

(Figure 1). Form {121} is a rare form, of rank 21 in order of increasing rarity (Bach, 1926), and is only mentioned here because the faces are comparatively large, give good signals on the goniometer, and would have been expected to demonstrate the tetartohedrism of wulfenite. However, instead of occurring on alternate corners only, it is present on all five corners of the measured crystal (the remaining three corners are not present, being in contact with the matrix); a possible explanation is that both right- and left-handed forms are represented, of equal perfection and development. Tetartohedrism, as illustrated in the figure, is shown by the shape of the pits on $m\{110\}$, and by small dull areas on the faces $e\{112\}$.

Measurements of the angles, 10 in all, between faces of {011} and between faces of {112}, lead to values of $65^\circ 49.5' \pm 0.5'$, $65^\circ 49.3' \pm 0.3'$, and $65^\circ 49.2' \pm 0.6'$ for the fundamental angle, and 2.2275 ± 0.001 for the axial ratio c/a . Williams (1966) has plotted values of c/a against content of Cr, As, V, and W in wulfenite, and shows it rising slowly from 2.2268 to just over 2.228 as the W content arises to 1.1%, thereafter (perhaps) dropping very rapidly with further increase in W content. Our value is entirely consistent with Williams' results. X-ray powder photographs of the Tsumeb material are a perfect match for wulfenite, and do not show the strong line at 4.96\AA which serves to distinguish stolzite (PbWO_4) from wulfenite, and which is present as a weak line in the pattern of a specimen of "chillagite" from Chillagoe.

The crystals are strongly, but irregularly, zoned. A brown core is overlain by blue wulfenite around the prism and lower pyramid, while the tips of the crystals and perhaps the whole outer surfaces are essentially colorless. Internal reflections show flaws round the core material, but the detail of the color distribution is obscured by the high refractive index and the brilliant luster of the faces. Small rough crystals on the matrix are pale blue or colorless. The material has been examined by electron microprobe in both laboratories and, although Ca, As, Cr, V, Ti, and W were looked for as minor constituents, only W was detected. About 1.3% WO_3 was found in the Smithsonian specimen, and 0.25% WO_3 in a fragment of BM 1976, 108. The latter, about $10 \times 8 \text{ mm}$, showed all three colors but there was no detectable difference in composition between them. It seems probable that the blue color is caused by partial reduction of Mo^{6+} to Mo^{4+} (compare ilsemannite).

We thank Paul Hicks, BM(NH), for the crystal drawing.

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Keyite: a new mineral from Tsumeb

by

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Abstract

Keyite, $(\text{Cu,Zn,Cd})_3(\text{AsO}_4)_2$, occurs as small blue prisms in cavities in tennantite ore from Tsumeb, Southwest Africa, associated with cuproadamite ($\text{Cu}:\text{Zn } 3:2$) and schultenite.

Microprobe analyses gave **CuO** 18.81, **Zn** 17.90, **CdO** 14.08, **PbO** 0.63, **CaO** 0.80, **MnO** 1.07, **As₂O₅** 45.36 (means of 6 analyses on 5 crystals), **Sum** 98.66%. D_{obs} n.d., but > 4.2 . Cell contents for 48 oxygens $6[(\text{Cu}_{1.19}\text{Zn}_{1.11}\text{Cd}_{0.55}\text{Mn}_{0.08}\text{Ca}_{0.07}\text{Pb}_{0.01})_{\text{sum } 3.01}\text{As}_{1.99}\text{O}_8]$, ideally $6[(\text{Cu,Zn,Cd})_3(\text{AsO}_4)_2]$ with $\text{Cu}:\text{Zn}:\text{Cd}$ near 2:2:1, for which $D_{\text{calc}} = 4.95$. Soluble in conc. HCl or HNO_3 , no water detected, blackens on heating. Monoclinic $I2_1$, or $I2/m$; a 11.65, b 12.68, c 6.87 \AA (± 0.01), β 98.95° ($\pm 0.05^\circ$), V 1002.5 \AA^3 . Strongest powder lines 3.29 vs(2), 2.876 vs(3), 2.795 vvs(1) (Cu-K α); 48 lines recorded.

