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Arthurite, a new copper-iron arsenate from Cornwall

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Summary. Thin apple-green crusts on several specimens from Hingston Down Consols mine, Calstock, Cornwall, proved to consist of a new mineral, alone or intimately mixed with pharmacosiderite (which it closely resembles), or with an unidentified mineral of the alunite-beudantite group having a 7.04, c 16.6 Å, or with both. The new mineral, for which the name arthurite is proposed, for Sir Arthur Russell and Mr. Arthur W. G. Kingsbury, who independently collected material and suggested that it might be new, gives X-ray powder photographs with their three strongest lines at 4.28, 4.81, and 6.97 Å; the photographs could be satisfactorily indexed on a monoclinic unit-cell with a 10.09, b 9.62, c 5.55 Å (all ± 0.01 Å), β $92.2^\circ \pm 0.2^\circ$, and containing $[\text{Cu}_2\text{Fe}_4(\text{AsO}_4)_3(\text{OH})_7 \cdot 6\text{H}_2\text{O}]$. Chemical analysis on 1.1 mg gave: CuO 16.8, Fe_2O_3 32.4, As_2O_5 34.3, H_2O 16.5 % (reduced to 100 % after deduction of 27.4 % quartz); sp. gr. 3.2 (calc. 3.07). Under the microscope arthurite is pale olive-green and very finely granular; n 1.78, birefringence low to moderate.

A SPECIMEN sent to us by Sir Arthur Russell in 1954 as a possible new mineral, from Hingston Down Consols mine, Calstock, Cornwall, gave a powder photograph distinct from any in our records, but the amount of material was too small for analysis at that date. Further specimens from the same locality received from Mr. Arthur W. G. Kingsbury in 1957 and later gave very similar photographs, but it became evident that only very small areas of the thin apple-green crusts were free from admixture with pharmacosiderite or an unidentified mineral of the alunite-beudantite family¹ or both, and the material was again set aside to await developments in analytical technique.

The problem was reopened as soon as a decimicrobalance, weighing to 0.1 μg , became available. Samples were collected from several specimens

¹ This mineral has a 7.04, c 16.6 Å, rather near the cell-dimensions of hidalgite; it proved to be too closely associated with arthurite and pharmacosiderite to give useful analytical data.

and were all checked by X-ray powder photographs; none proved free from pharmacosiderite, the hidalgite-like mineral, or quartz, and attempts at purification by flotation with bromoform were ineffective, the association being too intimate to permit of more than a small degree of

TABLE I. Chemical analyses of arthurite; all samples checked by X-ray powder photography.

	A	B	C	A'	B'	C'	D	E
CuO	12.1	8.4	12.4	16.8	17	14.5	17.7(?)	16.00
Fe ₂ O ₃	23.4	12.3	25.7	32.4	25	30.1	29.5	32.12
As ₂ O ₅	24.7	16.9	29.7	34.3	34	34.8	31.4	34.67
H ₂ O	11.9	11.9	17.6	16.5	24	20.6	—	17.21
Insol.	27.4	[50.5]	[14.6]	—	—	—	—	—
Sum	99.5	[100]	[100]	100.0	100	100.0	—	100.00

A. Arthurite plus quartz (X9556*e*; from B.M. 1964, 80; on 2.1 mg).

B. Arthurite plus much quartz (X378F(*c*); from B.M. 1964, 80; on 1.7 mg.).

C. Arthurite with some pharmacosiderite (X9555*f* and *g*; from B.M. 1964, 75; on 1.4 mg).

A', B', C'. Anal. A, B, C recalculated after deduction of insolubles.

D. Arthurite with some pharmacosiderite from Sir Arthur Russell's original specimen (X9554*d*; B.M. 1964, 74); partial analysis on 0.4 mg.

E. Theoretical composition of Cu₂Fe₄(AsO₄)₃(OH)₇.6H₂O.

concentration. The most suitable sample had quartz as the only impurity detectable by X-ray powder photographs, and portions of 1.1 and 1.0 mg of this were taken for analysis (A, table I). Other samples (B, C, D) gave confirmatory results.

Water was determined as loss of weight of the 1.1 mg sample on ignition just below red heat; the residue was dissolved in conc. HCl and the insolubles filtered off by placing a small piece of thick filter-paper in the drop of solution and sucking the liquid through it into a capillary tube, washed with dilute HCl, ignited and weighed. Ammonium citrate was added to the solution and the pH brought to approx. 9.0; copper and other heavy metals were extracted with diphenylthiocarbazone in CCl₄, and after acidification and extraction of excess reagent the iron was extracted with 0.1 % 8-hydroxyquinoline in chloroform and determined in this extract by colorimetry at 580 mμ. The diphenylthiocarbazone extracts were washed with 1:500 HCl and the washings examined for Pb, Zn, etc. (none was found); the copper-bearing CCl₄ layer was evaporated, diphenylthiocarbazone destroyed by gentle ignition, and the copper determined by colorimetry of its diethyldithiocarbamate complex in CCl₄ at 440 mμ. Arsenic was determined on the 1.0 mg sample by molybdenum-blue colorimetry after distillation as AsCl₃.

