

Crystal structure of minehillite: Twinning and structural relationships to reyerite

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ABSTRACT

The crystal structure of minehillite from Franklin, New Jersey, $(K,Na)_2Ca_{28}Zn_5Al_4Si_{40}O_{112}(OH)_{16}$, was solved and refined in space group $P\bar{3}c1$, $a = 9.777(2)$, $c = 33.293(2)$ Å, to $R = 0.022$ for 1510 unique reflections collected from a twinned crystal. Two twinned portions are related to each other by a twofold axis coincident with the $\bar{3}$ axis, which can result in apparent hexagonal symmetry for minehillite. The structure consists of a stacked sequence of three types of layer units: (1) an infinite sheet of edge-sharing Ca-(O,OH) polyhedra, (2) a single sheet of SiO_4 tetrahedra connected in oval and pseudo-hexagonal-shaped six-membered rings, and (3) a complex slab built of SiO_4 tetrahedra and AlO_6 octahedra into which alkali elements and Zn are accommodated. The first two units are identical to those found in the reyerite structure. The third is analogous to the double layer in reyerite but with significant differences. The SiO_4 tetrahedra in the complex slab in minehillite form two sheets of isolated pseudo-hexagonal six-membered rings that are connected by AlO_6 octahedra centered on the threefold axis, which are unusual features among layered silicate minerals. An average of five Zn atoms per cell partially occupy a highly distorted tetrahedral site.

INTRODUCTION

Minehillite was first described from Franklin, New Jersey, by Dunn et al. (1984) and classified as a member of the reyerite-truscottite-gyrolite group on the basis of its similarity in symmetry, unit-cell parameters, and chemical compositions to reyerite. The chemical analyses of their sample gave an empirical formula based on 128 O atoms per formula unit of $(K_{1.93}Na_{0.29})_{2.22}(Ca_{27.50}Mn_{0.10}Mg_{0.10}Fe_{0.14})_{27.88}Zn_{4.82}Al_{4.33}Si_{39.92}H_{15.22}O_{128}$. A close structural relationship between minehillite and reyerite was suggested by Dunn et al. (1984), but the role of Zn and the large difference between c parameters of the two minerals could not be explained. We herein present the details of the crystal structure of minehillite derived from the intensity data collected from a twinned crystal and comment upon the structural relationships among reyerite-group minerals. Our results are noteworthy in that the Al atoms are octahedrally coordinated.

EXPERIMENTAL METHODS

Numerous platy fragments of minehillite crystals from the type specimen NMNH no. C6412-1 (Dunn et al., 1984) were examined using precession methods and optical microscopy. The c -axis precession photographs showed different intensity distributions; some are hexagonal and some trigonal, although powder diffraction

patterns taken with a Gandolfi camera are identical. These observations suggested that minehillite is trigonal with a possible twofold twin axis coincident with the $\bar{3}$ axis. This twin law was confirmed by subsequent structure refinement. All crystals examined in this study appeared to be twinned, and most of them showed apparent hexagonal symmetry, as reported by Dunn et al. (1984), because there were nearly equal amounts of each twin component. The twinning geometry and mechanism are discussed below.

The dimensions of the crystal fragment used in the structure determination are given in Table 1. Overexposed precession photographs taken along [100], [110], [010], and [001] showed the point symmetry of $\bar{3}2/m$ and systematic absences suggested space group $P\bar{3}c1$.

The details of data collection and data reduction are given in Table 1. Standard reflections (also in Table 1) showed no significant deviations in the course of data collection. The intensity data were corrected for Lorentz and polarization effects, and absorption effects were corrected using an empirical ψ -scan technique, utilizing intensity data obtained from $\pm 180^\circ \psi$ scans at 10° intervals for six reflections. In the final cycle of full-matrix least-squares refinement, only reflections with $F_{obs} > 4\sigma_F$ were used.

