

The crystal structure of killalaite

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SUMMARY. The crystal structure of killalaite has been approximately determined, using a crystal from the original locality. The ionic constitution is $\text{Ca}_{3+x}(\text{H}_{1-2x}\text{Si}_2\text{O}_7)(\text{OH})$, with $x \approx 0.2$ for the crystal studied. Crystal data are: monoclinic pseudo cell with a 6.807, b 15.459, c 6.811 Å, β 97.76°, space group $P2_1/m$, $Z = 4$, $D_{\text{x-ray}} = 2.94 \text{ g cm}^{-3}$. Additional, very weak reflections indicate a B -centred monoclinic true cell with doubled a and c . The structure was determined using only the pseudo cell reflections, and includes one fractionally occupied Ca site; the larger true cell possibly arises from ordering of Ca atoms in these sites, together with associated small shifts of other atoms. There are weak indications that the degree of occupancy of this site may be variable. The X-ray powder pattern has been indexed and a calculated pattern is also given. A synthetic compound called 'Phase F' by Aitken and Taylor (1960) appears identical with or closely similar to killalaite.

KILLALAIT is a calcium silicate mineral found in a thermally metamorphosed limestone by Nawaz (1974). So far, only the one locality (Killala Bay, Ireland) is known. The killalaite occurs as grains sparsely distributed in rocks consisting mainly of calcite or other phases. Nawaz gave optical and X-ray powder data and concluded that the composition was $\text{Ca}_6\text{Si}_4\text{O}_{15}\text{H}_2$. This was based on a microprobe analysis together with a qualitative test for water, the content of which was obtained only by difference.

Determination of the structure. A crystal was extracted from a thin section under the microscope by Dr. Nawaz, to whom the author is much indebted. It was an irregular fragment some 0.2 mm in its largest dimension, and was mounted about an axis subsequently called b . It had a cleavage face that was called (001). Single-crystal X-ray photographs (b -rotation, hol and $h1l$ Weissenberg, $hol-h4l$ de Jong-Boumann, and hko , hkl , okl , and $1kl$ precession, all made with filtered Cu radiation) showed a monoclinic pseudo cell, which was subsequently refined from single-crystal diffractometer data (Mo- $K\alpha$, 0.7110 Å) to give a 6.807, b 15.459, c 6.811 Å, β 97.76° ($V = 710.2 \text{ Å}^3$), space group $P2_1$ or $P2_1/m$. There were additional, very weak reflections indicating a B -centred monoclinic true cell with doubled a and c . The cell derived by Nawaz (1974) from X-ray powder and morphological data is incorrect.

The crystal was then placed on a Hilger automatic linear diffractometer, which was used with molybdenum radiation to measure the intensities of 2052 independent pseudo-cell reflections (1425 observed) over a hemisphere of reciprocal space extending to $\sin^2\theta = 0.3$. Balanced filters were used and each reflection measured three times with each type of filter. Unobserved reflections were taken initially to have intensities equal to twice the estimated standard deviation obtained from counting statistics but at a late stage in the structure refinement these values were reduced to one-half. No absorption corrections were made. The intensities of equivalent reflections were averaged, structure amplitudes calculated, and preliminary estimates of scale and temperature factors obtained by Wilson's method. Intensity statistics, while inconclusive, suggested that a centre of symmetry was present and the space group was assumed to be $P2_1/m$. It was assumed that the composition was $\text{Ca}_6\text{Si}_4\text{O}_{15}\text{H}_2$, as found by Nawaz (1974), with $Z = 2$ for the pseudo cell, which gives an X-ray density of 2.78 g cm^{-3} . Nawaz (1974) found the density calculated from the refractive index to be 2.88 g cm^{-3} .

An attempt to solve the structure by symbolic addition failed, and the solution was obtained from inspection of the three-dimensional Patterson. The approximate coordinates of the Si and some of the Ca atoms were soon found, but it was not clear which were Si and which Ca, and considerable adjustments of coordinates with different combinations of assignments of atoms to sites had to be made by trial-and-error before the remaining atoms could be placed from a Fourier map. The pseudo structure then refined without difficulty using Fourier and block-diagonal least squares methods. During the refinement it became clear that the composition assumed was wrong, at least for the crystal examined, the composition of the formula unit being approximately $\text{Ca}_{6.4}\text{Si}_4\text{O}_{16}\text{H}_{3.2}$, with $Z = 2$. The Ca atoms in excess of 6 in this

