The crystal structure of harkerite

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Abstract

The lattice parameters of harkerite from Skye (Scotland) are: $a = 18.131$ A, $\alpha = 33,46°$, space group $R\bar{3}m$, twin plane (211). The crystal structure has been solved by Patterson, Fourier, and difference syntheses, then refined by least-squares procedures to a conventional $R = 0.067$ for the 1175 reflections with $F_o^2 > 3 \sigma(F_o^2)$; $R = 0.147$ for all 2695 measured reflections.

The crystal structure of harkerite is comparable with that of sakhaite. The idealized cell contents derived from the structural studies are:

harkerite $Ca_{24}Mg_8[AlSi_4(O,OH)_{16}]_2 (BO_3)_8(CO_3)_8(H_2O,Cl)$

sakhaite $2\{Ca_{24}Mg_8[(BO_3)_8 (BO_3)_8](CO_3)_8(H_2O)\}$,

the main difference between the structures being the replacement of the aluminosilicate group in harkerite (similar to the tetrahedral pentamer found in zunyite) by $4(BO_3)$ in sakhaite. Both minerals show a very marked pseudo-symmetry in the cubic space group $Fd3m$ ($a = 14.7$ A).

The crystal structure is based on an arrangement of oxygen and calcium atoms in an incomplete cubic closest packing, with Mg in octahedral sites, Si and Al in tetrahedral sites, and B or C in triangular holes. The Ca-coordination ranges from 8 to 10. Two carbonate groups are statistically placed on one of two inversion-related orientations. Some structural disorder follows from the mutual replacement among aluminosilicate, borate, or possibly other atomic groups (CO_3, OH, H_2O). Such substitutions would be also responsible for some discrepancies between the idealized and actual chemical composition of harkerite. The different ordering of the replacing groups accounts for possible harkerite polymorphs in the cubic pseudo-cell.

Introduction

Harkerite from skarn deposit in Skye (Scotland) was discovered and described by Tilley (1951); it is associated very intimately with calcite, which is a product of its alteration. Among various data, Tilley reports the density (2.959 at 20°C), the Laue symmetry (*m3m*), the lattice parameter ($a = 29.53$ A, with a marked pseudo-repeat distance $a/2 = 14.76$ A), and the chemical analysis, from which the following atomic content of the cubic pseudo-cell ($a = 14.76$ A) was derived: $20\ CaCO_3 \cdot Ca_{28}(Mg_{15.5}, Al_{3.5}, Fe_{0.5}^{3+}, Fe_{0.5}^{2+})(B_{11}, Si_{13})(O,OH,Cl)_{96}$. The complex crystal chemistry was considered tentative by Tilley, who wrote: "a further chemical analysis of selected material is much to be desired."

Pertsev (1961) found at Tas-Haiatah (Polar Yakutia-Siberia) a mineral which was first regarded as harkerite, and later assigned to the new species sakhaite: $Ca_{48}Mg_{16}(BO_3)_{28}(CO_3)_{16}(OH)_8Cl_4 \cdot 4H_2O$ (Ostrovskaya *et al.*, 1966). According to the latter authors, harkerite and sakhaite are very similar in their structural properties; *i.e.*, they have the same Laue symmetry, and the lattice parameter of sakhaite is equal to the pseudo-repeat distance of harkerite. Some differences are shown in the optical properties, sakhaite being isotropic and harkerite often anisotropic and zoned. They made a new chemical analysis on harkerite from Skye and obtained the pseudo-cell content:

$Ca_{48}Mg_{16}Al_3(SiO_4)_{12}(BO_3)_{15}(CO_3)_{18}(OH)_6Cl_2 \cdot 3H_2O$.
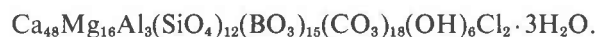
Further crystal-chemical studies on harkerite and its relations with sakhaite were carried out by Ostrovskaya (1969) and Davies and Machin (1970).

Chichagov *et al.* (1974) determined the crystal structure of synthetic sakhaite in the space group $F4_132$; the unit cell content ($a = 14.69$ A) obtained from the structural study was:

$$Ca_{48}Mg_{16}(BO_3)_{32}(CO_3)_{16} \cdot 2H_2O.$$
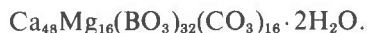
The "average" crystal structure of a Siberian harkerite described in the cubic pseudo-cell ($a = 14.73$ A; space group $Fd3m$) was published by Machin and Miehe (1976) just after our paper was completed. According to these authors, the idealized composition of harkerite is:

$$Ca_{48}Mg_{16}[Al(SiO_4)_4]_3[(BO_3)_{17}(CO_3)_3](CO_3)_{16} \cdot 4H_2O.$$

In the present study we started from the following idealized content of the pseudo-cell:

$$Ca_{48}Mg_{16}[AlSi_4(O,OH)_{16}]_4(BO_3)_{16}(CO_3)_{16}(H_2O,HCl)_2;$$

this atomic formula is halved in the true rhombohedral unit cell of harkerite from Skye.

Experimental

Two crystals of harkerite were examined with a Philips PW 1100 diffractometer: one of them was a single crystal with symmetry $R\bar{3}m$ and the second was a twin. Fig. 1 shows the relations among the different unit cells obtainable from the lattice of harkerite. The apparent cubic symmetry observed by the preceding authors (Tilley, 1951; Davies and Machin, 1970; Ma-
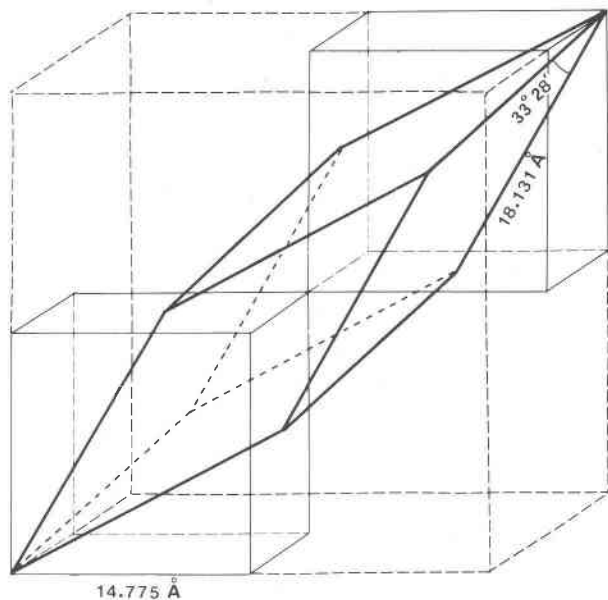

