

# The structure of reyerite, $(\text{Na},\text{K})_2\text{Ca}_{14}\text{Si}_{22}\text{Al}_2\text{O}_{58}(\text{OH})_8 \cdot 6\text{H}_2\text{O}$

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## Abstract

The crystal structure of reyerite,  $(\text{Na},\text{K})_2\text{Ca}_{14}\text{Si}_{22}\text{Al}_2\text{O}_{58}(\text{OH})_8 \cdot 6\text{H}_2\text{O}$ ,  $Z = 1$ , was refined in the space group  $P\bar{3}$ ,  $a = 9.765$ ,  $c = 19.067\text{Å}$ , 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  $P3$  or  $P\bar{3}$ , with cell dimensions  $a = 9.74$ ,  $c = 19.04\text{Å}$  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  $\text{Si}_6\text{O}_{18}$  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  $(\text{Na},\text{K})_2\text{Ca}_{14}\text{Si}_{22}\text{Al}_2\text{O}_{58}(\text{OH})_8 \cdot 6\text{H}_2\text{O}$  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.  $B_{\text{eq}}$  was calculated, for the atoms of the tetrahedral and octahedral sheets, as  $\frac{1}{3}\sum_{i=1}^3 U_{ii} a_i^2$ . 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	$m$	$o$	$x$	$y$	$z$	$B_{\text{eq}}$ or $B$ ( $\text{\AA}^2$ )
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

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  $\text{Cu-K}\alpha$  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.

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  $\text{Mo-K}\alpha$  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)  $\text{ \AA}$  obtained by Clement and Ribbe (1973) by least squares refinement of powder diffractometer data collected using  $\text{Cu-K}\alpha$  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  $\Sigma_1$  relation, whereas symbols  $A$ ,  $B$  and  $C^1$  were assigned to three additional reflections. In the course of the application of the  $\Sigma_2$  formula there were several indications that  $B = +$ , whereas  $A$  and  $C$  remained indetermined. 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  $\Sigma_2$  relationships; moreover they were indicated as positive by  $\Sigma_1$  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

<sup>1</sup> 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).

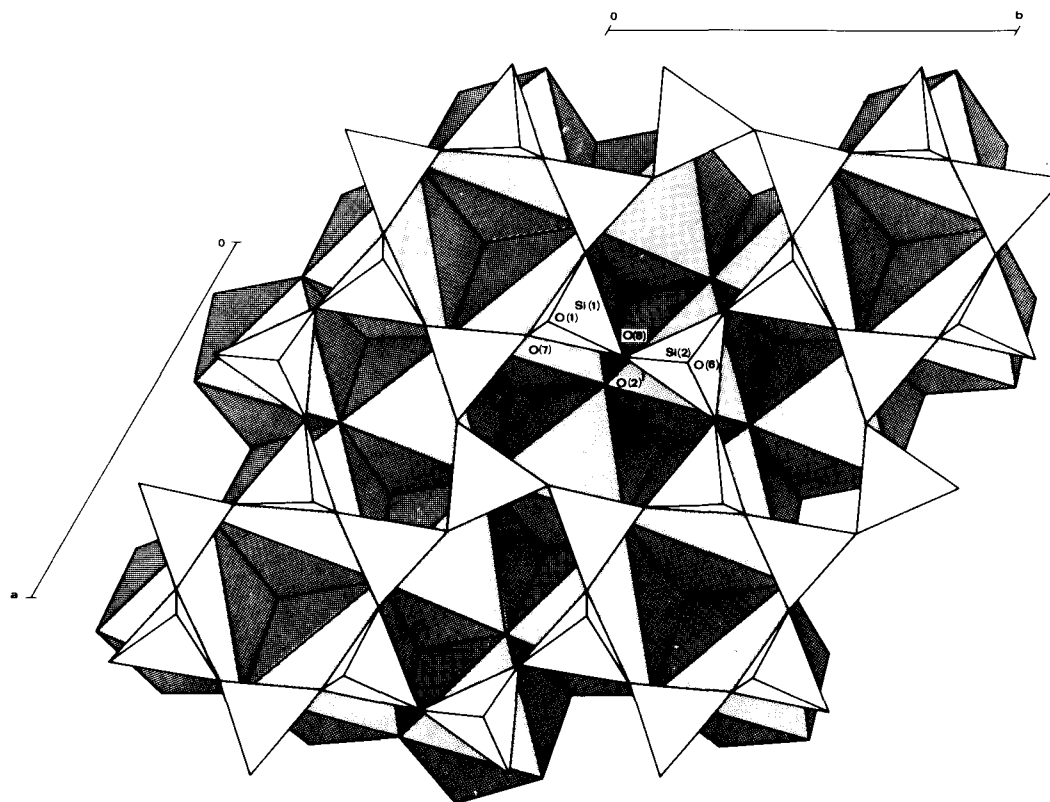


Fig. 1. Projection along  $c$  of the crystal structure of reyerite included in a slab between  $z \approx -0.25$  and  $z \approx 0.15$ . The figure shows the connection between the tetrahedral sheet  $S_1$  and the preceding octahedral sheet.

