NEW LEAD SULFANTIMONIDES FROM MADOC, ONTARIO—PART I

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ABSTRACT

A small prospect pit in Precambrian marble at Madoc, Ontario, contains at least eight new lead sulfantimonides and ten previously known sulfosalts. The compositions of the minerals were determined by microprobe analyses and determinative curves constructed by plotting the mol ratio of Pb/Sb_2 and Pb/As_2 against the density of known lead sulfarsenides and sulfantimonides.

Microprobe analyses of the new mineral *madocite* correspond to $7PbS.3(Sb, As)_2S_3$, but the true formula may be $17PbS.8(Sb, As)_2S_3$. Madocite is orthorhombic, $a = 27.2$, $b = 34.1$, $c = 2c' = 8.12$ Å, pseudocell space group $Pba2$ or $Pbam$, perfect {010} cleavage, $D_x = 5.98$ for $Z = 4$. The strongest lines of the powder pattern are 3.396 (10), 3.355 (9), 2.720 (8), 3.67 (7), 2.925 (6).

Veenite, $2PbS.(Sb, As)_2S_3$ with Sb:As = 5:3, has an orthorhombic pseudocell with $a' = \frac{1}{2}a = 4.22$, $b = 26.2$, $c = 7.90$ Å, space group $P2_1cn$ or $Pmcn$, $D_m = 5.92$, $D_x = 5.96$ for $Z = 8$. The x-ray powder pattern is like that of dufrenoysite, with strongest lines at 3.81 (10), 3.03 (9), 3.42 (8), 3.26 (8), 2.76 (7).

INTRODUCTION

For several years in the early 1920's, Geological Survey of Canada field parties under the direction of M. E. Wilson mapped the area around Madoc, Ontario. Part of the effort was directed toward examination of the economic mineral deposits, particularly those of fluorite. Field notes kindly lent to the writer by Dr. Wilson show that on July 5, 1924, one of his assistants examined a cluster of small prospect pits in marble in concession XIV, Huntingdon township. Impregnation of the marble by sphalerite, pyrite, and jamesonite was noted and about two pounds of grab sample material collected. This material was brought to the Geological Survey in Ottawa, and although no detailed mineralogical examination was carried out, sufficient work was apparently done to indicate that the suite contained an unidentified and possibly new sulfosalt. In 1960 Dr. S. C. Robinson drew attention to the specimen containing the unidentified mineral, and the writer subsequently reported (Jambor, 1962) that several new sulfosalts had been found in the Madoc material. In 1963, the writer rediscovered the prospect pits and collected additional mineral specimens. The Madoc suite contains at least 18 sulfosalts, of which half are new. The present paper is concerned principally with the determinative methods used for deriving the compositions of the Madoc sulfosalts, and includes descriptions of two of the new minerals.

GEOLOGICAL SETTING

The sulfosalts described here occur in lot 12, concession XIV, Huntingdon Township, on the farm of Mr. Ed Taylor of Madoc. The geology of the area has been described by Wilson (1921, 1940) and, more recently, by Hewitt (1964). The only consolidated rocks in the area are of probable Ordovician and Precambrian (Grenville) ages. In the vicinity of Madoc itself, the Paleozoic rocks are restricted to scattered outliers of Ordovician limestone belonging to the Black River and Trenton groups. The predominant rocks throughout the southern half of the Madoc area have been grouped by Hewitt (1964) into two units: (1) a metasedimentary unit consisting of marble, lime silicate rock, skarn, and (2) a plutonic unit consisting of granitic gneiss, hybrid granite gneiss, and granite pegmatite. According to Hewitt (1964, p. 4), the metasediments are of greenschist facies metamorphic grade. The Madoc sulfosalts occur within marbles of the aforementioned Precambrian metasedimentary unit, exposed at the margin of an intrusion belonging to the plutonic unit.

In the vicinity of the sulfosalt occurrence, the marbles strike 10 to 15 degrees northeast and dip about 80 degrees west. The marble is thin-bedded, with individual units typically being less than a foot thick. Most of the rock is white, and fine- to medium-grained, but portions are pale grey to cream-coloured. In rare cases, the rock is white, compact, and sufficiently massive that it is suitable for quarrying.

Calcite and dolomite are the principal constituents of the marble; magnesite is also present, but only in trace amounts. Very fine-grained, dense marble generally consists mostly of dolomite, whereas calcite predominates in coarser-grained material. In a few cases, fine-grained phlogopite is a major constituent, and both muscovite and phlogopite were noted in several places to be abundant along fractures and bedding surfaces.

The margins of the Precambrian plutonic unit are exposed approximately 900 feet east of the sulfosalt occurrence. The contact is not well exposed, and small irregular injections or apophyses have not been seen. Rather, the marble has apparently been warped in order to accommodate the pluton. In the one outcrop where both the plutonic and carbonate units are exposed together, the 10 to 15 degree northeasterly strike of the marble has been changed to 25 degrees northwest. Except for a small patch of amphibole, no megascopic mineralogical changes in the marble at the contact were observed. The plutonic unit is medium-grained and deep pink in the main mass, but is characteristically fine-grained and very pale pink to white for a few tens of feet at its periphery. Although the pluton has not been examined in detail, the main mass appears to be granite, but peripheral material has been substantially desilicated.