FIG. 1. The rhombohedral unit cell of harkerite and its relations with the large cubic cell due to the twinning ($a = 29.55$ A) and the small cubic pseudo-cell (actual cell for sakhaite).

chin and Miehe, 1976) in the large unit-cell follows from the twinning: an idealized pseudo-cubic twin aggregate is formed by four trigonal individuals, each of them having its three-fold axis parallel to one of the four three-fold axes of the cubic cell. If the indices of the reflecting planes are assigned in this F-centered pseudo-cubic lattice, the twin individuals contribute to each set of 48 "equivalent" reflections in the following way: if $h + k + l$ is even, the contributions of all individuals are superposed on all 48 reflections; on the contrary, if $h + k + l$ is odd, each twin individual gives rise to only 12 of such reflections, and no superposition occurs. In the latter case, a complete set of 48 exactly equivalent pseudo-cubic reflections is obtained only if four individuals having equal volumes are present.

In our twinned crystal formed by two individuals (77 and 23 percent in volume respectively), only 24 reflections were detected for each set of "equivalent" planes with $h + k + l$ odd, the intensities of 12 of them being about 3.5 times greater than those of the remaining ones. The twin plane is (211) in the rhombohedral lattice, corresponding to (010) in the pseudo-cubic lattice.

The rhombohedral parameters are: $a = 18.131(2)$ A, $\alpha = 33.46(2)°$. They were obtained by a least-squares procedure applied to the sine 2ϑ values of 25 reflections measured on a Philips diffractometer.

The intensities were collected from the single crystal (dimensions $0.22 \times 0.22 \times 0.30$ mm) using a Philips PW 1100 automated diffractometer and $MoK\alpha$ radiation monochromatized by a flat graphite crystal. A set of data was collected out to $2\vartheta = 60°$ by the ω-scan mode, with a symmetric scan range of 1.8°. The scan rate was 0.03°/sec; processing of the data was carried out in the manner described by Davies and Gatehouse (1973) to yield values of F_0 and $\sigma(F_0)$. The intensities of 2695 independent reflections were measured; of these, 1175 having $F_0^2 > 3\sigma(F_0^2)$ were used in the subsequent calculations. Three standard reflections, monitored at three-hour intervals, showed no variation in intensity greater than 2.5 percent. Neither absorption nor extinction correction were applied.

The average intensities of the reflections were quite different, depending on the parity groups of the indices; the ratios among $\bar{E}^2$'s were: eee:eoo:eeo:ooo $= 25:4:1.5:1$.[1] The strongest reflections ($h + k + l$ even) would be those uniquely present in a lattice based on the cubic pseudo-cell with $a = 14.78$ A (Fig.
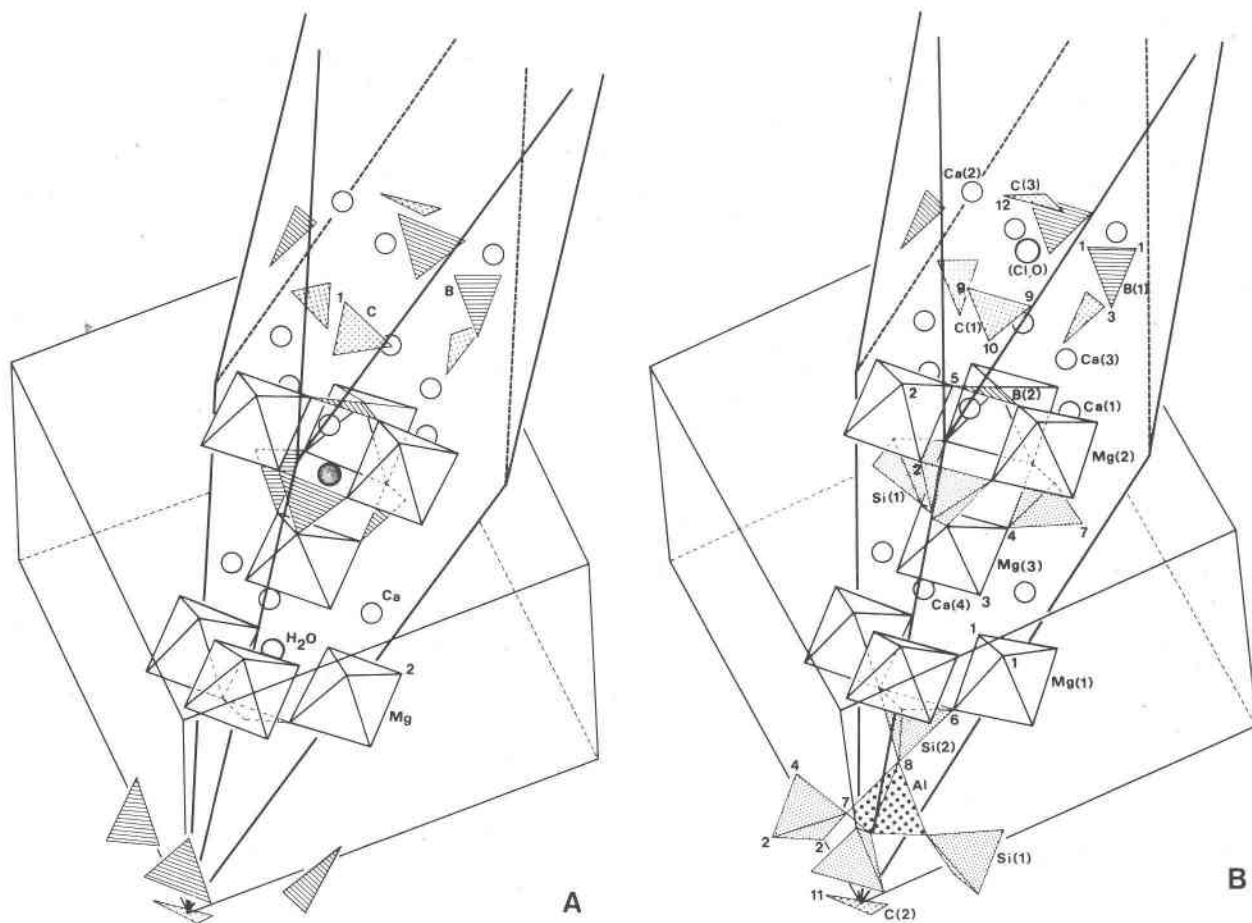
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[1] e = even, o = odd

