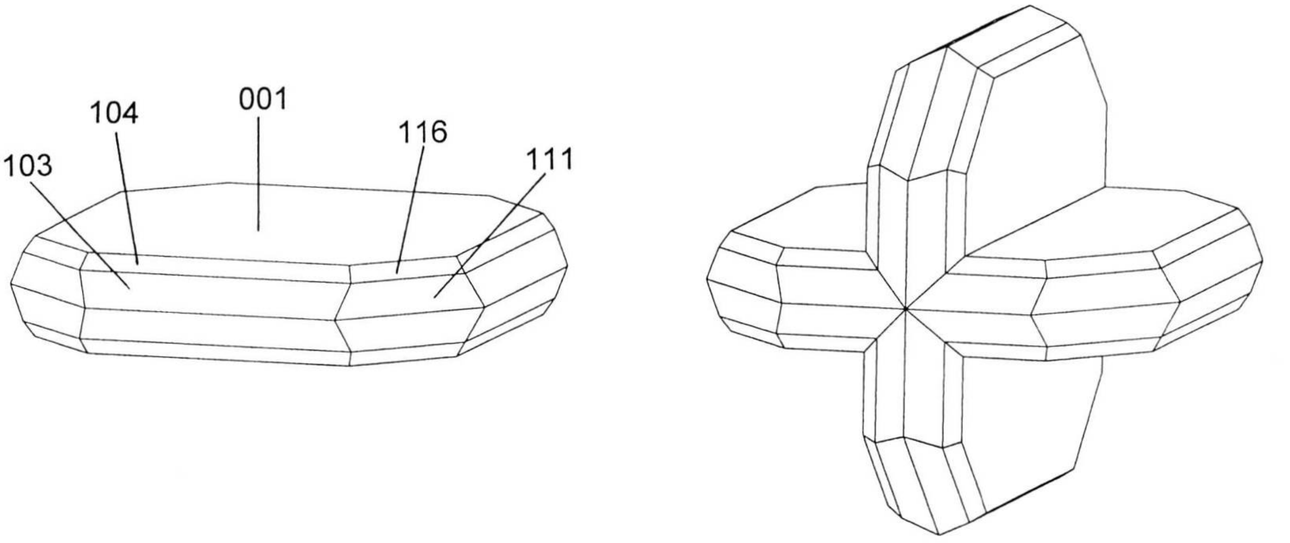

Fig. 2 Shape crystal drawings (Dowty, 1997) based on optical goniometry. Left: single crystal; right: penetration twin along (016).

Tab. 1 Physical and optical properties of quadratite from Lengenbach.

Habit:	extremely thin quadratic (octogonal) laminae, often translucent		
Forms:	pinacoid {001}, always strongly dominant first order bipyramids {103} and {104}, mostly small second order bipyramids {111} and {116}, dominant		
Twinning:	penetration along (016), see figure 2		
Colour:	in thin laminae reddish translucent, otherwise grey-metallic, opaque		
Streak:	reddish-brown		
Cleavage:	{001} perfect (micaceous); {110} distinct		
Tenacity:	thin laminae are ductile to flexible		
Hardness:	Mohs: ≤ 3 — according to microindentation $VHN_{10g} = 63$ (52–72)		
Density:	5.31 g/cm^3 (calculated)		
Ore microscopic data (MPV-STAT by WILD-LEITZ)			
Colour:	greyish-white with bluish tint		
Internal reflexions:	dark red reflexions along cleavage cracks (oil immersion)		
Pleochroism:	not observed (polished section ≈ parallel to {001})		
Bireflectance:	not observed (polished section ≈ parallel to {001})		
Reflectance values:	WTiC standard		
	Wavelength	Air	Oil
	470 nm	30.5–32.3	12.5–14.0
	543 nm	29.6–30.8	12.2–13.3
	587 nm	28.7–29.7	12.0–12.9
	657 nm	26.3–28.0	11.3-12.3

since the angle $(001{}^\wedge016) = 45.6°$, the twinning-plane undoubtedly is (016), see figure 2. The extremely thin laminae appear clearly translucent and under a transmission polarizing microscope produce an indistinct nearly uniaxial figure whose character is not interpretable. With increasing thickness the crystals turn to an opaque, metallic character. In polished section under the metal microscope, quadratite appears greyish-white, with a slight bluish tint. Due to the perfect, micaceous cleavage along the basis (001), polished sections could only be prepared parallel to this face. Therefore, they provided few information on anisotropy, bireflectance, and pleochroism. A full set of physical and optical properties is compiled in table 1.

2.2. X-RAY DIFFRACTION STUDY

The special ductile nature of the mineral provided some problems for the X-ray study. Therefore, powder data were derived mainly from diffraction patterns carried out by the Gandolfi technique (on single crystals). The patterns established with this device turned ot to be of superior quality compared to those obtained by common Debye-Scherrer-technique. The single-crystal investigation (Weissenberg and Precession methods) too, was impeded by the mineral's special properties, and was fully successful only with the better material found in 1993. The results of this study suggest some relationship to the mineral cernyite, though the mineral formula and space group symmetry are quite different compared to quadratite. We hope that in future we will be able to separate adequate material for a complete structure determination which could solve this problem. The results of the X-ray diffraction study are given in table 2.

