Schultenite, a new mineral, from South-West Africa.

By L. J. SPENCER, M.A., Sc.D., F.R.S.

With a chemical analysis by E. D. MOUNTAIN, M.A. Mineral Department, British Museum (Natural History).

[Read November 2, 1926.]

BARON A. DE SCHUL/TEN,¹ a political refugee from Finland, worked during the latter part of his life in the chemical laboratories of the Sorbonne in Paris. There he prepared in a crystallized form a number of minerals and compounds analogous to them. These were determined crystallographically and compared in isomorphous series. For example, having obtained crystals of artificial monetite,² CaHPO₄, he then proceeded to prepare the corresponding compounds in which strontium, barium, or lead take the place of calcium, and arsenic the place of phosphorus.³ In this series he determined the crystallographic constants and optical data for CaHPO4, SrHPO4, BaHPO4, PbHPO4, SrHAsO, and PbHAsO, Crystals of CaHAsO, were also obtained, but they were too small for measurement. Any of these compounds might be expected to occur in nature, but hitherto only monetite has been found as a mineral. His 'monétite arséniée de plomb' is the subject of the present note, and for it, as a mineral, the name schultenite is suggested. Baron Schulten presented to the British Museum collection in 1898 a small set of his artificial products, but unfortunately these include none of his monetite series.

¹ August Benjamin Friherre af Schultén (1856-1912); obituary notice, Min. Mag., 1913, vol. 16, p. 381.

² A. de Schulten, Reproduction artificielle de la monétite. Bull. Soc. Franç. Min., 1901, vol. 24, pp. 323-326.

—— Recherches sur le phosphate dicalcique. Reproduction artificielle de la brushite. Reproduction de la monétite par un nouveau procédé. Ibid., 1903, vol. 26, pp. 11-17.

³ A. de Schulten, Reproduction artificielle de monétites de baryum, de plomb et de strontium et de monétites arséniées de plomb et de strontium. Ibid., 1904, vol. 27, pp. 109-123. (Monétite arséniée de plomb, p. 113.) This compound, lead hydrogen orthoarsenate, $PbHAsO_4$, is the 'lead arsenate' of commerce, and was first prepared by J. J. Berzelius in 1819. It is used as an insecticide, especially in America in sprays for fruit-trees; and being practically insoluble in water it is no doubt responsible for the retention of arsenic in apples. H. Goguel¹ in 1895 obtained monoclinic crystals on which be determined some of the characters under the microscope. Later, in 1916, C. C. McDonnell and C. M. Smith,² in a detailed study of the several forms of lead arsenate, also gave some of the microscopic characters.

As yet only a single specimen representing the new mineral is known, but doubtless there are others in collections amongst the rich series of crystallized material that has come from the locality. This specimen [B.M. 1926, 205] was acquired in 1926 for the British Museum collection from Mr. Wilhelm Maucher of Munich, and was labelled 'Lanarkite: Tsumeb, Otavi, South-West Africa'. Although the mineral was incorrectly labelled lanarkite, there can be no doubt about the locality, for the specimen is very typical of the pseudomorphous crusts that have been found in abundance at Tsumeb. The lead chloro-arsenate (mimetite) is common at this locality.

The specimen shows a base of large (2 cm. across) crystals of yellowish anglesite which are altered on the surface and along cracks to bayldonite. Resting on the anglesite were tabular crystals probably of chessylite, and hexagonal prisms and rods no doubt representing mimetite; both of these are now completely changed to bayldonite. The bayldonite (a basic arsenate of lead and copper) is yellowish-green in the interior, and bluish-green and minutely crystalline on the surface. The new mineral rests on these pseudomorphs, and is somewhat intermixed with bayldonite.

The schultenite has the form of thin crystal plates which are perfectly transparent, clear, and colourless, and with a brilliant vitreous to almost adamantine lustre. The largest plates measure 1 cm. across with a thickness of 1 mm., and the smallest is about 1 mm. across. The material is brittle and easily crushed to a white powder; hardness $2\frac{1}{2}$.