The sulfosalts collected by the writer occurred in the marble over an area about 25 feet long and 5 feet wide, with the larger dimension being parallel to the strike of the carbonate beds. The locus of the site was a small prospect pit which has been enlarged and considerably deepened by blasting in 1966. According to H. R. Steacy (personal communication), there has been no decrease in the amount of sulfosalt material with depth; the occurrence may thus be more extensive than is indicated by the surface exposures. The principal sulfides and sulfosalts are sphalerite, pyrite, arsenopyrite, boulangerite, and jamesonite, with sphalerite being by far the most abundant. The minerals occur principally as small masses and minute stringers in the marble of the pit, and are also present as small disseminated grains in the adjacent area. Both fractures and bedding planes were favourable depositional sites. The principal silicates are chlorite, actinolite, and microscopically euhedral $2M_1$ muscovite, but none occurs in any abundance. Rare grains of plagioclase and euhedral, pale yellow tourmaline have been noted under the microscope.

Deposition of the epigenetic minerals was probably related to intrusion of the adjacent plutonic unit. The folding evident in some hand specimens, the warped appearance of the marble on the face of the pit, and the abundance of small mineralized fractures along deformed twinned calcite grains are probably manifestations of the adjustment required to accommodate the plutonic unit.

DETERMINATIVE METHODS

Electron microprobe analyses

All the new Madoc sulfosalts were analyzed by G. R. Lachance at the Geological Survey of Canada with a microprobe manufactured by Elion Instruments Inc., Burlington, New Jersey. For most of the minerals, the area traversed by the beam was 25 microns square; where there were indications of damage to the specimen surface, the area was increased to a 60 micron square. At 30KV, the intensities of the $K\alpha$ line of sulfur and $L\alpha$ line of antimony were measured with gypsum as the analyzing crystal; As$K\beta$ and Pb$L\beta$ were read using lithium fluoride. For the measured intensities, a minimum of two 100-second counts per element were obtained, and at least two spots were counted on any particular mineral grain.

The metals of lead and antimony and the following minerals were used as analytical standards: galena, Rossie, New York; stibnite, St. George, York Co., New Brunswick; kermesite, possibly from York Co., New Brunswick; boulangerite, Yale District, British Columbia; semseyite crystals, Kisbanya, Hungary; meneghinite, Bottino, Tuscany; jamesonite, Itos mine, Oruro, Bolivia (ROM 14506); jordanite, Binnental, Switzerland; and gratonite, Cerro de Pasco, Peru. Sartorite and dufrenoysite from Binnental were used as secondary arsenic standards. The elemental concentrations in the above minerals were calculated from the ideal formulae given in Berry & Thompson (1962). The net counts per second for the elements in the standards were plotted against the elemental concentrations and the resulting linear relationships (Figs. 1 and 2) were used as determinative curves for the unknown minerals. Concentrations in the unknowns all fall on the calibration curves, so that extrapolations are not necessary.

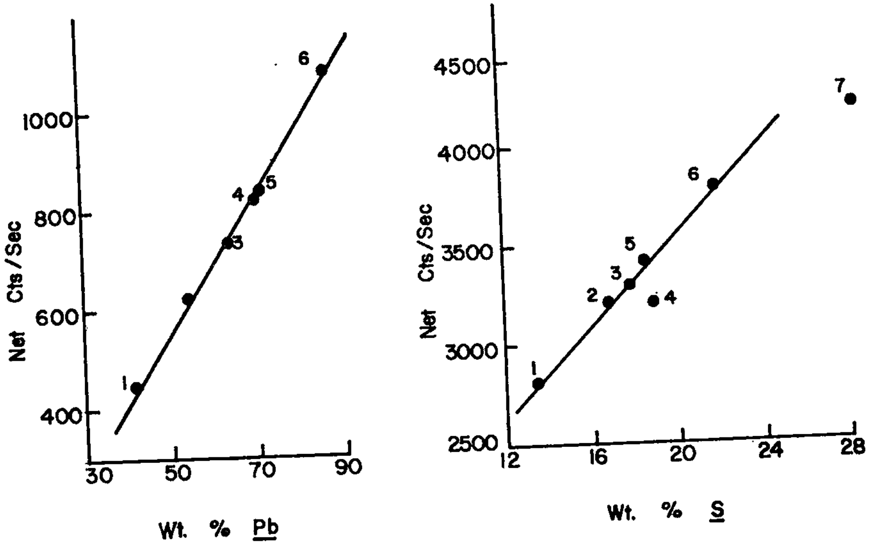

FIG. 1. Typical working curves for electron microprobe analyses of the Madoc sulfosalts. Pb standards are (1) jamesonite (2) semseyite (3) meneghinite (4) jordanite (5) gratonite (6) galena. S standards are (1) galena (2) meneghinite (3) gratonite (4) jordanite (5) semseyite (6) jamesonite (7) stibnite.

In addition to the reading of the standards before, during and after measurement of the unknowns, several sulfosalts of known composition were analyzed with the new minerals in order to check the accuracy of the results. From comparison with such control samples, the absolute error attached to the reported value of each major element is estimated to be ±3 per cent, but the sum of errors for the four elements in each complete analysis generally does not exceed 6 per cent. Reproducibility of the gross and net counts per second obtained from several spots on a grain was excellent. For both major and minor elements, the resulting analytical weight percentages obtained for each spot had to agree within ±2 per cent to be considered acceptable.

While the averages of the results obtained from many of the analyses are in excellent agreement with idealized formula requirements, substantially erroneous values are not rare. For example, the determined lead values for robinsonite were consistently 6 to 7 per cent higher than the theoretical requirements for $7PbS.6Sb_2S_3$, but there is no other evidence to suggest that the above formula is incorrect. Because of such unpredictable inconsistencies, the microprobe analyses have been used only as a guide in deriving the formulae of some of the new minerals; more reliance has been placed on the density determinative curves described below.

