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QUATERNARY COMPOUNDS IN THE SYSTEM Pb–Sb–S–Cl: DADSONITE AND SYNTHETIC PHASES

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ABSTRACT

Two Pb–Sb chlorosulfides have been synthesized hydrothermally at 200°C. Phase *Y* $Pb_{11}Sb_{10}Cl_4S_{24}$ is monoclinic, space group *P*2, *Pm* or *P*2/*m*, with *a* 19.42, *b* 4.06, *c* 15.19 Å, β 94°40′, $Z = 1$; its crystals are acicular. Phase *Y′* $Pb_{16}Sb_{15}Cl_7S_{35}$ or $Pb_{19}Sb_{18}Cl_8S_{42}$ also exhibits acicular crystals. Dadsonite and phases *Y* and *Y′* have similar X-ray properties and conditions of synthesis. Dadsonite also contains a small amount of chlorine (0.4%) as an essential component, and the new formula $Pb_{23}Sb_{25}ClS_{60}$ is proposed. The mineral has a new cell for which $b' = 2b = 8.22$ Å, $Z = 1$. In nature, dadsonite probably results from reaction of Pb–Sb ore with chlorinated solutions in the late stages of mineralization. Two groups are distinguished among Pb–Sb acicular sulfosalts: boulangerite group, crystals acicular [001] ($c \sim 4$ or 4 or 2 x 4 Å), and dadsonite group, crystals acicular [010] ($b \sim 4$ or 2 x 4 Å).

SOMMAIRE

Des synthèses par voie hydrothermale à 200°C ont permis d'obtenir deux chlorosulfures d'antimoine et de plomb. La phase *Y* $Pb_{11}Sb_{10}Cl_4S_{24}$, de facies aciculaire, est monoclinique, groupe spatial *P*2, *Pm* ou P2/*m*, avec *a* 19.42, *b* 4.06, *c* 15.19 Å, β 94°40′, $Z = 1$. La phase *Y′*, à cristaux également aciculaires, a comme formule $Pb_{16}Sb_{15}Cl_7S_{35}$ ou $Pb_{19}Sb_{18}Cl_8S_{42}$. La dadsonite présente des ressemblances avec les phases *Y* et *Y′* (diffraction X, conditions de synthèse). Elle contient également un peu de chlore (0.4%) comme constituant intrinsèque, d'où la nouvelle formule $Pb_{23}Sb_{25}ClS_{60}$, avec maille $b' = 2b = 8.22$. Å et $Z = 1$. Dans la nature, la dadsonite résulterait du remaniement de minerais de plomb et antimoine par des solutions fortement chlorurées lors des derniers stades de minéralisation. On distingue deux groupes parmi les sulfosels de Pb–Sb à cristaux aciculaires: le groupe de la boulangérite (allongement suivant [001] avec $c \sim 4$ ou 2 x 4 Å) et le nouveau groupe de la dadsonite (allongement suivant [010] avec $b \sim 4$ ou 2 x 4Å).

INTRODUCTION

Pb–Sb sulfosalts form a complex group usually divided into two subgroups: tabular (plagionite group) and acicular (boulangerite group). Some of the minerals are common and others rare, irrespective of their subgroup or Pb/Sb ratio (Moëlo *et al.* 1977). For instance, dadsonite is a rare acicular sulfosalt, whereas boulangerite (acicular) and semseyite (tabular), with similar Pb/Sb ratios, occur frequently.

Minor elements are critical for the stability of some members of the sulfosalt family, and thus may influence the relative abundance of members in natural occurrences. For instance, Hoda & Chang (1975) showed that a small amount of copper is essential to stabilize meneghinite at low temperatures, whereas Wang (1977) was unable to synthesize its copper-free analogue below 500°C. Two Pb–Sb chlorosulfosalts were obtained by hydrothermal synthesis in the present study, and it was found that chlorine plays an essential role in dadsonite, a situation analogous to that of copper in meneghinite. This accounts for the peculiar conditions required for the synthesis of dadsonite, and perhaps explains the rarity of the mineral in nature.

