Mineralogical Magazine, December 2009, Vol. 73(6), pp. 1027–1032

Dalnegroite, $Tl_{5-x}Pb_{2x}(As,Sb)_{21-x}S_{34}$, a new thallium sulphosalt from Lengenbach quarry, Binntal, Switzerland

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[*Received 16 October 2009; Accepted 14 December 2009*]

ABSTRACT

Dalnegroite, ideally $Tl_4Pb_2(As_{12}Sb_8)_{\Sigma 20}S_{34}$, is a new mineral from Lengenbach, Binntal, Switzerland. It occurs as anhedral to subhedral grains up to 200 μm across, closely associated with realgar, pyrite, Sb-rich seligmanite in a gangue of dolomite. Dalnegroite is opaque with a submetallic lustre and shows a brownish-red streak. It is brittle; the Vickers hardness (VHN_{25}) is 87 kg mm^{-2} (range: 69–101) (Mohs hardness ~3–3½). In reflected light, dalnegroite is highly bireflectant and weakly pleochroic, from white to a slightly greenish-grey. In cross-polarized light, it is highly anisotropic with bluish to green rotation tints and red internal reflections.

According to chemical and X-ray diffraction data, dalnegroite appears to be isotypic with chabournéite, $Tl_{5-x}Pb_{2x}(Sb,As)_{21-x}S_{34}$. It is triclinic, probable space group $P\bar{1}$, with a = 16.217(7) Å, b = 42.544(9) Å, c = 8.557(4) Å, α = 95.72(4)°, β = 90.25(4)°, γ = 96.78(4)°, V = 5832(4) Å^3, Z = 4.

The nine strongest powder-diffraction lines [d (Å) (I/I_0) (hkl)] are: 3.927 (100) ($\bar{2}$ 10 0); 3.775 (45) ($2\bar{2}2$); 3.685 (45) ($\bar{4}60$); 3.620 (50) (440); 3.124 (50) ($\bar{2}\bar{8}2$); 2.929 (60) ($4\bar{2}2$); 2.850 (70) ($\bar{4}42$); 2.579 (45) (0 $\overline{14}$ 2); 2.097 (60) (024). The mean of 11 electron microprobe analyses gave elemental concentrations as follows: Pb 10.09(1) wt.%, Tl 20.36(1), Sb 23.95(1), As 21.33(8), S 26.16(8), totalling 101.95 wt.%, corresponding to $Tl_{4.15}Pb_{2.03}(As_{11.86}Sb_{8.20})S_{34}$. The new mineral is named for Alberto Dal Negro, Professor in Mineralogy and Crystallography at the University of Padova since 1976.

Keywords: dalnegroite, new mineral, thallium, arsenic, sulphosalt, Lengenbach, Switzerland.

Introduction

Since the late eighteenth century the Lengenbach quarry, in Binntal, Switzerland, has been a unique source of a number of exclusive arsenic sulphosalts with additional elements including Tl, Pb, Ag and Cu. The quarry is the type locality for 27 new mineral species (Graeser *et al.*, 2008) and, to date, 15 Tl-sulphosalts have been discovered at this locality, of which twelve are new species including: imhofite $Tl_3As_{7.67}S_{13}$ (Burri *et al.*, 1965); edenharterite $TlPbAs_3S_6$ (Graeser and Schwander, 1992); jentschite $TlPbAs_2SbS_6$ (Graeser and Edenharter, 1997); sicherite $TlAg_2As_3S_6$ (Graeser *et al.*, 2001); and gabrielite $Tl_2AgCu_2As_3S_7$ (Graeser *et al.*, 2006).

Here, we report the description and characterization of a new Tl-sulphosalt from the Lengenbach quarry. Dalnegroite, ideally $Tl_{5-x}Pb_{2x}(As,Sb)_{21-x}S_{34}$ (x ~1) shows strong chemical and structural affinities with the mineral chabournéite, $Tl_4Pb_2(Sb,As)_{20}S_{34}$ (Johan *et al.*, 1981), and of which it is the As-dominant analogue.

The name of the new mineral honors Alberto Dal Negro (b. 1941), Professor of Mineralogy and Crystallography at the University of Padova since 1976, for his contribution to the discovery and crystal-structure determination of several new mineral species. The new mineral and its name have been approved by the Commission of New

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DOI: 10.1180/minmag.2009.073.6.1027

Minerals, Nomenclature and Classification, I.M.A. (IMA 2009-058). The holotype is deposited in the collections of the Museum of Mineralogy of the Department of Geosciences at the University of Padova under the catalogue number MMP M7620.

