

Crystal Chemistry of Beryllium

GEOLOGICAL SURVEY PROFESSIONAL PAPER 468



MOSS—CRYSTAL CHEMISTRY OF BERYLLIUM—PROFESSIONAL PAPER 468

Crystal Chemistry of Beryllium

By MALCOLM ROSS

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*A detailed discussion of the crystal chemistry
of all the known beryllium minerals*



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CONTENTS

	Page		Page
Abstract.....	1	The beryllium minerals—Continued	
Introduction.....	1	Gugiaite.....	16
The beryllium minerals.....	1	leucophanite.....	16
Aminoffite.....	2	meliphanite.....	18
Barylite.....	2	Milarite.....	19
Bavenite.....	3	Moraesite.....	19
Bertrandite.....	3	Bearsite.....	20
Beryl.....	5	Phenakite.....	20
Bazzite.....	6	Rhodizite.....	20
Beryllite.....	6	Roschéríte.....	20
Beryllonite.....	7	Spherobertrandite.....	21
Beryllsodalite.....	7	Swedenborgite.....	21
Bityite.....	8	Taaffeite.....	22
Bromellite.....	8	Tengerite.....	22
Chkalovite.....	9	Trimerite.....	22
Chrysoberyl.....	9	Väyrynenite.....	22
Epididymite.....	9	Euclase.....	23
Eudidymite.....	10	The beryllium compounds.....	23
Faheyite.....	10	Be(H ₂ O) ₄ SO ₄	23
Gelbertrandite.....	10	β-Be(OH) ₂	24
Hambergite.....	10	BeSO ₄	24
Harstigite.....	11	BeGeO ₄	24
Helvite.....	11	BeS.....	24
Danalite.....	11	BeSe.....	24
Genthelvite.....	11	BeTe.....	24
Herderite.....	13	BeSiN ₂	24
Gadolinite.....	13	BeCl ₂	24
Hsianghualite.....	14	Be(CH ₃) ₂	24
Hurlbutite.....	14	Basic beryllium acetate, Be ₄ O(CH ₃ COO) ₆	25
Karpinskyite.....	16	Beryllium phthalocyanine, BeC ₃₂ H ₁₆ N ₈	25
		The beryllium fluorides.....	25
		Conclusions.....	27
		References.....	28

ILLUSTRATIONS

		Page
FIGURE	1. The crystal structure of barylite.....	4
	2. The crystal structure of bertrandite (after Ito and West).....	4
	3. The crystal structure of bertrandite (after Solovieva and Belov).....	5
	4. The crystal structure of beryl.....	6
	5. The structure of the Si ₆ O ₁₈ ring in beryl.....	7
	6. The crystal structure of beryllonite.....	8
	7. The arrangement of tetrahedra and octahedra in layers I and II of chrysoberyl.....	10
	8. The crystal structure of hambergite.....	12
	9. The crystal structure of herderite.....	13
	10. The arrangement of the calcium polyhedra in herderite.....	13
	11. The arrangement of the yttrium and iron polyhedra in gadolinite.....	14
	12. The crystal structure of hurlbutite.....	15
	13. The crystal structure of melilite.....	16
	14. The arrangement of the calcium polyhedra in melilite.....	17
	15. The crystal structure of milarite projected on (10 $\bar{1}$ 0).....	18

FIGURE 16. The crystal structure of milarite projected on (0001).....	18
17. A comparison of the beryl and milarite structures.....	19
18. The crystal structure of swedenborgite.....	21
19. A comparison of the väyrynenite and euclase structures.....	23
20. The beryllium phthalocyanine molecule.....	25

TABLES

TABLE		Page
1. The beryllium minerals.....		2
2. Chemical composition of Bavenite.....		3
3. Charge distribution on the oxygen atoms in hurlbutite and danburite.....		15
4. Bond lengths in the hurlbutite structure.....		15
5. Crystallography of gugiaite, leucophanite, meliphanite, and the related minerals melilite and hardystonite.....		16
6. Chemical composition of gugiaite, leucophanite, and meliphanite.....		17
7. Bond lengths in milarite.....		19
8. The beryllium compounds.....		23
9. The beryllium fluoride compounds and their structural analogs.....		26
10. The beryllium-anion bond lengths.....		27