Crystals prismatic {001} to tabular {010}, commonly tapering or showing sub-parallel stacking on {010}. Dominant forms observed on SEM photos {010}, {110}, {210}, {011}, and perhaps {201}. Cleavage {001}, good. No twinning observed. Color deep sky-blue, streak pale blue. H $3\frac{1}{2}$ - 4. Biaxial, sign and 2V not determined, optic axial plane {010}. α 1.80, β n.d. (= b), γ 1.87. Strong dispersion of indicatrix: $\alpha:[001]$ $10\frac{1}{2}^\circ$ (Cd red), $11\frac{1}{2}^\circ$ (Hg yellow), $12\frac{1}{2}^\circ$ (Hg green), $9\frac{1}{2}^\circ$ (Hg violet).

Named for the mineral dealer Charles L. Key, who supplied the mineral for investigation. Name approved by IMA Commission in 1975. Type specimens in BM(NH).

Occurrence

Keyite was brought to our attention by Charles Key, who submitted for identification some minute blue crystals nestling at the base of much larger ($< 2 \text{ mm}$) crystals of cuproadamite on a matrix of tennantite. Since the specimen was from Tsumeb, we at first suspected the crystals of being stranskiite (triclinic $\text{CuZn}_2(\text{AsO}_4)_2$; Strunz, 1960), for which no powder data have yet been published. However, on discovering major cadmium in our mineral and establishing its symmetry as monoclinic, we became convinced that we were dealing with a new species. Stranskiite occurs on chalcocite at the 1000 m level at Tsumeb, but we have no information about which part of the mines our specimens came from.

Cuproadamite, the copper-rich variety of adamite, as small but abundant green prisms, has been associated with keyite on all the specimens we have seen, and it was the only other arsenate present on our original specimen (BM 1973,236). A subsequent specimen (BM 1975,660), first loaned by and later acquired from Mr. Luis Teixeira-Leite, carried large (ca. 2 cm) prisms of schultenite as well. The unusual habit of this new schultenite is the subject of a short note elsewhere in this volume. Keyite and cuproadamite appear to have crystallized more or less at the same time, since the keyite sometimes sits on and is sometimes partly enclosed by cuproadamite.

Table 1. Keyite: microprobe analyses

	1	2	3	4	5	6	Mean
CuO	19.23	18.76	20.22	16.84	19.80	18.01	18.81
ZnO	17.94	18.14	17.59	18.57	16.78	18.41	17.90
CdO	13.98	13.58	13.64	14.93	14.59	13.78	14.08
PbO	0.14	0.40	0.62	1.42	0.65	0.55	0.63
CaO	1.11	0.91	0.83	0.41	0.97	0.59	0.80
MnO	1.27	1.16	1.07	0.94	1.21	0.79	1.07
As₂O₅	45.54	45.40	45.57	45.02	44.96	45.68	45.36
Total	99.21	98.35	99.54	98.13	98.96	97.81	98.65

Cations calculated to 8 oxygen atoms

								S.D.
Cu	1.209	1.189	1.271	1.084	1.258	1.148	1.193	0.070
Zn	1.102	1.124	1.076	1.169	1.041	1.147	1.110	0.047
Cd	0.544	0.533	0.531	0.596	0.574	0.544	0.554	0.026
Pb	0.003	0.009	0.014	0.033	0.015	0.013	0.014	
Ca	0.098	0.082	0.073	0.037	0.087	0.053	0.072	
Mn	0.089	0.083	0.075	0.068	0.086	0.056	0.076	
As	1.982	1.992	1.983	2.006	1.976	2.015	1.992	0.015
(Sum)	3.045	3.020	3.040	2.987	3.061	2.961	3.019	

Columns 1 & 2, one crystal from BM 1973.236; columns 3 - 6, four crystals from BM 1975.660.
S.D. = standard deviation (major cations only).