TABLE I. Atomic parameters (coordinates as fractions of pseudo-cell edges; e.s.d.'s on last significant digit in parentheses; Ca5 has occupancy 0.43 ± 0.02)

Atom	Sym.	x/a	y/b	z/c	B_{iso}	Atom	Sym.	x/a	y/b	z/c	B_{iso}
Ca 1	1	0.3314 (3)	-0.0942 (2)	0.9308 (4)	1.24 (3)	0 2	1	0.690 (1)	-0.1463 (6)	0.662 (1)	1.9 (2)
Ca 2	1	0.7190 (4)	-0.0996 (2)	0.3330 (4)	1.89 (4)	0 3	1	0.004 (1)	-0.1440 (5)	0.919 (1)	1.0 (1)
Ca 3	m	0.0125 (6)	1/4	0.3375 (6)	1.86 (6)	0 4	1	0.672 (2)	0.0489 (8)	0.392 (2)	2.7 (2)
Ca 4	m	0.9299 (6)	1/4	0.8332 (6)	2.08 (6)	0 5	1	0.633 (1)	0.1316 (6)	0.731 (1)	1.6 (1)
Ca 5	m	0.520 (1)	1/4	0.487 (1)	1.2 (2)	0 6	1	0.957 (1)	0.1504 (5)	0.576 (1)	1.1 (1)
Si 1	1	0.8131 (4)	-0.0874 (2)	0.8374 (4)	1.00 (4)	0 7	1	0.884 (2)	0.0004 (7)	0.727 (2)	2.5 (2)
Si 2	1	0.7804 (4)	0.0833 (2)	0.6008 (4)	0.93 (4)	0 8	m	0.280 (2)	1/4	0.762 (3)	3.0 (3)
O 1	1	0.677 (1)	-0.0587 (5)	0.002 (1)	1.2 (1)	0 9	m	0.660 (2)	1/4	0.156 (2)	2.0 (2)

formula were present in a fractionally occupied site, which only became apparent at a fairly late stage in the refinement, and the occupancy fraction was obtained from the least-squares procedure. The hydrogen atoms were not located and their number was derived purely from consideration of charge-balance.

Using individual, isotropic temperature factors, the structure refined to $R = 0.147$ on all 2052 reflections (0.112 on observed reflections only). With anisotropic temperature factors, the corresponding values were 0.071 and 0.039, but the validity of this procedure for a pseudo-structure is uncertain. Attempts to locate the hydrogen atoms from difference electron-density maps failed. Analyses of the weighting scheme ($1/w = 1 + [(|F_o| - 50.0)^2 / 100.0]$) against $|F_o|$, $\sin^2\theta$, and k -index showed it to be satisfactory. Final difference electron-density maps showed a range of $\pm 0.6 \text{ e } \text{Å}^{-3}$ if anisotropic temperature factors were used, but with isotropic temperature factors, values from -3.0 to $+4.0 \text{ e } \text{Å}^{-3}$ were observed near to some of the heavier atoms.

Description of the structure. Table I gives the atomic parameters based on the isotropic refinement, Table II gives the more important bond lengths and angles, and figs. 1 and 2 show projections of the structure. The latter is based on Ca ions, pyrosilicate groups, and additional oxygen atoms (O8 and O9) that could conceivably be O^{2-} , OH^- , or H_2O . From reasoning that is given later, it was concluded that they are OH^- and that the constitutional formula is $\text{Ca}_{3+x}(\text{H}_{1-2x}\text{Si}_2\text{O}_7)(\text{OH})$, where $x \approx 0.2$ for the crystal studied. The structure is conveniently described in terms of layers parallel to (010) (fig. 2); layers of composition $[\text{Ca}_2(\text{H}_{1-2x}\text{Si}_2\text{O}_7)]^{-(1+2x)}$ alternate with ones of composition $[\text{Ca}_{1+x}\text{OH}]^{+(1+2x)}$. These latter layers include the statistically occupied calcium site, Ca 5. Of the other Ca atoms, Ca 1, Ca 2, and Ca 5 are in distorted octahedral coordination, while Ca 3 and Ca 4 are seven coordinated. The composition corresponds to an X-ray density of 2.94 g cm^{-3} .

