

The structure of reyerite, (Na,K)₂Ca₁₄Si₂₂Al₂O₅₈(OH)₈·6H₂O

STEFANO MERLINO

Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, 56100 Pisa, Italy

Abstract

The crystal structure of reyerite, (Na,K)₂Ca₁₄Si₂₂Al₂O₅₈(OH)₈·6H₂O, $Z = 1$, was refined in the space group $P\bar{3}$, $a = 9.765$, $c = 19.067\text{\AA}$, to $R = 0.064$ for 1540 reflections. The structure is composed of the following structural units: (a) tetrahedral sheets S_1 , with composition $(\text{Si}_8\text{O}_{20})^{8-}$, characterized by six-membered rings of tetrahedra; (b) tetrahedral sheets S_2 , characterized by six-membered rings of tetrahedra, with six tetrahedra pointing in one direction and two pointing in the other direction—the apical oxygens of these two tetrahedra connect two inversion-related S_2 sheets to build $S_2\bar{S}_2$ double sheets, with composition $(\text{Si}_{14}\text{Al}_2\text{O}_{38})^{14-}$ and ordered distribution of aluminum cations; (c) sheets O of edge-sharing calcium octahedra. The various structural units are connected through corner sharing according to the schematic sequence $\dots\bar{O}S_1OS_2\bar{S}_2\bar{O}\dots$; the corresponding composition is $[\text{Ca}_{14}\text{Si}_{22}\text{Al}_2\text{O}_{58}(\text{OH})_8]^{2-}$. The charge balance is restored by alkali cations which are placed, together with water molecules, in the cavities of the structure at the level of the double tetrahedral sheet.

KEYWORDS: reyerite, crystal structure, calcium silicates, Niakornak, Greenland.

Introduction

REYERITE was found by Gieseke in 1811 at Niakornak in Greenland and studied by Cornu and Himmelbauer (1906). It had a troubled history as a mineral species, being identified from time to time with gyrolite or truscottite. The various phases of that history were reported by Chalmers *et al.* (1964) in a very thorough study which contains comprehensive chemical analysis, infrared absorption, X-ray powder diffraction, single crystal diffraction and thermal weight loss data. They obtained the following crystal data: space group $P\bar{3}$ or $P\bar{3}$, with cell dimensions $a = 9.74$, $c = 19.04\text{\AA}$ and the cell content $\text{KCa}_{14}\text{Si}_{24}\text{O}_{60}(\text{OH})_5\cdot 5\text{H}_2\text{O}$ with minor replacement of Si by Na Al. On the basis of their data and the good basal cleavage of the mineral, they suggested a sheet structure characterized by the occurrence of Si_6O_{18} rings linked together into sheets by additional tetrahedra.

As regards the relations among the various calcium sheet silicates, Strunz and Micheelsen (1958) claimed the identity of reyerite with truscottite, and proposed that gyrolite is a water-expanded reyerite. Mamedov and Belov (1958) proposed for gyrolite and truscottite, identified with reyerite, a sheet structure characterized by a succession of calcium octahedral and silicon tetrahedral

layers, these last consisting of pentagonal and octagonal rings of alternatively up and down pointing tetrahedra.

In their paper on the synthesis and crystal chemistry of gyrolite and reyerite, Meyer and Jannarajs (1961) follow the suggestions of Strunz and Micheelsen (1958) as regards the identity of reyerite with truscottite, as well as the structural relationships between gyrolite and reyerite. However in the aforementioned paper Chalmers *et al.* (1964) concluded that reyerite closely resembles truscottite but that, because of marked differences especially in the infrared spectra, it seemed 'necessary to leave the question open as to whether truscottite should be regarded as a distinct mineral species'.

In a short note by Merlino (1972) the main features of the crystal structure of reyerite were given and the crystal chemical formula $(\text{Na,K})_2\text{Ca}_{14}\text{Si}_{22}\text{Al}_2\text{O}_{58}(\text{OH})_8\cdot 6\text{H}_2\text{O}$ was suggested. A subsequent paper on reyerite was published by Clement and Ribbe (1973) who found reyerite from a new locality in Brunswick, Virginia, and compared its chemical composition with that of samples from Greenland. Moreover these authors, unaware of the fact that the crystal structure of the mineral

Table 1. Atomic coordinates with, in parentheses, the estimated standard deviations. B_{eq} was calculated, for the atoms of the tetrahedral and octahedral sheets, as $\frac{1}{3} \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* a_i a_j$. A fixed isotropic thermal factor $B = 7.0 \text{ \AA}^2$ was assumed for the water molecules and the sodium cations. The coordinates of the two hydrogen atoms of the hydroxyl groups were obtained from the difference synthesis and a fixed $B = 3.0 \text{ \AA}^2$ was assigned to them. Multiplicity and occupancy are indicated as m and o respectively.