2.3. CHEMICAL COMPOSITION

First qualitative chemical data were obtained from EDS analyses on a SEM device (Cambridge Stereoscan Mark 2A, University of Basel), carried out with extremely fine laminae of about 0.1 mm in diameter. These analyses clearly pointed out that the mineral consisted of mainly Ag, Cd, As, and sulfur, a composition that was not known from a natural mineral, so far. Quantitative determinations, however, became feasible only with larger amounts of material discovered some years later. Chemical data are reported in table 3.

With the composition $Ag(Cd,Pb,Tl)(As,Sb)S_3$ for quadratite, the mineral obviously represents the first example of a Ag–Cd–As-sulfide in mineral systematics, altogether. Without a complete structure determination to date it is not possible to decide whether it belongs to the sulfosalt group s.str. (with AsS_3 pyramids) or to complex sulfides

Tab. 2 X-ray diffraction data of quadratite from Lengenbach.

$I_{visuell}$	d_{obs} (in Å)[1]	d_{calc}	h k l
30	4.23	4.239	0 0 8
50	3.19	3.203	1 1 6
100	2.77	2.750	2 0 0
< 10	2.39	2.403	2 1 3
10	2.33	2.312	2 1 5
10	2.145	2.136 2.119	2 0 10 0 0 16
10	2.090	2.091	1 0 15
10	2.040	2.055	1 1 14
80	1.960	1.970	2 0 12
10	1.878	1.895 1.875	2 2 4 1 0 17
10	1.827	1.830 1.817	3 0 1 2 0 14
30	1.783	1.789 1.770	2 1 13 3 0 5
30	1.759	1.767	2 2 8
70	1.679	1.679	2 0 16
40	1.664	1.664	2 1 15
70	1.598	1.602 1.576	2 2 12 3 0 11
20	1.536	1.544 1.524	3 1 10 3 2 1
30	1.435	1.433 1.433 1.424	1 1 22 2 2 16 1 0 23
10	1.380	1.375	4 0 0
30	1.299	1.309 1.308 1.292	4 1 5 4 0 8 3 3 2
60	1.274	1.274	4 0 10
30	1.245	1.257 1.237	2 0 24 1 1 26
10	1.237	1.236 1.230	4 0 12 4 2 0
20	1.224	1.226 1.224	4 2 2 1 0 27
10	1.210	1.211 1.202	3 3 10 4 2 6
10	1.177	1.181 1.178	4 2 8 2 0 26
20	1.156	1.156	4 2 10
30	1.136		
20	1.131		
10	1.0982		
10	1.0738		
30	1.0676		
20	1.0459		
20	1.0370		
20	1.0198		
30	0.9894		
40	0.9816		

[1] Gandolfi camera 114.6 mm Ø, FeK_{α} radiation, intensities visually estimated

Crystal system: tetragonal Space group: I4/amd

Lattice parameters (cell constants refined from Gandolfi powder data):

a = 5.499 (5) Å V = 1025 (2) $Å^3$
c = 33.91 (4) Å Z = 8
c/a = 6.165 (from lattice parameters)
= 6.19 (from optical goniometry)

(with AsS_4 tetrahedrons), though from the general aspect of the mineral an affiliation to the complex sulfides appears more probable. Another problem arises from the question if Cd may be substituted partly by Pb, as postulated by the mineral formula. There are few minerals known in nature containing Cd as a major element (NICKEL and NICHOLS, 1997), however, among about 10 well defined species, one of them seems to represent exactly the same uncommon substitution: for the sulfide mineral shadlunite $(Fe,Cu)_8(Pb,Cd)S_8$ a similar substutition is postulated by the authors (EVSTIGNEEVA et al., 1973).

Analytical work was carried out by means of an electron probe on one relatively large quadratite crystal (about 1 mm^2). The chemical data are reported in table 3. A BSE-image of quadratite (Fig. 3) proofs a remarkably homogeneous

Tab. 3 Chemical composition of quadratite.

	I	II	III
Ag	26.30	26.05 – 26.88	26.30
Cu	0.05	0.04 – 0.06	
Tl	0.49	0.46 – 0.57	
Cd	21.42	21.08 – 22.06	21.91
Pb	10.17	9.31 – 10.65	10.10
As	18.06	17.74 – 18.37	18.25
Sb	0.27	0.23 – 0.32	
S	23.61	23.29 – 24.11	23.44
Total	100.37	99.76 – 101.08	100.00
Structural formula (based on 24 sulfur atoms)			
Ag	7.95		8.0
Cu	0.03	$\Sigma = 7.98$	–.–
Cd	6.27		6.0
Pb	1.61		2.0
Tl	0.08	$\Sigma = 7.96$	–.–
As	7.92		8.0
Sb	0.07	$\Sigma = 7.99$	–.–
S	24		24

I mean of six analyses, leading to the empirical formula $(Ag_{7.95}Cu_{0.03})_{\Sigma=7.98}(Cd_{6.27}Pb_{1.61}Tl_{0.08})_{\Sigma=7.96}(As_{7.92}Sb_{0.07})_{\Sigma=7.99}S_{24}$

