SECOND OCCURRENCE OF BONATTITE[1]

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ABSTRACT

Bonattite, $CuSO_4.3H_2O$, first described from Elba by Garavelli in 1957, is present as vermiform aggregates in a sample from the Bonaparte River area, Lillooet District, British Columbia. The extreme indices of the B.C. mineral were determined as 1.559 and 1.615, in good agreement with the data obtained from synthetic material by Posnjak & Tunell (1929). The *x*-ray powder pattern of the Lillooet mineral is compared with those obtained from synthetic $CuSO_4.3H_2O$ and the Elba mineral.

Associated with the B.C. bonattite is a salmon-coloured sulphate of composition (Cu, Fe, Zn) $SO_4.H_2O$ with Cu:Fe:Zn = 100:94:19. The new mineral is water-soluble, and has a hardness of about 3. Partly indexed *x*-ray powder data are given; the strongest lines of the measured pattern are 3.46 (10), 4.72 (5), 3.08 (5), 4.85 (4), and 2.51 Å (4). The unit cell dimensions calculated from the powder photograph are: $a = 7.480$, $b = 7.424$, $c = 7.053$, $\beta = 114° 40'$. Assuming $Z = 4$, the calculated D is 3.281. The successful synthesis is briefly described.

BONATTITE

The trihydrate sulphate of copper, $CuSO_4.3H_2O$, a stable phase in the system $CuO\text{-}SO_3\text{-}H_2O$ (Posnjak & Tunell, 1929) was reported from Elba in 1957 by Garavelli as the new mineral, bonattite.

Bonattite has also been found as part of a fist-sized mineral sample taken from the Avoca claim, Bonaparte river, Lillooet District, British Columbia. This constitutes the second recorded occurrence.

Most of the specimen consists of a fine, powdery, salmon-coloured (Ridgeway's ochraceous-salmon) monohydrate sulphate which is surrounded by a thin cohesive outer crust of an olive-coloured iron arsenate admixed with quartz. The core of the specimen is somewhat vuggy and filled with the salmon-coloured sulphate and pale blue bonattite, both in vermiform units one to two millimeters in length. Each bonattite unit, however, consists of an aggregate of microcrystalline particles which are colourless in immersion oil, non-pleochroic, and show a pronounced change in relief on rotation of the microscope stage. Individual grains are too small to give an optical figure. According to Posnjak & Tunell (1929), synthetic $CuSO_4.3H_2O$ has the following indices of refraction: α 1.554, β 1.577, and γ 1.618. For bonattite, Garavelli (1957) obtained indices of 1.578 and 1.601; the Lillooet material has extreme indices of 1.559 and 1.615.

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$CuSO_4.3H_2O$ is monoclinic domatic, with $a:b:c = 0.432:1:0.552$; β 96°25′ (Scacchi, 1870). The compound is easily prepared by crystallization from acid solutions or dehydration of the pentahydrate Kohlschutter & Nitschmann, 1931; Hammel, 1939; Garavelli, 1957). Synthetic material for the present *x*-ray powder study was prepared by J. A. Maxwell by adding 55 ml. of concentrated sulphuric acid to 45 ml. of a solution saturated in copper sulphate at room temperature. The trihydrate was precipitated by heating on a hot water bath at 60–70° C for about 48 hours.

X-ray powder spacings of the Cape Calamita, Lillooet, and synthetic materials are compared to chalcanthite in Table 2. The Elba and synthetic material of Garavelli (1957) contain a few relatively strong lines which were not observed in the first patterns of the B.C. mineral and synthetic trihydrate prepared in this laboratory. These lines do, however, appear in subsequent powder patterns as the material is gradually transformed by hydration to chalcanthite. The lines recorded at 5.45 and 5.75 Å in the Cape Calamita bonattite do not appear in Garavelli's synthetic material, and Garavelli has suggested that these also are chalcanthite reflections.

Comparison of the chemical analyses is made in Table 1. The mean value of two analyses of bonattite reported by Garavelli (1957) corresponds to 85.15% trihydrate, the remainder being chalcanthite.

TABLE 1. BONATTITE, CHEMICAL COMPOSITION

	Cape Calamita	Lillooet, B.C.[a]	$CuSO_4.3H_2O$ (theoretical)
CuO	35.23	38.1	37.24
FeO	0.82		
MgO	0.25		
SO_3	36.49		37.47
H_2O	27.33		25.29

[a] *X*-ray fluorescence analysis by G. R. Lachance. Average of two determinations.