The crystals are monoclinic (holohedral) with the elements :

 $a:b:c = 0.8643:1:0.7181, \beta = 84^{\circ} 36',$

¹ H. Goguel, Contribution à l'étude des arséniates et des antimoniates cristallisés préparés par voie humide. Mém. Soc. Sci. Bordeaux, 1895, vol. 1, pp. 83-157. (Orthoarséniate diplombique, p. 135.)

² C. C. McDonnell and C. M. Smith, Journ. Amer. Chem. Soc., 1916, vol. 38, p. 2030. A summary of the chemical literature is there given.

as calculated from the measured angles cp, cl, and bl given in the following table. A few other measured angles are also added for comparison with the calculated angles, sufficient to show that good results were obtained.

		Mean.		Limits.	No.	. Calculated	•
cp = (001):(111)	•••	$45^{\circ}25^{\prime}$	45°	24'-45° 2	6′ 9	*	
cl = (001):(130)		88 3	88	2 - 88	6 6	*	
bl = (010):(130)		$21 \ 10^{1}_{2}$	21	8 - 21 1	3 8	*	
bp = (010) : (111)		62 12	62	3-62 2	23 16	62° 16′	
ce = (001):(011)		$35 \ 36$	35	32 - 35 4	0 6	35 34	
$st = (\bar{2}11) : (\bar{2}21)$	•••	$16 \ 33$	16	30 - 16 3	8 8	$16 \ 32$	

The complete list of sixteen forms and their angles is, however, given in a form of table (p. 153), which, it is believed, combines the advantages both of the arrangement in zones of interfacial angles (as adopted by Miller, Dana, Hintze, and Groth) and of the ϕ and ρ (longitude and latitude) angles employed in two-circle goniometry (as advocated by Goldschmidt). For monoclinic crystals the polar distances ρ are more conveniently taken from the fixed *b*-axis (the axis of symmetry), rather than from the arbitrary *c*-axis as done by Goldschmidt. The angle between any two faces lying in a zone containing one of the axial planes is at once given by the difference between two angles in the table. Such a table of angles can be quickly checked by placing a transparent stereographic net over the projection (fig. 3).

The crystals are all flattened parallel to the plane of symmetry b (010), parallel to which there is a good cleavage. The usual habit is rhombshaped (fig. 1), with much the appearance of crystals of gypsum. Α small (1 mm.) crystal of this type, which was mounted on the goniometer, is completely developed on all sides. Less often the pyramidfaces p(111) are partly or sometimes completely cut out by the basal plane c(001) (fig. 2). The prominent prism is l(130), and n(140) is usually present as narrow faces, but m(110) is only rarely represented. Small clino-dome faces e(011) sometimes border the basal plane when Except for p(111), all the pyramid-faces are the latter is present. quite small. The faces b(010) are prominently striated parallel to their intersection with the prism-faces; and when c(001) is present they also bear less prominent striations parallel to and close to the edge b/c. The prism-faces are faintly striated vertically. The basal plane and the pyramids are perfectly smooth, and give single sharp images when not confused by sub-parallel growth of the crystals.

The determination of the optical constants presented some difficulty and unfortunately is not complete. The crystals are very thin and brittle, and the thicker and better crystals on the single specimen

could not be sacrificed for cutting oriented plates and prisms. Measurements of the extinction-angle on the plane of symmetry gave readings varying from 19° to 28° to the prism-edge in the acute angle β , the mean being 24°. Owing to the high refraction, the optic axes do not emerge into air through b(010), and it was consequently at first thought that the optic axial plane was parallel to the plane of symmetry (as previously described for the artificial crystals). One optic axis is, however, visible through p(111). A small fragment broken approximately perpendicular to the plane of symmetry and the cleavage, and giving straight extinction, showed a wide-angle biaxial figure of positive sign with the optic axial plane perpendicular to the plane of symmetry. The angle was estimated under the microscope with a micrometer scale as $2E_a = 135^\circ$. By immersing a crystal in a trough of methylene iodide it was possible to observe the obtuse angle through b (010), and on the Fuess axial angle apparatus this was measured as $2H_{\circ} = 146^{\circ} 34'$ for sodium-light. Taking β as 1.9097 and for methylene iodide n = 1.742, this gives:

 $2V_a = 58^\circ 14'$ and $2E_a = 136^\circ 38'$ (Na).

