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# On bultfonteinite, a new fluorine-bearing hydrous calcium silicate from South Africa.

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[Read June 7, 1932.]

THIS new mineral was first found by a miner named Cann in 1903 or 1904 on the 480-foot level of the Bultfontein mine at Kimberley. It occurred, associated with calcite, apophyllite, and natrolite, in a large ' horse ' of dolerite and shale fragments enclosed in kimberlite. This huge inclusion, several hundred feet in height, undoubtedly formed part of the country-rock that now encloses the kimberlite pipe. The specimens of the new mineral were considered to be natrolite and were presented to Mr. A. F. Williams. Several years later the same mineral was found by Mr. C. E. Adams in the Dutoitspan mine, which is located about half a mile from the Bultfontein mine; he presented his specimens to the MacGregor Museum at Kimberley. Recently, Mr. Miller, Underground Manager of the Jagersfontein mine in Orange River Colony, discovered the new mineral in that mine, which is located 100 miles south-east of Kimberley.

<sup>1</sup> Mr. John Parry, Chief Chemist of the De Beers Consolidated Mines at Kimberley, died on October 6, 1931.

After the description of the new mineral afwillite<sup>1</sup> had been published, Mr. Williams realized that the specimens of bultfonteinite in his collection were different from natrolite and probably represented a new mineral. Accordingly, at his request, the material was investigated chemically by Mr. Parry, Chemist of the De Beers Consolidated Mines, and found to be unlike any mineral heretofore described. Likewise its crystallographical and optical properties, determined by Mr. Wright at Mr. Williams's request, proved that it is a new mineral of interesting properties.

The determinative work on this mineral has not been an easy matter and the results obtained are not of the highest accuracy because of its relatively poor crystallographical development, its intricate polysynthetic twinning phenomena, and its peculiar chemical composition. In this connexion it may be stated that without the use of the Fedorov universal stage the optical measurements which have been obtained would hardly have been possible.

The significant chemical feature of bultfonteinite is the presence of fluorine and its resemblance in chemical aspects to the mineral afwillite. The chemical analysis and tests were made chiefly on material from the Bultfontein mine. Part of a large pink radial spherulite measuring an inch and a half in diameter served for the several tests and determinations. This is the only radial spherulite of large size that has thus far been discovered. The remaining few specimens of the mineral are small radial spherulites, either attached to larger calcite crystals or to the country-rock matrix. Calcite and bultfonteinite were deposited in part simultaneously; however, the formation of bultfonteinite continued after that of calcite. Somewhat later small crystals of a second new mineral, a hydrous calcium sulphate, still to be described, were deposited. Individual crystals of bultfonteinite project out as radial extensions from small spherulites.

The methods followed in the chemical analysis were standard. In addition to the analysis a number of special tests were performed to ascertain the exact nature of the substance and its relation to afwillite.

From this analysis the formula  $2Ca(OH,F)_2.SiO_2$  can be deduced, although the agreement is not close, especially with reference to the silica and lime. A more exact agreement is given by the formula  $11Ca(OH,F)_2.5SiO_2$ . The analyses computed from these formulas

<sup>1</sup> J. Parry and F. E. Wright, Min. Mag., 1925, vol. 20, p. 277.

are listed in columns 4 and 5 of table 1. In both cases the alumina and ferric iron oxide are included with the lime. The material was carefully selected for the chemical analysis; examination of the large pink spherulite failed to reveal the presence of substances other than bultfonteinite.

Per cent. Molecular ratios. 2Ca(OH,F)2.SiO2. 11Ca(OH,F)2.5SiO2. SiO2 ... 26.50 ... 0.441228.5826.68 ... . . . ... ... Al<sub>2</sub>O<sub>3</sub>) 0.720.0055. . . . . . ... ... Fe<sub>2</sub>O<sub>3</sub> CaO ... 54.20 . . . 0.9666... 53.3754.79... ... . . . H,0 ... 13.36 0.741413.0613.40... . . . . . . ... ... F ... ... 8.81 0.46378.63 8.87 • • • ... ... ... ... 103.59103.64103.74 ... . . . ... Less O ... 3.71 3.74 . . . . . . . . . . . . 3.64. . . 99.88 100.00 100.00

 TABLE 1. Chemical analysis of bultfonteinite. (Analyst, John Parry.)

