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Luetheite, $Cu_2Al_2(AsO_4)_2(OH)_4.H_2O$, a new mineral from Arizona, compared with chenevixite

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SUMMARY. Luetheite was found at a small prospect in Santa Cruz County, Arizona, as crystals in vugs in rhyolite porphyry. A few specimens were found on the dump, none seen in place. Occurs in silicified porphyry (quartz–sericite–alunite) with chenevixite and hematite. Crystals indian blue inclining to greenish, H = 3, $D_{meas} = 4·28$.

Crystals monoclinic $2/m$ and tabular on a {100}, also a plane of distinct cleavage; other forms are {110}, {140}, {011}. Space group perhaps $P2_1/m$ with $a = 14·743$ Å, $b = 5·093$, $c = 5·598$, $\beta = 101°\ 49'$; strongest lines are 3·498Å (10), 310, 111; 7·208 (7), 200; 2·507 (5), 120, 510. Feebly pleochroic in pale blue in thin section, $\gamma = \beta > \alpha$. Indices are $\alpha = 1·752$, $\beta = 1·773$, $\gamma = 1·796$; $2V\gamma = 88°$ (calc.); dispersion is moderate $v > \rho$. $\alpha \parallel$ [010], γ: [001] 10° in obtuse β. Duplicate chemical analyses averaged CuO 28·9 %, Al_2O_3 18·4 %, As_2O_5 40·5 %, H_2O 9·3 % giving $2[Cu_2Al_2(AsO_4)_2(OH)_4.H_2O]$.

Named for R. D. Luethe, geologist for Phelps Dodge Corporation.

Chenevixite from Las Animas, Sonora, analysed to give $Cu_2Fe_2(AsO_4)_2(OH)_4.H_2O$. Powder data are close to luetheite, and the cell is monoclinic $2/m$, probably $P2_1/m$, with $a = 15·006$A, $b = 5·189$, $c = 5·724$, $\beta = 102°15$. The measured specific gravity is 4·38, $D_{calc.} = 4·59$. Crystals tabular on a {100} with a habit very similar to luetheite. Indices are $\alpha = 1·92$, $\beta = 1·96$, $\gamma = 2·04$, $2V\gamma_{calc.} = 75°$; $\alpha \parallel$ [010], γ nearly $\parallel$ [001].

Luetheite

LUETHEITE was first found by R. D. Luethe, a geologist for the Phelps Dodge Corporation. The occurrence is described by Mr. Luethe as follows: 'The specimen was collected from the dump of a short adit located 1·7 miles southeast of the Flux mine and 0·6 miles southwest of the Humboldt mine, Santa Cruz County, Arizona: specifically 31°27·95′N latitude, 110°44·45′W longitude. A thorough search of the outcrop and portal walls on subsequent visits failed to reveal any similar material; however, float from the talus slope above and southwest of the adit contains abundant chenevixite. I conclude that the specimen was incorporated in the overburden removed from the adit portal and that the source of the mineral is upslope from the adit. Chenevixite was noted also in the prominent cliff of rhyolite breccia about 400 feet above and 700 feet southwest of the adit.

The wall rocks at the adit portal are intensely altered and pyritized dacitic (or andesitic) lapilli tuff. The adit was driven southwest toward the rhyolite breccia, which appears to be a volcanic plug. The rhyolite breccia contains minor amounts of chenevixite and brochantite, presumably derived from enargite.'

Little can be added to his comments except to note that, in thin section, luetheite appears to occur mostly in voids created by dissolution of sanidine, as spherules of randomly arranged plates perched on the edges of the cavities. The rock otherwise has been intensely altered and is converted to a coarse aggregate of quartz, shreddy sericite, and occasional crystalloblasts of alunite. Chenevixite also occurs in the specimens but is more apt to invade the matrix of the rock. Where it occurs in cavities, it is plastered on the walls and seems older than the luetheite. Also present, but far less common, is cornubite. Brilliant crystals[1] of this species occur in cavities or fractures that seem later than the associated luetheite.