Site	m	o	x	y	z	B_{eq} or B (Å^2)
Ca(1)	2	1.00	2/3	1/3	0.1930(2)	0.87
Ca(2)	6	1.00	0.2437(2)	0.0502(2)	0.1698(1)	0.99
Ca(3)	6	1.00	0.3862(2)	0.4762(2)	0.1971(1)	0.88
Si(1)	6	1.00	0.2088(2)	0.3145(2)	0.0386(1)	0.63
Si(2)	2	1.00	1/3	2/3	0.0566(2)	0.61
Si(3)	6	1.00	0.3640(3)	0.2375(3)	0.3284(1)	0.79
Si(4)	6	1.00	0.1235(3)	0.3668(3)	0.3289(1)	0.72
Si(5)	2	1.00	2/3	1/3	0.4139(2)	0.69
Al(1)	2	1.00	1/3	2/3	0.4143(2)	0.68
O(1)	6	1.00	0.2157(7)	0.2622(7)	0.1178(3)	1.08
O(2)	6	1.00	0.4908(7)	0.0970(7)	0.1346(3)	1.13
O(3)	6	1.00	0.1337(7)	0.4136(7)	0.2473(3)	1.12
O(4)	6	1.00	0.4194(7)	0.2678(7)	0.2481(3)	1.20
O(5)	2	1.00	0	0	0.2198(6)	0.90
O(6)	2	1.00	1/3	2/3	0.1405(5)	0.79
O(7)	6	1.00	0.2623(7)	0.2381(7)	-0.0233(3)	1.11
O(8)	6	1.00	0.3176(7)	0.5044(7)	0.0253(3)	1.29
O(9)	6	1.00	0.2461(7)	0.3039(7)	0.3439(4)	1.66
O(10)	6	1.00	0.2669(8)	0.0496(7)	0.3460(3)	1.55
O(11)	2	1.00	1/3	2/3	0.5038(7)	2.63
O(12)	6	1.00	0.1625(7)	0.5076(7)	0.3826(4)	1.46
O(13)	6	1.00	0.5085(7)	0.3271(7)	0.3838(4)	1.78
O(14)	6	0.35	0.2901(95)	0.0169(59)	0.5021(27)	7.0
O(15)	6	0.53	0.3676(63)	0.0212(40)	0.4996(18)	7.0
O(16)	6	0.20	0.1669(120)	-0.0266(100)	0.5035(47)	7.0
Na(1)	2	0.17	0	0	0.4389(53)	7.0
Na(2)	6	0.12	0.5436(120)	0.0123(100)	0.4975(50)	7.0
Na(3)	6	0.09	0.1083(150)	0.0137(150)	0.4814(60)	7.0
H(1)	6	1.00	0.500	0.114	0.086	3.0
H(2)	2	1.00	0	0	0.270	3.0

The refinement was carried out with a new data set, collected by means of a Nicolet P3 four-circle diffractometer from a crystal fragment with dimensions $0.68 \times 0.16 \times 0.025 \text{ mm}^3$. The cell parameters, $a = 9.767$, $c = 19.067 \text{ \AA}$, obtained using Mo- $K\alpha$ radiation and a graphite monochromator ($\lambda = 0.71069 \text{ \AA}$), were in very good agreement with the values $a = 9.765$ (3), $c = 19.067$ (3) Å obtained by Clement and Ribbe (1973) by least squares refinement of powder diffractometer data collected using Cu- $K\alpha$ radiation and Si metal as an internal standard. Intensity data were collected for 1834 independent reflections with $2\theta < 50^\circ$, according to the $\omega/2\theta$ scan method. The instrument was permitted to vary the scan rate in relation to the intensity being measured. No absorption correction was applied (linear absorption coefficient $\mu = 17.5 \text{ cm}^{-1}$). Calculations were carried out on the Honeywell 66/80 computer of the Computing Centre of the University of Aberdeen. The programs were those of SHELX76 System (Sheldrick, 1976), modified for use on that computer by R. Alan Howie of the University of Aberdeen. Scattering factors were taken from International Tables for X-ray Crystallography (1974).

Determination and refinement of the structure

The structure was solved by the symbolic addition procedure using the photographic data set. The origin of the unit cell was fixed by assigning the positive sign to a reflection with odd l index and five more signs were obtained by the application of the Σ_1 relation, whereas symbols A , B and C^1 were assigned to three additional reflections. In the course of the application of the Σ_2 formula there were several indications that $B = +$, whereas A and C remained undetermined. Of the four possible sign combinations, that corresponding to both signs being positive was discarded because all the signs would be positive. That corresponding to both signs being negative was discarded on the basis of the following considerations: reflections 0014 and 0024 were indicated as C and AB respectively by the Σ_2 relationships; moreover they were indicated as positive by Σ_1 relationship with probabilities 0.89 and 0.88 respectively; therefore the probability that both are negative is low (0.02). The two remaining possibilities were tested: the three-dimensional E -map corresponding to the choice $A = +$, $C = -$, calculated with the contribution of 290 of the

¹ A Table presenting the statistical averages and distribution of E values, together with sign and symbol assignments, is deposited in the Mineralogical Library at the British Museum (Natural History).

was already known, proposed for reyerite a structure made up of modified mica sheets stacked normal to c .

Recently the crystal structural study of gyrolite (Merlino, 1988) made necessary a more thorough account of the structure of reyerite, as the architecture of gyrolite can be fully appreciated only in relation to that of reyerite and, as matter of fact, it was derived on the basis of the structure of reyerite. The present work is an extension of the 1972 note and offers a more complete account of the crystal structure of reyerite.

Experimental

The structure determination was carried out on a sample from Niakornak, kindly donated by H. F. W. Taylor, with intensity data collected by means of integrated Weissenberg photographs, using the Cu- $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The statistical averages and the distribution of the normalized structure factor magnitudes E gave evidence for the presence of a centre of symmetry: thus the space group $P\bar{3}$ was assumed for reyerite and this choice was subsequently confirmed by the results of the structure analysis.

