MOLYBDOMENITE FROM THE RANWICK URANIUM MINE, MONTREAL RIVER AREA, ONTARIO

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ABSTRACT

Molybdomenite has been found at the Ranwick Uranium Mine, where it occurs as small white to colourless blades closely associated with clausthalite. Molybdomenite has been synthesized and its chemical formula is established as $PbSeO_3$. The mineral is monoclinic with space group $P2_1$ or $P2_1/m$. Unit cell parameters are: $a = 6.86$, $b = 5.48$, $c = 4.50$ (all in Å), $\beta = 112°45'$, $Z = 2$.

INTRODUCTION

Historical review

The original description of molybdomenite given by Bertrand (1882) is quite sketchy and does not completely define the species. This was due, no doubt, to insufficient material and primitive mineralogical techniques. Goni & Guillemin (1953) restudied various selenites and selenates including molybdomenite, and published *x*-ray powder data and partial optical data for Bertrand's original specimens. They also proved, by qualitative tests, that molybdomenite is a lead selenite. The amount of material was too small for a quantitative analysis. Other than suggesting that molybdomenite was orthorhombic, they presented no crystallographic data.

Molybdomenite has been found at Cerro de Cocheuta, Mendoza, Argentina (the type locality); at the Trogtal, Harz, Germany (Goni & Guillemin, 1953); and at Pacajake, Bolivia, (Ahlfeld & Reyes, 1955). It may also be present in one of the deposits of the Magadanskaya oblast of the U.S.S.R. (Babkin, 1958) as reported by Sindeeva (1964). Of these reports, only the one by Goni & Guillemin contains diagnostic data for molybdomenite.

This paper records a new occurrence of molybdomenite and characterizes the species somewhat more fully than before.

During the fall of 1961, Dr. W. M. Tovell, Curator of Geology at the Royal Ontario Museum, took a collecting trip along the north shore of Lake Superior. One of the numerous mines which he visited was the Ranwick Uranium Mine, now operated as a tourist attraction by Mr.

R. R. Ranson of Sault Ste Marie, Michigan. Mr. Ranson kindly presented several specimens from the mine to Dr. Tovell, who subsequently turned them over to the writer. A preliminary examination of the specimens revealed the following main minerals: pitchblende; a galena-like mineral which was later identified as clausthalite; and calcite. In addition, a few white to colourless, adamantine crystals were observed in close association with the clausthalite. Thinking this material might be one of the rare lead selenites or selenates, the writer began a detailed study. Data from an x-ray powder pattern resembled the data given by Goni & Guillemin (1953) for molybdomenite except that the powder photograph of the Ranwick mineral contained many more lines.

It was apparent that additional material would be needed in order to continue the study. Mr. Ranson offered Dr. Tovell and the writer the run of his property, and we visited the mine in August, 1962 and 1963.

Location and geology

The Ranwick Uranium Mine is north of Sault Ste Marie (near Mile 72) on Highway 17 (Trans-Canada Highway). The mine is readily visible on the south side of the highway which here runs east–west. Access to the property is extremely easy and there are ample parking facilities.

The geology of the Montreal River Area has been studied in detail by Nuffield (1956). Most of the material in this section has been abstracted from Nuffield's report. Additional information has been supplied by Mr. Ranson. The area is underlain by Algoman (?) granite, "granite" gneiss, and minor syenite, which are cut by Lower Keweenawan diabase dikes. These dikes are numerous and may make up as much as 5 per cent of the rock. The dikes range in width from less than a foot to 600 feet. The longest dikes strike west to northwest and dip steeply to the north. Some of these have been traced for over two miles. Other dikes strike northeast and dip vertically or steeply to the southeast, while a few strike north.

The Ranwick Uranium Mine is situated on a northwest-striking, north-dipping diabase dike. The dike, now known as the Ranson dike, is about two miles long and the average width is 70 feet. Pitchblende was discovered near the south contact of the dike by Mr. Ranson in November of 1948. Since then, much trenching has been done across the dike and an adit was driven 1,049 feet along the footwall. From the adit, two crosscuts were driven 70 feet across the dike. Five other crosscuts of only a few feet in length were also driven. Pitchblende occurs in calcite-hematite veins in fractures near the diabase-granite contact. According to Mr. Ranson, most of the selenium-bearing samples came from a surface pit about 80 feet above the adit. The writer visited this pit with

Mr. Ranson and, although the pit was partially filled with water, several pitchblende-selenide specimens were collected. Only one of these contained molybdomenite. Fortunately, Mr. Ranson had collected a larger number of specimens from the pit before it was flooded and he kindly turned these over to the writer.