Chemistry

There is too little keyite for a full wet microchemical analysis, so all the analytical work has been done on a Geoscan electron probe microanalyzer. Element scans on a grain from the original specimen showed the presence of major Cu, Zn, Cd, and As, with minor amounts of Pb, Ca, and Mn; this was confirmed later on grains taken from four other specimens loaned to us. Six quantitative analyses were performed, two on opposite ends of a single grain from the original specimen and the remainder on four separate grains from a second specimen (table 1). Anglesite and wollastonite were used as standards for Pb and Ca, and pure elements for the others. Assuming $Z = 6$ (see below), the mean of the six analyses leads to the formula $6[(\text{Cu}_{1.19}\text{Zn}_{1.11}\text{Cd}_{0.55}\text{Mn}_{0.08}\text{Ca}_{0.07}\text{Pb}_{0.01})_{\text{SUM}} 3.01\text{As}_{1.99}\text{O}_8]$, idealizing to $6[(\text{Cu}, \text{Zn}, \text{Cd})_3(\text{AsO}_4)_2]$, with Cu:Zn:Cd nearly 2:2:1. The three principal cations show only a limited tendency to replace one another in the grains examined, with standard variations of 4 - 6%. It is interesting to note that, despite the evidence that keyite crystallized at about the same time, optical spectrography of the cuproadamite showed no trace of cadmium. This suggests that cadmium cannot be accommodated in the cuproadamite structure. A survey of several different specimens of cuproadamite shows considerable variation in the Cu:Zn ratio, but the crystals associated with keyite have Cu:Zn near 3:2; we are continuing work on this problem.

Keyite is readily soluble in concentrated acids. Tests for the presence of water were made, but no water was found; the mineral blackens on heating, and presumably loses much of the arsenic.

Crystal geometry

Single crystal rotation and Weissenberg X-ray photographs show keyite to be monoclinic, with a body-centered unit cell (systematic absences for $h+k+l$ odd). The space group possibilities are thus $I2$, Im , or $I2/m$, but we have not tested for centrosymmetry. Unit cell dimensions are given in Table 2, and

were refined from the powder data in the same table using the Weissenberg data in the indexing. Calculated d -spacings are not listed, but they are in close agreement for the assigned indices.

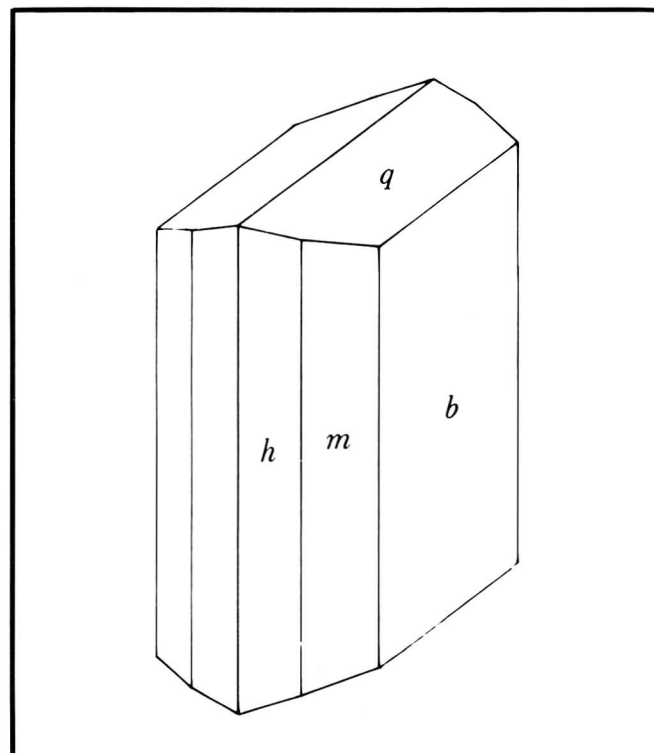


Figure 1. Idealized drawing of keyite, showing forms h [210], m [110], b [010], and q [011].