CRYSTAL CHEMISTRY OF BERYLLIUM

By MALCOLM ROSS

ABSTRACT

The present study is a compilation of the X-ray crystallography, chemistry, and crystal chemistry of all the known minerals containing essential amounts of beryllium. These minerals are: aminoffite, barylite, bavenite, bazzite, bearsite, bertrandite, beryl, beryllite, beryllonite, beryllsodalite, bityite, bromellite, chkalovite, chrysoberyl, danalite, epididymite, euclase, eudidymite, faheyite, gadolinite, gelbertrandite, genthelvite, gugiaite, hambergite, harstigite, helvite, herderite, hsianghualite, hurlbutite, karpinskyite, leucophanite, meliphanite, milarite, moraesite, phenakite, rhodizite, roschérite, spherobertrandite, swedenborgite, taaffeite, tenerite, trimerite, and väyrynenite. The X-ray crystallography and crystal structure of the following inorganic and organic beryllium compounds are also given: $\text{Be}(\text{H}_2\text{O})_4\text{SO}_4$, $\beta\text{-Be}(\text{OH})_2$, BeSO_4 , BeGeO_4 , BeS , BeSe , BeTe , BeSiN_2 , BeCl_2 , $\text{Be}(\text{CH}_3)_2$, $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$, $\text{BeC}_{22}\text{H}_{16}\text{N}_8$, and the beryllium fluorides. In all but one compound (beryllium phthalocyanine) beryllium is reported to be tetrahedrally coordinated. In beryllium phthalocyanine Be is in planar coordination. A summary of the bond distances between beryllium and the coordinating anions is presented. The average beryllium-oxygen bond distance in those structures believed to be accurately determined is 1.636 Å; the average Be-OH bond distance is 1.650 Å.

INTRODUCTION

Beryllium is one of the less abundant elements; recent estimates (Fleischer and Cameron, 1955; Warner and others, 1959) give 0.0005 to 0.0006 percent for the content of the earth's crust. This element occurs primarily in the igneous rocks where it is one of the last components to crystallize. In the early stages of magmatic crystallization the concentration of beryllium is low and it is thus not incorporated in any appreciable quantities in the structures of ferromagnesian silicates and feldspars. It tends to be concentrated in the late magmatic and early hydrothermal stages and crystallizes as an essential constituent in such minerals as beryl and chrysoberyl.

Sandell (1952) found the average Be content of seven granitic composites to be 3 ppm where the SiO_2 content varied between 68 and 78 percent. He found 4 ppm Be in $\text{An}_{28}\text{Ab}_{72}$, 1 ppm in microcline, and $\frac{1}{2}$ ppm in biotite. Sandell suggests the mechanism $\text{Be} + \text{Ca}$ for $\text{Na} + \text{Al}$ to account for the presence of Be in the feldspars.

The beryllium ion (Be^{2+}) has a radius of 0.33 Å (Green, 1959) and appears to be of a size that will permit it to readily substitute for tetrahedral Si^{4+} , Al^{3+} , P^{5+} and S^{6+} . If such a substitution occurs, the deficiency of positive charge must be adjusted for by replacement of other cations with ones of higher charge. For example, Rankama and Sahama (1950, p. 126) postulate that the small content of lanthanum sometimes present in potassium feldspar is a result of the substitution of La^{3+} for K^+ simultaneously with Be^{2+} for Si^{4+} . As will be discussed later, such substitution mechanisms, if they do occur, occur only to a very limited extent. This is probably because of the rather unsatisfactory distribution of charges on to the anions such that Pauling's rules are not very well obeyed.

The first part of this report is a compilation of the X-ray crystallography, chemistry, and crystal chemistry of all the known minerals containing essential amounts of beryllium. The second part is a presentation of the crystallography and crystal chemistry of a number of inorganic and organic beryllium compounds.

I would like to thank several of my colleagues for their help: C. L. Christ suggested this study of the crystal chemistry of beryllium, and he and Michael Fleischer made numerous suggestions for improving the manuscript; Douglas C. Alverson translated a number of Russian publications into English for me. I am also particularly indebted to Michael Fleischer for bringing to my attention much of the current Russian literature on the beryllium minerals.