SYNTHETIC PB–SB CHLOROSULFOSALTS

A new compound, designated phase *Y*, was obtained frequently with other tabular sulfosalts by reacting mixtures of galena and stibnite hydrothermally at 200°C. Phase *Y* crystallized if sufficient chlorine was present. Typical run conditions involved solutions of $PbCl_2$ ($>2 \times 10^{-2}$ molar) or other chlorine-bearing solutions such as $FeCl_3$ in which Cl^- was >2 ion-g/l. Run duration was usually 3 to 4 weeks.

Phase *Y* is acicular (Fig. 1) and generally consists of fibres less than 1 µm in diameter. These fibres are thin enough to permit light diffusion, and so macrosamples are red. Crystals up to 5 mm in length and 0.1–0.2 mm in thickness were obtained occasionally; these have a metallic lustre like that of natural Pb–Sb

FIG. 1. Phase *Y*: acicular facies (length of the fibres: 1 mm). M.E.B. photograph by P. Jeanrot (B.R.G.M.-C.N.R.S., Orléans).

sulfosalts, but in polished section red internal reflections are more abundant. A cleavage perpendicular to the elongation is clearly visible at high magnification (x 10000).

Crystallography

The X-ray powder diffraction pattern of a particularly well-crystallized sample of phase *Y* is given in Table 1. Weissenberg photographs show that phase *Y* is monoclinic, elongate along *b*, with *a* 19.42, *b* 4.06, *c* 15.19 Å, *β* 94.7°, *V* 1194 Å^3. As no systematic extinctions are present, the possible space groups are *P*2, *Pm*, or *P*2/*m*.

The fibre studied is twinned, with orthorhombic pseudosymmetry and pseudobinary axis [108]. Two crystallographic features point out this pseudosymmetry: (1) intense diffraction spots of $10\bar{8}$ and $12\bar{8}$ planes remain unchanged. The relation is: $c = 8d_{108}$ [c(calc.) = 15.19 Å and $8d_{10\bar{8}}$ (meas.) = 15.12 Å]. Furthermore, (2) the powder pattern shows many intense double lines such as $30\bar{5}$ and 205, $30\bar{4}$ and 204, $40\bar{5}$ and 305, $21\bar{5}$ and 115, $31\bar{5}$ and 215, *etc.* (Table 1).

Intense diffraction spots on the Weissenberg photographs show a subcell, related by the transformation matrix $(\frac{1}{4}.0.0)$ / (010) / $\left(\frac{1}{20}.0.\frac{2}{5}\right)$, with a' 7.72, b' 4.06, c' 3.80 Å, β 89.5°. In the pseudo-orthorhombic sublattice (*B* type), $\vec{a'}$ and $\vec{c'}$ are respectively on

