# OLSACHERITE, Pb<sub>2</sub>(SO<sub>4</sub>)(SeO<sub>4</sub>), A NEW MINERAL FROM BOLIVIA<sup>1</sup>

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### ABSTRACT

Olsacherite,  $Pb_2(SO_4)(SeO_4)$ , has been found in the Pacajake mine, Colquechaca, Bolivia, as an alteration product of penroseite. It is orthorhombic, 222, and occurs in colorless, well-formed crystals 0.1–1.5 mm long elongated on [010]. Morphological measurement showed the presence of four forms:  $\{010\}$ ,  $\{101\}$ ,  $\{111\}$  and  $\{1\overline{1}1\}$ . The space group is  $P22_12$ ; a=8.42, b=10.96, c=7.00 Å; a:b:c=0.7682:1:0.6387; vol. 645.98 ų; Z=4. Strongest lines in X-ray powder photographs in Å are: 3.338 (100), 3.234 (100), 3.015 (100), 2.086 (70), 2.786 (60), 3.845 (50).

Olsacherite is optically (–);  $\alpha=1.945$ ,  $\beta=1.966$ ,  $\gamma=1.983$ ,  $2V=80^\circ$ ; X=a, Y=c. The hardness is  $3-3\frac{1}{2}$ , density 6.55 g/cm³ (calc). Cleavage: {101} good, {010} fair. Calculations of oxides from an electron microprobe analysis yield in weight percent: PbO 71.2, SeO₃ 16.2, SO₃ 14.2 Total 101.6 which results in the empirical formula Pb₂(SO₄) (Se<sub>0.80</sub>So<sub>0.12</sub>O<sub>5.76</sub>). The ratio of S:Se close to 1:1 and the doubling of the b dimension compared to PbSO₄ suggests an ordered structure with a general formula Pb₂(SO₄)(Se<sub>1-x</sub>S<sub>x</sub>O₄). Olsacherite is named in honor of Juan A. Olsacher (1903–1964), former Professor of Mineralogy, Córdoba University, Argentina.

### Introduction

In 1953 Goni and Guillemin described a mineral from Pacajake,<sup>2</sup> Colquechaca, Bolivia and from Cacheuta,<sup>3</sup> Mendoza, Argentina. They referred to it only as an orthorhombic lead selenate and stated that it was impossible to give the mineral a name until the exact nature of kerstenite is known. Kerstenite is a poorly described lead selenium mineral.

Our interest was aroused in this mineral when, in checking the material from the Bolivian locality (Ahlfeld collection, Harvard University), we discovered that the space group differs from that suggested by Strunz (1966). A microprobe analysis showed that sulfur and selenium are both present indicating a formula, Pb(S,Se)O<sub>4</sub>.

This study is based only on the mineral from Bolivia, for none of the Argentine material was available. Even the specimen in the Museum National d'Histoire Naturelle, Paris studied by Goñi and Guillemin has disappeared.

A review of the literature indicates (see Historical Review) that the

- <sup>1</sup> Mineralogical Contribution No. 470 Harvard University.
- <sup>2</sup> Specimen N° 630-53 Laboratoire de Minerálogie, Sorbonne, Paris, France.
- $^3$  Specimen N° 104–1214 Museum National d'Histoire Naturelle, Paris, France, erroneously labeled "molybdomenite."

mineral deserves a proper name. We propose the name *olsacherite* in honor of Juan A. Olsacher (1903–1964), former Professor of Mineralogy at Córdoba University, Argentina, who studied selenium minerals of that country. Goñi and Guillemin have been consulted and they concur that the mineral should be named and agree to *olsacherite*.<sup>4</sup>

### HISTORICAL REVIEW

In 1839 Kersten (p. 277) gave a sketchy and qualitative account of a selenium mineral from Friedricksglück mine, near Hildburghausen, Thuringia, Germany. He mentioned that the mineral occurs in small spheres and botryoidal masses, has a sulfur yellow color, a hardness of 3 to 4 and a distinct cleavage in one direction. Qualitative test indicated that it is a *lead salt of selenious acid* with a small amount of copper, that is, a *selenite*.

