Ludlockite: a new mineral from Tsumeb

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Abstract

Ludlockite, **(Fe,Pb)As$_2$O$_6$**, was found as red needles in a cavity in sulfide ore from the 'germanite section' of the mines at Tsumeb, Southwest Africa, associated with zincian siderite. Analysis gave **PbO** 9.32, **Fe$_2$O$_3$** 21.63, **As$_2$O$_5$** 70.82, less 'oxygen deficiency' 1.69, sum 100.08 percent. Empirical cell content $Pb_{1\cdot2}Fe^{3+}_{7\cdot9}As^{3+}_{3\cdot1}As^{5+}_{14\cdot9}O_{55\cdot0}$ for $D_{obs.}$ 4.40, simplifying to nearly 9[(Fe,Pb)As$_2$O$_6$]. $Fe^{3+} >> Fe^{2+}$ by Mössbauer and E.S.R. Readily soluble in conc. HC1 or HNO_3, more slowly in dilute acids. On heating turns yellow, then black, losing As_2O_3; DTA curves given. Infra-red and Raman show no As-O bonds of AsO_4^{3-} or AsO_3^{3-} anions. Triclinic, P1 or P$\bar{1}$, *a* 10.41, *b* 11.95, *c* 9.86 Å (± 0.02), α 113.9°, β 99.7°, γ 82.7° (± 0.2°), V 1103 Å^3. Strongest powder lines (Co-K*α*) 8.81 vvs(1), 3.330 ms(3), 2.935 vs(2). Crystals elongated [100], flattened {0$\bar{1}$1}, other prominent forms {021}, terminal faces not determined. Cleavage {0$\bar{1}$1} micaceous, {021} perfect. Twinning lamellar, composition plane {0$\bar{1}$1}, twin law not established. Color red, streak light brown, lustre sub-adamantine. No fluorescence. Biaxial positive α 1.96, β 2.055, γ >2.11; γ near [100], optic axial plane *l* {011}. Pleochroic γ (orange yellow) > β (deep yellow) > α(yellow). Named for mineral dealers Frederick **Lud**low Smith and Charles **Locke** Key who found and supplied specimens for investigation. Name approved by IMA Commission in 1970. Type specimens in BM(NH).

Occurrence

Ludlockite was first observed in 1968 by Smith and Key, as an orange-brown earthy mass on the surface of a lump of ore that they had obtained from the 'germanite section' of the mines at Tsumeb, Southwest Africa. On splitting the lump they found a cavity lined with sharp brownish-yellow, 1 - 3 mm rhombs of zincian siderite, from which grew slightly diverging bundles of red-brown needles up to 4 mm long. These needles, the subject of this paper, have not been observed in contact with the sulfide ore. Siderite rhombs also occur singly and in groups on and impaled by the ludlockite needles (Fig. 3). An electron microprobe scan, by S. J. B. Reed, of a section of a siderite rhomb showed about 9% zinc at the surface, falling irregularly to about 5% zinc at the core, with corresponding variation in the iron content. An X-ray powder photograph confirms the identification as zincian siderite, and a bulk chemical analysis yields the formula **($Fe_{67\cdot5}Zn_{21\cdot8}Ca_{5\cdot6}Mn_{4\cdot2}$-$Mg_{0\cdot5}Pb_{0\cdot4}$)CO$_3$** with 3.6% admixed **Fe$_2$O$_3$**. Textural relationships have not been determined in the sulfide matrix, but the following species have been identified: tennantite, chalcocite, pyrite, bornite, germanite, siderite, and quartz.

Chemistry

Ludlockite is readily soluble in concentrated nitric or hydrochloric acids, more slowly when they are diluted. On heating it remains unchanged up to 400°C; between about 550° and

Figure 1. **Ludlockite: D.T.A. curves in air and in nitrogen (marked L). The bottom curve (marked K) is of karibibite in argon (after von Knorring *et al.*, 1973).**