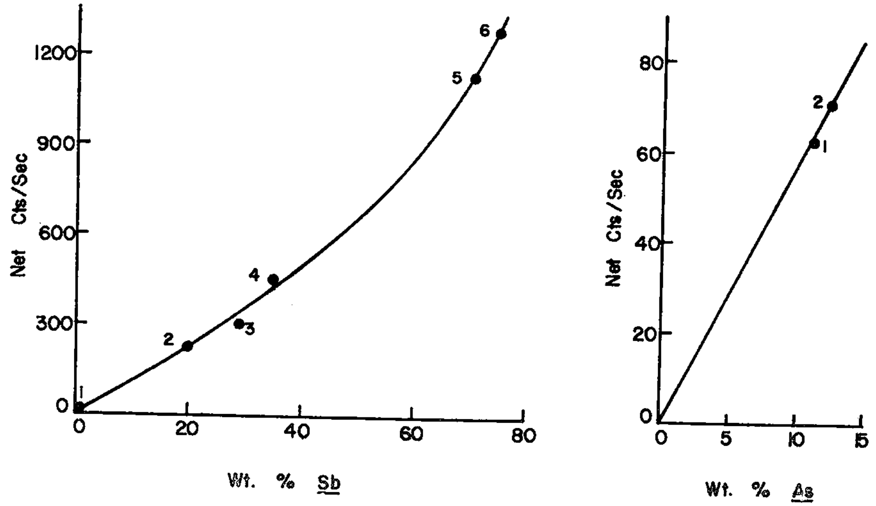

FIG. 2. Typical working curves for microprobe analyses of the Madoc sulfosalts. Sb standards are (1) gratonite (2) meneghinite (3) semseyite (4) jamesonite (5) stibnite (6) kermesite. As standards are (1) gratonite (2) jordanite.

Density determinative curves

As nearly all the new Madoc sulfosalts occur in quantities which preclude the possibility of measuring specific gravity by conventional methods, some new definitive criterion was necessary if the compositions of these complex minerals were to be obtained with some assurance of validity.

It has been known for many years that among the lead antimony sulfosalts there is an increase in density which corresponds to an increase in the weight per cent PbS present in a particular mineral. Robinson (1947, p. 33) plotted this relationship and concluded that it would be "useful as an approximate guide to the composition of any lead sulphantimonide, whose specific gravity is known". It could not serve as more than an approximate guide because the individual points of the plot are considerably scattered; the aforementioned composition-density trend is nevertheless clearly apparent. Kostov (1957) obtained a similar relationship by plotting the weight per cent As, Sb, or Bi of a sulfosalt against its density.

It seemed more logical to the present writer that molecular proportions rather than weight percentages should be considered. Utilization of this concept leads to the linear relationship shown in Fig. 3. The selection of densities used in drawing up the curve is given in Table 1.

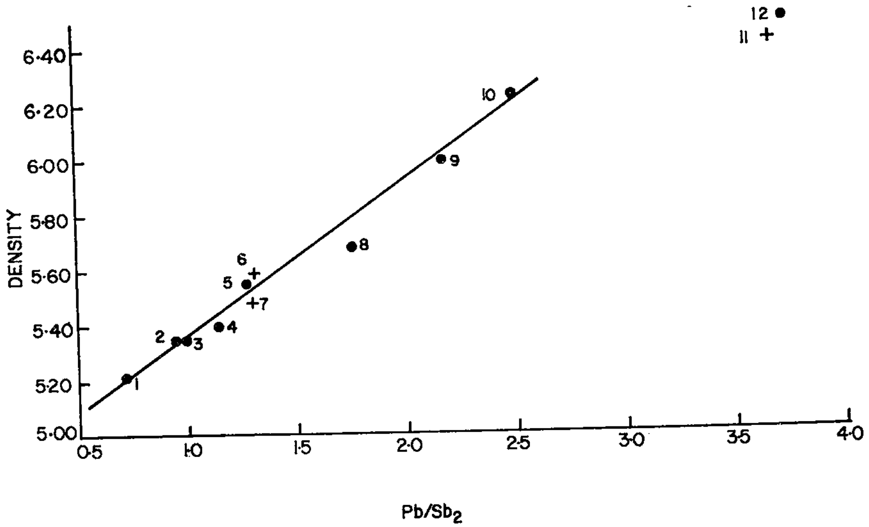

FIG. 3. Density determinative curve for Pb sulfantimonides: (1) fülöppite, (2) zinckenite, $6PbS.7Sb_2S_3$, (3) zinckenite, $6PbS.6Sb_2S_3$, (4) robinsonite, (5) plagionite, (6) jamesonite, (7) parajamesonite, (8) heteromorphite, (9) semseyite, (10) boulangerite, (11) meneghinite, (12) geocronite.

The two heaviest sulfosalts, that is, meneghinite and geocronite, do not fall along the straight line of the sulfantimonide curve. As meneghinite contains essential copper in its formula, only the apparently discrepant density of geocronite is of some concern. However, Douglass *et al.* (1954) obtained for geocronite from Park City, Utah, cell dimensions and analytical data which yield a calculated density of 6.70. The method of using the density determinative curves will be explained below; for now, it can be stated that they yield a predicted density of 6.76 for the above geocronite. The measured value may thus be too low.

