New data on glaucocerinite

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ABSTRACT. The strongest lines in the X-ray powder diffraction pattern of type material of glaucocerinite from Laurion (Greece), indexed on a hexagonal pseudocell, are 10.9 (100) (003), 5.45 (90) (006), 3.63 (80) (009), 2.62 (60) (012), 2.46 (60) (015), 2.231 (50) (018), and 1.981 Å (50) (0.1.11). The pseudocell parameters are a 3.0700(8), c 32.65(1) Å. Chemical analysis of topotype material yields the formula $[(Zn,Cu)_5Al_3(OH)_{16}][(SO_4)_{1.5} \cdot 9H_2O]$ based on a pyroaurite-like structure. The pseudocell parameters for this sample are a 3.057(3), c 32.52(5) Å. Optical data are $2V_\alpha \simeq 60°$, α 1.540, β 1.554, γ 1.562; D(meas.) = 2.4 ± 0.1 g/cm³, D(calc.) = 2.33 g/cm³. So-called 'woodwardite' from Caernarvonshire, Wales, is identified as the Cu-analogue of glaucocerinite. An '11 Å mineral' occurring together with carrboydite in Western Australia is shown to be the Ni-analogue of glaucocerinite. Alleged cotype glaucocerinite from Laurion is related to woodwardite and has the formula $[(Zn,Cu)_2Al(OH)_6][(SO_4)_{0.5} \cdot 3H_2O]$. This is a cation-ordered pyroaurite-type structure with hexagonal cell parameters a 5.306(2), c 26.77(2) Å. The strongest X-ray powder lines occur at 8.9 (100) (003), 4.47 (90) (006), 2.55 (60) (113), and 2.28 Å (50) (116).

KEYWORDS: glaucocerinite, woodwardite, Laurion, Greece, Caernarvonshire, Wales.

IN a paper on ktenasite from Modum (Norway) by Raade *et al.* (1977), mention is made of an unidentified mineral which microchemical tests showed to be a Cu–Zn–Al sulphate. Infra-red spectroscopy indicates the presence of $(SO_4)^{2-}$, H_2O, and probably also $(OH)^-$. The mineral occurs as pale-blue coatings in association with ktenasite and gypsum. Scanning electron micrographs reveal an aggregate of platy crystals, but the mineral gives only a very poor X-ray powder diffraction pattern with broad and diffuse lines: 11 s, 8.3 vs, 7.5 s, 4.13 w, 3.72 w, c.2.6 m(b), 1.53 Å w(b).

In an attempt to identify this phase we have

searched the literature for data on other minerals of similar composition, but unfortunately several of these are inadequately described, mostly without X-ray diffraction data. A good specimen of glaucocerinite from Laurion (Greece) was kindly supplied by the University of Vienna (specimen C 11.130) for comparison. Because the chemical analysis of this material was found to deviate considerably from that given in the original description, it was necessary to examine all the specimens of glaucocerinite from Laurion in the collections of the Natural History Museum of Vienna. New data on glaucocerinite obtained as a result of our unsuccessful attempt to identify the mineral from Modum mentioned above, are presented in this paper.

Type material

Glaucocerinite† was described as a new mineral from Laurion (Greece) by Dittler and Koechlin (1932), based on old material from the collections of the Natural History Museum of Vienna. From their analytical data, obtained on two samples of only 50 mg each (cf. Table III), Dittler and Koechlin derived the formula $Zn_{13}Al_8Cu_7(SO_4)_2O_{30} \cdot 34H_2O$. A more plausible formula is suggested by Strunz (1970): $(Zn,Cu)_{10}Al_4(SO_4)(OH)_{30} \cdot 2H_2O$.

The two original specimens of glaucocerinite have catalogue numbers G 1377 and G 1378 (Dittler and Koechlin, 1932) and give identical X-ray powder patterns (Table I, col. 1). We regard these as the genuine type specimens of glaucocerinite. An additional specimen, not mentioned by Dittler and Koechlin, is G 4526 which gives the same pattern plus additional lines of smithsonite.