The following chemical behaviour characterizes bultfonteinite. The powder rubbed down with a little water and then filtered yields a solution showing strong alkaline reaction with litmus and phenolphthalein. The alkali in solution was found to be calcium hydroxide and that only. The fine powder moistened first with water and then mixed with dilute hydrochloric acid and shaken vigorously produces a firm clear jelly. On treating the powder with strong acids great heat is at once generated. When 0.1 gram of the substance is treated with water and then with 10 c.c. of half-normal hydrochloric acid a clear solution is obtained almost at once. When a definite amount of powdered bultfonteinite is shaken with a measured quantity of pure water and titrated at convenient intervals with standard acid, it is found that calcium hydroxide is being continuously dissolved, until, after a prolonged contact of several days, a total limiting amount of 41.2 % lime (CaO) is taken up. When a definite quantity of bultfonteinite powder is dissolved in a measured quantity of standard acid and the unused acid is determined, it is found that the amount of lime thus taken up is 41.2 %. When, however, the bultfonteinite powder is first strongly heated over a blast-lamp and then placed in prolonged contact with pure water, measurements show that the total limiting quantity of lime taken up is 16.8 % lime (CaO).

These reactions are easily understood if the formula is written  $2Ca(OH)_2 \cdot 2SiO_2 + CaF_2 \cdot Ca(OH)_2$ . The total amount of lime entering

into solution on prolonged contact with water is then represented by  $Ca(OH)_2$  in the second part of the formula. On heating to a high temperature calcium metasilicate is formed; only the free CaO not combined with silica or fluorine is then reacted upon by water. Expressed in these terms the analysis reads:

		1.	1a.	2.	2a.
SiO <sub>2</sub>		 26.50	26.53	26.50	26.64
$Al_2O_3$ $Fe_2O_3$	•••	 0.72	0.72		—
CaÖ*	• • •	 24.74	24.77	24.74	24.87
CaO†		 16.46	16.48	16.77	16.86
$CaF_2$		 18-10	18.12	18.10	18.20
H <sub>2</sub> O		 13.36	13.38	13.36	13.43
		99.88	100.00	99.47	100.00

 TABLE 2.
 Recast of analysis of bultfonteinite.

\* Portion of lime which on heating combines with silica to form calcium metasilicate.

 $\dagger$  Excess of free lime over and above that needed to form calcium metasilicate.

In column 1 the alumina and iron oxide are listed; but in column 2 they are combined with the lime and are treated as entering with the lime into the silicate. In column 1 the total free lime available for solution in water is 41.2 %. On heating to a high temperature calcium metasilicate is formed and only the excess lime, or 16.5 %, is available to enter into solution according to column 1; 16.8 % according to column 2. In columns 1 *a* and 2*a* the percentages are adjusted to 100 %.

Chemical similarities with afwillite.—The mineral afwillite occurs under conditions quite similar to those obtaining for bultfonteinite. The composition of afwillite may be written  $3CaO.2SiO_2.3H_2O$  or  $2H_2CaSiO_4.Ca(OH)_2$ . Like bultfonteinite, afwillite powder, when shaken with pure water and titrated with standard acid, loses lime continuously, until after 36 hours nearly the whole of the lime has gone into solution. On heating over a blast-lamp, however, only  $23\cdot17$  % lime is dissolved even after 72 hours' contact with water. This quantity represents the lime which, on heat treatment, is in excess of the amount needed to form the metasilicate. Afwillite is completely soluble in acid; the amount of acid used in this operation is exactly equivalent to the lime required for the complete afwillite molecule. It is possible to express the composition of bultfonteinite in terms of afwillite plus fluorite and calcium hydroxide, thus :

3CaO.28	5iO2.3	BH <sub>2</sub> O	•••		•••	75.53 %
Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>2</sub>	ł		•••	•••		0.72
CaF <sub>2</sub>	••••					18.10
Ca(OH) <sub>2</sub>			•••	•••	•••	5.40
						99.75

The question arises: Does bultfonteinite represent possibly a product formed as the result of the attack of a fluorine- or hydro-fluoric acid-bearing solution on afwillite? The amount of calcium hydroxide equivalent to  $18\cdot10\%$  CaF<sub>2</sub> is  $17\cdot17$ ; this amount added to the 5.40 calcium hydroxide already present yields 22.57. In afwillite the free Ca(OH)<sub>2</sub> amounts to  $21\cdot64\%$  as computed, or 23.1% as determined. This agreement is quite remarkable, and suggests that possibly the afwillite molecule was attacked, its silicate of lime removed, and its calcium hydroxide partially disintegrated by fluorine.

On heating in a blowpipe or gas flame, fragments of bultfonteinite become dull white and porcelain-like. No decrepitation or traces of melting were observed; the fragments glow intensely at higher temperatures and show the calcium flame reaction. Examined under a microscope the white material obtained on heating was turbid and evidently decomposed.

When powdered bultfonteinite is heated in a dry test-tube, water is given off freely and condenses at the cold end of the tube. A series of heating experiments was made at the Geophysical Laboratory to ascertain the amount of water liberated at different temperatures. The powdered material was heated in a platinum crucible in an electric resistance furnace; temperatures were read with the aid of a platinum, and platinum + 10 % rhodium, thermo-element and a millivoltmeter. Two different runs were made on two different samples. The results are listed in table 3.