TABLE 1. MEASURED DENSITIES OF SOME LEAD SULFANTIMONIDES

Name	Composition	PbS/Sb_2	Density	Reference
Fülöppite	$3PbS.4Sb_2S_3$	0.750	5.23	Palache *et al.* (1944)
Zinckenite	$6PbS.7Sb_2S_3$	0.857	5.36	Harris (1965)
	$PbS.Sb_2S_3$	1.000	5.36	Nuffield (1945)
Robinsonite	$7PbS.6Sb_2S_3$	1.167	5.40*	Berry *et al.* (1952)
Plagionite	$5PbS.4Sb_2S_3$	1.250	5.56	Nuffield *et al.* (1944)
Heteromorphite	$7PbS.4Sb_2S_3$	1.750	5.73	Palache *et al.* (1944)
Semseyite	$9PbS.4Sb_2S_3$	2.250	6.03	Nuffield *et al.* (1944)
Boulangerite	$5PbS.2Sb_2S_3$	2.500	6.23	Berry (1940b)
Geocronite	$27PbS.7Sb_2S_3$	3.86	6.5	Douglass *et al.* (1954)
Jamesonite	$4PbS.FeS.3Sb_2S_3$	1.33	5.63	Berry (1940a)
Parajamesonite	$4PbS.FeS.3Sb_2S_3$	1.33	5.48	Zsivny *et al.* (1947)
Meneghinite	$Cu_2S.26PbS.7Sb_2S_3$	3.71	6.36	Palache *et al.* (1944)

*Calculated.

Because there are substantial variations among published density values of sulfarsenides, a good determinative curve can be constructed only if some arbitrary selection of the available data is made. For example, the measured and calculated densities of sartorite, $PbS.As_2S_3$, are respectively given as 5.10 and 5.07 in Palache *et al.* (1944), but the calculated value from the cell dimensions of Nowacki *et al.* (1961) is 4.968 and the observed value stated to be 5.05. On the other hand, the calculated density of synthetic sartorite, based on the cell dimensions given by Rösch & Hellner (1959), is 5.12. Similar discrepancies are present for other sulfarsenides. It was felt that the measured densities of dufrenoysite and sartorite should be reliable and these values have therefore been used in Fig. 4. Similarly, the calculated values for rathites and baumhauerite as given by Le Bihan (1962) have been accepted *in toto.* The complete listing of data used in the construction of Fig. 4 is given in Table 2. With the exception of rathite I and gratonite, an excellent linear relationship is obtained. For rathite I the cell dimensions given by Nowacki *et al.* (1964) yield a calculated density of 5.256, in much better agreement with the determinative curve. Gratonite falls so far off the curve that it has not been plotted on Fig. 4. The probable explanation for the deviation is that gratonite is rhombohedral and is the only sulfosalt known to have lead in five-fold co-ordination. The remaining sulfarsenides possess monoclinic or lower symmetry. Thus, the synthetic trigonal and cubic phases of sartorite synthesized by Rösch & Hellner (1959) likewise do not satisfactorily plot on the determinative curve. On the other hand, the position of zinckenite on the sulfantimonide curve is unaffected, presumably because, despite the hexagonal symmetry, the mineral is structurally similar to the other lead sulfantimonides.

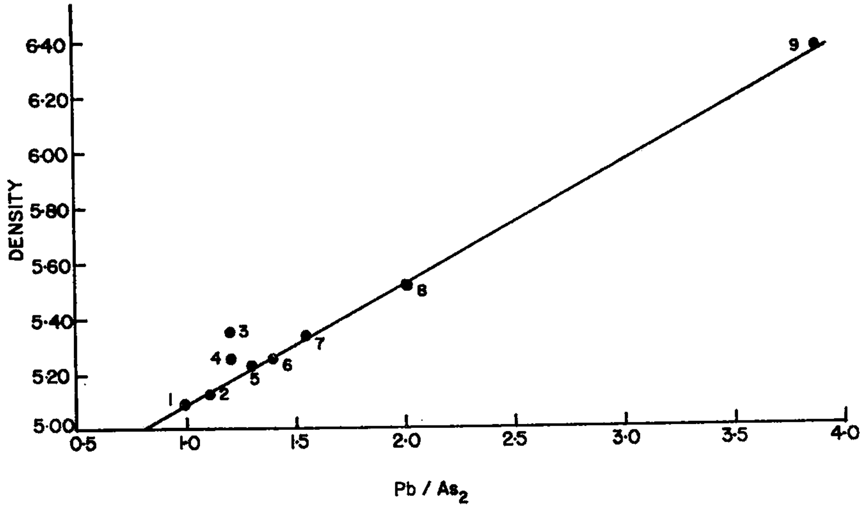

FIG. 4. Density determinative curve for Pb sulfarsenides: (1) sartorite, (2) baumhauerite, Ī, (3) rathite I of Le Bihan, (4) rathite I of Nowacki *et al.*, (5) baumhauerite, 1, (6) rathite II, (7) rathite Ia, (8) dufrenoysite, (9) jordanite.

TABLE 2. MEASURED (*m*) AND CALCULATED (*c*) DENSITIES OF LEAD SULFARSENIDES

Name	Composition	PbS/As_2	Density	Reference
Sartorite	$PbS.As_2S_3$	1.00	5.10(*m*)	Palache *et al.* (1944)
Baumhauerite, Ī	$Pb_{10}As_{18}S_{36}$	1.11	5.13(*c*)	Le Bihan (1962)
Rathite I, III	$Pb_{12}As_{20}S_{40}$	1.20	5.35(*c*)	Le Bihan (1962)
Baumhauerite, 1	$Pb_{11}As_{17}S_{36}$	1.29	5.22(*c*)	Nowacki (1964)
Rathite II	$Pb_9As_{13}S_{28}$	1.38	5.27(*c*)	Le Bihan (1962)
Rathite Ia	$Pb_{14}As_{18}S_{40}$	1.56	5.34(*c*)	Le Bihan (1962)
Dufrenoysite	$2PbS.As_2S_3$	2.00	5.53(*m*)	Palache *et al.* (1944)
Jordanite	$27PbS.7As_2S_3$	3.86	6.38(*m*)	Palache *et al.* (1944)
Gratonite	$9PbS.2As_2S_3$	4.50	6.22(*m*)	Palache *et al.* (1944)

It may be noted that in Table 2 the sulfarsenide formulae are given in either structural or component form. The latter has been used extensively because of its convenience, but the form does become awkward in the case of non-stoichiometric compounds. In this regard, it should be noted that in Figs. 1 and 2 the ratios Pb/Sb_2 and Pb/As_2 are used rather than Pb/Sb_2S_3 and PbS/As_2S_3. The determinative curves are thus independent of sulfur stoichiometry.