Although Nuffield (1956) reports only pitchblende, calcite, and hematite from the Ranwick mine, later studies by Nuffield (personal communication) disclosed the following species: klockmannite, native selenium, and malachite. In addition to the foregoing minerals identified by Nuffield and the molybdomenite described in this paper, the writer has identified only clausthalite and a few secondary uranium minerals.

MINERALOGY OF MOLYBDOMENITE

General features and appearance

The Ranwick molybdomenite occurs as flat, bladed crystals up to 0.5 mm in length. The crystals are colourless to white and have a pearly to adamantine lustre. Molybdomenite is translucent to transparent. It is invariably associated with clausthalite, from which it is derived.

Crystallographic characteristics

No euhedral crystals were available, so the entire crystallographic study was carried out by means of *x*-rays.

X-ray data. A crystal was mounted on a Buerger precession camera and oriented with the blade axis parallel to the spindle axis. After several films had been taken, it became apparent that the mineral was not orthorhombic as deduced by Goni & Guillemin (1953), but rather, monoclinic. From numerous films taken at small angular intervals, provisional a^* and c^* axes were located normal to the spindle axis. Using these axes, 0 –, 1 –, and 2 – level films were obtained. The crystal was then reoriented with the *b*-axis as the precession axis and 0 –, 1 –, and 2 – level photographs were taken. Measurements from these films yielded unit cell parameters which were used to index the *x*-ray powder data. More precise cell parameters were then calculated from the indexed powder data. The only systematic extinctions observed from the single-crystal films were $0k0$ where k was odd.

The unit cell of molybdenite is defined as follows:

Space group $P2_1$ or $P2_1/m$
$a = 6.86$ Å
$b = 5.48$ Å
$c = 4.50$ Å
$\beta = 112°45^{1}$
$a:b:c = 1.252:1:0.821$

Using a cell volume of 156 Å^3 and a measured specific gravity of 7.07, $Z = 2$ (1.99 by actual calculation).

The indexed x-ray powder data for molybdomenite are given in Table 1 All d-spacings permitted by the space group were calculated down to $d = 1.554$ Å. The pattern was produced in a camera of 114.6 mm diameter using Ni-filtered Cu radiation. Also included in Table 1 are

TABLE 1. X-RAY POWDER DATA FOR MOLYBDOMENITE.

	Molybdomenite Ranwick mine, Montreal River area, Ontario, Canada ROM, M26131			Molybdomenite Cerro de Cacheuta, Mendoza, Argentina Type specimen from Muséum National d'Histoire Naturelle, No. 99,561				Synthetic molybdomenite	
	This study Camera diameter 114.6 mm Radiation Cu/Ni			This study* Camera diameter 57.3 mm Radiation Cu/Ni		Goni & Guillemin (1953) Camera diameter ? Radiation Cu/Ni		This study Camera diameter 114.6 mm Radiation Cu/Ni	
kkl	d(calc)	d(obs)	I	d(obs)	I	d(obs)	I	d(obs)	I
100	6.33 Å	6.29 Å	½	6.37 Å	½			6.22 Å	½
$10\bar{1}$	4.318	4.31	½	4.35	1			4.32	½
001	4.150	4.13	6	4.15	6	4.16 Å	4	4.12	3
110	4.143					3.59	2		
$11\bar{1}$	3.392	3.40	7	3.43	7	3.40	7	3.39	7
011	3.308	3.31	9	3.32	9	3.32	7	3.30	8
$20\bar{1}$	3.176	3.16	8	3.17	7	3.17	4	3.14	9
200	3.165								
101	2.982	2.98	3	2.99	5	3.00	2	2.97	1
$21\bar{1}$	2.746								
020	2.740	2.741	10	2.756	10	2.75	10	2.735	10
210	2.739								
111	2.619	2.618	2	2.636	2	2.62	2	2.616	1
120	2.514								
$12\bar{1}$	2.313								
021	2.286								
$30\bar{1}$	2.268								
$10\bar{2}$	2.244	2.248	4	2.264	5	2.26	3	2.246	4
$20\bar{2}$	2.159								
201	2.148								
300	2.110								
$31\bar{1}$	2.095	2.093	2	2.090	6b			2.097	½
$11\bar{2}$	2.077								
002	2.075	2.071	5			2.08	2	2.071	6
$22\bar{1}$	2.075								
220	2.072								
121	2.018	2.013	3	2.023	5	2.02	2	2.017	2
$21\bar{2}$	2.009								
211	2.000	1.998	2					1.996	2
310	1.969	1.962	1	1.965	2			1.960	1
012	1.940	1.943	1					1.945	½
$30\bar{2}$	1.888	1.888	2	1.892	3	1.86	2	1.887	1