The agreement between these runs is only fairly good; the escape of the water at the different temperatures is remarkably slow, and very long exposures at a given temperature are required if equilibrium is to be attained; many of the exposures in these runs were not of sufficient duration to insure equilibrium. The results do show, however, that the water given off is all of the same kind and is water of constitution and not water of crystallization as in the zeolites.

The greater part of the water escapes between  $250^{\circ}$  and  $350^{\circ}$  C. The mineral afwillite behaves in the same manner on heating and loses its water gradually, but more rapidly at  $300^{\circ}$  than at any other temperature.

Temperature in degrees C.	Time in hours of exposure at the given temperature.	Cumulative total percentage loss in weight.
First run, Nov. 9	to 12, 1931. Weight of sa	mple 0-4208 gram.
$250^{\circ}$	1.25	0.60
$250 - 255^{\circ}$	16-67	1.90
350	2.17	4.42
350	2.50	9.10
350	17.50	12.50
350	. 4.00	12.50
600	2.00	12.98
600	16.75	12.98
900	3.50	13.17
1000	2.00	13.28
Second run, Nov.	20 to 25, 1931. Weight o	f sample 0-8130 gram.
110°	2.00	0.09
300-310°	19.67	3.49
270-300	23.30	3.63
500	3.00	12.99
500	19.67	12.99
700	29.75	13.05
870-900	16.25	13.52
1000	6.25	14.13

TABLE 3. Loss of water by bultfonteinite at different temperatures.

Blowpipe tests.—Heated in a closed tube, fragments of the mineral lose water which gathers in the restricted neck of the tube; at the same time they become white and porcelain-like. Before the blowpipe the needles glow intensely with the characteristic brilliance of lime-bearing minerals and become white and enamel-like; but they do not melt; even sharp edges show little evidence of rounding.

Specific gravity.—The specific gravity of bultfonteinite was found by immersion in pure benzene ( $C_6H_6$ ), which has no solvent action on it, to be 2.73.

Crystallographical properties.—In the specimens thus far collected, bultfonteinite occurs in the form of small radial spherulites and groups of small radiating acicular crystals measuring from 0.5 to 2 mm. in length. Many of the minute crystals are colourless and water-clear. In masses, especially in the single large radial spherulite, the colour is pale pink. The prismatic crystals are well

		d'=tanp.	0.0831	8	: :		:	:	:	:	:	0.7628	0.6120	0.5477	0.4776	I ·0532	0.9817	1.3057	1.2319	1.2020	1.1625	1.2699	2.2106
	= 0.0828 = 24° 37′	у'.	0-0755	8 :	: :	:	:	ĩ	:	:	:	0.7648	$\overline{0}.6137$	0.0834	0.0677	0.0912	0.0598	0.7805	0.7491	$\overline{0}.5880$	0.6294	0.4280	0.7962
	345 d 753 8 966	$\mathbf{x}'$ (Prisms $\mathbf{x}$ :y).	0.0346	64.858	2.8249	$\overline{2}$ ·1321	1.4439	1.5112	0.7301	0.7469	$\overline{2}.9147$	0.0346	0.0346	0.5435	0.4743	1.0525	0.9833	1.0525	$\overline{0}.9833$	1.0525	$\overline{0}.9833$	0.5435	2.0704
Triclinic.)	x <sub>0</sub> = 0.03 h = 0.03 h = 0.99	η.	4°19′	0 53	19 29	<u>1</u> 7 54 <sup>.</sup>	$\frac{34}{2}$ 42	33 30	$\frac{53}{52}$ 52	53 15	$\overline{69}$ 38	37 17	$\overline{3}$ ] 25	4 11	3 29-	3 35	2 26	28 13	28 04	22 01	24 07	20 33	19 05
inite. (	。]7′ 。59′ 。44′	منه	1° 58′ 0 00	89 07	70 30	72 05	55 18	56 30	36 08	36 45	20 22	1 34	1 41	$\frac{28}{20}$	$\overline{25}$ 16	$\frac{46}{16}$ 16	44 22	$\frac{39}{2}$ 37	38 08.	$\frac{42}{2}$ 09	39 41	26 29	<b>58 15</b>
of bultfonte	а В = 91 90	70.	4° 19′ 00 00	~~ ;	: :	ĩ	:	:	:	:	:	37 24	$\overline{3}1$ 32	4 46	3 52	5 I2·	3 25.	37 58	$\frac{36}{50}$	$\overline{30}$ 27.	32 11	23 10	38 31·
stal angles	- 0-6756 - 1 - 0-6873	ξ0.	1° 59′ 0 00	38	:	:	:	:	:	:	:	1 59	1 59	28 31	$\overline{25}$ 22.	$\frac{46}{28}$	44 31	$\frac{46}{28}$	44 31	46 28	44 3I	28 31 <sup>.</sup>	64 13
LE 4. Cry	 ఉద్ర	ъ.	4° 45′ 00 00	00 . Na	: :	:	:	:	:	:	:	37 20	31 28	28 42	25 32	46 29	44 28	52 $33$	50 56	50 14	49 18	34 35	65 39
TAB	$\lambda = 85^{\circ} 41$ $\mu = 87^{\circ} 57$ $\nu = 89^{\circ} 07$	<i>ф</i>	$24^{\circ} 37'$	00 0 89 07	70 30	107 54	55 18	123 30	36 08	143 15	159 38	2 35	176 46	$81 \ 16$	<u>8</u> 1 53	<u>8</u> 5 03	86 31	$\overline{53}$ 26.	52 42	119 11	122 37	51 47	68 58
	145 869	Miller.	(100)	(000)	(210)	(210)	(010)	(110)	(120)	(120)	(140)	(011)	$(1\overline{1}0)$	(102)	$(\bar{1}02)$	(101)	(101)	(111)	(III)	$(1\overline{1}1)$	$(\overline{\mathbf{III}})$	(112)	(211)
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		No.	-i °	iri	4.	ю.	6.		œ	<u>б</u>	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.

