NEW LEAD SULFANTIMONIDES FROM MADOC, ONTARIO
PART 3—SYNTHESES, PARAGENESIS, ORIGIN

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ABSTRACT

At least eleven artificial sulfosalts have been prepared by heating various mixtures of galena, stibnite, and orpiment in closed tubes. Among these are the new Madoc sulfosalts playfairite, madocite, guettardite, and two lead sulfantimonides which have no mineral counterparts.

From oldest to youngest, the depositional sequence at Madoc is sulfides, arsenic-rich sulfosalts, and antimony-rich and copper-bearing sulfosalts. Precipitation of the Pb-Sb-As sulfosalts initially followed a trend of decreasing activity of As_2S_3 and probably terminated with increasing activity of Sb_2S_3 in the system. The observed paragenesis is believed to have resulted principally from the greater solubility of arsenic as compared to antimony, with temperature effects becoming a more important control toward the terminal stages of deposition.

Introduction

The geological setting and detailed mineralogy of the Madoc sulfosalt deposit were given in Parts 1 and 2 of this study (Jambor 1967 a, b.) This paper (Part 3) concludes the series.

SYNTHESES

Syntheses in the system Pb-Sb-As-S were carried out primarily to demonstrate the existence of certain mineral species in the system and to obtain data on the mutual substitution of Sb and As in lead sulfosalts.

The only modern work on the Pb-Sb-S system is that of Robinson (1947, 1948), who used both dry fusion and hydrothermal techniques and obtained eight artificial sulfantimonides by the latter method. Rösch & Hellner (1959) had considerable success in obtaining lead sulfarsenides by hydrothermal methods, but to the writer's knowledge, no study on the Pb-Sb-As-S system has been attempted. The crude experimental work reported below is not a systematic study of the phases in the system; rather it represents an effort directed towards obtaining a maximum diversity of artificial sulfosalt products.

Materials and apparatus

Virtually all syntheses in this study were carried out using galena from the Rossie lead mine, St. Lawrence Co., New York, stibnite from St. George, York Co., New Brunswick, orpiment from Yakutiya, Siberia,

U.S.S.R., and pharmaceutical grade sulfur. After grinding, these were combined in stoichiometric proportions to obtain stock material con-conforming to about eighty different hypothetical sulfosalts.

In the present study, any charge loaded into an appropriate vessel which was heated to promote reaction between the contained compounds and subsequently yielded a new metallic phase or phases is considered to constitute a "run." Approximately 275 runs were carried out, and in addition, about 50 charges were loaded but subsequently blew up. Over 90% of the runs were carried out in sealed tubes of either fused silica or pyrex glass having inside diameters of 3 to 4 mm and lengths of 5 to 8 cm. Most charges consisted of 250 to 600 mg of hypothetical sulfosalt and 20 to 30 mg of excess sulfur.

In about 40 runs compression of the charge and reduction of free space about it was accomplished by the insertion of close-fitting glass rods. This substantially decreased the problem of volatilization and subsequent segregation of arsenic and antimony in the vessels. A few experiments using gold tubes were also attempted and proved to be feasible for sulfosalt synthesis.

Tuttle-type cold seal bombs of commercial manufacture were used for most of the hydrothermal runs. Nearly all dry (non-hydrothermal) charges were heated in a portable oven equipped with a temperature regulator and thermocouple with 50°C graduations. The thermocouple was calibrated with a millivolt potentiometer but the temperatures obtained were probably no more accurate than $\pm 25°C$. Although the tubes containing the charges were placed in a horizontal position in the oven, it was found that segregation of stibnite and arsenic could not be prevented. Presumably a significant temperature gradient is present in the oven.

All synthetic products were systematically examined with a binocular microscope, and x-ray powder diffraction patterns of the discernible sulfosalt phases were obtained with 57 mm cameras. As this method of identification is somewhat unreliable, approximately 260 of the products were also initially examined by means of Guinier x-ray patterns.

Conditions of synthesis

A resumé of the products obtained and the general conditions of synthesis is given in Table 1. The products obtained in the high temperature work were derived from 55 charges heated to 1,000°C in evacuated silica tubes for 2 to 7 hours. The hydrothermally synthesized sulfosalts were obtained from 18 runs in which the charge contained water as a constituent; in 5 of these, Na$_2$S was also added. The temperature in almost all cases was 400 to 500°C, and the heating times ranged from 4 to

TABLE 1. SYNTHETIC SULFOSALTS OBTAINED IN THIS STUDY

1. By high temperature (1,000°C) synthesis (quenched in water)

robinsonite, $7PbS \cdot 6Sb_2S_3$ zinckenite, $6PbS \cdot 7(Sb,As)_2S_3$(?)
boulangerite, $5PbS \cdot 2Sb_2S_3$ phase K-1, Pb sulfantimonide
madocite, $17PbS \cdot 8(Sb,As)_2S_3$ phase AN, Pb sulfantimonide
jordanite, $27PbS \cdot 7As_2S_3$ baumhauerite, Pb sulfarsenide
dufrenoysite, $2PbS \cdot As_2S_3$

2. By hydrothermal synthesis

robinsonite   zinckenite
boulangerite   phase K-1
madocite   semseyite, $9PbS \cdot 4Sb_2S_3$
rathite II   baumhauerite

3. By heating of dry charges at moderate ($\sim$400°C) temperatures

robinsonite   zinckenite
boulangerite   phase K-1
madocite   phase AN
geocronite, $27PbS \cdot 7Sb_2S_3$ guettardite, $9PbS \cdot 8(Sb,As)_2S_3$
jordanite   playfairite, $16PbS \cdot 9(Sb,As)_2S_3$
dufrenoysite

865 hours. Heating times for the remainder of the runs (category 3, Table 1) ranged from 3.5 to 1,463 hours.