THE BERYLLIUM MINERALS

Apparently, 43 minerals have been described that contain an essential amount of beryllium.¹ These are listed in table 1. Some of these minerals are of doubtful validity and several have questionable chemical formulas. The various minerals are discussed individually. If known, the unit-cell dimensions, space group, densi-

¹ For the purposes of this report an "essential amount of beryllium" is defined as the amount of beryllium needed to fill at least 50 percent of the equipoints of one set of equivalent positions in the crystal structure.

ties, and number of formulas per unit cell are given.² Chemical analyses or references to lists of chemical analyses are given for most of the minerals. For a few minerals, where there appears to be no question of the validity of the chemical formula, the chemical composition is not discussed. The crystal structures of more than half of the beryllium minerals are known or partly known and these are discussed in detail.

The present study will not touch on the mineralogy or petrology of these minerals. These subjects are considered in great detail in the recent book, "The Geochemistry of Beryllium and Genetic Types of Beryllium Deposits," by the Russian mineralogist, A. A. Beus (1960).

The mineral kolbeckite, once believed to be a phosphate or silicophosphate of beryllium, has been shown

TABLE 1.—The beryllium minerals

Name	Formula
Aminoffite	Ca ₂ (Be,Al)Si ₂ O ₆ (OH) ₂
Barylite	BaBe ₂ Si ₂ O ₇
Bavenite	Ca ₄ (Be,Al) ₄ (Si,Al) ₉ O ₂₆ (OH) ₂ ?
Bazzite	R ⁺ (Sc,Al,Fe,Mg) ₂ Be ₃ Si ₆ O ₁₈ ?
Bearsite	Be ₂ (AsO ₄)(OH).4H ₂ O?
Bertrandite	Be ₄ Si ₂ O ₇ (OH) ₂
Beryl	Al ₂ Be ₃ Si ₆ O ₁₈
Beryllite	Be ₃ Si ₂ O ₇ (OH) ₄ .2H ₂ O?
Beryllonite	NaBePO ₄
Beryllousodalite	Na ₄ BeAlSi ₄ O ₁₂ Cl
Bityite	(Ca,Na,K)(Al,Li,Mg) ₂₋₃ (Si,Al,Be) ₄ O ₁₀ (OH) ₂
Bromellite	BeO
Chkalovite	Na ₂ (BeSi ₂ O ₆)
Chrysoberyl	Al ₂ BeO ₄
Danalite	Fe ₄ Be ₃ Si ₃ O ₁₂ .S
Epididymite	NaBeSi ₃ O ₇ (OH)
Euclase	AlBeSiO ₄ (OH)
Eudidymite	NaBeSi ₃ O ₇ (OH)
Faheyite	(Mn,Mg,Na)Be ₂ Fe ₂ ²⁺ (PO ₄) ₄ .6H ₂ O
Gadolinite	Fe ₂ YBeSi ₄ O ₄ .O
Gelbertrandite	Be ₄ Si ₂ O ₇ (OH) ₂ .3H ₂ O?
Genthelvite	Zn ₄ Be ₃ Si ₃ O ₁₂ .S
Gugiaite	Ca ₂ BeSi ₂ O ₇
Hambergite	Be ₂ (BO ₃)(OH)
Harstigit	(Ca,Mn,Mg) ₇ Be ₄ Si ₃ (O,OH,F) ₂₃₋₂₄ ?
Helvite	Mn ₄ Be ₃ Si ₃ O ₁₂ .S
Herderite	CaBePO ₄ (F,OH)
Hsianghualite	Li ₂ Ca ₃ Be ₃ (SiO ₄) ₃ F ₂
Hurlbutite	CaBe ₂ (PO ₄) ₂
Karpinskyite	Na ₂ (Be,Zn,Mg)Al ₂ Si ₆ O ₁₆ (OH) ₂ ?
Leucophanite	(Ca,Na) ₂ Be(Si,Al) ₂ (O,F,OH) ₇
Meliphanite	(Ca,Na) ₂ Be(Si,Al) ₂ (O,F,OH) ₇
Milarite	KCa ₂ (Be ₂ Al)(Si ₁₂ O ₃₀). ¹ / ₂ H ₂ O
Moraesite	Be ₂ (PO ₄)(OH).4H ₂ O
Phenakite	Be ₂ SiO ₄
Rhodizite	NaKLi ₄ Al ₄ Be ₃ B ₁₀ O ₂₇ ?
Roschérite	(Ca,Mn,Fe) ₃ Be ₃ (PO ₄) ₃ (OH) ₃ .2H ₂ O
Spherobertrandite	Be ₃ (Si ₂ O ₇)(OH) ₄ ?
Swedenborgite	NaBe ₄ SbO ₇
Taaffeite	(Be,Mg)(Al,Fe) ₂ O ₄
Tengerite	(Y,Ce)BeCO ₃ (OH) ₃ ?
Trimerite	Ca(Mn,Fe,Mg) ₂ (BeSiO ₄) ₃
Värynenite	(Mn,Fe)BePO ₄ (OH)