An accurate specific gravity could not be obtained owing to the intimate intergrowth with other minerals; most material appeared to remain suspended in a CHBr₃-CH₂I₂ mixture of sp. gr. 3.2; the calculated sp. gr. for a unit cell of the dimensions given below and containing Cu₂Fe₄(AsO₄)₃(OH)₇.6H₂O is 3.07. Together with the X-ray data (below)

these results show that the mineral is one not hitherto recognized, and we propose the name *arthurite* (pronounced \bar{A} -RTHERRAIT) in honour of Sir Arthur Russell and of Mr. Arthur W. G. Kingsbury, both of whom have made outstanding contributions to our knowledge of the minerals of Britain.

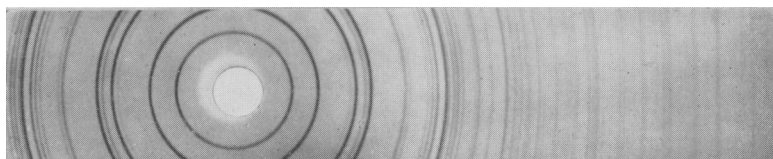


FIG. 1. X-ray powder photograph of arthurite. Co- $K\alpha$ radiation, 11.46-cm diameter camera.

Under the microscope, the arthurite is pale olive-green, with a low-to-medium birefringence and no marked pleochroism; owing to its finely granular nature, only a mean refractive index, n 1.78, could be measured.

X-ray powder photographs were taken of several samples of arthurite; two samples¹ gave identical results, which are given in table II and are believed to represent the pure mineral, because all these lines are present with the same relative intensities on all the films, no matter what impurities are present, and because apart from five extremely weak lines this pattern can be indexed efficiently; failure to index was one of the criteria used to reject earlier films as representing impure specimens and we persisted until the results in table II were obtained. On all the specimens on which it has been identified, the arthurite forms a thin apple-green crust; it is always microcrystalline and unoriented. On one sample the surface of the crust was a dull yellowish grey, but the interior was green; a sample from this crust contained scorodite, which was also present in small amount on part of the original specimen from Sir Arthur Russell. On most of the specimens, however, the impurities, which seem to be concentrated near the surface of the crusts, are pharmacosiderite (fairly well crystallized) or a member of the alunite-beudantite group (see above) or both; the crust does not come away from the matrix cleanly, and many samples contained more or less quartz or fluorite from the matrix.

Trial and error showed that if the first three lines of the powder photograph are indexed as 100, 110, and 200, a well-populated rectangular

¹ The samples taken for X-ray study were usually only about 10–30 μ g; samples of 1–3 mg were collected for chemical analysis with some difficulty.

TABLE II. X-ray powder data for arthurite (Co- $K\alpha$ radiation, 11.46 diam. camera), indexed on a unit cell having: a 10.09, b 9.62, c 5.55 Å, β 92.2°. Systematic absences to be expected for space-group $P2_1/c$ are indicated by an asterisk (*), but are probably accidental (see text)