Occurrence

The Lengenbach Pb-Zn-As-Tl-Ba mineralization occurs in Triassic dolomitic rocks hosted in Penninic nappes which reached lower amphibolites facies during Alpine metamorphism. Sulphide melts, rich in As, Pb and Tl, coexisting with hydrothermal fluids, line cavities with a number of As-Ag-Pb-Tl sulphosalt/sulphide assemblages. Geological and metallogenic data concerning the deposit are summarized by Hofmann and Knill (1996) and Knill (1996).

The sample containing dalnegroite was provided by Luca Debattisti, an amateur collector who collected the sample at the Lengebach quarry in the summer of 2006. Dalnegroite, along with abundant realgar and pyrite, is hosted in centimetre-scale irregular cavities in the marble, where it forms anhedral to subhedral crystals (200–300 μm long) dark grey in colour, or occurs as tiny parallel aggregates (Fig. 1). It shows no obvious twinning, inclusions or intergrowths with other minerals. The mineral assemblage also includes Sb-rich hutchinsonite, jordanite, Sb-rich seligmanite and sinnerite.

Physical properties

Dalnegroite is opaque with a submetallic lustre and possesses a brownish-red streak. It is brittle with an uneven fracture and no cleavage. Unfortunately, the density could not be measured because of the small grain-size; the calculated density is 4.82 g cm^{-3} (on the basis of the empirical formula based on 34 S atoms). Microindentation measurements carried out with a VHN load of 25 g gave a mean value of 87 kg mm^{-2} (range 69–101), corresponding to a Mohs hardness of 3–3½.

In plane-polarized reflected light, dalnegroite is highly bireflectant and weakly pleochroic from white to a slightly greenish-grey. In cross-polarized light, the mineral is highly anisotropic with bluish to green rotation tints and red internal reflections. Reflectance measurements were made in air with a MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. Filament temperature was approximately 3350 K. Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.1 mm. Reflectance percentages (R_{min} and R_{max}) for dalnegroite for the four standard COM wavelengths are: 45.6, 46.1 (471.1 nm); 46.1, 46.6 (548.3 nm); 46.3, 47.0 (586.6 nm); 46.4, 47.1 (652.3 nm) respectively. Figure 2 shows the reflectance percentages obtained for dalnegroite

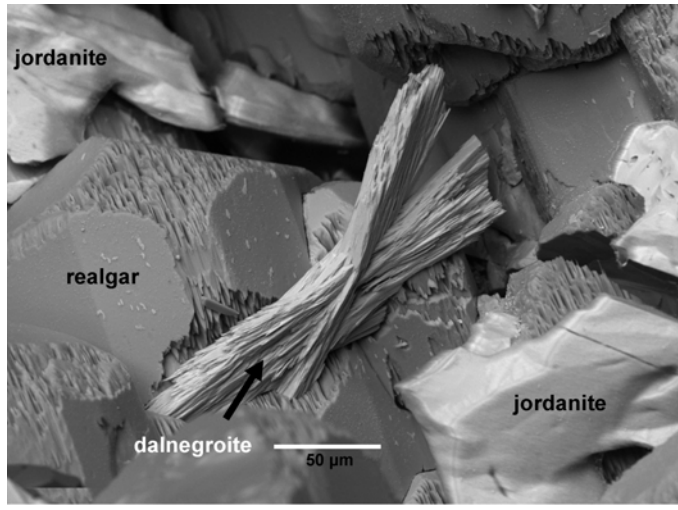

FIG. 1. BSE image of dalnegroite associated with jordanite and corroded crystals of realgar. Scale bar is indicated.

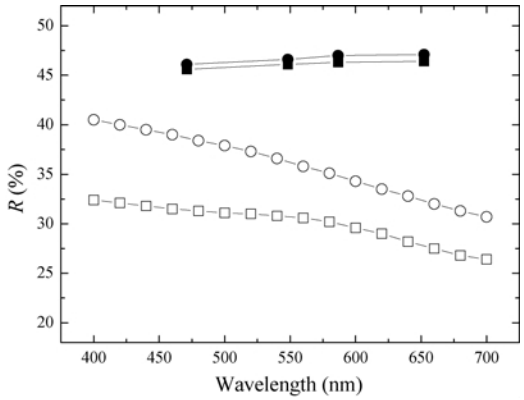

FIG. 2. Reflectivity curves for dalnegroite in air. Open symbols refer to chabournéite, $Tl_{5-x}Pb_{2x}(Sb,As)_{21-x}S_{34}$ (Johan *et al.*, 1981), filled symbols refer to dalnegroite (this study). Circles and squares refer to R_{max} and R_{min} values respectively.

and those measured by Johan *et al.* (1981) for chabournéite, $Tl_{5-x}Pb_{2x}(Sb,As)_{21-x}S_{34}$, with which it is isotypic, as we discuss below.