Details of the starting compositions, temperatures, and durations of all the runs are not particularly significant; many of the sulfosalts were obtained under an extremely wide variety of conditions whereas others (e.g. playfairite) were obtained by chance in conditions which are unlikely to be duplicated. Appropriate data for individual minerals are given below. The sulfosalt products were readily categorized into two principal types correlative with the conditions under which the minerals were synthesized. Charges which were heated to 1,000°C and subsequently quenched in water had a mirror-like exterior surface and an interior which was either massive or consisted of compact material radially arranged. In both cases small vesicles were the principal cause of the low and erratic specific gravity values obtained by Berman balance measurement of the best selected fragments of fusion material.

Charges heated to less than 500°C, as in most of the runs, yielded fine granular aggregates which were occasionally pulverulent but generally of sufficient rigidity that they could be extruded from the tubes in coherent, rod-shaped masses. Commonly, these masses had fine-grained crystal tufts projecting toward the open (free space) end of the tube. Likewise, microscopic examination of the main charges showed them to consist of loosely spherulitic aggregates of acicular crystals held together with additional non-crystallized sulfosalt material. With the exception of robinsonite and zinckenite, the acicular crystals and tufts proved to be too small for single crystal work.

Boulangerite, $5PbS \cdot 2Sb_2S_3$. Boulangerite is one of the commonest

synthetic lead sulfantimonides. In this study, it was obtained from an extremely wide range of starting compositions, from both dry and hydrothermal charges, and was also obtained in the complete range of temperatures used (1,085 to 395°C). Although the mineral was also synthesized from charges containing minor amounts of arsenic, it is not known whether the element was taken into the boulangerite structure. In this connection, ten synthetic samples which gave the best boulangerite x-ray powder patterns were closely examined, and although slight variations in cell dimensions were noticeable, they could not be correlated with the arsenic or water content of the starting materials, or the duration of the runs. Starting compositions containing substantial amounts of arsenic generally yielded madocite rather than boulangerite; the only critical requirement for boulangerite synthesis thus appears to be the necessity of keeping the starting material low in arsenic.

Robinsonite, $7PbS \cdot 6Sb_2S_3$. Like boulangerite, robinsonite is a common and easily synthesized mineral. It has been obtained from starting compositions ranging from $PbS:Sb_2S_3 = 4:1$ to 3:4. Where this ratio exceeded 4:1, robinsonite did not form in either hydrothermal or dry runs. The mineral was also obtained in runs containing arsenic, but there is no evidence that this element was taken into the structure. The best conditions for synthesis appear to be a starting composition with $PbS:Sb_2S_3$ near 1:1, and heating of a dry charge. Wet charges generally yield zinckenite.

Because of differences in the intensities of a few lines of the x-ray powder pattern as given by Berry *et al.* (1952), there was some difficulty in the initial identification of the synthesized robinsonites. A crystal from one of the runs (BR-6, starting composition $3PbS \cdot 4Sb_2S_3$, heated at 580°C for 50 hours) was therefore mounted about the axis of elongation and rotation and zero-level Weissenberg photographs were obtained. The measured cell dimensions are in good agreement with those reported by Berry *et al.* (1952) for synthetic material:

	BR-6		Berry *et al.* (1952)
d_{100}	16.7 Å	d_{100}	16.40 Å
d_{010}	17.7	d_{010}	17.52
c	3.97	c	3.97
γ^*	88°10′	γ^*	88°10′

Baumhauerite and rathite II, lead sulfarsenides. Baumhauerite was obtained in two runs, neither of which contained antimony in the starting material. In the dry synthesis, a starting composition of $19PbS \cdot 13As_2S_3$ was heated for 3.5 hours at 1,000°C in an evacuated silica tube and quenched in cold water. The product is apparently homogenous but does not

give a very sharp x-ray powder pattern. In an essentially identical run (heating time 3 hours), the product gave such poor patterns that the material was classified as being amorphous. Charges containing a predominance of antimony over arsenic, but otherwise fired under identical conditions, consistently yielded madocite.

Baumhauerite was also obtained hydrothermally from a starting composition of $13PbS \cdot 9As_2S_3$ heated to 406°C for 865 hours. The silica capsule exploded at the terminal stage of the run, but a good sulfosalt yield was obtained from the bomb. The products obtained were baumhauerite, rathite II, and zinckenite. Antimony contamination was confirmed by x-ray spectrographic examination of the product.

Dufrenoysite, $2PbS \cdot As_2S_3$. Dufrenoysite was obtained in seven runs, all of which were dry charges. Only two were heated in pyrex tubes, the remainder being high temperature (1,000°C) quenches. In all cases the starting material contained no antimony, and neither veenite nor antimonian dufrenoysite was obtained in the present series of experiments. Starting compositions ranged from $9PbS \cdot As_2S_3$ to $13PbS \cdot 9As_2S_3$. Charges containing lead in excess of the formula requirements of dufrenoysite also contained major amounts of galena in the product. Excess arsenic is readily volatilized to an amorphous phase and hence does not appear as a contaminant in x-ray powder patterns.