TABLE 1. X-RAY POWDER DATA FOR PHASE Y $Pb_{11}Sb_{10}Cl_4S_{24}$

I_{est}	d_{mes}	d_{calc}	hkl
1/2	11.5	11.45	101
1	7.54	7.55	002
1	7.23	7.23	$10\bar{2}$
2	6.83	6.84	102
1	6.22	6.20	$20\bar{2}$
1/2	4.76	4.72	302
1/2	4.63	4.62	$20\bar{3}$
2	4.30	4.32	203
1	4.25	4.23	$40\bar{2}$
2	4.15	4.13	$30\bar{3}$
2	4.06	4.07	010
1	3.92	3.93	402
4	3.86	3.87 (3.86)	500 $(11\bar{1})$
10	3.83	3.82 3.83 3.82	$50\bar{1}$ 111 303
1/2	3.76	3.76	$10\bar{4}$
4	3.67	3.68 (3.67)	501 $(21\bar{1})$
8	3.58	3.58 (3.56)	012 $(50\bar{2})$
2	3.54	3.54	$11\bar{2}$
1	3.49	3.50	112
10	3.41	3.42	204
10	3.39	3.38	304
1	3.32	3.33 3.32	502 212
1/2	3.20	3.21	$60\bar{1}$
3	3.18	3.18	$31\bar{2}$
3	3.09	3.08 (3.10) (3.08)	312 (113) (411)
2	3.07	3.07	$30\bar{4}$
2	3.05	3.05	$21\bar{3}$
1	3.01	3.02	$41\bar{1}$
1/2	2.956	2.962	213
1	2.934	2.932	$41\bar{2}$
2	2.826	2.824 2.817 (2.825)	$30\bar{5}$ 205 (412)
8	2.801	2.803	510
2	2.785	2.785 (2.784)	$51\bar{1}$ 313
8f	2.717	2.727 2.711	511 $(41\bar{3})$
1	2.664	2.660	$40\bar{5}$
1	2.638	2.652	305
2f	2.609	2.618 2.599	214 $31\bar{4}$
2	2.575	2.578 (2.587)	512 413
1/2	2.526	2.529	702
1	2.445	2.443	$61\bar{2}$
3	2.387	2.388	$21\bar{5}$
3	2.382	2.386	115
2	2.344	2.342 (2.351)	703 (612)
5	2.321	2.319 2.318 2.316	$31\bar{5}$ $61\bar{3}$ 215
3	2.258	2.252 (2.250)	$80\bar{3}$ (802)
1/2	2.230	2.229 2.226	$71\bar{2}$ $41\bar{5}$
1/2	2.211	2.221	315
2	2.195	2.192	$50\bar{6}$
1/2	2.139	2.139 2.143 2.142	$01\bar{6}$ $11\bar{6}$ $20\bar{7}$
1	2.118	2.117 (2.116) (2.113) (2.110)	$51\bar{5}$ $(80\bar{4})$ (803) (116)
1	2.100	2.104	901
1/2	2.076	2.074	$31\bar{6}$
1/2	2.063	2.059	216
1/2	2.041	2.037 2.039	$90\bar{3}$ 811
10	2.032	2.033	020
1	2.011	2.009	$41\bar{6}$
1	1.982	1.990	316
1	1.973	1.967 1.970	$80\bar{5}$ $81\bar{3}$
2	1.948	1.949 (1.942)	122 $(70\bar{6})$
1	1.934	1.934 1.930 1.932 (1.937)	$\underline{10}00$ $51\bar{6}$ $22\bar{2}$ $(90\bar{4})$
1/2	1.900	1.899	714
8	1.891	1.893 (1.895)	$10\bar{8}$ $(21\bar{7})$
3	1.882	1.877 (1.883) (1.875)	$81\bar{4}$ (117) $(91\bar{2})$
1/2	1.869	1.864	$60\bar{7}$
2	1.837	1.840	223
2	1.826	1.825	$32\bar{3}$
1/2	1.807	1.806	422
2	1.795	1.795 (1.800)	$52\bar{1}$ (520)
2	1.777	1.779	521
1/2	1.756	1.763	$\underline{11}01$
8	1.744	1.748 1.742	224 $32\bar{4}$
1/2	1.726	1.728 1.730	616 417
1	1.702	1.704 1.700 1.700	$90\bar{6}$ $42\bar{4}$ 621
1	1.695	1.694 1.689	$61\bar{7}$ $\bar{6}08$
5	1.648	1.650 1.649	$32\bar{5}$ 225
+ many lines			
3	1.442	1.445 1.440	419 619

Data, obtained with Cu *Kα* radiation, were indexed with *a* 19.42, *b* 4.06, *c* 15.19 Å, β 94.7°. Camera: Guinier-de Wolff; internal standard: quartz. Intensities were estimated visually; f: line is not sharp; (hkl): weak diffraction spot on Weissenberg photograph.

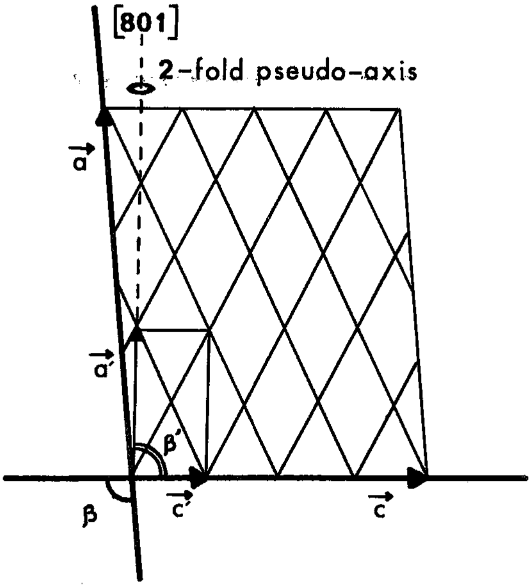

FIG. 2. Phase *Y*: geometric relations between lattice, sublattice and pseudo-orthorhombic twinning in the (010) plane.

