

Schultenite from King County, Washington, USA; a second occurrence, and review

R. FALLS

Department of Mineralogy and Geology, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario,
Canada M5S 2C6

B. CANNON

Bart Cannon Minerals, 1041 NE 100 Street, Seattle, Washington, USA 98125

AND

J. A. MANDARINO

Department of Mineralogy and Geology, Royal Ontario Museum, 100 Queen's Park, Toronto, and Department of
Geology, University of Toronto, Toronto, Ontario, Canada M5S 2C6

ABSTRACT. Schultenite, PbHAsO_4 , known only from Tsumeb, Namibia, has been identified from a second occurrence: near North Bend, King County, Washington, USA. It occurs as euhedral crystals in a quartz-arsenopyrite-galena vein. It has a measured density of $6.07(3) \text{ g/cm}^3$ and a calculated density of $6.079(4) \text{ g/cm}^3$. The white to colourless crystals have a white streak, adamantine lustre, and fluoresce dull yellow under long wave ultraviolet light. Schultenite is monoclinic. Pa or $P2_1/a$; the unit cell parameters refined from the X-ray powder diffraction data are: a 5.827(3), b 6.743(3), c 4.847(3) Å, β 95.34(5)°; V 189.6(1) Å³; $Z = 2$; $a:b:c = 0.8642:1:0.7188$. The forms $\{010\}$, $\{001\}$, and $\{322\}$ were observed on the Washington schultenite crystals.

KEYWORDS: schultenite, King County, Washington.

PbHAsO_4 has long been known as a synthetic compound and has had widespread use as an insecticide. Details on the synthesis of this compound are summarized by McDonnell and Smith (1916) and by Mellor (1929). Notable among the studies cited is that of de Schulten (1904) who carried out a rather extensive crystallographic study of the synthetic material. The compound was discovered as a mineral on a specimen from Tsumeb, South West Africa. It is quite appropriate that Spencer (1926) named the mineral schultenite in view of de Schulten's earlier work. Spencer's description was extended by the X-ray diffraction study carried out by Claringbull (1950). All the data for the mineral were obtained from a single specimen in the British Museum (Natural History). Embrey and Hicks (1977), working with two specimens obtained several years later, were able to add

two more forms to Spencer's original list. These later specimens probably came from a deeper part of the Tsumeb deposit and are associated with cuprian adamite and keyite on a matrix of dark red tennantite and (on one specimen) milky quartz. Hänni *et al.* (1978) presented new data for stranskiite, and noted that it was associated with adamite, olivenite, schultenite, and galena. Their specimen came from Tsumeb, the type locality for both stranskiite and schultenite, but it is from the lower zone of oxidation 950 m below the surface, 31st level, E9 pillar.

This paper describes a new occurrence of schultenite in the state of Washington, USA.

New occurrence

Schultenite is a minor constituent of a quartz-arsenopyrite vein in the granodiorite of the Miocene Snoqualmie Batholith in King County, Washington, USA. The occurrence (longitude 121° 36' W, latitude 47° 29' N, about 60 km due east of the city of Seattle) was exposed in a logging road cut on the ridge between Granite Lake and Gifford Lake at an elevation of 1300 m, 13 km east of the town of North Bend. The vein dips vertically and strikes N50° W. It is 12 to 30 cm wide with wall linings of poorly formed quartz crystals (1 to 4 cm long) and a nearly solid filling of coarsely crystalline arsenopyrite. Euhedral arsenopyrite crystals up to 3 cm in diameter occur occasionally in small vugs. The vein has been partially oxidized to a depth of one metre below the shallow soil-cover.

One of the authors (B.C.) trenched this vein to a depth of 2 m and for a distance of 3 m. The excavation uncovered a single vertical zone 12 cm in diameter and at least 2 m deep which contained a number of minerals in addition to arsenopyrite and quartz. The lower metre of this zone hosted galena, sphalerite, and chalcopyrite. The upper, oxidized portion of this zone contained partially decomposed sulphides, scorodite, mimetite, schultenite, smithsonite, beudantite, anglesite, cerussite, aurichalcite, iron oxides, and an unidentified Pb-Ag-Bi mineral.

The secondary minerals occurred in vugs up to $4 \times 8 \times 10$ cm and in the interstices between sulphide crystals. The vugs have been divided into five different types, depending on their mineral assemblages. The type of mineral assemblage which was present in a particular vug appeared to depend upon the size of the vug, the associated sulphide minerals and the relationship of the vug to the oxidation front (fig. 1).