† English spelling; as Glaukokerinit (in German) in the original paper. The spelling Glaucokerinit (glaucokerinite) as quoted by Palache *et al.* (1951) and by others is erroneous, as pointed out by Hey (1962).

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TABLE I. *X-ray powder diffraction data for glaucocerinite and related minerals*

hkl	1			2			3			4		
	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I
003	10.9 A	10.88 A	100	10.9 A	10.84 A	100	10.9 A	10.95 A	100	10.8 A	10.82 A	vs
006	5.45	5.442	90	5.41	5.420	50	5.46	5.475	60	5.40	5.408	s
009	3.63	3.628	80	3.62	3.613	30	3.66	3.650	50	3.60	3.605	ms
012	2.62	2.624	60	2.62	2.613	15	2.613	2.621	40	2.59	2.584	m
015	2.46	2.462	60	2.45	2.452	15	2.454	2.462	20b	2.44*	2.427	mb
	2.41†		10									
107	2.311	2.310	15									
018	2.231	2.228	50	2.216	2.219	5				2.21*	2.199	wb
0.0.15	2.180	2.177	10									
0.1.11	1.981	1.980	50	1.972	1.972	10				1.96	1.958	wb
	1.927†		10									
1.0.13	1.825	1.826	15									
0.1.14	1.751	1.753	25									
1.0.16	1.618	1.619	15									
110	1.535	1.535	40	1.522* }	1.529	5b	1.535	1.533	5b	1.51	1.511	m
113	1.521	1.520	40	}	1.514							
116	1.477	1.477	25									
1.0.19	1.443	1.443	10									
119	1.414	1.414	15									

	a 3.0700(8) A	a 3.057(3) A	a 3.066(4) A	a 3.022(2) A
	c 32.65(1)	c 32.52(5)	c 32.8(1)	c 32.45(5)
	V 266.5(1) A^3	V 263.3(5) A^3	V 267(1) A^3	V 256.7(5) A^3

1. Glaucocerinite, Laurion, Greece. Type specimen G 1378 from Naturhistorisches Museum Wien. 9 cm Debye-Scherrer camera, Fe radiation, Mn filter. Visual intensities.

2. Glaucocerinite, Laurion, Greece. Analysed material, sample C 11.130 from Institut für Mineralogie und Kristallographie der Universität Wien. 9 cm Debye-Scherrer camera, Fe radiation, Mn filter. Visual intensities.

3. 'Woodwardite', Caernarvonshire, N. Wales. From JCPDS card No. 17-132.

4. '11 A phase', Carr Boyd Rocks, W. Australia. From Nickel and Clarke (1976).

b = broad line.   † could not be indexed.   * not used for calculation of cell parameters.

Two other cotype specimens, G 2172 and H 858, are mentioned in the original description. X-ray powder data for G 2172 as well as a partial chemical analysis (Table III, col. 5) were obtained from two small grains as received from the Natural History Museum of Vienna. The powder patterns of this sample and H 858 are identical and resemble that of woodwardite (Table II, col. 1). The same pattern was obtained from an additional specimen, G 2173. However, examination of other samples from specimen G 2172 gave powder patterns of glaucocerinite. Thus it is likely that both minerals are present on this specimen though indistinguishable by the naked eye. Specimen G 1370 is identical in appearance to G 2173, but its X-ray pattern was not recorded by us. Another sample (without number) received from the Museum in Vienna and labelled 'research material of Koechlin', was shown by X-ray analysis to consist of aurichalcite. This mineral was also identified from specimen K 2934, which was acquired in 1934 after the publication of Dittler and Koechlin's (1932) paper on glaucocerinite.

X-ray powder data

Glaucocerinite. The X-ray powder patterns obtained from type specimen G 1378 and one of the minerals analysed by us (C 11.130) correspond, except that the former is of better quality and shows more reflections (Table I, cols. 1 and 2).