Direct-method programs in the Molen software package (Fair, 1990) were used for phase determination without considering the twin factor, and a relative scale factor for F_{obs} and an overall temperature factor were determined based on Wilson statistics. The structure model derived from direct methods and subsequent Fourier electron density maps was reasonable in terms of bond

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TABLE 1. Crystal data and experimental details

Crystal data	
Crystal dimensions (mm)	0.150 × 0.150 × 0.030
Space group	$P\bar{3}c1$ (no. 165)
Unit-cell parameters	
<i>a</i> (Å)	9.777(2)
<i>c</i> (Å)	33.293(2)
<i>V</i> (Å ³)	2755.7(9)
<i>Z</i>	1
Data collection and refinement	
Twin ratio	0.644(1):0.356
Diffractometer	CAD4/graphite-monochromated MoK α
θ limits (°)	1–25
Reciprocal space	$\pm h, \pm k, \pm l$
Standards	
Orientation	two per 600 reflections
Intensity	three per 2 h
Total data	10256
Unique data	1932
Data $F_{obs} > 4\sigma_f$	1510
<i>R</i>	0.022
<i>R</i> _{int}	0.033
Goodness of fit	1.05
Final difference-Fourier maps (e/Å ³)	
(+)	0.69
(-)	0.36

lengths and the measured chemical composition. On the basis of this model, however, the full-matrix least-squares refinement converged only to $R = \sim 0.23$.

The SHELXL-93 programs were then utilized for the final-stage least-squares refinement. The twin components were included by means of a transformation matrix (see below), and the refinement quickly converged to $R = 0.06$, with all atoms isotropic. The refined twin ratio of the two components was 0.644(1):0.356. After converting displacement parameters to anisotropic, all non-H atomic positions except for Zn behaved predictably; the

TABLE 2. Atomic parameters for minehillite structure

Atom	Equi-point	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)
K	2	0	0	1/4	0.0231(8)
Zn	6	0	0.49431(9)	1/4	0.0098(3)
Al	4	1/3	2/3	0.25112(6)	0.0080(3)
Ca1	4	1/3	2/3	0.11288(4)	0.0098(3)
Ca2	12	0.91036(8)	0.38794(9)	0.11169(2)	0.0100(2)
Ca3	12	0.75653(9)	-0.05187(9)	0.09618(2)	0.0113(2)
Si1	4	2/3	1/3	0.03155(5)	0.0074(4)
Si2	12	0.7581(1)	0.1246(1)	0.18744(3)	0.0076(2)
Si3	12	0.8727(1)	0.2386(1)	0.31193(3)	0.0071(2)
Si4	12	0.8934(1)	0.2080(1)	0.02173(3)	0.0079(2)
O1	4	0	0	0.1229(1)	0.015(9)
O2	4	2/3	1/3	0.0793(1)	0.0107(9)
O3	12	0.1000(3)	0.6077(3)	0.07794(8)	0.0121(6)
O4	12	0.7246(3)	-0.0516(3)	0.19881(8)	0.0129(6)
O5	12	0.5871(3)	-0.2682(3)	0.14137(8)	0.0122(6)
O6	12	0.1729(3)	0.5100(3)	0.21832(7)	0.0104(6)
O7	12	0.2949(3)	0.0565(3)	0.19824(8)	0.0155(6)
O8	12	0.5135(3)	0.3478(3)	0.21654(7)	0.0106(6)
O9	12	0.4103(3)	0.2746(3)	0.14053(8)	0.0118(6)
O10	12	0.2600(3)	0.2371(3)	0.01397(7)	0.0134(6)
O11	12	0.5035(3)	0.1897(3)	0.01354(8)	0.0135(6)
O12	12	0.2654(3)	0.0464(3)	0.06664(8)	0.0136(6)
H1	4	0	0	0.141(2)	0.02
H2	12	0.115(6)	0.610(6)	0.059(1)	0.02

TABLE 3. Selected interatomic distances (Å) and O-Zn-O angles (°) for minehillite structure

