

Plumboselite, $\text{Pb}_3\text{O}_2(\text{SeO}_3)$, a new oxidation-zone mineral from Tsumeb, Namibia

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Abstract Plumboselite, ideally $\text{Pb}_3\text{O}_2(\text{SeO}_3)$, is a new selenite (IMA2010–028) from the Tsumeb mine, Namibia. It occurs as fibres on clausenthalite and is also associated with smithsonite, mimetite and vaterite. Plumboselite occurs in subparallel to divergent clusters of thin, flattened, colourless fibres up to 0.3 mm in length, but not exceeding 5 μm in width and 2 μm in thickness. The fibres are elongated parallel to $[001]$ and flattened on $\{010\}$, with $\{010\}$ the only form observed. The crystals have a dull to adamantine lustre and a white streak. The tenacity is brittle and the Mohs hardness is estimated to be between 2 and 3. Plumboselite crystals are optically biaxial with parallel extinction and are length fast in all orientations. The Gladstone-Dale relationship predicts $n_{\text{av}}=2.115$. The high indices of refraction and small crystal size prevented the determination of other optical properties. The calculated density is 7.814 g/cm^3 . The empirical formula (based on 5 O atoms) is $\text{Pb}_{2.92}\text{Ca}_{0.01}\text{Se}_{1.03}\text{O}_5$. Plumboselite is orthorhombic, space group $Cmc2_1$, $a=10.5384(11)$, $b=10.7452$

(13), $c=5.7577(7) \text{ \AA}$, $V=651.98(12) \text{ \AA}^3$ and $Z=4$. The five strongest lines in the powder X-ray diffraction pattern are [d_{obs} in $\text{Å}/(I)/hkl$]: 3.155/(100)/221; 1.956/(26)/042,402; 2.886/(22)/311,002; 1.713/(21)/223; 2.691/(17)/040. The crystal structure was solved from single-crystal X-ray diffraction data and refined to $R_1=0.0371$ on the basis of 200 unique reflections with $F_o>4\sigma F$. The structure is based on double $[\text{O}_2\text{Pb}_3]$ chains of edge-sharing oxo-centered $[\text{OPb}_4]$ tetrahedra along c , between which are sited SeO_3 triangles. The two independent Pb^{2+} atoms and the Se^{4+} atom have stereochemically active lone electron pairs.

Introduction

As noted by one of the authors (WWP) in his introduction to the Tsumeb issue of the *Mineralogical Record* (Wilson 1977), “Tsumeb is most likely the greatest of the great (mineral localities).” This assessment was based upon its prolific production of “classic” mineral specimens of remarkable size and beauty, as well as an incredible diversity of rare and unusual species. Currently, the Tsumeb mine in the Otjikoto Region of Namibia ($19^\circ 15' \text{ S}$, $17^\circ 42' \text{ E}$) is recognised as the type locality for 60 new minerals and 266 mineral species in total (G. Gebhard pers. comm.).

In the 1970s and 1980s, Dr. John Innes served as mineralogist for the Tsumeb Corporation and was instrumental in the discovery of many unusual specimens. Among them, were three specimens of clausenthalite, which represent the first reported occurrence of a selenium-bearing mineral at Tsumeb. Gebhard (1999) noted that “The clausenthalite crystals are covered by the only known selenate from Tsumeb GS 19, still under investigation.” Unknown “GS 19”, to which Gebhard referred, is actually a selenite, rather than a selenate. It is described herein as a new mineral.

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The name is in reference to the mineral's chemical composition, *plumbo* (for lead) and *sel* (for selenite). The mineral and name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2010–028). The holotype specimen is preserved in the collections of the Mineral Sciences Department, Natural History Museum of Los Angeles County, catalogue number 63264.

