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Ardaite—a new lead-antimony chlorosulphosalt

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ABSTRACT. The first occurrence of new mineral ardaite (a chlorine sulphosalt) has been discovered in the Madjarovo polymetallic ore deposit (Bulgaria). The average composition is Pb 56.50, Ag 0.04, Sb 22.48, S 15.56, Cl 3.78, total 98.36 wt.%. The formula is $Pb_{20-18}\ Sb_{12-24}S_{34-36.5}Cl_{6-8}$. The mineral occurs as fine acicular aggregates associated with galena, nadorite, a Cl-bearing robinsonite and Cl-bearing semseyite, pyrostilpnite, silver- bearing tetrahedrite and anglesite.

NEW types of natural compounds—lead-antimony chlorosulphosalts with a chlorine content of up to 4.2 wt.% have recently been discovered in the Madjarovo polymetallic ore deposit, Bulgaria (Breskovska *et al.*, 1978*a* and *b*, 1979, 1980). Further investigations of these sulphosalts with a high chlorine content enabled us to identify ardaite (initially named 'chlorine falkmanite') as an independent species. The mineral was named after the Arda river, which runs through the Madjarovo ore deposit. The mineral and its name were approved by the Commission on New Minerals and Mineral Names of the IMA in February 1980.

Description of ardaite. Ardaite is visible only under the microscope. It occurs as fine-grained aggregates (up to 50 μm in size) of individual acicular crystals (1-2 μm). The associated minerals (fig. 1) are galena, a Cl-bearing robinsonite and Cl-bearing semseyite, pyrostilpnite, Ag-bearing tetrahedrite, anglesite, nadorite. The ardaite is frequently intergrown with nadorite, but is also found as isolated inclusions in galena. No chlorine has been detected in the associated galena, pyrostilpnite and Ag-bearing tetrahedrite.

Ardaite is anisotropic and appears greenish-grey in the Madjarovo assemblage (galena, nadorite), with a distinct bireflectance. Its reflectivity, measured for eight wavelengths is as follows: 440nm 31.3-33.2; 480nm 32.1-34.4; 520nm 32.3-35.1; 580nm 31.7-34.7; 620nm 31.1-33.9; 660nm 30.6-32.8; 700nm 30.3-31.8; 740nm 30.2-30.9. One grain was measured—anal. 6 (Table II), the measured area being 10 microns in diameter. (App. PIOR, with silicon (Si) and pyrite (FeS_2) as standards).

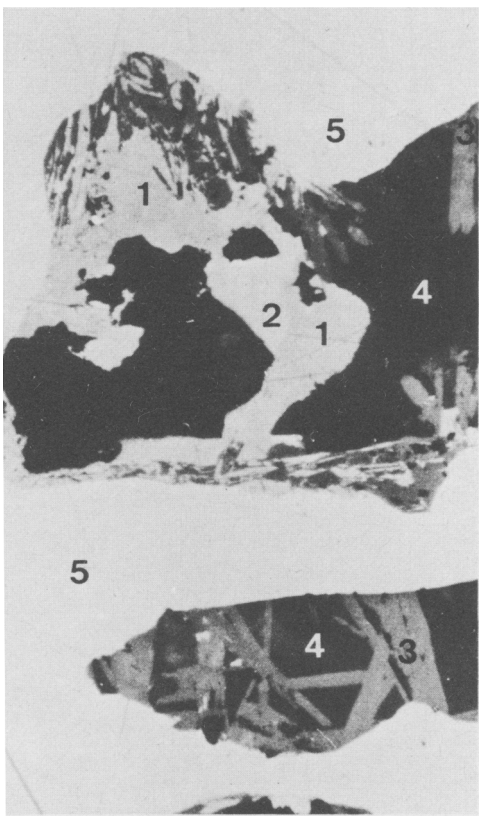

FIG. 1. Chlorine sulphosalts from Madjarovo ore deposit and their paragenesis: 1. Ardaite; 2. Chlorine-containing robinsonite; 3. Nadorite; 4. Anglesite; 5. Galena; × 120.