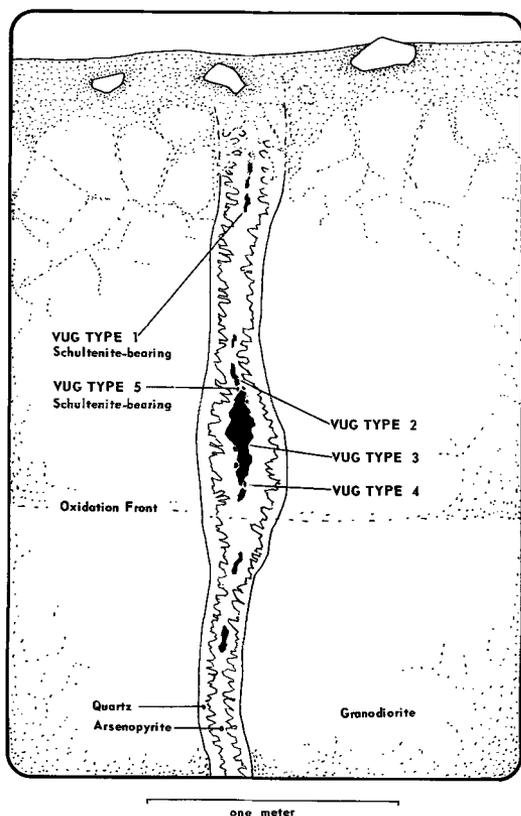


FIG. 1. An idealized cross-section through the schultenite-bearing vein.

Vug type 1 was the most common and contained yellowish-brown, botryoidal scorodite coating arsenopyrite. In the rare cases where galena was present schultenite also occurred. Approximately twenty individual crystals and groups of schultenite were collected from this type of vug. These crystals are 0.5 to 4 mm in length, pale yellow in colour and show a bladed habit. Most of the crystals protruded from the walls of the vugs and they were usually well isolated from each other. The vugs of this type reached a maximum size of $1 \times 2 \times 4$ cm, but most were under $1 \times 1 \times 0.5$ cm.

Vug type 2 was also a common one and contained dull, yellowish orange cerussite pseudomorphs after mimetite. Colourless anglesite crystals up to 1 mm partially encrusted some of the cerussite. Beudantite, in greenish brown coatings and pale yellowish 0.5 mm crystal tufts, was an associate in some type 2 vugs.

Vug type 3 had only one representative, and hosted no schultenite, but its dimensions were the largest of any encountered ($10 \times 8 \times 4$ cm). This vug contained partially oxidized sphalerite crystals up to 4 cm with galena, arsenopyrite, and quartz. Most of this vug had been thickly coated with cerussite and anglesite and with minor beudantite and mimetite, in a similar fashion to vug type 2. The unique feature of this vug was the presence of sky-blue, botryoidal aurichalcite, and colourless to pale grey smithsonite crystals up to 2 mm long.

Vug type 4 was the least common and occurred as solution cavities within the thicker galena concentrations. These cavities were lined with water clear, equant anglesite crystals of 1 to 2 mm.

Vugs of type 5 were abundant and contained the greatest number of schultenite crystals. These vugs were actually interstitial cavities between sulphide crystals. Most of these vugs were less than $1 \times 1 \times 0.5$ cm. In most cases galena was partly altered to a very friable unidentified black mineral containing Bi, Ag, and Pb. Approximately fifty schultenite specimens were found in these vugs along with columnar clusters of glassy, pale yellow tapering mimetite crystals up to 3 mm, tufted acicular bundles of snow white, younger generation mimetites up to 1.5 mm, and rare colourless cerussite prisms up to 2 mm. The schultenite crystals from these vugs often displayed attached crystal tufts of mimetite. These schultenite crystals were colourless and were much sharper than the schultenites from vug type 1, most appearing similar to the idealized habit shown by Palache *et al.* (1951). Several specimens showed excellent 'fishtail' twins. The schultenite crystals from these vugs reached a maximum length of 3.5 mm.

It could be significant to note that schultenite did not occur at the lowest extent of the oxidized zone.