The optical orientation of the crystals is: optic axial plane perpendicular to the plane of symmetry and lying in the obtuse angle β ; $a(Bx_o) = b, \beta: c = -24^\circ, \gamma(Bx_a): c = +66^\circ$; sign positive. These directions are plotted on the stereographic projection (fig. 3).

Refractive indices were determined by the prism method of minimum deviation through the natural prism given by the faces l(130) (130), the refracting angle on the crystal employed being measured as $42^{\circ} 22'$. In such a prism the path of the light is symmetrical through the prism in the direction of the axis of symmetry; and the vibration-directions β and γ lie in the plane of symmetry, though not parallel and perpendicular to the refracting edge of the prism. The use of natural prisms of orthorhombic crystals in this connexion is well recognized, when the vibration-directions are parallel and perpendicular to the refracting edge; but for monoclinic crystals I have not been able to find any mention of this method in the text-books on crystallography With white light the schultenite prism gave two and crystal-optics. long and widely separated spectra, indicating high dispersion and strong birefringence. The crystal used was small and readings could not be obtained for lithium- and thallium-light. The values determined for sodium-light are:

 $\beta = 1.9097$ and $\gamma = 1.9765$ (Na).

Calculated from β , γ , and 2V, the value of α is 1.8903.



Crystals and Stereographic Projection of Schultenite.

Forms of Schultenite and the normal angles of each to the three axial planes. Angle to

			<u>`</u>	
Forms.		a (100).	b (010).	c (001).
b(010)		90° 0′		90° 0'
c (001)		84 86	90° 0′	
$= h(210) \dots$		$23 \ 17$	66 43	85 2
m (110)		40 43	49 17	86 0
(120)		$59^{+}50$	30^{-10}	87 17
1 (130)		$68 \ 50$	21 10	88 3
n (140)		73 48	$16 \ 12$	88 30
e (011)		85 36	54 26	35 34
[abs. (101)]		47 4	90 0	$37 \ 32$
[abs. (102)]	•••	107 55	90 0	$23 \ 19$
[abs.(101)]	•••	126 33	90 0	41 57
[abs. (201)]	•••	147 87	90 0	63 1
1 m (828)		50 0	70 41	41 32
n(111)	•••	52 55	61 16	45 25
$p(111) \dots p(122)$	•••	57 40	51 44	51 29
1 0 (202)	•••	62 0	48 84	56 52
$- \pi (121) \dots$	•••	104 19	55 89	40 49
r(122,, 111)	•••	104 40	60 1	49 54
$q(111) \dots$	•••	140 1	69 59	61 57
$= s(211) \dots$	•••	1444 L 1960 L	50 00	69 56
t (221)	•••	152 1	02 20	00 60

The question of the crystallographic orientation must now be considered, since the one here adopted differs from that of Schulten for the artificial crystals. He gave the elements as a:b:c = 0.7212:1:0.8704, $\beta = 84^{\circ} 23'$, and the forms recorded by him were $g^{1}(010)$, m(110),

 $e^{1}(011)$, $b^{\frac{1}{2}}(\bar{1}11)$, and $b^{1}(\bar{1}12)$. Groth ¹ adopts Schulten's orientation but letters the forms $b \ m \ q \ \omega \ i$ respectively. The difference amounts only to an interchange of the *a* and *c* axes; but to get the crystals into parallel position one must be rotated through $84\frac{1}{2}^{\circ}$ and then turned over (180° about the new *c*-axis). The first and last indices of the forms must also be interchanged, but this affects only some of the forms. The following tabular comparison shows the differences, and at the same time shows that Schulten's measured angles (except those on which the calculations are based) are in closer agreement with my values than with his own calculated values.

