

apple-green to bluish-green colour, encrusting the walls of minor fractures cutting the malachite-rich shells around djurleite masses, and on the walls of small cavities. The formation of the arsenate apparently took place during a second, late phase of oxidation. No crystal forms could be distinguished in the smooth, slightly lustrous crusts at  $\times 1000$ .

Identification was made on the basis of X-ray powder data and qualitative X-ray fluorescence and electron microprobe examination. The powder pattern, taken with a Guinier focusing camera and Fe- $K\alpha$  radiation, shows no significant variations from that found by Davis and Hey (1964) for two samples of the type-material from the Hingston Down Consols Mine, Calstock, Cornwall, at least up to  $d\ 2\ \text{\AA}$ . No evidence of the presence of pharmacosiderite, intimately associated with the Cornish arthurite, was detected, although an extremely thin surficial coating of brochantite yielded a few weak lines in the powder patterns.

X-ray fluorescence analysis of several small particles of the green crust revealed the presence of major copper, iron, and arsenic, and these three elements were further confirmed by microprobe scanning of an impregnated mount of the same powder.

Arsenates are comparatively rare in the oxidized zones of copper deposits in this region, although Sillitoe (1969) has identified duftite, bayldonite, and conichalcite, each from the near-surface zones of a single mine. This rarity presumably reflects that of hypogene enargite in the majority of the deposits, and the occurrence of arthurite at Potrerillos probably derives from the minor enargite that is present in the ore (March, 1935).

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## The cell-contents of arthurite redetermined

IN the original description of arthurite (Davis and Hey, 1964), we noted a discrepancy between the X-ray and chemical data: the cell dimensions, chemical analysis, and

density led to 3  $\text{AsO}_4$  groups per unit cell, whereas the absent diffractions indicated the space-group  $P2_1/c$ , which has only twofold and fourfold positions.

A tiny crystal has since been found, making it possible to confirm the unit cell and space-group by single-crystal methods, and to obtain data for a complete structure (Davis, in preparation), which indicates a cell content  $M_6(\text{RO}_4)_4(\text{OH})_4 \cdot 8\text{H}_2\text{O}$ . An electron microprobe analysis by Dr. S. J. B. Reed (table I, column E) cleared up the discrepancy: the Hingston Down Consols mine material contains 2.4 % P and 1.3 % S, equivalent to 5.5 %  $\text{P}_2\text{O}_5$  and 3.2 %  $\text{SO}_3$ , or in terms of the above unit cell formula to 0.82  $\text{PO}_4^{3-}$  and 0.44  $\text{SO}_4^{2-}$ .

TABLE I. *Analyses of arthurite from Davis and Hey (1964) recalculated taking account of the presence of P and S, together with a micro-probe analysis by S. J. B. Reed (col. E) and the composition deduced from the X-ray structure assuming As:P:S = 7:2:1.  $A_1, B_1, C_1$  atomic ratios to 6(Cu+Fe);  $A_2, B_2, C_2$  the analyses recalculated to 100 %, allowing for 19.2, 41.8, and 5.9 % insolubles respectively.  $\Sigma R = \text{As} + \text{P} + \text{S}$*

	$A_1$	$B_1$	$C_1$	Theor.		$A_2$	$B_2$	$C_2$	E	Theor.
Cu	2.05	2.4	1.96	2	CuO	15.3	16	13.3	17.5	14.93
Fe	3.95	3.6	4.04	4	$\text{Fe}_2\text{O}_3$	29.7	23	27.5	27.6	29.96
As	2.90	3.4	3.25	2.8	$\text{As}_2\text{O}_5$	31.3	31	31.7	36.5	30.20
$\text{H}_2\text{O}$	8.9	15	12.3	9.8	$\text{P}_2\text{O}_5$	[5.5]	[5.5]	[5.5]	5.5	5.33
$\Sigma R$	4.16	4.6	4.5	4	$\text{SO}_3$	[3.2]	[3.2]	[3.2]	3.2	3.01
					$\text{H}_2\text{O}$	15.0	21	18.8	[9.7]	16.57

Recalculation of the three analyses of our 1964 paper to a basis of 6(Cu+Fe) gives the ratios shown under  $A_1, B_1, C_1$ , in table I; it would seem that either all the arsenic determinations or the phosphorus and sulphur figures are slightly high. Of the three analyses, A fits the cell contents deduced from the X-ray work best, but the insolubles appear to have been seriously contaminated, probably by about 90  $\mu\text{g}$  of dust. The analyses have therefore been recalculated to 100 %, incorporating the sulphur and phosphorus figures and taking insolubles by difference, in columns  $A_2, B_2, C_2$ . The theoretical composition for  $\text{Cu}_2\text{Fe}_4(\text{RO}_4)_4(\text{O},\text{OH})_4 \cdot 8\text{H}_2\text{O}$  with As:P:S = 7:2:1 is also given; for this composition the calculated specific gravity is 3.29 (observed, 3.2). We have assumed in calculating the theoretical composition that replacement of  $\text{AsO}_4^{3-}$  by  $\text{SO}_4^{2-}$  is balanced by  $\text{O}^{2-}$  for  $\text{OH}^-$ , but it is possible that it might be balanced by replacement of  $\text{Fe}^{3+}$  by  $\text{Fe}^{2+}$  or by a small deficiency in the metal positions.

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