X-RAY POWDER DATA FOR MOLYBDOMENITE. contd.

hkl	d(calc)	d(obs)	I	d(obs)	I	d(obs)	I	d(obs)	I
$31\bar{2}$	1.785	1.783	2	1.791	4	1.76	2	1.783	2
102	1.779								
130	1.755								
$32\bar{1}$	1.747								
$12\bar{2}$	1.736	1.738	2					1.742	2
$40\bar{1}$	1.716	1.714	1					1.710	1
$22\bar{2}$	1.696								
112	1.692	1.691	2	1.695	2vb			1.691	3
221	1.690								
$13\bar{1}$	1.682								
031	1.672	1.672	1					1.676	½
320	1.672								
022	1.654								
301	1.642	1.640	2	1.647	1			1.638	2
$41\bar{1}$	1.637								
$40\bar{2}$	1.588								
$23\bar{1}$	1.584	1.582	2	1.588	2			1.585	2
400	1.582								
230	1.582								
311	1.573								
131	1.558	1.554	2	1.563	2			1.558	2
		1.519	3	1.526	2			1.517	4
		1.491	½	1.497	½			1.494	½
		1.450	2	1.457	3			1.452	3
		1.426	1	1.435	2			1.430	1
		1.407	1					1.408	2
				1.401	1				
		1.394	1					1.395	1
		1.370	1	1.375	½			1.376	1
		1.343	<½	1.351	½			1.344	½
		1.314	½	1.316	1			1.316	1
		1.294	1	1.299	2			1.294	2
		1.276	1	1.284	1			1.278	3
		1.262	½	1.264	1			1.262	2
		1.236	½	1.241	½			1.240	1
		1.224	1	1.230	1			1.226	5

*Note: The following additional lines were observed and are probably due to chalcomenite: 5.37(½), 4.93(½), 3.85(½), 3.55(1), 2.550(1), 2.380(½), 2.309(½), and 1.753(4).

the data given by Goni & Guillemin (1953) for type molybdomenite and data obtained by the writer for both type molybdomenite and synthetic molybdomenite. The type specimen was made available by Mlle. S. Cailliere, Muséum National d'Histoire Naturelle, Paris.

Physical and optical properties

The natural crystals of molybdomenite were too small for specific gravity determinations. We did, however, measure the specific gravity of eleven fragments of synthetic molybdomenite by means of a Berman balance. Under a binocular microscope, three of the fragments revealed numerous pores caused by the fusion process used for synthesizing the compound. These porous fragments gave consistently lower specific gravities than the others. Consequently, they were eliminated from consideration. The average value for the remaining eight fragments is 7.07 ± 0.05. The specific gravity calculated from the unit cell data is 7.12.

Molybdomenite has two cleavages parallel to the length of the crystals. A good cleavage lies in the plane of the blades, parallel to $\{001\}$. The orientation of the other cleavage could not be determined but it is parallel to some plane in the $\{h0l\}$ family.