The sulfarsenide determinative curve is quite sensitive to arsenic stoichiometry and hence it could not have been constructed without the precise compositional data obtained by recent structural studies.

Equivalent data have not been obtained for lead sulfantimonides and hence stoichiometric proportions have been used in all cases. This may be one reason for the greater scatter of the points on the determinative curve. On the other hand, because the atomic weights of lead and antimony are closer than those of lead and arsenic, there is a decrease in sensitivity to minor Pb:Sb variations. The sensitivity in an equivalent determinative curve for the sulfosalts of lead and bismuth (atomic wts. 207 and 209 respectively) should likewise be further decreased, but there are too few minerals of this type to provide a good check.

Applications

As a simple example of the application of the sulfantimonide determinative curve, the synthetic sulfosalt prepared by Robinson (1948, p. 65) and described as "Phase II" is examined. Although insufficient material was available for a specific gravity determination, Robinson obtained unit cell dimensions of $a = 19.16$, $b = 4.12$, $c = 17.39$ kX, $\beta = 96°24'$, and a polarigraphic molal ratio of Pb:Sb = 3.4:5.4, the latter being close to the formula for plagionite, $5PbS.4Sb_2S_3$.

The density (D) of a mineral is equal to MZ/NV, where M is the molecular weight of the compound, Z is the number of formula weights per unit cell, N is Avogadro's number (6.023×10^{23}), and V is the cell volume. As neither Z nor density is known, the initial value sought is D/Z. For "Phase II" the cell dimensions cited yield a volume of 1,364 Å^3, and if the composition $9PbS.7Sb_2S_3$ is considered, then D/Z 5.514 with $Z = 1$. From the determinative curve, the above composition leads to a predicted density of about 5.54. Robinson's "Phase II" is thus $9PbS.7Sb_2S_3$.

A more complex situation arises when the sulfosalt is at some intermediate position in an Sb-As solid solution series. Although naturally-occurring examples were previously limited to geocronite and zinckenite, this type of solid solution is common in the Madoc sulfosalts. Provided that the Sb:As ratio of such a mineral is known, its formula can be predicted by marking off the appropriate interval between the combined sulfarsenide and sulfantimonide determinative curves. Practice has shown that for a pure lead sulfantimonide, the calculated and graphically predicted densities should generally agree to within 0.1 gm/cm^3. The error is larger for solid solution members, but agreement should generally be within 0.2 gm/cm^3.

The determinative curves have been used extensively in deriving the formulae of the new Madoc sulfosalts. Their predicted and calculated densities should therefore always approximately coincide.

The Madoc Sulfosalts

The sulfides and sulfosalts identified in the Madoc suite are listed in Table 3. All new mineral names have been approved by the Commission on New Minerals and Mineral Names, I.M.A. Type specimens have been deposited with the National Mineral Collection, Ottawa.

Sphalerite is by far the most abundant mineral in the list, and nearly all of it is of the iron-rich, dark brownish-black variety. A few grains of pale amber sphalerite were also noted, but these occur as isolated grains in the marble and hence yield no useful information. The commonest sulfosalt associate of the zinc sulfide is boulangerite.

Pyrite and arsenopyrite are common. They are typically euhedral and up to 4 mm in largest dimension. Arsenopyrite characteristically occurs in clusters of euhedral crystals forming veinlets, whereas pyrite is generally present as single grains. Some grains of pyrite have corroded margins, a feature not evident in arsenopyrite. The minerals have been observed in contact with each other in a few cases: no unequivocal age relationships are evident.

Table 3. Sulfides and Sulfosalts in the Madoc Suite

New minerals are marked with an asterisk

Sulfides		
Sphalerite	Pyrite	Arsenopyrite
Chalcopyrite	Galena	
Sulfosalts		
Boulangerite	Jamesonite	Tetrahedrite
Veenite*	"Geocronite"	Bournonite
Madocite*	Playfairite*	Launayite*
Twinnite*	Sorbyite*	Sterryite*
Guettardite*	Zinckenite	Robinsonite
Semseyite	Mineral QM	Antimonian Baumhauerite

Chalcopyrite occurs only in minute amounts and is associated principally with the copper-bearing sulfosalts tetrahedrite and bournonite. The latter occurs as very narrow rims around anhedral tetrahedrite and as microscopic veinlets which cut the lead sulfosalts. Galena is also rare at Madoc. It is associated principally with "geocronite,"[1] particularly where there are indications that small vugs are present in the marble.

Nearly all of the Madoc sulfosalt material consists of boulangerite and jamesonite. Tetrahedrite, geocronite, and veenite are common but much less abundant. For the most part the remaining sulfosalts are identifiable only in polished sections. Two of the new ones are described below.

[1] The identification is tentative.

MADOCITE

Madocite (may-dok-ite) is named for Madoc, Ontario, the locality from which the mineral was first identified. Madocite has also been discovered in specimens labeled "robinsonite" from Owyhee Co., Idaho. Boulangerite and jamesonite are associated sulfantimonides in both cases.