developed in the prism-zone, but the terminal faces are either lacking or so poorly developed that reflections are extremely difficult to obtain on the goniometer. The reflection signals, when obtainable, are not sharp, but are drawn out because of rounding and imperfections in the development of the faces. Examined under a highpower binocular or on the goniometer, the prism-faces are found to be finely striated, after the manner of plagioclase felspars with fine polysynthetic twinning. The result is that single clear reflection signals are uncommon when crystals are measured on the goniometer. Although more than 35 selected small crystals were measured on the goniometer, the angles fluctuated appreciably, and the angles listed in table 4 may be in error  $\pm 10'$ . Many of the crystals measured were 0.3 mm. or less long and 0.1 mm. wide. Small crystals were selected purposely in the hope of reducing the effects of the intricate polysynthetic twinning; but even on such minute crystals, which were water-clear, the prism-faces were striated and the terminal faces were poorly developed. The best development of terminal faces was found on the ends of the radial units of the large pink spherulite. Unlike the small spherulites, no acicular crystals projected beyond the general spherical surface of this spherulite, which consisted essentially of the terminal facets of the radiating crystals. Examined under a high-power binocular, these facets were seen also to be striated; but in many cases more coarsely so than was the case with the small crystals. A number of these facets were broken off from the spherulite and served for both optical and crystallographical measurements.

The crystallographical measurements were all made on a Goldschmidt two-circle goniometer with reducing attachment and a strong concentrated filament light source. From the averages of the weighted measurements thus obtained the crystallographical elements were computed; in addition, all observed position angles were plotted in gnomonic projection and the most probable positions of the several faces were ascertained graphically. On the crystals certain faces are invariably present; others less frequently. In table 5 are listed the faces that were found on each one of the 31 crystals measured on the goniometer. It was difficult in certain cases to decide whether a given face belonged to the crystal in normal position or to one of the intercalated twins.

The angle between the faces (100) and (010) is  $89^{\circ} 07'$ ; this angle is so nearly equal to  $90^{\circ}$  that when twinning occurs with the twinning-

