

*Connellite, buttgenbachite, and tallingite*

(With Plate II)

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**T**HERE are many basic copper chlorides and sulphates which occur as minerals but have received little recent crystallographic study. Yet copper is a widely distributed element and many of these minerals are the products of corrosion and weathering of copper and copper ores.

In 1948 we were able to confirm the earlier goniometric work of G. F. Herbert Smith (1906) that paratacamite and atacamite are not identical species (Max H. Hey, 1950) and showed that the two minerals give different X-ray powder patterns. This result was further extended by Clifford Frondel (1950) to a single crystal and thermal study of paratacamite, in the course of which he measured the rhombohedral unit-cell dimensions and showed that this mineral can be artificially produced by various methods as well as by the action of salt-water on copper. We now find from an X-ray study of all atacamites and paratacamites labelled as such in the British Museum collections, that only one occurrence of the orthorhombic mineral itself is known in the British Isles, namely at Roughtongill.<sup>1</sup> It is paratacamite, not atacamite that occurs at the famous Cornish locality, Botallack mine, St. Just.

FrondeI (1950) also studied copper chlorides related to paratacamite and was supplied by us with specimens not only of paratacamite itself but also of tallingite and botallackite. Frondel came to the conclusion that botallackite  $\text{Cu}_4(\text{OH})_6\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  is a mineral with optical properties and X-ray powder pattern entirely different from those of paratacamite and 'of other known copper minerals as far as could be determined'. He gave powder data in his paper, and we have since obtained almost identical spacings and relative intensities. So far as is known at present botallackite is a species in its own right, but we know neither its symmetry nor its crystal structure. Moreover, its formula rests upon one chemical analysis by A. H. Church (1865).

FrondeI suspected, from the two specimens available to him, that tallingite is identical with paratacamite. Our own X-ray photographs of tallingite, however, showed that it should rank as an independent

<sup>1</sup> B.M. 31622a, bought of Mr. D. Lowry, 1860.

species. We therefore intended to publish powder data for tallingite as soon as we could satisfy ourselves that Church's analyses of the mineral were not analyses of a mixture of tallingite and paratacamite, the two minerals being usually closely associated.

At that time A. W. G. Kingsbury, who had been collecting many specimens from the forsaken dumps and mines of Cornwall, also suspected that tallingite was of species rank. He had enlisted the help of H. Neumann and later of J. Hartley in the Dept. of Geology, University of Leeds, to take X-ray photographs of many of his specimens and also of species he supposed to be relevant to his investigations. Most fortunately Hartley took powder photographs of connellite and found them to be identical with tallingite. This information Kingsbury generously placed at our disposal.

Connellite occurs in slender hexagonal blue prisms at many Cornish localities; Grand Central mine, Tintic district, Utah; and in Namaqualand; South Africa.<sup>1</sup> Powder photographs of specimens from these localities are identical (table I), and we have confirmed Hartley's identification of tallingite. We have also shown that tallingite like connellite contains sulphate as well as chloride. Our photographs are reproduced in pl. II, figs. 1-3, together with the pattern for buttgenbachite (fig. 4), which A. Schoep (1927) considered to be closely related to connellite (Hey, 1950). All the powder patterns (table I) are almost identical in the positions of the diffraction lines and their relative intensities; and all diffraction lines observed for connellite from 13.7 down to 2.29 Å. have been indexed, using the appropriate Bunn chart and the axial ratio  $c/a$  derived from our single crystal measurements. Rotation, oscillation, and Weissenberg equi-inclination photographs (pl. II, fig. 5) have been about the  $c[0001]$  and  $b[11\bar{2}0]$  axes of a prism of connellite from B.M. 60566, St. Day United Mines, Cornwall.<sup>2</sup> These confirm hexagonal symmetry and yield a simple rhomb-based cell with dimensions  $a = 15.82$ ,  $c = 9.14$  Å. The only systematic absences recorded for all the observed diffractions are of the type  $hh\bar{2}hl$  for  $l$  odd. Hence the space-group may be  $D_{3h}^4 - C62c$ ,  $C_{6v}^4 - C6mc$  or  $D_{6h}^4 - C6/mmc$ ; and H. A. Miers (1894) failed to detect any pyroelectricity in the mineral. The ratio  $c/a$  is exactly one-half of the value of the axial ratio  $c/a = 1.1562$  obtained for a crystal of connellite by N. Story-Maskelyne (1863) on a single-circle goniometer. Based upon our axial ratio obtained by X-ray measurements Maskelyne's form  $(10\bar{1}1)$  now becomes  $(20\bar{2}1)$ .