Hydrogen-atom positions. The shortness of the O2-O4 distance (2.87 Å ; fig. 1) shows that

it is a hydrogen bond, and if one were to postulate an idealized structure in which the Ca 5 sites were all empty, the most obvious constitution would be $\text{Ca}_3(\text{HSi}_2\text{O}_7)(\text{OH})$, with O8 and O9 as the OH groups. This leaves it open as to whether the H atom of the HSi_2O_7 group is attached to O2 or O4, and also how the charge-balance is maintained when some of the Ca 5 sites are occupied. The incorporation of Ca atoms in these sites can presumably only be balanced by omission of H atoms, but it is not immediately obvious which these are likely to be.

TABLE II. *Interatomic distances (Å) and angles (degrees). E.s.d.'s on last significant figures in parentheses*

Ca 1 to	Ca 2 to	Ca 3 to	Ca 4 to	0 - Ca - O angles below 150°
0 1 2.398 (9)	0 1 2.324 (9)	0 2 2.585 (10)	0 3 2.351 (8)	Ca 1 Min. 0 3 - 0 9 74.2 (3)
0 1 2.410 (9)	0 2 2.389 (10)	0 3 2.387 (8)	0 5 2.746 (10)	Max. 0 1 - 0 3 106.4 (3)
0 3 2.347 (8)	0 4 2.360 (12)	0 6 2.305 (10)	0 6 2.358 (10)	Ca 2 Min. 0 6 - 0 8 73.2 (4)
0 4 2.303 (11)	0 5 2.427 (9)	0 9 2.549 (15)	0 8 2.492 (18)	Max. 0 4 - 0 6 115.2 (4)
0 5 2.353 (9)	0 6 2.345 (9)			Ca 3 Min. 0 2 - 0 3 62.3 (3)
0 9 2.484 (4)	0 8 2.414 (5)			Max. 0 2 - 0 9 133.5 (4)
Ca 5 to	Si 1 to	Si 2 to	0 2 to	Ca 4 Min. 0 5 - 0 6 60.4 (3)
0 2 2.292 (11)	0 1 1.609 (9)	0 4 1.603 (12)	0 4 2.867 (12)	Max. 0 3 - 0 5 135.1 (3)
0 5 2.523 (11)	0 2 1.640 (10)	0 5 1.613 (9)		Ca 5 Min. 0 5 - 0 8 72.2 (4)
0 8 2.652 (19)	0 3 1.605 (8)	0 6 1.614 (9)		Max. 0 5 - 0 9 117.8 (4)
0 9 2.558 (16)	0 7 1.654 (12)	0 7 1.649 (12)		
Angles at Si 1		Angles at Si 2		
0 1 - 0 2 111.8 (5)		0 4 - 0 5 113.5 (6)		
0 1 - 0 3 115.2 (4)		0 4 - 0 6 112.3 (6)		
0 1 - 0 7 108.7 (5)		0 4 - 0 7 108.7 (6)		Si - O - Si angle at 0 7 138.1 (7)
0 2 - 0 3 105.2 (5)		0 5 - 0 6 106.8 (5)		Si - O(11)O angle at 0 4 98.5 (5)
0 2 - 0 7 106.1 (5)		0 5 - 0 7 109.0 (5)		
0 3 - 0 7 109.4 (5)		0 6 - 0 7 106.4 (5)		

In an attempt to clarify these problems, the method of Donnay and Allman (1970) was used, in which the following procedure is adopted: (i) For each cation (Ca or Si), any oxygen is considered as bonded if it lies at a distance $L \leq L_{\text{max}}$, where $L_{\text{max}} = 3.25 \text{ \AA}$ for Ca and 2.13 \AA for Si. (ii) The mean length, \bar{L} , of the bonds formed by the cation is calculated. (iii) The ideal bond valence, v_i , for the cation is defined as the cation charge divided by the number of bonded oxygen atoms. (iv) A quantity p for the cation is defined as $\bar{L}/(L_{\text{max}} - \bar{L})$. (v) The bond valence, v , for each bond formed by the cation is calculated, using the formula $v = v_i(\bar{L}/L)^p$ if $L \leq \bar{L}$, or the formula $v = v_i(L_{\text{max}} - L)/(L_{\text{max}} - \bar{L})$ if $\bar{L} \leq L \leq L_{\text{max}}$. (vi) For each oxygen the sum of the bond valences, Σv , is calculated; if v approximates to 2, 1, or 0, the oxygen is assumed to carry 0, 1, or 2 H atoms respectively. Substantial deviations from these integral values indicate hydrogen bonding, and from the values it is possible to decide which of the oxygen atoms most probably carries the hydrogen atom.