FIG. 2. The crystal structure of (a) sakhaite, (b) harkerite. The contours of the real cubic cell of sakhaite and the pseudo-cell of harkerite are drawn.

1): actually the intensities of such reflections are nearly consistent with cubic symmetry in an F-centered lattice.

The crystal structure was solved in the space group $R\bar{3}m$ through Patterson syntheses followed by several electron density and difference syntheses. At the end of the least-squares refinement, with anisotropic thermal parameters, and taking into account the partial structural disorder described in a following section, the conventional R-index was 0.067 for the 1175 reflections used in the calculation; for the different parity groups of the indices we obtained: $R(eee) = 0.049$, $R(eoo) = 0.062$, $R(eeo) = 0.105$, and $R(ooo) = 0.119$. The R index including all 2695 reflections measured was 0.147. The observed and calculated structure amplitudes are compared in Table 1.[2]

Comparison between the crystal structures of harkerite and sakhaite

The crystal structure of harkerite can be suitably explained in comparison with that of sakhaite: Figure 2a shows the latter structure (Chichagov et al., 1974) described in the rhombohedral unit-cell of harkerite (Fig. 2b). In the upper part of the rhombohedral cell (not drawn), the atoms repeat in harkerite through inversion and in sakhaite through simple translation. The most evident difference between the structures is the substitution of two $AlSi_4O_{16}$ groups for eight BO_3 ions per unit cell.

Most of the atoms (Ca,Mg and its coordinated oxygens, B and, partially, C) lie nearly in the same positions in both structures: also the sites of Si in harkerite are very close to the positions of B in sakhaite. Table 2 compares the atomic parameters of both minerals, and Table 3 gives the anisotropic thermal parameters of the atoms in harkerite.

TABLE 2. Final positional parameters of harkerite compared with those of sakhaite

Atom	Point symmetry	Number of positions	x	y	z	Atom	Point. symmetry	Number of positions	x	y	z
		Harkerite R3̄m						Sakhaite F4₁32			
Mg(1)	2/m	3	1/2	0	0				1/2	0	0
Mg(2)	2/m	3	0	1/2	1/2	Mg	32	8	0	1/2	1/2
Mg(3)	3m	2	0.2486(1)	x	x				1/4	1/4	1/4
Ca(1)	m	6	0.1936(1)	x	0.6723(3)				0.1930	x	0.6710
Ca(2)	m	6	0.3168(1)	x	-0.1982(3)	Ca	2	24	0.3070	x	-0.1710
Ca(3)	m	6	0.5592(2)	x	0.0725(3)				0.5680	x	0.0460
Ca(4)	m	6	-0.0659(1)	x	0.4498(3)				-0.0680	x	0.4540
O (1)	1	12	0.0768(5)	0.5679(5)	-0.2099(4)				0.0835	0.5635	-0.2125
O (2)	1	12	0.4107(5)	-0.0436(5)	0.7077(4)				0.4245	-0.0555	0.7045
O (3)	m	6	0.3180(3)	x	0.0394(6)	O(2)	1	48	0.3165	0.3325	0.0365
O (4)	m	6	0.1694(3)	x	0.4653(6)				0.1675	0.1835	0.4635
O (5)	m	6	0.4300(3)	x	0.2054(6)				0.4435	0.4275	0.2035
O (6)	m	6	0.0575(3)	x	0.3024(6)				0.0725	0.0565	0.2965
B (1)	m	6	0.3176(4)	x	-0.0323(8)				0.3240	x	-0.0400
Si(1)	m	6	0.1361(2)	x	0.6039(3)	B	3	16	0.1760	x	0.5400
B (2)	3m	2	0.3548(2)	x	x				0.3580	x	x
Si(2)	3m	2	0.1293(1)	x	x				0.1420	x	x
C (1)	m	6	0.2748(5)	x	-0.2917(10)				1/4	1/4	3/4
C (2)	3̄m	1	0	0	0	C	32	8	0	0	0
C (3)	3m	2 §	0.4895(5)	x	x				1/2	1/2	1/2
Al	3m	2	0.0639(1)	x	x						
(O,Cl)	3m	2 §	0.4543(5)	x	x	H₂O	23	8 †	0.3125	x	x
O (7)	m	6	-0.0390(4)	x	0.2383(8)						
O (8)	3m	2	0.0975(2)	x	x						
O (9)	1	12	0.1708(6)	0.3776(6)	-0.2558(6)				0.1890	0.3110	-0.1890
O(10)	m	6	0.2779(5)	x	-0.3660(9)	O(1)	2	24	0.1890	0.3110	-0.3110
O(11)	2	6 §	-0.1208(12)	-x	0				-0.1220	-x	0
O(12)	m	6 §	0.5606(7)	x	0.3462(13)				0.6220	1/2	0.3780

§ occupancy 1/2; † occupancy 1/8.
Parameters of sakhaite (Chichagov et al.,1974) are converted to the same rhombohedral unit cell as harkerite.
Standard deviations are indicated in parentheses in terms of last significant figures.