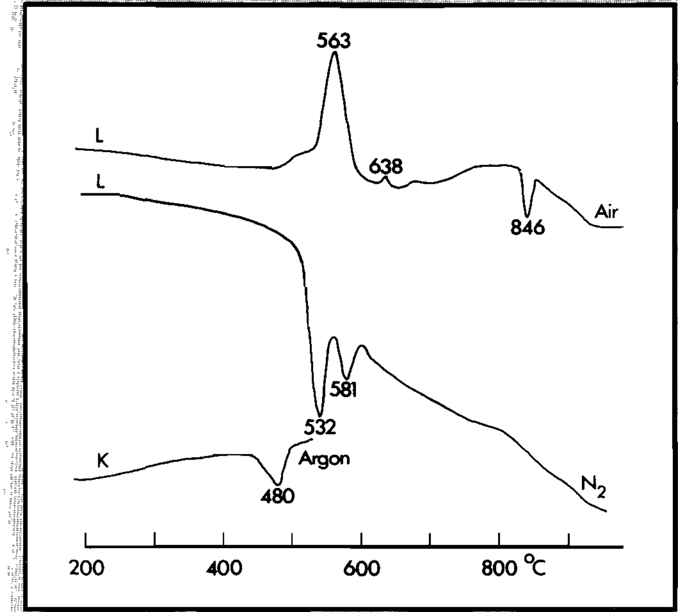
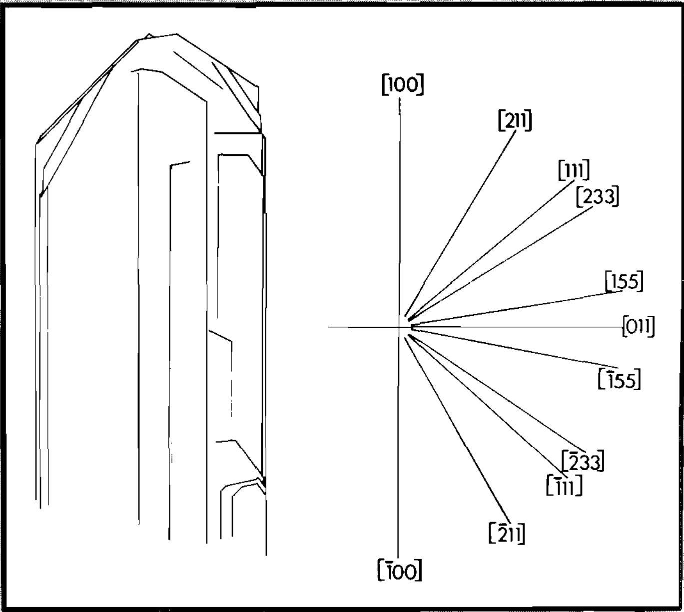


Figure 2. **Ludlockite: composite drawing on {011} showing traces of terminal edges, and the possible zones to which they may be referred.**



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† Note: the pale yellow product is unoriented with respect to the original fibers, and is fine-grained. It has not been identified. The three strongest powder lines are 3.10Å (1), 3.02 (2), and 3.33 (3), and the highest observed spacing was 8.3 Å.

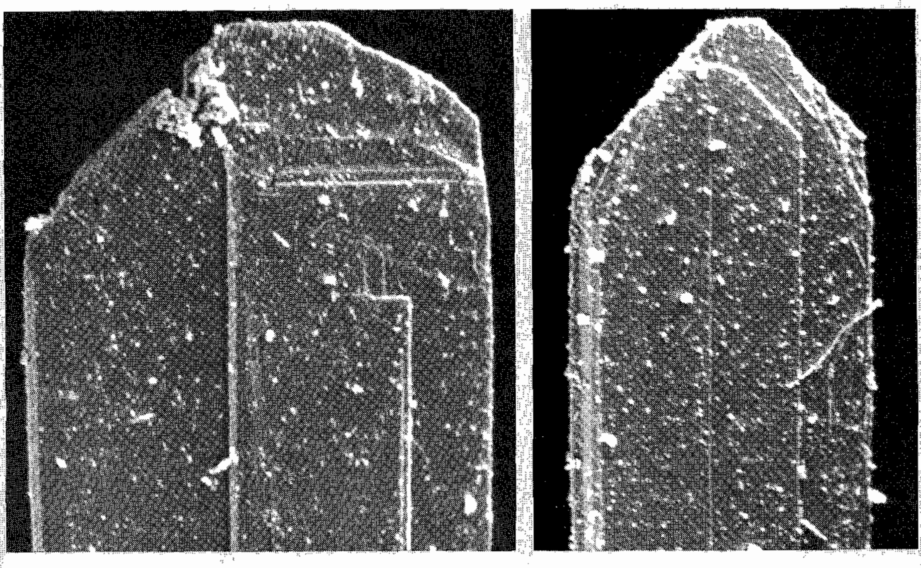


Figure 3 and 4. **Ludlockite: crystal laths on {011}, showing terminal edges and twinning. SEM, 1000x**

