

*New data for dumortierite.*

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*Summary.* New chemical, optical, and X-ray data have been obtained for dumortierite. The unit cell, space group  $Pcmm$ , contains  $4[(Al,Fe)_2BSi_3O_{18}]$ . Brown gem quality material from Ceylon has  $\alpha$  1.6860, black,  $\beta$  [001],  $\beta$  1.722, deep red-brown, and  $\gamma$  1.7229, brown, with  $2V_\alpha$  13°,  $r > v$ . X-ray powder data are given.

**A** NATIVE-CUT, dark red-brown, transparent gemstone weighing 0.369 g. bought in Ceylon by Kenneth Parkinson in 1950 was submitted to us in 1951 for determination after measurements of its physical properties (see below) had failed to provide an identification. An X-ray powder photograph of material scraped with a diamond from the girdle of the stone proved it to be dumortierite; the photograph was practically identical with one of a purple dumortierite from San Diego Co., California (B.M. 1905,6), and in reasonable agreement with the data of N. L. Bowen and R. W. G. Wyckoff (1926). As the stone was a single crystal it was ideally suitable material for the determination of the unit-cell dimensions of the mineral, which had not previously been obtained, probably because it is rarely found in this condition: most apparently single crystals consist of parallel aggregates of intimately twinned needles. Mr. B. W. Anderson, who had purchased the stone and submitted it to us for identification, readily agreed to have it recut so as to provide material for the X-ray study and for chemical analysis.

Rotation and powder X-ray photographs gave the cell-dimensions:  $a$   $11.79 \pm 0.01$ ,  $b$   $20.209 \pm 0.002$ ,  $c$   $4.7015 \pm 0.001$  Å., and axial ratios  $a:b:c = 0.5834:1:0.2326$ . Systematic diffraction absences indicate the space-group  $Pcmm$  ( $D_{2h}^{16}$ ), assuming holohedral symmetry; they are:  $hk0$  only observed for  $(h+k)$  even,  $0kl$  only for  $l$  even.

Dumortierite crystals are usually very poorly developed and multiply twinned on  $m$  {110}, giving aragonite-like sixlings (E. Bertrand, 1880); the only goniometric data in the literature are: J. S. Diller (1881) observed the prism  $m$  {110} and cleavage plane  $a$  {100}, with  $am$  28° (30° 16' calc. from the X-ray data). G. Linck (1899) observed a prism of

69° 6' angle, probably {250} (calc. (250):(250) 68° 52'). And W. T. Schaller (1905) studied crystals from Clip, Arizona, and from Harlem, New York, which gave rather poor reflections; he deduced axial ratios  $a:b:c = 0.8897:1:0.6871$ , and indexed his observed forms  $a$  {100},  $b$  {010},  $l$  {120},  $g$  {320}, more rarely  $m$  {110} and  $n$  {210}, and very rarely (once each)  $d$  {102} and  $v$  {203}; referred to the X-ray unit cell Schaller's results give remarkably good agreement considering the nature of his material: transformation, Schaller to X-ray, [200/030/001],  $a:b:c = 0.5931:1:0.2290$ ,  $a$  {100},  $b$  {010},  $l$  {310},  $g$  {110},  $m$  {230},  $n$  {430},  $d$  {101},  $v$  {403}.

Few chemical analyses of dumortierite have been made, and several of these are imperfect or were made on material of doubtful purity. Spectrographic examination of our material showed that apart from the principal elements Si, Al, Fe, and B there were only traces of Ti and Sn. Similar results, except that the trace elements detected were Mn, Ti, Mg, and Cu, were also obtained for three other specimens of dumortierite: B.M. 67299 from Clip, Yuma Co., Arizona; B.M. 81006 from California;<sup>1</sup> B.M. 1905,6 from San Diego Co., California; and B.M. 1925,612 from Ashby, Addington Co., Ontario. The fragments of gem material available (B.M. 1953,76) weighed 34 mg.; analysis, on 9 mg., gave the data included in table I (the low total is due to a slight leak in the crucible used for the sodium carbonate fusion, and should not affect the ratios of the oxides). The state of oxidation of the iron was not determined because of the small amount of material available.

With the observed cell-dimensions and density, and neglecting the water as an impurity, probably adsorbed on the powder prepared for analysis, the empirical unit cell contents included in table I are calculated; they show a reasonably close approximation to  $4[(Al,Fe)_7BSi_3O_{18}]$ , which with Al:Fe = 20:1 and the observed cell-dimensions would require the percentage composition and density given under 'calc.' in table I.