Sc	hulten.	Spencer.			
Angle.	Obs.	Cale.	Angle.	Calc.	
(010);(110)	$54^{\circ} \ 20'$	*	(010): (011)	54° 26′	
(011):(110)	63 46	*	(110):(011)	64 4	
(011):(110)	$71 \ 15$	*	$(\bar{1}10):(011)$	$71 \ 16$	
(010):(011)	$49 \ 13$	49° 6′	(010):(110)	$49 \ 17$	
$(010):(\bar{1}11)$	$60 \ 1$	59 50	$(010):(\bar{1}11)$	6 0 1	
(010):(112)	68 55	$68 \ 48$	(010):(211)	68 58	
$(\bar{1}10):(\bar{1}11)$	$35 \ 17$	35 20	$(011):(\bar{1}11)$	$35 \ 27$	
$(\bar{1}12):(\bar{1}11)$	20 59	21 0	$(\bar{2}11)$: $(\bar{1}11)$	20 58	

On the natural crystals now described the zone chosen by Schulten for the prism-zone is frequently not developed (fig. 1), and when it is present [bec] the prism-faces *e* are always small. Further, it is to be noted that the orientation here adopted is the same as the earlier one shown in the figure of H. Goguel (1895), whose paper is not mentioned by Schulten and was apparently unknown to him.

There remains the question of the optical orientation, which has been given incorrectly by previous authors for the artificial crystals. Goguel and Schulten both state that the optic axial plane is parallel to the plane of symmetry (this has been dealt with above). Goguel measured under the microscope the angle β as 83° 24', and McDonnell and Smith (1916) give the corresponding value 84°; but both these authors give the extinction as being in the obtuse (not acute) angle β , their values to the prism-edge being +21° to 22° (for n_p [i.e. β]) and +29° respectively. Schulten gives the extinction-angle as 38° in the obtuse angle, which in the second orientation is equivalent to $32\frac{1}{2}°$ in the acute angle β . The statement of obtuse for acute angle is evidently a slip, and the variation 21° to $32\frac{1}{2}°$ (compare 19° to 28° above) may perhaps be due to dispersion.

¹ P. Groth, Chem. Kryst., 1908, vol. 2, p. 822.

154

It may be mentioned that the data recorded above for the natural crystals were all determined before the identity of the mineral with the artificial crystals was established by Mr. Mountain's analysis. The substance could not be identified from the crystallographic data alone, since a copy of Fedorov's 'Tables for Crystallo-chemical Analysis' was not available.

Pseudomorphs of anglesite after schultenite (?).—Another specimen [B.M. 1922, 338] from Tsumeb, acquired from Mr. W. Maucher in 1922, was labelled 'Anglesite pseudomorphous after a monoclinic mineral (lanarkite? or gypsum?)'. This shows lath-shaped tabular crystals up to $1\frac{1}{2}$ cm. long which are completely changed to an aggregate of small crystals of anglesite and stained with a later thin deposit of bayldonite. Most of the pseudo-crystals are merely hollow crusts, and, consisting of an aggregate of anglesite crystals, the form is not always distinct. Terminated crystals, however, show a form suggestive of fig. 1, and it is possible that these are really pseudomorphs of anglesite after schultenite.

Chemical Analysis of Schultenite.

The total weight of available material was 0.2981 gram. The crystal fragments were collected by Dr. Spencer and contained only a minute trace of bayldonite, the copper of which was not sufficient to determine. A specific gravity¹ determination by the pyknometer method gave a corrected value of 5.943.

The analysis was made on 0.2917 gram. The water was determined as loss of weight on heating to incipient fusion. The residual powder was dissolved in a small quantity of dilute nitric acid and the lead was precipitated as lead sulphate. Subsequently the arsenic was estimated as sulphide after prolonged reduction by hydrogen sulphide. The analysis gave the following results:

					Molec, r	atios.		Calculated.
PbO		•••	63.97		0.287	2	•••	$64 \cdot 24$
As_2O_5		••• ·	52.18		0.140	1	•••	33.17
H_2O			2.88	•••	0.160	.1	•••	2.59
			99.03					100.00

This corresponds with the formula 2PbO.As₂O₅.H₂O or PbHAsO₄.

¹ Specific gravity of the artificial crystals 6.076 (Schulten, 1904), 6.053 (McDonall and Smith, 1916).