<sup>1</sup> Also at Bisbee, Arizona, but no specimen is available to us for X-ray or chemical study.

<sup>2</sup> Probably from the C. F. Greville collection, purchased 1810.

TABLE I. X-ray powder data for connellite, buttgenbachite, and tallingite in A.

hkil	$d_{\text{calc}}$	Connellite.		Buttgenbachite.		Tallingite.	
		$I$	$d$	$I$	$d$	$I$	$d$
1010	13.70	vvs	13.70	vvs	13.70	vvs	13.20
1120	7.90	vvs	8.00	vvs	7.95	vvs	8.00
2020	6.85	vvw	6.90	—	—	—	—
2021	5.48	m	5.51	mw	5.51	m	5.53
2130	5.18	ms	5.20	ms	5.20	s	5.20*
0002	4.57	m	4.59	m	4.59	m	4.59
3030	4.57						
1012	4.34	m	4.35	mw	4.35	m	4.32
1122	3.97	vw	3.98	vw	3.98	vvw	3.98
2240	3.97						
3140	3.80	m	3.82	m	3.82	m	3.82
2022	3.80						
2132	3.43	m	3.48	m	3.44	m	3.42
3032	3.23	vs	3.27	s	3.27	vs	3.22
1013	2.97	vw	2.96*	vw	2.93*	vvw	2.98*
2242	3.00						
3251	2.97						
4150	3.00						
4151	2.84	vw	2.85	vvw	2.85	—	—
5050	2.74	vvs	2.75	vvs	2.75	vvs	2.74
3252	2.59	ms	2.62	m	2.61*	ms	2.61
5051	2.62						
3360	2.64	m	2.59	—	—	—	—
4260	2.59						
4152	2.50	s	2.51	s	2.51	s	2.51
5160	2.46	vvw	2.46	vvw	2.47	—	—
5161	2.37	w	2.38	w	2.38	vvw	2.38
5052	2.35						
6060	2.28	vvs	2.29	vvs	2.30	vvs	2.28*
		mw	2.25	mw	2.26	—	—
		mw	2.20	mw	2.20	mw	2.19
		w	2.09	vw	2.10	vw	2.09
		w	2.04	vw	2.05	vw	2.03
		mw	1.98	mw	1.98	mw	1.98
		vw	1.91	vw	1.92	vvw	1.91
		vw	1.855	vvw	1.861	vvw	1.853
		mw	1.811	mw	1.811*	mw	1.804
		mw	1.799	—	—	—	—
		ms	1.754	m	1.760	mw	1.756
		vvw	1.725	vvw	1.730	vvw	1.723
		vw	1.673	vw	1.680	vvw	1.674
		vvw	1.644	vvw	1.649	vvw	1.642
		vs	1.613	vs	1.621	vs	1.613
		m	1.580	m	1.587*	m	1.578
		w	1.546	vw	1.549	w	1.546
		vw	1.520	vvw	1.520	vvw	1.516
		s	1.488	ms	1.488*	s	1.488
		vvw	1.464*	—	—	—	—
		vw	1.443	—	—	vvw	1.440
		w	1.419	w	1.422	vw	1.417
		mw	1.392	mw	1.399	mw	1.392
		vw	1.371	vw	1.377	vw	1.371
		w	1.354	vw	1.356	vw	1.353
		vvw	1.333	vvw	1.333	vvw	1.333
		ms	1.313	ms	1.305	ms	1.312

Order of decreasing intensity: vvs, vs, s, ms, m, mw, w, vw, vvw. Broad lines are asterisked.

The cell dimensions of connellite, tallingite, and buttgenbachite are within the errors of determination with small cameras identical. Moreover, single crystal photographs of connellite and buttgenbachite about the  $[0001]$  axis are superposable. It is clear that, as H. Buttgenbach (1926) suggested, connellite and buttgenbachite are isomorphous; it is an unusual type of isomorphism,  $\text{SO}_4''$  being replaced by  $2(\text{NO}_3')$ , a replacement that is presumably possible because  $\text{SO}_4''$  is only a minor, though essential, constituent.