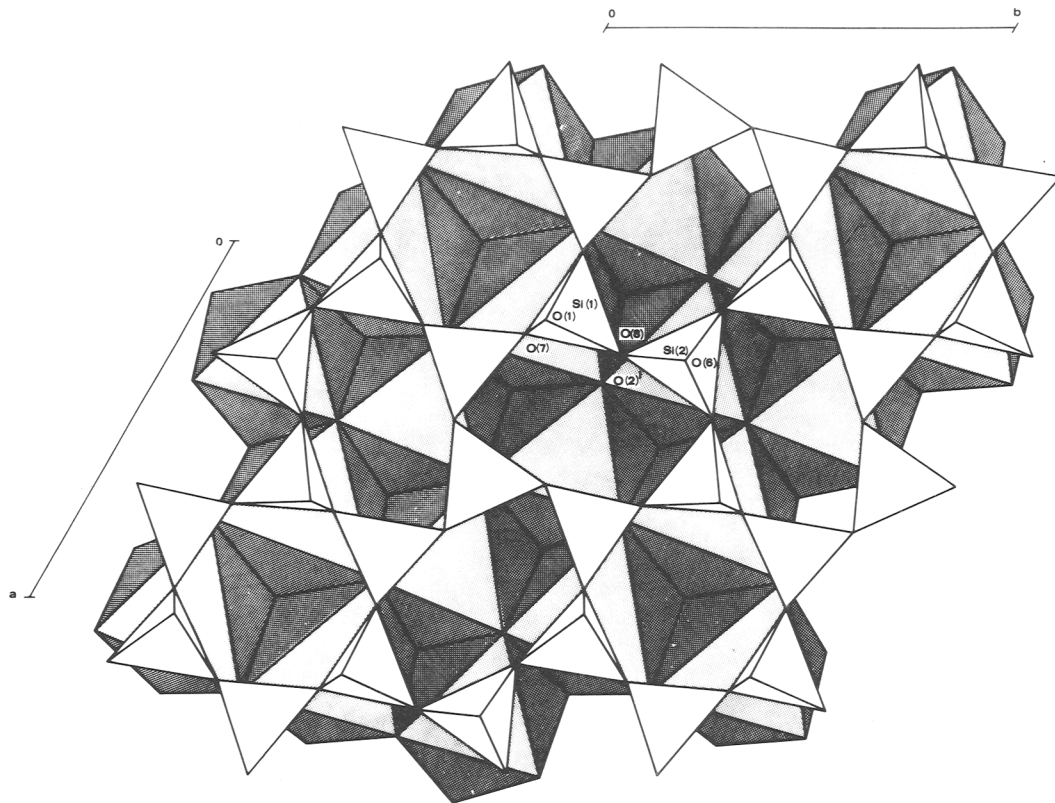


FIG. 1. Projection along c of the crystal structure of reyerite included in a slab between $z \approx -0.25$ and $z \approx 0.15$. The figure shows the connection between the tetrahedral sheet S_1 and the preceding octahedral sheet.

largest E_s , clearly showed distinct maxima which, on the basis of their heights, were attributed to calcium and silicon atoms, as well as a number of lower peaks among which the positions of oxygen and hydroxyl ions were selected on the basis of crystal chemical considerations. The structure was completed, locating the alkali cations and water molecules, and then refined to a $R = 0.095$ for 1322 measured reflections.

In the subsequent structure refinement, carried out with the diffractometer data set, all the atoms, apart from the alkali cations and water molecules with partial occupancies, were initially placed in the positions found in the preceding stage carried out with photographic data. After three cycles of least squares refinement the atom set was completed by means of a difference Fourier synthesis, which gave the position of the missing water molecules O(14), O(15) and O(16) located with partial occupancy on adjacent sites, and alkali cations, distributed with low occupancies in two sites

Na(1) and Na(2): their nature was established on the basis of crystal chemical considerations. More cycles of least squares refinement were carried out: because of the strong correlation between occupancy factors and thermal parameters, a common fixed isotropic thermal parameter was given to the water molecules and alkali cations; anisotropic thermal parameters were introduced for the other atoms. After four least squares block diagonal refinement cycles, a difference Fourier synthesis was calculated: two distinct peaks near O(2) and O(5) positions were attributed to hydrogen atoms; another peak, at 0.10, 0.02, 0.48, was attributed to an alkali cation Na(3) with very low occupancy. These atoms were introduced in the least squares refinement, assuming, for the hydrogen atoms, fixed positional and thermal parameters. Two final cycles led to $R = 0.064$ for 1540 reflections with $F_0 \geq 2\sigma(F_0)$. The reflections were weighted according to the reciprocal of the variance, estimated from the counting statistics; the

final R_w value was 0.063. The refinement was stopped at this point since the ratio of the shift to the error was less than 0.3 for the parameters of all the atoms with full site occupancy.

The atomic coordinates are given in Table 1. Observed and calculated structure factors, as well as anisotropic thermal parameters for the atoms in the tetrahedral and octahedral sheets, are deposited in the Mineralogy Library at the British Museum (Natural History).

Description and discussion of the structure

The crystal structure of reyerite is represented in Figs. 1, 2 and 3. It is composed of the following structural units: (a) a tetrahedral sheet, with composition $(\text{Si}_8\text{O}_{20})^{8-}$ and characterized by six-membered rings; (b) a tetrahedral double sheet, with composition $(\text{Si}_{22}\text{Al}_2\text{O}_{38})^{14-}$; (c) a sheet of edge-sharing calcium octahedra. These structural units are stacked through corner sharing as illustrated in Fig. 3. Alkali cations and water molecules are located in the cavities of the structure at the level of the double tetrahedral sheet.