The powder patterns of glaucocerinite from Laurion and so-called 'woodwardite' from Caernarvonshire, Wales, as reported in the JCPDS files (cf. Table I, col. 3), are identical. Nickel (1976) has previously shown that the Welsh mineral is different from the original Cornish woodwardite (cf. Meixner, 1940), and our data show that it is closely related to glaucocerinite.

In their description of the new mineral carrboydite (a hydrated sulphate of nickel and aluminium) Nickel and Clarke (1976) mention an associated '11 Å phase' of similar composition. The X-ray powder diffraction pattern of the '11 Å phase' is similar to, although distinguishable from that of carrboydite, which is converted to the '11 Å phase' by immersion in boiling water. It is concluded by

TABLE II. *X-ray powder diffraction data for minerals related to woodwardite*

	1				2			3	
hkl	d_{obs}	d_{calc}	I	hkl	d_{obs}	d_{calc}	I	d_{obs}	I
003	8.9 A	8.92 A	100	003	8.6 A	8.52 A	100	9.1 A	vs
006	4.47	4.462	90	006	4.25	4.258	90	4.43	wb
009	2.98	2.975	20						
110	2.65	2.653	30	101	2.64	2.637	30	2.58	m
113	2.55	2.543	60	012	2.60	2.596	60		
116	2.28	2.280	50	015	2.35	2.353	30		
119	1.98	1.980	30	018	2.04	2.040	20		
1.1.12	1.70*	1.708	20						
300	1.53	1.532	30	110	1.53	1.531	50	1.50	m
303	1.51	1.510	30	113	1.51*	1.506	30		
1.1.15	1.48	1.481	20						
306	1.45	1.449	20						

a 5.306(2) = $\sqrt{3}\cdot3.063$ A
c 26.77(2)
V 652.9(7) = $3\cdot217.6$ A^3

a 3.061(2) A
c 25.55(5)
V 207.3(4) A^3

a 3.00 A
c ~27.3
V ~212 A^3

1. Laurion, Greece. Specimen H 858 from Naturhistorisches Museum Wien. 9 cm Debye-Scherrer camera, Fe radiation, Mn filter. Visual intensities.
2. Laurion, Greece. Specimen G 2173 from Naturhistorisches Museum Wien. 9 cm Debye-Scherrer camera, Fe radiation, Mn filter. Visual intensities.
3. Cornwall, specimen BM 40035 (from Nickel, 1976).

b = broad line.   * not used for calculation of cell parameters.

Nickel and Clarke (1976) that the '11 Å phase' is probably a more hydrated form of carrboydite. As can be seen from Table I (cols. 2 and 4) the diffraction pattern of the '11 Å phase' is almost identical to that of glaucocerinite analysed by us, thus it can be regarded as the Ni-analogue of glaucocerinite.

The powder patterns in Table I are closely related to those of sulphate-exchanged takovite at relative humidities $> 50\%$ (Bish, 1980) and hydrohonessite (Nickel and Wildman, 1981; Bish and Livingstone, 1981). We have been able to index all the patterns in Table I on hexagonal cells. The indices are consistent with rhombohedral symmetry $(-h+k+l = 3n)$. However, we could not index two weak lines in the pattern of G 1378, nor could we relate them to any known impurity. They may in fact indicate a lower true symmetry for glaucocerinite, which would be in agreement with the optical data for sample C 11.130, although our attempts at indexing this pattern on various monoclinic and orthorhombic cells were unsuccessful.

Woodwardite-related mineral. Powder data for specimen H 858 from Laurion are very close to those for woodwardite from Cornwall, published by Nickel (1976) (Table II). Material taken from specimen G 2173 gave partly a pattern identical

with that of H 858, and partly a very similar pattern with some spacing differences (Table II, col. 2). This pattern was found to be very close to that given by another sample of woodwardite from Cornwall, supplied by the Natural History Museum of Vienna (specimen Aa 5079, examined by Meixner, 1940). The variations in these powder patterns may be due to different degrees of hydration of the mineral. Samples of so-called woodwardite from County Cork, Ireland, were found to be X-ray amorphous.