The copper determination of the B.C. sample, in good agreement with the theoretical value given above, indicates that the Lillooet mineral approximates $CuSO_4.3H_2O$. The material used for analysis was handpicked under a fifty-power binocular microscope and stored in two small sealed bottles almost immediately after the hand specimen was broken open and the sulphate exposed. After approximately one week in an air-conditioned laboratory (75° F., 45% humidity), the remainder of the exposed bulk sample and the original *x*-ray powder spindle have partly altered to the pentahydrate, chalcanthite. This transformation was not accompanied by any outward change in the appearance of the sample.

TABLE 2. BONATTITE AND CHALCANTHITE X-RAY POWDER DATA

$CuSO_4.3H_2O$ (Garavelli, 1957)		Cape Calamita (Garavelli, 1957)		Lillooet, B.C.[a]		$CuSO_4.5H_2O$ (Garavelli, 1957)	
d(Å)	I	d(Å)	I	d(Å)meas.	I(est.)	d(Å)	I
5.10	68	5.09	65	5.11	7	10.5	8
4.85	30	4.83	33	4.86	3	6.11	8
4.72	26	4.69	18			5.77	27
4.42	100	4.40	100	4.42	10	5.72	27
3.96	44	3.96	37	3.97	3	5.46	100
3.69	16	3.69	9			5.21	16
3.65	52	3.65	54	3.65	6	5.13	16
3.43	48	3.42	50	3.42	5	4.83	5
3.29	10	3.28	9			4.71	63
3.25	64	3.24	67	3.25	6	4.66	60
3.18	40	3.18	35	3.19	4	4.28	15
3.01	40	3.00	39	3.01	6	3.98	67
2.972	22	2.970	21	2.97	2	3.70	30
2.819	42	2.814	43	2.82	4	3.54	20
2.747	10	2.743	26			3.45	15
2.660	6	2.660	6			3.30	18
				2.593	1/2	3.27	13
2.557	8	2.550	6	2.550	1/2	3.18	16
2.498	40	2.494	39	2.498	5	3.05	25
				2.428	1/2	2.911	7
2.420	12	2.420	9			2.865	27
				2.404	1/2	2.825	33
2.353	16	2.349	11	2.354	1	2.790	7
2.277	36	2.275	33	2.278	4	2.747	15
2.213	14	2.211	9	2.208	1	2.660	12
2.104	14	2.103	11	2.106	2	2.564	7
2.080	16	2.079	11	2.081	2	2.530	3
1.947	10	1.938	11	1.950	1	2.420	13
				1.935	1/2	2.409	16
1.902	10	1.900	9	1.908	1	2.355	5
				1.869	1	2.333	7
1.827	10	1.824	9	1.827	1		
1.763	10	1.762	11	1.762	1	Plus many additional lines	
				1.740	1/2		
1.724	10	1.722	11	1.724	1		
1.694	16	1.693	15	1.702 1.693	2		
				1.670	1/2		
1.659	12	1.658	15	1.660	1		
				1.650	1/2		
1.641	10	1.638	6	1.637	1/2		
1.614	18	1.613	20	1.616	3		

[a] Norelco camera, diameter 11.46 cm. Nickel-filtered copper radiation.

THE MONOHYDRATE SULPHATE

The salmon-coloured powdery to vermiform mineral, mentioned earlier as forming the bulk of the hand specimen, is a new mineral. X-ray powder diffraction photographs of the mineral show it to be related to the kieserite group, and this was substantiated by a chemical analysis.

TABLE 3. CHEMICAL ANALYSIS OF SALMON-COLOURED SULFHATE

		Recalculated to 100 after eliminating insol.	Ratios		Theoretical contents
CuO	20.3	21.43	.269		
FeO	17.2	18.16	.253	.573	1
ZnO	3.9	4.11	.051		
As_2O_5	0.4	0.42			
SO_3	41.73	44.05		.550	1
$H_2O\pm$	11.20	11.83		.657	1
Insol.	2.95				
TOTAL	97.68	100.00			

ANALYSTS: G. R. Lachance and S. Courville. Cations determined in triplicate by x-ray fluorescence method.

Spectrographic analysis of the original sample gave, in addition to the above elements, minor Si, trace Mg, Mn, Ca, Ni, faint trace Ba, B, Ag, Al. Microscopic examination of the insoluble residue showed it to be quartz.

Neglecting the small amount of arsenic present, the formula derived from the above analysis is approximately $(Cu_{.49}, Fe_{.46}, Zn_{.09}) (SO_4)_1 . (H_2O)_{1.2}$. This can be considered as $(Cu, Fe, Zn)SO_4 . H_2O$, with Cu:Fe:Zn = 100:94:19. The Lillooet mineral is thus the only member of the kieserite group in which copper is the dominant cation.