Crystallography

Madocite is elongated and striated along [001], but otherwise the morphology is not known. Weissenberg and precession studies indicate that the mineral is orthorhombic, with $a = 27.2\,\text{Å} \pm 0.2$, $b = 34.1 \pm 0.2$, $c = 8.12 \pm 0.05$; $a{:}b{:}c{:}0.7977{:}1{:}0.2381$. Rotation photographs show a strong pseudoperiod, with $c' =$ half c. For the pseudocell, all orders of hkl, $hk0$, and $00l$ are present. The following systematic extinctions are evident:

$h0l$: present only with h even.

$0kl$: present only with k even.

The space group of pseudocell is therefore *Pba*2 (No. 32) or *Pbam* (No. 55).

The indexed *x*-ray powder pattern of madocite from Madoc is given in Table 4. Powder patterns of material dug out from polished sections of the Idaho specimens proved to be identical to patterns of the Madoc mineral.

Properties

The colour and streak of madocite are metallic grey-black. The mineral has a perfect {010} cleavage and conchoidal fracture. The Talmage hardness is $B+$, and the mean Vickers hardness with a 50 gram load is 155 (141–171). The indentation is generally square and is accompanied by cleavage fractures. In polished section, madocite shows strong reflection pleochroism from white to grey, the intensity being only slightly less than that of boulangerite. The anisotropism is strong, but also slightly less than that of boulangerite. Madocite is negative to $HgCl_2$, $FeCl_3$, KCN, and HCl. Prolonged reaction with 40% KOH tarnishes the mineral iridescent. Concentrated HNO_3 and 1:1 HNO_3 immediately tarnish iridescent, then black.

Reflectivity

Reflectivity measurements on the Madoc sulfosalts were obtained at the Mines Branch, Ottawa, using the apparatus described by Nickel (1966), and silicon as a standard. As nearly all the determinative work

TABLE 4. X-RAY POWDER DATA FOR MADOCITE

Cu $K\alpha$ radiation, 114.6 mm diameter camera. Indexed with pseudocell dimensions $a = 27.2$, $b = 34.1$, $c' = 4.06$ Å

I Est.	d Meas.	d Calc.	hkl
$<\frac{1}{2}$	13.4	13.6	200
$<\frac{1}{2}$	12.6	12.6	210
$<\frac{1}{2}$	10.8	10.6	220
1	8.7	8.8	310
		8.7	230
$\frac{1}{2}$	7.20	7.22	240
1	6.76	6.80	400
$<\frac{1}{2}$	6.20	6.21	340
$<\frac{1}{2}$	4.80	4.80	170
$\frac{1}{2}$	4.53	4.53	600
$<\frac{1}{2}$	4.36	4.38	620
		4.36	460
1	4.22	4.21	180
$<\frac{1}{2}$	4.07	4.06	001
3	3.94	3.96	470
		3.93	560
5	3.87	3.87	211
		3.86	710
		3.86	380
1	3.78	*	
7	3.67	3.68	311
		3.68	231
		3.68	730
2	3.53	3.54	241
		3.52	331
1	3.50	3.50	390
10	3.396	3.400	800
		3.398	341
9	3.355	3.355	580
$\frac{1}{2}$	3.242	3.239	511
4	3.110	3.109	590
		3.105	680
4	3.028	3.024	601
6	2.925	2.923	631
4	2.824	2.824	561
2	2.795	2.797	381
8	2.720	2.720	10.0.0
		2.714	291

I Est.	d Meas.	I Est.	d Meas.	I Est.	d Meas.	I Est.	d Meas.
$<\frac{1}{2}$	2.663	3	2.345	$\frac{1}{2}$	2.021	1	1.802
$<\frac{1}{2}$	2.604	1	2.263	1	1.980	$<\frac{1}{2}$	1.770
$\frac{1}{2}$	2.570	$\frac{1}{2}$	2.211	$<\frac{1}{2}$	1.962	5	1.741
$<\frac{1}{2}$	2.522	$<\frac{1}{2}$	2.150	$<\frac{1}{2}$	1.940	$<\frac{1}{2}$	1.701
$<\frac{1}{2}$	2.460	2	2.130	$\frac{1}{2}$	1.923	$<\frac{1}{2}$	1.678
$<\frac{1}{2}$	2.427	$<\frac{1}{2}$	2.077	2	1.897	$<\frac{1}{2}$	1.658
$\frac{1}{2}$	2.404	4	2.032	4	1.877	$\frac{1}{2}$	1.630

*Several possible indices.

on the Madoc sulfosalts was done on the material collected in 1925, in some cases only one or two grains suitable for reflectivity measurements were available for a particular mineral. All the new Madoc minerals are bireflecting and hence the data obtained probably only approximate the maximum and minimum reflectivities.

In the case of madocite, only the maximum reflectivity was determined. With the {010} cleavage visible the maximum values at λ470, 546, 589, and 650 are 44.5, 42.3, 40.4 and 37.9% respectively.