[801] and [001] of the primitive lattice (Fig. 2); this shows the relation between the substructure and the pseudo-orthorhombic twinning.

Chemical composition

Because the synthesis of phase *Y* specifically required Cl-bearing solutions, the presence of structural Cl was anticipated and confirmed by electron-microprobe analyses (Table 2). Phase *Y* has a S/Cl ratio close to 6, and the set of smallest-integer stoichiometric coefficients consistent with the analytical data is $Pb_{11}Sb_{10}Cl_4S_{24}$. This formula and the cell volume give Z = 1, which is acceptable with the proposed space groups. The calculated density is ≃ 6.13 g/cm³.

TABLE 2. MICROPROBE ANALYSES OF PHASES Y AND Y'

	Phase Y 1	2	3	4	5	Av.	Standard deviation	at. %	$Pb_{11}Sb_{10}Cl_4S_{24}$ at. %	wt. %
Pb	52.2	50.4	49.9	50.9	52.3	51.1	1.1	22.1	22.4	51.7
Sb	28.1	27.4	28.2	28.8	28.1	28.1	0.5	20.6	20.4	27.7
S	17.8	17.5	18.1	17.2	17.4	17.6	0.4	49.1	49.0	17.4
Cl	3.4	3.2	3.0	3.4	3.2	3.2	0.2	8.2	8.2	3.2
Σ	101.5	98.5	99.2	100.3	101.0	100.0	1.3			

	Phase Y' 1	2	3	4	5	Av.	Standard deviation	at. %	a	b
Pb	51.0	49.7	50.0	49.2	52.2	50.4	1.2	21.6	50.9	50.7
Sb	27.2	28.7	28.4	28.5	28.1	28.2	0.6	20.6	28.1	28.3
S	17.2	18.1	17.0	17.7	16.9	17.4	0.5	48.3	17.2	17.3
Cl	3.6	3.7	3.9	4.2	3.8	3.8	0.2	9.5	3.8	3.7
Σ	99.0	100.2	99.3	99.6	101.0	99.8	0.8			

a: $Pb_{16}Sb_{15}Cl_7S_{35}$; b: $Pb_{19}Sb_{18}Cl_8S_{42}$. Automated CAMEBAX microprobe (B.R.G.M.-C.N.R.S. Orléans). Programming and analysis: C. Gilles, R. Giraud and G. Remond. Analytical conditions: 15 kV, 12nA, counting time 5 s. Standards: PbS (Pb *Mα*), Sb_2S_3 (Sb *Lα*), ZnS (S *Kα*), $Pb_5(PO_4)_3Cl$ (Cl *Kα*).

The plausibility of the above formula can be checked by comparing the atomic density of (Cl+S) in the following two cases:

(1) $Pb_{11}Sb_{20}Cl_4S_{24}$: there are 28 (Cl + S) atoms for a cell volume of 1194 Å³; thus $D_{at.(Cl+S)} \backsimeq 23.5 \times 10^{-3}$ at./Å³. (2) The weighted average for a mixture of $PbCl_2$ and a boulangerite-like phase ($2PbCl_2 + Pb_9Sb_{10}S_{24}$) has: in $PbCl_2$, $D_{at.(Cl)} \backsimeq 26 \times 10^{-3}$ at./Å³, and in boulangerite or semseyite $D_{at.(S)} \backsimeq 22 \times 10^{-3}$ at./Å³. Thus the mixture has $D_{at.(Cl+S)} \backsimeq \left[\left(26 \times \frac{1}{7}\right) + \left(22 \times \frac{6}{7}\right)\right] \times 10^{-3} \backsimeq 22.6 \times 10^{-3}$ at./Å³, or 27.0 (Cl + S) atoms for V = 1194 Å³. These calculations support our assumption.