With the exception of the oxygens from O(7) to O(12) (shared oxygens in the aluminosilicate group and CO_3-oxygens) in harkerite and O(1)-oxygens from carbonate ions in sakhaite, all the atoms are nearly related by a center of symmetry at 1/4, 1/4, 1/4, corresponding to 1/2, 1/2, 1/2 in the cubic pseudo-cell; also pairs of different atoms (B/Si and Al/(Cl,O) are involved in this pseudo-symmetry. As a consequence, a pseudo-repeat ½[111] occurs in harkerite, corresponding to the true translation in sakhaite.

In spite of the different space groups ($R\bar{3}m$ for harkerite and $F4_132$ for sakhaite), the majority of the atoms in both structures have a symmetry very near to that of $Fd3m$ in the cubic pseudo-cell. In sakhaite the sites of all atoms are either perfectly or very nearly [for O(2)] consistent with this space group; only the number of O(1)-oxygens from CO_3 ions would be doubled with respect to the actual number of CO_3-oxygens in sakhaite.

The atomic parameters of harkerite from Skye, transformed into the corresponding parameters of the cubic pseudo-cell, are compared in Table 4 with those obtained by Machin and Miehe (1976) from Siberian harkerite: the coordinates of the atoms which would be equivalent in the space group $Fd3m$ were averaged to obtain comparable data. The agreement is very satisfactory; some minor discrepancies (differences in the coordination around Ca atoms or in the chemical composition) are either a consequence of the atomic parameters of Siberian harkerite being an "average" of the real parameters, or a consequence of the crystal-chemical nature of harkerite.

In sakhaite the carbonate oxygens lie on two-fold axes, whereas in harkerite C(1) and C(2) have their

TABLE 3. Anisotropic temperature factors of harkerite ($\times 10^4$)

Atom	$B_{eq.}$	β_{11}	β_{22}	β_{33}	$-\beta_{12}$	$-\beta_{13}$	$-\beta_{23}$	Atom	$B_{eq.}$	β_{11}	β_{22}	β_{33}	$-\beta_{12}$	$-\beta_{13}$	$-\beta_{23}$
Mg(1)	0.59	18(4)	25(3)	25(3)	6(2)	6(2)	19(3)	Mg(2)	0.61	17(4)	22(2)	22(2)	9(2)	9(2)	10(3)
Mg(3)	0.52	23(3)	23(3)	23(3)	12(1)	12(1)	12(1)								
Ca(1)	1.16	28(1)	28(1)	47(2)	10(1)	18(1)	18(1)	Ca(2)	1.82	44(2)	44(2)	76(3)	17(2)	28(1)	28(1)
Ca(3)	1.90	55(2)	55(2)	75(3)	16(2)	34(1)	34(1)	Ca(4)	1.17	32(1)	32(1)	61(3)	13(1)	23(1)	23(1)
O(1)	2.08	108(7)	76(6)	33(4)	64(5)	23(5)	15(4)	O(2)	1.87	74(5)	62(5)	42(5)	28(4)	33(4)	20(4)
O(3)	1.73	59(5)	59(5)	49(7)	18(6)	29(4)	29(4)	O(4)	1.74	91(6)	91(6)	35(6)	66(7)	20(3)	20(3)
O(5)	1.66	59(5)	59(5)	46(7)	22(6)	27(4)	27(4)	O(6)	2.22	120(8)	120(8)	32(7)	101(8)	15(3)	15(3)
B(1)	0.74	21(5)	21(5)	36(8)	8(6)	14(4)	14(4)	Si(1)	1.53	46(2)	46(2)	54(3)	14(3)	26(1)	26(1)
B(2)	0.81	28(8)	28(8)	28(8)	13(4)	13(4)	13(4)	Si(2)	1.41	41(4)	41(4)	41(4)	18(2)	18(2)	18(2)
C(1)	1.87	57(7)	57(7)	70(11)	2(8)	41(6)	41(6)	C(2)	2.73	71(22)	71(22)	71(22)	30(12)	30(12)	30(12)
C(3)	1.23	29(16)	29(16)	29(16)	12(9)	12(9)	12(9)								
Al	1.20	43(3)	43(3)	43(3)	20(1)	20(1)	20(1)	(O,Cl)	3.90	135(13)	135(13)	135(13)	63(7)	63(7)	63(7)
O(7)	3.88	126(9)	126(9)	78(9)	105(10)	20(4)	20(4)	O(8)	3.68	155(13)	155(13)	155(13)	76(7)	76(7)	76(7)
O(9)	4.62	97(7)	113(8)	141(9)	43(6)	2(6)	102(7)	O(10)	4.32	224(12)	224(12)	109(11)	159(13)	58(6)	58(6)
o(11)	6.09	106(13)	106(13)	131(24)	-62(16)	92(15)	92(15)	O(12)	2.49	66(12)	66(12)	44(14)	45(14)	13(7)	13(7)

Standard deviations are indicated in parentheses in terms of last significant figures.
$B_{eq.}$ (Å^2) is the equivalent isotropic temperature factor proposed by Hamilton, 1959.
The anisotropic temperature factor has the form: $exp(-h^2\beta_{11} -k^2\beta_{22} - l^2\beta_{33} -2hk\beta_{12} -2hl\beta_{13} -2kl\beta_{23})$.

oxygens on mirror planes; the CO_3 triangles are rotated around an axis perpendicular to their plane to avoid a steric hindrance, which otherwise would occur between CO_3 oxygens and APO_4 oxygens. The C(2) carbonate group has the same position in both minerals. In harkerite, C(2) lies on a center of symmetry and C(3) is very near a center. This fact could suggest an acentric symmetry, but the positions of the $C(2)O_3$ oxygens on twofold axes and those of $C(3)O_3$ oxygens on mirror planes give contradictory indication for the possible space group, i.e. $R32$ and $R3m$ respectively. For the space group $R\bar{3}m$, both carbonate ions must be statistically placed in either one orientation or their centrosymmetrical counterpart. This implies that also the (Cl,O) atom, which lies very near to C(3), plays a similar role. When one of the centrosymmetrical C(3) carbonate ions is present, the nearest (Cl,O) site would be vacant, and its inversion equivalent would be occupied.