hkl	$\sin^2 \theta$ calc.	$\sin^2 \theta$ obs.	d obs.	I	hkl	$\sin^2 \theta$ calc.	$\sin^2 \theta$ obs.	d obs.	I
100	0.00788	0.00785	10.08	vs	420	0.16072	—	—	—
010	0.00866	—	—	*	041	0.16461	—	—	—
110	0.01654	0.01652	6.97	vvs (3)	411	0.16519	0.16482	2.203	ms
001	0.02605	—	—	*	222	0.16596	—	—	—
200	0.03152	0.03156	5.04	w	302	0.16852	0.1684	2.180	vvw
101	0.03283	—	—	*	240	0.17008	—	—	—
020	0.03464	—	—	—	141	0.17139	—	—	—
011	0.03471	0.03470	4.81	vvs (2)	337	0.17161	—	—	—
101	0.03503	—	—	*	141	0.17359	—	—	—
—	—	0.0374	4.62	vvvw	222	0.17476	0.17418	2.143	mw
210	0.04018	0.04017	4.48	m	312	0.17718	—	—	—
111	0.04149	—	—	—	331	0.17821	0.17834	2.118	w
120	0.04252	—	—	—	302	0.18172	—	—	—
111	0.04369	0.04364	4.28	vvs (1)	032	0.18214	—	—	—
—	—	0.0532	3.88	vvvw	421	0.18237	0.18243	2.097	mw
201	0.05537	—	—	*	132	0.18782	0.1885	2.061	vw
201	0.05977	—	—	*	312	0.19038	0.1908	2.048	w
021	0.06069	—	—	—	421	0.19117	—	—	—
—	—	0.0610	3.62	vvvw	132	0.19222	—	—	—
211	0.06403	—	—	—	241	0.19393	0.1932	2.035	vwB
220	0.06616	—	—	—	500	0.19700	—	—	—
121	0.06747	0.06758	3.44	ms	241	0.19833	—	—	—
211	0.06843	—	—	—	322	0.20316	—	—	—
121	0.06967	—	—	—	430	0.20402	0.2033	1.984	mwB
300	0.07092	0.07095	3.36	w	510	0.20566	—	—	—
030	0.07794	—	—	*	232	0.20926	0.2093	1.955	w
310	0.07958	—	—	—	340	0.20948	—	—	—
130	0.08582	0.08597	3.05	mw	322	0.21636	—	—	—
221	0.09001	0.09003	2.983	m	050	0.21650	—	—	—
301	0.09367	—	—	*	501	0.21755	0.2172	1.919	vvwB
221	0.09441	0.09442	2.912	s	232	0.21806	—	—	—
—	—	0.0980	2.858	vvvw	402	0.22148	—	—	—
301	0.10027	—	—	*	150	0.22438	—	—	—
311	0.10233	0.10213	2.801	vs	431	0.22567	0.22498	1.887	mw
031	0.10399	—	—	—	511	0.22621	—	—	—
002	0.10420	—	—	—	501	0.22855	—	—	*
320	0.10556	0.10495	2.768	mw	412	0.23014	0.2298	1.866	vvw
311	0.10893	—	—	—	520	0.23164	—	—	—
230	0.10946	—	—	—	341	0.23223	—	—	—
102	0.10988	0.10957	2.703	m	003	0.23445	—	—	*
131	0.11077	—	—	—	431	0.23447	—	—	—
012	0.11286	—	—	—	511	0.23721	—	—	—
131	0.11297	0.11369	2.655	m	341	0.23883	0.23853	1.833	vw
102	0.11428	—	—	—	further:				
112	0.11854	0.11867	2.600	m	d obs.	I	d obs.	I	
112	0.12294	0.1221	2.559	vvw	1.816	vw	1.463	mw	
400	0.12608	0.1260	2.520	vvw	1.789	wBB	1.446	mwB	
321	0.12831	—	—	—	1.752	vvw	1.428	vvw	
202	0.13132	0.13124	2.473	w	1.729	mw	1.417	vw	
231	0.13331	—	—	—	1.712	w	1.402	vw	
410	0.13474	0.13468	2.438	m	1.694	mwB	1.379	mwB	
321	0.13491	—	—	—	1.669	vw	1.353	vwB	
231	0.13771	—	—	—	1.657	vvw	1.326	mwB	
040	0.13856	0.1385	2.403	vw	1.639	vw	1.301	vw	
022	0.13884	—	—	—	1.613	vvw	1.286	vw	
212	0.13998	—	—	—	1.605	w	1.273	vw	
202	0.14012	—	—	—	1.591	w	1.255	w	
122	0.14452	0.14488	2.349	vw	1.574	vvw	1.231	w	
140	0.14644	—	—	—	1.558	vw	1.227	w	
401	0.14773	—	—	*	1.540	vvw	1.202	vvw	
212	0.14878	—	—	—	1.528	mw	1.170	vw	
330	0.14886	0.14855	2.321	mw	1.518	wB	1.144	vvw	
122	0.14892	—	—	—	1.499	vw	1.131	vvw	
—	—	0.1538	2.28	vvvw	1.490	vvw	1.117	w	
411	0.15639	—	—	—	1.482	vw	1.103	w	
401	0.15653	—	—	*	and 11 more broad lines				

zone of reflections is present, with odd orders of $0k0$ probably absent; assuming that the rectangularity of this zone is not accidental, the symmetry must be monoclinic or higher. The first line not indexable as $hk0$ has d 4.28 Å, and there are only four other lines of this type with spacings larger than 2.8 Å; assuming these five are of type hkl , they may be indexed by a modification of Vand's method,¹ and give a unique solution with b as the monoclinic symmetry axis: a 10.09, b 9.62, c 5.55 Å (all ± 0.01 Å), β $92.2^\circ \pm 0.2^\circ$. Values of $\sin^2\theta$ for all possible diffractions as far as d 1.83 Å have been calculated (table II); they agree well with the observed values, and the good proportion of possible diffractions actually observed at spacings greater than 2.5 Å suggests that the cell is most probably correct. There are, however, a number of extremely weak lines that cannot be indexed on this cell and do not appear to be due to impurities. They could be indexed by doubling a or b or both.

No diffractions of type $0k0$ with k odd or $h0l$ with l odd were observed, which would lead to the space-group $P2_1/c$. In this space-group there are only twofold and fourfold equivalent positions, whereas the cell-dimensions, analysis, and density indicate a cell-content $\text{Cu}_2\text{Fe}_4(\text{AsO}_4)_3(\text{OH})_7 \cdot 6\text{H}_2\text{O}$ (with some uncertainty over the water content), in which the number of AsO_4 groups is odd; it does not seem possible that the chemical data or density could be far enough out to lead to even numbers of Cu, Fe, and As atoms in the unit cell, and both the 'systematic' absences must be accidental, leading to space groups $P2$, Pm or $P2/m$. Confirmation of the unit-cell, space-group, and water content must await the discovery of better crystallized material.

¹ V. Vand, *Acta Cryst.*, 1948, vol. 1, p. 290.