	BULTFONTEINITE, A NE									E	w	MINERAL						FROM SOUTH				A	FI	153								
	(211)	1	I	I	I	I	١	I	I	1	I	I	I	i	I	I	1	1	I	Ι	I	I	j	1	I	I	1	I	Ι	I	×	: 1
	(112)	1	ł	I	I	I	I	I	I	I	I	I	I	I	ſ	ł	I	Ι	I	I	I	I	I	I	×	1	I	I	I	I	1	1
	([[]]	ł	Ι	I	I	I	1	1	1	!	I	I	ł	I	i	I	I	ŀ	. 1	I	I	[	I	:	1	I	ſ	I	×	ł	×	.
	([[]])	I	Ι	1	ł	!	I	ł	1	I	I	I	١	I	ł	1	ł	I	I	ł	I	l	I	I	ł	×	1	×	×	ł	×	1
	(111)	I	I	ſ	I	I	ł	I	١	I	I	Ι	i	1	I	I	ł	i	I	;	I	ſ	I	I	ſ	ł	I	Ι	I	I	×	1
	(111)	I	I	I	1	i	ł	ł	I	I	I	I	ſ	1	I	Ι	i	i	ł	I	I	I	I	I	I	×	t	I	Ι	×	×	×
	$(0\bar{1}1)$	I	;	I	×	1	i	I	i	Ι	Ι	Ι	I	ł	I	ł	i	i	I	I	' 	i	I	:	I	ł	×	I	i	1	I	I
inite.	(011)	I	:	I	Ι	Ι	Ι	I	1	I	I	I	[	1	ł	J	I	Ι	I	I	Ι	i	I	I	I	×	×	×	×	×	×	I
ltfonte	$(\bar{1}02)$	I	I	1	ł	I	I	I	I	I	ł	1	I	1	I	ſ	ł	}	I	х	Ι	I	×	I	!	1	I	I	I	1	I	I
s of bu	(102)	ł	I	I	I	I	I	I	I	ł	×	I	I	×	I	I	I	I	I	×	I	I	×	1	I	I	ſ	1	I	l	×	1
crystal	$(\bar{1}01)$	1	1	I	1	1	1	1	I	I	×	l	I	I	I	Ι	I	T	I	I	ţ	I	I	I	I	I	I	;	×	ł	I	I
es on	(101)	ł	I	Ι	I	I	I	I	I	١	I	I	ł	I	I	1	I	I	I	1	I	;	I	١	I	×	×	I	ł	×	×	×
ved fac	$(2\overline{1}0)$	1	I	I	I	I	I	I	×	×	I	I	×	I	I	×	I	I	I	I	I	I	I	I	I	I	I	l	I	I	ł	I
Obser	(210)	I	I	ł	I	×	I	I	I	I	[	I	l	ſ	١	I	I	I	I	ł	I	×	I	I	×	1	I	1	i	1	I	I
LE 5.	$(1\bar{4}0)$	ł	!	1	I	×	I	I	I	×	i	ł	I	I	I	×	I	1	Ι	I	I	I	I	I	I	I	×1	I	I	I	I	1
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	$(1\overline{1}0)$	1	×	×	×	×	×	×	I	I	×	×	×	×	Ι	×	I	I	×	l	×	×	×	×	×	ł	I	×	×	I	I	I
	(110)	×	×	×	×	l	×	×	×	×	×	x	×	×	1	I	ł	I	×	I	I	×	×	×	×	I	×	I	Ι	l	l	×
	(100)	I	I	ł	×	1	I	I	l	I	l	1	I	×	·I	1	Ι	Ļ	I	1	×	×	×	×	×	×	×	×	×	×	×	×
	(010)	×	×	×	×	×	x	×	I	x	×	×	×	×	×	×	×	×	×	×	×	×	×	×	x	×	×	×	×	×	×	×
	(100)	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×	×
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axis normal either to (100) or to (010) the face in twinning position almost coincides in position with the second pinacoid, with the result that the faces are finely striated and do not yield good reflection signals even on the most minute crystals. Twinning actually does occur on both faces and the result is commonly an interpenetrating polysynthetically twinned group in which lamellae of four different crystallographic orientations can be distinguished optically when examined in convergent polarized light or on the Fedorov universal stage.



FIG. 1. Observed crystal-forms of bultfonteinite in gnomonic projection. FIG. 2. Gnomonic projection of the crystal-forms of bultfonteinite in the normal position and in the three twinning positions.

Cleavages parallel to (100) and (010) are fairly good. It is difficult to determine the degree of perfection of the cleavage because of the minute size of the prisms, the polysynthetic twinning, and the nearly parallel growth of the crystals. The fracture is conchoidal. Lustre vitreous. Hardness  $4\frac{1}{2}$ .

The positions of the several crystal-forms are shown assembled in gnomonic projection in fig. 1. As a result of the interpenetrating polysynthetic twinning and the near approach of the angles, (100): (010), (001): (100), and (001): (010), to a right angle there appear clustered around each face in the projection the corresponding twinning positions of the face, as shown in fig. 2; thus for the face g(101), the larger clear circle, labelled 1, marks the position of the

face in undisturbed position; the circle 2 with the horizontal diameter is the face in twinning position, the twinning-plane being (010). The circles 3 and 4 show the positions of the ( $\overline{101}$ ) faces brought into twinning positions by twinning on the front pinacoid (100). On any single crystal not all the faces shown in figs. 1 and 2 were observed; but the optical tests show the four interpenetrating



F1G. 3.

FIG. 4.

FIG. 3. Crystal of bultfonteinite as it would appear if twinning were not present and if the several faces were well developed.

FIG. 4. Crystal of bultfonteinite showing faces on crystal in normal position and other faces in twinning positions to them.

polysynthetically twinned groups so well that on a single crystal the four positions of the optical ellipsoid could be satisfactorily ascertained with the aid of a Fedorov stage. By themselves and before the optical data had been obtained the effort to disentangle the crystal-angle values of measurement was unsuccessful. Had the crystal been opaque the determination of the crystal system and especially of the character of the twinning would not have been possible.

The general development of the crystals is shown in figs. 3 and 4, in which the upper portion of the acicular prisms only is given. Fig. 3 illustrates a crystal as it would appear were it not twinned; fig. 4 shows the positions of the faces in a polysynthetically twinned crystal. The terminations represented in the figures are too sharply

drawn to be a correct illustration of the actual end faces of the greater number of crystals. However, the facets of the crystals exposed on the surface of the large pink spherulite are in part clean cut and appear as indicated in figs. 3 and 4. The terminal faces on the small acicular crystals are so poorly developed that it is only with great difficulty that reflection signals can be obtained from them on the goniometer.