The calculations were made both assuming the Ca 5 sites to be empty and assuming them to be occupied. The results (Table III) indicate in both cases that O8 and O9 are hydroxyl groups. If the Ca 5 sites are assumed to be empty, O2 carries a hydrogen atom, which is hydrogen bonded to O4. If they are assumed to be occupied, this hydrogen atom is absent. Incorporation of a Ca atom into the Ca 5 site is thus balanced by omission of two H atoms

from the O2 atoms of pyrosilicate groups, and these will presumably be the two O2 atoms to which the Ca atom is attached.

The true structure has not been solved, but preliminary consideration of the intensities of the weak reflections unindexable on the pseudo-cell showed that the larger cell cannot arise solely from ordering of atoms in the Ca 5 sites. It could arise indirectly from this cause, if the presence

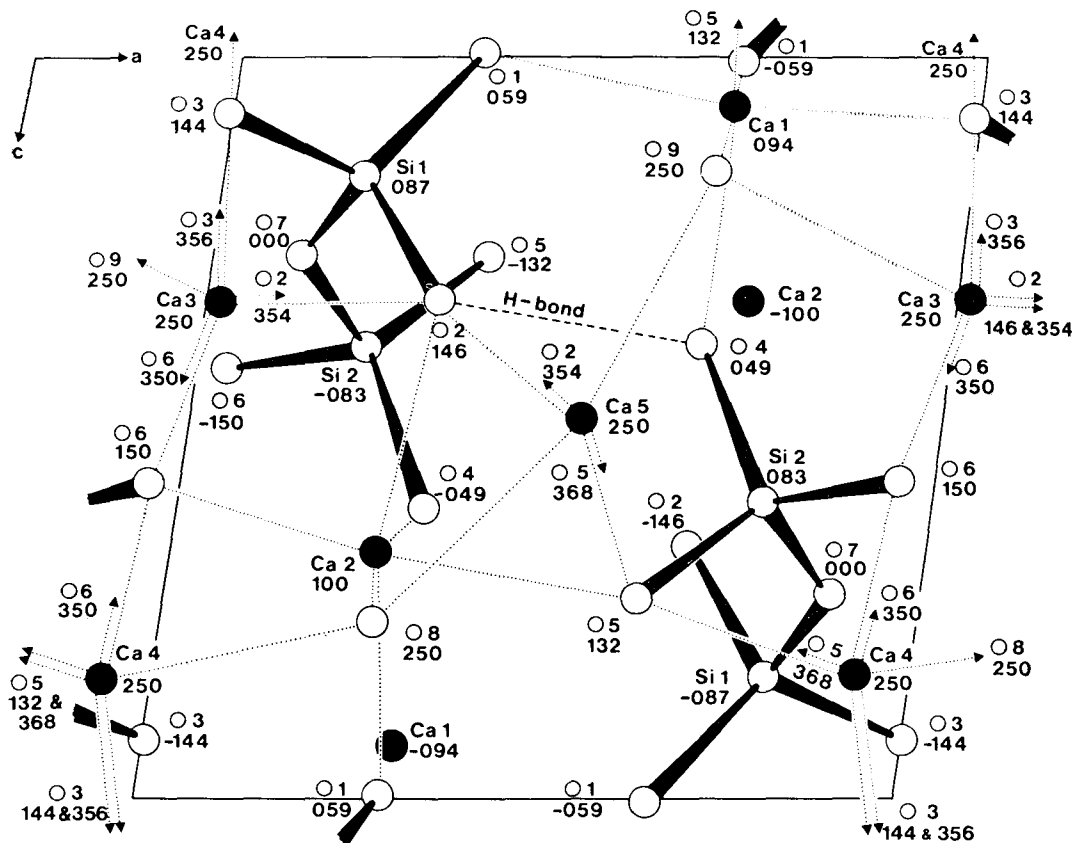


FIG. 1. Killalaite: projection along b for $-0.15 < y/b < 0.25$. Heights as $1000 y/b$.

or absence of an atom in such a site causes small shifts in positions of the other atoms. It is highly probable that this is the case, since the O2–O4 distance may be expected to increase if O2 does not carry a hydrogen atom, and this in turn is likely to affect the positions of other atoms. The apparent anisotropy of some of the heavier atoms may well arise partly or wholly in this way.

X-ray powder pattern, constancy of composition, and comparison with synthetic material. Table IV, col. 2, gives the powder pattern calculated from the pseudo-cell and atomic parameters given in Table I, assuming Debye-Scherrer geometry and Cu radiation. It is in moderate agreement with the observed pattern (col. 1), which was obtained using a 114.85-mm-diameter camera with visual estimation of relative intensities. No material remained on which it might have been possible to obtain a pattern at higher resolution by means of a Guinier camera.