The pattern of H 858 was indexed best on a hexagonal cell with $a = \sqrt{3}\cdot a'$, and the indexing of the two other patterns in Table II is consistent with the honessite indexing (Bish and Livingstone, 1981). The indices of both types of cell are in accordance with rhombohedral symmetry.

Chemical composition

Glaucocerinite. Our new analysis of glaucocerinite (specimen C 11.130) is presented in Table III (col. 2). It is not easy to explain the large difference between this and the original analysis published by Dittler and Koechlin, 1932 (Table III, col. 1); only the Al_2O_3 concentrations are comparable, and the SO_3 content we found is about twice that reported by Dittler and Koechlin (1932). We suspect that the

analytical data reported in the original description may be grossly in error, perhaps because of problems associated with the analysis of small samples. It is more difficult to explain the discrepancy in the analyses as a result of the presence of contaminants. Furthermore, it is worth noting that in their description of glaucocerinite, Dittler and Koechlin (1932) report that the original analysis attempt, in which 1 g of material was consumed, 'failed completely'. Unfortunately, it is not clear which cotype specimen was analysed for Dittler and Koechlin's description, or if the analysed substance was a composite.

TABLE III. *Chemical analyses (in weight per cent)*

	1	2	3	4	5
CuO	19.26	11.6	34.48	7.41	5.96
ZnO	37.95	28.7	0.30	35.2	34.2
Al_2O_3	15.40	15.4	16.5	13.5	12.0
Na_2O				1.00	
SO_3	5.79	11.8		10.5	
H_2O	22.00*	30.9		30.2	
CO_2				2.43	
Total	100.40	98.4		100.24	

1. Glaucocerinite, Laurion, Greece. Analysts: E. Dittler and W. Freh, in Dittler and Koechlin (1932).
   * H_2O^-(110°C) 16.31%, H_2O^+(110-500°C) 5.69% (air-dried material).

2. Glaucocerinite, Laurion, Greece. Specimen C 11.130 from Institut für Mineralogie und Kristallographie der Universität Wien. Analyst: C.J. Elliott. Cl^- was sought but not detected. Spectrographic analysis shows traces of Mg, Fe, Ni, and Si.

3. 'Woodwardite', Caernarvonshire, N. Wales. Specimen NMW 27.111 GR 443. Analyst: V.K. Din.

4. Laurion, Greece. Specimen H 858 from Naturhistorisches Museum Wien. Analyst: V.K. Din.

5. Laurion, Greece. Specimen G 2172 from Naturhistorisches Museum Wien. Analyst: V.K. Din.

The determination of water in glaucocerinite posed special problems. The crushed material dried at 110 °C was unstable and gained steadily in weight on the microbalance [Dittler and Koechlin (1932) report that water amounting to 16.31 wt. % of the mineral is lost below 110 °C]. The procedure we usually follow to determine the H_2O content of minerals or rocks using a C,H,N elemental analyser (Din and Jones, 1978) is not suitable for materials like glaucocerinite, which lose water very easily, since an indeterminate amount of water may be removed from the sample by a pre-analysis purge of the instrument with dry helium. The purge is an essential part of the analysis sequence because it flushes the system of air introduced with the sample. In order to minimize any water loss, samples of 'as received' glaucocerinite were analysed in nickel micro-capsules plugged with silica wool—a procedure which yielded results within

$\pm 5\%$ (relative) of theoretical for $CuSO_4 \cdot 5H_2O$. By comparison, results were $> 10\%$ (relative) low when analysis was attempted without a silica wool plug. The data from the water determinations on five samples of specimen C 11.130 covered the range 26.0-30.9 % (analyst: C. J. Elliott). We have selected the highest result as probably being nearest to the true value, an assumption supported to some degree by the reasonable formula calculated from the analytical data. The low summation (98·4 %) for C 11.130 could be due to experimental error in the H_2O determination. Although 0·7 % of CO_2 was found in one C,H,N analysis and carbonate is shown to be present from the IR spectrum, this figure could not be confirmed because of a problem with the calibration of the elemental analyser CO_2 detector system. A spectrographic examination showed the presence of small amounts of Si and Mg together with traces of Fe and Ni.