² The following abbreviations will be used in this work:

a, b, c: α, β, γ-unit-cell edges; unit-cell angles

V=volume of unit cell

D_m=measured density

D_c=calculated density

Z=number of formula units per unit cell

Å=angstrom unit (10⁻⁸cm)

kX=0.997984 times Å. Unit-cell edges are assumed to be in angstrom units for substances described after 1948 and in kX units for substances described prior to 1949. Unless otherwise noted, the numerical values of the unit-cell edges are those originally presented in the references.

by Mary E. Mrose, U.S. Geological Survey (oral communication, 1962), to be a scandium phosphate with the formula Sc(PO₄).2H₂O.

AMINOFFITE



CRYSTALLOGRAPHY

[Hurlbut, 1937]

Tetragonal:

a	13.8	kX	D _m	2.94	g/cm ³
c	9.8	kX	Z	12	
V	1866	kX ³	D _c	3.03	g/cm ³

Space group: I4/mmm

CHEMICAL COMPOSITION

[Hurlbut, 1937, p. 292. Numbers of ions on the basis of Si=2.00]

	Weight percent	Ratios		Weight percent	Ratios
SiO ₂	42.49	2.00	CaO	40.27	2.03
Al ₂ O ₃	4.41	.13	H ₂ O	6.45	1.01
BeO	6.20	.70			
Fe ₂ O ₃	.31	.01		100.32	
MnO	.19	.01			



CRYSTAL STRUCTURE

This mineral may be related structurally to the minerals of the melilite group.

BARYLITE



CRYSTALLOGRAPHY

[Smith, 1956; Abrashev and Belov, 1962]

Orthorhombic:

a	9.80 ± 0.01	Å	D _m	4.03	g/cm ³
b	11.65 ± 0.03	Å	Z	4	
c	4.71 ± 0.02	Å	D _c	4.08	g/cm ³
V	526	Å ³			

Space group: Pn2₁a, piezoelectric
X-ray powder data (Smith, 1956)

CHEMICAL COMPOSITION

[Numbers of ions on the basis of Si=2.00]

	Aminoff (1925)		Palache and Bauer (1930)	
	Weight percent	Ratios	Weight percent	Ratios
SiO ₂	35.51	2.00	36.42	2.00
BeO	16.01	2.17	15.77	2.08
BaO	47.43	1.05	46.49	1.00
CaO	.42	----	----	----
MgO	.21	----	.29	----
PbO	----	----	.11	----
FeO	----	----	.19	----
Fe ₂ O ₃	.04	----	----	----
Al ₂ O ₃	.05	----	----	----
H ₂ O	.57	----	.40	----
	100.24		99.67	

CRYSTAL STRUCTURE

[Abrashev and Belov, 1962]

The barylite structure is found to be composed of linked BeO₄ and SiO₄ tetrahedra. Each of two corners

of the BeO₄ tetrahedra are shared with another BeO₄ group and one SiO₄ group. Each of the other two corners are shared with an SiO₄ group. The SiO₄ groups link together in pairs to form Si₂O₇ double tetrahedra. One corner of each SiO₄ tetrahedron is shared with a like group, one corner with two BeO₄ groups, and two corners with a single BeO₄ tetrahedron. The BeO₄ tetrahedra link to form pyroxenelike chains oriented parallel to the *c*-axis. The repeat distance along the chains is 4.71 Å (the *c*-dimension), and is the length measured parallel to *c* of two linked BeO₄ tetrahedra. The Si₂O₇ groups are oriented with the Si-Si axes parallel to *b* and link the (BeO₃)_n⁴ⁿ⁻ chains together to form the three-dimensional structure shown in figure 1. Large cavities appear in the framework and are composed of four Si₂O₇ groups and four BeO₄ tetrahedra, two each from two different (BeO₃)_n⁴ⁿ⁻ chains. Into these large cavities fit the barium ions. These ions are in approximately twelvefold coordination.