Occurrence and paragenesis

Plumboselite is known to occur on only three specimens. All three specimens were collected by the late John Innes, probably from the same isolated occurrence. While no information appears to have survived regarding the specific location of this occurrence in the mine, we assume it to be in the second oxidation zone, on or in the vicinity of the 30 level, because this was the part of the mine being actively exploited in the late 1970s, around the time the clausthalite specimens were found. The holotype specimen was previously in the collection

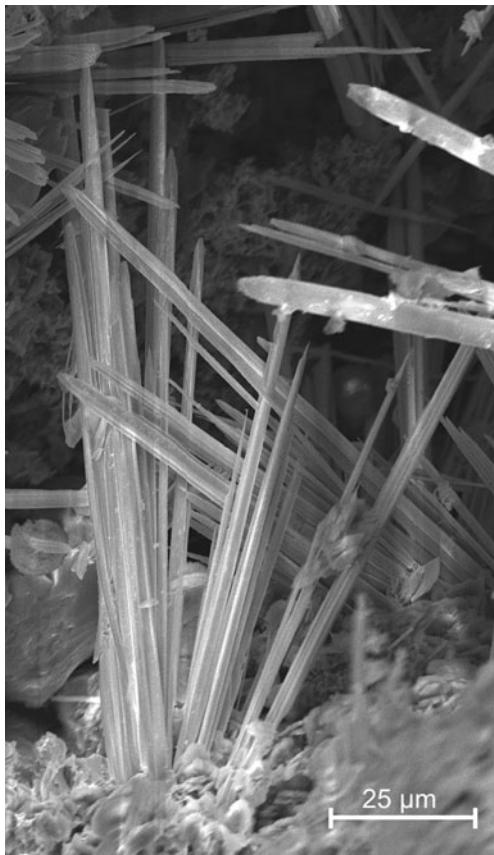


Fig. 1 SEM image of plumboselite

Table 1 Electron microprobe analytical data for plumboselite

Constituent	Wt.%	Range	Stand. Dev.	Probe Standard
CaO	0.09	0–0.34	0.12	Diopside
PbO	84.92	83.49–86.66	1.09	Galena
SeO ₂	14.95	13.18–17.20	1.40	Se metal
Total	99.96	97.00–101.10	1.36	

Table 2 X-ray powder diffraction data for plumboselite

I_{obs}	$d_{\text{obs}}(\text{Å})$	$d_{\text{calc}}(\text{Å})$	I_{calc}	hkl
7	7.5822	7.5212	4	1 1 0
5	5.3271	5.3721	2	0 2 0
		5.2660	2	2 0 0
2	4.5644	4.5710	1	1 1 1
2	3.9411	3.9274	2	0 2 1
100	3.1549	3.1482	100	2 2 1
22	2.8858	2.8870	2	3 1 1
		2.8781	23	0 0 2
17	2.6912	2.6861	17	0 4 0
11	2.6395	2.6330	18	4 0 0
1	2.5253	2.5255	2	2 0 2
3	2.3014	2.2985	4	3 3 1
12	2.1965	2.2095	3	2 4 1
		2.1942	2	1 3 2
		2.1870	3	4 2 1
		2.1794	3	3 1 2
26	1.9561	1.9637	22	0 4 2
		1.9427	23	4 0 2
13	1.8864	1.8803	20	4 4 0
21	1.7129	1.7091	29	2 2 3
11	1.6289	1.6263	26	2 6 1
12	1.6051	1.6026	29	6 2 1
11	1.5767	1.5741	22	4 4 2
2	1.5241	1.5237	2	3 3 3
		1.5204	2	0 6 2
2	1.4971	1.5042	1	5 5 0
		1.4986	1	6 0 2
		1.4969	1	2 4 3
		1.4898	2	4 2 3
3	1.4429	1.4390	5	0 0 4
2	1.3463	1.3485	1	7 3 1
		1.3430	3	0 8 0
3	1.3189	1.3188	1	5 3 3
		1.3167	2	4 6 2
		1.3165	5	8 0 0
		1.2711	12	2 6 3
17	1.2711	1.2705	12	2 6 3
		1.2693	3	2 8 1
		1.2685	6	0 4 4