The site assigned to (Cl,O) became apparent on one of the last difference syntheses; such an atom was taken as ½Cl + ½O in the calculation of the structure amplitudes in order to obtain a reasonable thermal factor. This site, which lies in a cavity of the crystal structure, is vacant in sakhaite. The site which in sakhaite is incompletely occupied by H_2O corresponds in harkerite to an empty position among SiO_4 tetrahedra belonging to four aluminosilicate groups

TABLE 4. Comparison of the positional parameters of Skye harkerite with those of Siberian harkerite (Machin and Miehe, 1976)

	Skye				Siberia		
Atom	x	y	z	Atom	x	y	z
Mg(1-3)	0.0003	x	x	Mg	0	0	0
Ca(1-4)	0.1248	x	-0.1238	Ca	1/8	1/8	-0.1215
B(1-2)	0.2112	x	x	(B,C)	0.2134	x	x
Si(1-2)	0.2423	x	x	Si	0.2429	x	x
Al	0.3722	x	x	Al	3/8	3/8	3/8
C(1-3)	0.4850	x	x	C	0.4851	x	x
O(1-6)	-0.0059	x	0.1388	O(2)	-0.0063	x	0.1385
O(7-8)	0.3067	x	x	O(3)	0.3065	x	x
O(9-12)	-0.0150	-0.0224	0.5838	O(1)	-0.0081	-0.0278	0.5831
(O,Cl)	0.4086	x	x	H_2O	0.4101	x	x

(Fig. 2a,b). The role of the (Cl,O) atom is not clear. It has six equal large distances (3.18 A) with three Ca(2) atoms and three O(12) oxygens from a C(3) carbonate ion.

Bond distances and angles are listed in Table 5. The octahedral coordination of magnesium is similar in both minerals; the mean Mg–O distance is 2.06 A (2.05 A in sakhaite). Some differences occur in the coordination of calcium (Fig. 3). In sakhaite Ca is bonded to six oxygens from the borate triangles and two oxygens from the carbonate groups in a kind of irregular square antiprism. Ca(1) and Ca(4) have the same coordination in harkerite; Ca(3) has two more contacts with carbonate oxygens, and similarly Ca(2) has further contacts with oxygens of the C(3) carbonate ion, either one or two, according to the presence

TABLE 5. Interatomic distances and angles in harkerite

Ca(1a)-polyhedron
O(2 a)	2.402(4) A	×2
O(2 t)	2.660(4)	×2
O(5 b)	2.503(2)	×2
O(10f)	2.348(6)	
O(11g)	2.373(8)	
mean	2.481 A	

Ca(2a)-polyhedron
O(1 a)	2.566(5) A	×2
O(1 p)	2.604(4)	×2
O(6 b)	2.707(3)	×2
O(9 a)	2.668(6)	×2
one of the following:		
O(12i)	2.596(4)	×2
O(12q)	2.330(12)	
means	2.602 – 2.628 A	

Ca(3a)-polyhedron
O(2 b)	2.613(4) A	×2
O(3 q)	2.692(6)	
O(4 r)	2.691(3)	×2
O(5 a)	2.663(6)	
O(9 h)	2.653(7)	×2
O(10h)	2.630(3)	×2
mean	.2.653 A	

Ca(4a)-polyhedron
O(1 b)	2.597(4) A	×2
O(3 k)	2.540(2)	×2
O(4 j)	2.377(5)	
O(6 a)	2.356(6)	
O(9 b)	2.341(5)	×2
mean	2.461 A	

Mg(1a)-octahedron
O(1 c)	2.034(4) A	×4
O(6 e)	2.088(5)	×2
mean	2.052 A	

Mg(2a)-octahedron
O(2 c)	2.103(4) A	×4
O(5 e)	2.002(5)	×2
mean	2.069 A	

Mg(3a)-octahedron
O(3 a)	2.067(6) A	×3
O(4 a)	2.044(6)	×3
mean	2.056 A	

Al-tetrahedron
O(7 a)	1.755(7) A	×3
O(8 a)	1.726(10)	
mean	1.748 A	

O(1 c)^O(1 d)	94.7(2)°	×2
^O(1 m)	85.3(2)	×2
^O(1 l)	180.0(0)	×2
^O(6 e)	85.6(2)	×4
^O(6 n)	94.4(2)	×4
O(6 e)^O(6 n)	180.0(0)	

O(2 c)^O(2 d)	94.9(2)°	×2
^O(2 t)	85.1(2)	×2
^O(2 s)	180.0(0)	×2
^O(5 e)	84.5(2)	×4
^O(5 u)	95.5(2)	×4
O(5 e)^O(5 u)	180.0(0)	

O(3 a)^O(3 e)	89.5(3)°	×3
^O(4 e)	86.0(2)	×6
^O(4 a)	173.6(3)	×3
O(4 a)^O(4 e)	92.2(2)	×3

| O(7 a)^O(7 e) | 111.1(3)° | ×3 |
| ^O(8 a) | 107.8(3) | ×3 |

Si(1a)-tetrahedron
O(2 t)	1.572(4) A	×2
O(4 a)	1.608(5)	
O(7 j)	1.658(7)	
mean	1.603 A	

Si(2a)-tetrahedron
O(6 a)	1.560(6) A	×3
O(8 a)	1.629(10)	
mean	1.577 A	

B(1a)-triangle
O(1 p)	1.358(5) A	×2
O(3 a)	1.312(8)	
mean	1.343 A	

B(2a)-triangle
| O(5 a) | 1.354(6) A | ×3 |

O(2 t)^O(2 v)	111.4(3)°	
^O(4 a)	107.1(2)	×2
^O(7 j)	111.4(2)	×2
O(4 a)^O(7 j)	108.1(4)	

| O(6 a)^O(6 e) | 110.1(2)° | ×3 |
| O(8 a) | 108.9(3) | ×3 |

| O(1 p)^O(1 m) | 117.4(6)° | |
| ^O(3 a) | 121.1(3) | ×2 |

| O(5 a)^O(5 e) | 120.0(0)° | ×3 |

C(1a)-triangle
O(9 a)	1.252(7) A	×2
O(10a)	1.257(9)	
mean	1.254 A	

C(2a)-triangle
| O(11a) | 1.261(12) A | ×3 |

C(3a)-triangle
| O(12a) | 1.293(12) A | ×3 |

(O,Cl a)
| Ca(2 f) | 3.175(6) A | ×3 |
| O(12 w) | 3.178(16) | ×3 |

| O(9 a)^O(9 c) | 119.2(8)° | |
| ^O(10a) | 120.4(4) | ×2 |

| O(11a)^O(11e) | 120.0(0)° | ×3 |

| O(12a)^O(12e) | 120.0(0)° | ×3 |

Standard deviations are indicated in parentheses in terms of last significant figures.

