X-ray investigation of hillebrandite.

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HILLEBRANDITE was first characterized by Wright[1] as a white, fibrous mineral with the composition $2CaO.SiO_2.H_2O$, optical properties α_{Na} $1 \cdot 605 \pm 0 \cdot 005$, γ_{Na} $1 \cdot 612 \pm 0 \cdot 003$, moderately weak birefringence, parallel extinction, optic axial angle 2E between 60 and 80°, and density $2 \cdot 692$. X-ray powder data were first published by Vigfusson,[2] but these have not been substantiated by later investigators (Clark and Bunn,[3] McMurdie and Flint,[4] and Heller and Taylor[5]). Synthetic dicalcium silicate β-hydrate has been found to resemble hillebrandite closely.

The present sample of hillebrandite from Velardeña, Durango, Mexico, was kindly supplied by the Building Research Station. It consisted of short, white fibres with optical properties compatible with those described by Wright. The hillebrandite fibres were associated with hibschite, identified optically (n about $1 \cdot 67$), and with wollastonite, identified optically and by X-rays.

The results of a chemical analysis of the present sample are shown in table I. If it is assumed that all the CO_2 is present as calcite, that the sample contains hibschite, wollastonite, and gypsum, and that Al replaces Si, and all other cations replace Ca, the resulting composition of hillebrandite approximates to $Ca_2SiO_4.H_2O$ (column 2b).

The density of the sample was found to be $2 \cdot 69$. The density of the lighter fraction of a sample separated once with liquid of specific gravity about $2 \cdot 70$ and boiled to eliminate occluded air was $2 \cdot 67$. The corrected density, allowing for the presence of calcite, hibschite, and wollastonite, is $2 \cdot 66$.

[1] F. E. Wright, Amer. Journ. Sci., 1908, ser. 4, vol. 26, p. 551.

[2] V. A. Vigfusson, Amer. Journ. Sci., 1931, ser. 5, vol. 21, p. 74. [M.A. 5–45.]

[3] L. M. Clark and C. W. Bunn, Journ. Soc. Chem. Industry, 1940, vol. 59, p. 155. [M.A. 8–116.]

[4] H. F. McMurdie and E. P. Flint, Journ. Res. Nat. Bur. Standards, U.S.A., 1943, vol. 31, p. 227. [M.A. 9–45.]

[5] L. Heller and H. F. W. Taylor, Journ. Chem. Soc. London, 1952, p. 2535. M.A. 12–83.]

TABLE I. Chemical analyses of hillebrandite.

	1.	2.	2a.	2b.	2c.	
SiO_2 ...	32·59	30·49	30·71	0·511	Si(Al) ...	12·3
Al_2O_3 ...	0·23	2·16	1·26	0·012	Ca, &c. ...	24·0
CaO ...	57·76	56·13	57·75	1·030	O	48·2
TiO_2 ...	0·02	0·01	0·01	—	H_2O ...	12·1
Fe_2O_3 ...	0·15	0·28	0·32	0·002		
MnO ...	0·01	0·03	0·03	—		
MgO ...	0·04	0·28	0·32	0·008		
Na_2O ...	0·03	0·02	0·02	—		
K_2O ...	0·05	0·07	0·08	0·001		
CO_2 ...	—	1·12	—	—		
SO_3 ...	—	0·19	—	—		
H_2O-		0·14	—	—		
H_2O+ ...	9·36	8·80	9·50	0·527		
	100·24	99·72	100·00			

1. Hillebrandite, Terneras mine, Velardeña, Durango, Mexico. Analyst, E. T. Allen (F. E. Wright, loc. cit.). Total iron as Fe_2O_3.
2. Hillebrandite, Velardeña, Durango, Mexico. New analysis by F. J. McConnell, Building Research Station. H_2O+, loss at 110–950° less CO_2.
2a. Column 2 after deducting impurities: 2·54 % calcite, 0·42 % gypsum, 4·4% wollastonite, and 4·4 % hibschite ($Ca_3Al_2Si_2O_8(OH)_4$), and adjusted to 100%.
2b. Column 2a expressed in molecular ratios.
2c. Unit-cell contents.

The crystallites composing the hillebrandite fibres were fairly well alined in the fibre direction but otherwise showed random orientation. J. D. Bernal and N. Joel, working on some of the fibres, had previously determined the unit-cell dimensions as: a 16·32, b 3·63, c 11·84 Å., $\alpha = \beta = \gamma = 90°$ (private communication).

In the course of the present investigation one single crystal of hillebrandite was found among the fibres. It was needle-shaped, about $85 \times 20 \times 20 \mu$ with straight extinction and positive elongation. Oscillation, rotation, and Weissenberg photographs were taken. The rotation photographs about the needle-axis were entirely compatible with rotation photographs of the fibres about the fibre-axis, which in turn were in good agreement with the powder data obtained from samples of the crushed material. The latter were the same as those previously described (Heller and Taylor, loc. cit.) and are reproduced here in table II. The line at 2·70 Å. was observed to vary in intensity and is therefore attributed, at least partly, to the presence of another substance and corresponds to the strongest line of hibschite.[1] The strongest lines of wollastonite and calcite could not be detected.

The unit-cell dimensions deduced from this crystal were a 16·60,

[1] A. Pabst, Amer. Min., 1942, vol. 27, p. 783. [M.A. 8–359.]

