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The Chemical Composition and Optical Characters of Chalybite from Cornwall.

By A. HUTCHINSON, M.A., Ph.D.

Demonstrator of Mineralogy in the University of Cambridge.

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THE acquisition by the Cambridge Mineralogical Museum of a series of well-crystallized specimens of chalybite, raised within recent years from the mines in the neighbourhood of Camborne in Cornwall, afforded a favourable opportunity for an investigation of the chemical composition and optical characters of this substance. This seemed the more desirable since no analysis of the chalybite crystals from the Camborne district appears to have been published, and our knowledge of the optical characters of the substance is confined to some observations of Ortloff[1] on material containing large quantities of manganese carbonate from Wolfsberg in the Harz.

The specimen examined by Ortloff was of a pale yellow colour and had a cleavage angle of 72° 55′. Its composition was as follows:— $FeCO_3$, 77·32; $MnCO_3$, 17·04; $MgCO_3$, 5·42; $CaCO_3$, 0·86; total, 100·64. The refractive indices for D light, determined by means of

[1] Zeits. Phys. Chem., 1896, vol. xix, p. 215.

a prism of which the orientation is not stated, were: $\mu_o = 1{\cdot}93409$, $\mu_e = 1{\cdot}62185$.

The crystals used in the experiments described below were essentially combinations of the basal plane with a rhombohedron, and somewhat resembled octahedra in appearance[1]. The crystals measured from 5 to 10 mm. along the edges of the basal plane and were implanted on quartz. The faces were rough and uneven and did not lend themselves to a determination of the forms present.

On breaking up the crystals they yielded perfectly transparent cleavage fragments of a pale yellow colour. Some of the larger crystals were selected for the purpose of making into prisms, and from the remainder some 7 grams of pure fragments were obtained, and these were submitted to chemical analysis after determinations of the cleavage angle and specific gravity had been made.

Angle between the cleavage planes.—This was found to vary somewhat in the larger crystals, but a number of small fragments which gave good reflections yielded values lying between 73° 5′ and 73° 0½′. Mean value 73° 2½′.

Specific Gravity.—The specific gravity was determined by the aid of a pycnometer which contained 9·9782 grams of water at 17·7° C. Corrections were applied for weighing in air and for the temperature of the water. Two independent determinations made on the same sample gave the following results:—

Sp. gr. at 16·9°/4° = 3·938. (Weight of chalybite used, 5·6336 grams.)
„ „ 17·1°/4° = 3·936. („ „ 5·6207 „)

Chemical Analysis.—The mineral was completely soluble in hydrochloric acid. After oxidation, the iron and manganese were separated by a double precipitation with ammonium acetate. As traces of calcium and magnesium were found in the filtrate after the separation of the manganese, a special determination of these constituents was made. For this purpose iron and manganese were removed by precipitation as sulphides, the filtrate was evaporated to dryness in a platinum dish, ammonium salts were removed by ignition, and the calcium and magnesium estimated in the minute residue. One determination of carbon dioxide was made; it agreed very closely with the amount required to combine with the oxides.

[1] Compare fig. 3, p. 276, of Dana's 'System of Mineralogy,' 6th edit., 1892.

The results are exhibited in the following table:—

TABLE I.

	I.	II.	III.	IV.	V.
FeO	61·15	61·02	—	—	61·08
MnO	1·12	1·13	—	—	1·12
CaO	0·10	0·12	0·09	—	0·10
MgO	—	0·14	0·11	—	0·13
CO_2	—	—	—	38·19	38·19
					100·62

I. Weight of substance taken, 1·2027 gram. The iron and manganese were separated by ammonium acetate, the calcium precipitated as oxalate, and the presence of magnesium proved qualitatively in the filtrate.

II. Weight of substance taken, 0·9608 gram. The iron and manganese were separated as sulphides from the calcium and magnesium.

III. Weight of substance taken, 1·0973 gram. Calcium and magnesium alone determined after removal of the iron and manganese as sulphides.

IV. Weight of substance taken, 1·0238 gram. Carbon dioxide determined by absorption in potash.

V. Mean result.

If the quantities of the respective carbonates are calculated from the mean percentages of the oxides we obtain:—

$FeCO_3$	98·43
$MnCO_3$	1·82
$CaCO_3$	0·18
$MgCO_3$	0·26
	100·69

From the above results it is clear that this chalybite is nearly pure ferrous carbonate.

Optical Characters.—As there was not at my disposal an apparatus for grinding faces on crystals in any desired direction, the prisms employed for finding the refractive indices were cut arbitrarily by hand, and the orientation of the faces subsequently determined by measuring the angles that they made with the cleavage planes. The substance is easily ground down on a glass plate with fine emery, and an excellent polish can be given to it by means of rouge.

The prisms were set in each case to give minimum deviation for the ordinary ray, the deviation of the extraordinary ray was then determined without altering the position of the prism, and finally the angle at which the light was incident on the first face of the prism was found. The measurements were made for lithium, sodium, and thallium light, incident on each of the two faces of the prism in turn.