K-O4 (× 6)	3.008(3)	Al-O6 (× 3)	1.896(3)
O7 (× 6)	3.161(3)	O8 (× 3)	1.906(3)
Mean	3.085	Mean	1.901
Ca1-O3 (× 3)	2.361(3)	Ca3-O3	2.316(3)
O5 (× 3)	2.425(3)	O1	2.346(2)
Mean	2.393	O12	2.425(3)
		O5	2.444(3)
Ca2-O3	2.309(3)	O9	2.489(3)
O5	2.393(3)	O12	2.567(3)
O9	2.411(3)	O10	2.826(3)
O2	2.419(2)	Mean	2.487
O12	2.420(3)		
O9	2.430(3)	Si3-O6	1.602(3)
Mean	2.397	O5	1.606(3)
		O4	1.623(3)
Si1-O2	1.588(5)	O7	1.630(3)
O11 (× 3)	1.624(3)	Mean	1.615
Mean	1.615		
Si2-O9	1.609(2)	Si4-O12	1.591(3)
O8	1.609(3)	O10	1.621(3)
O7	1.624(3)	O11	1.626(3)
O4	1.629(3)	O10	1.632(3)
Mean	1.618	Mean	1.618
Zn-O6	1.933(2)	O6-Zn-O6	138.0(2)
O6	1.933(2)	O6-Zn-O8 (× 2)	111.8(1)
O8	1.936(2)	O6-Zn-O8 (× 2)	84.3(1)
O8	1.936(2)	O8-Zn-O8	135.5(2)
Mean	1.935	Mean	110.9
H1-O1	0.62(8)	H2-O3	0.64(4)

Wyckoff 6*f* Zn site (0,*x*, 1/4) had relatively large anisotropic displacement parameters. Given that minehillite has about five Zn atoms per cell (Dunn et al., 1984), the occupancy factor of the Zn site was varied in the final refinement cycles and converged to 0.802(1), in good agreement with the chemical formula. The chemical formula of Dunn et al. (1984) suggested a minor substitution of Na at the K site; thus, the occupancy factor of K also was refined to $K_{occ} = 0.948(6)$, indicating possible Na substitution at the K site. To complete the structure model, a Fourier difference map was used to locate H atoms. The standard deviation of the peak, σ , was 0.1 e/Å³. On the difference map, there were 14 peaks higher than the background (3 σ), as suggested by Nelson and Guggenheim (1993). Two of the peaks (1.12 and 0.97 e/Å³) were substantially higher than the rest (<0.70 e/Å³) and were assigned as H positions. The H positional parameters were refined in the final cycle of refinement with displacement parameters fixed. The final full-matrix least-squares refinement of 165 parameters, including positional parameters, anisotropic displacement parameters, a scale factor, a secondary extinction factor, occupancy factors of Zn and K sites, and a twin factor, converged to $R = 0.022$. Details are given in Table 1. The atomic coordinates and displacement parameters are given in Table 2, and Table 3 lists the selected bond lengths and angles. Tables 4 and 5 contain anisotropic displacement parameters and observed and calculated structure factors.¹

¹ A copy of Tables 4 and 5 may be ordered as Document AM-95-575 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