Tetrahedral sheets. The new and unexpected feature in the crystal structure of reyerite is the presence of two different tetrahedral sheets. Both sheets can be described as made up by two-dimensional connection of groups of four tetrahedra. In the first sheet, S_1^1 , the group is built up by an Si(2) tetrahedron in special position along a threefold axis and three crystallographically equivalent groups, as described in Fig. 1, to give an infinite sheet with composition $(\text{Si}_8\text{O}_{20})^{8-}$, characterized by the presence of two kinds of six-membered rings of tetrahedra; the first, with trigonal symmetry, presents alternatively up and down pointing tetrahedra: this kind of sequence is conveniently denoted as 1,3,5; the second, with oval shape, has three down pointing tetrahedra, followed by three up pointing tetrahedra, and may be denoted as 1,2,3-ring (Fig. 1).

In the sheet S_2 there are two crystallographically independent groups of four tetrahedra, made up

by Si(5) and Al up-pointing tetrahedra linked to three symmetry-related down-pointing tetrahedra Si(3) and Si(4) respectively (Fig. 2). Each group is connected to three groups of the other type to build a two-dimensional sheet. As in the case of S_1 , two kinds of six-membered rings are also present in S_2 : the first is an almost hexagonal ring of down-pointing tetrahedra; the second with oval shape, may be denoted as a 1,4-ring, composed of two separated pairs of down-pointing tetrahedra, connected by up-pointing Si(5) and Al tetrahedra.

The S_1 and S_2 sheets may also be described as formed by the connection of four-repeat chains, the translational unit presenting three tetrahedra pointing in one direction and one tetrahedron pointing in the opposite direction: in the S_1 sheet inversion equivalent chains follow each other, whereas in the S_2 sheet similar, although crystallographically independent chains, follow each other.

Clement and Ribbe (1973) in their crystal chemical study of reyerite proposed three structures for the tetrahedral sheets. Their suggestion was exceedingly good: the structural schemes *a* and *b* in Fig. 1 of their paper (Clement and Ribbe, 1973) closely approximate the actual shape of sheets S_2 and S_1 respectively. To obtain a perfect match, the four tetrahedra placed along the threefold axes in the schemes *a* and *b* must be reversed. However they obviously could not anticipate either that aluminum cations are ordered in the S_2 sheet, or that the S_2 sheet is connected to an inversion-related \bar{S}_2 sheet through the apical oxygen atoms of Si(5) and Al tetrahedra to build a double $S_2\bar{S}_2$ sheet with chemical composition $(\text{Si}_{14}\text{Al}_2\text{O}_{38})^{14-}$. Reyerte is therefore the first example of a mineral species with mixed tetrahedral sheets, according to Zoltai's classification (Zoltai, 1960).

The bond distances in the various tetrahedra are given in Table 2*. The values of the bond distances clearly indicate that aluminum cations are perfectly ordered in the Al site. The Al-O(11)-Si(5) angle of 180° is quite unusual and it is probable that O(11) atoms present positional

¹ The sheets S_1 and S_2 were called $T(1)$ and $T(2)$ respectively in the short preliminary note (Merlino, 1972).

*In Tables 2 and 3, in Fig. 1, as well as in the text, the atoms are related to the corresponding atoms in the asymmetric unit as follows:

i	atom at	$x - y$	x	$-z$	viii	atom at	$1 - y$	$1 + x - y$	z
ii	atom at	$1 - x$	$-y$	$1 - z$	ix	atom at	y	$y - x$	$-z$
iii	atom at	$-x$	$-y$	$1 - z$	x	atom at	$1 + x - y$	x	$1 - z$
iv	atom at	$y - x$	$-x$	z	xi	atom at	x	$-1 + y$	z
v	atom at	$-y$	$x - y$	z	xii	atom at	y	$y - x$	$1 - z$
vi	atom at	$1 - x$	$1 - y$	$1 - z$	xiii	atom at	$x - y$	x	$1 - z$
vii	atom at	$1 + y - x$	$1 - x$	z	xiv	atom at	$1 - y$	$x - y$	z