I_{obs} and d_{obs} from profile fitting using JADE 9.1

I_{calc} and d_{calc} calculated from crystal structure using JADE 9.1

Table 3 Data collection and structure refinement details for plumboselite

Diffractionmeter	Rigaku R-Axis Rapid II
X-ray radiation/power	MoK α ($\lambda=0.71075$ Å)/50 kV, 40 mA
Temperature	298(2) K
Structural Formula	Pb ₃ O ₂ (SeO ₃)
Space group	<i>Cmc</i> 2 ₁
Unit cell dimensions	<i>a</i> =10.5384(11) Å <i>b</i> =10.7452(13) Å <i>c</i> =5.7577(7) Å
<i>Z</i>	4
Volume	651.98(13) Å ³
Density (for above formula)	7.952 g/cm ³
Absorption coefficient	82.807 mm ⁻¹
<i>F</i> (000)	1280
Crystal size	38×5×2 μm
θ range	3.79 to 18.84°
Index ranges	-9≤ <i>h</i> ≤9, -9≤ <i>k</i> ≤9, -4≤ <i>l</i> ≤5
Reflections collected/unique	1110/258 [<i>R</i> _{int} =0.0802]
Reflections with <i>F</i> _o >4σ <i>F</i>	200
Completeness to $\theta=27.48^\circ$	98.7%
Max. and min. transmission	0.8519 and 0.1450
Refinement method	Full-matrix least-squares on <i>F</i> ²
Parameters refined	35
GoF	0.897
Final <i>R</i> indices [<i>F</i> _o >4σ <i>F</i>]	<i>R</i> ₁ =0.0371, <i>wR</i> ₂ =0.0650
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0500, <i>wR</i> ₂ =0.0715
Extinction coefficient	0.00016(6)
Largest diff. peak/hole	+1.025/-1.110 e/Å ³
Flack parameter	0.06(8)

$R_{int} = \frac{\sum |F_o^2 - F_c^2|}{\sum F_o^2}$
 $GoF = S = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]^2}{(n-p)} \right\}^{1/2}$. $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$
 $wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2} \right\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where *a* is 0, *b* is 0 and *P* is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$

of one of the authors (WWP) and another specimen remains in his collection. The third specimen is currently in the collection of Dr. Mark Feinglos.

Plumboselite occurs on clausthalite and clearly formed as an oxidative alteration thereof. Other associated minerals on the specimens include smithsonite, mimetite and vaterite.

Physical and optical properties

Plumboselite occurs in subparallel to divergent clusters of thin, flattened, colourless fibres up to 0.3 mm in length, but not exceeding 5 μm in width and 2 μm in thickness (Fig. 1). The fibres are elongated parallel to [001] and flattened on {010}, with {010} the only form

Table 4 Atomic coordinates and displacement parameters (Å²) for plumboselite

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Pb1	0.0	0.8816(2)	0.814(2)	0.0204(14)	0.0197(19)	0.0162(17)	0.025(2)	-0.007(5)	0.0	0.0
Pb2	0.24794(19)	0.11233(14)	0.8125(8)	0.0199(11)	0.0200(14)	0.0207(14)	0.0190(16)	0.002(5)	0.006(3)	-0.0053(10)
Se	0.5	0.8698(6)	0.8652(15)	0.024(5)	0.000(5)	0.032(5)	0.041(15)	0.001(5)	0.0	0.0
O1	0.138(2)	1.000(7)	0.048(13)	0.029(8)						
O2	0.5	0.723(3)	0.765(9)	0.015(12)						
O3	0.624(3)	0.930(3)	0.717(5)	0.028(10)						

Table 5 Selected bond distances (Å) in plumboselite

Se–O2	1.68(4)	Pb2–O1	2.16(6)
Se–O3(×2)	1.69(3)	Pb2–O1	2.26(6)
<Se–O>	1.687	Pb2–O3	2.44(3)
		Pb2–O3	2.73(3)
Pb1–O1(×2)	2.35(6)	Pb2–O2	2.886(13)
Pb1–O1(×2)	2.46(6)	Pb2–O3	3.70(3)
Pb1–O2	2.83(5)	Pb2–O3	3.71(3)
Pb1–O2	3.36(5)	<Pb2–O>	2.848
<Pb1–O>	2.635		

observed. Plumboselite fibres are transparent, have a dull to adamantine lustre and a white streak. The hardness is estimated to be between 2 and 3. The tenacity is brittle, no cleavage or parting was observed and the fracture could not be ascertained due to the size of the fibres. The density could not be measured because it is greater than those of available high-density liquids and there is insufficient material for physical measurement. The calculated density is 7.814 g/cm^3 based upon the empirical formula and single-crystal unit cell.

Optically, plumboselite is biaxial, however the sign, $2V$ and dispersion could not be determined due to the size of the crystals and the indices of refraction are higher than available index fluids. The Gladstone-Dale relationship (Mandarino 1981) predicts $n_{av}=2.115$. The optical orientation could only be partially determined: $X=c$. The extinction is parallel and fibres are length fast in all orientations.