TABLE II.   X-ray powder data of natural hillebrandite.

d (Å.).	Int.	d (Å.).	Int.	d (Å.).	Int.	d (Å.).	Int.
8·2	mw	2·45	w	1·64	w	1·360	vvw
6·7	vw	2·37	s	1·62	mw	1·350	vvw
5·8	w	2·26	ms	1·61	mw	1·335	vvw
4·76	vs	2·23	ms	1·57	mw	1·325	w
4·06	mw	2·10	vvw	1·56	vvw	1·300	vvw
3·52	mw	2·06	ms	1·54	w	1·280	vvw
3·33	vs	1·96	ms	1·530	vw	1·220	vvw
3·02	s	1·93	m	1·525	vw	1·205	vvw
2·92	vvs	1·87	ms	1·505	vvw	1·190	w
2·82	s	1·85	m	1·500	vvw	1·180	w
2·76	s	1·81	s	1·470	w	1·175	w
2·70	w*	1·75	m	1·450	vw	1·120	vw
2·67	w	1·72	mw	1·430	vw	1·115	vvw
2·63	mw	1·69	vvw	1·415	vw	1·095	vw
		1·67	vvw	1·365	vvw		

* This line varied in intensity for different samples taken from the same lump of mineral. It corresponds to the strongest line of hibschite.

b 7·26, c 11·85 Å., $\alpha = \beta = \gamma = 90°$. The b(needle)-axis showed strong pseudo-halving. Reflections on the weak layer-lines were streaks elongated in the direction of the layer-lines. It was not possible to detect these reflections on photographs of an imperfectly oriented fibre, which accounts for Bernal and Joel's value of 3·63 Å. for the length of the b-axis.

Using the analysis and density previously deduced, it follows that the number of formula-units of $2CaO.SiO_2.H_2O$ per cell is 12·1 (column 2c of table I) or 12 in the ideal case.

The determination of the true structure of hillebrandite can be simplified as a first approximation by considering only the pseudo-structure which is obtained when the weak intermediate layer-lines in the b-direction are neglected. The layer-lines are so weak that the pseudo-structure cannot differ substantially from the true structure.

A complete set of oscillation photographs was taken about the b-axis and sufficient oscillation photographs about the c-axis to estimate all the $0k0$ reflections. Weissenberg photographs were also taken of the $h0l$, $h2l$, and $h4l$ zones. (Photographs of the weak zones $h1l$ and $h3l$ would have required excessively long exposures.) The series of oscillation photographs about the b-axis show that there is a plane of symmetry perpendicular to b for all the reflections. For the pseudo-structure there are also planes of symmetry perpendicular to the other two axes.

This is confirmed by the Weissenberg photographs. For the true structure, however, there is some evidence that there may be no further planes of symmetry. On two successive photographs, both of which show the (11$\bar{2}$) and (11$\bar{3}$) reflections together with reflections (112) and (113), the former were respectively stronger than the latter. (These indices refer to the true cell.) As these reflections are streaks, however, the difference in intensity may also be due to a cutting-off effect. The symmetry of the true structure may therefore be monoclinic (with a β angle of 90°), but the evidence is ambiguous. The pseudo-structure is orthorhombic.

The following are the only systematic absences observed for the true structure: $h0l$ reflections absent for h odd and $0k0$ reflections for k odd. The space-group is therefore compatible with $P2_1/a$. This is, however, subject to some uncertainty, due to the weakness and streakiness of the reflections on the intermediate layer-lines.

For the pseudo-structure, in which b 3·63 Å., the following are the only observed systematic absences, hkl reflections absent for $h+k$ odd and $0kl$ reflections for k odd or l odd, with the only observed exception of (001), which is very weak. (These indices, of course, refer to the pseudo-cell.) Although this reflection was observed on oscillation and rotation photographs of the single crystal and of fibres, and also on powder photographs of hillebrandite and of synthetic dicalcium silicate β-hydrate, and therefore appears to be genuine, it is so weak that its presence cannot indicate a significant departure from the space-group otherwise deduced. The absences, neglecting the (001) reflection, are characteristic of space-groups $Ccmm$, $Ccm2$, and $Cc2m$. These space-groups have 16-fold general, and 8- or 4-fold special positions. The pseudo-cell of hillebrandite contains 6 silicon and 30 oxygen atoms. It is therefore not apparent how the cell content may be reconciled with the observed space-group. This problem requires elucidation.

Hillebrandite is one member of a series of hydrated calcium silicates which resemble each other and the anhydrous mineral wollastonite in crystallizing with a fibrous habit, and in having a repeat distance of 7·26 Å. with strong pseudo-halving in the needle or fibre direction. These have been described by Bernal,[1] who also discussed the possible significance of the strong 3·65 Å. repeat distance. However, it appears from the present results that the occurrence of the weak, intermediate layer-lines and the type of stacking disorder indicated by the streakiness

[1] J. D. Bernal, Proceedings of the Third International Symposium on the Chemistry of Cements, London, 1952, in the press.

of the reflections on these layer-lines cannot be ignored even as a first approximation.

A Patterson map in the (010) projection was calculated for hillebrandite, but was not found very helpful at this stage. It was therefore decided to postpone further attempts at interpreting the structure, pending a thorough reinvestigation of the structure of wollastonite which is in progress in this laboratory.