In order to confirm the nature of the chlorine in the sulphosalts, a synthesis of Pb-sulphoantimonites in chlorine-containing media was made (Bortnikov *et al.* 1979). The experiments were carried out in evacuated quartz ampules in eutectic melts of NH_4Cl-LiCl at a temperature of 300 °C and in an aqueous solution of NH_4Cl and NaCl at a temperature of 250–400 °C and pressure 500 atm., using standard techniques (Nekrassov and Bortnikov, 1976; Moh and Taylor, 1971). Starting components were synthetic FeS,PbS,Sb_2S_3,Ag_2S and the temperature of the experiment was kept up within ±5 °C. The products of the synthesis included the sulphoantimonites of Pb and Fe: boulangerite, jamesonite, robinsonite, zinckenite, semseyite, dadsonite, heteromorphite, launayite, plagionite and phases A, B, and C. In most of the synthesized phases Cl was detected in amounts up to 4.5 wt.%. Apart from crystals of the sulphosalt phases, no other Cl-bearing compounds were found among the products of the synthesis. The synthesized phase *A* (system Fe–Pb–Sb–S; eutectic melts NH_4Cl–LiCl at 300 °C) is similar to ardaite in terms of both composition and electron and X-ray diffraction patterns.

Crystallography. The electron diffraction studies of the selected area of specimen 5 and of the synthetic phase *A* indicated their structural analogy. In the diffraction patterns of the a^*c^* plane, strong and weak reflections alternate along the shortest axis (the c^* axis), thus indicating the presence of a superstructure along this axis. The diffraction pattern fits a monoclinic cell with a 21.97, c 8.05 Å, with a subcell $c = 2c'$ and β 103°. The b dimension

TABLE I. *X-ray powder patterns of ardaite*

		1			2		3		4	
No.	*hkl*	*I*	$d_{meas.}$	$d_{calc.}$	*I*	*d*	*I*	*d*	*I*	*d*
1	500	10	4.30	4.30	2	4.24	1	4.31	—	—
2	150	10	4.15	4.14	—	—	—	—	—	—
3	102	10	4.02	4.02	—	—	—	—	—	—
4	302	15	3.83	3.82	2	3.90	3	3.88	—	—
5	102	20	3.71	3.725	1	3.65	—	—	—	—
6	341	16	3.55	3.545	—	—	10	3.47*	—	—
7	621	100	3.39	3.391	10	3.43	10	3.40	10	3.38
8	332	79	3.36	3.360	—	—	—	—	—	—
9	541	20	3.28	3.283	—	—	—	—	—	—
10	042	16	3.15	3.148	4	3.13	—	—	1	3.07
11	361	15	3.03	3.036	—	—	10	2.98*	—	—
12	052	56	2.87	2.874	—	—	—	—	—	—
13	171	37	2.82	2.820	8	2.83	3	2.83	7	2.83
14	370	30	2.78	2.780	1	2.75	—	—	—	—
15	342	15	2.71	2.709	—	—	—	—	—	—
16	362	10	2.59	2.589	—	—	—	—	1	2.54
17		5	2.37	—	2	2.36	—	—	—	—
18		5	2.30	—	—	—	—	—	1	2.32
19		5	2.28	—	2	2.28	—	—	—	—
20		10	2.25	—	—	—	—	—	—	—
21		20	2.15	—	—	—	—	—	2	2.12
22		42	2.10	—	2	2.05	10	2.11*	4	2.00
23		5	2.03	—	—	—	—	—	—	—
24		5	1.960	—	—	—	—	—	—	—
25		5	1.941	—	—	—	—	—	—	—
26		5	1.910	—	3	1.900	2	1.905	1	1.903
27		5	1.875	—	—	—	2	1.803*	—	—
28		5	1.803	—	—	—	—	—	—	—
29		20	1.781	—	—	—	—	—	—	—
30		10	1.725	—	—	—	1	1.732	—	—

1, 2—synthetic phase *A*; 3, 4—natural ardaite. 1—Diffractometer DRON, Cu-$K\alpha$ radiation, Ni filter (anal. T. N. Dokina, IGEM, Moscow, USSR); 2, 3, 4—Powder camera RKD, 57.3 mm diam., unfiltered Fe radiation, micromethod (anal. A. A. Anisimova, IGEM, Moscow, USSR). The asterisks denote galena reflections.

is determined only for the synthetic phase, where its value is 21.3 Å. The X-ray powder diffraction pattern of the natural material is close to that of the synthetic (Table I) and the unit cell parameters of the former have been calculated *a* 22.09, *b* 21.11, *c* 8.05 Å, β 103° 01′; V = 3657.776 Å^3.

Chemical composition. The chemical composition of the ardaite was determined by means of a Cameca MS-46 electron probe microanalyser. Analyses of six natural ardaite grains (nos. 1-6) and of the synthetic *A* phase (no. 7) using PbS (for Pb), $CuFeS_2$ (for S), Sb and Ag metals, as well as NaCl (for Cl) as standards, are given in Table II. The measurements have been made under the following conditions: voltage, 20 kV; specimen current, 10-30 nA; size of the beam, 1-3 μm. Processing of the counts and correction of the relative intensities was carried out using the 'NR-1 programme' in a Hewlett-Packard 9380 computer (Tsepin and Boronihin, 1979).

