NEW OBSERVATIONS ON MATILDITE

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ABSTRACT

A study of matildite from another occurrence in the Camsell River Area, N.W.T. is reported. The mineral occurs as pure irregular grains in a deposit containing native silver, native bismuth and Co-Ni arsenides and in which galena has not been identified.

Single crystal studies and reflectivity measurements confirm the hexagonal symmetry postulated by Geller & Wernick, but with the *a*-cell dimension doubled, yielding values of

$$a = 8.12;\ c = 19.02\ \text{Å}$$

Electron probe microanalysis shows that the mineral is homogeneous with a formula of $Ag_{0.95}Bi_{1.00}S_{1.97}$ which agrees very well with the ideal formula $AgBiS_2$.

Microhardness values (25-gram load) range from VHN 59 to 76.

INTRODUCTION

The first occurrence of matildite in Canada was reported by Ellsworth (1916) who identified the mineral in ores of the O'Brien Mine, Cobalt, Ontario. Other reported occurrences include Glacier Gulch, B.C. (Pratt 1931) and the Camsell River Silver Mines, N.W.T. (Thompson, 1953).

A characteristic feature of matilidite in most of the occurrences from widely separated regions of the world is its intergrowth in galena which form Widmanstätten-like structures. In the deposits of the Cobalt area two types of galena-matildite intergrowths were observed. In the first type matildite occurs as irregular blebs with no systematic orientation in galena. In the second texture (Walker, 1916) it occurs as oriented microintergrowths in galena. Thompson reports that one of the more interesting microscopic features of the ore from the Camsell River Silver Mines is the fairly abundant galena-matildite exsolution intergrowths which exhibit a Widmanstätten texture.

On the other hand, Pratt reports that matildite from Glacier Gulch is found closely associated with tetradymite with apparently no galena.

The identification of matildite from ores of another locality in the Camsell River Area, N.W.T., is worth mentioning in that matildite occurs as pure irregular grains in a deposit containing native silver, native bismuth and Co-Ni arsenides and in which galena has not been identified.

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The purpose of this paper is to record the occurrence and to add new data which have not been previously reported for matildite.

GENERAL DESCRIPTION

The matildite locality is on the Camsell River, 4 miles south of its mouth at Conjuror Bay on Great Bear Lake, and about 35 miles south of the producing silver mine of Echo Bay Mines at Port Radium. This location corresponds to latitude 65°36′14″ and longitude 118°06′45″.

Silver deposits have been known in the general area for many years. In 1932 silver was discovered 4 miles upstream on what is generally known as the Camsell River Silver Mines property (Lord, 1951). This property has been investigated sporadically in both underground and surface workings, and in 1967 some high-grade ore was bagged from surface workings.

In 1960 the matildite-bearing deposit was investigated by Eldorado Mining and Refining Limited. Four holes totalling 942 feet were drilled, with 6 samples from one 10.3-foot section assaying over 20 oz. silver per ton. Within this section a length of 0.4 ft. assayed 1492 oz. silver per ton, 9.55% bismuth and 3.16% cobalt. In 1967 a total of about 10,000 feet in 31 holes was drilled (by Terra Mining and Exploration Limited) to test the deposit to a depth of 300 feet.

For the geology and rock types of the area, the reader is referred to Map 1055A, Geological Survey of Canada (Brown, 1958).

The deposit consists of veins within, parallel to, and rarely in cross-fractures in, a sheared andesitic tuff and fractured rhyolite formation within a northwest-striking nearly vertical sequence of more massive acidic tuffs and flows. The formation of sheared tuff and fractured rhyolite is about 50 feet thick and contains disseminated chalcopyrite, pyrite and pyrrhotite that have weathered to produce a gossan.

The surface exposure of the deposit consists of a transverse vein about 14 inches in width, which contains heavy Co-Ni arsenides, coarsely crystalline native bismuth, matildite, and minor amounts of chalcopyrite and bismite. Only the arsenides and native bismuth are megascopically visible. The main arsenides in the samples are safflorite, skutterudite and rammelsbergite and the minor ones gersdorffite, pararammelsbergite and cobaltite. The matildite is the only silver-bearing mineral in the surface specimens, although native silver is fairly abundant in drill core. Niccolite has also been identified.

The matildite occurs as large irregular grains measuring up to 500×700 microns in size. These grains are relatively free of inclusions except for a few small blebs of native bismuth. Replacement textures indicate that matildite and native bismuth formed simultaneously and are younger than the arsenides.

In reflected light matildite is medium grey, and weakly to moderately anisotropic with colours ranging from light grey to dark grey. The mineral is very brittle and has an uneven fracture.