Jordanite, $27PbS \cdot 7As_2S_3$, *and geocronite*, $27PbS \cdot 7Sb_2S_3$. The pure arsenic end-member of jordanite was obtained in five runs, one of which was a high temperature quench, and the remainder being oven-heated samples. All syntheses were under dry conditions. The $PbS:As_2S_3$ mol ratios of the charges ranged from 4:1 to 2:1. In three of the runs, the charges were heated to 405°C for 120 hours. The cell dimensions calculated from the x-ray powder pattern (Table 2) are $a = 8.92$, $b = 31.88$, $c = 8.457$ Å, $\beta = 117°43'$. For $27PbS \cdot 7As_2S_3$ the calculated density is 6.38 gm/cc, which is identical to the measured value reported for jordanite in Palache, Berman & Frondel (1944).

Geocronite was obtained in three runs in which the $PbS:Sb_2S_3$ ratios of the starting compositions were 5:1, 6:1, and 7:1. All were heated at 395°C for 571 hours. The products obtained were mixtures of geocronite and galena, plus small amounts of another unidentified sulfosalt. In none of the runs was arsenic recorded as being present in the starting material. To ensure that no error had been made in the recording of the conditions of synthesis, the geocronite products were checked by x-ray spectroscopy. The Sb-As ratio was found to be about 20:1, which makes the arsenic content sufficiently low as to be inconsequential even if all of it is in the geocronite.

X-ray powder patterns of synthetic jordanite and geocronite are very similar, but the pattern of the latter is very slightly contracted in the low

TABLE 2. X-RAY POWDER DATA FOR JORDANITE, CuKα$_1$ radiation; indexed with $a = 9.82$, $b = 31.88$, $c = 8.457$ Å, $\beta = 117°43'$.

I_{est}	d_{meas}(Å)	d_{calc}(Å)	hkl
$<\frac{1}{2}$	7.25	7.23	$\bar{1}11$
$\frac{1}{2}$	7.09	7.08	120
$\frac{1}{2}$	6.75	6.78,6.73	$021,\bar{1}21$
$\frac{1}{2}$	6.34	6.34	130
$\frac{1}{2}$	6.11	6.12	031
$\frac{1}{2}$	5.46	5.46	041
$\frac{1}{2}$	4.96	4.96	150
$\frac{1}{2}$	4.84	4.84	$\bar{1}51$
1	4.447	4.449,4.446	$\bar{2}01,111$
$<\frac{1}{2}$	4.403	4.408,4.406	$160,\bar{2}11$
$\frac{1}{2}$	4.322	4.321	$\bar{1}61$
1	4.191	4.192	$\bar{1}12$
$<\frac{1}{2}$	4.106	4.104	$\bar{2}31$
$<\frac{1}{2}$	3.987	3.985	080
$\frac{1}{2}$	3.945	3.948,3.945	$200,170$
$\frac{1}{2}$	3.889	3.891	071
2	3.829	3.833	220
$<\frac{1}{2}$	3.738	3.743,3.735	$002,\bar{1}42$
6	3.696	3.701,3.687	$230,\bar{2}12$
$\frac{1}{2}$	3.640	3.644	022
$<\frac{1}{2}$	3.620	3.615	$\bar{2}22$
7	3.534	3.538,3.531	$240,032$
4	3.500	3.504	$\bar{2}32$
4	3.385	3.388	042
5	3.367	3.365	$\bar{2}42$
$<\frac{1}{2}$	3.230	3.228	052
1	3.209	3.208	$\bar{2}52$
10	3.188	3.188	$0.10.0$
	3.169	3.169	260
5	3.056	3.060	062
6	3.045	3.043	$\bar{2}62$
4	2.983	2.983	270
$\frac{1}{2}$	2.919	2.919	221
4	2.893	2.892	072
5	2.880	2.877	$\bar{2}72$
$\frac{1}{2}$	2.859	2.860,2.859	$\bar{3}12,231$
2	2.802	2.805	280
	2.799	2.798	132
1	2.777	2.781,2.772	$191,\bar{3}32$
2	2.726	2.728,2.726	$082,142$
1	2.703	2.701	$\bar{3}42$
$\frac{1}{2}$	2.680	2.681,2.677	$\bar{2}33,\bar{3}51$
$<\frac{1}{2}$	2.659	2.657	$0.12.0$
$\frac{1}{2}$	2.637	2.640,2.632	$152,300$
$\frac{1}{2}$	2.620	2.623,2.618	$310,\bar{3}52$
1	2.593	2.597,2.593,2.591	$320,261,\bar{2}.10.1$
$<\frac{1}{2}$	2.572	2.574	092
$<\frac{1}{2}$	2.566	2.563	$\bar{2}92$

