'Plumbogummite' from Roughten Gill, Cumberland

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[Taken as read 2 November 1967]

Summary. X-ray, infra-red, and optical studies suggest that the bluish-grey crust (previously described as plumbogummite) on arsenian pyromorphite from Roughten Gill, Cumberland, is a carbonate-bearing mix-crystal of plumbogummite, hinsdalite, and hidalgoite with a 7·018 Å, c 16·784 Å; a_{rh} 6·907, α 61° 3′; ω 1·680, ϵ 1·698.

During a reinvestigation of the pyromorphite group of minerals, (Förtsch, 1964), a sample (Fö 63) from Roughten Gill, Cumberland, was encountered, which is zoned, ranging from an arsenian pyromorphite (*circa* 12 mol. % mimetite) to a campylite (*circa* 50 mol. % mimetite), and is encrusted by a bluish-grey mineral. This sample was obtained from the Mineralogical Museum, University of Bonn, Germany. Although the bluish-grey mineral was labelled as a silicate of zinc (Bonn 335/9, 775), its X-ray powder pattern is similar to that of hidalgoite (ASTM 6–0380, Smith *et al.*, 1953); but their d-values differ noticeably. A similarity in structure could, nevertheless, be assumed.

Miers (1897, 1900) describes material from Roughten Gill that corresponds to the material investigated: '. . . This beautiful blue substance occurs as a crust which generally lies directly upon the vein quartz, and usually has crystals of pyromorphite dispersed upon it. The pyromorphite crystals are sometimes quite fresh, but are often surrounded by a zone of hitchcockite [= plumbogummite], and on some specimens are only represented by hollow pseudomorphs consisting entirely of hitchcockite; . . .' Hartley (1900) published chemical analyses of the blue mineral and of plumbogummite from various localities, and Miers (1900) gave optical observations on the minerals analysed by Hartley. The close relationship of the minerals hamlinite [goyazite], florencite, plumbogummite, beudandite, and svanbergite is discussed by Prior (1900).

Plumbogummite from Cherokee, Georgia, U.S.A., is listed as No. 2–0683 in the ASTM data file and the accompanying refractive indices are taken from Winchell (1951, p. 229). Owing to the imperfect d-values and the absence of lattice constants as well as Miller indices, new *d*-spacings (table I) and lattice constants are now presented for the Roughten Gill mineral.

X-ray powder data were obtained with a Guinier-type AEG-camera developed by Jagodzinski, using monochromatic Cu-$K\alpha$ radiation and silicon as an internal standard. The pattern (table I) could be indexed on the assumption that the mineral has a structure similar to that of hidalgoite. Reflections were present only when $-h+k+l = 3n$, indicating a rhombohedral space-group. The unit cell dimensions are: a 7·018 ± 0·002 Å, c 16·784 ± 0·003 Å, c/a 2·3915; a_{rh} 6·907 ± 0·002 Å, α 61° 3′ ± 2′. Calculated $\sin^2\theta$ from these parameters are in good agreement with the measurements.

FIG. 1. X-ray powder photograph of 'plumbogummite' Fö 63, Roughten Gill, Cumberland, taken in Guinier camera with Cu-$K\alpha$ radiation. 4θ-range 30° to 125° (actual size). Si-standard lines are marked with dots, Vaseline (v), quartz (q), unidentified (x).

The *d*-spacings of a hinsdalite from Colettes (Nicolas and de Rosen, 1963) are included in table I for comparison; there is a good agreement between the *d*-values of these two minerals and it therefore seems as though one of them, or possibly both, were incorrectly identified. The *d*-values of hinsdalite from the type locality, Lake City, Hinsdale County, Colorado, listed by Nicolas and de Rosen (1963) and on the ASTM card No. 14–185 respectively, differ slightly from each other as well as from those of hinsdalite from Colettes and 'plumbogummite' from Roughten Gill.