Following W. E. Ford (1902) we have rejected those analyses in the literature that show no boron<sup>2</sup> or that show appreciable alkalis (A. Damour, 1881; R. B. Riggs, 1887; P. Jannasch in J. Romberg, 1893; W. Schimpff in G. Linck, 1899; H. A. Weber, 1900). There remain

<sup>1</sup> Purchased in 1896, and therefore probably from Dehesa, San Diego Co.

<sup>2</sup> These include the only analysis yet made of material from the original locality, Beaunan, vallée de l'Iseron, Rhône, France; if the boron is assumed to be mainly included with the  $Al_2O_3$  (cf. Min. Mag., 1941, vol. 26, p. 128), this analysis falls in line with the rest.

TABLE I. Chemical composition, optical properties, and empirical unit-cell contents of brown gem dumortierite, B.M. 1953,76, from Ceylon; together with the calculated composition and density for the idealized formula  $4[(\text{Al},\text{Fe})_7\text{BSi}_3\text{O}_{18}]$  with  $\text{Al}:\text{Fe} = 20:1$ . Optical data, density, and hardness by B. W. Anderson.

	Obs.	Calc.			
$\text{SiO}_2$	32.7	31.00	Si	12.9	$\alpha$ 1.6860, black, $\perp$ [001]
$\text{Al}_2\text{O}_3$	55.5	58.44	Al	25.7	$\beta$ 1.722, deep red-brown
$\text{Fe}_2\text{O}_3$	4.4	4.58	Fe	1.3	$\gamma$ 1.7229, brown
$\text{B}_2\text{O}_3$	4.9	5.98	B	3.3	$2V_\alpha$ $13^\circ$ , $r > v$
$\text{H}_2\text{O}$	0.4	--	O	71.2	
Total	97.9	100.00	(Si + Al + Fe + B)	43.2	Twinned, composition plane $\perp$ [001], optic axial planes of twin-members are at $58^\circ$ obs. ( $60^\circ$ $32'$ calc. from X-ray cell dimensions). Hardness $8\frac{1}{2}$ .
$D_{40}^{20^\circ}$	3.41	3.450			
	$\pm 0.02$				

eleven analyses, which have been recalculated to a basis of 72 oxygen atoms (excluding  $\text{H}_2\text{O}$ ) and are compared with our new analysis in table II; it will be seen that they agree well with the formula  $4[(\text{Al},\text{Fe})_7\text{BSi}_3\text{O}_{18}]$ . Unfortunately few of the analyses are directly linked with full optical data. Water has often been regarded as an essential constituent of dumortierite, but the 0.4 % found in the gem material would only correspond to 1.0 (OH) per unit cell, and the minimum number of equivalent positions in space-group *Pcmn* is 4; we conclude that the appreciable amounts of water shown in several analyses are either adsorbed on the very finely fibrous material or due to incipient alteration, though the possibility of isomorphous replacement, perhaps of the type  $R^+\text{OH} \leftrightarrow \text{AlO}$ , cannot be excluded.

W. T. Schaller (1905) assumed that the titanium of anal. 5 was present as  $\text{Ti}_2\text{O}_3$  and the iron as  $\text{Fe}_2\text{O}_3$ , both replacing  $\text{Al}_2\text{O}_3$ , and this assumption was followed by T. L. Walker in presenting anal. 8 and by S. K. Chatterjee in anal. 11; the mineral is practically insoluble in acids, including hydrofluoric, and it is clear that there was no experimental evidence for the assumption. In anal. 10 by F. Raoult, the titanium is again reported as  $\text{Ti}_2\text{O}_3$ ; neither Raoult nor Losert (anal. 9) states how the state of oxidation of the mineral was determined, and without knowing the method used it is impossible to assess the probable accuracy of this difficult determination. Fortunately the amounts of Fe and Ti are small, so that the uncertainty as to their state of oxidation does not appreciably affect the atomic ratios calculated on a basis of 72 oxygen atoms.

The only refractive index data for analysed material are for anals. 8, 9, 11, and 12, and are not adequate to draw any definite conclusions about

TABLE II. Chemical data for dumortierite recalculated to a basis of 72 oxygen atoms. Analyses showing no boron and analyses showing appreciable alkalis have been omitted. Total iron as Fe<sup>III</sup>, except in anal. 9 and 10; Ti as Ti<sup>IV</sup>.