X-RAY CRYSTALLOGRAPHY

Ramdohr (1938) studied matildite in detail and found the low-temperature (β) form, corresponding to natural matildite, to be orthorhombic with $a = 8.14$, $b = 7.87$, $c = 5.69$ Å. Since the lattice dimensions had been obtained from powder patterns alone, Graham (1951) prepared single crystals of β-$AgBiS_2$ by hydrothermal techniques, and by Weissenberg studies, confirmed an orthorhombic structure. However, the cell dimensions that he obtained were $a = 3.926$, $b = 4.054$, $c = 5.673$ Å. The two cells are related in the following manner: a_G = approx. $1/2b_R$ and b_G = approx. $1/2a_R$. These values explain the powder pattern better than the dimensions proposed by Ramdohr, but the indexing was still not wholly satisfactory. Recently, Geller & Wernick (1959) studied several ternary semi-conducting compounds with sodium chloride-like structures which included $AgBiSe_2$ and $AgBiS_2$, and reported that β-$AgBiS_2$ is hexagonal rather than orthorhombic, with cell elements $a = 4.07$, $c = 19.06$ Å.

Since the cell dimensions of matildite have never been determined on natural material, a small fragment was mounted for single-crystal precession studies. Because of the poor reflections obtained from the mineral, only zero-level photographs were studied. The films confirm the hexagonal symmetry but provide evidence that the a dimension of the Camsell River matildite is double that reported by Geller & Wernick, the newly determined cell parameters being $a = 8.22$ and $c = 19.14$ Å. For more accurate cell dimensions, the x-ray powder data given in Table 1 were indexed, which yielded values of $a = 8.12$, $c = 19.02$ Å.

The x-ray powder data for natural matildite agree very well with that given by Geller & Wernick for synthetic β-$AgBiS_2$, and are more complete than the data published by Berry & Thompson (1962) which have several extraneous lines due to impurities of galena.

COMPOSITION

The composition of matildite was determined with a Jeolco electron probe microanalyzer operated at a gun voltage of 25 kilovolts and a beam current of 0.15 microamperes. Metallic silver and bismuth, and

TABLE 1. *X*-RAY DIFFRACTION DATA FOR MATILDITE NICKEL-FILTERED COPPER RADIATION

Hexagonal $a = 8.12$, $c = 19.02$ Å

I(est.)	*d*(meas.)	*hkl*	*d*(calc.)	*I*(est.)	*d*(meas.)	*hkl*	*d*(calc.)
3	6.311	003	6.340	½	1.600	045	1.596
2	3.453	021	3.457	2	1.580	137	1.584
8	3.302	022	3.298	1(B)	1.468	229	1.464
2	3.166	006	3.170	2	1.412	048	1.414
1	3.074	023	3.075	2	1.333	01.14	1.334
10	2.827	024	2.827	2	1.282	239	1.282
2	2.582	025	2.582	3	1.246	336	1.245
1	2.356	026	2.354	½	1.225	246	1.225
1	2.149	027	2.150	½	1.175	03.14	1.175
5	2.029	220	2.030	1	1.161	248	1.160
6	1.966	028	1.969	2	1.125	249	1.125
2	1.729	0011	1.729	½	1.101	066	1.099
3	1.709	226	1.709	½	1.087	346	1.086
1	1.671	038	1.669	½	1.073	160	1.072
1	1.650	044	1.649				

TABLE 2. ELECTRON PROBE MICROANALYSIS

Element	Weight %	Atomic Prop.
Ag	27.3	0.95
Bi	56.0	1.00
Pb	n.d.*	—
Cu	n.d.	—
Sb	n.d.	—
S	16.9	1.97
	100.2	

*n.d. = looked for but not detected.

the following minerals, were used as standards: cosalite ($Pb_2Bi_2S_5$), bismuthinite (Bi_2S_3), aramayoite ($Ag(Sb,Bi)S_2$), stephanite (Ag_5SbS_4). The elemental concentrations in the above minerals were calculated from their ideal formulae. In addition, absorption corrections were carried out according to the modified Philibert-formula (Duncumb & Shields, 1964) using the mass absorption coefficients published by Heinrich (1964).

To determine the homogeneity of the mineral, several areas on different grains were analyzed and the average number of counts used to derive the composition. The mineral was considered to be homogeneous, since the variation in counts from one spot to the other was less than the variation expected from the counting statistics. Other elements looked for, but not detected, were lead, copper and antimony. Results of the analysis are given in Table 2.

Based on the unit-cell dimensions $a = 8.12$, $c = 19.02$ Å and composition corresponding to the theoretical formula $AgBiS_2$, the cell contains twelve formula units giving a calculated density of 6.99.

MICROHARDNESS

The microhardness of matildite was determined with the aid of a Leitz Durimet Vickers hardness tester equipped with polarizing filters and rotating stage. The sample was mounted in araldite and polished on lead laps with graded diamond abrasives down to 0–2 microns in diameter. Final buffing was done on a cloth lap with magnesium oxide paste.

The indentation time for all measurements was kept constant at 25 seconds.

Since the microhardness of ore minerals can be strongly affected by the crystallographic orientation of the mineral, and this was the case for matildite, the mineral was aligned at maximum extinction and both diagonals carefully measured for each indentation.