The X-ray powder diffraction photograph (fig. 1) shows, besides the Si (internal standard), Vaseline (sample preparation) and quartz lines, some very weak lines that could not be accounted for. If, however, the a constant is trebled, possible indices are obtained for these lines:

hkil	$51\bar{6}1$	$34\bar{7}2$	$31\bar{4}8$	$11\bar{2}9$	$2.10.\overline{12}.1$	$9.2.\overline{11}.7$
$\sin^2\theta_{\text{obs.}}$	0·05771	0·07450	0·15740	0·17661	0·22400	0·28710
$\sin^2\theta_{\text{calc.}}$	0·05752	0·07457	0·15825	0·17624	0·22375	0·28748

The only value that lies slightly outside the experimental error is that of $31\bar{4}8$. Unfortunately, the proposed trebling of the a value could not be verified by single crystal photographs.

TABLE I. X-ray powder data for 'plumbogummite' (Fö 63) from Roughten Gill, Cumberland. Guinier-camera, Cu-$K\alpha$ radiation (λ 1·5418 Å), a 7·018±0·002 Å, c 16·784±0·003 Å, c/a 2·3915, space group $R\bar{3}m$ or $R3m$, intensities: visual estimate, B = broad; all permitted values of $\sin^2\theta$ are shown up to 0·37261. For comparison d-values of hinsdalite from Colettes (Nicolas and de Rosen, 1963, p. 382).

'plumbogummite'							hinsdalite	
4θ	$\sin^2\theta_{\text{obs.}}$	$\sin^2\theta_{\text{calc.}}$	$hkil$	hkl	I/I_0	d	d	I
30·95	0·01810	0·01819	$10\bar{1}1$	100	vs	5·726	5·704	65
31·6	0·01890	0·01898	0003	111	mw	5·609	5·59	10–40
36·0	0·02446	0·02452	$01\bar{1}2$	110	mw	4·928	4·923	10
							4·543	5
					vw	(4·26)*		
41·7	0·03274	(0·03375)	(0004)†					
42·8	0·03447	(0·03507)	$(10\bar{1}3)$†		mw	(4·152)‡		
47·6	0·04252				w	(3·738)‡		
50·7	0·04814	0·04826	$11\bar{2}0$	$10\bar{1}$	ms	3·513	3·513	55–35
51·55	0·04974	0·04984	$10\bar{1}4$	211	mw	3·456	3·455	25
53·3	0·05311	(0·05277)	(0005)†		w	(3·345)*		
55·6	0·05771	(0·05670)	$(11\bar{2}2)$†		vw	(3·209)§		
56·9	0·06038				vvs	(3·137)‖		
60·1	0·06720	0·06646 0·06725	0201 $11\bar{2}3$	$11\bar{1}$ 210	vvs	2·973	2·97	100
60·8	0·06874	0·06882	$01\bar{1}5$	221	mw	2·940	2·937	10–15
62·6	0·07277	0·07279	$20\bar{2}2$	200	mw	2·858	2·860	20–15
63·35	0·07450				vw	(2·824)§		
64·0	0·07598	0·07594	0006	222	m	2·796	2·79	25–55
72·0	0·09549				vw	(2·495)‡		
73·0	0·09807	0·09810	$02\bar{2}4$	220	m	2·461	2·46	20
79·2	0·11474	0·11472	$21\bar{3}1$	$20\bar{1}$	mB	2·276	2·276	20–16
80·05	0·11712	0·11709	$20\bar{2}5$	311	m	2·253	2·254	10
80·9	0·11951	0·11945	$10\bar{1}7$	322	ms	2·230	2·23	60–70
81·45	0·12107	0·12105	$12\bar{3}2$	$21\bar{1}$	mB	2·216	2·218	35–40
82·6	0·12437	0·12421	$11\bar{2}6$	321	m	2·186	2·189	20
89·45	0·14475	0·14479	$03\bar{3}0$ $30\bar{3}0$	$11\bar{2}$ $2\bar{1}\bar{1}$	wB	2·025		
90·0	0·14645	0·14637	$21\bar{3}4$	310	mB	2·014	2·015	15
91·55	0·15124	0·15110 (0·15163)	$01\bar{1}8$ $(11\bar{2}7)$†	332	mw	1·982	1·98	15
							1·958	5
93·5	0·15740	(0·15323)	$(30\bar{3}2)$†		vvw	(1·943)§		
94·7	0·16122				vs	(1·92)‖		
95·5	0·16381	0·16378	$0\bar{3}\bar{3}3$ $30\bar{3}3$	$22\bar{1}$ 300	msB	1·903	1·905	40–25
96·0	0·16543	0·16535	$12\bar{3}5$	320	wB	1·895		
96·75	0·16786	0·16772	$02\bar{2}7$	331	w	1·881		
97·7	0·17092	0·17087	0009	333	vvw	1·864		
98·5	0·17362				vvw	(1·850)‡		
99·4	0·17661				vwB	(1·834)§		
100·4	0·17995	(0·17854)	$(30\bar{3}4)$†		vw	(1·817)*		
							1·774	3
104·25	0·19303	0·19305	$22\bar{4}0$	$20\bar{2}$	msB	1·752	1·754	25–15
106·1	0·19943	0·19936	$20\bar{2}8$	422	mwB	1·725	1·727	5
109·45	0·21115	0·21125	$13\bar{4}1$	$21\bar{2}$	mB	1·675		
109·7	0·21213	0·21204	$22\bar{4}3$	$31\bar{1}$		1·673	1·673	5
110·8	0·21608	0·21598	$21\bar{3}7$	421	mwB	1·658	1·658	7
		0·21758	$31\bar{4}2$	$30\bar{1}$				
111·65	0·21914	0·21909	$11\bar{2}9$	432	mB	1·646	1·646	
112·1	0·22113	0·22074	$03\bar{3}6$ $30\bar{3}6$	330 411	¶	1·639	1·641	10
112·35	0·22178					(1·6367)‖		
113·0	0·22400				vvw	(1·628)§		
		(0·22681)	$(22\bar{4}4)$†					
113·8	0·22695	0·22704	$1.0.\bar{1}.10$	433	mw	1·618	1·616	7
117·95	0·24253	0·24290	$13\bar{4}4$	$32\bar{1}$	vvw	1·564		