In 1850, Dana (p. 504) indicated that the mineral is a *lead selenate* and in 1868 (p. 669) without further information he named this mineral kerstenite with the comment, "May it be a selenate, or is it only a mixture?". The name kerstenite is used in the seventh edition, Vol. II, of Dana's System of Mineralogy (1951) but with the possibility that molybdomenite, PbSeO<sub>3</sub>, described by Bertrand (1882) is synonymous.

Later Goñi and Guillemin (1953) and Mandarino (1965) confirmed molybdomenite as a valid species. Finally, Goñi and Guillemin (1953) described the natural compound, referred to in the Introduction, which they believed to be PbSeO<sub>4</sub>.

We have then a situation in which a mineral name (kerstenite) proposed by Dana was given to a natural substance not described by him; whose properties are practically unknown; and with the apparent impossibility of finding a specimen from the locality described by Kersten. If the name kerstenite is to be preserved it means refraining from naming all minerals containing lead, selenium and oxygen, discovered after Kersten's paper (1839). If so, molybdomenite (Bertrand 1882), the accepted name for monoclinic PbSeO<sub>3</sub>, must go. Furthermore, Mandarino (1965, p. 157) states there are at least two polymorphs of PbSO<sub>3</sub> and quotes Morse in reporting polymorphs of PbSO<sub>4</sub>. Also, according to Mellor, (1930, 10, p. 883) and Jones and Rothschild (1958) there are several other compounds composed of these three elements. Sindeeva (1964, p. 87), in discussing the mineralogy of selenium, expresses the idea that the name kerstenite should be abandoned.

Moreover, since kerstenite was originally described as a selenite and its habit, color, and cleavage do not check with those of the selenate mineral described by Goñi and Guillemin (1953) and in this paper, we believe that Pb<sub>2</sub>(SO<sub>4</sub>)(SeO<sub>4</sub>) is a species that deserves its own name.

### OCCURRENCE

Olsacherite occurs in the Pacajake mine, near Hiaco, Bolivia about  $24~\rm km~ENE$  of Colquechaca on the east slope of the Central Cordillera. The geology of the area was described by Brock and Ahlfeld (1937), and according to them the deposit is a vein enclosed in Devonian sandstone that strikes N 30° W and dips 65° SW.

In this deposit the primary minerals are: penroseite, clausthalite, naumannite, tiemannite, pyrite, siderite, barite, hematite, calcite; and

 $<sup>^4</sup>$  The mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA.

the secondary minerals: cerussite, anglesite, wulfenite, limonite, chalcomenite, ahlfeldite, and native selenium (Herzenberg and Ahlfeld, 1935; Block and Ahfeld, 1937; Palache, 1937; Herzenberg, 1944 and 1945). Olsacherite is an alteration product of penroseite and occurs very sparingly in well formed crystal coating the walls of small cracks or cavities.

In the Cerro Cacheuta, Province of Mendoza, Argentina is a deposit with a mineralogy similar to that of Pacajake, Bolivia (Olsacher, 1939, Ahlfeld and Angelelli, 1948). From this locality Goñi and Guillemin (1953) described a mineral identical (?) with the one from Bolivia here called olsacherite. Their specimen was unavailable for the present study.

## Morphology

The crystals of olsacherite from Bolivia are in the form of sharp, fine needles ranging in length from 0.1 to 1.5 mm with the length 10–15 times the width. Five of the larger crystals were measured on the two-circle reflecting goniometer. Using the resulting axial ratios and following the rule that c < a < b the crystals are elongated on [010] as indicated in Figure 1. This orientation seems desirable for it corresponds to the usual

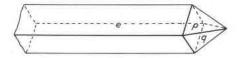


Fig. 1. Olsacherite crystal.

orientation of the closely related mineral anglesite. However, it differs from that of Goñi and Giullemin (1953) who took  $\epsilon$  as the axis of elongation. Many crystals present a very steep pyramidal habit giving them the shape of long acute needles as illustrated in the photograph of the Goñi and Guillemin paper. The measured angles and axial ratios are given in Table 1.