TABLE II. Unit-cell contents of connellite and buttgenbachite.

	A	B	C	C*	D	E	F	G	G*
Cu <sup>++</sup>	36.4	38.5	39.3	37.8	37.6	37.6	35.8	36.1	37.1
Cl'	8.4	7.2	9.0	8.6	7.8	8.1	8.2	6.8	7.0
SO <sub>4</sub> ''	2.4	1.7	1.6	1.5	1.6	1.95	—	—	—
NO <sub>3</sub> '	—	—	—	—	0.5	0.2	—	4.0	4.1
H <sub>2</sub> O	38.3	36.0	36.2	34.8	38.8	38.0	—	38.6	39.7
Sp. gr.	3.364	3.396	3.54	—	—	—	—	3.33	—

A Connellite, Camborne, Cornwall. S. L. Penfield, 1891. Analysis on 0.074 gram.

B Connellite, Calumet and Arizona mine, Bisbee, Arizona. C. Palache and H. E. Merwin, 1909. Analysis on 0.73 gram of selected material.

C 'Ceruleofibrite', Bisbee, Arizona. E. F. Holden, 1922, with corrections, 1924. Water by difference.

C\* Holden's analysis recalculated assuming a specific gravity of 3.41.

D Connellite, Czar mine, Bisbee, Arizona. W. E. Ford and W. M. Bradley, 1915. Specific gravity assumed to be 3.41.

E Connellite, Grand Central mine, Eureka, Tintic district, Utah. W. E. Ford and W. M. Bradley, 1915. Specific gravity assumed to be 3.41.

F 'Footcite', Copper Queen mine, Bisbee, Arizona. G. A. Koenig, 1891. Analysis on 0.0165 gram; SO<sub>3</sub> not tested for, but later shown to be present in the type material.

G Buttgenbachite, Likasi, Belgian Congo. A. Schoep, 1925.

G\* Schoep's analysis recalculated assuming a specific gravity of 3.424.

Owing to the small percentage of  $\text{SO}_4''$  present, to the rarity of the mineral, and to the frequent presence of other copper minerals accompanying it, the chemical formula of connellite is still in doubt. We have calculated the empirical unit-cell contents for all the available analyses accompanied by specific gravity determinations, and obtain the results in columns A-C of table II; these show a marked variation in all constituents, and by themselves would leave the formula still in doubt. But it will be noted that the observed specific gravity for Holden's analysis C (1922) is in marked disagreement with the other two; we therefore redetermined the specific gravity of connellite, using the same Cornish specimen<sup>1</sup> (B.M. 60566) as was used for the determination of unit-cell

<sup>1</sup> This specimen was tested for sulphate and nitrate and was found to contain sulphate only.

dimensions, and obtained the value  $D_4^{18} 3.41 \pm 0.01$ , in close agreement with Palache and Merwin (1909) and fairly close agreement with Penfield (1891). Adopting this new value for the specific gravity of connellite, a recalculation of Holden's analysis gives C\*; two analyses by Ford and Bradley (1915), in which account was taken of the possible presence of nitrate but no specific gravity was determined, give D and E when combined with our specific gravity and cell-size determinations, and an old, incomplete analysis by Koenig (1891) of footeite gives F (footeite was shown to be identical with connellite by Ford and Bradley).

We next proceeded to calculate the unit-cell content of buttgenbachite (table II, col. G), using Schoep's analysis and specific gravity, and we were surprised to find that the copper content was apparently lower than for connellite. Suspecting that Schoep's specific gravity might be in error, we redetermined the specific gravity on a type specimen<sup>1</sup> (B.M. 1933,267), and obtained the much higher value  $3.42_4 \pm 0.01$ , leading to the unit-cell contents given in table II, col. G\*.

Remembering that the possible space-groups for connellite and buttgenbachite have only even numbers of equivalent positions, it is evident that the unit-cell contains  $38\text{Cu}''$ ,  $8\text{Cl}'$ , and  $2\text{SO}_4'$  or  $4\text{NO}_3'$ , but the water content is less certain. Most of the analyses suggest  $38\text{H}_2\text{O}$ , but the calculated specific gravity for this formula is distinctly higher than that observed, both for connellite and buttgenbachite, and the careful analysis of Palache and Merwin, on specially selected material, suggests  $36\text{H}_2\text{O}$ , which gives a calculated specific gravity nearer to the observed value.