TABLE I—*continued*

'plumbogummite'							hinsdalite	
4θ	$\sin^2\theta_{obs.}$	$\sin^2\theta_{calc.}$	*hkil*	*hkl*	I/I_0	*d*	*d*	*I*
119·3	0·24740	0·24763	$12\bar{3}8$	431	vvw	1·550		
120·0	0·25000	(0·24816)	$(30\bar{3}7)$†		vvw	(1·541)*		
		0·25952	$40\bar{4}1$	$3\bar{1}\bar{1}$				
123·1	0·26180	0·26188	$31\bar{4}5$	410	mwB	1·505	1·506	3
124·15	0·26583	0·26585	$04\bar{4}2$	$22\bar{2}$	w	1·495	1·493	7
124·95	0·26891	0·26900	$22\bar{4}6$	420	mB	1·4865	1·487	5
125·6	0·27145	0·27135	$0.1.\bar{1}.11$	443	vw	1·479		
126·55	0·27513	0·27531	$0.2.\bar{2}.10$	442	msB	1·4697	1·469	15
129·6	0·28710	(0·28509)	$(31\bar{4}6)$†		vvw	(1·438)§		
130·6	0·29107	0·29116	$40\bar{4}4$	400	mwB	1·4289		
		(0·30352)	$(1.1.\bar{2}.11)$†					
133·8	0·30383	0·30378	0.0.0.12	444	vw	1·3985		
134·8	0·30785	0·30778	$32\bar{5}1$	$30\bar{2}$	w	1·3894		
		0·31015	$04\bar{4}5$	$33\bar{1}$				
135·9	0·31229	0·31251	$13\bar{4}7$	430	mw	1·3804		
		0·31411	$23\bar{5}2$	$31\bar{2}$				
136·7	0·31553	0·31556	$03\bar{3}9$ $30\bar{3}9$	441 522	mw**	1·3725		
137·6	0·31919	0·31961	$2.0.\bar{2}.11$	533	vvw	1·3645		
138·25	0·32184				m	(1·3589)‖		
138·65	0·32354	0·32357	$2.1.\bar{3}.10$	532	¶	1·3555		
142·2	0·33804	0·33785	$14\bar{5}0$ $41\bar{5}0$	$21\bar{3}$ $3\bar{1}\bar{2}$	mw	1·3259		
		0·33943	$32\bar{5}4$	$41\bar{1}$				
143·65	0·34404	0·34416	$31\bar{4}8$	521	vvw	1·3142		
145·55	0·35193	0·35204	$1.1.\bar{2}.12$	543	w	1·2994		
146·7	0·35674	0·35683	$14\bar{5}3$ $41\bar{5}3$	$32\bar{2}$ $40\bar{1}$	m	1·2907		
		0·35841	$23\bar{5}5$	$42\bar{1}$				
		0·36078	$40\bar{4}7$	511				
148·35	0·36344	0·36393	$22\bar{4}9$	531	vvw	1·2783		
149·3	0·36764	0·36788	$1.2.\bar{3}.11$	542	w	1·2714		
150·45	0·37249	0·37261	$1.0.\bar{1}.13$	544	mw	1·2632		