Phase Y′

A fibrous compound similar to phase *Y*, here called phase *Y′*, was synthesized in only one run. Experimental conditions were almost the same as for phase *Y*. Despite the fibrous

TABLE 3. X-RAY POWDER DATA FOR PHASE Y'

I_{est}	d_{mes}	I_{est}	d_{mes}	I_{est}	d_{mes}	I_{est}	d_{mes}
1/2	10.71	1/2	3.47	3	2.686	2	2.088
1/2	7.46	1/2	3.43	1	2.665	1	2.057
2	6.71	3	3.36	1/2	2.625	1/2	2.049
1/2	5.60	1	3.32	1	2.590	10	2.030
1	5.01	3	3.24	1/2	2.511	1	2.021
1/2	4.49	1/2	3.20	2	2.499	1	1.967
2	4.23	1/2	3.16	1	2.440	1	1.952
2	4.18	1/2	3.12	1/2	2.413	1	1.934
2	4.05	1	3.08	2	2.378	1	1.911
1	4.02	2	3.03	2	2.337	4	1.883
1/2	3.96	1/2	2.99	2	2.302	1	1.873
2	3,86	4	2.93	1	2.289	2	1.830
8	3.79	1	2.91	1/2	2.257	3	1.788
3	3.74	1	2.90	2	2.206	1	1.749
5	3.60	1/2	2.855	1	2.157	2	1.741
8	3.55	7	2.797	2	2.142	1	1.645
5	3.53	10	2.747	1	2.125		

Data were obtained using Cu *Kα* radiation and a Guinier-de Wolff camera. Intensities are estimated visually

TABLE 4. MICROPROBE ANALYSES OF DADSONITES

	Ech. A (8 analyses)			Ech. B (5 analyses)			Ech. C (6 analyses)			Ech. D (10 analyses)				$Pb_{23}Sb_{25}Cl\,S_{60}$	
	a	b	at. %	a	b	at. %	a	b	at. %	a	b	at. %	error		at. %
Pb	49.6	0.8	21.5	48.1	0.4	20.9	49.2	0.7	21.3	48.7	0.6	21.0	0.2	48.7	21.1
Sb	30.6	0.5	22.5	31.1	0.3	22.9	31.2	0.2	22.9	31.3	0.3	22,9	0.2	31.2	22.9
S	19.7	0.3	55.2	19.7	0.2	55.2	19.6	0.4	55.0	19.7	0.1	55.1	0.3	19.7	55.1
Cl	0.35	0.05	0.8	0.41	0.04	1.0	0.30	0.09	0.8	0.38	0.07	1.0	0.2	0.36	0.9
Σ	100.2 ± 1.1			99.3 ± 1.0			100.3 ± 0.6			100.1 ± 1.0					
Valency balance			- 0.6 %			- 0.8 %			+ 0.5 %				- 0.3 %		

Specimens A, B: Wolfsberg, Germany; C, D: Saint-Pons, France. For analytical conditions, see Table 2.
a: average, b: standard deviation.

habit of *Y'*, the phase is poorly crystalline and single-crystal data could not be obtained. A very intense line at 2.03 Å in the X-ray powder pattern (Table 3) is probably related to the periodicity along the elongation direction, as it is for phase *Y*.

Microprobe analyses indicate that *Y'* has more chlorine than phase *Y* (Table 2). Stoichiometric formulas consistent with the analyses are $Pb_{16}Sb_{15}Cl_7S_{35}$ and $Pb_{19}Sb_{18}Cl_8S_{42}$.

CHLORINE IN DADSONITE

Phase *Y* and dadsonite are structurally similar, as is exemplified by their diffraction patterns. That the synthesis conditions required to form dadsonite and phase *Y* also are similar can be inferred from the literature: previous authors were unable to obtain dadsonite in dry systems or hydrothermally without chlorine (Jambor 1968), whereas dadsonite was obtained when Cl-bearing solutions were used (Robinson 1948, Nekrasov & Bortnikov 1975).

Microprobe analyses confirm the presence of Cl in four samples of dadsonite (Table 4): (A) a thin film of dadsonite microfibres on euhedral plagionite; (B) mm-wide veinlets of dadsonite in quartz, with partial replacement of plagionite; (C) mixed dadsonite fibres up to 1 cm long and tenths of a mm wide; (D) dadsonite fibres included in calcite, associated with bournonite. The first two samples (A and B) are from Wolfsberg (Germany) and were supplied by P. Sainfeld (Mineralogical Collection of Ecole des Mines de Paris). Samples C and D are from the recently discovered Saint-Pons deposit, France (Cervelle *et al.* 1979), and were supplied by J. and A. Davaux and J. Féraud.