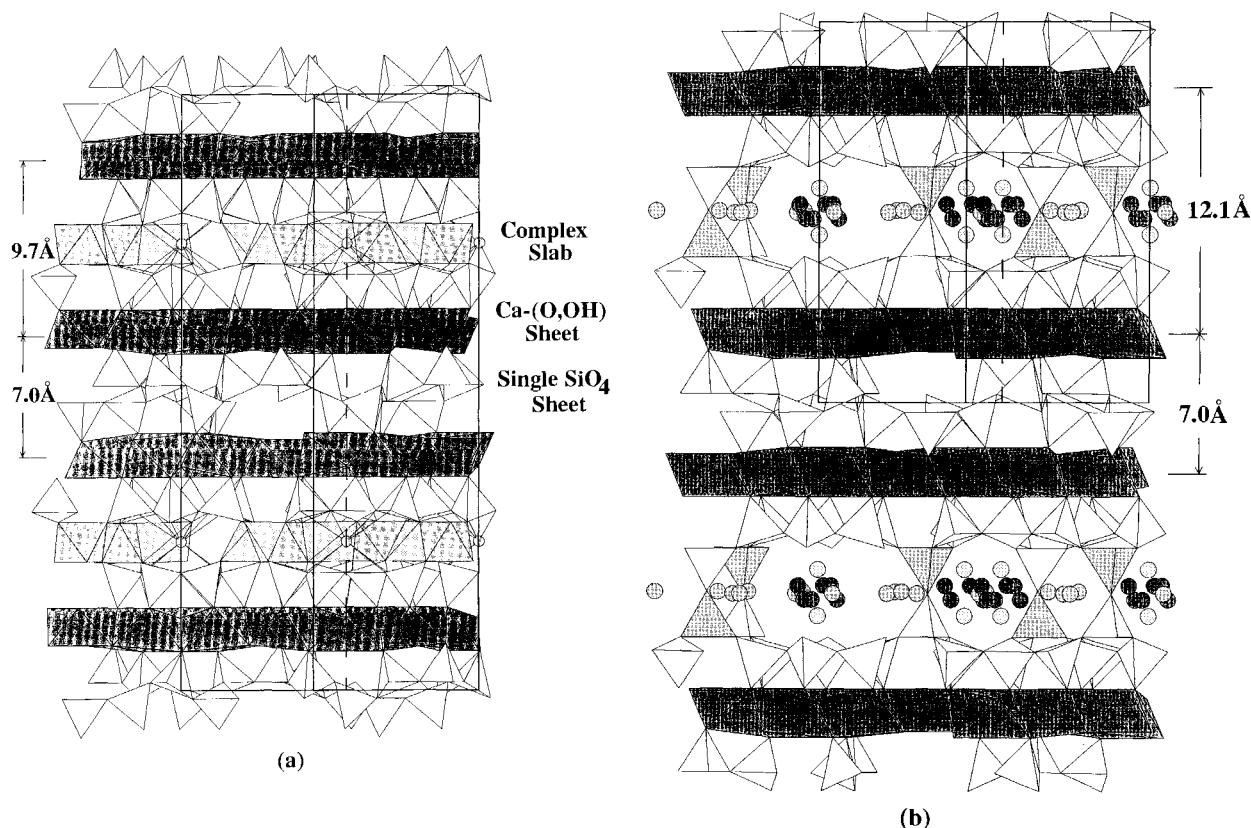


Fig. 1. Projections of the minehillite structure (a) and the reyerite structure (b) onto (210). The unit cell is outlined. The shading of polyhedra from dark to light is Ca-(O,OH) polyhedra, AlO_6 octahedra (minehillite) and AlO_4 tetrahedra (reyerite), and ZnO_4 tetrahedra. The SiO_4 tetrahedra are unshaded. Alkali atoms in both structures are denoted by circles. For clarity, the H_2O molecules are omitted from the reyerite structure.

DISCUSSION OF THE STRUCTURE

The layered structure of minehillite and its structural relationship with reyerite (Merlino, 1988a) are depicted in Figure 1. The minehillite cell is composed of four Ca-(O,OH) polyhedral sheets containing three symmetrically distinct Ca sites, two single sheets of SiO_4 tetrahedra (Si1 and Si4), and two complex structure slabs of Si-O (Si2, Si3), Al-O, Zn-O, and K-O polyhedra. Minehillite has twice the number of the analogous structure units per cell as reyerite. The Ca-(O,OH) polyhedral sheet and SiO_4 tetrahedral single sheet are nearly identical to those of reyerite described by Merlino (1988a), to whom the reader is referred for detailed descriptions of these structural units. The structure slabs, termed double layers in the reyerite structure by Merlino (1988a), fundamentally differentiate the minehillite and reyerite structures (Fig. 2).

Structure slab of SiO_4 tetrahedra and AlO_6 octahedra

The unique feature of the minehillite structural slab is the framework of mixed SiO_4 tetrahedra and AlO_6 octahedra, into which Zn and K atoms are accommodated. The structure slab (Figs. 1 and 2) consists of two sandwiching sheets of SiO_4 tetrahedra; in each sheet, SiO_4 tetrahedra share two corners with each other to form iso-