Table 1. Olsacherite Angle Table Rhombic; Disphenoidal—222  $a:b:c=0.7662:1:0.6345\ p_0:q_0:r_0=0.8281:0.6345:1\\q_1:r_1:p_1=0.7662:1.2076:1\ r_2:p_2:q_2=1.5760:1.3051:1$ 

	Forms	φ	$\rho = C$	$\phi_1$	$\rho_1 = A$	$\phi_2$	$\rho_2 = B$
b	010	0° 00′	90° 00′	90° 00′	90° 00′	_	0° 00′
e	101	90 00	39 38	0 00	50 22	50° 22′	90 00
p	111	52 32	46 13	32 24	55 02	50 22	63 57
$\overline{q}$	1 <u>T</u> 1	127 28	46 13	-32 24	55 02	129 38	116 03

Although the morphology suggests that the crystals belong to the crystal class 2/m2/m2/m, a positive pyroelectric response indicates that the crystal class is 222 or mm2.

# Physical and Optical Properties

Olsacherite has good  $\{101\}$  and fair  $\{010\}$  cleavage; the crystals are very brittle and tend to break along the  $\{010\}$  cleavages yielding short prisms with rhombic cross sections. The hardness is  $3-3\frac{1}{2}$ . The crystals are colorless, partially transparent with a colorless streak and vitreous luster; some of them present a very thin whitish coating with a dull luster.

Due to the extremely small amount of material it was not possible to measure the specific gravity. However, the density, calculated using the chemical composition and cell dimensions, was determined as  $6.55 \, \mathrm{g/cm^3}$ . This, as is to be expected, is greater than the density of anglesite which is 6.36. The optical properties are given in Table 2.

TABLE 2. OPTICAL PROPERTIES OF OLSACHERITE

# X-RAY STUDY

The unit cell dimensions were determined from precession photographs (Mo/Zr) for zero, first and second layers with a and c as precession axes. The unit cell data are presented in Table 3; the cell dimensions were refined using X-ray powder data (Table 4).

Precession photographs of exposures as long as 48 hours showed 0k0 reflections only with k=2n; this leads to the space group  $P22_12$ . However, in photographs of the hk0 layer many of the spots defined by h+k= odd are extremely weak and many are missing, especially those with low indices. This suggests the possibility that the odd 0k0 spots could not be seen because of weakness rather than omission. If this is the case, the space group could be P222, Pmm2 or Pmmm, for which there are no conditions for reflection. A positive pyroelectric test eliminates Pmmm, but it leaves the remote possibility that it could be one of the other two.

TABLE	3	HALL	CELL	Пата

	PbSO <sub>4</sub> <sup>a</sup>	$Pb_2(SO_4)(SeO_4)^b$	PbSeO <sub>4</sub> c
	Anglesite	Olsacherite	Synthetic
a	8.47Å	8.42	8.60Å <sup>a</sup>
b	5.39	$10.96$ $\pm 0.01$ Å	5.63
c	6.94	7.00	7.12
Cell volume	$316.8\text{Å}^3$	$645.98\AA^{3}$	$344.7 \rm{\AA}^3$
Space group	Pnma	$P22_{1}2$	Pnma
Z	4	4	4
a:b:c	1.574:1:1.290	0.7682:1:0.6387	1.528:1:1.265
Density			
g/cm³(calc)	6.36	6.55d	6.78

<sup>&</sup>lt;sup>a</sup> Data from Strunz (1966).