Chemical composition

Quantitative wavelength-dispersive electron-microprobe analyses (7 points) were carried out on plumboselite

Table 6 Bond valence sums for plumboselite

	Pb1	Pb2	Se	Sum
O1	0.454 x2↓	0.669		2.031
	0.363 x2↓	0.545		
O2	0.170	0.152	1.425	1.895
	0.058			
O3		0.378	1.387 x2↓	2.011
		0.189		
		0.029		
		0.028		
Sum	1.862	1.990	4.199	

Pb²⁺–O bond strengths from Krivovichev and Brown (2001) and Se⁴⁺–O bond strengths from Brese and O'Keeffe (1991)

needles with a Cameca SX50 electron microprobe at the Department of Earth and Ocean Sciences, University of British Columbia. Operating conditions were 20 kV, with beam current of 5 nA and a 1 μm beam diameter. Raw intensity data was corrected using a PAP matrix correction (Pouchou and Pichoir 1984). No other elements were detected by energy dispersive spectroscopy. The results, as well as the standards used, are provided in Table 1.

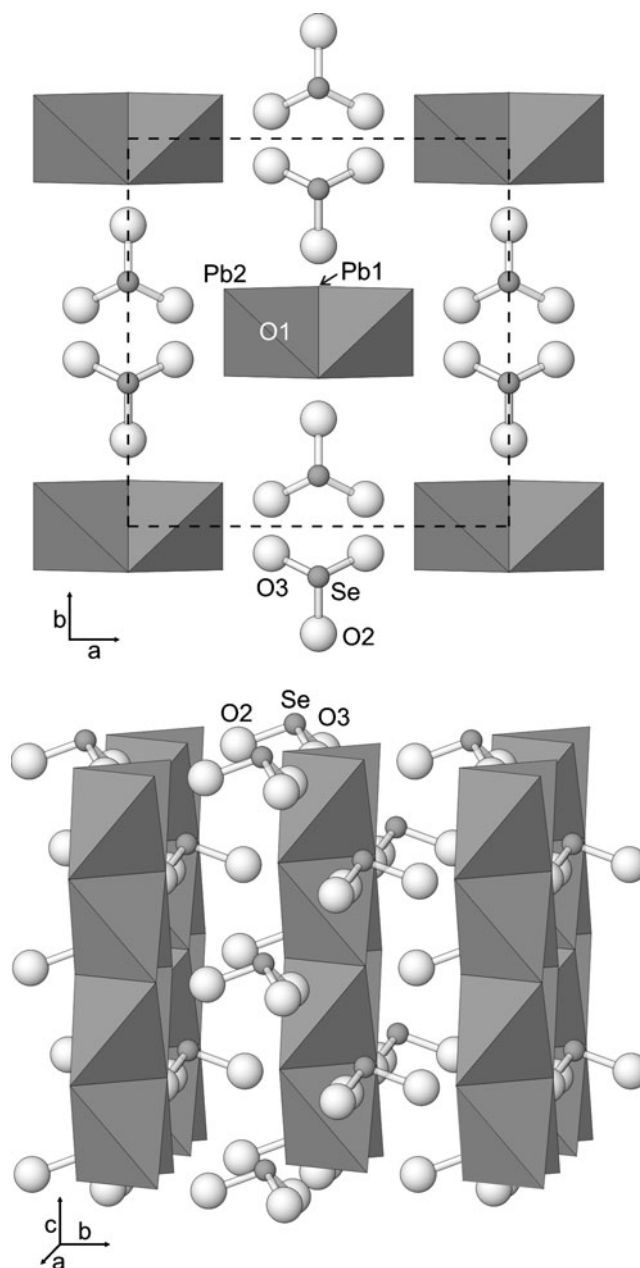
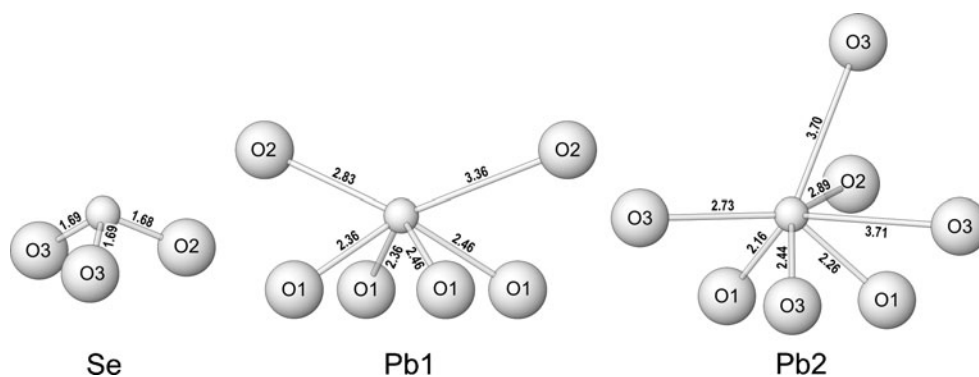
**Fig. 2** Crystal structure of plumboselite