A number of hydroxy-sulphates with powder patterns similar to those of glaucocerinite or woodwardite have been shown to possess pyroaurite- or sjögrenite-type structures in which brucite-like positively charged layers containing the cations Mg^{2+}, Ni^{2+}, Fe^{3+}, and Al^{3+} alternate with negatively charged interlayers [so called by Allmann (1968)] containing exchangeable anionic groups (mainly sulphate and carbonate) plus variable amounts of water. These minerals are motukoreaite (Brindley, 1979), carrboydite and the related '11 Å phase', honessite and hydrohonessite (Nickel and Wildman, 1981; Bish and Livingstone, 1981), and mountkeithite (Hudson and Bussel, 1981) (cf. Table IV). Review papers on these types of structure were published by Allmann (1970) and Taylor (1973). A calculation based on 8 cations per brucite-like layer gives the following empirical formula for glaucocerinite, confirming its relationship to minerals of the trigonal pyroaurite group: $[(Zn,Cu)_{4.98}Al_{3.02}(OH)_{16}]^{3.02+}[(SO_4)_{1.47}(OH)_{0.08} \cdot 9.10H_2O]^{3.02-}$. The formula can also be written $(Zn,Cu)_{10}Al_6(SO_4)_3(OH)_{32} \cdot 18H_2O$ with $Zn:Cu \simeq 7:3$. Possible variations in the $Zn:Cu$ ratio were tested by determining Cu and Zn by atomic absorption spectrophotometry in another portion of the analysed material (C 11.130) and in the type material G 1378 (analyst: V. K. Din). The results are CuO 11.2, ZnO 28.1 wt. % (close to the values in Table III) and CuO 13.4, ZnO 26.8 wt. %, respectively, which correspond to $(Zn_{7.10}Cu_{2.90})_{\Sigma 10.00}$ and $(Zn_{6.62}Cu_{3.38})_{\Sigma 10.00}$.

The differential thermal analysis curve of the glaucocerinite sample C 11.130 (fig. 1) shows two large endothermic peaks at 205 and 320 °C, with a small shoulder around 285 °C. The loss of water starts at c.80 °C. There is also a small endothermic deflection around 580-590 °C.

Table IV. *Double-layer minerals with brucite-like layers* $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}$
and interlayers $[(A^-_x,A^{2-}_{\frac12 x})\cdot nH_2O]^{x-}$

Mineral	M^{2+}	M^{3+}	$M^{2+}:M^{3+}$	A^-,A^{2-}	c' (A)[†]
Hydrotalcite*/Manasseite**	Mg	Al	3:1/2:1	CO_3^{2-}	7.6-7.7
Pyroaurite*/Sjögrenite**	Mg	Fe	3:1	"	7.8
Stichtite*/Barbertonite**	Mg	Cr	3:1	"	7.8
Desautelsite	Mg	Mn	3:1	"	7.8
Takovite	Ni	Al	3:1	"	7.5
Reevesite	Ni	Fe	3:1	"	7.6
Comblainite	Ni	Co	3:1	"	7.6
Meixnerite	Mg	Al	3:1	OH^-	7.6
unnamed (Lapham, 1965)	Mg	Ni		"	7.7
unnamed (Jambor and Boyle, 1964)	Ni	Ni		"	7.6
Chlormagaluminite	Mg	Al	2:1	Cl^-,CO_3^{2-}	7.7
Iowaite	Mg	Fe	4:1	Cl^-	8.1
Motukoreaite	Mg	Al	1.58:1	SO_4^{2-}	11.2
Mountkeithite	Mg	Fe	3.67:1	CO_3^{2-},SO_4^{2-}	11.3
Carrboydite	Ni	Al		SO_4^{2-}	10.3
"11 A phase"	Ni	Al		"	10.8
Honessite	Ni	Fe	3:1		8.9
Hydrohonessite	Ni	Fe	3:1	"	10.8
Glaucocerinite	Zn	Al	1.67:1	"	10.9
Caernarvonshire mineral	Cu	Al		"	10.9
Laurion mineral H 858	Zn	Al	2:1	"	8.9
Woodwardite	Cu	Al	2:1	"	9.1