There are weak indications that the composition of killalaite may vary slightly. Nawaz's

TABLE III. *Coordination of the oxygen atoms*

Electrostatic bond valences (ν) and sums ($\Sigma\nu$) are calculated by the method of Donnay and Allman (1970), contributions from H atoms to the sums being omitted.

Oxygen no.	Bonded to	Distance (Å)	ν	$\Sigma\nu$ (Ca 5 sites empty)	$\Sigma\nu$ (Ca 5 sites occupied)	Conclusion
1	Si 1	1.609	1.04	2.04	2.04	Si-O ⁻
	Ca 1	2.398	0.33			
	Ca 1	2.410	0.32			
	Ca 2	2.324	0.35			
2	Si 1	1.640	0.98	1.54	1.97	Ca 5 empty: Si-O-H, H-bonded to O 4, Ca 5 occupied: Si-O
	Ca 2	2.389	0.33			
	Ca 3	2.585	0.23			
	Ca 5	2.292	0.43			
3	Si 1	1.605	1.04	2.04	2.04	Si-O ⁻
	Ca 1	2.347	0.35			
	Ca 3	2.387	0.31			
	Ca 4	2.351	0.34			
4	Si 2	1.603	1.04	1.75	1.75	Si-O ⁻ ; if Ca 5 is empty accepts H-bond from O 2.
	Ca 1	2.303	0.37			
	Ca 2	2.360	0.34			
5	Si 2	1.613	1.01	1.86	2.17	Si-O ⁻
	Ca 1	2.359	0.35			
	Ca 2	2.427	0.31			
	Ca 4	2.746	0.19			
	Ca 5	2.523	0.31			
6	Si 2	1.614	1.01	2.04	2.04	Si-O ⁻
	Ca 2	2.345	0.35			
	Ca 3	2.305	0.34			
	Ca 4	2.358	0.34			
7	Si 1	1.654	0.94	1.88	1.88	Si-O-Si
	Si 2	1.649	0.94			
8	Ca 2	2.414	0.32	0.92	1.18	OH ⁻
	Ca 2	2.414	0.32			
	Ca 4	2.492	0.28			
	Ca 5	2.652	0.26			
9	Ca 1	2.484	0.29	0.83	1.13	OH ⁻
	Ca 1	2.484	0.29			
	Ca 3	2.549	0.25			
	Ca 5	2.558	0.30			

Phase F; they considered the composition to be approximately $5\text{CaO}\cdot 3\text{SiO}_2\cdot 2\text{H}_2\text{O}$. The X-ray powder pattern (Table IV, col. 3) suggests that 'Phase F' is probably identical with or closely similar to killalaite. The mean refractive index was reported as 1.62; for killalaite Nawaz (1974) found α 1.635, γ 1.642.

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Errata: Table IV, col. 5, line 37, for 143— read 143+;
 col. 12, line 32, for 136 read 136.