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  $\text{Si}(2)$  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  $\text{Si}(5)$  and Al up-pointing tetrahedra linked to three symmetry-related down-pointing tetrahedra  $\text{Si}(3)$  and  $\text{Si}(4)$  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  $\text{Si}(5)$  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  $\text{Si}(5)$  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  $180^\circ$  is quite unusual and it is probable that O(11) atoms present positional

<sup>1</sup> 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	$1-y$	$x-y$	$z$

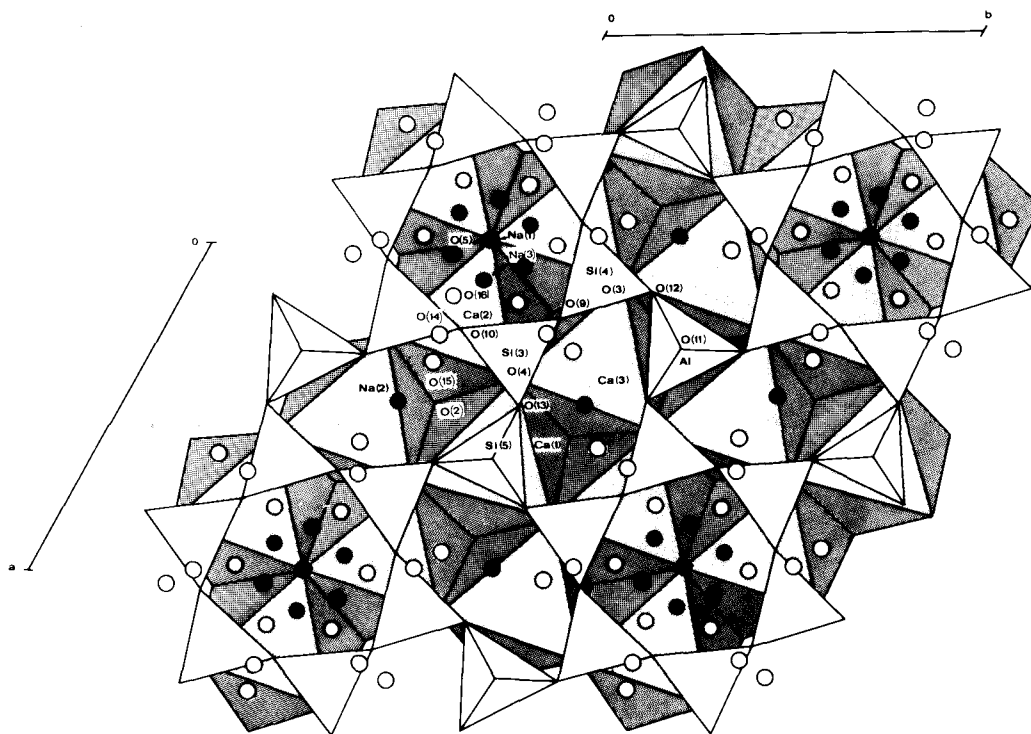


FIG. 2. Projection along  $c$  of the crystal structure of reyerite included in a slab between  $z \approx 0.15$  and  $z \approx 0.50$ . The figure shows the connection between the tetrahedral sheet  $S_2$  and the octahedral sheet  $O$ . White and black circles represent water molecules and sodium 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  $3600\text{ cm}^{-1}$ , due to hydroxyl groups coordinated only to calcium cations, 'was resolved into two components under grating resolution,

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

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  $S_2S_2$  tetrahedral sheet. The stacking sequence in reyerite can be conveniently represented by the scheme  $\bar{O}S_1OS_2\bar{S}_2\bar{O} \dots$ , and is illustrated in Fig. 3; the corresponding composition is  $[\text{Ca}_4\text{Si}_{22}\text{Al}_2\text{O}_{58}(\text{OH})_8]^{2-}$ . The charge balance is restored by alkali cations which are placed, together with water molecules, in the cavities of