* trigonal polytype; ** hexagonal polytype; † basal spacing.

Caernarvonshire mineral. Through the courtesy of the National Museum of Wales we obtained two samples of the so-called woodwardite. One, with specimen No. NMW 27.111 GR 443 (as examined by Nickel, 1976), is labelled 'Woodwardite, coating
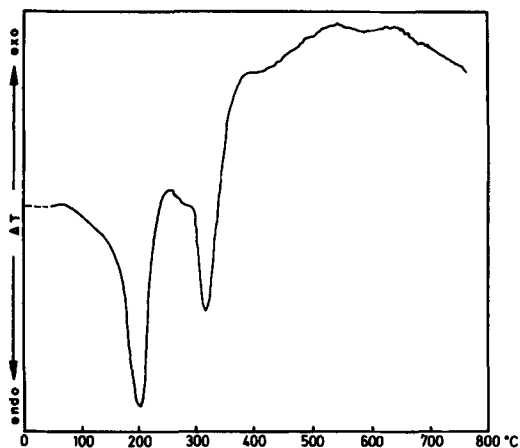

FIG. 1. DTA curve of glaucocerinite from Laurion, Greece (specimen C 11.130), recorded using a DuPont 900 thermal analyser. Sample weight c.30 mg. Rate of heating 10 °C/min in air at 1 atm. Reference material Al_2O_3.

grass, Simdde Dallhuan, Drws-y-coed, Nantlle, Carnarvonshire', and the other is labelled 'Woodwardite, coating bracken, Ffriddgoch Mine, Dolgelley, Merionethshire', No. NMW 27.111 GR 464. The diffraction patterns given by these samples are very weak and diffuse, but correspond with the data given on JCPDS card No. 17-132. A partial AAS analysis of the former is reported in Table III. From this it is clear that the Welsh 'woodwardite' is probably the Cu-analogue of glaucocerinite.

Nickel (1976) reported a Cu : Al ratio in the range 0.62–0·82 for the Welsh mineral (electron microprobe analysis), which is disturbing because it does not fit with our results and we are unable to explain this discrepancy. We have not continued our investigations of this material because we have not been able to obtain sufficiently pure samples.

Woodwardite-related mineral. A complete microchemical analysis of sample H 858 is given in Table III (col. 4). Only one measurement of the H_2O and CO_2 contents was possible because of the limited amount of material available. The procedure followed differed slightly from that described above for specimen C 11.130. The sample was weighed into an aluminium micro-capsule and covered with a weighed amount of powdered tin. The empty part of the capsule was crimped and folded to exclude air and protect the contents from the pre-analysis

purge with dry helium, then the sample was analysed according to the standard procedure for the instrument.

A partial analysis of sample G 2172 is also presented in Table III (col. 5). The agreement between the analyses of H 858 and G 2172 suggests that the samples are the same mineral, though it should be noted that G 2172 was found to contain also material giving a glaucocerinite pattern (see the section headed *Type material*).