* quarts. † indices not conforming to rhombohedral criteria. ‡ Vaseline.
§ unidentified lines (see text for trebling of *a* constant). ‖ Si-standard.
¶ camouflaged by Si. ** plus quartz.

Single crystal rotation photographs, taken with the axis of the fibre bundle as the rotation axis, resemble a powder photograph with distinct shape orientation due to the fact that the fibres are very fine and subparallel (fig. 2). If the stronger reflections are associated with the corresponding layer lines, their *hkl*'s agree with those obtained from the powder pattern; the fibre axes correspond to the *c*-axis.

Optical study. The refractive indices measured in Na-light are intermediate between those of hidalgoite (Smith *et al.*, p. 1219) and hinsdalite from Hinsdale County (Dana, 1951, p. 1004), and much higher than those of plumbogummite from Canton Mine, Georgia (Dana, 1951, p. 831):

hidalgoite mean	n 1·705–1·713	
'plumbogummite'	ω 1·680±0·002	ϵ 1·698±0·002
hinsdalite	1·670	1·689
plumbogummite	1·653±0·01	1·675±0·01

A thin section parallel to (0001) of the zoned arsenian pyromorphite host shows the 'plumbogummite' to have grown in rhythmic shells. The sub-parallel orientation of the fibres as well as their orientated relationship to the host can be seen under crossed nicols (fig. 2).

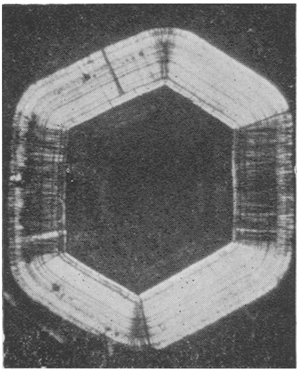

FIG. 2. Zoned arsenian pyromorphite (dark) with rhythmic layers of 'plumbogummite' (light). Fibre axes of 'plumbogummite' (dark in the east and west segments) are parallel to the thin section. Crossed nicols, × 37. (Actual width of crystal is 1 mm.)

Chemical data. If the chemical analysis of plumbogummite from Roughten Gill by Hartley (1900) is compared with the theoretical composition as calculated from the formula $PbAl_3H[(OH)_6/(PO_4)_2]$, a relative deficiency of P_2O_5 and PbO and a surplus of Al_2O_3 and H_2O are observed (table II). Furthermore, CO_2 is not accounted for.

When recalculating the chemical analysis of Hartley (table II) the CO_2 was not regarded as an impurity, as no carbonates were detected in the X-ray powder pattern, and C therefore is believed to substitute for P. It is suggested that the CO_3 ions are accompanied by an equivalent number of OH in the replacement of PO_4. Not only is the charge balance maintained, but the tetrahedral coordination for P-position atoms is also preserved. Part of the surplus Al is also assigned to tetrahedral positions with twice the number of OH accompanying them. In order to maintain the charge balance, still more OH has to take the place of O, and the remaining OH is converted to H_2O. This type of substitution does, however, produce a decrease in total charges in the structure. Other possibilities would be to retain eight oxygen in the formula and to balance the charges with hydrogen ions, or to bring in only the equivalent amount of OH for C and Al, and then balance with hydrogen ions (table II).