lated, pseudohexagonal rings individually centered on the $\bar{3}$ axes (Fig. 2). The basal planes of the SiO_4 tetrahedra in both sheets are nearly parallel to (001), with the apical vertices pointing away from each other. The isolated rings around the $\bar{3}$ axes in the two sheets are connected by the opposite triangular faces of AlO_6 octahedra centered on the threefold axes, forming a two-dimensional network of SiO_4 tetrahedra and AlO_6 octahedra. In contrast, the analogous reyerite structural slab consists of a SiO_4 and AlO_4 tetrahedral framework (Fig. 2); the SiO_4 pseudohexagonal rings around the $\bar{3}$ axes, essentially identical to those of minehillite, are linked by an extra AlO_4 tetrahedron in one sheet and an extra SiO_4 tetrahedron in the other (Fig. 1). These SiO_4 and AlO_4 tetrahedra are centered on one threefold axis and share a common apical O, which is also on the threefold axis and links the tetrahedral sheets to form the slab framework. As a result, the structure slab of minehillite is about 2.42 Å thinner than that of reyerite (Fig. 1), accounting for the significant difference in the *c*-parameters ($c_{\text{minehillite}} = 33.293 \text{ \AA}$, $2 \times c_{\text{reyerite}} = 38.134 \text{ \AA}$; Merlino, 1988a). The AlO_6 octahedral coordination in minehillite requires about 30° rotation of the two pseudohexagonal SiO_4 rings about the $\bar{3}$ axis relative to each other (Fig. 2). The reduction in thickness

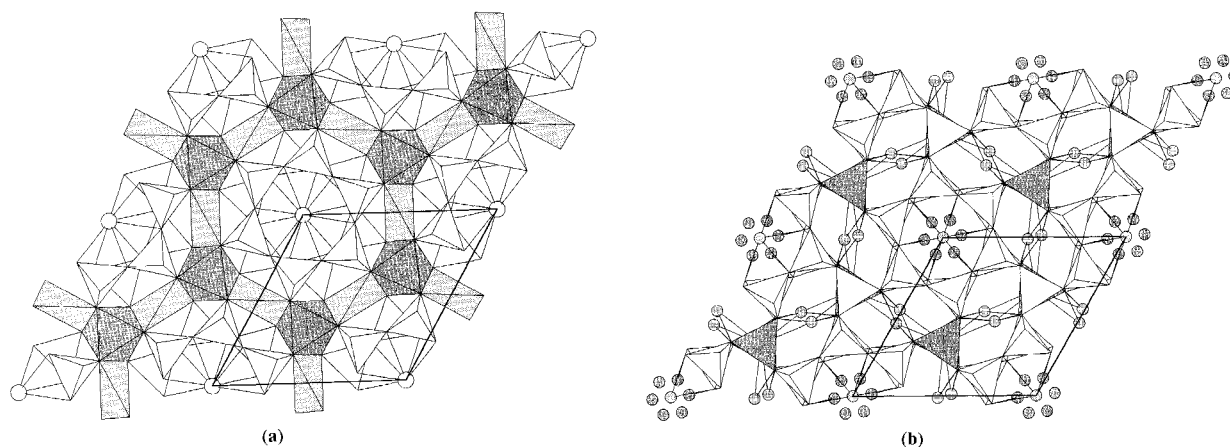


Fig. 2. The (001) projections of the complex structural slabs in minehillite (a) and reyerite (b). The unit cell is outlined. Polyhedral shadings are the same as in Fig. 1. Alkali positions are denoted by circles. The alkali-O bonds in minehillite are plotted in solid lines, and those in reyerite are omitted. For clarity, the H₂O molecules in the reyerite slab are not shown.

and relative rotation of tetrahedral rings in the minehillite structure slab dramatically reduce the size of cavities relative to those observed in the reyerite structure slabs (Merlino, 1988a), accounting for only a single alkali site and the absence of H₂O molecules in the minehillite structure. Instead, a single alkali site at the center of two pseudo-hexagonal rings on each $\bar{3}$ axis and a distorted tetrahedral site suitable for Zn are generated, if not caused by Zn, within the structure slab of minehillite. Minehillite is, therefore, the first example of a layered silicate mineral species with a layer unit built of mixed SiO₄ tetrahedra and AlO₆ octahedra that contains isolated SiO₄ six-membered rings.