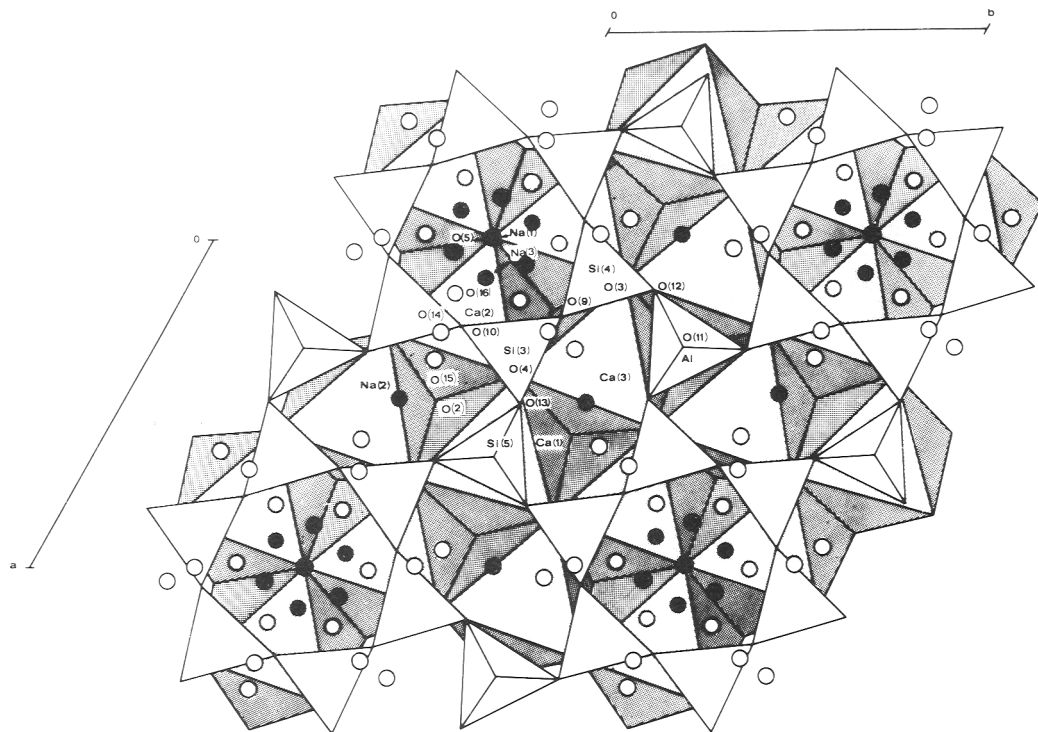


Fig. 2. Projection along c of the crystal structure of reyerite included in a slab between $z \approx 0.15$ and $z \approx 0.50$. The figure shows the connection between the tetrahedral sheet S_2 and the octahedral sheet O . White and black circles represent water molecules and sodium cations located, with partial occupancies, at $z \approx 0.5$ inside the double tetrahedral sheet. In the figure the Na(2) cation is located, for the sake of simplicity, on the inversion centre at $(\frac{1}{2}, 0, \frac{1}{2})$, although it is located some little way from this point.

disorder, being distributed around the threefold axis so that the Al–O(11)–Si(5) group assume a bent configuration; the relatively high thermal parameters of O(11) seem indicative of such distribution.

Octahedral sheet. Three independent calcium cations, Ca(1), Ca(2) and Ca(3), occur in the octahedral sheet O . The nature of the ligands was easily determined: the oxygen atoms of the octahedral sheet which are coordinated also to silicon cations correspond to oxide anions, whereas the remaining oxygen atoms, O(2) and O(5), correspond to hydroxyl anions. In fact the two located hydrogen atoms H(1) and H(2) are linked to O(2), with sixfold multiplicity, and to O(5), with twofold multiplicity, respectively. It seems useful to remark that this is in keeping with the results of the infrared absorption studies by Chalmers *et al.* (1964), who observed that the sharp absorption band near 3600 cm^{-1} , due to hydroxyl groups coordinated only to calcium cations, 'was resolved into two components under grating resolution,

showing then a principal peak at 3639 cm^{-1} with a much weaker subsidiary one at 3612 cm^{-1} .'

Ca(1), Ca(2) and Ca(3) cations are coordinated by three, four and five oxide anions respectively, the octahedral coordination being completed by three, two and one hydroxyl anions respectively. A seventh weak bond is formed by Ca(2) cation: it is reported in Table 4, but not represented in the figures. The octahedra are connected by edge sharing to build infinite sheets with seven octahedra within the unit net and chemical composition $[\text{Ca}_7\text{O}_{10}(\text{OH})_4]^{4-}$.

Stacking of the sheets. Two inversion-related octahedral sheets, O and \bar{O} , are present in the unit cell, both sandwiched between a single S_1 and a double $S_2\bar{S}_2$ tetrahedral sheet. The stacking sequence in reyerite can be conveniently represented by the scheme $\bar{O}S_1OS_2\bar{S}_2O\dots$, and is illustrated in Fig. 3; the corresponding composition is $[\text{Ca}_{14}\text{Si}_{22}\text{Al}_2\text{O}_{58}(\text{OH})_8]^{2-}$. The charge balance is restored by alkali cations which are placed, together with water molecules, in the cavities of

Table 2. Bond distances, in Å, in tetrahedral and octahedral sheets, with the estimated standard deviations in parentheses.

Si(1) - O(1)	1.606 (7)	Si(4) - O(12)	1.600 (8)
0(7)	1.616 (8)	0(3)	1.611 (6)
0(8)	1.632 (6)	0(9)	1.621 (9)
0(7) ⁱ	1.636 (8)	0(10) ^v	1.621 (7)
Si(2) - O(6)	1.600 (10)	Si(5) - O(11) ^{vi}	1.569 (14)
0(8) x3	1.627 (7)	0(13) x3	1.620 (8)
Si(3) - O(4)	1.601 (6)	Al - O(11)	1.706 (14)
0(9)	1.607 (9)	0(12) x3	1.723 (5)
0(13)	1.624 (7)		
0(10)	1.625 (6)		
Ca(1) - O(2) x3	2.356 (6)	Ca(3) - O(2) ^{vii}	2.334 (7)
0(4) x3	2.408 (7)	0(3) ^{viii}	2.400 (7)
		0(4)	2.419 (8)
Ca(2) - O(2)	2.319 (7)	0(6)	2.420 (5)
0(5)	2.376 (5)	0(3)	2.422 (7)
0(1)	2.431 (8)	0(1)	2.438 (6)
0(4)	2.458 (6)		
0(3) ^{iv}	2.485 (7)	0(2) - H(1)	0.95
0(1) ^{iv}	2.537 (8)	0(5) - H(2)	0.95
0(7) ^{ix}	2.880 (8)		

the structure at the level of the double tetrahedral sheet.