The assumption of a pyroaurite-like structure for the woodwardite-related mineral H 858 is consistent with its powder data. Based on 3 cations per brucite-like layer the empirical formula is

$$[(Zn,Cu)_{2.00}Al_{1.00}(OH)_6]^{1.00+}$$
$$[(H_3O)_{0.30}Na_{0.12}(SO_4)_{0.50}(CO_3)_{0.21} \cdot$$
$$2.91H_2O]^{1.00-}.$$
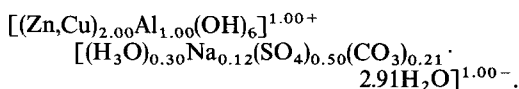
The large cations Na^+ and H_3O^+ have been placed tentatively in the interlayer to neutralize the 'excess' CO_3^{2-}. A simplified version of the formula is $(Zn,Cu)_4Al_2(SO_4)(OH)_{12} \cdot 6H_2O$, which is virtually the formula usually quoted for woodwardite (Palache *et al.*, 1951), except that Zn > Cu and the water content is greater. A close relationship between this Laurion mineral and woodwardite is evident from the X-ray powder data (Table II). The ratio of Cu:Al in Cornish woodwardite was reported to be 1.73–2.03 by Nickel (1976).

Physical properties

Glaucocerinite. The general appearance of the glaucocerinite material analysed by us is consistent with the description given by Dittler and Koechlin (1932), e.g. the softness (like wax) and the uneven distribution of the blue colour. The mineral forms botryoidal incrustations consisting of fibrous to platy aggregates and it shows parallel extinction with positive elongation, $2V_\alpha \simeq 60°$, α 1.540, β 1.554, γ 1.562 (all ±0.002, measured in white light). From the Gladstone–Dale relationship this gives a density of 2.45 g/cm³ using k values from Larsen and Berman (1934) or 2.38 g/cm³ using the values of Mandarino (1976).

The densities of two small fragments of apparently non-porous material of C 11.130 were measured using a Berman balance and toluene at 18 °C. The means of four determinations on each fragment were: 2.47 ± 0.02 g/cm³ for a piece weighing 5.6 mg and 2.52 ± 0.02 g/cm³ for a 4.8 mg piece. The latter had a rust-coloured coating on part of the surface, probably increasing the density. Three larger pieces, probably porous (7.5, 13.9, and 21.6 mg), gave results in the range 2.25–2.36 g/cm³. In conclusion, a value 2.4 ± 0.1 g/cm³ is adopted for the measured density of glaucocerinite C 11.130. The calculated density for this sample is 2.33 g/cm³.

Dittler and Koechlin (1932) report a specific gravity of 2.749 (which seems rather high for such a hydrated compound), γ 1.542 ± 0.001 in Na-light, and high birefringence. However, their data are not consistent. Based on their chemical analysis and specific gravity, the Gladstone–Dale relationship gives $\bar{n}$ 1.574 (k values from Larsen and Berman, 1934) or $\bar{n}$ 1.589 (k values from Mandarino, 1976).

The refractive indices depend strongly on the water content of a mineral, which may to some extent explain the difference in these values. The discrepancy in the density data is harder to understand (could it be a printing error for 2.479?). It should be mentioned that the specific gravity reported by Dittler and Koechlin is close to that for cyanotrichite, which can be similar to glaucocerinite in appearance, and which is known to occur at Laurion.

We conclude that the original chemical and physical data for glaucocerinite may be either partly erroneous or obtained in part from one or more minerals closely resembling glaucocerinite. Cyanotrichite, aurichalcite, and chalcoalumite are among the possible candidates for confusion with glaucocerinite, as are some still imperfectly known minerals in the group of Zn–Cu–Al sulphates.

Woodwardite-related mineral. Optical data for sample H 858 are as follows: parallel extinction, positive elongation, low birefringence, n_{max}. 1.558 ± 0.002 in white light (optical character could not be determined).
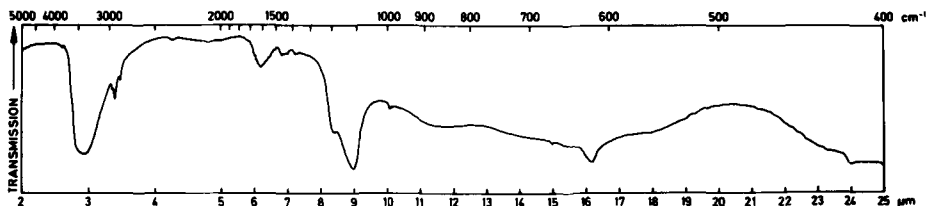

FIG. 2. Infra-red spectrum of glaucocerinite from Laurion, Greece (specimen C 11.130). KBr microdisc technique, recorded by G. C. Jones at the British Museum (Natural History), Department of Mineralogy.