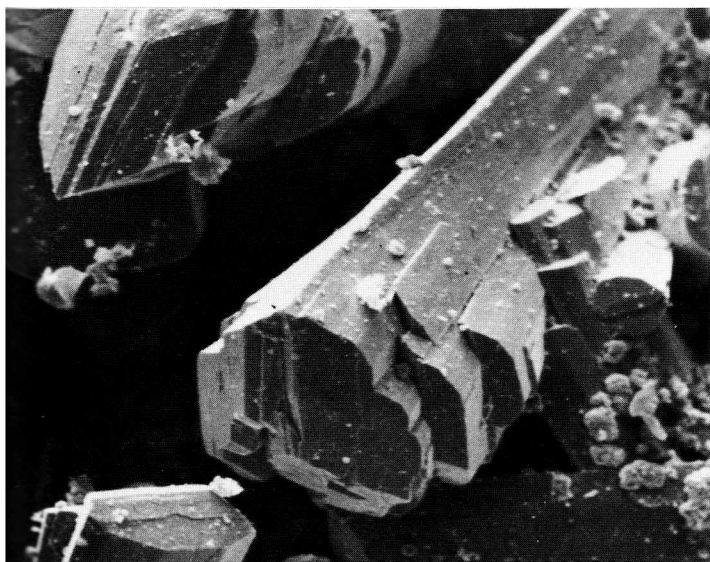


Figure 2. Keyite crystals showing forms $h\{210\}$, $m\{110\}$, $b\{010\}$, and $q\{011\}$; the largest crystal shows the terminal form $\{201\}$ (?). SEM, 500x.

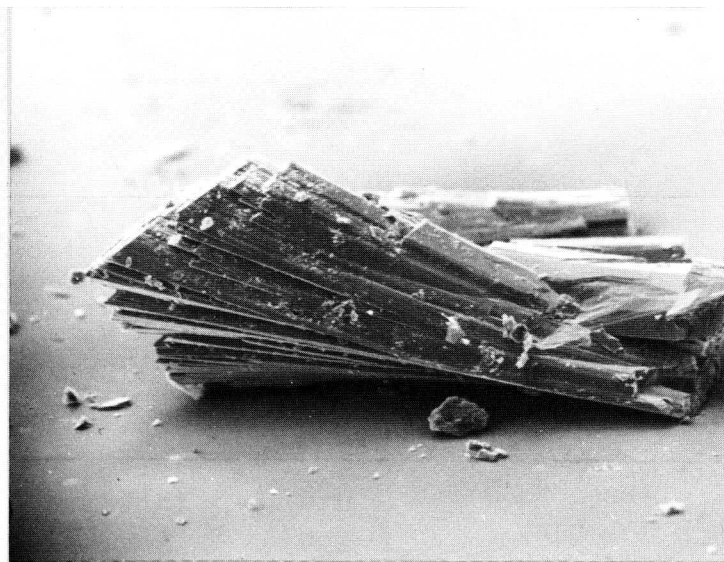


Figure 3. Keyite: a typical sub-parallel group of crystals. The apparent size of $\{011\}:(011)$ is increased by divergence. SEM, 500x

The specific gravity is greater than 4.2, shown by crystals sinking in Clerici solution, but we were unable to measure it more accurately than this. To obtain a density of this order, bearing in mind that the possible space groups require an even number of formula units in the unit cell, we are proposing that $Z = 6$ leading to a calculated density of 4.95. A second approach to the estimation of the unit cell contents was made using the average value of 20 \AA^3 for the volume occupied by oxygen atoms in other copper arsenates of known structure. The unit cell volume is 1002 \AA^3 , so we get about 50 oxygen atoms, and the nearest multiple of 8 to this (there are eight oxygen atoms in two AsO_4 groups) is 48, once again suggesting that $Z = 6$.

Crystal morphology

Keyite crystals are as large as $0.25 \times 0.1 \times 0.04 \text{ mm}$, but are usually much smaller, and it may be seen from the scanning electron microscope (SEM) photographs (Fig. 2-5) that the larger 'crystals' are aggregates of tablets in sub-parallel position. We had no success in trying to measure crystals with the optical goniometer, but comparison of calculated angles with the SEM photographs shows the dominant forms to be $b\{010\}$, $m\{110\}$, $h\{210\}$, $q\{011\}$, and perhaps $\{201\}$ (seen only on the largest, tapering crystal in Figure 2). An idealized crystal is drawn in Figure 1. Under the microscope separated tablets lie flat on $\{010\}$, and give a measured value of $\beta = 98^\circ 50'$. There is a good $\{001\}$ cleavage. No twinning has been observed, re-entrant angles being caused by the sub-parallel growth. Calculated interfacial angles are $(110):(1\bar{1}0) 84.45^\circ$; $(011):(0\bar{1}1) 56.31^\circ$.