TABLE IV. X-ray powder patterns

1.		2.			3.		1.		2.			3.	
Killalaite Observed		Killalaite Calculated Peak heights			Phase F Observed		Killalaite Observed		Killalaite Calculated Peak heights			Phase F Observed	
d	I _{rel}	d	I _{rel}	hkp	d	I _{rel}	d	I _{rel}	d	I _{rel}	hkp	d	I _{rel}
7.40	3	7.73	12	020	7.7	6	1.720	5	1.720	4	322+	—	—
6.75	10	6.74	16	100	6.7	6	—	—	1.710	3	303	—	—
(5.45	1)	—	—	—	—	—	—	—	—	—	—	—	—
5.10	25	5.08	24	120	5.02	20	1.688	35	1.690	12	104+	1.692	20
4.97	3	4.865	5	111	4.85	(13)	1.673	35	1.687	12	004, 361+		
4.50	5	4.476	4	101	—	—	1.620	(30)	1.674	18	272+	1.671	45
(4.35	5)	—	—	—	—	—	—	—	1.623	6	333	1.625	13
3.86	(30)	3.864	25	040	3.84	20	—	—	1.605	7	243+	1.606	6
3.38	30	3.371	27	200+	3.40	6	1.566	3	1.573	6	272+	1.572	9
3.30	10	3.295	14	012	—	—	—	—	1.565	4	224+		
3.19	25	3.193	23	201	3.18	13	1.550	3	1.554	4	124, 421	—	—
3.09	25	3.089	48	220	3.11	20	—	—	1.550	5	144, 441+	—	—
(3.03	80)	—	—	—	(3.03	9)	—	—	1.530	7	092+	1.529	13
2.97	2	2.949	8	221	2.93	6	1.520	(30)	1.527	6	432		
2.85	2	2.863	19	201	—	—	—	—	1.516	5	431+	—	—
2.824	100	2.820	100	032+	2.83	100	—	—	1.513	5	192, 291	—	—
2.724	60	2.714	37	132+	2.70	45	—	—	1.493	4	303	—	—
2.650	5	2.647	7	151	2.649	9	1.469	8	1.486	3	313, 154	—	—
2.560	30	2.574	36	060	2.565	67	—	—	1.473	3	291+	1.475	6
2.540	30	2.539	28	240+	2.533	6	—	—	1.468	4	144+	—	—
—	—	2.504	10	231	—	—	—	—	1.440	3	413+	1.446	6
—	—	2.461	6	142	(2.392	6)	—	—	1.427	4	292+	—	—
—	—	2.434	5	222	—	—	1.413	(40)	1.422	5	324+	—	—
—	—	2.406	3	061, 160	—	—	—	—	1.414	13	461, 164+	1.415	45
2.275	(45)	2.301	20	142+	2.305	45	1.357	5	1.392	4	433+	—	—
—	—	2.281	5	052	—	—	—	—	1.351	3	164+	1.361	6
2.250	10	2.248	20	300+	2.257	45	1.285	5	1.288	5	471, 0.12.0	1.285	13
2.224	45	2.223	27	310, 301+	2.224	45	(1.233	5)	1.285	3	404, 511		
2.150	3	2.159	5	023+	—	—	—	—	—	—	—	—	—
—	—	2.138	6	123, 242	2.141	6	—	—	1.167	2B	491+	1.172	6
—	—	2.101	6	152	2.092	6	—	—	1.140	2B	4.10.1, 463+	1.142	6
2.055	10	2.047	13	260+	2.050	9	1.108	10	1.111	3	2.10.4, 365	—	—
—	—	2.028	6	171	2.026	9	—	—	1.108	6	136, 1.10.4+	1.113	9
—	—	2.005	5	261+	—	—	—	—	1.098	3	1.13.2, 2.13.1	1.096	6
1.975	15	1.974	11	252+	—	—	—	—	1.083	3	611, 523+	—	—
—	—	1.943	6	043, 340	1.970	13	—	—	1.079	3	2.13.2+	1.079	6
1.920	(30)	1.930	8	080, 143-	1.939	9	—	—	1.062	3	136+	—	—
—	—	1.916	11	261, 162	1.914	13	1.044	(20)	1.052	3	543+	—	—
(1.876	30)	—	—	—	—	—	—	—	1.043	2B	633+	—	—
—	—	1.864	3	233	—	—	—	—	—	—	—	—	—
—	—	1.858	3	180	—	—	—	—	—	—	—	—	—
1.849	2	1.848	5	072	1.848	6	—	—	—	—	—	—	—
1.815	10	1.813	6	252+	—	—	—	—	—	—	—	—	—
1.766	5	1.764	6	203	1.773	6	—	—	—	—	—	—	—
1.748	15	1.749	13	172, 271	1.746	20	—	—	—	—	—	—	—

Where an observed spacing and intensity are together enclosed in parentheses, the peak is attributed wholly to impurity; where only the intensity is so enclosed the peak is attributed partly to impurity.
 Col. 1: Killalaite (Nawaz, 1974); the dominant impurity is calcite, of which the only peaks listed are ones considered by Nawaz to be partly due to killalaite. Col. 3: Phase F (Aitken and Taylor, 1960); intensities converted to numerical scale on basis vs = 100, s = 67, ms = 45, m = 30, mw = 20, w = 13, vw = 9, vvw = 6.
 The calculated pattern (col. 2) gives positions and heights of peaks assuming CuK α radiation and Cauchy line profiles with a half-height half-width of $\pm 0.1^\circ 2\theta$. All peaks of height > 2.5 are listed. For each peak, indices are normally given for all reflections contributing more than about 33% of the total integrated intensity, in decreasing order of their contributions, and '+' denotes that the listed reflections contribute less than about 85% of the total integrated intensity. Indices relate to the pseudo cell.