640°C, it becomes khaki and then pale yellow, losing nearly 29% of its weight in 20 hr.+ In the closed tube a sublimate of As_2O_3 is formed. Above 780°C it becomes brownish black, with the formation of Fe_2O_3. It was not observed to fuse before decomposition.

Qualitative optical spectrography showed major lead, iron, and arsenic, with minor amounts of germanium and aluminum that were not detected chemically nor by microprobe. Electron microprobe analyses at 30 points on three crystals showed no sign of inhomogeneity; they have not been repeated since 1969, when methods of accurately determining lead and arsenic in the presence of each other had not been perfected (their spectra contain overlapping lines), and the results are not given here.

Wet microchemical analyses were made on several portions varying from ⅓ to 16 mg, to develop the method of separation and to determine the state of oxidation. Briefly, the mineral was dissolved in a mixture of conc. HCl and ICl, and titrated with KIO_3 solution to obtain the 'oxygen deficiency' or overall state of oxidation (Hey, 1974). The resulting solution was then reduced with hydrazine hydrochloride, the arsenic precipitated and separated as As_2S_3, and finally weighed as ammonium magnesium arsenate. Iron was extracted from the solution after acidification with HCl, and weighed as the 8-hydroxyquinolate. After removal of chloride, lead was precipitated from nitric acid solution as the 'thionalide' complex, and weighed.

The average of the results considered to be most reliable is given in table 1. Wet chemistry did not distinguish between Fe^{2+} and Fe^{3+}, nor between As^{3+} and As^{5+}, but the determined 'oxygen deficiency' corresponds to 10.4% As_2O_3. Semiquantitative Mössbauer measurements by A. D. Law, and electron spin resonance measurements by J. R. Thyer, showed Fe^{3+} to be considerably in excess of Fe^{2+}, so part of the arsenic is present in ludlockite as As^{3+}. The analysis is presented with all the iron expressed as Fe^{3+}; to do otherwise at this stage would be an empty exercise in numerology.

Unit cell contents based on the measured specific gravity of 4.40 and cell volume 1103 Å³ are given in table 1. Since these can only be a guide, in the absence of a full structure determination, we have recalculated to a basis of 54 oxygen atoms per unit cell in order to obtain a provisional simplified formula (and for no other reason): $\mathbf{9[(Fe^{3+},Pb)(As^{5+},As^{3+})_2O_6]}$. The reduction to 54 oxygen atoms, etc., leads to a calculated specific gravity 4.32.

Differential thermal analysis (in air and in nitrogen) curves were obtained by B. D. Mitchell on 10 mg samples, and are reproduced in fig. 1 together with that of karibibite in argon (von Knorring *et al.*, 1973, p. 270). The exothermic peak (563°C) in air may be due to oxidation of the small amount of Fe^{2+}, and the endothermic effects (530 - 580°C) in nitrogen may be connected with the loss of As_2O_3, but since we have done no further work in this direction any interpretation must remain speculative.

Preliminary attempts were made to synthesize ludlockite, without success.

Crystal geometry

Ludlockite is triclinic, Laue class $\bar{1}$, space group P1 or P$\bar{1}$ (centrosymmetry not determined). Unit cell dimensions and angles were obtained from precession photographs, and are given for the Donnay-Nowacki reduced (primitive) cell in table 2. The powder data were obtained on a Philips 114.6 mm camera (Co - Kα radiation) and are given in table 4. These data, together with Guinier data, were used in the refinement of the cell dimensions; details will be given in another paper, to be published elsewhere, dealing with the twinning geometry and morphology at greater length.

The structure has yet to be determined. Unit cell contents are given in table 1.