This imperfect development of the end faces is probably due to the fine polysynthetic twinning and consequent near approach of the several twinned faces to a common position, so that no one of the faces could develop properly and only a general roughness resulted. In the prism-zone the conditions are different; only two sets of directions, instead of four, are brought near together by the twinning and give rise, as in the plagioclase felspars, to twinning-lamellae and fine striations, but not to the rough, imperfect development noted on the end faces. When the crystallographical measurements were first undertaken, the rough end terminations on the minute crystals were considered to be the result of later attack and etching by circulating solutions from which the sulphate crystals were deposited. This may also have been a factor, but the fact that the prism-faces showed no evidence of attack and are sharply defined makes it probable that subsequent etching was not the only factor. Against this view may, however, be cited the much better terminal development in the larger crystals of the pink spherulite, which may have been formed under conditions somewhat different from those of the small colourless spherulites.

Optical determinations.—It might be supposed that optical measurements on water-clear crystals, even though they measure only a few tenths of a millimetre in thickness and a millimetre in length, would be a simple task. In the present case, however, the intricate polysynthetic twinning on two planes, approximately at right angles one to the other and so fine that satisfactory interference-figures in convergent polarized light are extremely difficult to obtain, renders the task unusually trying and time-consuming. Had it not been for the Fedorov stage methods, it is doubtful that satisfactory results could have been obtained.

Under the microscope the mineral exhibits medium refringence, medium birefringence, and fine polysynthetic twinning-lamellae. The acicular crystals exhibit, parallel with the prism-axis, fine twinning-lamellae with high extinction-angles. The extinction-angle on (010) is  $c: \gamma' = 27^{\circ}$  to  $29^{\circ}$ ; on (100)  $c: \gamma' = 46^{\circ}$  to  $48^{\circ}$ . Flakes normal to the prism-axis show two sets of interpenetrating twinninglamellae crossing nearly at right angles as in microcline. In convergent polarized light the interference-figures that can be obtained are, in general, unsatisfactory. On sections nearly normal to the prism-axis an optic axis may be seen in the field; the axial bar is slightly curved and points toward  $\gamma$  as acute bisectrix. The optic axial angle, ascertained on sections of this kind by measuring the angle between the bisectrix and the optic axis, was found to be approximately  $2E = 130^{\circ}$ . Dispersion of the optic axes is barely perceptible with  $2V_r > 2V_r$  apparently. On a section nearly normal to the optic axes, the plane of the optic axes includes an angle of approximately  $47^{\circ}$  with the traces of the twinning-lamellae. The optical sign is positive.

The refractive indices were measured in sodium-light both by the immersion method and on an Abbe crystal refractometer on polished plates cut from the large spherulite. On these plates the maximum and minimum refractive indices were found to be, for sodium-light,  $a = 1.587 \pm 0.002$ ,  $\gamma = 1.597 \pm 0.002$ . Many attempts were made to measure  $\beta$  by the immersion method; but they were not successful because of the intricate twinning phenomena. The refractive index,  $\beta$ , was found, on computation from the optic axial angle and the refractive indices, a and  $\gamma$ , to be  $\beta = 1.590$ . The principal birefringences from these values are:  $\gamma - a = 0.010$ ,  $\gamma - \beta = 0.007$ ,  $\beta - a = 0.003$ .

Measurements with the aid of the Fedorov stage were made on a number of sections; at first on thin sections cut from the large spherulite approximately normal to the radiating group. Experience soon proved that, although some measurements could be obtained on these sections, the lack of satisfactory crystal outlines and of the possibility of determining the crystal orientation on a given section would prevent this method from obtaining the desired data. The effort was then made to mount small definitely oriented crystals and to grind and polish thin plates normal to the prism-axis. This method failed because of the minute size of the crystals. Recourse was then had to a special instrument devised for the purpose. This apparatus is shown in fig. 5 (actual size) in which A is the side view in section, B the front view, and C the plan or top view. The device is made from a block M of brass, on top of the upright end of which a straight bronze spring a is clamped by a screwed brass plate k. At the inner end of this spring a brass angle piece is attached by

a screwed brass plate d. To the upright side of the angle piece a section of a razor-blade c is clamped by a second screwed brass plate. When the spring is raised and then released, the razor-blade strikes a sharp blow against the smooth upper surface of the brass support. The apparatus is enclosed by plates of microscope object glass ( $25 \times 46$  mm.) cemented to the brass support M; in addition, the top is



FIG. 5. Apparatus for splitting off thin flakes of a crystal normal to its prism-axis. A is the side view, B front view, and C plan.

covered by a similar glass plate and held in position by the observer during the operation. The plates prevent the escape and loss of the minute crystal flakes chipped off by the razor-blade.