The average Cl content of dadsonite in these samples is 0.3 to 0.4 wt. %, distinctly detectable with the microprobe (16 cps for a background of 6 cps). The Cl content of the Saint-Pons dadsonite was also confirmed by wet-chemical analysis in collaboration with M. Garcia and D. Dagorne (B.R.G.M.-M.G.A., Orléans). The analysis involved dissolution of a 200-mg sample in 1N HNO_3, addition of tartaric acid to prevent precipitation of Sb oxychlorides, and titration by potentiometry with a $Ag–Hg_2SO_4$ electrode. The Cl content obtained, 0.42%, is in good agreement with the microprobe results.

Crystal-chemical interpretation

Various halogen-bearing sulfides are known: Sb chlorosulfides (Bothorel 1958), Bi iodosulfides (Miehe & Kupčík 1971); Bi and Cu chlorosulfides (Lewis & Kupčík 1974); Bi and Cu bromosulfide (Mariolacos & Kupčík 1975), Bi, Cu and Pb iodosulfide (Ohmasa & Mariolacos 1974), Fe, K and Li chlorosulfide, the synthetic analogue of djerfisherite (Tani 1977). None of these compounds shows any replacement of sulfur by halogens. In the three compounds whose structures are known, sulfur and halogens occupy specific sites and share distinct chemical bonds. This is particularly clear in the djerfisherite-type compound, where there is only one chlorine atom for 26 sulfur atoms.

A similar structural role for chlorine probably also applies to dadsonite and to phases *Y* and *Y'*. Because the chlorine content of dadsonite is 0.4%, the unit cell defined by Jambor (1969) would have to contain only half an atom of chlorine. Therefore, the Saint-Pons dadsonite was re-examined by single-crystal methods. Oscillation photographs about the needle (*i.e.*, *b*) axis show weak diffraction spots between layers 0 and 1, thus indicating a superstructure with $b' = 2b = 8.22$ Å, and a cell volume twice that obtained by Jambor (1969). The stoichiometric formula proposed for dadsonite therefore becomes $Pb_{23}Sb_{25}ClS_{60}$, close to Jambor's formula of $Pb_{11}Sb_{12}S_{29}$, *i.e.* $Pb_{23}Sb_{25}ClS_{60}$ =

$2(Pb_{11}Sb_{12}S_{29}) + PbSbClS_2$. However, the addition of the ($PbSbClS_2$) group increases the calculated density from 5.76 g/cm^3 in the original formula to 6.01 g/cm^3 in the new.

NATURAL FORMATION OF DADSONITE AND ANALOGOUS COMPOUNDS

The natural formation of dadsonite through direct precipitation from hydrothermal solutions would imply simultaneous saturation in sulfides (PbS and Sb_2S_3) and lead chloride. It is generally assumed that Pb is hydrothermally transported as chloride complexes and is precipitated by decomposition of these complexes (Anderson 1973). Therefore, precipitation occurs as Cl activity decreases, and this is not favorable for the formation of dadsonite.

It seems more likely that dadsonite is the product of a reaction between lead–antimony ore and highly chlorinated solutions that may be present during the late stages of mineralization. Indeed, dadsonite is always associated with other Pb–Sb sulfosalts, *e.g.*, robinsonite at Pershing County, Nevada and plagionite at Wolfsberg, Germany (Jambor 1967); jamesonite at Madoc, Ontario (Jambor 1967) and in the ore from the Giant Yellowknife property, N.W.T. (Coleman 1963). All of the above sulfosalts have a Pb/Sb ratio lower than that of dadsonite. At Madoc, Yellowknife and Wolfsberg, dadsonite is obviously later than the associated sulfosalts as indicated by replacement and fracture-filling relationships. It is possible, therefore, that highly chlorinated solutions reacted with the older sulfosalts in a nearly closed system. This natural simulation of the experimental conditions used to synthesize dadsonite is rarely attained, as is indicated by the infrequent occurrences of the mineral. Natural formation of phases *Y* and *Y′* seems even more unlikely because of their relatively high chlorine content. Nevertheless, Breskovska *et al.* (1978) have reported microprobe analyses of chlorine-bearing Pb–Sb sulfosalts from the Madjarovo deposit (Bulgaria) whose compositions are close to those of phases *Y* and *Y′*. Crystallographic data are not available to verify the apparent similarity.