Zn crystal chemistry

Dunn et al. (1984) demonstrated that minehillite has about five Zn per unit cell, which is in excellent agreement with the present site occupancy refinement for Zn (4.81 per cell). Thus, only about five Zn atoms reside in the $6f(x,0,1/4)$ site, with partial occupancy due to the requirement for charge balance. The Zn atoms are coordinated by four O atoms (2 × O6, 2 × O8) in a severely distorted tetrahedron, which shares two short edges with two AlO₆ octahedra (Fig. 2). The Zn-O bond lengths are typical, ranging from 1.933 to 1.936 Å, whereas the O-Zn-O angles, varying from 84.3 to 138.0° (Table 3), represent the largest variation for O-Zn-O tetrahedral angles recorded in the literature. Zn occurs in minehillite but not in reyerite and may be responsible for the formation of minehillite instead of reyerite.

OH content

A bond valence calculation for all atoms except H, given in Table 6, shows that O1 and O3 sites are substantially underbonded, consistent with the assignment of adjacent H positions on the final difference map. However, as is typical with X-ray diffraction results, the observed O-H bond lengths (Table 3) in minehillite are unrealistically

short, compared with typical O-H bond lengths (~0.95 Å) observed for OH groups by neutron diffraction (Ferraris and Franchini-Angela, 1972; Chiari and Ferraris, 1982). The 16 observed OH groups per unit cell account for the entire H₂O content of minehillite from the chemical analysis (Dunn et al., 1984); all the OH groups reside in the Ca-(O,OH) polyhedral sheets. The single-step loss of H₂O in the DTA-TGA curves (Dunn et al., 1984) with a peak at 775 °C is consistent with OH⁻ as the only hydrous species.

Twinning geometry and mechanism

The geometrical relationship between the cells of the twin individuals can be expressed as: $(a,b,c)_{\text{twin1}} = R(a',b',c')_{\text{twin2}}$, where R is the transformation matrix:

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

This relationship represents merohedral twinning, which gives no extra reflections that would violate the trigonal symmetry or systematic absences defined by the space group, $P\bar{3}c1$. However, the intensities of reflections from a given twin component were modified by the overlapping reflections from the other component. If a twinned crystal consists of equal amount of two twin components, an apparent hexagonal symmetry results, as observed by Dunn et al. (1984) and in this study on many other crystals. Fortunately, the crystal used in this structure determination is dominated by one twin individual (64%). Thus, direct methods and Fourier routines still were successful in finding non-H atoms in the structure, on the basis of the intensity data collected from this twinned crystal.

In light of the transformation matrix (R) and Figure 2, the twinning mechanism of minehillite is immediately clear: the twinning is caused by the relative rotation of the SiO₄ sheets in the complex structure slab. In each unit cell, two structure slabs are related by the center of sym-

TABLE 6. Bond valences* (vu) for minehillite

	K	Zn	Al	Ca1	Ca2	Ca3	Si1	Si2	Si3	Si4	Total
O1						0.36 × 3→					1.08
O2					0.30 × 3→		1.10				2.0
O3				0.35 × 3↓	0.40	0.39					1.14
O4	0.09 × 6↓							0.98	1.00		2.07
O5				0.29 × 3↓	0.32	0.27			1.05		1.93
O6		0.54 × 2↓	0.50 × 3↓						1.06		2.10
O7	0.06 × 6↓							1.00	0.98		2.04
O8		0.53 × 2↓	0.50 × 3↓					1.04			2.07
O9					0.30 0.29	0.24		1.04			1.88
O10						0.10				1.01 0.98	2.09
O11							1.00 × 3↓			1.00	2.00
O12					0.29	0.29 0.20				1.10	1.88
Total	0.90	2.14	3.0	1.92	1.90	1.95	4.10	4.06	4.09	4.09	

Note: multiplicities are indicated by ×.

* Constants from Brese and O'Keeffe (1991).

metry required by the space group. Thus, the relative rotation of the two SiO_4 sheets in one slab is, for example, clockwise, and the relative rotation in the other slab must be counterclockwise. In the next cell, however, the first slab can be either clockwise or counterclockwise without affecting the coordination environments of other elements. Thus, the orientation of the subsequent cell can be either conformable with the previous one or rotated by 60° about the $\bar{3}$ axis; the latter orientation is related to the original cell by the twin law. As a result, twinning is common, perhaps even inevitable, in minehillite. On the other hand, the structure slabs in reyerite do not have this orientation freedom without violating the rule of Al-O-Al avoidance and modifying the coordination of non-framework cations within the slab. Thus, twinning is not expected in reyerite.