The list of spacings given in Table 4 were derived from powder photographs (Cu/Ni) with intensities obtained from visual estimation. These values agree well with those reported by Goñi and Guillemin (1953) for the mineral from Cacheuta, Argentina, and correspond closely to those of synthetic PbSeO<sub>4</sub> (Goñi and Guillemin, 1953; Jones and Rothschild, 1958) and anglesite (Swanson and Fuyat, 1954, p. 67). Because of this similarity of d spacings, Strunz (1966) included PbSeO<sub>4</sub> in the Barite Group with space group Pnma. Popovkin and Simanov (1962) give the unit cell dimensions of synthetic PbSeO<sub>4</sub> and assign it to the same space group. Olsacherite, in composition lies between PbSO<sub>4</sub> and PbSeO<sub>4</sub> with a and c cell dimensions close to those of these compounds. However, its b dimension is approximately twice that of the others and it has a different space group (Table 3).

## CHEMICAL COMPOSITION

There was insufficient material available for a wet chemical analysis of olsacherite. Accordingly an electron microprobe analysis was made by Dr. John Drake and a water determination by Mr. William Sabine, both of Harvard University. Using a highly sensitive technique a one milligram sample gave less than one per cent H<sub>2</sub>O. The mineral is, therefore, considered to be anhydrous. The electron probe determinations showed the presence of only lead, sulfur and selenium and yielded in weight percent: Pb 66.1, Se 10.1, S 5.7. The chemical composition expressed in terms on oxides is given in Table 5. The analysis yields the empirical

b This study.

e Popovkin and Simonov (1962) Å converted from kX units.

 $<sup>^</sup>d$  Density calculated for  $\mathrm{Pb_2}(\mathrm{SO_4})(\mathrm{Se_{0.80}S_{0.12}O_{3.76}}).$ 

Table 4, X-ray Powder Data for Olsacherite

Olsacherite (Pacajake, Bolivia) This study				Olsacherite(?) (Cacheuta, Argentina) Goñi and Guillemin (1953)		PbSeO; (Synthetic) Goñi and Guillemin (1953)		PbSO <sub>4</sub> (Synthetic) Swanson and Fuyat (1954)	
$I^n$	d(obs)b	d(calc)e	Lk.º	I	$d({ m obs})$	I	$d({ m obs})$	1	d(obs
10	5_40	5.383	101					3	5.381
1	4_82	4.832	111					100	
40	4.316	4.315	021	40	4.32	50	4.31	87	4.26
10	4.210	4,210	200	0.88	2102	2.57	1.01	01	1.20
50	3.845	3.840	121	50	3 84	35	3.86	57	2 04 /
30	3.614	3.608	201	15	3.62	15	3_63	23	3,813
30	3.503	3,50	002	15	3.50				3.622
00	0.500	(3_339	220			25	3.51	33	3,479
100	3.338	3.334	012	100	3.35	75	3.36	86	3.333
100	3.234	∫3.239	031	100	3 24	75	3.25	71	3.220
		3_232	102						
100	3.015	3.013	221	100	3.01	100	3,03	100	3,001
60	2.786	2.784	122	40	2.78	35	2.79	35	2,773
35	2.743	2.740	040	40	2.73	35	2.74	46	2,699
20	2.610	∫2.614	212	25	2.62	15	2.62	8	2.618
20	2.010	2.605	301						
2	2.533	2.534	311						
25	2,416	2.416	222			25	2.42	17	2.406
10	2.355	2.353	321			1 777		<1	2.355
20	2.299	2.296	240	15	2.29	15	2.30	20	2,276
10	2,252	2.249	103		-1	10	2.50	5	2.235
30	2.182	2.182	241	25	2.18	15	2_19	7	2.193
		-1102	211	20	2.10	13	2_19	26	
1	2.121	2.121	331						2,164
		(2.090	142	50	2.08	~ ~	2 00	5	2.133
70	2.086	2.080	123	30	2.00	75	2,09	76	2.067
40	2.036	2.033	322	10	2 02				
40	2.020	2.033	401	40	2.03	50	2.04	34	2.031
40	2.020	,		4.0	4000		7.742	48	2.028
30	1.966	1.966	033	20	1.97	10	1.98	21	1.973
	4 04 5	1.965	420						
1	1.913	1,913	223		24/35/2			3	1.095
20	1.887	1.888	341	1.5	1.89			6	1.879
1	1.853	1.858	052						
35	1.794	1.794	303	15	1,79	25	1.80	15	1.793
2	1.750	1.750	004					8	1.741
1	1.734	1.738	143						
		1.714	104			25	1.72	[ 3	1,716
15	1.709	1.711	342		- 7		530 E	16	1.703
		1.705	323					(10	+
-		1.677	351					7	1.656
5	1.677	1.676	260		3.			,	1+050
		1.637	501, 243			35	1.64	3	1.648
15	1.636	1.635	124		- 1	30	1.424		1-040
20	1-625	1.621	441	10	1.62		1	10	4 (04
10	1.591	1.590	162	101	4.02			19	1.621
		∫1.570						10	1.611
5	1.569		153					6	1_571
		1.569	521				S 100		
10	1 273	1.551	134			20	1.53	2	1.542
10	1.552	1.550	224					1	1.525
		1.549	352						
30	1,502	$\int 1.503$	171, 512, 423					15	1.493
-		1.501	343						