Italic letters refer to the following positions:

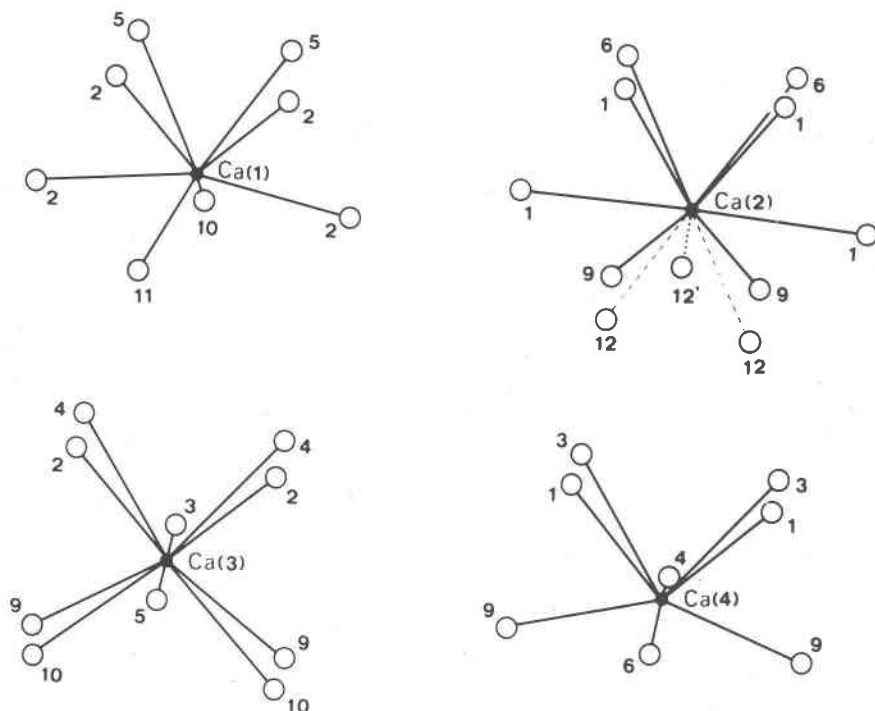| a) | x | y | z | | b) | x | z | y | | c) | y | x | z | | d) | y | z | x |
e)	z	x	y		f)	x	y	1+z		g)	y	z	1+x		h)	1+z	y	x
i)	y	z	x-1		j)	-x	-y	1-z		k)	-z	-y	1-x		l)	1-y	-x	-z
m)	1-y	-z	-x		n)	1-z	-x	-y		p)	-z	1-y	-x		q)	1-x	1-y	-z
r)	1-z	1-x	-y		s)	-y	1-x	1-z		t)	-y	1-z	1-x		u)	-z	1-x	1-y
v)	1-z	-y	1-x		w)	1-x	1-y	1-z									

FIG. 3. The coordination around calcium atoms in harkerite. The pairs Ca(1)–Ca(2),Ca(3)–Ca(4),O(1)–O(2),O(3)–O(4),O(5)–O(6) are pseudo-equivalent. The differences in the coordination between pseudo-equivalent Ca atoms arise from the positions of CO_3 oxygens, O(9–12). The bonds Ca(2)–O(12) sketched in dotted or dashed lines are alternative possibilities.

or absence of such CO_3 groups in either centro-symmetrical positions. The mean Ca–O distances in the polyhedra with coordination 8 (2.46–2.48 A) are comparable with those in sakhaite (2.46 A); the mean distances Ca–O are 2.60 and 2.65 A in the polyhedra with coordination 9 and 10 respectively.

The mean C–O distance, 1.27 A, is comparable in both minerals, whereas the average B–O lengths are somewhat lower in harkerite (1.35 instead of 1.39 A); B–O distances ranging from 1.34 to 1.38 A (mean 1.365 A) are typical for triangular borates: the values in harkerite thus cannot be considered low enough to demonstrate substitution of CO_3 for BO_3. As expected, Si–O distances are longer for the oxygens shared with Al (mean 1.64 A) with respect to the unshared ones (mean 1.57 A).

Topological features and disorder in the crystal structure of harkerite

Oxygen and calcium atoms are nearly ordered on an incomplete cubic closest packing (105 atoms are present instead of the theoretical 128 per rhombohedral unit cell). Sets of four non-equivalent layers of such atoms are perpendicular to the [111]-direction at a distance of about 2.1 A, symmetrically arranged

through twofold axes and inversion centers. Figure 4 a–d shows the atoms which make up the layers (large circles) together with those lying between the layers. The four drawings are sections of the crystal structure converted into the hexagonal unit cell (a = 10.440 A, c = 51.300 A) and projected along the three-fold axis.