The twinning in minehillite has no apparent effects on

the atomic positions in the Ca-(O,OH) polyhedral and SiO_4 single tetrahedral sheets. Even within the structure slab, the effects are limited only to the atomic positions involved in two independent SiO_4 tetrahedra (Si2 and Si3) (Fig. 2). The K, Al, and Zn positions are the same in the two orientations of the cells. Thus, it is possible to derive the structure model from the twinned intensity data.

Structural relationships among the minerals of the reyerite group

Analogous to that of minehillite, the crystal structure of the other minerals in the reyerite group, including reyerite $[(\text{Na},\text{K})_2\text{Ca}_{14}\text{Si}_{22}\text{Al}_2\text{O}_{58}(\text{OH})_8 \cdot 6\text{H}_2\text{O}]$: Merlino, 1988a], gyrolite $[\text{NaCa}_{16}\text{Si}_{23}\text{AlO}_{60}(\text{OH})_8 \cdot 14\text{H}_2\text{O}]$: Merlino, 1988b], and truscottite $[\text{Ca}_{14}\text{Si}_{24}\text{O}_{58}(\text{OH})_8 \cdot x\text{H}_2\text{O}]$: Lachowski et al., 1979], consist of three major structure units: a Ca-(O,OH) sheet, a SiO_4 single sheet, and com-

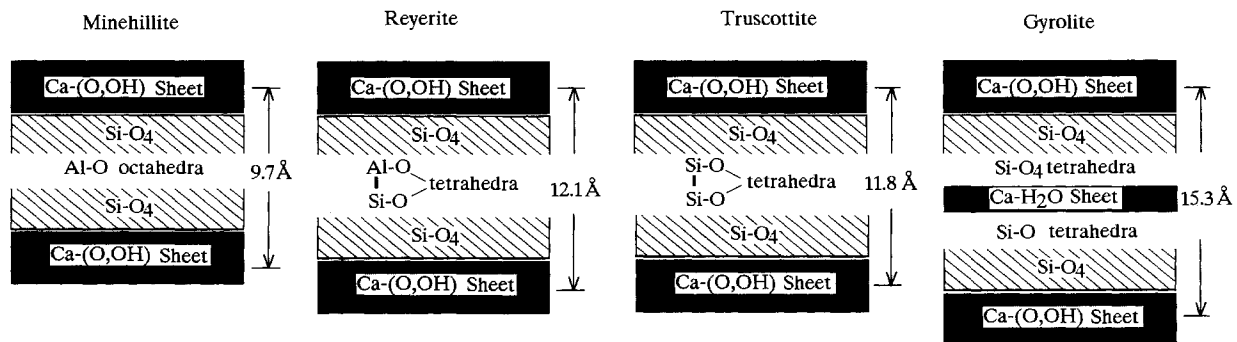


Fig. 3. Comparison of the simplified structure slabs of the reyerite group minerals sandwiched by the Ca-(O,OH) sheets (black). Within each of the slabs the two SiO_4 sheets (striped) are connected by different subunits, which are denoted.

plex structure slabs. The geometries of the Ca-(O,OH) and single SiO₄ sheets are nearly identical in these minerals, whereas structural variations occur primarily in the slabs (Fig. 3). The differences in thickness of the structure slab reflect the different linkages between the two sandwiching SiO₄ sheets shown in Figure 3. In minehillite, the two SiO₄ sheets are linked by one AlO₆ octahedron; in reyerite the sheets are connected by one AlO₄ and one SiO₄ tetrahedron and in truscottite the sheets are connected by two SiO₄ tetrahedra. The two sheets in the gyrolite slab are separated by a sheet of Ca-(H₂O) polyhedra. In light of the twin mechanism in minehillite, twinning should be common in truscottite and gyrolite.

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