[1] A hasty measurement of one crystal quickly confirmed the triclinic symmetry assigned in the original description by Claringbull *et al.* (1959).

Physical properties. Luetheite occurs as spherules of well-formed crystals up to 0·2 mm in largest dimension. The colour is indian blue (RHS–118B) but the streak is white. With surficial alteration, the colour inclines to pale green. No fluorescence was observed in long or short wavelength U.V. The hardness on Mohs scale is 3, and crystals are brittle although thin cleavage foliae tend to bend before rupturing. The specific gravity was estimated by the sink-float method in Clerici solution at 22·5 °C as 4·28±0·05 (using measured rutile and adamite as standards). Owing to the cellular boxworks-like structure of crystal aggregates, erroneously low reading were obtained on the Berman balance.

Crystallography and optics. It was only with some difficulty that measurable crystals or partial crystals were separated for goniometry. Three crystals were successfully studied, however, and at least the major forms could be recognized. Crystals are monoclinic, and no evidence was found to indicate that they are not $2/m$. They are tabular on *a* {100} and modified by *m* {100}, *o* {140}, and *d* {011}. A typical crystal is shown in fig. 1.

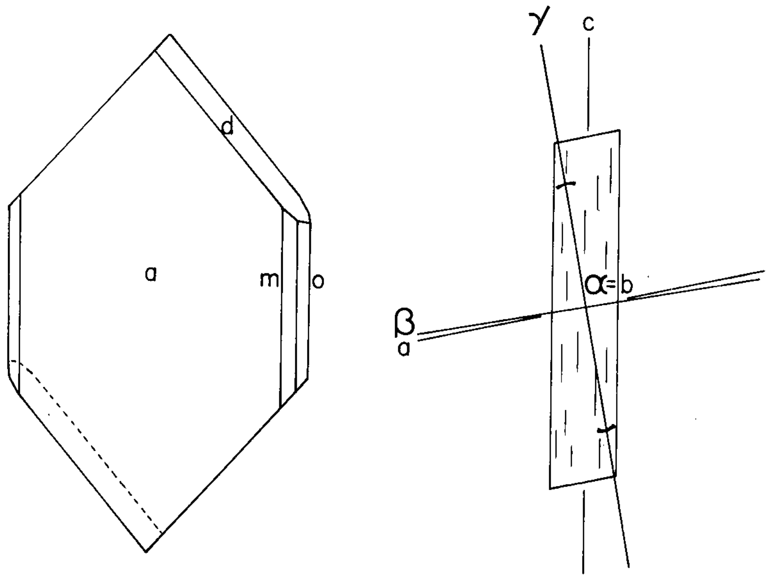

FIG. 1. Crystal form and optical orientation of luetheite.

Cleavage is fair to good on *a* {100} and enhanced by grinding. In thin section, crystals showing cleavage are either length fast or slow with parallel or near-parallel extinction. Basal plates give a nearly centred flash figure. In overall appearance, both in hand specimen and thin section, luetheite resembles chalcoalumite. Pleochroism is feeble, all directions showing pale blue, with $\gamma = \beta > \alpha$. Dispersion is small with $v > \rho$. The indices were determined for the Na *D* line as $\alpha = 1{\cdot}752$, $\beta = 1{\cdot}773$, $\gamma = 1{\cdot}796$, thus $2V\gamma_{\text{cal.}}$ is 88°. The optic orientation is shown in fig. 1.

X-ray analysis. Powder data for luetheite are given in Table I. Single crystals examined by Weissenberg and rotation methods gave cell dimensions $a = 14{\cdot}743$Å, $b = 5{\cdot}093$, $c = 5{\cdot}598$, $\beta = 101°49'$. The space group in the orientation chosen appears to be $P2_1/m$ but many reflections are weak and $P2_1/a$ is a possibility. With a cell volume of 411·4Å^3, and Z = 2, the calculated density is 4·40 g/cm^3.