Physical properties

Keyite appears to scratch adamite, but not fluorite, so $H = 3\frac{1}{2} - 4$. The color is deep sky-blue, and the streak is pale blue; on hand specimen, green light reflected from the associated cuproadamite tends to mask the color of keyite. There is no fluorescence in U.V. radiation.

Optical properties

Keyite is strongly pleochroic in shades of blue: γ (deep

blue) $> \beta$ (greenish blue) $> \alpha$ (pale blue). The optic axial plane is $\{010\}$. Refractive indices for sodium light are $\alpha 1.80$, β not determined, $\gamma 1.87$. There is strong dispersion of the indicatrix, and crystals lying on $\{010\}$ show purple and greenish extinctions in white light. Extinction angles $\alpha:[001]$, all in the acute angle β , are $10\frac{1}{2}^\circ$ (Cd red), $11\frac{1}{2}^\circ$ (Hg yellow), $12\frac{1}{2}^\circ$ (Hg green), and back to $9\frac{1}{2}^\circ$ (Hg violet). Interference figures showing the optic axes and their dispersions have not been observed, and $2V$ and the optic sign have not been determined.

Discussion

The superficial resemblance between keyite and stranskiite is striking, and it is unfortunate that we have not been able to obtain any of the latter for study. Apart from the cadmium and the Cu:Zn ratio, the simple formulae and the refractive indices are much the same. The crystal symmetry, however, is entirely different and there is no integral ratio between the unit cell volumes. The higher symmetry of keyite, and the non-integral numbers of the cations in the unit cell, taken in conjunction with a larger oxygen volume (20.9 \AA^3) than for stranskiite (19.1 \AA^3), lead us to speculate that keyite may be a disordered polymorph of stranskiite, possibly stabilized by the cadmium. Sidney Williams has recently sent us for comparison a powder photograph of a fragment of the type specimen of stranskiite, given to him by the Tsumeb Corporation. The strongest lines are 3.131 (10), 2.789 (5), and 2.505 (5); neither they nor the pattern as a whole show any resemblance to those of keyite. We are working to complete our description of the morphology and optical properties of keyite.

Name and type specimens

Keyite was approved by the I.M.A. Commission on New Minerals and Mineral Names in March 1975. The name is for Charles L. Key, mineral dealer of Canton, Connecticut, who has supplied the Museum with many fine and rare specimens over the last few years. Holotype specimens, BM 1973.236 and BM 1975.660, are in the mineral collection, British Museum (Natural History).

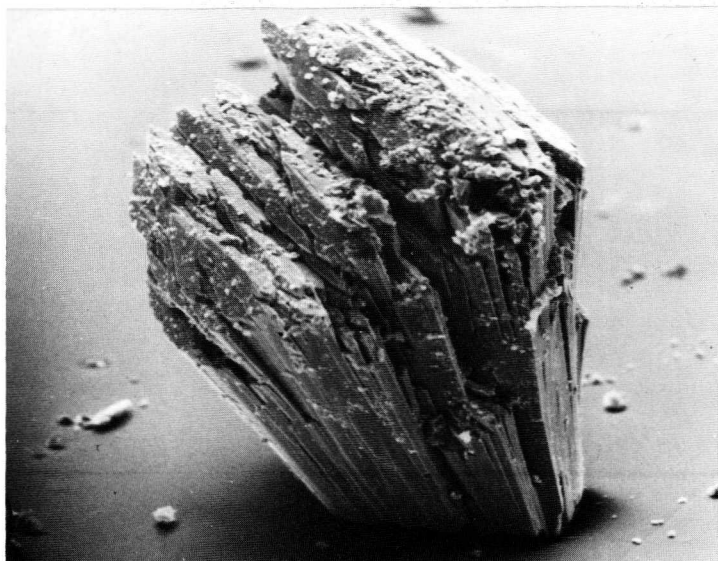


Figure 4. Keyite: composite crystal showing typical roughness of faces. SEM, 500x