The writer can add very little to the optical properties of molybdomenite. His highest refractive index liquid (2.10) was lower than the refractive indices of the Ranwick molybdomenite. The orientation of the optical indicatrix could not be determined because the material was too fibrous, nor was it possible to resolve the difference in optic sign previously recorded for this material: optically positive by Bertrand (1882) and optically negative by Goni & Guillemin (1953). The modern techniques available to Goni & Guillemin make the writer more inclined to accept their data, which follow:

Biaxial negative
parallel extinction (presumably for sections parallel to the *b*-axis)
sign of elongation positive
$2V$ near 80°
$n_p = 2.12$, $n_g = 2.14$

Assuming a composition of $PbSeO_3$ and a calculated specific gravity of 7.12, the Gladstone-Dale rule was applied to the mineral, using the revised values for the specific refractive energies given by Mandarino (1964). An "average" refractive index of 2.11 was obtained. The observed average was 2.13.

Chemical characteristics

Again, material was insufficient for a quantitative analysis. Two methods were explored to obtain the chemical composition of molybdomenite: (1) *x*-ray spectrographic determination of the Pb/Se ratio and (2) synthesis.

X-ray spectrographic determination. Mr. Donald C. Harris, Assistant Curator of Mineralogy at the Royal Ontario Museum, determined the ratio of lead to selenium in the Ranwick molybdomenite by using the following samples as standards:

1. synthetic $PbSeO_3$ (Levy)
2. synthetic $PbSeO_3$ (Mrose)
3. synthetic $PbSeO_3$ (Mandarino)

Samples 1 and 2 were kindly supplied by Miss Mary Mrose of the United States Geological Survey; sample 3 was synthesized at the Royal Ontario Museum.

The analyses were made with a Norelco *x*-ray spectrograph equipped with a vacuum sample chamber (in which the sample is inverted), a pulse height analyser, and a scintillation counter.

One to two milligrams of each sample were concentrated inside a sample holder on the centre of the Mylar. Mr. Harris determined the peak intensities of the Pb*Lα* and Se*Kα* lines, and then calculated the ratios of the intensities of Pb*Lα* to Se*Kα* (see Table 2).

TABLE 2. *X*-RAY SPECTROGRAPHIC DETERMINATION OF Pb*Lα*/Se*Kα* ratios

Sample No.	Material	Pb*Lα*/Se*Kα* ratio corrected for background
1	$PbSeO_3$ synth. (Levy)	0.915
2	$PbSeO_3$ synth. (Mrose)	0.928
3	$PbSeO_3$ synth. (Mandarino)	0.927
4	Molybdomenite, Ranwick mine	0.932

Since the ratio of the intensity of the Pb*Lα* line to that of the Se*Kα* line is practically constant, it follows that the ratio of the Pb to Se is the same (1:1) in all the samples. This fact, however, does not conclusively define molybdomenite. We cannot assign a formula of $PbSeO_3$ to molybdomenite from these data alone because we may be dealing with a "basic" selenite, such as $Pb_2Se_2O_7$, in which Pb/Se is also 1:1.

Synthesis. Mellor (1930) lists various procedures for synthesizing $PbSeO_3$ and $Pb_2Se_2O_7$. These include:

1. Precipitation by adding selenious acid or an alkali selenite to a solution of lead chloride or lead nitrate.
2. Fusion of lead selenate.
3. Treatment of lead dioxide with selenious acid (a small amount of lead selenate is also produced).

Mrose (personal communication) produced $PbSeO_3$ by the precipitation method. *X*-ray powder data for synthetic $PbSeO_3$ are given by Goni & Guillemin (1953). It is not stated how their material was synthesized, but it was probably by precipitation. A.S.T.M. card 4-0710 lists *x*-ray powder data for synthetic $PbSeO_3$ prepared by the Wyandotte Chemicals Corporation, Wyandotte, Michigan. According to Keuntzel (personal communication) no record remains of the analysis nor has any of the material been preserved. The writer synthesized $PbSeO_3$ by two methods. First, solutions of lead nitrate and potassium selenite were mixed to form a precipitate of $PbSeO_3$. In the second method, a mixture of PbO and SeO_2 in a molecular ratio of 1:1 was fused in a sealed evacuated Vycor tube and allowed to cool slowly. Because of the great affinity of SeO_2 for water, the SeO_2 was heated in an oven for several hours at a temperature above 100° C and then placed in a desiccator for several days. The

TABLE 3. PARTIAL X-RAY POWDER DATA FOR VARIOUS SAMPLES OF SYNTHETIC $PbSeO_3$. Cu$K\alpha$ RADIATION USED FOR ALL PATTERNS.