Chemistry. Spectrographic and microchemical analysis of luetheite showed only traces of Ca in addition to the essential constituents. Copper was then determined by atomic absorption (with a correction for possible suppression by Al), As was determined in the U.V. as AsI_3, and Al found colorimetrically by eriochrome cyanine R.

Water was determined (and clearly visible) by the Penfield method but some experimentation was necessary to avoid loss of As_2O_3. A part of the water is lost readily during early stages of heating but the majority lost only just before a portion of As_2O_3 begins to sublime on the tube walls. The results of these analyses are presented in Table II, and they lead to $Cu_{3\cdot97}Al_{3\cdot90}(AsO_4)_{3\cdot94}(OH)_{7\cdot82}\cdot1\cdot74H_2O$ or $Cu_2Al_2(AsO_4)_2(OH)_4\cdot H_2O$. The low sum of the analysis is surely due to traces of admixed quartz and sericite, which were seen in the beakers following initial digestion; owing to the small amounts involved it was not possible to determine them as 'insol.'.

TABLE I. *X-ray powder data for luetheite:* Cr-$K\alpha$

I	d_{meas}	d_{calc}	*hkl*	*I*	d_{meas}	d_{calc}	*hkl*	*I*	d_{meas}	d_{calc}	*hkl*	*I*	d_{meas}
7	7·208 Å	7·215 Å	200	2	3·610 Å	3·608 Å	400	3	2·454	2·453 Å	$11\bar{2}$	½	2·021 Å
		4·806	101	10	3·498	3·497	310			2·454	$51\bar{1}$	1	1·904
2	4·801	4·803	110			3·496	111	2	2·426	2·424	$21\bar{2}$	5	1·803
		4·810	300	1	3·132	3·140	211			2·401	220	3	1·471
1	4·065	4·161	210	1	2·943	2·944	410	2	2·402	2·405	600	3	1·401
		4·049	$30\bar{1}$(?)	3	2·546	2·546	020			2·403	202	4	1·270
2	3·745	3·740	$11\bar{1}$	5	2·507	2·508	120	2	2·251				
		3·730	011			2·511	510	½	2·176				

TABLE II. *Chemical analysis of luetheite*

	1	2	3	4	5	6
CuO	29·8	28·0	—	28·9	29·8	29·19
Al_2O_3	18·2	18·5	—	18·4	18·9	18·71
As_2O_5	40·5	40·5	—	40·5	41·7	42·18
H_2O	—	—	9·3	9·3	9·6	9·92
				97·1	100·0	100·00

1, 2. Cu, Al, and As on 759 μg and 1440 μg respectively; M. Duggan, analyst.
3. Average of 4 analyses on 508, 236, 5653, and 4147 μg.
4. Average analysis.
5. Average analysis recalculated to 100 %.
6. Theory for $Cu_2Al_2(AsO_4)_2(OH)_4.H_2O$.

Taken to ignition in the closed tube luetheite fuses to a greenish slag. It is sparingly soluble in cold 1:1 HCl or in hot 1:1 HNO_3, but readily dissolves in hot 1:1 HCl. Luetheite is also unaffected by perchloric acid (hot or cold), and cold 1:1 H_2SO_4 or KOH. It dissolves easily in hot H_2SO_4 and, heated in 40 % KOH, it turns a distinctive chocolate brown colour.

Chenevixite

Since first described by Pisani (1866), chenevixite has remained an ill-defined species. Although well known at present, at least upon the basis of its powder data and general appearance, there was some confusion in older literature.

The species was named for Richard Chenevix, the first (1801) to analyse an iron-bearing copper arsenate. Both Pisani's chenevixite and the mineral studied by Chenevix came from Cornwall.