Fig. 3 Se, Pb1 and Pb2 coordinations in plumboselite. In each case, the stereoactive lone electron pairs are oriented approximately upwards



The empirical formula (based on $\text{O}=5$) is $\text{Pb}_{2.92}\text{Ca}_{0.01}\text{Se}_{1.03}\text{O}_5$. The simplified formula is $\text{Pb}_3\text{O}_2(\text{SeO}_3)$, which requires PbO 85.78 and SeO_2 14.22, total 100 wt%.

X-ray powder diffraction data

X-ray powder-diffraction data (Table 2) were collected on a Rigaku R-AXIS Rapid II curved imaging plate micro-diffractometer using monochromatized $\text{MoK}\alpha$ radiation at the Natural History Museum of Los Angeles County. Unit-cell parameters, derived from whole pattern fitting using JADE 9.1 software are: $a=10.5505(8)$, $b=10.7601(9)$ and $c=5.7671(5)$ Å and $V=654.71(9)$ Å³, which are in good agreement with those obtained from the single-crystal study (see below).

Single crystal X-ray diffraction

The structure data collection was performed using the same instrument noted above. The Rigaku CrystalClear software package was used for processing of the structure data, including the application of an empirical absorption correction. Application of a shape-based absorption correction was found to be unsuitable because of the very small and thin nature of the fibre. Note that because of the small crystal size the dataset was limited to a resolution of 1.1 Å ($\theta=18.84^\circ$). This thwarted our efforts to refine anisotropic displacement parameters for the O atoms. The structure was solved by direct methods using SIR92 (Altomare et al. 1994) and the location of all atoms was straightforward. SHELXL-97 (Sheldrick 2008) was used for the refinement of the structure. The details of the data collection and the final structure refinement are provided in Table 3. The final atomic coordinates and displacement parameters are in Table 4. Selected interatomic distances are listed in Table 5 and bond valences in Table 6.

Description of the structure

The crystal structure of plumboselite is identical to that of synthetic $\text{Pb}_3\text{O}_2(\text{SeO}_3)$ as described by Krivovichev et al. (2004) and Kim et al. (2009). The structure contains two Pb atoms, one Se atom and three O atoms in the asymmetric unit. The structure is based on double $[\text{O}_2\text{Pb}_3]$ chains of edge-sharing oxo-centered $[\text{OPb}_4]$ tetrahedra along c , between which are sited SeO_3 triangles (Fig. 2). The lone pairs for both Pb^{2+} atoms and the Se^{4+} atom are stereoactive, as evidenced by the lopsided geometries of the Pb^{2+} and Se^{4+} coordinations (Fig. 3). Kim et al. (2009) pointed out the importance of the stereoactivity of the Se^{4+} in determining the non-centrosymmetric symmetry of the phase and, consequently, its piezoelectric and pyroelectric properties.

The average Pb1-O and Pb2-O bond lengths are 2.635 and 2.848 Å, respectively, and the average Se-O bond length is 1.687 Å. All values are consistent with typical oxysalt minerals, as well as those lengths reported by both Krivovichev et al. (2004) and by Kim et al. (2009). Note that we have included Pb-O bonds up to a bond-length of 3.71 Å; however, an O2 at a distance of 3.68 Å from Pb1 is not included because it is on the same side of the Pb as are the four short Pb-O bonds and, therefore, it is unlikely to contribute to the Pb1 coordination.

Numerous minerals and synthetic phases have oxo-centered $[\text{OPb}_4]$ tetrahedra (Siidra et al. 2008). Of these compounds, only twelve have $[\text{O}_2\text{Pb}_3]$ chains, and only three are minerals: chloroxiphite (Finney et al. 1977), mendipite and damaraite (Krivovichev and Burns 2001). Among all of these phases, the plumboselite structure-type is unique.

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