Properties

Because of the fine-grained character of the sulphate, only approximate refractive indices are determinable. These are compared in Table 4 with the optical properties of the end member compounds, $CuSO_4 . H_2O$ and $FeSO_4 . H_2O$. The latter is the well-known mineral szomolnokite; the existence of a pure natural copper member has not been established.

The Lillooet mineral is quite soft, probably having a hardness of 3–3½. It is slowly soluble in cold water. Under a candle flame, the mineral rapidly turns mauve and within a minute, to a rusty colour (Ridgeway's hazel).

TABLE 4. COMPARISON OF OPTICAL PROPERTIES AND S.G. OF Cu AND Fe MONOHYDRATE SULPHATES

	$CuSO_4 . H_2O$[a]		Lillooet mineral		$FeSO_4 . H_2O$[b]
α	1.626	α'(?)	1.610	α	1.591
β	1.671			β	1.623
γ	1.699	γ'(?)	1.636	γ	1.663
γ–α	0.073			γ–α	0.072
$2V$	(–) 75°			$2V$	(+) 80°
D	3.0–3.3		3.30 (suspension)		3.035 (meas.)
D	3.321 (calc.)		3.281 (calc.)		3.092 (calc.)

[a] Optical data taken from Kordes (1960); calculated D from Pistorius (1961).

[b] Data from Palache, Berman, & Frondel (1951); calculated D from Pistorius (1960).

X-ray powder photographs of the Lillooet mineral were taken on a 57.3 mm. diameter camera using manganese-filtered iron radiation. The measured spacings, corrected for film shrinkage, and the visually estimated intensities are listed in Table 5. The following unit cell dimensions were calculated from the powder pattern:

$$a\ 7.480\ \text{Å} \quad b\ 7.424\ \text{Å} \quad c\ 7.053\ \text{Å}$$
$$\beta\ 114°\ 40' \quad a:b:c = 1.008:1:0.9500$$

The calculated specific gravity for 4[(Cu, Fe, Zn)$SO_4.H_2O$] is 3.281.

TABLE 5. *X*-RAY POWDER DATA FOR LILLOOET MINERAL

I(est.)	*d*(meas.) Å	*d*(calc.) Å	*hkl*
4	4.85	4.861	011
5	4.72	4.710	$11\bar{1}$
1	3.71	3.712	020
10	3.46	3.488	111
2	3.34	3.318	$21\bar{1}$
2	3.26	3.260	120
5	3.08	3.046	$20\bar{2}$
1	2.56	2.554	$12\bar{2}$
4	2.51	2.511	220
½	2.43	2.430	022
½	2.37	2.360	$31\bar{1}$
1	2.30	2.293	$13\bar{1}$
2	2.23	2.230	$11\bar{3}$
1*vb*	{2.09	2.093, 2.095	122, 131
	{2.07	2.059	$23\bar{1}$
2	1.98	1.969	202
1	1.95	1.959	$31\bar{3}$
½	1.86	1.854, 1.856	$40\bar{2}$, 040
1	1.84	1.850	311
½	1.76	1.760	$20\bar{4}$
½	1.73	1.740	222
½	1.70	1.699, 1.705	$13\bar{3}$, 400
3	1.67	1.679, 1.680	$41\bar{3}$, $23\bar{3}$
½	1.61	1.607, 1.607	004, 042
1	1.60	1.590	$22\bar{4}$
1	1.58	1.585	$24\bar{2}$
½	1.54		
½	1.51		
½	1.46		
1	1.44		

The selection rules from the indexed powder pattern permit a space group of *A*2/*a* or *Aa*. If isostructural with kieserite, the Lillooet mineral is monoclinic prismatic with space group *A*2/*a*.

Synthesis

Preparation of the synthetic analogue of the Lillooet mineral was accomplished by dissolving in water various proportions of $CuSO_4.H_2O$