Infra-red examination. Because very little material of the 'plumbogummite' was available, only an infra-red absorption spectrum was recorded. Hidalgoite, the As-analogue of hinsdalite, was used for comparison. A sample (U.S. Nat. Museum No. 112728) was kindly supplied through the courtesy of Mr. R. L. Smith. The infra-red absorption spectra were recorded in the 4000 to 670 cm^{-1} (2·5–15 μ) region on a Perkin-Elmer 221 Infrared Spectrometer equipped with NaCl prism, at sample concentrations of 1·2 mg in 11-mm diameter KBr discs.

TABLE II. Chemical composition of the 'plumbogummite' from Roughten Gill compared with the theoretical composition of plumbogummite; with possible interpretations of the analysis.

	1	2		1*a*
PbO	37·03	38·44	Pb	0·93
Al_2O_3	28·74	26·32	Al	3·19
P_2O_5	18·64	24·425	P	1·48
CO_2	3·12	—	C	0·40
H_2O	12·73	10·845	H	7·95
Sum	100·26	100·00	O	14·19

1. 'Plumbogummite', Roughten Gill, anal. E. G. J. Hartley, 1900.
2. Theoretical composition of plumbogummite, $PbAl_3H(PO_4)_2(OH)_6$.
1*a*. Atomic ratios calculated for 6 cations (Pb, Al, P, and C).

Possible structural formulae (see text)

$Pb_{0\cdot 93}Al_{3\cdot 07}[(P_{1\cdot 48}C_{0\cdot 40}Al_{0\cdot 12})O_{6\cdot 43}(OH)_{1\cdot 57}/(OH)_6].0\cdot 38H_2O$
or
$Pb_{0\cdot 93}Al_{3\cdot 07}H_{1\cdot 57}[(P_{1\cdot 48}C_{0\cdot 40}Al_{0\cdot 12})O_8(OH)_6].0\cdot 38H_2O$
or
$Pb_{0\cdot 93}Al_{3\cdot 07}H_{0\cdot 93}[(P_{1\cdot 48}C_{0\cdot 40}Al_{0\cdot 12})O_{7\cdot 36}(OH)_{0\cdot 64}/(OH)_6].0\cdot 38H_2O$

The absorption spectra obtained are reproduced in fig. 3. The wavenumbers of the bands are: for 'plumbogummite' Fö 63, 3413, 3125, 2358, 1636, 1470, 1412, 1182, 1101, 1030, 866, 797, 778, and 689 cm^{-1}, and for hidalgoite U.S.N.M. 112728, 3448, 3067, 2358, 1633, 1210, 1079, 1015, 967, and 860 cm^{-1}. The original spectra are filed at the Physikalisch Chemischen Institut, Freiburg University, Freiburg im Breisgau, Germany, nos. 16459 and 16458 respectively. Using Moenke's (1962) published spectra cards it was possible to identify the bands resulting from OH, SO_4, and AsO_4 in the case of hidalgoite. 'Plumbogummite', on the other hand, gave a spectrum with more bands although, according to its ideal formula, it should have fewer. Owing to superposition of bands, the transmission is lower over a wide range of the spectrum. Bands due to hydroxyl and water are clearly visible in the 3 μ and 6 μ regions. The double band in the 7 μ region is allotted to CO_3. It is interesting to note that Gulbrandsen *et al.* (1966) also found a double band in the 7 μ region in a carbonate-bearing apatite. They attribute it to the different environment of the CO_3 ion in apatite compared with calcite where only one band is present. Similar reasons can be advanced for the double band in 'plumbogummite' because cerussite, too, exhibits only one band (Adler and Kerr, 1963, p. 127). This seems to be in accordance with the structural formula as calculated from Hartley's analysis.