Due to the close-packing arrangement of oxygen and calcium atoms, vertices, edges, and faces are largely shared between coordination polyhedra, as can be easily seen with the aid of Figure 4. The B triangles share every vertex with one Mg-octahedron and one Ca-polyhedron; in addition they share the edges with Ca polyhedra. The same feature is shown by the vertices and the edges involving unshared oxygens in the Si tetrahedra of the aluminosilicate groups. C(1)- and C(3)-carbonate triangles share both vertices and edges with Ca polyhedra, whereas the C(2)-carbonate triangle shares every vertex with two Ca-polyhedra. Six of the eight faces of the Mg octahedra are shared with Ca polyhedra. The sharing scheme between the Ca polyhedra is as follows: two vertices are common with equivalent polyhedra on the same layer, four faces are shared with polyhedra of Ca atoms lying on the adjacent (upper and lower) layers, four vertices are shared with Ca polyhedra
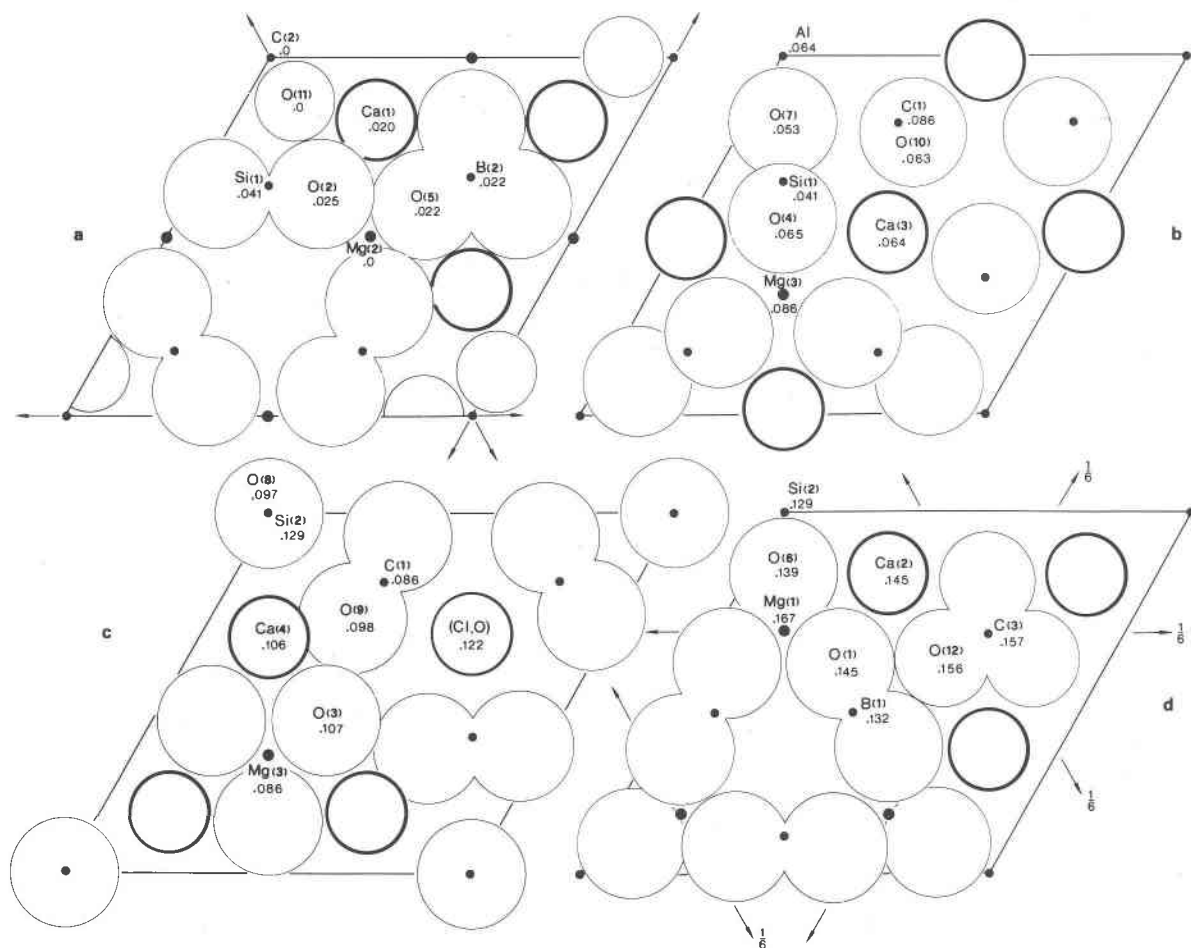
FIG. 4. Projection slabs along [001] of the crystal structure of harkerite in hexagonal unit cell: (a) $0 < z < 0.04$, (b) $0.04 < z < 0.08$, (c) $0.08 < z < 0.125$, (d) $0.125 < z$ 0.167.

lying on the layers following the adjacent ones; two of the latter sharings are lacking for the Ca(4) polyhedron. Other aspects of the crystal structure of harkerite, common with that of sakhaite, are discussed in the paper by Chichagov *et al.* (1974).

In the last stage of the least-squares refinement, a systematic disagreement between observed and calculated structure factors was noticed for the reflections having $h + k + l$ odd: F_0's were always lower than F_c's, and their R index was 2–3 times larger than that for the reflections with $h + k + l$ even. The former reflections are essentially due to the loss of the ½[111] repeat which follows from the presence of aluminosilicate and borate groups in inversion-related pairs; if these groups would repeat through a real ½[111] translation, harkerite could be well described in the cubic pseudo-cell with an acentric space group.

The agreement between observed and calculated structure factors for the reflections with $h + k + l$ odd could be improved by a partial replacement of $AlSi_4O_{16}$ by $4BO_3$ and vice-versa in the ordered structure, so as to increase the portion of the crystal structure with true ½[111] repeat. This was accomplished by matching a fraction X of the atomic positions in the unit cell with the fraction $1 - X$ of their inversion-related counterparts with respect to the pseudo-center of symmetry at 1/4, 1/4, 1/4. The best ratio $X : (1 - X) = 86 : 14$ was obtained after repeated applications of the least-squares method and reference to difference maps.

Both harkerite and sakhaite show the B_{eq} temperature factors of carbonate oxygens somewhat higher than those of the remaining oxygens (Table 3); the thermal vibrations of O(9), O(10), and, particularly, O(11) are largely anisotropic in harkerite. Such results could be also due to some disorder in the posi-

TABLE 6. Charge balance in harkerite

Atom	H	Al	Si(1)	Si(2)	B(1)	B(2)	C(1)	C(2)	C(3)	Mg(1)	Mg(2)	Mg(3)	Ca(1)	Ca(2)	Ca(3)	Ca(4)	Sum
O (1)				0.99						0.34				0.42°		0.24	1.99
O (2)		1.02									0.33		0.52°		0.20		2.07
O (3)			1.02									0.33			0.20	0.48°	2.03
O (4)		0.99										0.34		0.40°		0.26	1.99
O (5)					1.00						0.34		0.52°		0.20		2.06
O (6)				1.01						0.32				0.40°		0.26	1.99
O (7)	0.25	0.75	0.97														1.97
O (8)	0.25	0.75		0.97													1.97
O (9)						1.33								0.21	0.20	0.26	2.00
O(10)						1.33							0.28		0.40°		2.01
O(11)							0.67							0.28°			0.95 §
O(12)								0.67							0.34°°		1.01 §

° sum of two bond strengths; °° sum of three bond strengths; § occupancy 1/2

tions of the carbonate oxygens, which, as seen above, are involved only in the irregular coordination of Ca atoms.