In table III the analyses of table II are compared with the calculated percentage compositions and specific gravities for the two possible pairs of formulae:

Connellite:  $2[\text{Cu}_{19}\text{Cl}_4\text{SO}_4(\text{OH})_{32} \cdot 2$  (or perhaps  $3)\text{H}_2\text{O}]$

Buttgenbachite:  $2[\text{Cu}_{19}\text{Cl}_4(\text{NO}_3)_2(\text{OH})_{32} \cdot 2$  (or perhaps  $3)\text{H}_2\text{O}]$

It remains to consider the nature of Church's tallingite (1865), which our X-ray study has shown to belong to the connellite-buttgenbachite group. Chemical tests showed that the blue crusts of tallingite contain sulphate; nitrate is either absent or quite small in amount. Tallingite is therefore an impure connellite.

The original tallingite analysis shows CuO 66.24 %, Cl 11.33 %, and Church mentioned in a footnote that a little sulphate was present among other impurities; he assigned this sulphate amounting to 0.3 %  $\text{SO}_3$ , to

<sup>1</sup> This specimen was tested for sulphate and nitrate and was found to contain nitrate only.

gypsum. This sulphate we now presume to have come from the connellite. The Cu : Cl ratio is 2.6, while in paratacamite it is 2, and in connellite 4.75. The material analysed was probably mainly paratacamite

TABLE III. Comparison of analyses with calculated percentage compositions of connellite and buttgenbachite.

	A	B	C	D	E	F	G	Connellite.				Buttgenbachite	
								4H <sub>2</sub> O	6H <sub>2</sub> O	4H <sub>2</sub> O	6H <sub>2</sub> O	4H <sub>2</sub> O	6H <sub>2</sub> O
CuO	72.3	75.96	73.8	73.38	73.41	71.7	71.56	74.62	73.96	73.60	72.97		
Cl	7.4	6.37	7.5	6.82	7.05	7.1	6.02	7.00	6.94	6.91	6.85		
SO <sub>3</sub>	4.9	3.43	3.6	3.15	3.84	—	—	3.95	3.95	—	—		
N <sub>2</sub> O <sub>5</sub>	—	—	—	0.72	0.30	—	5.40	—	—	5.26	5.21		
H <sub>2</sub> O	17.2	16.07	15.04	17.13	16.81	—	17.34	16.01	16.75	15.79	16.52		
Sum*	100.1	100.41	99.67	99.7	99.82	—	99.04	100.00	100.00	100.00	100.00		
Sp. gr.	3.364	3.396	3.54	—	—	—	3.33	3.396	3.426	3.443	3.473		

\* After deduction of O for Cl.

Columns A–G correspond to A–G of table II. In the last four columns are given the calculated compositions and specific gravities for connellite and buttgenbachite assuming 4 or 6 molecules of water (exclusive of hydroxyl water) per unit cell.

with perhaps 10–20 % of connellite and 5 % or more of adsorbed water. The fibrous to enamel-like crusts of tallingite are obviously by no means uniform, and vary in colour from a greenish-blue to a deep royal blue; this darker material was also analysed by Church, who described it as another new copper chloride, more basic than tallingite, but he did not give it a new name and it has always been classed in mineral collections as a variety of tallingite. Church's analysis of this dark blue variety shows 67.25 % CuO, and 8.73 % Cl, a Cu : Cl ratio of 3.4, which would correspond to a mixture of about equal quantities of paratacamite and connellite; again, the water content is very high, and Church's analysis, giving nearly 5 % lost in vacuo at room temperature, shows that much of it is adsorbed. On all the specimens the dark blue connellite is very closely associated with lighter coloured material, and it is evident that Church was unable to isolate the connellite for analysis.