I_{est}	d_{meas}	I_{est}	d_{meas}	I_{est}	d_{meas}	I_{est}	d_{meas}
$<\frac{1}{2}$	2.548	3	2.228	1	2.048	$<\frac{1}{2}$	1.871
$\frac{1}{2}$	2.529	2	2.220	2	2.029	$<\frac{1}{2}$	1.866
$<\frac{1}{2}$	2.497	$<\frac{1}{2}$	2.203	$<\frac{1}{2}$	2.011	$<\frac{1}{2}$	1.857
$<\frac{1}{2}$	2.483	$<\frac{1}{2}$	2.178	$<\frac{1}{2}$	2.003	1	1.847
$\frac{1}{2}$	2.427	$<\frac{1}{2}$	2.165	$<\frac{1}{2}$	1.991	1	1.843
	2.420	$<\frac{1}{2}$	2.154	1	1.972	3	1.833
1	2.391	$<\frac{1}{2}$	2.140	$<\frac{1}{2}$	1.965	3	1.824
$<\frac{1}{2}$	2.369	$<\frac{1}{2}$	2.129	2	1.943	1	1.808
$<\frac{1}{2}$	2.343	4	2.113	$\frac{1}{2}$	1.914	$<\frac{1}{2}$	1.791
$<\frac{1}{2}$	2.329	$<\frac{1}{2}$	2.099	$<\frac{1}{2}$	1.903	$<\frac{1}{2}$	1.778
3	2.245	1	2.083	$<\frac{1}{2}$	1.894	3	1.762
1	2.239	2	2.052	1	1.884	1	1.752

2θ region. From the (0.10.0), (260), (062), ($\bar{2}$62), (270), and (072) powder diffraction lines, the cell dimensions of the synthetic geocronite are $a = 8.97$, $b = 32.03$, $c = 8.47$ Å, $\beta = 117°45'$. For $27PbS \cdot 7Sb_2S_3$, the calculated density is 6.81 gm/cc. Extrapolation of the density determinative curve for lead sulfantimonides (Jambor 1967a) leads to a predicted density of about 6.97 for geocronite. It may be that the determinative curve bends slightly when the Pb-Sb ratio is very high, but this and other possible explanations for the discrepancy have no factual support as yet. Directly related to this problem is the recent study of the substructure of jordanite by Wuensch & Nowacki (1966), who have tentatively suggested that the composition of jordanite may be $Pb_{26}As_{14}S_{46}$. However, the cell dimensions reported above for synthetic jordanite and the dimensions obtained by Wuensch & Nowacki both yield calculated densities in the range 6.15–6.17 for $Pb_{26}As_{14}S_{46}$. The calculated density is thus too low. Although the formula $Pb_{27}As_{14}S_{48}$ has therefore been retained for jordanite in the present paper, the equivalent formula for geocronite is not as satisfactory. The available data suggest that the jordanite-geocronite series has a more generalized formula, namely $Pb_{26+x}X_{14}S_{46-48}$. If this assumption is validated in the forthcoming detailed structural study of jordanite by Wuensch & Nowacki, then the problem regarding the high calculated density of geocronite will be eliminated. (Geocronite with $x = 0$ and Sb:As = 3:1 will have a density of about 6.46 gm/cc).

Zinckenite, $6PbS \cdot 7Sb_2S_3$ *or* $PbS \cdot Sb_2S_3$. Zinckenite was obtained in several runs, both dry and hydrothermal. The mineral forms most readily from starting compositions having a $PbS:Sb_2S_3$ ratio close to 1:1. Although guettardite tends to appear in charges having a very high arsenic content, coexisting zinckenite is also commonly present. X-ray examination of the zinckenite indicates that substantial but indefinite amounts of arsenic are taken into the lattice of the mineral. The principal manifestation of this arsenic uptake is shrinkage of the lattice. For example, the zinckenite diffraction lines indexed as 0004 and $0.18.\overline{18}.0$ in Berry & Thompson (1962) were measured on Guinier films of zinckenite from Bridge River, British Columbia (Nuffield 1946), and synthetic material from hydrothermal run BR-31 (starting composition $PbS \cdot (Sb,As)_2S_3$ with Sb:As = 3:1, plus excess S; heated 45 hrs. at 435°C). Quartz was used as an internal standard. The results compare as follows:

	Bridge River	BR-31
d_{0004}	2.162 Å	2.153 Å
$d_{0.18.\overline{18}.0}$	2.135	2.123
a	44.4	44.1
c	8.65	8.61

Madocite, $17PbS \cdot 8(Sb,As)_2S_3$. Madocite is easily synthesized and, on the basis of the present experiments, is the commonest product to form from four-component charges in the antimony-rich portion of the Pb-Sb-As-S system. Madocite was obtained in 3 of the hydrothermal runs, in 22 of the high temperature quenches, and in over 40 of the dry, moderate-temperature runs. Synthesis of the mineral is easiest when the starting material contains a substantial quantity of arsenic (Sb/As = 2 or 3).

Guettardite, $9PbS \cdot 8(Sb,As)_2S_3$. Guettardite was obtained in 22 runs, all of which were oven-heated dry charges. The starting material in all cases contained substantial quantities of arsenic. Zinckenite was generally also present in the synthetic product. Associated madocite was less common.

Some variations in the x-ray powder patterns of synthetic guettardite were noted. These variations are not due to contamination, as there are shifts among the 2θ values for certain pairs of lines. The shifts are relatively small, but their nature is such that the similarity of the powder patterns of guettardite and twinnite is increased. Because of the structural similarity of the two minerals, it seems reasonable to postulate the existence of a relationship in which guettardite, simplified as $Pb(Sb,As)_{2-x}S_{4-1.5x}$ undergoes a crystallographic transformation to twinnite, $Pb(Sb,As)_2S_4$, as x decreases.

Semseyite, $9PbS \cdot 4Sb_2S_3$. No attempt was made to duplicate the experiments carried out by Robinson (1947), who was particularly successful in synthesizing members of the plagionite group. In the few hydrothermal runs attempted here, semseyite was obtained with certainty in only one. The starting material with composition $7PbS \cdot Sb_2S_3$ and aqueous Na_2S added, was heated at 406°C and 16,000 p.s.i. for 865 hours. The product was semseyite and major galena.