Chemistry and density

Microprobe analyses of madocite are given in Table 5. The analytical values correspond almost exactly with $7PbS.3(Sb,As)_2S_3$ and the average Sb:As ratio about 9:2. The volume of the pseudocell is 3,766 Å^3 and for $7PbS.3Sb_2S_3$ the D/Z value is 1.19. With $Z = 5$ the calculated

TABLE 5. MICROPROBE ANALYSES OF MADOCITE

	1	2	3	Average
Pb	54	55	56	55
Sb	24.5	21.5	21.5	22.8
As	3	2.3	4	3.1
S	20	19.8	20	19.9
	101.5	98.6	101.5	100.8

	Atomic ratios		Formula ratio
Pb	.2654	1	17
Sb	.1875	0.862	14.07
As	.0414		
S	.6215	2.342	39.8

Analytical Formula: $17PbS.8(Sb, As)_{1.84}S_{3.26}$
Idealized Formula: $17PbS.8(Sb, As)_2S_3$

density is 5.95 as compared to the predicted value of about 6.10. The correspondence is thus not altogether satisfactory, and the required number of formula weights is unacceptable. An alternative possibility is $9PbS.4Sb_2S_3$, which yields $D/Z = 1.548$; with $Z = 4$, $D = 6.19$ as compared to the determinative curve value of about 6.05 for this composition. A final possibility is that the formula of madocite is $17PbS.8Sb_2S_3$, which with $Z = 4$ (true cell) yields a density of 5.98 as compared to the predicted value of 5.99. The last formula is preferred as $9PbS.4Sb_2S_3$ corresponds to the composition of semseyite.

Occurrence

Although madocite is rare in the specimens collected in 1924, it has been observed in several polished sections of recently collected material. The mineral is closely associated with jamesonite and boulangerite, particularly the latter. As these minerals are among the most widely distributed lead sulfantimonides at Madoc, the opportunities of collecting additional madocite specimens are good.

Synthesis

A brief description of the synthesis of madocite and several additional lead sulfosalts will be given at a later date. Madocite has been prepared by hydrothermal and pyrosynthesis techniques and was found to be the commonest product formed by moderate heating (425° C) of dry charges in the antimony-rich portion of the Pb – Sb – As – S system.

VEENITE

Veenite is named in honour of R. W. van der Veen, eminent metallographer. The mineral is chemically the antimony analogue of dufrenoysite, but a name with this connotation, such as stibdufrenoysite (Nowacki, 1964)*, has not been used because there is as yet no proof that veenite and dufrenoysite are completely identical in structure. Veenite is the most abundant new sulfosalt at Madoc. It does not occur in weathered specimens, but masses up to ¾ inch diameter have been found *in situ* at the site of the original prospect pit.

Crystallography

Several fragments of veenite have been examined by single crystal methods. Rotation photographs about the elongation axis show a pronounced 4.2 Å pseudocell and weaker diffraction rows which indicate that the true axial dimension is double that of the pseudoperiod. The complete cell dimensions are compared to those of dufrenoysite in Table 6. For the pseudocell, all orders of *hkl* and *0kl* reflections are present; *h00*, *0k0*, and *00l* are present only when even; *hk0* is present only when $h + k$ is even, and *h0l* appears only when *l* is even. The symmetry of the pseudocell is orthorhombic and the systematic extinctions lead to the possible orthorhombic space groups $P2_1cn$ or *Pmcn*. The symmetry of the true cell is not known.

TABLE 6. UNIT CELL DIMENSIONS OF DUFRENOYSITE AND VEENITE

	Dufrenoysite (Berry, 1953)	Veenite
a	8.41 Å	2 × 4.22 = 8.44 Å
b	25.85	26.2
c	7.88	7.90
β	90° 30′	
a:*b*:*c*	0.3253:1:0.3048	0.322:1:0.304

The *x*-ray powder pattern of veenite closely resembles that of dufrenoysite, but is contracted in the low 2θ region. The measured and calculated *d*-spacings of veenite are given in Table 7.

Properties

Most veenite is massive or occurs as disseminated anhedral grains. The only available single crystal is more than half a millimeter long. The elongation is along [100] and the prism zone almost equant, but slightly flattened on {010}. The faces are roughened and grooved, and give such indistinct signals on the optical goniometer that even crude measurements cannot be obtained. In addition to this crystal, a few loose

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*See also *stibiodufrenoysite* used by Burkart-Baumann *et al. N. Jb. Mineral. Mh.* 353 (1966).

TABLE 7. *X*-RAY POWDER DATA FOR VEENITE

114.6 mm camera and Cu $K\alpha$ radiation. Indexing based on pseudocell dimensions of $a = 4.22$, $b = 26.2$, $c = 7.90$ Å

I Est.	*d* Meas.	*d* Calc.	*hkl*	*I* Est.	*d* Meas.	*d* Calc.	*hkl*
1	7.63	7.56	011	5	2.74	2.74	132
1	6.80	6.77	021	½	2.73	2.73	091
1	5.86	5.86	031	1	2.640	2.638 2.638	142 171
½	5.05	5.04	041	<½	2.603	2.620	0.10.0
2	4.36	4.37 4.37	051 060	<½	2.480	2.487	0.10.1
3	4.15	4.16	110	<½	2.458	2.458	181
1	3.93	3.95	002	5	2.386	2.395	190
10	3.81	3.82	061	½	2.342	2.343	092
1	3.60	3.60	032	½	2.286	2.292 2.284	191 172
4	3.58	3.58	121	½	2.268	2.280	0.11.1
8	3.42	3.42	131	3	2.246	2.255	063
8	3.26	3.28	080	3	2.231	2.225	113
5	3.23	3.23	141	½	2.179	2.183 2.183	0.10.2 0.12.0
4	3.16	3.15	052	½	2.164	2.164 2.164	133 182
9	3.03	3.03 3.03	151 081	½	2.136	2.142	1.10.1
5	2.93	2.93	062	4	2.107	2.114 2.108	143 400
<½	2.88	2.88	102				
5	2.83	2.83	161				
7	2.76	2.80	170				

I Est.	*d* Meas.	*I* Est.	*d* Meas.	*I* Est.	*d* Meas.	*I* Est.	*d* Meas.
2	2.058	<½	1.894	1	1.771	<½	1.608
<½	1.989	1	1.877	<½	1.743	<½	1.581
½	1.958	½	1.850	½	1.707	½	1.566
1	1.942	2	1.834	<½	1.698	½	1.546
<½	1.932	½	1.813	<½	1.667	½	1.527
<½	1.918	½	1.790				

imperfect fragments have been used in *x*-ray work. These are bladed, being thinnest on {010}, elongated and striated along [100].