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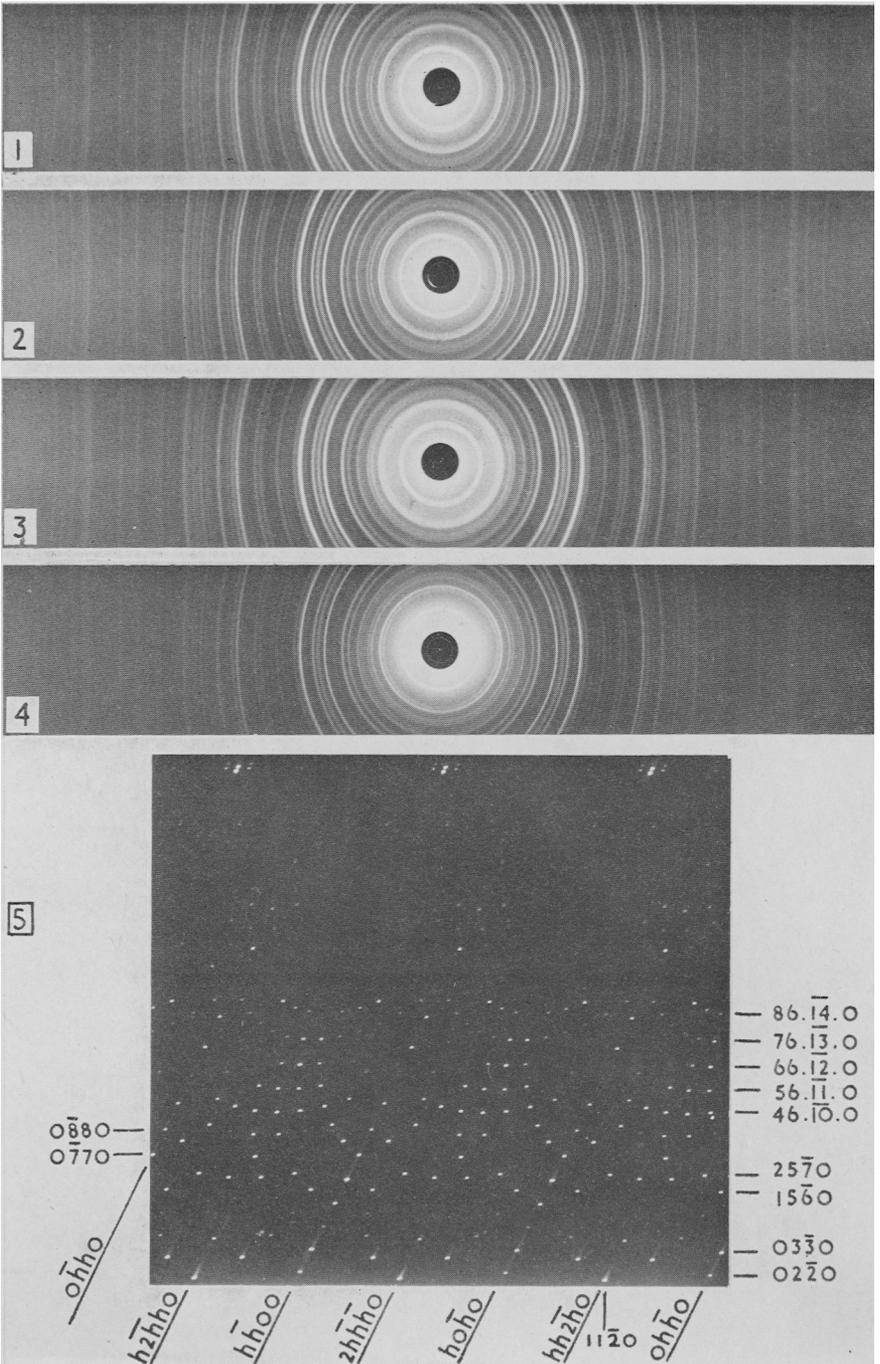
## EXPLANATION OF PLATE II

FIGS. 1-4. X-ray powder photographs in 6 cm. diameter camera, Cu-K $\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ).

1. Connellite, from Concordia mine, Namaqualand, South Africa. B.M. 32446.
2. Connellite, from St. Day United mines, Gwennap, Cornwall. B.M. 60566.
3. Tellingite, from Botallack mine, St. Just, Cornwall. B.M. 36530.
4. Buttgenbachite, from Likasi, Katanga, Belgian Congo. B.M. 1933,267.

FIG. 5. Zero-layer, normal beam, Weissenberg X-ray photograph about [0001] of connellite crystal from St. Day United mines, Gwennap, Cornwall. B.M. 60566; 6 cm. diameter camera, Cu-K $\alpha$  radiation.

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