The bond lengths were found to have the following range in angstroms:

	Angstroms
(8) Si-O-----	1.63-1.70
(8) Be-O-----	1.64-1.70
(12) Ba-O-----	2.82-3.34

BAVENITE



CRYSTALLOGRAPHY

[Claringbull, 1940. For chemical composition of bavenite see table 2]

Orthorhombic:

a-----	19.34 kX	D _m -----	2.74 g/cm ³
b-----	23.06 kX	Z-----	4
c-----	4.95 kX	D _x -----	2.80 g/cm ³
V-----	2208 kX ³		

X-ray powder data (Fleischer and Switzer, 1953)

BERTRANDITE



CRYSTALLOGRAPHY

[Solovieva and Belov, 1961; Ito and West, 1932]

Orthorhombic:

a-----	8.73 Å	V-----	612 Å ³
b-----	15.31 Å	Z-----	4
c-----	4.58 Å	D _x -----	2.58 g/cm ³

Space group: Cmc2₁, pyroelectric

CHEMICAL COMPOSITION

[Dana, 1892, p. 546. Numbers of ions on the basis of Si=2.00]

	Weight percent			Ratios		
	(1)	(2)	(3)	(1)	(2)	(3)
SiO ₂ -----	49.60	49.26	51.8	2.00	2.00	2.00
BeO-----	42.62	42.00	39.6	4.13	4.10	3.67
CaO-----			1.0			.04
Fe ₂ O ₃ -----	Tr.	1.40			.02	
Al ₂ O ₃ -----	Tr.					
H ₂ O-----	7.94	6.90	8.4	1.07	.93	1.08
	100.16	99.56	100.8			

CRYSTAL STRUCTURE

[Ito and West, 1932; Solovieva and Belov, 1961]

The bertrandite structure, as Ito and West postulate it, is built up of linked SiO₄, BeO₄, and BeO₂(OH)₂ tetrahedra. The structure is based on an arrangement of close-packed oxygen atoms with beryllium and silicon occupying tetrahedral holes. This model is depicted in figure 2 which shows the bertrandite structure projected on (001).

One half of the silicon tetrahedra form infinite SiO₃ chains parallel to *c* which alternate with two infinite BeO₃ chains to form strips of the composition Be₂SiO₆. The BeO₄ and SiO₄ tetrahedra within this strip are positioned with their bases parallel to (001). Successive tetrahedra in this strip are joined up in such a way that

TABLE 2.—Chemical composition of bavenite

[Samples 1-5, Fleischer and Switzer, 1953; 6, Beus, 1960, p. 45-49; 7, Switzer and Reichen, 1960. Numbers of ions on the basis of 26.00 oxygens and 2.00 OH]

	1		2		3		4		5		6		7	
	Weight percent	Ratios												
SiO ₂ -----	57.11	8.90	57.25	8.91	58.92	9.13	59.13	9.35	57.64	9.11	55.25	8.82	57.04	9.05
Al ₂ O ₃ -----	9.60	.89	9.89	.91	6.88	.63	7.00	.64	6.46	.60	8.26	.85	9.62	.94
Fe ₂ O ₃ -----	.11		.10		.07		7.14	2.67	7.66	2.91	1.18		.60	2.10
BeO-----	6.60	2.47	6.33	2.38	7.72	2.88	7.14	2.67	7.66	2.91	7.00	2.69	5.52	2.10
CaO-----	24.30	4.06	24.35	4.06	23.26	3.86	23.90	3.98	23.96	4.06	24.15	4.13	23.44	3.99
MnO-----					.01		.01							
MgO-----					.13	.03	.05	.01					.22	
Na ₂ O-----					.44	.07	.10	.02						
H ₃ O ⁺ -----	1.87	.97	1.90	.99	2.41	1.25	2.46	1.28	3.56	1.88	4.00	2.13	2.86	1.51
H ₂ O-----					.06		.06	.32					.14	
Other-----	.31		.31		.04		.16				.74			
	99.90		100.13		99.94		100.01		99.60		100.58		99.44	