In addition to the main elements Pb, Sb, S, and Cl (fig. 2), ardaite sometimes contains a small amount of Ag. The Pb/Sb ratio of ardaite is close to that of falkmanite, $Pb_3Sb_2S_6$, formerly discarded. For that reason we had provisionally called it 'chlorine-falkmanite' in previous publications (Breskovska *et al.*, 1979). As can be seen from the analyses (Table II) the composition of ardaite is not constant. The amount of lead in the synthetic *A* phase is somewhat smaller than that of the natural ardaite.

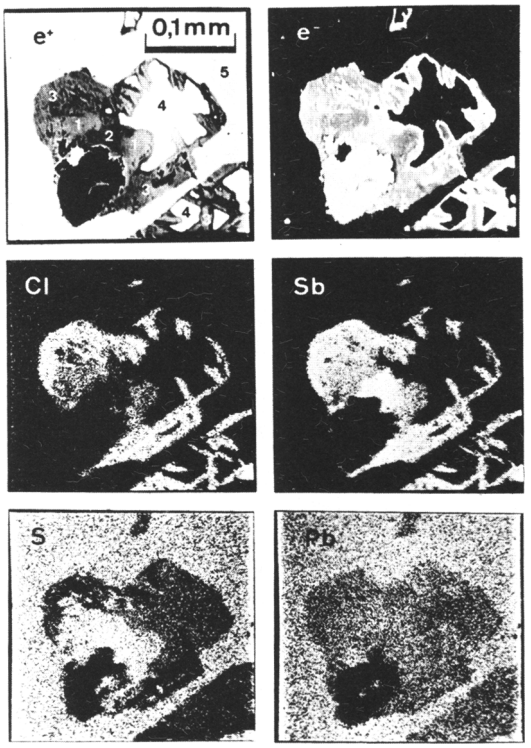

FIG. 2. Distribution of elements in: 1. Ardaite; 2. Chlorine-bearing robinsonite; 3. Nadorite; 4. Anglesite; 5. Galena.

TABLE II. *Electron microprobe analysis of ardaite and synthetic phase A*

No.	Pb	Ag	Sb	S	Cl	Total
1	57.82	0.06	21.10	15.04	4.16	98.18
2	57.70	—	21.52	14.93	3.83	97.98
3	56.95	—	22.31	15.62	3.56	98.44
4	55.89	—	22.75	15.58	4.02	98.24
5	55.93	—	22.79	16.78	3.02	99.52
6	54.72	0.16	24.10	15.40	4.06	98.74
7	52.29	—	26.47	16.57	4.50	99.83
8	56.50	0.04	22.48	15.56	3.78	98.36

Formula of ardaite on Pb+Ag+Sb = 32

No.	Pb	Ag	Sb	S	Cl	Pb/Sb	Cl/S
1	19.72	0.04	12.24	33.18	8.30	1.61	0.25
2	19.57	—	12.43	32.73	7.59	1.57	0.23
3	19.20	—	12.80	34.03	7.01	1.50	0.21
4	18.90	—	13.10	34.06	7.95	1.44	0.23
5	18.89	—	13.11	36.64	5.96	1.44	0.16
6	18.14	0.10	13.76	32.98	7.86	1.33	0.24
7	17.19	—	14.81	35.20	8.64	1.16	0.25
8	19.06	0.03	12.91	33.96	7.46	1.49	0.22

1-6, natural material; 7, synthetic phase A; 8, average of analysis 1-6.

Alternative variants of ardaite's ideal formula were obtained on the basis of electron microprobe analysis data. The first is based on Pb+Sb = 10 atoms in the unit cell, while the second, which includes the measured range of composition, namely $Pb_{20-18}Sb_{12-24}S_{34-36.5}Cl_{6-8}$ is based on Pb+Sb = 32 atoms. The second variant is more acceptable, because in this case the value of calculated density (6.17-6.32 g/cm^3, where Z = 2 agrees well with the assumed values based on the known density of boulangerite and meneghinite (Jambor, 1967). Both $Pb_{20}Sb_{12}S_{34}Cl_8$ and $Pb_{19}Sb_{13}S_{35}Cl_7$ could be put forward as formulae of ardaite. The first is in agreement with analysis 1. The second, however, is more acceptable, because it is closer to the average analysis.