Alkaline cations and water molecules. As previously stated, the maxima in the Fourier syntheses outside the tetrahedral and octahedral sheets were attributed to alkaline cations or water molecules on the basis of the known chemical data and crystal chemical considerations. The positions and occupancies of the alkali cations were refined assuming the scattering factor for sodium.

The bond distances in the coordination polyhedra around Na(1), Na(2) and Na(3) are given in Table 3. Na(2) is located near an inversion centre and its inversion related Na(2)ⁱⁱ is at a dis-

tance of 0.77 Å, so the two sites cannot be simultaneously occupied. Both sites are coordinated by six oxygen atoms from the tetrahedral double sheet: the coordination is completed by two water molecules O(14) and O(15)ⁱⁱ, when the Na(2) site is occupied, and by O(14)ⁱⁱ and O(15) when the Na(2)ⁱⁱ site is occupied. Na(1) is linked on one side to three O(10) oxygen atoms, with three more distant O(9) atoms at 3.28 Å, on the other side to six O(14) water molecules at nearly 3 Å. Na(3) is linked to only one oxygen atom of the tetrahedral framework and its coordination is completed by water molecules: the bonded molecules were found by listing all the Na(3)-O distances less than 3.0 Å and excluding the oxygen atoms too close to Na(3). The three ligands O(15)ⁱⁱⁱ, O(15)^{iv} and O(15)^v cannot be simultaneously present, as O(15)ⁱⁱⁱ is too close (1.78 Å) to the other two ligands.

It should be remarked that although the positions and occupancies of the alkali cations were refined assuming the scattering factor for sodium, the coordination and bond distances for the Na(1) site indicate it is more apt to host potassium cations.

Crystal chemical considerations

The results of the crystal structure analysis may be summarized by the following ideal crystal chemical formula: $(\text{Na}, \text{K})_2\text{Ca}_{14}\text{Si}_{22}\text{Al}_2\text{O}_{58}(\text{OH})_8 \cdot 6\text{H}_2\text{O}$.

It would remark that what appears well established by the structural study is the presence of 2 Al, 22 Si, 8 hydroxyls and 14 Ca cations, with possible minor substitution by x Na cations. This obviously constrains the number of alkali cations, which must be equal to $2 + 2x$. Because of the zeolitic character of the reyerite structure at the level of $S_2\bar{6}_2$ sheet, the alkali cations, and water molecules as well, may be highly dispersed within the double tetrahedral sheet and the alkali content 1.7 (Na + K), corresponding to the combined site occupancies of Na(1), Na(2) and Na(3), pro-

Table 3. Bond distances, in Å, in the coordination polyhedra around Na(1), Na(2) and Na(3). Estimated standard deviations are given in parentheses.

Na(1) - O(10)	x3 2.98 (6)	Na(2) - O(13) ^{xiv}	2.63 (9)	Na(3) - O(10)	2.94 (12)
0(9)	x3 3.28 (6)	0(12) ^x	2.64 (9)	0(16) ^v	2.30 (28)
0(14)	x3 3.01 (10)	0(11) ^{vi}	2.74 (9)	0(14) ^{xiii}	2.37 (14)
0(14) ^{xiii}	x3 2.98 (14)	0(12) ^{iv}	2.86 (9)	0(14) ^{xii}	2.50 (20)
		0(11) ^{xii}	2.95 (8)	0(15)	2.52 (17)
		0(13) ^{xii}	3.03 (9)	0(16) ^{iv}	2.60 (21)
		0(14)	2.50 (16)	0(16) ⁱⁱⁱ	2.77 (21)
		0(16) ⁱⁱ	2.76 (18)		

Table 4. Chemical formulae, calculated on the basis of 24(Si+Al) cations, obtained from the four known analyses of Niakornak reyerite.

	A	B	C	D
Si	22.1	22.2	21.9	21.9
Al	1.9	1.8	2.1	2.1
Ca	14.4	14.4	13.3	13.6
Na	1.9	n.d.	1.3	2.7
K	0.8	n.d.	n.d.	1.1
O	62.8	61.5	60.9	62.5
H ₂ O	9.4	9.3	10.8	4.8

A. Chalmers *et al.* (1964); analyst R.A. Chalmers.

B. Cornu and Himmelbauer (1906).

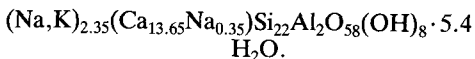
C. Bøggild (1908); analyst C. Christensen.

D. Clement and Ribbe (1973).

bably indicates only the lower limit of the actual value.

To obtain the correct number of alkali cations we have to rely on the indications derived from the chemical data. The chemical formulae reported in Table 4 were obtained from the four known chemical analyses of reyerite from Niakornak, assuming 24 (Si + Al) cations. The most complete analysis is that by Chalmers *et al.* (1964) and indicates 2.7 alkali cations. The microprobe analysis given by Clement and Ribbe (1973) shows a low water and high alkali content, although the K/Na ratio closely corresponds to that found by Chalmers *et al.* (1964): it is possible that, because of the zeolitic character of reyerite, not only some water was driven off by the heat of the electron beam, but also that the measured alkali contents can be affected by an apparent increase due to the easy migration of Na and K (Rinaldi, 1981; Chandler, 1973).