Chemical data

A preliminary chemical analysis using a JEOL 5610 LV equipped with an EDS detector (Bayerisches Geoinstitut, Bayreuth, Germany) did not indicate the presence of any elements with Z >9 other than Tl, Pb, As, Sb and S. The chemical composition was then determined using wavelength dispersive analysis (WDS) by means of a JEOL JXA-8200 electron microprobe (accelerating potential 20 kV, probe current 20 nA, final beam diameter 2 μm, with counting times of 20 s on peaks and 10 s on backgrounds. Element standards used for WDS analysis were as follows: Pb metal (Pb-$M\alpha$ line); synthetic TlI and TlBr (Tl-$M\alpha$ line); Sb metal (Sb-$L\beta_1$ line); synthetic InAs (As-$L\alpha$ line); natural FeS_2 (S-$K\alpha$ line). Analytical data are given in Table 1. The crystal fragment was found to be quite homogeneous within analytical error (11 analyses on different spots). The concentration ranges (in wt.%) for the elements measured are: Pb 8.5–12.4; Tl 19.6–21.5; Sb 22.2–25.6; As 21.0–21.8; S 26.0–26.4. The empirical formula, based on a total of 34 sulphur atoms is $Tl_{4.15}Pb_{2.03}(As_{11.86}Sb_{8.20})S_{34}$. The simplified formula is $Tl_{5-x}Pb_{2x}(As,Sb)_{21-x}S_{34}$ (x ~1).

X-ray Diffraction

Three fragments of dalnegroite were extracted from a polished section and checked for diffraction quality using Oxford Diffraction Xcalibur 3 and STOE STADI4 (with CCD detector) single-crystal diffractometers. The fragments gave extremely broad X-ray diffraction profiles, thus indicating the powder study as the only possible means of X-ray investigation. Fully indexed 114.6 mm Gandolfi camera X-ray powder data (Ni-filtered Cu-$K\alpha$) are presented in Table 2. The intensities were measured with an automated

TABLE 1. Electron microprobe analyses and atomic ratios for the selected dalnegroite crystal.

	1	2	3	4	5	6	7	8	9	10	11	mean
Pb	11.15	9.96	9.93	8.60	11.23	8.46	9.49	10.77	12.38	8.80	10.18	10.09
Tl	20.33	20.07	20.06	20.39	19.76	21.50	21.15	20.65	19.56	20.76	19.77	20.36
Sb	23.73	24.66	25.23	25.57	23.85	24.03	24.10	22.56	22.18	23.63	23.94	23.95
As	21.51	21.56	21.13	21.09	21.16	21.45	21.05	21.50	21.84	21.21	21.11	21.33
S	26.13	26.37	26.20	26.06	26.04	26.30	26.15	26.17	26.17	25.99	26.22	26.16
Total	102.85	102.62	102.55	101.71	102.04	101.74	101.94	101.65	102.13	100.39	101.22	101.89
Atomic ratios based on 34 S atoms												
Pb	2.24	1.99	1.99	1.74	2.27	1.69	1.91	2.17	2.49	1.78	2.04	2.03
Tl	4.15	4.06	4.08	4.17	4.05	4.36	4.31	4.21	3.99	4.26	4.02	4.15
Sb	8.13	8.37	8.62	8.78	8.20	8.18	8.25	7.72	7.59	8.14	8.17	8.20
As	11.98	11.90	11.73	11.77	11.82	11.87	11.71	11.95	12.14	11.87	11.71	11.86

Probe standards: Pb (metal); TlI, TlBr (synthetic); Sb (metal); InAs (synthetic);FeS_2 (natural)
Average errors: Pb = 1.5%, Tl = 1.0%, Sb = 1.2%, As = 0.5%, S = 0.8%

densitometer. The unit-cell parameters were derived by means of the program *TREOR* (Werner *et al.*, 1985) and by comparison with the isotypic chabournéite, $Tl_{5-x}Pb_{2x}(Sb,As)_{21-x}S_{34}$ (Nagl, 1979; Johan *et al.*, 1981). Dalnegroite is triclinic with refined unit-cell parameters, based on 63 reflections between 7.20 and 1.785 Å, of: a = 16.217(7) Å, b = 42.544(9) Å, c = 8.557(4) Å, α = 95.72(4)º, β = 90.25(4)º, γ = 96.78(4)º, V = 5832(4) Å^3, Z = 4.