Three prisms were prepared. The first (I) was cut with its refracting edge not far removed from parallelism with the optic axis, and its refracting angle was $42° 36\frac{1}{2}'$. After a series of measurements had been made, this prism was re-ground and re-polished and its refracting angle reduced to $39° 13'$. A new series of determinations was then made with this prism, which will be referred to in future as (I a). This prism was of a pale yellow colour, and its faces, though small, about 6 sq. mm. in area, were good and afforded perfect images of the slit. The second prism (II) was larger, the area of its faces being about 20 sq. mm.: it was made from very perfect material, and the faces were excellent. Its refracting angle was $53° 41'$. The third prism (III), refracting angle $47° 45\frac{1}{2}'$, was about the same size as the last, and made from equally good material, but the angle between the two cleavage planes used for finding the orientation of the artificial faces was abnormal, being $73° 48'$ instead of $73° 2\frac{1}{2}'$, and this discrepancy makes the true value of the principal extraordinary index as found by this prism a little uncertain.

Calling the prism faces P and S, and two of the cleavage planes R and R_1 respectively, the six angles between these four planes were measured. The values obtained for each prism are given in the following table:—

TABLE II.

Prism.	PS	PR	PR_1	SR	SR_1	RR_1
	° ′	° ′	° ′	° ′	° ′	° ′
I.	137 23½	65 58	120 6	131 52	93 24	106 59
I a.	140 47	63 26	119 13½	130 43	93 12	106 59
II.	126 19	80 33	125 49½	107 22	106 38½	73 3
III.	132 14½	176 0	77 5	51 41	69 3½	106 12

As the prisms were set to give the minimum deviation of the ordinary ray, the corresponding indices of refraction can be calculated from the formula $\mu_o = \dfrac{\sin \dfrac{A+D_o}{2}}{\sin \dfrac{A}{2}}$, where D_o is the deviation observed and A the refracting angle of the prism.

The velocity of the extraordinary wave and the direction of its normal in the crystal can be found by the method used by Glazebrook[1] in his verification of the law of double refraction in Iceland-spar. Let ϕ and ψ be the angles of incidence and of emergence respectively, ϕ' and ψ' the corresponding angles made by the wave-normal inside the prism, D_e the angle of deviation, and A the angle of the prism. Then we have

$$\phi + \psi = D_e + A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

$$\phi' + \psi' = A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

$$\tan\frac{\phi'-\psi'}{2} = \tan\frac{\phi'+\psi'}{2}\tan\frac{\phi-\psi}{2}\cot\frac{\phi+\psi}{2} \quad . \qquad (3)$$

From these formulae, since D_e, A, and ϕ are known, ϕ' and ψ' can be calculated.

If, now, V (= 1) is the velocity of light in air and v its velocity in the crystal, we have

$$\frac{V}{v} = \frac{\sin\phi}{\sin\phi'} = \frac{\sin\psi}{\sin\psi'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

The velocities v were calculated in each case from ψ and ψ' as well as from ϕ and ϕ'; the values thus obtained agreed very closely, and the mean of the two was taken as the true value. The following table (III) gives the values of D_o, D_e, ϕ, and $\frac{1}{v}$ for each prism.

From a knowledge of the angles made by the prism faces with the cleavage planes (Table II) we can calculate the angle between the optic axis and the wave-normal to which the velocity v corresponds. Then if v_o and v_e be the two principal wave-velocities, we have

$$v^2 = v_o^2\cos^2\theta + v_e^2\sin^2\theta \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

whence the principal extraordinary index, μ_e, can be found.

The method of calculating the value of θ is illustrated by the accompanying stereogram[2], which represents the case of prism I. The faces of the crystal are referred to a rectangular axial system OX, OY, OZ, and the crystal is so placed that the edge between the two cleavage planes RR_1 is parallel to the axis OZ, while the angles between Rr_1 and RR_1 are bisected by X and Y respectively. P is the pole of one face of the prism, S the pole of the other, while s is the pole at the other end

[1] Phil. Trans. Roy. Soc., 1880, vol. clxxi, p. 421.

[2] In the figure the faces P and S are slightly removed from their true position for the sake of clearness. In an accurate drawing K and L would lie very close together. OZ is normal to the paper at O.

TABLE III.

Prism.		Light incident on P.			Light incident on S.		
		Li.	Na.	Tl.	Li.	Na.	Tl.
I.	D_o	42° 41½′	43° 10½′	43° 35½′	42° 42½′	43° 11½′	43° 37′
	D_e	30 7	30 19½	30 32	30 9½	30 19½	30 32½
	ϕ	35 7	35 7	35 7	36 12	36 12	36 12
	$\frac{1}{v}$	1·6316	1·6356	1·6395	1·6328	1·6359	1·6401
I a.	D_o	38° 18′	38° 41½′	39° 4½′	38° 18′	38° 41′	39° 4½′
	D_e	27 28	27 38	27 47½	27 38	27 47	27 56½
	ϕ	38 47	38 47	38 47	40 1	40 1	40 1
	$\frac{1}{v}$	1·6326	1·6364	1·6399	1·6337	1·6371	1·6387
II.	D_o	60° 58½′	61° 45½′	62° 30′	60° 58½′	61° 45′	62° 28½′
	D_e	45 50	46 8	46 25½	44 45	45 5	45 21½
	ϕ	57 19¾	57 19¾	57 19¾	57 54½	57 54½	57 54½
	$\frac{1}{v}$	1·6785	1·6827	1·6867	1·6613	1·6661	1·6700
III.	D_o	50° 14′	50° 48′	51° 20½′	50° 13½′	50° 48′	51° 20′
	D_e	39 25	39 41	39 57½	40 3½	40 21	40 37
	ϕ	48 48	48 48	48 48	49 40¾	49 40¾	49 40¾
	$\frac{1}{v}$	1·6977	1·7021	1·7066	1·7063	1·7111	1·7156