If we assume as correct the alkali cations and water molecules content indicated by Chalmers *et al.* (1964) the resulting crystal chemical formula for Greenland reyerite is:

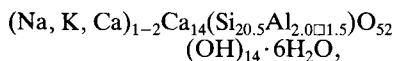


The Ca content closely corresponds to that indicated by Clement and Ribbe (1973), with a calculated density of 2.590 g cm^{-3} , to be compared with the value 2.578 g cm^{-3} reported by Bøggild (1908).

As regards the water content the agreement with the chemical data by Chalmers *et al.* (1964), as well as by Cornu and Himmelbauer (1906) and Bøggild (1908) is satisfactory. Moreover Chalmers *et al.* (1964) by weight loss studies determined that water is lost in two steps, the first, corresponding to the loss of 5.8 water molecules is completed at 400°C , the second one, which begins at 650°C , corresponds to the loss of 3.6 water molecules. They attribute the two steps to the loss of water present in reyerite as water mole-

cules and hydroxyl anions respectively, which is in good agreement with the six water molecules and the eight hydroxyl ions indicated by the structure analysis.

Chemical and crystallographic data are also known for reyerite from Brunswick County, Virginia (Clement and Ribbe, 1973) and from Isle of Mull, Scotland (Cann, 1965). Whereas reyerite from Virginia appears quite similar to that from Greenland, apart some differences in the alkali contents, reyerite from Scotland shows a much higher water content together with a deficiency of 1.5 atoms from the expected 24(Si + Al) atoms in the unit cell. Assuming that $1.5(\text{O}_4\text{H}_4)^{4-}$ substitute for $(\text{SiO}_4)^{4-}$ anions (Cann, 1965), the following formula may be suggested for reyerite from Mull:



with some substitution of Ca by Mg and Fe in the octahedral sheet.

Chalmers *et al.* (1964) made a thorough comparison of the infrared absorption spectra of reyerite, natural truscottite and synthetic preparations obtained hydrothermally from mixtures of $\text{Ca}(\text{OH})_2$ and SiO_2 gel. They found a close analogy between the spectra of natural truscottite on one side and the synthetic preparations on the other side, including the preparation obtained from Meyer and Jaunarais (1961) and described as reyerite from those authors: the preparations must therefore be classified as synthetic truscottites.

They observed appreciable differences between reyerite and truscottite in the region at $600\text{--}850 \text{ cm}^{-1}$, namely in the region associated with Si–O–Si linkages, and in the band at 1640 cm^{-1} , attributed to molecular water. However reyerite has also 'features in common with natural truscottite and the synthetic preparations, particularly in the $400\text{--}650 \text{ cm}^{-1}$ region, and the absorption of their ionic hydroxyl groups occurs at identical frequencies, although that of natural truscottite is weaker and broader than the others' (Chalmers *et al.*, 1964).

Reyerite and truscottite present significant differences in chemical composition, with higher water, alkali and aluminum contents in reyerite, and also in the length of their *c* parameters.

All the differences in chemistry, infrared spectra, as well as in crystallographic parameters, may be explained assuming that reyerite is characterized, in comparison with natural and synthetic truscottite, by the presence of two ordered Al cations in the unit cell. This clearly explains the chemical features of reyerite: the substitution of