II range of data

III theoretical composition for the simplified formula $8 \times Ag(Cd_{0.8}Pb_{0.2})AsS_3$ (based on a zell content Z = 8)

Microprobe: JEOL JXA–8800M (20 kV, 5×10^{-8} A), JEOL on-line ZAF correction using Berger & Seltzer's J/Z plus Philibert's and Duncumb & Reed's absorption correction

Standards: Ag (pure), Cu (pure), $TlSbS_2$ (Tl, Sb), CdS (Cd, S), PbS (Pb), InAs (As)

chemical composition of the mineral, though it is very closely intergrown with other sulfide mineral phases (jordanite, pyrite).

3. Occurrence, associated minerals

The mineral quadratite occurs in cavities formed by hydrothermal activity in the white Lengenbach dolomite. Different from the various new Tl-sulfosalts discovered within the past few years (see GRAESER and EDENHARTER, 1997, e.g.), which are strictly associated with minerals of extremely high contents in arsenic (minerals like realgar, orpiment, etc.), quadratite exclusively occurs together with phases poorest in arsenic, mainly in association with galena, jordanite ($Pb_{14}(As,Sb)_6S_{23}$), pyrite, and, occasionally, sphalerite, lengenbachite and few hatchite. In most cases, quadratite is closely intergrown with jordanite, and even contains inclusions of this mineral (see Fig. 3). Quadratite is undoubtedly the product of a late hydrothermal activity by which galena, sphalerite, and jordanite were leached and partly dissolved. Silver was leached from galena (Ag-contents between 1'000-5'000 ppm), cadmium from sphalerite (Cd-contents between 1'000-2'000 ppm), arsenic and thallium presumably from jordanite and pyrite (thallium). The concentrations of minor elements in galena and sphalerite are taken from GRAESER (1969, 1971). The characteristically corroded crystals of galena and sphalerite proof the leaching process by hydrothermal fluids.

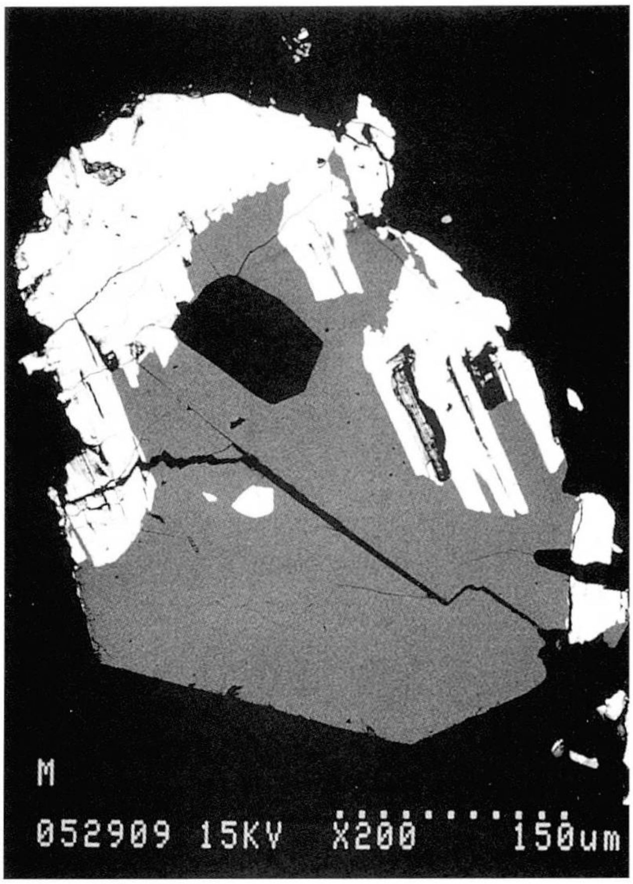

Fig. 3 BSE-image of quadratite (dark grey), jordanite (light grey), and pyrite (black idiomorphic inclusion). Diameter of sample about 0.3 mm.

Within the first years after its discovery, quadratite remained an extremely rare species in Lengenbach, presumably as a consequence of its very small dimensions. In 1997, however, more than 30 quadratite samples existed in the official exploitation list of the "Arbeitsgemeinschaft Lengenbach". Obviously the eyes of the collectors became used to the mineral and, in particular, from the knowledge of the mineral's special occurrence, potential quadratite-bearing samples were easily discernible.

Acknowledgements

Monika and Walter Gabriel, the first discoverers of the unknown mineral kindly put all their material at our disposal for investigation. Several other collectors (Markus Ecker, Ralph Cannon, e.a.) provided us with larger samples and thus enabled the accomplishment of the study that led to the proposal for the new mineral species. Mikosch Siegel put an excellent crystal at our disposal for photographic purpose, splendidly carried out by W. Gabriel. We are greatly obliged to R. Guggenheim, M. Düggelin, and D. Mathys (SEM laboratory, University of Basel), who contributed the first chemical data of the mineral. Martin Kunz (ETH Zürich) provided valuable recommendations for the improvement of the text.

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