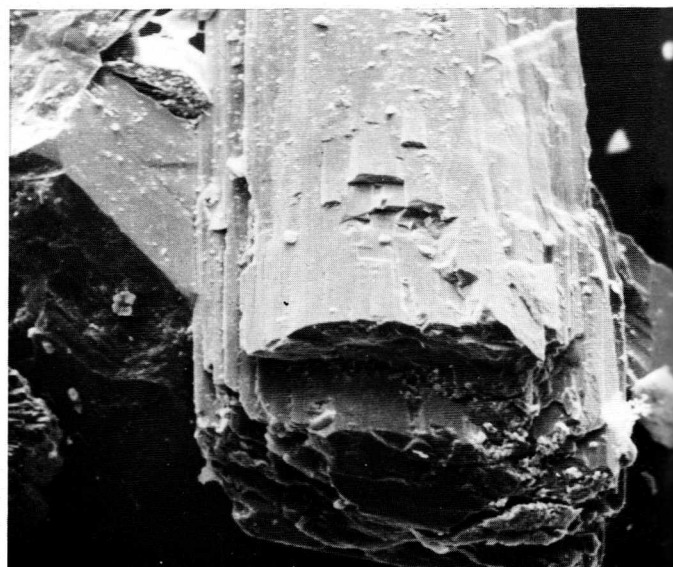


Figure 5. Keyite: composite crystal lying on and in a 'cuproa-damite' crystal. SEM, 500x

Acknowledgements

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Reference

STRUNZ, H. (1960). Stranskiit, ein neues Mineral. *Naturwiss.* **47**, 376 [Abstracts in *Amer. Mineral.* **45**, 1315; *Mineral. Abstr.* **15**, 213]. See also structure determination by K. Plieth and G. Sanger, *Zeits. Krist.* **124**, 91-100 [*Mineral. Abstr.* **19**, 271]

Table 2. Keyite: X-ray powder data (Cu-K α , camera dia. 114.6 mm)

<i>d</i> obs	<i>I</i> obs	hkl	<i>d</i> obs	<i>I</i> obs	hkl	<i>d</i> obs	<i>I</i> obs
6.41	ms	020, 10 $\bar{1}$	2.515	mwB	222, 132	1.718	w
5.97	vvw	011	2.386	w	40 $\bar{2}$, 34 $\bar{1}$	1.700	m
4.46	vw	21 $\bar{1}$, 12 $\bar{1}$	2.320	mw-mB	312, 042, 33 $\bar{2}$	1.644	ms
4.27	vvw	220	2.266	vw	510	1.602	vwB
4.15	w	121	2.230	w	25 $\bar{1}$, 42 $\bar{2}$, 24 $\bar{2}$, 341, 013	1.566	mwB
3.89	vw	211	2.160	vvw	431, 103, 52 $\bar{1}$, 251	1.534	w
3.69	mw	310				1.529	vw
3.59	vw	30 $\bar{1}$, 031	2.131	w	440	1.498	vw
3.40	w	002	2.080	vw	501	1.485	vw
3.29	vs(2)	11 $\bar{2}$	2.036	w-mw	40 $\bar{2}$, 123, 51 $\bar{2}$, 15 $\bar{2}$	1.456	w
3.15	m	23 $\bar{1}$, 20 $\bar{2}$, 301, 32 $\bar{1}$				1.437	vw
			1.990	w	033, 323	1.413	w
3.02	vw	112	1.980	vw	260, 521, 213	1.406	w
2.978	vw	022	1.911	vvwB		1.384	mw
2.876	vs(3)	400	1.868	vwB		1.379	vvw
2.795	vvs(1)	22 $\bar{2}$, 321, 240	1.805	vvw		1.346	vwBB
2.740	mw	141	1.760	mw			
2.638	wB	132, 420					

Unit cell dimensions: a 11.65 Å (\pm 0.01), b 12.68 (\pm 0.01), c 6.87 (\pm 0.01), β 98.95° (\pm 0.05), V 1002.5 Å³.

Space group I2, Im, or I2/m. $Z = 6[(\text{Cu,Zn,Cd})_3(\text{AsO}_4)_2]$. $D_{\text{obs}} > 4.2$, $D_{\text{calc}} 4.95$.