Crystal morphology

Ludlockite crystals are commonly lath-shaped, but a few are almost equant in cross-section. Most of them are 15 - 40 mm long, 0.05 - 0.1 mm wide, and 0.008 - 0.025 mm thick. Many taper slightly, some have a twist about the needle axis, and the

Table 1. Ludlockite: Chemical analysis and cell contents

		Ratios		Cell contents		
PbO	9.32	Pb	0.04175	1.22	1.20	1.24
Fe_2O_3	21.63	Fe	0.2709	7.91	7.77	8.05
As_2O_5	70.82	As	0.6163	18.00	17.67	18.33
	101.77	O	1.8833	55.00	[54]	[56]
Less O	1.69	Sum of cations		27.13	26.64	27.62
Total	100.08%	Dobs. /Dcalc.		4.40	4.32	[4.48]

Empirical formula $\mathbf{Pb_{1\cdot2}Fe^{3+}_{7\cdot9}As^{3+}_{3\cdot1}As^{5+}_{14\cdot9}O_{55\cdot0}}$ (assuming all iron to be ferric)

Note: water was sought, but not found; minor Ge and Al were detected spectrographically, but not chemically.

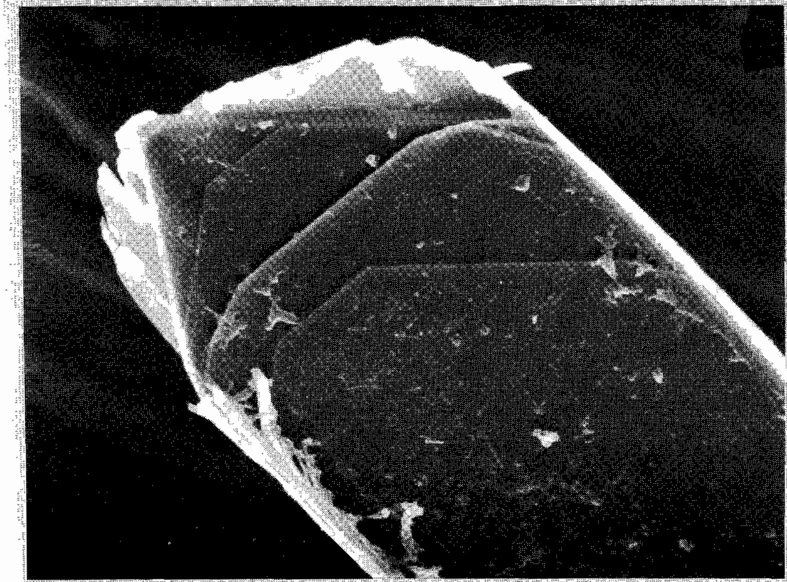


Table 2. Ludlockite: crystallographic data

Triclinic, P1 or P$\bar{1}$	*a* 10.41 Å ± 0.02 Å	α 113.9° ± 0.2°
	b 11.95 ± 0.02	β 99.7° ± 0.2°
Cell volume 1103 ± 3 Å^3	*c* 9.86 ± 0.02	γ 82.7° ± 0.2°

D_{obs} 4.40 ± 0.05, $D_{calc.}$ 4.32 (see text).

Z = 9[(Fe^{3+}.Pb)(As^{5+}.As^{3+})$_2$O$_6$] (simplified, see text and Table 1)

Figure 5. (top left) **Ludlockite: crystal on {011}, showing multiple twinning. SEM, 2000x**

Figure 6. (above) **Ludlockite: crystal with bruised point, showing {011} (broad), {021} (narrow), and unindexed terminal faces; tapering edges of the latter suggest that the twin plane may not be the plane of composition. SEM, 2000x**

Figure 7. (below) **Ludlockite: crystal lath distorted by handling, demonstrating flexibility and the two perfect cleavages. SEM, 1000x**

Table 3. Ludlockite: morphological data - some possible angles

Interfacial angles in zone [100]