TABLE I. *Physical properties and unit cell parameters of schultenite*

	1	2	3	4	5	6	7
<i>a</i>	—	—	—	5.83	5.820(9)	5.8421(6)	5.827(3) Å
<i>b</i>	—	—	—	6.76	6.750(8)	6.7545(6)	6.743(3) Å
<i>c</i>	—	—	—	4.85	4.850(6)	4.8575(6)	4.847(3) Å
β	—	—	—	95.5°	95.9(2)°	95.40(1)°	95.34(5)°
Vol.	—	—	—	190.4	189.5(3)	190.83	189.6(1) Å ³
2 <i>V</i> _{meas.}	—	—	58° 14'	—	—	medium	—
2 <i>V</i> _{calc.}	—	—	—	—	—	59° 12'	—
α	—	—	1.8903(calc.)	—	—	1.890	—
β	—	—	1.9097	—	—	1.910	—
γ	—	—	1.9765	—	—	1.976	—
D _{meas.}	6.076	6.042	5.943	—	—	—	6.07
D _{calc.}	—	6.053	—	6.06	6.08	6.041	6.079

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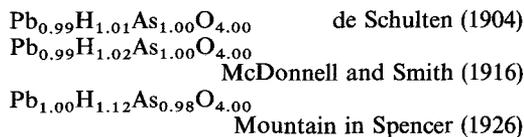
1. de Schulten, 1904.
2. McDonnell and Smith, 1916.
3. Spencer, 1926.
4. Claringbull, 1950.
5. Refined from the powder data of Claringbull, 1950 (this study).
6. Morris *et al.*, 1977.
7. This study (refined from the powder data).

Natural and synthetic schultenite

Appearance and physical properties. Synthetic schultenite is known as well-formed platy crystals and as formless masses and powders, but the mineral only occurs as euhedral crystals. It is transparent and varies from colourless through white to yellowish and has a white streak. The lustre is brilliant vitreous to almost adamantine. The hardness is 2½. The mineral is brittle and has a good {010} cleavage.

The Washington schultenite occurs as well-formed crystals from 1 to 4 mm long. They are colourless to white with a white streak and have a subadamantine lustre. The good {010} cleavage was observed on broken crystals. Unlike the specimens of Tsumeb schultenite in the collections of the Royal Ontario Museum, the Washington schultenite fluoresces a dull yellow under long wave ultraviolet light. Table I lists the physical properties of synthetic and natural schultenites.

Chemical data. The results of three chemical analyses are given in Table II where they are compared with the theoretical composition of the compound. Two of the analyses were carried out on synthetic material by de Schulten (1904) and by McDonnell and Smith (1916), while the third was done on the mineral by Mountain, whose data are given by Spencer (1926). The empirical formulae (based on 4 oxygen ions) derived from the three sets of analytical data are:



No analysis was made of the Washington schultenite. An X-ray fluorescence scan showed only Pb and As. The ratio of the height of the Pb-*Lβ* peak to the height of the As-*Kβ* peak is almost identical to the ratio of the heights of the same peaks in a scan of Tsumeb schultenite.

TABLE II. *Chemical data for schultenite and synthetic schultenite*

Ref.	H ₂ O	PbO	As ₂ O ₅	Total	Mol. wt.
1	2.59	64.30	33.11	100.00	347.12
2	2.63	64.08	(33.29)	(100.00)	345.66
3	(2.67)	64.20	33.13	(100.00)	345.87
4	2.88	63.97	32.18	99.03	345.51

Notes:

1. Ideal composition, wt. %.
 2. de Schulten (1904); As₂O₅ by difference.
 3. McDonnell and Smith (1916); water by difference.
 4. Mountain in Spencer (1926).
- Molecular weights calculated by the method given by Mandarino (1981b).

Crystallographic data. Optical goniometric studies by de Schulten (1904) showed that synthetic PbHAsO_4 is monoclinic. That study gave the following morphological data: $a:b:c = 0.7212:1:0.8704$, $\beta = 84^\circ 23'$. Spencer (1926), working on natural crystals, interchanged de Schulten's a and c axes, and obtained the axial ratio $a:b:c = 0.8643:1:0.7181$ with $\beta = 84^\circ 36' (95^\circ 24'$ in the modern convention). He found sixteen forms on the crystals from Tsumeb: $\{001\}$, $\{010\}$, $\{210\}$, $\{110\}$, $\{120\}$, $\{130\}$, $\{140\}$, $\{011\}$, $\{323\}$, $\{111\}$, $\{232\}$, $\{121\}$, $\{122\}$, $\{111\}$, $\{211\}$, and $\{221\}$. After transformation to Spencer's axes, de Schulten's forms, $\{010\}$, $\{110\}$, $\{011\}$, $\{111\}$, and $\{112\}$, became Spencer's $\{010\}$, $\{011\}$, $\{110\}$, $\{111\}$, and $\{211\}$, respectively. Palache *et al.* (1951) recalculated the axial ratio from Spencer's complete data (Spencer used only three angles for his calculations) and obtained $0.8649:1:0.7201$ and $\beta = 95^\circ 23\frac{1}{2}'$. Embrey and Hicks (1977) reported two new forms, $\{101\}$ and $\{113\}$, from a study of new specimens from Tsumeb.