Phase K-1, lead sulfantimonide. This artificial product, arbitrarily named phase K-1, was obtained in one hydrothermal run and is a common product in both high temperature quenches and oven-heated dry charges of widely ranging composition. The sulfantimonide is a definite new phase in the system Pb-Sb-S. Although the compound forms in the presence of abundant arsenic, no evidence of partial substitution for antimony in the lattice has been found.

X-ray powder data for phase K-1 are given in Table 3. The powder pattern resembles that of boulangerite and could easily be mistaken for a mixture containing that mineral. As yet phase K-1 has no known naturally occurring counterpart. Unfortunately, fibrous synthetic crystals proved to be too small for single crystal study.

In order to obtain an estimate of the composition of phase K-1, three synthetic samples selected on the basis of their apparent homogeneity

TABLE 3. X-RAY POWDER DATA FOR SYNTHETIC PHASE K-1, CuKα_1 radiation

I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)
$<\frac{1}{2}$	9.4	2	3.24	$<\frac{1}{2}$	2.615	$\frac{1}{2}$	1.776
$\frac{1}{2}$	7.6	$\frac{1}{2}$	3.16	1	2.590	3	1.737
$\frac{1}{2}$	6.8	1	3.15	$\frac{1}{2}$	2.573	$<\frac{1}{2}$	1.713
$<\frac{1}{2}$	6.27	$<\frac{1}{2}$	3.12	$<\frac{1}{2}$	2.570	$\frac{1}{2}$	1.688
$\frac{1}{2}$	6.13	1	3.10	$\frac{1}{2}$	2.519	1	1.659
$\frac{1}{2}$	4.29	$\frac{1}{2}$	3.06	$\frac{1}{2}$	2.440	$<\frac{1}{2}$	1.613
$<\frac{1}{2}$	4.17	5	3.00	1	2.424	$\frac{1}{2}$	1.588
1	4.12	1	2.98	$\frac{1}{2}$	2.380	$<\frac{1}{2}$	1.569
2	4.07	1	2.961	1	2.368	$\frac{1}{2}$	1.541
1	4.00	3	2.957	1	2.320	1	1.506
3	3.88	1	2.93	$\frac{1}{2}$	2.285	$<\frac{1}{2}$	1.488
$<\frac{1}{2}$	3.82	1	2.91	1	2.225	$<\frac{1}{2}$	1.475
$<\frac{1}{2}$	3.78	1	2.88	1	2.165	$<\frac{1}{2}$	1.447
10	3.72	1	2.86	$\frac{1}{2}$	2.132	$<\frac{1}{2}$	1.384
$\frac{1}{2}$	3.67	2	2.80	$<\frac{1}{2}$	2.074	$\frac{1}{2}$	1.375
2	3.63	6	2.78	4	2.009	$<\frac{1}{2}$	1.350
1	3.57	2	2.77	1	1.984	$\frac{1}{2}$	1.331
3	3.46	3	2.74	1	1.936	$\frac{1}{2}$	1.313
1	3.43	1	2.697	2	1.884	1	1.286
6	3.42	1	2.673	$\frac{1}{2}$	1.839	$\frac{1}{2}$	1.266
$\frac{1}{2}$	3.32	$\frac{1}{2}$	2.640	$\frac{1}{2}$	1.804		

(d-values 2.961 and 2.957 bracketed together)

TABLE 4. X-RAY POWDER DATA FOR SYNTHETIC LEAD SULFANTIMONIDE PHASE AN; 57 mm camera, CuKα radiation

I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)
$\frac{1}{2}$	4.11	10	3.43	$<\frac{1}{2}$	2.69	6	2.043
$\frac{1}{2}$	4.07	5	3.37	$<\frac{1}{2}$	2.65	1	1.999
1	4.01	2	3.24	$\frac{1}{2}$	2.50	$<\frac{1}{2}$	1.957
5	3.95	$\frac{1}{2}$	3.22	1	2.41	$<\frac{1}{2}$	1.927
$<\frac{1}{2}$	3.85	1	3.12	1	2.325	$<\frac{1}{2}$	1.900
4	3.78	1	2.95	$\frac{1}{2}$	2.283	$\frac{1}{2}$	1.862
1	3.67	5B	2.92	1	2.212	1	1.751
2	3.56	5	2.77	$<\frac{1}{2}$	2.135	$\frac{1}{2}$	1.711
6	3.51	5	2.73	$<\frac{1}{2}$	2.071	$<\frac{1}{2}$	1.685
4	3.47						

were examined by x-ray spectroscopy. The PbS:Sb$_2$S$_3$:As$_2$S$_3$ mol ratios were as follows: 1:0.38:0.03; 1:0.47:0; 1:0.42:0. The formula ratio is thus close to 24PbS·10Sb$_2$S$_3$, and as the starting composition of two of the samples was 24PbS·11Sb$_2$S$_3$, it is likely that the formula of phase K-1 is in the neighbourhood of 12PbS·5Sb$_2$S$_3$.

Phase AN, lead sulfantimonide. Phase AN was obtained in 7 runs, 5 of which were high temperature (1,000°C) quenches. As nearly all 57 mm films of the phase are identical, the results are too repetitive to avoid the conclusion that a distinct lead sulfantimonide phase is present. The x-ray powder pattern (Table 4) is similar to those of other lead sulfantimonides, but in detail it is distinctive and easily recognizable.