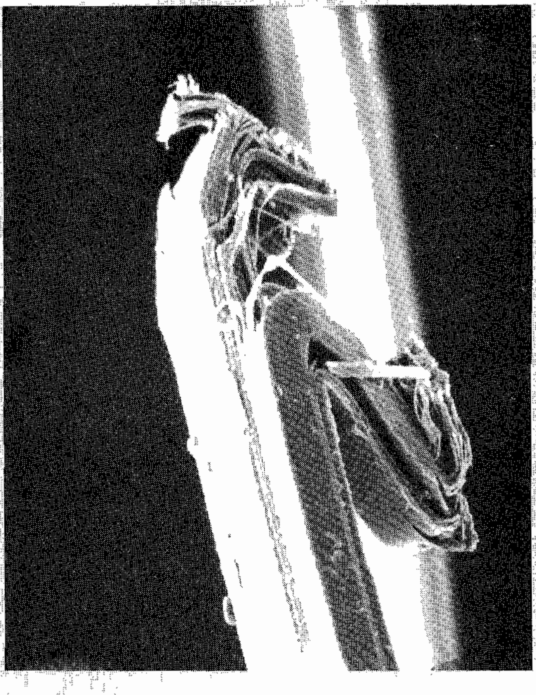
(0$\bar{1}\bar{1}$):	(0$\bar{4}$1)	(001)	(0$\bar{5}$1)	(011)	(0$\bar{4}$1)	(0$\bar{3}$1)	(021)
calc.	47.4°	48.0°	51.1°	77.7°	79.1°	82.9°	90.6°
obs.		*ca* 50°			*ca* 79°		*ca* 90°

Interzonal angles (angles between edges on {0$\bar{1}\bar{1}$})

[$\bar{1}$00] or [100]*	[011]*	[155]	[$\bar{1}$55]*	[233]	[233]*	[111]	[$\bar{1}$11]*	[211]	[$\bar{2}$11]*
calc.	90.7°	99.2°	100.5°	122.5°	123.5°	130.5°	131.3°	149.8°	150.2°
obs.	90 ± 1°	99½ ± 1°		121 ± 4°		134 ± 2°		148 ± 2°	

Table 4. Ludlockite: X-ray powder data
(camera dia. 114.6 mm; Co-K α radiation).

d(Å)	I_{obs}	hkl	*d* (Å)	$I_{obs.}$	hkl	*d* (Å)	$I_{obs.}$	hkl
10.90	m	010	4.47	mB	002 (&c)	3.330	ms(3)	23$\bar{1}$ (&c)
8.81	vvs (1)	011	4.41	mw	0$\bar{2}$2	3.216	vw	1$\bar{3}$2 (&c)
7.76	vvw	110	4.20	vvw	201	3.160	ms	32$\bar{1}$.2$\bar{2}\bar{1}$
7.22	vvw	10$\bar{1}$.1$\bar{1}$0	4.11	w	2$\bar{1}$1	3.060	w	3$\bar{1}$2 (&c)
5.88	w	011	3.94	wB	0$\bar{3}$1.2$\bar{1}\bar{1}$	2.978	mw	003 (&c)
5.41	vvw	12$\bar{1}$	2.69	m	22$\bar{2}$	2.935	vs (2)	0$\bar{4}$1 (&c)
5.19	vw-w	1$\bar{1}\bar{1}$	3.60	mw	20$\bar{2}$,2$\bar{2}$0	2.863	ms	212,1$\bar{3}\bar{1}$ (&c)
4.98	vw	120	3.57	vw	2$\bar{2}$1	2.793	mw-m	3$\bar{2}$0,122
4.74	mB	210 (&c)	3.453	vvw	130 (?)			



only reflections we have been able to get on the optical goniometer have been very poor and confined to the prism zone [100]. Scanning electron micrographs, fig. 3 - 6, show that the terminations of the needles are variable and that all crystals are multiply twinned.

The crystals are all elongated along the *a*-axis [100], and are flattened on {0$\bar{1}$1}; the only other face that we have identified with certainty is {021}. It is a feature of the geometry of ludlockite that some of the angles are close to 90°, making for difficulty in identifying unambiguously the inter-edge angles measured from SEM photographs. Thus (0$\bar{1}$1):(021) is 90.6°, and [100]:[011] is 90.7° (Fig. 2); further, the face normal (021) and the zone axis [011] are within 0.9° of each other so that we can say no more at present about the twinning than that the composition plane is {0$\bar{1}$1}. Some relevant comparisons between calculated and observed interfacial and inter-edge angles are given in Table 3.