It is suggested that a double band due to SO_4 is partly superimposed on the PO_4 doublet in the 8 to 11 μ region. The band at 866 cm^{-1} seems to indicate AsO_4. Although the material was hand-picked under a binocular microscope, part of the AsO_4 could be due to very minute campylite crystals, which are dispersed on the 'plumbogummite'.

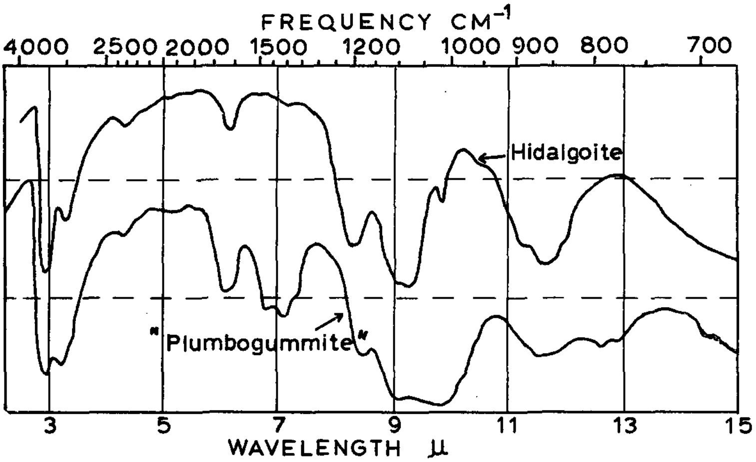

FIG. 3. Infra-red absorption spectra of hidalgoite (U.S. Nat. Museum, No. 112728) and 'plumbogummite' (Fö 63), from Roughten Gill, Cumberland (bottom).

Another absorption band (v_3) of the CO_3 ion, however, falls in the same region, and it is therefore difficult to evaluate how much AsO_4, if any, contributed to that absorption band. The bands at 797 cm^{-1} and 778 cm^{-1} correspond to quartz, the presence of which is indicated by the X-ray powder photograph, while the small band at 689 cm^{-1} could be due to the v_4 mode of the CO_3 ion.

Discussion. The *d*-values of hinsdalite (Nicolas and de Rosen, 1956, p. 382) are in good agreement with those of the 'plumbogummite' of the present investigation (table I). Regarding the composition of this hinsdalite only qualitative chemical results are given (p. 383), namely P, Pb, Al present, and SO_4-reaction positive, and its chemical formula is thus only tentative.

If the components PO_4, SO_4, CO_3, and AsO_4, as suggested by the infra-red spectrum, are in fact present, then the 'plumbogummite' under discussion would be a carbonate-bearing mix-crystal of hinsdalite, plumbogummite, and hidalgoite. Such a composition is also in closer agreement with the measured refractive indices. Unfortunately, Miers (1900) did not determine the refractive indices of the sample analysed by Hartley (1900). Regarding the hinsdalite from Colettes, Nicolas and de Rosen only mention that it is uniaxial positive with first-order yellow interference colours (presumably thin section-thickness).

A mix-crystal containing hidalgoite and hinsdalite in equal proportions would imply that the atomic ratio $(As+P):S = 1:1$; a mineral of such a composition would have higher refractive indices than the mineral under discussion. Although the exact proportions of P, S, and As are not known, it can be deduced from the infra-red absorption spectrum that PO_4 is much in excess of AsO_4. If it is kept in mind that the v_2 mode of the CO_3 ion is partly superimposed on the AsO_4 band in the 11 to 12 μ region, then the possibility of a carbonate-bearing mix-crystal of plumbogummite and hinsdalite is not ruled out.

Acknowledgements. The writer wishes to express gratitude to Prof. H. Wondratschek for his support and supervision in the Department of Mineralogy at Freiburg University, where most of the research was carried out. Professor R. Mecke, director of the Physikalisch-Chemische Institut at Freiburg University generously permitted the use of an infrared spectrometer. The award of a DAAD exchange-bursary is gratefully acknowledged. The Deutsche Forschungsgemeinschaft made the investigation possible by providing essential instruments. Appreciation is expressed to Dr. E. A. Retief for critically reading the manuscript.

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[*Manuscript received 23 November 1966*]