Synthesized by	Levy				Mrose Precipitation		This study Precipitation		Wyandotte Chemicals Corporation ASTM 4-0710		This study Fusion of $PbO + SeO_2$		Molybdomenite Ranwick Mine, Ontario	
	d(obs)[1]	I	d(obs)[2]	I	d(obs)[2]	I	d(obs)[2]	I	d(obs)	I	d(obs)[3]	I	d(obs)[3]	I
	5.95	3	5.91	2	5.99	3	5.91	3			6.22	½	6.29	½
	4.44	2			4.41	2	4.41	1			4.32	½	4.31	½
	4.28	3	4.29	1	4.25	1	4.23	2	4.13	50	4.12	3	4.13	6
	3.89	2	3.85	2	3.88	4	3.86	3	3.39	60	3.39	7	3.40	7
	3.76	3			3.75	1	3.72	3	3.31	70	3.30	8	3.31	9
	3.48	4	3.50	3	3.50	4	3.47	4	3.14	40	3.14	9	3.16	8
	3.26	10	3.24	10vb	3.22	10b	3.20	10b			2.97	1	2.98	3
	3.19	5												
	2.95	5	2.97	8b	2.95	9	2.94	8	2.74	100	2.735	10	2.741	10
	2.83	3			2.814	8	2.814	6			2.616	1	2.618	2
			2.772	9vb										
	2.77	5			2.764	8			2.24	50	2.246	4	2.248	4
	2.74	5			2.739	8	2.715	9			2.097	½	2.093	2
	2.57	3			2.571	1	2.550	2	2.07	50	2.071	6	2.071	5
			2.522	4b										
	2.51	3			2.501	3	2.495	4	2.02	40	2.017	2	2.013	3
	2.39	2	2.392	1	2.386	2	2.380	½			1.996	2	1.998	2
	2.28	2	2.292	1	2.281	1	2.275	1			1.960	1	1.962	1
					2.196	½	2.191	½			1.945	½	1.943	1
	2.14	3	2.137	6	2.137	7	2.132	5b	1.89	30	1.887	1	1.888	2
	2.05	3	2.053	4	2.058	5	2.049	6	1.78	30	1.783	2	1.783	2
	2.01	2			2.010	½	2.006	1	1.73	30	1.742	2	1.738	2
	1.97	3	1.997	5	1.977	5	1.973	6			1.710	1	1.714	1
			1.930	1	1.930	2	1.926	3			1.691	3	1.691	2
									1.68	30				
			1.892	½	1.888	½	1.885	1			1.676	½	1.672	1
			1.820	1b	1.821	5	1.817	4			1.638	2	1.640	2
					1.784	6	1.772	3b	1.58	30	1.585	2	1.582	2
	1.76	3	1.762	7b										
					1.750	6	1.750	7	1.55	30	1.558	2	1.554	2

Note—b = broad, vb = very broad [1]Goni & Guillemin (1953) [2]Mandarino, camera diameter 57.3 mm. [3]Mandarino, camera diameter 114.6 mm.

material was weighed on a Mettler Gram-Atic balance, quickly, to prevent water from being taken up by the SeO_2. During the fusion process, no evidence of water was observed, indicating that a truly anhydrous compound was synthesized.

Partial *x*-ray powder data for all these synthetic products are compared in Table 3. The first three substances are clearly identical, but do not give the molybdomenite pattern. The remaining three samples (the $PbSeO_3$ produced by the Wyandotte Chemicals Corporation, the sample prepared by the writer and the Ranwick mineral) give essentially the same *x*-ray powder patterns—molybdomenite. The Ranwick molybdomenite has already been proved identical to the molybdomenite from Argentina (see Table 1).

From the above evidence, there seems to be little doubt that the chemical formula of molybdomenite is $PbSeO_3$. It is also clear that there are at least two polymorphs of $PbSeO_3$. Mrose (personal communication) has found a similar situation in samples of $PbSeO_4$. The writer's precipitated $PbSeO_3$, upon fusion, inverts to molybdomenite. A powder pattern for such a product showed all the lines of molybdomenite plus some lines from the precipitated $PbSeO_3$ (due to incomplete fusion).

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