Infra-red spectra

The IR spectrum of the analysed glaucocerinite is shown in fig. 2. Sulphate bands occur at 415 (v_2, weak), 620 (v_4, medium), 990 (v_1, weak), and 1110 cm^{-1} (v_3, strong), with a shoulder at 1180 cm^{-1} which is another $v_3(SO_4^{2-})$ frequency. Water bands occur at 3390 (stretching; strong, broad) and 1610 cm^{-1} (bending; medium). The presence of small amounts of carbonate is indicated by weak bands at 670 (v_4), 1385, and 1465 cm^{-1} (v_3).

Additional spectra were recorded at Institut für Kristallographie der Universität Karlsruhe (KI microdisc technique). In this case, absorption bands for sample C 11.130 at 370 (very weak), 430, 625, 830 (broad), 985 (very weak), 1110, 1170 (shoulder), 1615, and c.3500 cm^{-1} (broad) were observed, with no trace of $(CO_3)^{2-}$ bands. It is remarkable indeed, that this spectrum and that of sample H 858 differ only in that the presence of a small amount of $(CO_3)^{2-}$ is indicated in the latter. This similarity is a corollary of the basic structural identity of the two minerals. The IR spectrum of 'woodwardite' from Wales (NMW 27.111 GR 443) is very similar to the spectra discussed above; the differences are in the degree of absorption in the low-frequency region. A minor amount of $(CO_3)^{2-}$ is shown to be present. The IR spectrum of the Welsh mineral as given by Nickel (1976) is broadly similar, but far less detailed.

Discussion

All minerals known to have pyroaurite- or sjögrenite-type structures are listed in Table IV. Most of the natural compounds apparently have a fixed $M^{2+}:M^{3+}$ cation ratio, usually 3:1. The crystal structure determinations for sjögrenite and pyroaurite (Allmann and Lohse, 1966; Ingram and Taylor, 1967; Allmann, 1968) and for a hydrotalcite with a cation ratio 2:1 (Allmann and Jepsen, 1969) indicate disordered cation distributions in the octahedral brucite-like layers. On the other hand, various synthesized compounds possessing either of the two-layer structures mentioned show a large variation in the ratios $M^{2+}:M^{3+}$, viz. about 4:1–1.5:1 (Allmann, 1970), 5:1 and 2:1 (Gastuche *et al.*, 1967), 4:1–2:1 (Miyata, 1980), and 5.7:1–2.7:1 (Hashi *et al.*, 1983). A tendency to cation ordering in cases where the cation ratio is 2:1, with a supercell having $a = \sqrt{3} \cdot a'$, was noted by Gastuche *et al.* (1967), Taylor (1969), and Bish (1980). The woodwardite-related Laurion mineral H 858 described here is exactly analogous. The $M^{2+}:M^{3+}$ ratio of 1.67:1 for glaucocerinite is within the limits for synthetic materials reported by Allmann (1970).

Brindley and Bish (1976) demonstrated that a plot of the weighed mean cation radius against unit-cell parameter a for pyroaurite structures is almost a straight line; our data for samples C 11.130 and H 858 fit this line very closely.

Two recent finds of woodwardite were reported by Weil *et al.* (1975) from the Vosges (France) and by Yakhontova *et al.* (1981) from E. Siberia. The former is stated to give an X-ray powder diagram exactly matching JCPDS pattern 17-132, and can therefore be identified as glaucocerinite or a closely related mineral. The powder diagram of the Russian mineral is substantially different from either glaucocerinite or woodwardite.

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