CONCLUSIONS

Djerfisherite (Fuchs 1966) was the first known example of a natural chlorosulfide; dadsonite is the second example and the first chlorosulfosalt (Moëlo 1978). Phases *Y*, *Y′* and dadsonite illustrate the existence of a new chemical group, namely, quaternary compounds in the system Pb–Sb–S–Cl. In these, as in other known halogen sulfides, chlorine plays a specific crystallochemical role that is distinct from that of sulfur. Because of the very different electronegativity values of Cl and S, mutual replacement of these elements is difficult. The special crystallochemical character of Cl permits the formation of discrete compounds with very low atomic ratios of Cl/S. For example, djerfisherite has about 1 wt. % Cl and 1 Cl atom to 26 S; dadsonite has about 0.4 wt. % Cl, and 1 Cl atom to 60 S. Although in dadsonite only 1 Cl atom among the 109 atoms of the unit cell seems to have been sufficient to induce a specific structure, in other cases it seems that Cl can be accommodated without appreciable structural disruption or reorganization. For example, Breskovska *et al.* (1978) report that boulangerite and jamesonite, hydrothermally synthesized at 300–400°C, contain small amounts of structural chlorine. The incorporation of Cl in these minerals may reflect the relatively high temperature of synthesis, and it is probable that Cl substitution for S is more restricted in nature.

Other sulfosalts which are difficult to synthesize in the system Pb–Sb–S may reflect the

TABLE 5. CONSTITUENT SPECIES OF THE DADSONITE GROUP

Name	Formula	Pb/Sb(+As)at.	b	2^d param.	3^d param.	β	Space group
SORBYITE	$Pb_{17}(\underline{Sb},As)_{22}S_{50}$	0.77	8.28	44.9	26.4	113°25'	C2,Cm or C2/m
LAUNAYITE	$Pb_{22}(\underline{Sb},As)_{26}S_{61}$	0.85	8.04	42.6	32.3	102°05'	C2,Cm or C2/m
PLAYFAIRITE	$Pb_{16}(\underline{Sb},As)_{18}S_{43}$	0.89	8.29	21.3	45.4	92°30'	P2,Pm or P2/m
DADSONITE	$Pb_{23}Sb_{25}Cl\ S_{60}$	0.92	8.22	19.05	17.33		P2,Pm or P2/m
PHASE Y'	$Pb_{16}Sb_{15}Cl_7S_{35}$ or $Pb_{19}Sb_{18}Cl_8S_{42}$	1.05	4.06 ?	?	?	?	?
PHASE Y	$Pb_{11}Sb_{10}Cl_4S_{24}$	1.10	4.06	19.42	15.19	94°40'	P2,Pm or P2/m
STERRYITE	$Pb_{12}(\underline{Sb},As)_{10}S_{27}$	1.20	8.20	42.6	32.3	90°	Pba2 or Pbam

Most data are from Jambor (1967).

need for the presence of Cl, as is the case for dadsonite. Among these, the following Pb–Sb–(As) sulfosalts from the Madoc deposit (Jambor 1967) were thought to be prime candidates as they have crystallographic analogies with dadsonite: sorbyite, launayite, playfairite and sterryite. However, Jambor has reported (written comm., 1979) that only playfairite contains Cl(<0.2 wt. %).

Crystallographic similarities among the above Madoc minerals, dadsonite, phase *Y* and probably phase *Y′* define a sulfosalt group (Table 5) with three features in common: (1) the *b* axis is close to 4 Å (or 2 x 4 Å); whereas one of the two others is close to 20 Å (or 2 x 20 Å); (2) monoclinic (except for sterryite, which is orthorhombic), and acicular along *b*. In contrast, the boulangerite group is acicular along *c*. This peculiarity had been noted for dadsonite ("mineral Q") by Coleman (1953). (3) Pb/(Sb,As) atomic ratio close to 1. Thus the axis of elongation distinguishes two groups of Pb–Sb acicular sulfosalts, namely, the boulangerite and dadsonite groups.