The small crystal from which sections are to be split off normal to the axis is now placed with its prism-axis normal to the razor-blade and underneath its edge. All these operations are done under a binocular magnifying 20 diameters. The top glass plate is now placed in position. The razor-blade is raised slightly with the aid of a small screw-driver or rod placed under the angle plate at d, and supported, as a lever, at k. The screw-driver is withdrawn slightly and the spring released. The razor-blade descends rapidly, like a guillotine, and decapitates or chips off a thin flake normal to the prism-axis of the crystal. After some practice it was found that

several sections, retaining the complete outline of the prism-zone, could be obtained by this method from a single crystal.

A suitable section was then mounted on the Fedorov stage and the positions of its principal optical directions with reference to the crystallographical directions were measured. Twenty-three crystal sections were thus measured. Many other sections were mounted, but were discarded for one reason or another. On several of the



FIG. 6. The principal optical directions and crystal-faces of bultfonteinite in stereographic projection.

FIG. 7. Stereographic projection of the principal optical directions in a bultfonteinite crystal in normal position and in the three twinning positions.

sections the optical orientation of all four twinning-lamellae could be measured. The results of the measurements are listed in table 6. The positions of the principal optical directions thus measured with reference to the crystallographical directions are shown in stereographic projection in figs. 6 and 7. In fig. 6 the directions are given for the single crystal; in fig. 7 the positions of the principal optical directions in the four different twinning-lamellae are plotted.

TABLE 6. Angular positions of principal optical directions in bultfonteinite.

			¢	5.		ρ.	ł	<u></u> .	η	0.	į		η	
a			$\overline{2}4^{\circ}$	00′	$55^{\circ}$	00′	- <u>3</u> 0°	00′	$52^{\circ}$	30′	ī9°	00′	<b>48°</b>	30′
β			$\overline{1}32$	30	66	00	$\overline{5}9$	00	$\overline{5}6$	· 30	$\overline{4}2$	30	38	00
γ		•••	111	00	44	30	42	30	$\overline{1}9$	30	41	00	15	00
A1			57	30	<b>24</b>	30	<b>21</b>	00	- 14	00	20	30	13	00
A <sub>2</sub>	•	· · ·	131	00	75	<b>3</b> 0 ·	71	00	68	30	47	00	$\overline{3}9$	30

The results of the measurements of the optic axial angle on different sections by the Fedorov stage method in white light are listed in table 7. In each case only the angle between an optic axis and  $\gamma$  or

No.	v.	No.	v.	No.	v.	No.	v.
2	34.0°	9	37·5°	16	40·0°	20	35∙0°
3	35.0	10	<b>33</b> ·0	17	37.5	21	<b>3</b> 9•0
4	33.0	11	34.0	18	<b>40</b> ·0	<b>22</b>	<b>31</b> .0
5	38.0	12	<b>34</b> ·0	19	31.0	,,	37.5
6	34.0	13	38.0	,,	35.0	23	38.0
7	34.5	14	32.0	,,	34.0		
8	35.5	16	37.5		28-0		

TABLE 7. Measurement of half the optic axial angle of bultfonteinite.

a could be obtained. At steeply inclined positions of the sections the twinning-lamellae overlapped to such a degree that measurements were not possible. The weighted average of these values is  $V=35^{\circ}$ ,  $2V = 70^{\circ}$ , and  $2E = 132^{\circ}$ .

Comparison with other fluorine-bearing hydrous calcium silicates.— Two other minerals, custerite<sup>1</sup> and zeophyllite,<sup>2</sup> have chemical compositions that bear some resemblance to that of bultfonteinite. The compositions and other data on these minerals and also on hillebrandite<sup>3</sup> are assembled in table 8.

The formula for custerite is commonly written  $Ca_2HFSiO_4$ ; it may, however, be written  $CaO.Ca(OH,F)_2.SiO_2$ . In this form its resemblance to the formulae for hillebrandite,  $CaO.Ca(OH)_2.SiO_2$ , and bultfonteinite,  $2Ca(OH,F)_2.SiO_2$ , is apparent. In custerite part of the hydroxyl, OH, of hillebrandite is replaced by fluorine. In custerite and hillebrandite half of the calcium oxide is still intact, the oxygen of the second half being replaced by OH and F; whereas in bultfonteinite none of the CaO remains as such, the calcium being entirely taken up by OH and F.

These three minerals show with phenolphthalein a strong alkaline reaction, indicating the presence, in aqueous solution, of calcium hydroxide. The minerals are easily soluble in hydrochloric acid. Afwillite, whose formula may be written  $3Ca(OH)_2.2SiO_2$ , exhibits similar chemical behaviour.

The mineral zeophyllite, on the other hand, bears little resemblance

<sup>1</sup> J. B. Umpleby, W. T. Schaller, and E. S. Larsen, Amer. Journ. Sci., 1913, ser. 4, vol. 36, pp. 385-394.