Table 4 (Continued)

Plsacherite (Pacajake, Bolivia) This study				Olsacherite(?) (Cacheuta, Argentina) Goñi and Guillemin (1953)		PbSeO <sub>4</sub> (Synthetic) Goñi and Guillemin (1953)		PbSO <sub>4</sub> (Synthetic) Swanson and Fuyat (1954)	
$I^n$	d(obs)b	d(calc)c	hk.e	I	d(obs)	I	d(obs)	I	d(obs)
		1.478	234						
1	1.475	1.475	044						
		1.472	314						
5	1.463	1.462	522					7	1.467
5 2	1.454	1.453	144						
		1.437	433					8	1.441
5	1.435	1.435	540					4	1.429
		1.433	324						
2	1.420	1.418	163						
5	1.405	∫1.405	541					3	1.406
3	1,405	1.403	600, 362					4	1.391
1	1,382							2	1.385
5	1.369							<b>[6</b>	1.371
	1.309							7	1.368
2	1.359							4	1.348
2	1.337							5	1.341
5	1.328						- 1		
Plus	14 addition	al lines							

<sup>&</sup>lt;sup>a</sup> Visual estimation.

formula  $Pb(S_{0.56}Se_{0.40})O_{3.88}$ . The ratio or S:Se close to 1:1, and the doubling of the b axis, as compared to minerals of the barite group, suggest that there is not a simple substitution of Se for S, but rather an ordered structure in which ions of these elements have in general their

TABLE 5. CHEMICAL COMPOSITION OF OLSACHERITE

	1 Wt. %	2 Wt. % recalculated		Atomic proportions with Pb=2
PbO	71.2	70.1	Pb	2.00
$SeO_3$	16.2	15.9	Se	0.80
$SO_3$	14.2	14.0	S	1.12
			O	7.76
	-	-		
Total	101.6	100.0		

<sup>&</sup>lt;sup>a</sup> John Drake, analyst. Electron microprobe analysis.

<sup>&</sup>lt;sup>b</sup> The observed values obtained using Cu K $\alpha$  = 1.54178 Å; Cu K $\alpha$ <sub>1</sub> = 1.54051 Å; Ni filger; camera diameter 114.59 mm.

 $<sup>^{\</sup>circ}$  The calculated values were obtained and indexed by means of an I.B.M. 7094 Computer, using a program for calculations of all possible spacings using h, k and l values from 8 to -8.

own sites. The formula could then be written  $Pb_2(SO_4)(SeO_4)$  or for the mineral with slightly less selenium than sulfur as  $Pb_2(SO_4)(Se_{1-x}S_xO_4)$ .

Dr. Jun Ito synthesized several compounds intermediate to PbSO<sub>4</sub> and PbSeO<sub>4</sub>. X-ray powder photographs of them were all similar to the X-ray powder photograph of olsacherite. However, the crystals were too small for single crystal X-ray study, and thus the range of composition involving a doubling of the b axis could not be determined.

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