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REFERENCES

ANDERSON, G. M. (1973): The hydrothermal transport and deposition of galena and sphalerite near 100°C. *Econ. Geol.* **68**, 480-492.

BOTHOREL, P. (1958): Chlorosulfures d'antimoine. *In* Nouveau Traité de Chimie Minérale XI (P. Pascal, ed.), Masson et Cie, Paris.

BRESKOVSKA, V. V., MOZGOVA, N. N., BORTNIKOV, N. S. & TSEPIN, A. T. (1978): Chlorine-containing sulphosalts from the Madjarovo polymetallic deposit in Bulgaria. *XIth Gen. Meet., Int. Mineral Assoc.* **1**, 136-137 (Abstr.).

CERVELLE, B. D., CESBRON, F. P., SICHÈRE, M.-C. & DIETRICH, J. (1979): La chalcostibite et la dadsonite de Saint-Pons, Alpes de haute Provence, France. *Can. Mineral.* **17**, 601-605.

COLEMAN, L. C. (1953): Mineralogy of the Yellowknife Bay area, N.W.T. *Amer. Mineral.* **38**, 506-527.

FUCHS, L. H. (1966): Djerfisherite, alkali copper-iron sulfide: a new mineral from enstatite chondrites. *Science* **153**, 166-167.

JAMBOR, J. L. (1967): New lead sulfantimonides from Madoc, Ontario. 2. Mineral descriptions. *Can. Mineral.* **9**, 191-213.

——— (1968): New lead sulfantimonides from Madoc, Ontario. 3. Syntheses, paragenesis, origin. *Can. Mineral.* **9**, 505-521.

——— (1969): Dadsonite (minerals Q and QM), a new lead sulphantimonide. *Mineral. Mag.* **37**, 437-441.

HODA, S. N. & CHANG, L. L. Y. (1975): Phase relations in the pseudo-ternary system $PbS–Cu_2S–Sb_2S_3$ and the synthesis of meneghinite. *Can. Mineral.* **13**, 388-393.

LEWIS, J., JR. & KUPČÍK, V. (1974): The crystal structure of $Bi_2Cu_3S_4Cl$. *Acta Cryst. B* **30**, 848-852.

MARIOLACOS, K. & KUPČÍK, V. (1975): Die Kristallstruktur des $Bi_2Cu_3S_4Br$. *Acta Cryst. B* **31**, 1762-1763.

MIEHE, G. & KUPČÍK, V. (1971): Die Kristallstruktur des $Bi(Bi_2S_3)_9J_3$. *Naturwiss.* **58**, 219.

MOËLO, Y. (1978): Rôle des constituants mineurs dans la formation des sulfoantimoniures de plomb. *C.-R. Soc. franç. Minéral. Crist.* (séance du 15 décembre 1977). *Suppl. Bull. Minéral.* **101**, 11 (Abstr.).

———, PICOT, P. & LAFORÊT, C. (1977): Inventaire des occurrences françaises de sulfoantimoniures de plomb. *In* Résumé des Principaux Résultats Scientifiques et Techniques du Service Géologique National pour 1977. *Suppl. Bull. Bur. Rech. Géol. Minières*, 48-49.

NEKRASOV, I. YA. & BORTNIKOV, N. S. (1975): The system $Pb–Sn–Sb–S–H_2O$ at 300-500°C and the genesis of the ores of "Bolivian" type. *In* MAWAM Symposium 1974: *Metallization Associated with Acid Magmatism* (M. Stemprok, ed.), *Geol. Surv., Prague* **1**, 280-283.

OHMASA, M. & MARIOLACOS, K. (1974): The crystal structure of $(Pb_{1-x}Bi_x)\,Bi_2Cu_2Cu_{2-x}S_5I_2$ ($x = 0.88$). *Acta Cryst.* B **30**, 2640-2643.

ROBINSON, S. C. (1948): Synthesis of lead sulphantimonites. *Econ. Geol.* **43**, 293-312.

TANI, B. S. (1977): X-ray study of $K_6LiFe_{24}S_{26}Cl$, a djerfisherite-like compound. *Amer. Mineral.* **62**, 819-823.

WANG, N. (1977): Synthesis and crystal data of a Cu-free "meneghinite". *Can. Mineral.* **15**, 115-116.

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