Chemical composition of harkerite

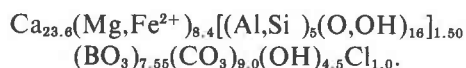Table 6 shows the charge balance (Ferguson, 1974) for the ideal cell content:

$$Ca_{24}Mg_8[AlSi_4(O,OH)_{16}]_2(BO_3)_8(CO_3)_8(H_2O,HCl),$$
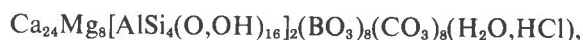
$D_{calc} = 3.00$. In the calculation the bond strengths were considered inversely proportional to the cation-oxygen distances; one hydrogen in the aluminosilicate group was considered statistically bonded to the four shared oxygens, 3×3 O(7) and O(8), whose nearest neighbors with atoms not belonging to the tetrahedral coordinations are O(7)–Ca(4) = 3.05, O(7)–O(9) = 3.29, O(8)–Ca(4) = 3.14 and O(8)–O(9) = 3.38 A. (H$_2$O, HCl) was neglected in the calculation because of its unclear crystal-chemical behavior. The charge balance is satisfactory.

The chemical analyses reported in the papers by Tilley (1951) and Ostrovskaya et al. (1966) show excess carbonate and deficient aluminosilicate and borate contents with respect to the above ideal composition of harkerite. A recalculation of the unit cell content from such analyses, made on the basis of the structural results and a sum of divalent cations equal to 32, gives
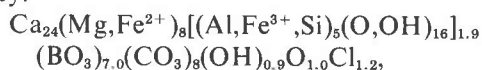
Tilley:

$$Ca_{23.8}(Mg,Fe^{2+})_{8.2}[(Al, Fe^{3+},Si)_5(O,OH)_{16}]_{1.75}$$
$$(BO_3)_{6.45}(CO_3)_{9.8}(OH)_{0.8}O_{0.9}Cl_{1.1};$$

Ostrovskaya et al.:

$$Ca_{23.6}(Mg,Fe^{2+})_{8.4}[(Al,Si)_5(O,OH)_{16}]_{1.50}$$
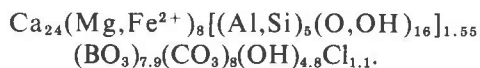$$(BO_3)_{7.55}(CO_3)_{9.0}(OH)_{4.5}Cl_{1.0}.$$
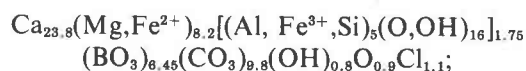
Two explanations of these discrepancies can be given: (1) according to Tilley, the alteration of harkerite yields fine-grained calcite, which can be removed only with some difficulty, and the excess CO$_2$ could then be due to calcite included in the analyzed samples; (2) some further replacements of aluminosilicate and borate groups by CO$_3$ and also (OH,H$_2$O), as suggested by Davies and Machin (1970), could occur. The structural study cannot give a conclusive answer to either alternative.

The following unit cell contents are obtained after deducting from the chemical analyses the excess CO$_2$ as Ca- and Mg-carbonates:

Tilley:

$$Ca_{24}(Mg,Fe^{2+})_8[(Al,Fe^{3+},Si)_5(O,OH)_{16}]_{1.9}$$
$$(BO_3)_{7.0}(CO_3)_8(OH)_{0.9}O_{1.0}Cl_{1.2},$$

Ostrovskaya et al.:

$$Ca_{24}(Mg,Fe^{2+})_8[(Al,Si)_5(O,OH)_{16}]_{1.55}$$
$$(BO_3)_{7.9}(CO_3)_8(OH)_{4.8}Cl_{1.1}.$$

Such stoichiometric units approach the ideal unit cell contents, but still some deficiencies remain for the aluminosilicate and borate groups.

The replacement of some B by C in the triangular ions would not significantly change the agreement between observed and calculated structure factors; on the other hand the observed B–O distances, as written above, do not confirm this substitution, and the

charge balance would be made worse by some replacement of B by C.

The $B_{eq.}$ thermal factors of Al,Si and their shared oxygens are somewhat higher than those for B,Mg and its coordinated oxygens (Table 3). Such evidence could be also interpreted as a deficiency of aluminosilicate groups in the actual structure, the unshared oxygens of the SiO_4-tetrahedra being replaced by (OH, H_2O). Both unit cell contents obtained after the deduction of some Ca–Mg carbonates would closely approach the ideal composition if this substitution is considered.

Some questions are still open about harkerite, for instance the extent of the mutual substitution among aluminosilicate, borate or other atomic groups (CO_3, OH, H_2O) and whether harkerite polymorphs are possible as a consequence of the ordering of the replacing groups. As for the former question, Barbieri *et al.* (1976) made a critical examination of several chemical analyses of harkerites (and also sakaites) from various localities. These authors found recently and studied a harkerite from Albano (Italy). This mineral is cubic, with a lattice parameter equal to that of sakhaite (pseudo-repeat for harkerite from Skye): the chemical composition is comparable with that of other harkerites, but chlorine is absent. Thus the harkerite from Albano seems to be a polymorph of the mineral from Skye. Starting from the ideal chemical formula written above, one can predict two polymorphs based on the sakhaite unit cell: a centrosymmetrical one showing complete disorder in the substitution of aluminosilicate for borate groups, and an acentric ordered polymorph when the above mentioned ½[111] repeat is strictly followed.

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