Cleavage on {0$\bar{1}$1} is perfect and micaceous, and on {021} perfect, with the result that the crystals readily fray at the ends to a bunch of cleavage fibers (Fig. 7).

Infra-red and Raman spectra

Infrared spectra have been recorded for us by C. J. Elliott, and Raman spectra by W. P. Griffith, but the curves are not reproduced here. The infrared spectrum is very similar to that of karibibite. Neither type of spectrum shows any sign of As-O bonding, with the oxygen atoms attached singly to arsenic as in compounds containing isolated AsO_3^{3-} or AsO_4^{3-} anions. Instead, both show strong bands at around 480 cm^{-1} which are characteristic of -As-O-As- 'stretches', and which are shown by arsenolite and claudetite (minerals with structures known to contain fully-shared oxygen atoms).

Physical properties

Crystals of ludlockite are very flexible and sectile, and cleave readily. The color is a rich red (R. H. S. 182A), and the streak is light brown (R. H. S. 172C). There is no fluorescence visible in either long- or short-wave U.V. (compare karibibite, which fluoresces yellow). The lustre is sub-adamantine. The hardness is difficult to determine, but appears to be about 1½ - 2. The specific gravity was determined on samples of about 10 mg, using a Berman balance and ethylene dibromide as immersion liquid; values of 4.40 to 4.33 were obtained, and it was assumed that the higher value was more reliable with an estimated accuracy of about 1%. We may be wrong, and the true value may prove to be lower (see Table 1).

Optical properties

Ludlockite has near-orthorhombic optics, and laths are length-slow with straight extinction. An obtuse bisectrix interference figure is to be seen through the laths, with the optic axial plane perpendicular to the plane of flattening and parallel to the length. The optic sign is positive, but the optic axes were not observed on the universal stage even at the limits of tilt; sections were cut across the crystals (embedded in resin), but no acute bisectrix figure was seen. Thus 2V(+) and the dispersion are not known. An extinction angle of about 3° (γ: [100]) was observed on a few laths with {011} vertical, but the sense was not determined. Attempts were made to 'un-twin' the crystals by pulling off {0$\bar{1}$1} cleavage flakes, but the extinction remained straight. Refractive indices for sodium light were obtained by immersion in Cargille liquids: $\alpha \simeq 1.96$, nearly $\perp$ [0$\bar{1}$1]; $\beta = 2.055 \pm 0.005$, nearly // [011]; $\gamma > \sim 2.11$, with γ:[100] $\simeq$ 3°. The pleochroism scheme is γ (orange-yellow) > β (deep yellow) > α (yellow), and all colors deepen rapidly with increasing thickness.

Name and type specimens

Ludlockite was approved by the I.M.A. Commission on New Mineral Names in February 1970. The name is for Frederick **Lud**low Smith III and Charles **Locke** Key, who found the mineral and presented it to the Mineral Department, British Museum (Natural History). Type specimens are numbered BM 1969,215 and 216.

Discussion

The only other species that are essentially arsenates or arsenites of iron and lacking structural water are angelellite ($Fe_4As_2O_{11}$; 1959), karibibite ($Fe_2As_4(O,OH)_9$; 1973) and schneiderhöhnite ($Fe_8As_{10}O_{23}$; 1973). Karibibite comes closest to ludlockite in appearance and Fe:As ratio, but the possibility of identity was disposed of in correspondence with Professor Sahama before its description was published (von Knorring *et al.*, 1973); the quickest field distinction between the two is that karibibite fluoresces yellow in short wave U.V., whereas ludlockite does not fluoresce at all.

Despite the As:O ratio of 1:3, most of the As in ludlockite is present as As^{5+}. Pending determination of the structure, the evidence that we have given above and its physical resemblance to claudetite suggest that ludlockite contains sheets or bands of AsO_6 octahedra sharing the corner oxygen atoms with each other. The volume per oxygen atom is a measure of the closeness of packing of a structure, and for ludlockite is 20 Å^3 (1103 /55). This value is about the same as those for scorodite (19) and for parasymplesite and symplesite (20 ±); claudetite (25½), arsenolite (28), schneiderhöhnite (25½), and karibibite (24½) are more loosely packed, and angelellite (17) is more closely packed.

Acknowledgements

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