Arsenic was present in the starting material of all the runs and in 6 of

these the $PbS:(Sb,As)_2S_3$ ratio was 1:1. The formula ratio of phase AN is probably closer to 6:5, the relative increase in lead occurring by volatilization of arsenic in the runs.

Playfairite, $16PbS \cdot 9(Sb,As)_2S_3$. Playfairite was obtained in only one run; madocite was an associated product. The dry starting composition of $13PbS \cdot 9(Sb,As)_2S_3$ with Sb:As = 3:1, was heated to 405°C for 168 hours and a pulverulent, heterogeneous product obtained. It appears that playfairite formed at the top of the charge, that is, adjacent to the column of open space, whereas madocite was predominant in the bottom portion.

Summary of sulfosalt syntheses

A resumé of the conditions under which the various sulfosalts were synthesized is given in Table 1. In the Pb-As-S system, the following artificial sulfosalts were obtained: dufrenoysite, jordanite, rathite II, and baumhauerite. Because of the conditions of synthesis, products appearing in the Pb-Sb-S system cannot generally be isolated from those appearing in the antimony-rich portion of the Pb-Sb-As-S system. In the latter, the following sulfosalts were obtained: boulangerite, robinsonite, madocite, semseyite, zinckenite, phase K-1, phase AN, geocronite, guettardite and playfairite.

The experiments have also demonstrated that significant amounts of arsenic may be taken into the lattice of zinckenite and madocite. Phase K-1, phase AN, playfairite, madocite, guettardite, and geocronite have been synthesized, or identified in synthetic products, for the first time.

PARAGENESIS

Introduction

Studies of the age relationships of the Madoc sulfosalts are based almost wholly on the small amount of material which was collected in 1924. Despite this limitation, the scheme outlined below may be of value as an indication of the generalized sequence which has been followed in the evolution of the sulfosalts at Madoc.

Age relationships

Because several of the sulfosalts occur in very sparse amounts, it has not been possible to satisfactorily delimit the relative ages of some of the minerals. The sequence that has been deduced is summarized in Table 5. Oldest minerals are listed at the top, and the progression is toward the younger minerals at the bottom. Vertical arrows indicate that the youngest possible age of a particular mineral was not established. For

TABLE 5. RELATIVE AGES OF THE MADOC SULFOSALTS AND SULFIDES

			Approximate Sb/As
Early	pyrite, arsenopyrite, galena		
	sphalerite (+chalcopyrite?)		
	baumhauerite		1.0
	guettardite		1.1
	veenite		1.5
	twinnite		1.5
	sorbyite, sterryite		2.8, 3
	jamesonite ↓		
		zinckenite, QM	
	madocite		4.5
	boulangerite ↓		8
		geocronite	
	playfairite, launayite	↓	8, 12
	tetrahedrite		
	bournonite, chalcopyrite		
Late	semsyite		

example, sterryite and sorbyite replaced veenite, but the relationship of sterryite and sorbyite to minerals lower (younger) in the sequence is not known.

Only a few brief explanatory notes for Table 5 will be made. Veining of one mineral by another has been virtually the only criterion used to establish a relative age. Pyrite, arsenopyrite, and galena are grouped together as being the oldest minerals in the suite. Galena is cut by sphalerite, which is in turn veined by the sulfosalts. Guettardite cuts baumhauerite, twinnite cuts veenite, and jamesonite has replaced veenite. Because baumhauerite and guettardite have not been seen in contact with the numerous younger lead sulfantimonides which cut veenite, they are assumed to have preceded veenite in the depositional sequence. The only remaining ambiguity involves geocronite, semseyite, and the copper-bearing sulfosalts. Geocronite appears to have preceded bournonite whereas semseyite appears to have followed it; this depositional order is, however, not firmly established.