Initially, a load of 100 g was applied, but excessive fracturing and large indentations required the load to be decreased to 50 g and finally to 25 g and 15 g. The majority of the indentations were made with the latter two loads.

Results of the measurements are given in Table 3. By averaging the shortest and longest diagonals, a range of HV values were obtained for each load. The mean microhardness value is given in brackets. For matildite, a load of 25 g gave the most satisfactory indentation.

TABLE 3. MICROHARDNESS OF MATILDITE

Load in g	Number of Identations	Range of VHN* in kg/mm^2
15	12	53.0–68.0 (60.5)
25	10	59.1–76.3 (67.7)
50	2	64.9–85.7 (75.3)
100	2	72.7–74.2 (73.5)

*Vickers hardness number.

REFLECTIVITY

The apparatus used for measuring the reflectivity of matildite was a Leitz MPE microscope photometer equipped with type FS-9-A photomultiplier tube, two six-volt storage batteries connected in parallel, and a Veril B200 continuous-band interference filter. Silicon was used as a reference standard.

The silicon standard was supplied by the Commission of Ore Microscopy of the International Mineralogical Association and had been calibrated by the National Physical Laboratory in Great Britain. The reflectivity values for silicon were taken from the NPL report reference N2538, dated August 22, 1966.

The sections of matildite were prepared for measurement by the polishing procedure outlined above for microhardness. To avoid errors in reflectivity values due to relief of the mineral produced by polishing on the cloth lap, only the centres of large grains were measured.

The results of the reflectivity measurements of four standard wavelengths, for five randomly oriented grains, are given in Table 4. Measurements taken at maximum and minimum reflectance on two of these grains which gave the most pronounced anisotropic effects for the spectrum from 450 mμ to 630 mμ are plotted in Fig. 1.

In a recent paper, Cameron (1963) pointed out that the reflectivity of a uniaxial or biaxial grain in air in normally incident plane-polarized light is a function of the orientation of the polished section of the grain with respect to the crystallographic axes and the vibration plane of the

TABLE 4. REFLECTIVITY (%) OF MATILDITE

Wavelength (mμ)	470	546	589	650
Range	44.2–45.3	43.8–44.9	43.4–44.4	42.6–44.0
Mean	44.8	44.4	44.9	43.6

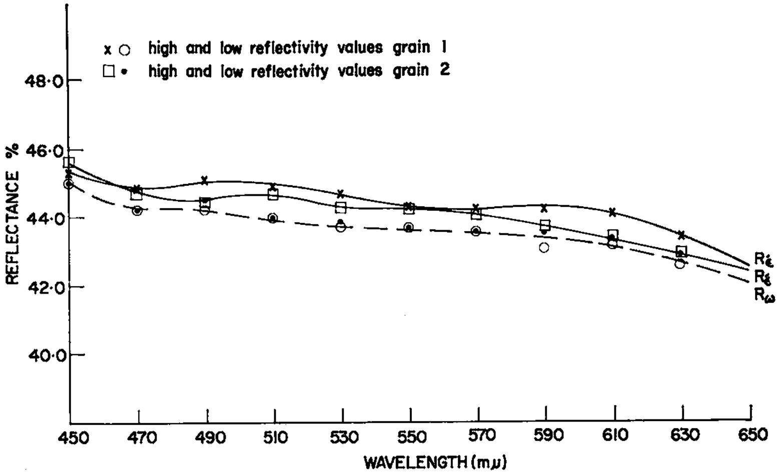

FIG. 1. Reflectivities R_ω and R_ϵ', of Matildite from Camsell River.

polarizer. If a mineral is uniaxial, either the lowest or highest reflectivity values for randomly oriented grains, at a particular wavelength, will be constant, within the error of measurement, whereas the other set of values will vary. The set of constant values represents the vibration direction of the ordinary ray (R_ω) and the other set of values involve components of the extraordinary ray (R_ϵ) to varying degrees depending on orientation. If the low values are constant and the high values variable, the mineral is uniaxial positive ($R_\omega < R_\epsilon$).

The values obtained for matildite and plotted in Fig. 1 show that the low values are nearly the same, while the high values vary. This indicates that the mineral is uniaxial positive and that it is thus in the hexagonal or tetragonal system.

The results of the reflectivity measurements and the single-crystal photographs obtained in this study, add further support to the work of Geller & Wernick, which shows that matildite is hexagonal rather than orthorhombic.

ACKNOWLEDGMENTS

The authors are very grateful to the following personnel in the Mineral Sciences Division of the Mines Branch: to J. M. Stewart and P. E. Porteous for the *x*-ray diffraction work, to E. H. Nickel for assistance in the reflectivity measurements, and to E. J. Gabe for the computer programme used in indexing the powder data.

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Manuscript submitted April 10, 1968, emended October 28, 1968

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