Relationship to chabournéite

According to Moëlo *et al.* (2008), the structural formula proposed for chabournéite by Nagl (1979) for a *b*/2 sub-cell is $Tl_8Pb_4Sb_{21}As_{19}S_{68}$. This formula was questioned by Johan *et al.* (1981), who proposed the formula $Tl_{21}(Sb,As)_{91}S_{147}$ for the unit cell of the Pb-free member, but this formula shows clearly a sulphur excess (when normalized to the same number of atoms as in the structural formula obtained by Nagl (1979) that is incompatible with the modular topology of the crystal structure. According to the substitution $Tl^+ + (Sb, As)^{3+} \rightarrow 2\ Pb^{2+}$, demonstrated by Johan *et al.* (1981), the general simplified formula should be written as $Tl_{5-x}Pb_{2x}(Sb,As)_{21-x}S_{34}$. The Pb-free pole ($x$ = 0) corresponds to $Tl_5(Sb,As)_{21}S_{34}$, while the Pb-rich composition studied by Nagl ($x \sim 1$) is close to $Tl_4Pb_2(Sb,As)_{20}S_{34}$. Hence, dalnegroite is the As-dominant analogue of the chabournéite studied by Nagl (1979) having $x \sim 1$. The two minerals have very similar X-ray powder-diffraction

TABLE 2. X-ray powder data for dalnegroite.

I	$d_{(meas.)}$	$d_{(calc.)}$	h	k	l	I	$d_{(meas.)}$	$d_{(calc.)}$	h	k	l
20	7.20	7.2065	$\bar{1}$	$\bar{2}$	1	10	2.853	2.8576	2	8	2
10	6.78	6.7933	$\bar{2}$	4	0	**70**	**2.850**	**2.8522**	**$\bar{4}$**	**4**	**2**
35	4.67	4.6614	$\bar{2}$	8	0	30	2.827	2.8265	$\bar{4}$	$\bar{4}$	2
25	4.27	4.2564	0	$\bar{2}$	2	20	2.813	2.8154	4	2	2
15	4.21	4.2031	0	10	0	5	2.768	2.7681	$\bar{2}$	10	2
5	4.10	4.0924	0	2	2	20	2.760	2.7619	2	$\overline{12}$	2
5	4.09	4.0916	0	$\bar{4}$	2	25	2.735	2.7350	$\bar{4}$	6	2
40	4.02	4.0253	4	0	0	25	2.710	2.7093	2	14	0
100	**3.927**	**3.9226**	**$\bar{2}$**	**10**	**0**	40	2.702	2.7012	$\bar{4}$	$\bar{6}$	2
25	3.921	3.9182	$\bar{4}$	4	0	20	2.618	2.6126	2	10	2
5	3.813	3.8136	0	4	2	10	2.613	2.6121	$\bar{6}$	6	0
25	3.810	3.8126	0	$\bar{6}$	2	25	2.590	2.5900	$\bar{2}$	16	0
45	**3.775**	**3.7750**	**2**	**$\bar{2}$**	**2**	**45**	**2.579**	**2.5791**	**0**	**$\overline{14}$**	**2**
20	3.690	3.6935	2	$\bar{4}$	2	30	2.547	2.5448	4	6	2
45	**3.685**	**3.6850**	**$\bar{4}$**	**6**	**0**	5	2.493	2.4990	4	12	0
50	**3.620**	**3.6177**	**4**	**4**	**0**	25	2.390	2.3881	4	8	2
25	3.600	3.6033	$\bar{2}$	$\bar{4}$	2	5	2.315	2.3153	$\bar{2}$	14	2
40	3.551	3.5561	2	10	0	20	2.198	2.1968	6	$\bar{8}$	2
35	3.524	3.5265	$\bar{2}$	4	2	15	2.194	2.1938	$\bar{2}$	$\overline{16}$	2
20	3.392	3.3967	$\bar{4}$	8	0	30	2.141	2.1410	0	16	2
25	3.379	3.3807	$\bar{2}$	$\bar{6}$	2	15	2.133	2.1332	$\bar{4}$	18	0
30	3.363	3.3617	$\bar{2}$	12	0	20	2.127	2.1266	6	$\overline{10}$	2
25	3.287	3.2865	$\bar{2}$	6	2	**60**	**2.097**	**2.0964**	**0**	**2**	**4**
20	3.277	3.2766	2	$\bar{8}$	2	10	2.050	2.0501	$\bar{6}$	10	2
10	3.151	3.1553	0	8	2	5	2.027	2.0266	$\bar{8}$	2	0
50	**3.124**	**3.1235**	**$\bar{2}$**	**$\bar{8}$**	**2**	10	2.000	2.0001	$\bar{6}$	16	0
20	3.113	3.1167	2	6	2	15	1.998	1.9975	2	$\bar{8}$	4
5	3.097	3.0974	$\bar{4}$	10	0	15	1.958	1.9579	$\bar{6}$	12	2
30	3.084	3.0803	2	12	0	5	1.910	1.9105	0	22	0
20	2.949	2.9490	$\bar{4}$	0	2	15	1.893	1.8919	6	14	0
60	**2.929**	**2.9360**	**4**	**$\bar{2}$**	**2**	5	1.785	1.7845	$\bar{8}$	$\bar{4}$	2
30	2.916	2.9145	4	$\bar{4}$	2						