Chenevix refers to an earlier occurrence of an iron–copper arsenate, a piece given to Proust by Hatchett who, in turn had received it from Peter Pallas. Pallas was said to have obtained it in Siberia. I find no mention of this, however, in Pallas's *Voyages* (1794).

The mineral analysed by Chenevix (see Table IV, col. 4) sounds, from his few tantalizing comments, as though it could have been chenevixite, and his analysis is close to modern results and to the generally accepted calculated analysis.

However, de Bournon (1801) describes the analysed material quite differently. A specific gravity of 3·4 is given as well as a blue colour. Two crystals are figured also. His description clearly does not refer to chenevixite. It is worth noting, however, that de Bournon and Chenevix exchanged arbitrary sample numbers to avoid prejudice, and confusion could possibly have resulted.

For this brief study, I used chenevixite from several localities: Chuquicamata, Chile (B.M. 1959, 406);[1] Wheal Gorland, Cornwall (B.M. 1972, 39 and B.M. 1958, 125); Las Animas, Sonora; Naco, Sonora; and Patagonia, Arizona (the luetheite locality). The Cornish and Chilean samples gave distinctly inferior patterns, and optical examination suggests that the broad, hazy lines are due solely to a grain size too small for diffraction work. The powder data did show, however, that all specimens were chenevixite, and further work was based largely on Las Animas material. Powder data for both Mexican localities are presented in Table III. The refined cell constants found from this data are: Las Animas, $a = 15{\cdot}006$Å, $b = 5{\cdot}189$, $c = 5{\cdot}724$, $\beta = 102^\circ\ 15'$; Naco $a = 14{\cdot}985$Å, $b = 5{\cdot}170$, $c = 5{\cdot}658$, $\beta = 102^\circ\ 55'$.

TABLE III. *X-ray powder data for chenevixite:* Cr-*K*α *radiation, 114 mm Wilson camera*

Naco, Sonora			Las Animas, Sonora			
I	d_{meas}	d_{calc}	I	d_{meas}	d_{calc}	hkl
3	7·318	7·303	4	7·322	7·332	200
1	5·573	5·588	—	—	—	$10\bar{1}$
1	4·980	4·967	—	—	—	$20\bar{1}$
1	4·867	4·876	1	4·888	4·892	101
		4·874			4·892	110
		4·869			4·888	300
2	4·218	4·220	2	4·130	4·235	210
		4·137			4·142	$30\bar{1}$
1B	3·801	3·795	5	3·817	3·818	$11\bar{1}$
		3·772			3·804	011
—	—	—	2	3·658	3·666	400
10	3·543	3·544	10	3·557	3·558	310
		3·524			3·559	111
—	—	—	2	3·238	3·237	$31\bar{1}$
1	3·160	3·160	2	3·194	3·194	211

Naco, Sonora			Las Animas, Sonora			
I	d_{meas}	d_{calc}	I	d_{meas}	d_{calc}	hkl
6	2·983	2·983	5	2·994	2·994	410
—	—	—	1B	2·812	2·797	002
					2·820	$20\bar{2}$
					2·812	311
					2·805	401
1	2·585	2·585	3	2·594	2·594	020
4	2·542	2·545	7	2·553	2·555	120
		2·543			2·543	510
2	2·502	2·480	4	2·504	2·504	$11\bar{2}$
		2·502			2·504	$51\bar{1}$
5	2·465	2·458	3	2·481	2·478	$21\bar{2}$
1	2·436	2·437	5	2·448	2·446	220
		2·434			2·444	600
					2·446	202

Crystallography. Single crystals were found in the Las Animas material but were too small to measure on the two-circle goniometer. It was apparent from thin section study, however, that their habit is virtually identical to that of luetheite, i.e. tabular on *a* {100} with a diamond-shaped outline in that plane.

Rotation and Weisenberg patterns taken on b^* verified the cell constants previously assigned on the basis of powder data, and again suggested the space group $P2_1/m$, or possibly $P2_1/a$.