Massive veenite is steel-grey in colour and resembles tetrahedrite. Small fragments observed under the binocular microscope are black and opaque. The streak is black, but a faint brownish tint is observable under the microscope when finely ground material is smeared on a white background. The perfect cleavage present in dufrenoysite is not observed, but veenite has a pronounced and characteristic conchoidal fracture. Veenite is very brittle, much more so than pure antimony sulfosalts, but less so than the pure arsenic member.

In polished section veenite is white with weak reflection pleochroism from white to pale pinkish grey. Upon rotation of the microscope stage, adjacent twin lamellae are discernible but not at a casual glance. The anisotropism of veenite is only moderate. Twin lamellae are prominent with partly crossed nicols, but at 45° with crossed nicols the colour is dark grey. Minimum and maximum reflectivities at the four standard wavelengths are 39.5–45.5%(470), 37.6–43.2, 36.3–42.0, 34.3–39.9% (650). The Talmage hardness determined in polished section is $C-$, and the average Vickers hardness with a 50 gm load is 164 (156–172). Either star or radial fractures invariably accompany the indentation. Fractures parallel to the twinning are relatively rare. Shell fracturing is associated with only five to ten per cent of the indentations and occurs as a single lobe about the same size as the area of impression.

KOH (40%) tarnishes veenite iridescent and HNO_3 tarnishes it black. KOH generally brings out the polysynthetic twinning also evident under partly crossed nicols.

Chemistry and density

One corner of the largest of the specimens collected in 1924 was found to have a mass of veenite, approximately 0.5 inches in diameter. Examination of a polished section of this mass showed that the minerals most likely to contaminate an analysis of it would be calcite and boulangerite, but that these were generally concentrated at the periphery of the section. The material subsequently dug out of the section was analyzed by *x*-ray spectroscopy and classical techniques. The presence of major Pb, Sb, As, and the absence of minor elements was indicated by optical spectrographic analysis; *x*-ray spectroscopic examination gave a high Sb:As ratio, with Sb estimated to be 14 per cent. Quantitative *x*-ray analysis for lead by G. R. Lachance gave the following results:

Sample wt., mg.	%Pb
20.0	50.8
25.0	49.0
17.1	52.1
26.0	50.4
Av.	50.6

Problems were encountered with the two samples submitted for wet chemical analysis (Table 8). Two synthetic control samples analyzed at the same time gave, for the arsenic-plus-antimony fraction, an arsenian precipitate too high in weight, and an antimony content too low. This must be borne in mind when considering the analysis given in Table 8 for the natural veenite. The results are nevertheless in fair agreement with the idealized formula requirements.

Microprobe analyses of three grains of veenite in polished sections are given in Table 9. The average analysis is in good agreement with the proposed formula. All analyses without exception indicate that in veenite

TABLE 8. CHEMICAL ANALYSIS OF TWO SAMPLES OF MADOC VEENITE

Analyst: Sydney Abbey, *Analytical Chemistry Section*

		*	$CaCO_3$ deducted	Atomic ratios	Formula ratios
Sample A, 238.1 mg.					
Pb	50.3	50.3	50.76	.245	2
Sb	major	21.2	21.39	.176	2.27
As	7.6	7.6	7.76	.102	
S	20.0	20.0	20.18	.629	5.14
CaO	0.6	0.9 ($CaCO_3$)			
R_2O_3	<0.1	100.0	100.0		
MgO	<0.1				
Sample B, 345.1 mg.					
Pb	50.4	50.4	50.61	.244	2
Sb	major	20.5	20.58	.169	2.31
As	8.4	8.4	8.43	.113	
S	20.3	20.3	20.38	.636	5.21
CaO	0.3	0.4 ($CaCO_3$)	100.00		
R_2O_3	<0.1	100.0			
MgO	<0.1				

*CaO converted to calcite:Sb by difference.

Idealized formula $2PbS.(Sb, As)_2S_3$

Formula from "A" $2PbS.(Sb, As)_{2.27}S_{3.14}$

Formula from "B" $2PbS.(Sb, As)_{2.31}S_{3.21}$

TABLE 9. MICROPROBE ANALYSES OF THREE GRAINS OF VEENITE

Analyst: G. R. Lachance

	Analyses 1	2	3	Average	Atomic ratios	Proportions
Pb	53.5	53	51	52.5	0.2534	2.00
Sb	19.5	19.5	20	19.7	0.1616	1.27
As	6.0	7.5	7	6.8	0.0912	0.72
S	22.0	19.2	21.5	21.2	0.6518	5.15
	101.0	99.2	99.5	100.2		

Average of microprobe analyses: $2PbS.(Sb, As)_{2.00}S_{3.14}$

Idealized formula: $2PbS.(Sb, As)_2S_3$

there is a substantial predominance of antimony over arsenic, the approximate ratio being Sb:As = 5:3. With this composition and cell dimensions of $a = 8.43$, $b = 26.2$, $c = 7.90$ and $Z = 8$, the calculated density for veenite is 5.96. The predicted density from the combined Sb-As determinative curves is 5.76, substantially lower than the calculated value, but nevertheless of the right order of magnitude. Sample "B" used in the chemical analysis gave a density of 5.92 gm/c.c. measured by pycnometer.

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