of the normal on S, hence P*s* represents the internal prism angle A. One end of the optic axis emerges at T, and the angle ZT can be calculated from the cleavage angle RR_1. From the spherical triangles PRX, Pr_1X, the angle PX can be found, for we have

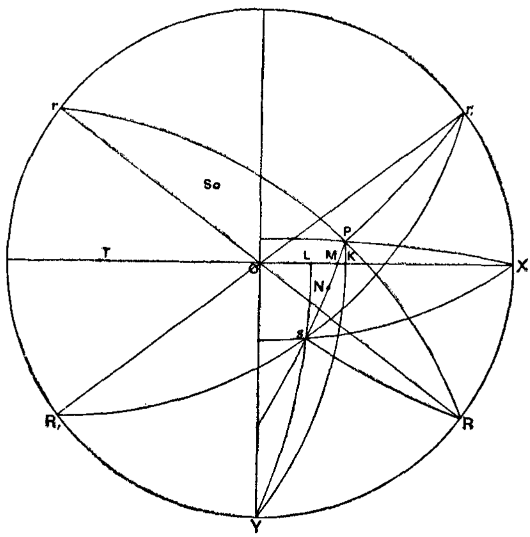
$$\cos PX = \frac{\cos \frac{PR + Pr_1}{2} \cos \frac{PR - Pr_1}{2}}{\cos \frac{Rr_1}{2}}.$$

Similarly, we can find PY, *s*X, and *s*Y.

The angle *s*M can be found by the formula

$$\cot sM = \frac{\sin PK}{\sin sL \sin Ps} + \cot Ps,$$

for we know $PK = PY - 90°$, $sL = 90° - sY$, and $Ps = A$. From the right-angled spherical triangle *s*LM, in which we know *s*L and *s*M, we can find LM and the angle LM*s*. Again, from the right-angled spherical triangle *s*LX we can find LX and so obtain the value of $TM = 90° - LX + LM + ZT$. The position of emergence in P*s* of the wave-normal N is known, for we have determined the angles ϕ' and



ψ' which it makes with the normals to the prism faces. Hence from the spherical triangle TMN, in which the sides TM, MN, and the angle TMN are known, we can find the side $TN = \theta$, the angle between the wave-normal and the optic axis. The values calculated for θ are given in Table IV.

TABLE IV.

Prism.		Light incident on P.			Light incident on S.		
		Li.	Na.	Tl.	Li.	Na.	Tl.
		° ′	° ′	° ′	° ′	° ′	° ′
I.	θ	96 26½	96 27	96 27½	96 19⅓	96 19	96 18⅓
I a.	θ	95 43½	95 44	95 45	97 10	97 9⅓	97 8½
II.	θ	60 38½	60 42½	60 46½	66 21½	66 17	66 13
III.	θ	54 26¼	54 24	54 22	51 58	52 0	52 2

The following table (V) contains the values of μ_o and of μ_e obtained from each prism according as the light was incident on P or on S.

TABLE V.

Prism.	Light incident on face.	μ_o			μ_e		
		Li.	Na.	Tl.	Li.	Na.	Tl.
I.	P	1·8648	1·8733	1·8807	1·6291	1·6331	1·6370
	S	1·8651	1·8736	1·8811	1·6303	1·6335	1·6377
	Mean	1·8649	1·8734	1·8809	1·6297	1·6333	1·6373
I a.	P	1·8655	1·8734	1·8812	1·6306	1·6344	1·6379
	S	1·8655	1·8733	1·8812	1·6307	1·6340	1·6376
	Mean	1·8655	1·8733	1·8812	1·6306	1·6342	1·6377
II.	P	1·8643	1·8724	1·8801	1·6304	1·6340	1·6375
	S	1·8643	1·8723	1·8798	1·6295	1·6336	1·6368
	Mean	1·8643	1·8724	1·8799	1·6299	1·6338	1·6371
III.	P	1·8642	1·8722	1·8798	1·6281	1·6310	1·6344
	S	1·8641	1·8722	1·8797	1·6275	1·6310	1·6344
	Mean	1·8642	1·8722	1·8798	1·6278	1·6310	1·6344

It will be seen that the results exhibit a satisfactory degree of concordance; those yielded by prism II are probably nearest to the truth.