<sup>2</sup> A. Pelikan, Sitzungsber. Akad. Wiss. Wien, Abt. 1, 1902, vol. 111, p. 334; also F. Cornu, Min. Petr. Mitt. (Tschermak), 1905, vol. 24, p. 127.

<sup>3</sup> F. E. Wright, Amer. Journ. Sci., 1908, ser. 4, vol. 26, pp. 551-553.

			Βt	Γ.	ГF	01	JT.	EI	NI	TE	3,	A	N	EW	М	INE	RA	L	FF	lo	М	so	UT	н	A	FR	(CA	ł		161
	phyllite.	Molec. ratios.	0.647	0.017	0.001	I	0.004	167.0	0.006	0.003	0.499	0.433					$I_4F_2Si_3O_{11}$	2.76	3	Easy	abobedral-	tohedral		1	1	1.55		$-27^{\circ}$	egative	c = c
	Zec	%	38.84	1.73	0.10	ļ	0.17	44.32	0.38	0.24	8.98	8.23		102.99	3.47	99.52	$Ca_4F$				Rhon	tetar	_					•	ă	
ium silicates.	brandite.	Molec. ratios.	0.540	0.002	l	0.001	0.001	1.030	0.001	0.001	0.502	I	ļ				$(OH)_2.SiO_2$	2.69	5-6	fficult	orhombic	10) <del>؟</del>		$\pm 0.005$	1	$\pm 0.003$		- 802	gative	
pdrous calc	Hille	%	32.59	0.23		0.15	0.04	57.76	0.03	0.05	9.36	none	0.03	100.24			CaO.Ca			Ā	Orthe		<u></u>	I-605		1.612	0 B	99	ne	v
nite with other hy	sterite.	Molec. ratios.	0.536			0.004	0.030	0.984	.1	]	0.294	0.427					$OH,F)_2.SiO_2$	2.91	ũ	fficult	noclinic	(110)	(100)	$3 \pm 0.005$	$0\pm0.005$	$3\pm0.005$	60°	05	sitive	$\iota: \gamma = 6.5^{\circ}$
bultfontei	Cui	%	32.17	 ~	 ~	1.00	1.19	55-11	i		5.30	8.12		102.89	3.42	99-47	CaO.Ca(			ñ	Moi	100)		1.586	1.589	I-598	,	T	od	$b = \alpha, \alpha$
Comparison of	onteinite.	Molec. ratios.	0.441	0.006	000-0	ł	l	296.0	.	ļ	0.741	0.464	1				$H,F)_2.SiO_2$	.73	$4\frac{1}{2}$	Heult	clinic	(100) 1 (100)	), (100)	$\pm 0.002$	$\pm 0.002$	$\pm 0.002$	70	32°	sitive	veak iclinic
TABLE 8.	Bultfe	%	26.50	010	71.0		1	54.20	1	I	13.36	8.81	l	103-59	3.71	99.88	2Ca(OI	61		Dit	Tri	010)	010)	1.587	1.590	1.597	. •	-	od ,	T.
			:		:	:	:	:	:	:	i	:	:		:		÷	:	:	:	÷		:		:	÷	÷	÷		axes
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			SiO,	$Al_{s}O_{s}$	$Fe_0$	$Fe_{3}O_{4}$	MgO	CaO	$Na_{2}O$	$K_{s}\bar{O}$	$H_{2}^{-}O$	Ĩ.	Ti02,		Less 0		Formu	Specifi	Hardn	Fusibi	Cryst.	Cleava	Twin-1	ſ	The Irac	ADIMIT	Optic	ang	Optics	Optice

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either in chemical behaviour or in its optical and other properties with custerite and bultfonteinite. In composition it appears to be a solution of  $4CaO.3SiO_2$  and  $4Ca(OH,F)_23SiO_2$  in the proportion of 1 to 7 approximately.

The refractive indices and the birefringences of bultfonteinite and custerite are identical, within the limits of error; both minerals are



FIG. 8. X-ray diffraction pattern of a prismatic fragment of bultfonteinite.

biaxial, optically positive with approximately equal optic axial angles. However, the extinction-angles and other relations between crystallographical and optical properties are so different that the two minerals can be readily distinguished under the microscope. Hillebrandite is orthorhombic and resembles neither custerite nor bultfonteinite in its optical and crystallographical properties.

X-ray photograph of bultfonteinite.—The photograph, fig. 8, was taken by, and through the courtesy of, Mr. H. S. Roberts of the Geophysical Laboratory. The crystal diffraction pattern of fig. 8 was obtained by rotating a prismatic sliver from the pink spherulite in the axis of the X-ray apparatus. The effect of the twinning is clearly shown in this photograph; but the relations are so complex that no effort was made to analyse the photograph critically.