Chemical relationships

In order to obtain a better indication of the chemical changes which took place during the deposition of the metallic minerals, their approximate antimony–arsenic ratios are given in Table 5. Although, as was mentioned earlier, the ages of some of the minerals have not been
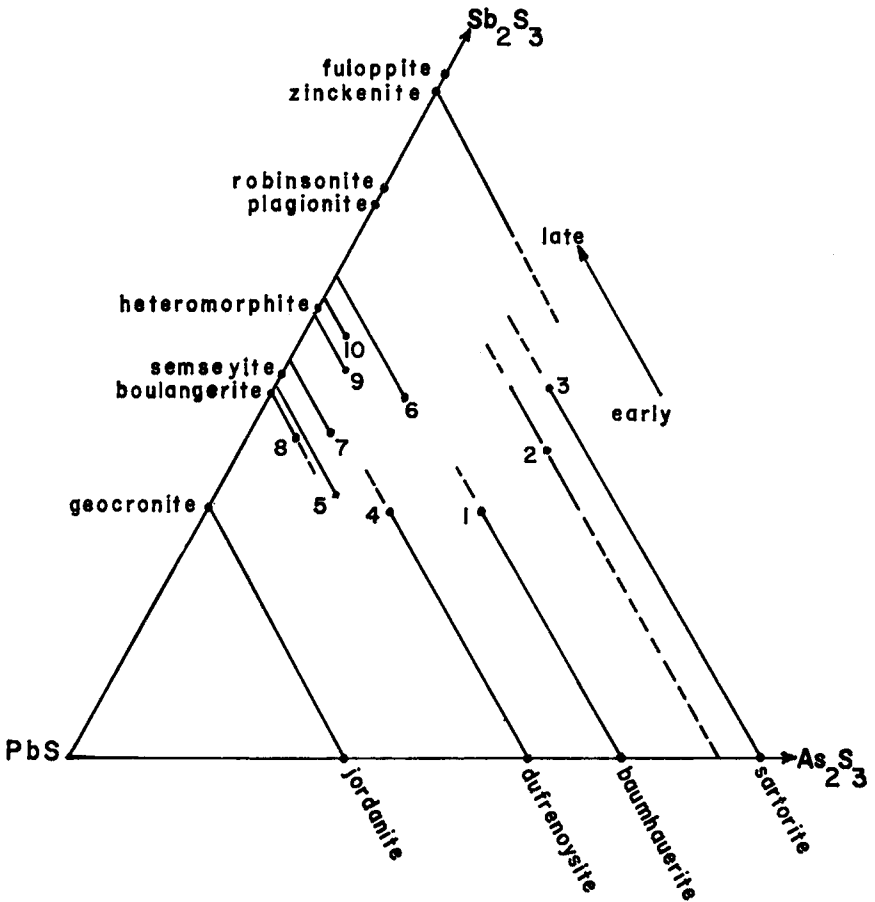
FIG. 1. Composition diagram and depositional sequence of the Madoc sulfosalts. (1) antimonian baumhauerite (2) guettardite (3) twinnite (4) veenite (5) sterryite (6) sorbyite (7) madocite (8) arsenian boulangerite (9) playfairite (10) launayite. Stoichiometric compositions have been assumed for all minerals. The position of baumhauerite is approximate and, on the basis of the microprobe analyses, could be shifted to the right (closer to the As_2S_3 apex).

established with certainty, in the following discussion the listing given in Table 5 is assumed to be correct.

The depositional trends of the elements are more readily visualized if plotted on a triangular diagram such as that shown in Fig. 1. The apices of the triangle are galena (PbS), stibnite (Sb_2S_3), and orpiment (As_2S_3). As most lead sulfarsenides and sulfantimonides plot in the lead-rich portion of the triangle, this area has been expanded and arrows used to indicate the directions of the stibnite and orpiment end-points. The

molecular ratios of all the well-defined sulfosalt minerals on the PbS-Sb_2S_3 join have been plotted on the figure, but only the relevant sulfarsenides are included. The extent of Sb-As solid solution is also indicated.

It is well known (McKinstry & Kennedy 1957) that for minerals along the PbS-Sb_2S_3 join, galena in ore deposits generally forms first and is followed by lead sulfantimonides and then stibnite. In other words, there is a progressive enrichment in the more volatile component, and hence the high PbS:Sb_2S_3 ratios of the early sulfantimonides are lowered towards a 1:1 ratio in the terminal stages of lead sulfosalt deposition. A similar sequence is known (McKinstry & Kennedy 1957) for the minerals along the PbS-As_2S_3 join; that is, galena is precipitated first and orpiment last. There are no equivalent data for the system Pb-Sb-As-S, but it is assumed here that arsenic, being lighter and smaller than antimony, will be the more mobile element of the pair. The dominating factor, however, should be the superior mobility of sulfur, and from the aforementioned PbS-Sb_2S_3 and PbS-As_2S_3 systems, it is apparent that sulfosalts containing the least amount of sulfur should precipitate first if the principle of progressive enrichment in the most volatile component is adhered to.

The oldest sulfosalts at Madoc are baumhauerite (1), guettardite (2), twinnite (3), and veenite (4). From the composition diagram (Fig. 1) it is evident that the PbS:$(Sb,As)_2S_3$ ratios of these four minerals show no fixed trend towards either increase or depletion. From oldest to youngest, however, the four minerals do show a progressive decrease in arsenic relative to antimony in the $(Sb,As)_2S_3$ solid solution. This can be seen in Fig. 1 by projecting lines from the PbS apex through the points representing the compositions of the Madoc sulfosalts. The trend of decreasing arsenic ratios is also apparent when the above minerals are compared as a group to the other lead sulfantimonides, the latter lying much closer to the PbS-Sb_2S_3 join. Likewise, the group as a whole shows that in the initial stage of deposition the most volatile components decreased rather than increased.

Following the above minerals, the next stage in the depositional scheme is marked by the appearance of jamesonite. As iron is an essential constituent of this mineral, its composition does not lie on the PbS-Sb_2S_3-As_2S_3 plane. However, the sequence madocite (7), boulangerite (8), playfairite-launayite (9–10) is again in harmony with precipitation according to decreasing As-Sb ratios. As was mentioned earlier, both arsenian and non-arsenian boulangerites occur in the Madoc suite. Theoretically, the non-arsenian boulangerite should be consistently younger than madocite, but this has not been proved, possibly because of the limited number of observations.

The principle of precipitation according to decreasing As ratios in the

sulfantimonides is so well adhered to that it would appear that sorbyite and sterryite are correctly positioned in Table 5; that is, they have not replaced any of the minerals lower in the sequence. There is too little evidence to indicate whether the sulfosalts on the PbS-Sb$_2$S$_3$ join follow the geocronite (older)–semseyite (younger) trend, but if so, then the complete hypothetical paragenetic sequence for the lead sulfantimonides conforms to the listing given in Table 6.