The strongest intensities are reported in bold.

TABLE 3. Comparison between dalnegroite and chabournéite.

	Dalnegroite	Chabournéite
Reference	This study	(Nagl, 1979; Johan *et al.*, 1981)
Chemical formula	$Tl_{5-x}Pb_{2x}(As,Sb)_{21-x}S_{34}$ (x ~1)	$Tl_4Pb_2(Sb,As)_{21}S_{34}$
Unit-cell parameters	a = 16.217(Å)	a = 16.320(Å)
	b = 42.544(Å)	b = 42.636(Å)
	c = 8.557(Å)	c = 8.543(Å)
	α = 95.72(º)	α = 83.98(º)
	β = 90.25(º)	β = 89.06(º)
	γ = 96.78(º)	γ = 83.20(º)
	V = 5832(4) Å^3	V = 5870 Å^3
Density (calc.)	4.819 g cm^{-3}	4.88 g cm^{-3}
VHN_{25}	69–101 Kg mm^{-2}	78–124 Kg mm^{-2}
Strongest diffraction lines (Å)	3.927, 2.850, 2.929, 2.097, 3.620, 3.124, 2.775, 3.685	3.573, 2.135, 2.808, 3.928, 3.358, 2.853, 2.709

patterns and, consequently, very similar unit-cell parameters (Table 3). The a and b parameters of dalnegroite are slightly shorter than those of chabournéite (Nagl, 1979) owing to the smaller size of As relative to Sb.

One of the difficulties encountered during a description of a complex metallic mineral for which a complete crystal-structure characterization is not possible because of small crystal size, complex twinning and/or intergrowths, is the valence state of the elements. On the basis of the analysed formula $Tl_{5-x}Pb_{2x}(As,Sb)_{21-x}S_{34}$ for dalnegroite, the formal charge balance is assumed by considering the normal valence states of the elements: Tl^+, Pb^{2+}, As^{3+}, Sb^{3+} and S^{2-}. Furthermore, it should be pointed out that dalnegroite could be also described by a triclinic unit cell with $b' = b/2$ = 21.272 Å, as all the measured reflections have $k = 2n$. Moreover, the a and c values of dalnegroite depend only on the presence of one reflection (i.e. hkl: $\bar{1}2\bar{1}$). A recent single-crystal X-ray diffraction study of chabournéite (Bonaccorsi, pers. comm.) indicates that its a and c parameters are halved and that the structure is centrosymmetric (i.e. $P\bar{1}$). As a full structural study of dalnegroite remains to be carried out, discussion of charge balance, degree of metallic bonding, unit-cell type and possible structural models must await the availability of better crystals.

Acknowledgements

The authors wish to thank Anke Potzel and Detlef Krauße from Bayerisches Geoinstitut (Bayreuth, Germany) for access to the WDS electron microprobe facility and Luca De Battisti for providing the sample. The manuscript took advantage from the revision of Anna Garavelli and Yves Moëlo. Financial support was provided by P.R.I.N 2006047943.

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ERRATUM

Dalnegroite, $Tl_{5-x}Pb_{2x}(As,Sb)_{21-x}S_{34}$, a new thallium sulphosalt from Lengenbach quarry, Binntal, Switzerland

In the above paper by Nestola *et al*., published in the December 2009 issue of *Mineralogical Magazine*, a mineral was incorrectly named. All references, including that in Fig. 1, to jordanite ($Pb_{14}As_6S_{23}$), should be replaced by sartorite ($PbAs_2S_4$).

Under the heading of Occurrence, the authors also wish to point out that the sample containing dalnegroite was provided by Luca De Battisti, a mineral collector, who collected the sample at the Lengenbach quarry in the summer of 2006.