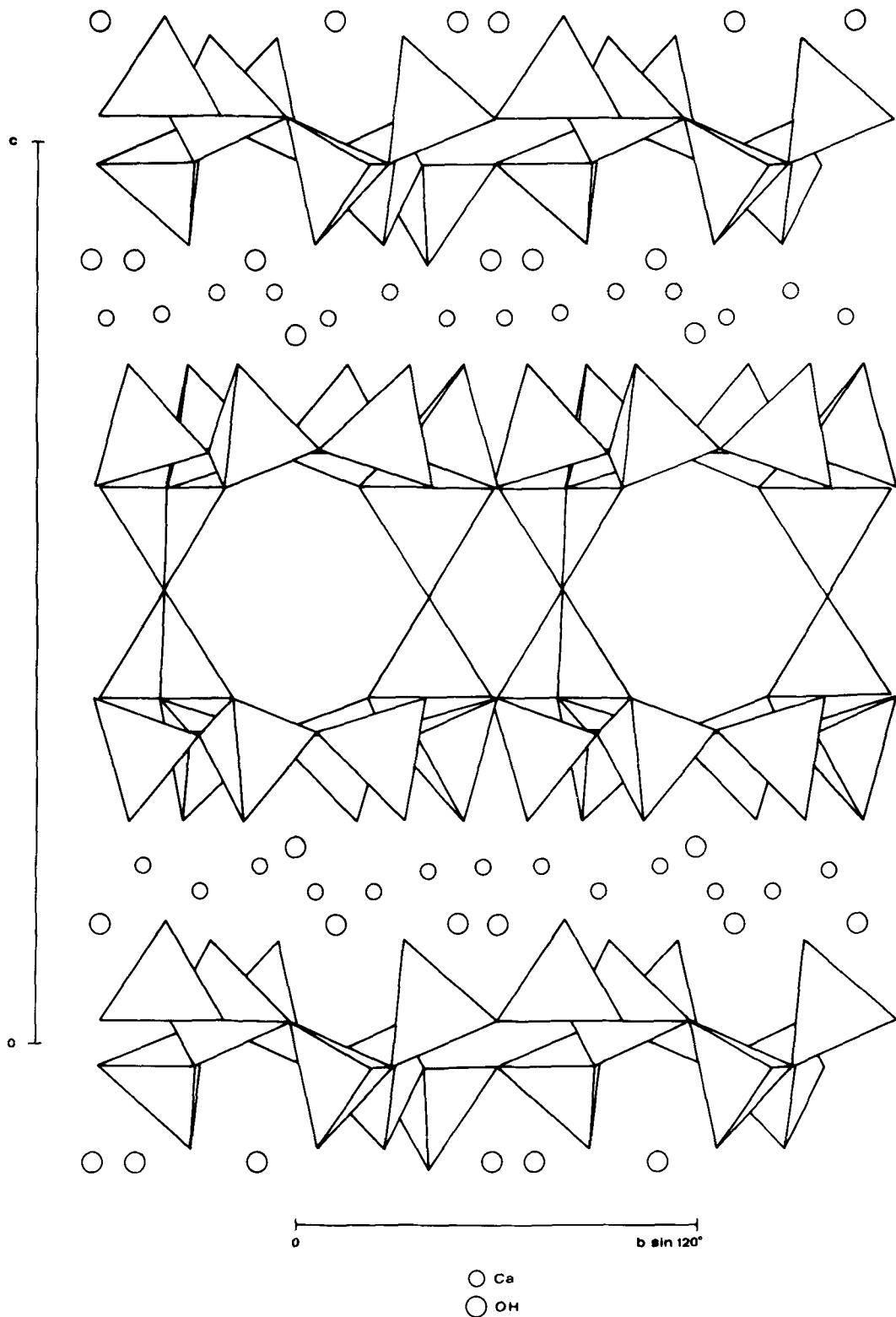


FIG. 3. The crystal structure of reyerite as viewed along a . Small and large open circles represent calcium cations and hydroxyl groups respectively. The water molecules and alkali cations inside the double tetrahedral sheet are not represented in the figure.

Si by Al cations requires not only the introduction of alkali cations in the cavities of the S_2S_2 sheet, where Al is located, to restore the charge balance, but also the introduction of water to complete the coordination of the alkali cations.

This model is completely consistent with the indications of the absorption spectra; the differences in the band at 1640 cm^{-1} can be explained with the different water content in reyerite and truscottite, whereas the differences in the region $600\text{--}850\text{ cm}^{-1}$ are related to the presence of Si–O–Al linkages in reyerite. These considerations suggest for truscottite the following crystal chemical formula: $\text{Ca}_{14}\text{Si}_{24}\text{O}_{58}(\text{OH})_8 \cdot x\text{H}_2\text{O}$ with $0 < x < 6$.

Lachowski *et al.* (1979) studied by analytical electron microscopy and X-ray powder diffraction eleven specimens of natural and synthetic truscottite, including gyrolite–truscottite intergrowths. They conclusively demonstrated that, in the absence of substitutions, the formula of truscottite is $\text{Ca}_{14}\text{Si}_{24}\text{O}_{58}(\text{OH})_8 \cdot 2\text{H}_2\text{O}$. Truscottite thus appears, from the synthetic standpoint, as the counterpart of reyerite obtained where aluminum and alkali cations are absent: however it can also accommodate some Al, probably randomly distributed, with increase in the c parameter, as well as K cations, thus approaching the composition of reyerite (Lachowski *et al.*, 1979).

Acknowledgements

The author is indebted to all the friends and colleagues of the Department of Chemistry of the University of Aberdeen, where he carried out the intensity data collection and structure refinement. In particular he is very grateful to H. F. W. Taylor and L. Dent Glasser, who

made the facilities of the Department available and to R. A. Howie and D. C. Neill Swindells for their generous help in data collection and computer calculations. Support by 'Centro di studio per la Geologia strutturale e dinamica dell'Appennino', C.N.R., is acknowledged.

References

- Bøggild, O. B. (1908) *Medd. Grønland*, **34**, 91.
 Cann, J. R. (1965) *Mineral. Mag.* **35**, 1.
 Chalmers, R. A., Farmer, V. C., Harker, R. I., Kelly, S. and Taylor, H. F. W. (1964) *Ibid.* **33**, 821.
 Chandler, J. A. (1973) *J. Microscopy*, **98**, 359.
 Clement, S. C. and Ribbe, P. H. (1973) *Am. Mineral.* **58**, 517.
 Cornu, F. and Himmelbauer, A. (1906) *Tschermaks Mineral. Petrogr. Mitt.* **25**, 519.
 International Tables for X-ray Crystallography (1974) Vol. IV. Birmingham: Kynoch Press.
 Lachowski, E. E., Murray, L. W. and Taylor, H. F. W. (1979) *Mineral. Mag.* **43**, 333.
 Mamedov, Kh. S. and Belov, N. V. (1958) *Dokl. Akad. Nauk SSSR*, **121**, 720.
 Merlino, S. (1972) *Nature Physical Science*, **238**, 124.
 ——— (1988) *Mineral. Mag.* **52** (in press).
 Meyer, J. W. and Jaunarajs, J. L. (1961) *Am. Mineral.* **46**, 913.
 Rinaldi, R. (1981) In *Microscopia elettronica a scansione* (Armigliato, A. and Valdrè, U., eds.) Lab. di Micr. Elett., Univ. di Bologna.
 Sheldrick, G. M. (1976) *SHELX 76. A program for crystal structure determination*. Univ. of Cambridge, England.
 Strunz, H. and Micheelsen, H. (1958) *Naturwiss.* **45**, 515.
 Zoltai, T. (1960) *Am. Mineral.* **45**, 960.

[Manuscript received 5 January 1987; revised 31 March 1987]