	1.	2.	3.	4.	5.	6.	7.	7a.	8.	9.	10.	11.	12.	13.
Si	12.37	11.00	11.56	11.83	11.13	12.04	11.28	11.22	11.86	12.89	11.84	11.50	13.0	12
Al	29.44	29.86	29.00	28.17	28.94	27.83	27.86	28.43	27.90	25.77	28.17	28.87	26.1	28
Fe <sup>III</sup>	—	—	0.07	0.11	0.07	0.03	0.74	0.75	0.32	0.48	0.21	0.07	1.3	—
B	1.77	3.36	3.51	3.95	3.59	4.08	3.78	3.86	3.61	3.81	3.37	3.66	3.3	4
R	0.57	0.07	—	—	0.42	—	0.57	0.57	0.51	1.10	0.70	0.06	—	—
Σ*	31.78	33.29	32.58	32.23	33.02	31.94	32.95	33.04	32.30	31.16	32.45	32.66	30.7	32
H <sub>2</sub> O, %	1.34	1.72	1.41	2.14	1.52	2.09	2.12	2.12	1.32	1.27	1.29	1.00	0.4	0
Sp. gr.	—	—	3.319	3.226— 3.43	3.306	3.211— 3.302	—	—	3.309	—	3.28	3.27	3.41	3.390†

1, 2. Clip, Yuma Co., Arizona. J. E. Whitfield anal. in J. S. Diller, 1889;  $R = 0.30 \text{ Mg} + 0.19 \text{ Na} + 0.08 \text{ K}$  in anal. 1, 0.07 P in anal. 2.

3. Clip, Yuma Co., Arizona. W. E. Ford, 1902.

4. San Diego Co., California. W. E. Ford, 1902.

5. Dehesa, San Diego Co., California. W. T. Schaller, 1905;  $R = 0.42 \text{ Ti}$ ;  $2E = 33^\circ \text{ Li}$ ,  $37^\circ \text{ Na}$ ,  $42^\circ \text{ Cu}$ .

6. Harlem, New York City. W. E. Ford, 1902.

7. Washougal River, Skamania Co., Washington. W. T. Schaller, 1905; known to contain some sphene and some andalusite;  $R = 0.28 \text{ Ti} + 0.29 \text{ Ca}$ .

7a. Anal. 7 recalculated after deducting Ti and Ca as sphene ( $2\frac{1}{2}\%$ ).

8. Ashby, Addington Co., Ontario. E. W. Todd anal. in T. L. Walker, 1922;  $R = 0.02 \text{ Ti} + 0.04 \text{ Mn} + 0.45 \text{ Mg}$ ;  $\alpha$  1.659, Berlin-blue, = [001],  $\beta$  1.684 and  $\gamma$  1.686 colourless;  $2V_c$   $52^\circ$ .

9. Kuklík hill, Kutná Hora, Bohemia. J. Losert, 1956;  $R = 0.03 \text{ Ti} + 0.25 \text{ Fe}'' + 0.40 \text{ Mg} + 0.01 \text{ Mn} + 0.41 \text{ Ca}$ ;  $\alpha$  1.660 greenish-yellow,  $\beta$  1.667 and  $\gamma$  1.683 colourless.

10. Soavina, Ankofa, Madagascar. F. Raoult anal. in A. Lacroix, 1922;  $R = 0.19 \text{ Ti} + 0.10 \text{ Fe}'' + 0.10 \text{ Mg} + 0.14 \text{ Ca} + 0.14 \text{ Na} + 0.02 \text{ K}$ ;  $\alpha$  deep cobalt blue.

11. Mogra, Bhandara district, Central Provinces, India. S. K. Chatterjee, 1930;  $R = 0.06 \text{ Ti}$ ;  $\alpha$  1.678 deep lilac,  $\beta$  1.685, and  $\gamma$  1.688 colourless;  $H$ , 7.

12. Ceylon (B.M. 1953, 76). This paper; for optical data see table I.

13.  $4[(\text{Al}, \text{Fe})_7\text{BSi}_3\text{O}_{18}]$ .

\* Sum of all atoms except Si and O.

† Calc. for  $\text{Fe}'' = 0$ .

the effect of composition on refractive index: the highest refractive indices ever recorded for dumortierite are for the iron-rich Ceylon material (anal. 12), but it is difficult to see what the considerable difference between the refractive indices of the Kutná Hora (anal. 9) and Mogra (anal. 11) materials can be attributed to.