The Washington schultenite occurs as single crystals, 'fishtail' twins, fan-shaped aggregates and radiating groups. The individual crystals show a bladed habit, flattened on $\{010\}$ and elongated on

$\{001\}$. Most of the crystals are unsuitable for goniometry due to twinning or poor faces. However, the forms $\{001\}$, $\{010\}$ and $\{322\}$ were identified on one broken crystal.

Table III is a new angle table based on the high-precision unit cell parameters determined by Morris *et al.* (1977). It contains data on all the forms recognized by de Schulten (1904), Spencer (1926), Embrey and Hicks (1977), and this study.

An X-ray powder diffraction pattern of the new schultenite was produced in a Debye-Scherrer camera of 114.6 mm diameter using $\text{Cu-K}\alpha$ radiation. The data from this pattern are essentially the same as those published by Claringbull (1950) and by Morris *et al.* (1977) and are not reproduced here for that reason.

Only one single-crystal study has been carried out on schultenite. The data obtained from that study by Claringbull (1950) are given in Table I where they are compared with the unit cell parameters refined from the X-ray powder diffraction data for synthetic PbHAsO_4 published by Morris *et al.* (1977). Also included are the values refined from the powder data obtained from the Washington schultenite and from the powder data given by Claringbull (1950).

TABLE III. Angle table for schultenite

Monoclinic prismatic, $2/m$
 $a:b:c = 0.8649:1:0.7192$; $\beta = 95^\circ 24'$;
 $\rho_0:q_0:r_0 = 0.8315:0.7160:1$
 $r_2:p_2:q_2 = 1.3966:1.1613:1$; $\mu = 84^\circ 36'$
 $\rho_0 0.8352, q_0 0.7192, x_0 0.0945$

Forms	ϕ	ρ	ϕ_2	$\rho_2 = B$	C	A
$\{001\}$	90° 00'	5° 24'	84° 36'	90° 00'	0° 00'	84° 36'
$\{010\}$	0 00	90 00	—	0 00	90 00	90 00
$\{140\}$	16 11	90 00	0 00	16 11	88 30	73 49
$\{130\}$	21 10	90 00	0 00	21 10	88 03	68 50
$\{120\}$	30 08	90 00	0 00	30 08	87 17	59 52
$\{110\}$	49 16	90 00	0 00	49 16	85 55	40 44
$\{210\}$	66 43	90 00	0 00	66 43	85 02	23 17
$\{011\}$	7 29	35 58	84 36	54 23	35 37	85 37
$\{101\}$	90 00	42 55	47 05	90 00	37 31	47 05
$\{113\}$	57 16	23 55	69 33	77 20	19 34	70 04
$\{111\}$	52 17	49 37	47 05	62 14	45 26	52 57
$\{\bar{1}11\}$	-45 50	45 55	126 31	59 59	49 53	121 01
$\{221\}$	-47 37	64 53	147 36	52 23	68 55	131 58
$\{323\}$	62 43	46 17	47 05	70 39	41 32	50 02
$\{232\}$	40 45	54 55	47 05	51 41	51 31	57 43
$\{121\}$	32 53	59 43	47 05	43 31	56 54	62 02
$\{122\}$	-24 11	38 15	107 54	55 37	40 43	104 42
$\{322\}$	-58 10	53 44	-40 49	64 49	121 38	133 14
$\{211\}$	-65 28	60 00	147 36	68 56	64 56	141 59

Notes: All elements and angles in this table are based on the unit cell parameters determined by Morris *et al.* (1977).

Conclusions

The crystallographic, physical, and chemical data for schultenite are remarkably constant for both natural and synthetic material. Using the mean refractive index of the Tsumeb mineral ($\bar{n} = 1.9255$), the calculated density ($D = 6.06 \text{ g/cm}^3$), the chemical data and the Gladstone-Dale constants given by Mandarino (1981a), the compatibility index is -0.034 which is excellent on the scale proposed by Mandarino (1979, 1981a). Using the density calculated from the refined cell parameters gives -0.027 , also excellent. For the synthetic material, using the data given by Morris *et al.* (1977), the compatibility index is also -0.034 (excellent). Assuming the same optical data and the ideal chemical composition, the Washington schultenite and the synthetic material studied by de Schulten (1904) each have a compatibility index of -0.027 (excellent). Similarly, the synthetic material described by McDonnell and Smith (1916) has a compatibility index of -0.034 (excellent).

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