There is little question that the cell found by Villarroel (1964) is incorrect. Both his powder data, and that of Pierrot and Walter (1961) fit chevenixite in a crude way and seem to represent that species.

The optic orientation is likewise very similar to that of luetheite and was determined in thin section with the universal stage. The orientation found is $\alpha \parallel [010]$, γ near [001] (the angle varies a bit for Naco and Patagonia crystals, never more than $\pm 5^\circ$). The indices (Na–*D*) for Las Animas material are $\alpha = 1{\cdot}92$, $\beta = 1{\cdot}96$, $\gamma = 2{\cdot}04$, $2V\gamma_{calc} = 73^\circ$. Chenevixite strongly resembles olivenite and cornubite in thin section, and its pleochroism is, like those species,

[1] B.M. numbers refer to samples from the British Museum (Natural History).

negligible. It can be easily distinguished from mottramite and vauquelinite by its habit, however, although of similar colour.

Chemistry. Two new analyses are presented here (see Table IV) and they verify the formula $Ca_2Fe_2(AsO_4)_2(OH)_4.H_2O$ assigned by most authors. Water was determined on separate samples by the Penfield method and again some experience and care was required to avoid loss of As_2O_3.

All older analyses known to me are presented in Table IV. The analysis of Chenevix is tantalizingly close to theory and it is tempting to think he did indeed analyse chenevixite. He thought he was analysing a mixture, but it sounds as if the contaminant was quartz. In fact, most Cornish chenevixite I have seen is intimately intergrown with quartz.

TABLE IV. *Chemical analyses of chenevixite*

	1	2	3	4	5	6	7	8
CuO	26·4	26·7	26·40	22·5	31·70	26·88	26·31	19·15
Fe_2O_3	27·0	26·2	26·50	27·5	25·10	26·94	27·76	22·27
As_2O_5	37·7	38·2	38·14	33·5	32·20	34·62	35·14	35·52
H_2O	8·5	8·5	8·97	12	8·66	9·25	9·33	12·32
	99·6	99·6	100·01	98·5	100·30	100·35	99·80	100·41

1, 2. Analyses by M. Duggan on 783 and 2206 μg respectively; H_2O by S.A.W. on 4·489 mg, 256 μg, and 576 μg.
3. Theory for $Cu_2Fe_2(AsO_4)_2(OH)_4.H_2O$.
4. Chenevix, 1801; incl. 3 % SiO_2 insol.
5. Pisani, 1866; also 0·34 % CaO, 2·30 % P_2O_5.
6. Mackenzie, 1885; also 0·55 % CaO, 0·23 % MgO, 1·17 % Al_2O_3, 0·71 % silica insol.
7. Hillebrand, 1883; also 0·44 % CaO, 0·16 % MgO, 0·66 % Al_2O_3, 0·40 % silica residue.
8. Mingaye (in Smith, 1926); also 0·06 % Bi_2S_3, 2·11 % Al_2O_3, 0·98 % CaO 0·06 % MgO, 0·30 % soluble silica, trace of P_2O_5, and 7·64 % silica residue.

Discussion. From the foregoing data, it seems evident that luetheite and chenevixite are isostructural. Whether or not they are isomorphous is another matter. The best information is provided by the Patagonia locality where both species occur. Here, there is little evidence of mixing, and when luetheite replaces chenevixite, there is an abrupt colour change. Also luetheite occurs only in iron-deficient rock; in samples with visible hematite, only chenevixite was noted. Luetheite also alters back to chenevixite where iron-bearing solutions penetrate the rock; in such fractures chenevixite and hematite occur together. Oddly, the alteration of luetheite to cornubite seems characterized by the presence of hisingerite rather than hematite.

Several pieces of luetheite were found at the type locality, representing some hundreds of milligrams of the mineral. Specimens will be given to the British Museum (Natural History) and the University of Arizona.

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