TABLE III. X-ray powder data for brown gem-quality dumortierite from Ceylon (B.M. 1953,76). Cu-K $\alpha$  radiation, camera diameter 6 cm.; the three strongest lines are numbered.

<i>d</i> , Å.	<i>l</i> .	<i>d</i> , Å.	<i>l</i> .	<i>d</i> , Å.	<i>l</i> .	<i>d</i> , Å.	<i>l</i> .
5.85	s(1)	2.66	w	1.93	vvw(b)	1.476	vvw
5.06	m(2)	2.54	vw	1.871	vvw	1.463	vvw
4.26	mw	2.48	vvw	1.831	vw	1.449	vvw
3.84	mw	2.41	vvw	1.781	vw	1.334	mw
3.43	m	2.34	vw	1.729	vvw	1.297	w
3.33	vvw	2.24	vvw	1.656	vw(b)	1.267	vvw
3.22	m	2.19	vw	1.617	vw	1.247	vvw
3.07	w	2.09	ms(3)	1.544	vw(b)		
2.91	m(b)	2.01	vvw	1.506	vvw		

Among the most notable features of dumortierite are its deep colour, intense pleochroism, and wide range of colour. For vibrations parallel to  $\beta$  and  $\gamma$  it is commonly colourless or very pale yellow, but yellow (E. D. Wilson, 1929), orange-yellow (R. von Auel, 1931), red-brown (this paper), and pale tints similar to  $\alpha$  in hue have also been recorded, always with absorption  $\beta > \gamma$ . For vibrations parallel to  $\alpha$  the commonest colour is deep cobalt-blue or deep Berlin-blue, but many other colours have been reported.<sup>1</sup> A. Damour (1881) suggested that the deep blue colour was due to a trace of Ti<sub>2</sub>O<sub>3</sub>, W. T. Schaller (1905) assigned the deep purple-red colour of San Diego Co. material to 1½% of Ti<sub>2</sub>O<sub>3</sub>, and A. B. Peck (1926) assigned the blue colours to Ti<sub>2</sub>O<sub>3</sub> and the red to TiO<sub>2</sub>, but the evidence to support these opinions is quite inadequate

<sup>1</sup> Purple-brown (A. Brammell, 1928; A. W. Groves, 1928); various hues of green (G. Linck, 1899; E. Rimann, 1914; T. L. Walker, 1922; J. Losert, 1956); various hues of crimson or violet (J. Romberg, 1893; H. Rösler, 1902; W. T. Schaller, 1905; E. Rimann, 1914; F. Němec, 1935); yellow (J. Losert, 1956); brownish-black (this paper). Also much lighter tints, from salmon-pink (A. Lacroix, 1893), lilac (S. K. Chatterjee, 1919, 1930), pink (F. MacMurphy, 1930), or pale blue-violet (E. S. Larsen, 1921) to pale yellow (J. Losert, 1956). The optical orientation is uniformly reported as  $\alpha = [001]$ ,  $\beta = [010]$ ,  $\gamma = [100]$ , except that S. Kilpady and A. S. Dave (1954) reported  $\beta = [100]$ ,  $\gamma = [010]$  for material from Garrah, India; but as they also report twinning on  $m \{110\}$  and cleavage  $a \{100\}$ , with  $am = 61^\circ$ , whereas all other records show twinning on  $m \{110\}$  and cleavage  $a \{100\}$  with  $am$  about  $30^\circ$ , it seems more likely that their material had the normal optical orientation and twinning, but a cleavage or parting parallel to  $b \{010\}$  instead of the usual cleavage  $a \{100\}$ .

(cf. A. Lacroix, 1922, p. 402). N. L. Bowen and R. W. G. Wyckoff (1926) observed that blue material from Clip, Arizona, lost its colour at 800° C., but showed no appreciable change in the X-ray powder pattern. J. Losert (1956) observed that green Bohemian material when heated in air goes yellow, and suggested that this is due to oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>, but does not appear to have brought analytical evidence to support this conclusion. The observed percentages of Fe and Ti in the deep-blue material from Clip and Harlem are very small, and it is doubtful if the origins of the colour of dumortierite can be satisfactorily explained in terms of colouring oxides; unusually stable colour-centres, perhaps connected with minor isomorphous replacements, seem a more probable cause, but the mineral is usually finely fibrous and intergrown with other minerals, making an identification of minor replacements very difficult.

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