TABLE 6. HYPOTHETICAL PARAGENETIC SEQUENCE FOR
LEAD-ANTIMONY-ARSENIC SULFOSALTS AT MADOC,
ONTARIO

Oldest	antimonian baumhauerite
	guettardite
	veenite
	twinnite
	sorbyite
	sterryite
	madocite
	arsenian boulangerite
	geocronite
	playfairite
	launayite
	boulangerite
	semseyite
	mineral QM
	robinsonite
Youngest	zinckenite

Boulangerite appears in two positions in Table 6 because its compositional variability is known. So far, veenite is the only other Madoc sulfosalt in which Sb-As variations have been recognized; this feature, with its manifold potential ramifications, was encountered so recently that analytical data have not yet been obtained. The x-ray powder patterns do, however, indicate that the composition variation is toward a more antimony-rich member than the previously analyzed material reported in Part 1.

Conclusions

The lead-antimony sulfosalts were deposited in an orderly sequence which corresponds to decreasing activity of As$_2$S$_3$ in the Pb-Sb-As-S system. For sulfosalts lying very close to, or along the PbS-Sb$_2$S$_3$ join, the depositional trend may have been towards increasing activity of Sb$_2$S$_3$.

The early appearance of arsenic-rich minerals (veenite, twinnite, guettardite, baumhauerite) can thus be explained by the fact that the As:Sb activity ratio decreased rather than increased. Had the trend been towards increasing As$_2$S$_3$ activity with time, these minerals would

have formed late, or alternatively, the effect might have been to extend the amount of As substitution in sulfantimonides such as boulangerite.

Origin

The general geological environment in which the Madoc sulfosalts occur was given in Part 1 (Jambor 1967a). One aspect not mentioned previously is the possibility that a crude zonal arrangement of the sulfosalts may be present. Specimens collected to date show that the sulfosalts disseminated in the marbles around the pit are antimony-rich (predominantly boulangerite and jamesonite) whereas arsenic-rich sulfosalts such as veenite appear to be restricted to the pit itself.

Intrusion of the marbles by the nearby granitic pluton is believed to have provided both a partial structural control and a metal source. No simple theory can account for all of the observed paragenetic relations. The oldest minerals (pyrite, arsenopyrite, galena, sphalerite) constitute an assemblage typical of many mineral deposits; the observed sequence, with sphalerite younger than galena, deviates from the general trend of mineral deposition in ore deposits. The absence of copper-bearing sulfosalts can also be considered anomalous as these normally precede lead sulfosalts. In the intermediate and final depositional stages, the progressive decrease of lead sulfosalts rich in arsenic is contrary to what is expected in an arsenic-antimony solid solution series. The relative decrease in arsenic chemical potential could result from a rise in temperature, a decrease in pressure, or a combination of these. However, if the semi-metal content of the ore-forming medium available at the site at the time of deposition is currently represented by the bulk chemical composition of all the sulfosalt minerals, then pressure-temperature changes on this very antimony-rich material cannot alone account for the relatively late precipitation of antimony or the apparent zonal arrangement of the sulfosalts—both of these should be the reverse of what is now found.

The mineral compositions and paragenetic relationships of the Madoc sulfosalts indicate that, with increasing time, the cumulative effect was to have arsenic progressively taken out of the system; until arsenic was essentially exhausted, however, its removal appears to have had little effect on the antimony. Assuming that antimony and arsenic were available in solution, the solubilities of their simple compounds indicate that the arsenic-bearing sulfosalts would precipitate first; the antimony compounds, being less soluble, would remain in solution longer (sulfides that are least soluble in terms of their activity product constants behave as if they were the most soluble in the ore-forming fluid; Barton 1959).

The antimony-rich compounds would therefore be among the youngest minerals deposited and would also be expected to penetrate farthest into the country rock, thus explaining both the sequence and zoning. Copper, being the least soluble cation present, would combine with antimony to form compounds late in the sequence, as is the case, but the limited avail-ability of the metal would preclude any extensive penetration into the country rock.

Some antimony would undoubtedly be precipitated with the arsenic. Upon exhaustion of arsenic, however, an arbitrarily selected P-T variable (temperature) would by default become the principal control. With its progressive decline with time the relative chemical potential of Sb_2S_3 would increase and the normal sequence boulangerite-semseyite-zinckenite would ensue.

The only sulfosalt deposit with which Madoc is comparable is Lengen-bach, Binnental, Switzerland. A recent description of the reopened Lengenbach quarry and its mineralogy (predominantly Pb, Ag, As sulfosalts) is given in the excellent comprehensive report by Graeser (1965). He has attributed the origin of the sulfosalts to arsenic-bearing solutions which re-worked a pre-Alpine sulfide deposit consisting mainly of galena, sphalerite, and pyrite. Applying Graeser's theory to Madoc, we could assume that an older sulfide deposit (pyrite and galena only) was attacked and modified by solutions from the adjacent granitic pluton. Although it is not accepted here, there is no strong evidence to either support or disprove the theory: the old, pre-sphalerite age of the galena is somewhat favourable; the general paucity of galena and, more impor-tant, its absence in the outer zone of disseminated mineralization, is strongly unfavourable. With the necessity of a pre-existing sulfide body, one more element of chance would thus be added to the conditions needed to form the Madoc deposit. Paradoxically, it is this added factor that makes the theory appealing, for the uniqueness of Madoc and Lengenbach is an eloquent testimonial of the rarity with which all the prerequisites are fulfilled.

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