$Pb_{17}Sb_{15}S_{35}Cl_9$ is put forward as an ideal formula for the synthetic *A* phase. Its calculated density is 6.11 g/cm^3, where Z = 2.

TABLE III. *Unit cell dimensions of chlorine sulphosalts and sulphosalts of lead with similar X-ray diffraction patterns*

Mineral	Formula	Pb/(Sb+As)	Cell dimensions (Å) a_0	b_0	c_0	Reference
Ardaite	$Pb_{17}Sb_{15}S_{35}Cl_9$	1.14	22.09	21.11	8.05	103° 01′ author's data
Playfairite	$Pb_{16}Sb_{18}S_{43}$	0.89	45.4	8.29	21.3	92° 30′ Jambor, 1967
Launayite	$Pb_{22}Sb_{26}S_{61}$	0.85	42.6	8.04	32.3	102° 05′
Sorbyite	$Pb_{17}(Sb,As)_{22}S_{50}$	0.77	44.9	8.28	26.4	113° 25′

It is interesting to note that correlations exist between the amounts Pb and Sb as well as between Cl and S (the correlation coefficients being −0.924 and −0.862 respectively), which is good reason for assuming isomorphism between these pairs of elements. It could be shown that the substitution Pb^{2+}-Sb^{3+} is accompanied by a substitution S^{2-}-Cl^{-}. This would involve an increase in the Cl content accompanied by an increase in Pb. No such increase was observed, which means that the isomorphism in ardaite is of a rather complex character (Breskovska *et al.*, 1981).

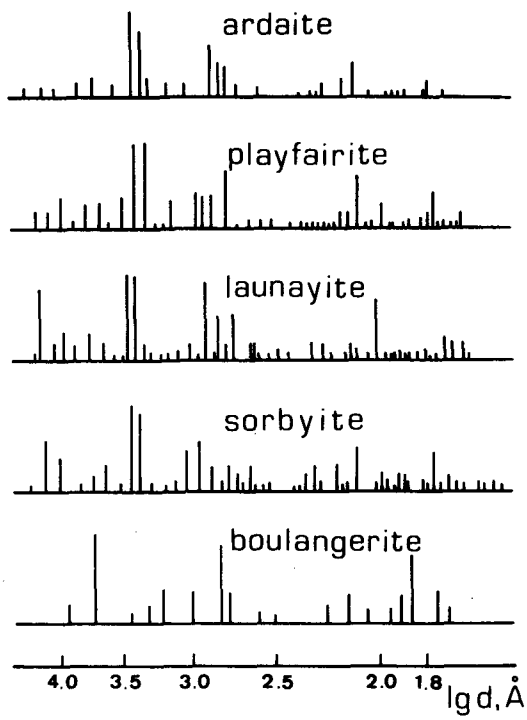

FIG. 3. Comparison of the X-ray powder patterns of ardaite, playfairite, launayite, sorbyite, and boulangerite.

Correlation between ardaite and lead sulphoantimonites. According to its basic components, particularly Pb and Sb, ardaite is related not only to the previously discarded $Pb_3Sb_2S_6$ (falkmanite), but also to the synthetic meneghinite (Cu-free meneghinite, Jambor, 1975; Wang, 1977) and to boulangerite. Nevertheless the X-ray powder diffraction pattern differs from these compounds. At the same time the X-ray powder diffraction patterns of ardaite and the *A* phase agree with those of lead sulphosalts with a lower Pb content (Pb/Sb ranging from 0.9 to 1.1), i.e. playfairite, launayite, and sorbyite (fig. 3). There is a distinct relationship between the size of the unit cell of the minerals presented in Table III. The shortest edge is practically identical for all compounds, the parameter *a* is approximately equal to half of the *a* dimension established by J. Jambor for sulphosalts from Madok (Jambor, 1967). A similar interrelation is established also by Moëlo (1979) for the minerals mentioned above, for dadsonite and the synthetic *Y* phase of $Pb_{11}Sb_{10}S_{24}Cl_4$. However dadsonite and the *Y* phase, which have compositions much closer to the *A* phase, are much more similar to jamesonite in their unit cell dimensions (Breskovska *et al.*, 1980). Thus the crystallographic data obtained for ardaite and the *A* phase lead to the assumption that the presence of Cl is stabilizing a launayite-type structure in the high-Pb system Pb–Sb–S, while the absence of Cl is stabilizing a structure resembling that of boulangerite and Cu-free meneghinite.

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