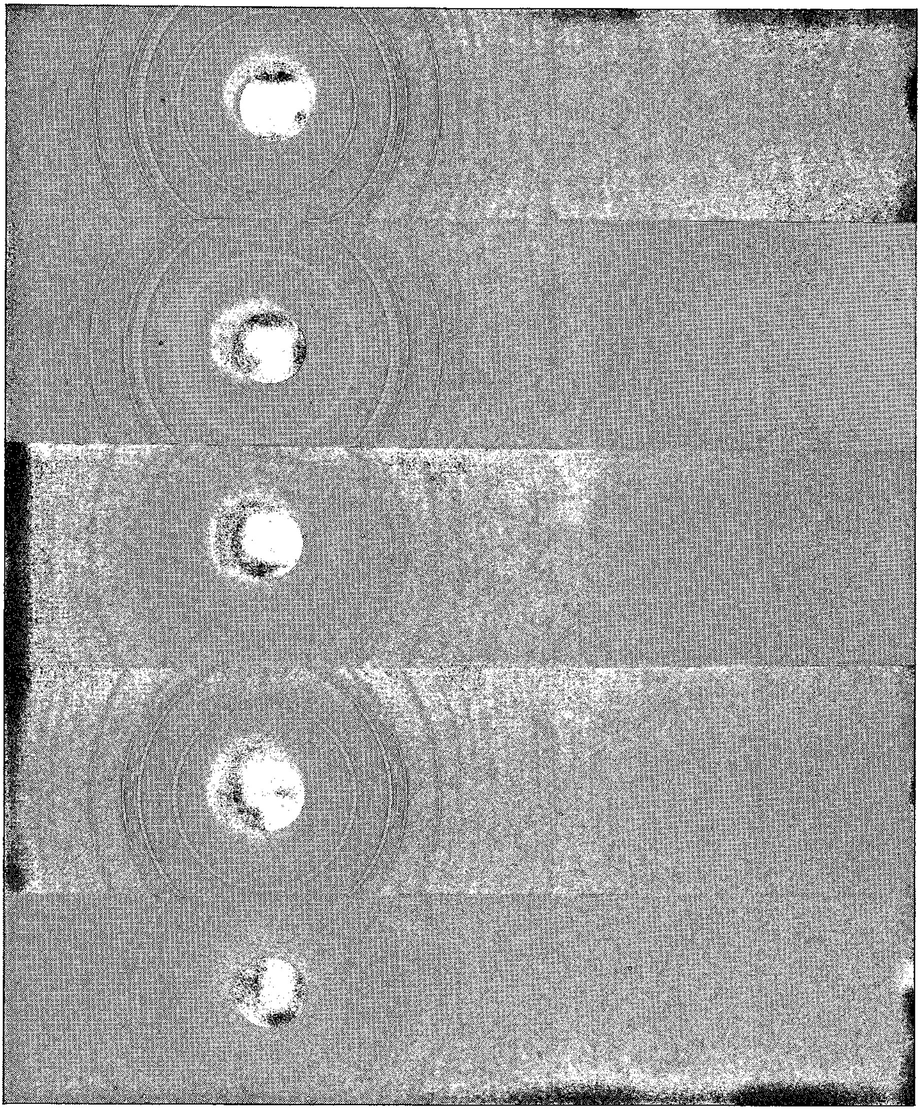

FIG. 1. Top to bottom (1) synthetic $FeSO_4.H_2O$ (2) szomolnokite, Tyrol; contains major Fe, low minor Cu, trace Si,Mg,Mn,Ca (3) synthetic $(Cu,Fe)SO_4.H_2O$ with Cu:Fe 4:3 (4) Lillooet salmon-colored mineral (5) synthetic $CuSO_4.H_2O$.

All films taken with 57.3 mm. cameras and manganese-filtered iron radiation. Lines at 4.13 Å (black dots) are from vaseline used as a binding agent for the *x*-ray powder spindles.

and $FeSO_4.H_2O$, and evaporating the solutions at a constant temperature of about 100° C. The precipitates were identified by the x-ray powder method.

The results of the study can be briefly summarized as follows:

1. Up to and including Cu:Fe = 1:2, the szomolnokite type of x-ray pattern is obtained.[2]
2. The powder pattern of the Lillooet mineral is duplicated in the range Cu:Fe = 1:1 to Cu:Fe = 4:3 (Fig. 1).
3. The $CuSO_4.H_2O$ type of pattern is obtained from precipitates containing copper in the ratio Cu:Fe = 2:1 and above.

It may be found objectionable to name the Lillooet monohydrate because the Cu:Fe ratio is approximately 1:1 and the mineral is thus not close to the theoretical end member. Should a complete series from $CuSO_4.H_2O$ to $FeSO_4.H_2O$ be found in nature, the series could be arbitrarily divided at Cu:Fe = 1:1, with szomolnokite being used to designate the iron-rich members of the series and a new name given to the copper-rich portion of which the Lillooet mineral would be a part.

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[2] Small variations apparently exist in the x-ray patterns of pure synthetic $FeSO_4.H_2O$. The most recently published patterns by Kubisz (1960) and Pistorius (1960) differ from one another; both also deviate slightly from the pattern shown in Fig. 1.

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