1. Ca_{4.00}(Be,Al)_{4.15}(Si,Al)_{9.00}O₂₆(OH)₂
 2. Ca_{4.00}(Be,Al)_{4.11}(Si,Al)_{9.00}O₂₆(OH)₂
 3. (Ca,Mg,Na)_{4.03}(Be,Al)_{4.14}Si_{9.15}O₂₆(OH)₂
 4. (Ca,Mg,Na)_{4.03}(Be,Al)_{4.05}Si_{9.35}O₂₆(OH)₂

5. Ca_{4.06}(Be,Al)_{4.11}Si_{9.11}O₂₆(OH)₂
 6. Ca_{4.13}(Be,Al)_{4.21}(Si,Al)_{9.00}O₂₆(OH)₂
 7. Ca_{3.99}(Be,Al)_{3.95}Si_{9.05}O₂₆(OH)₂

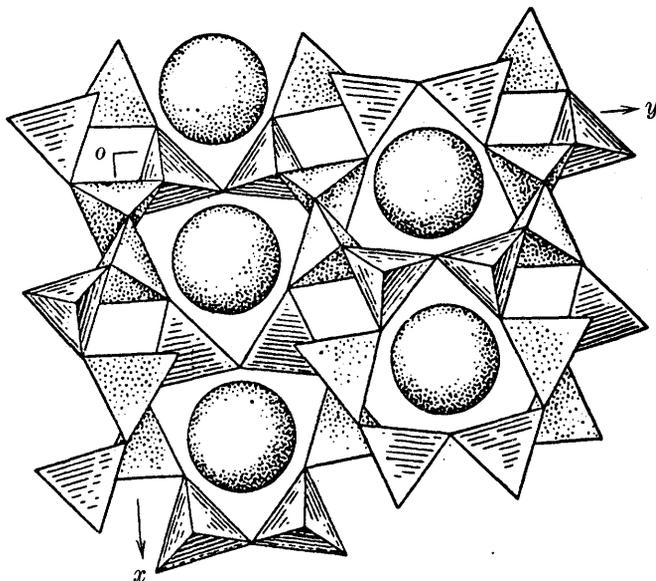


FIGURE 1.—The crystal structure of barylite, $\text{BaBe}_2\text{Si}_2\text{O}_7$. Reprinted from Abrashev and Belov, 1962. The stippled tetrahedra are the BeO_4 groups; the lined tetrahedra are the SiO_4 groups. The large circles represent barium atoms. The $(\text{BeO}_2)_{\infty}$ chains run parallel to the c -axis.

the apex of one becomes a corner of the base of the next. The two types of chains link into the Be_2SiO_6 strips by sharing two corners of each base. All oxygen atoms in the BeO_4 tetrahedra coordinate two beryllium atoms and one silicon atom. The basal oxygens in the SiO_4 tetrahedra coordinate two Be atoms and one silicon atom. The apical oxygens of each SiO_4 tetrahedra coordinate two silicon atoms only.

The Be_2SiO_6 strips alternate with strips of the composition $\text{Be}_2\text{O}_3(\text{OH})_2$. These latter strips consist of infinite $\text{BeO}_2(\text{OH})_2$ chains lying parallel to c . The $\text{BeO}_2(\text{OH})_2$ tetrahedra that form these chains link in the same manner as the BeO_4 and SiO_4 tetrahedra but are oriented so that the apices point in the opposite direction. The $\text{BeO}_2(\text{OH})_2$ chains are linked into the strips by sharing one corner of each base.

The two types of strips link into a three-dimensional network as shown in figure 2. Additional SiO_4 tetrahedra are situated between the strips. Each oxygen atom of these tetrahedra coordinates one silicon atom and two beryllium atoms. The two oxygen atoms of

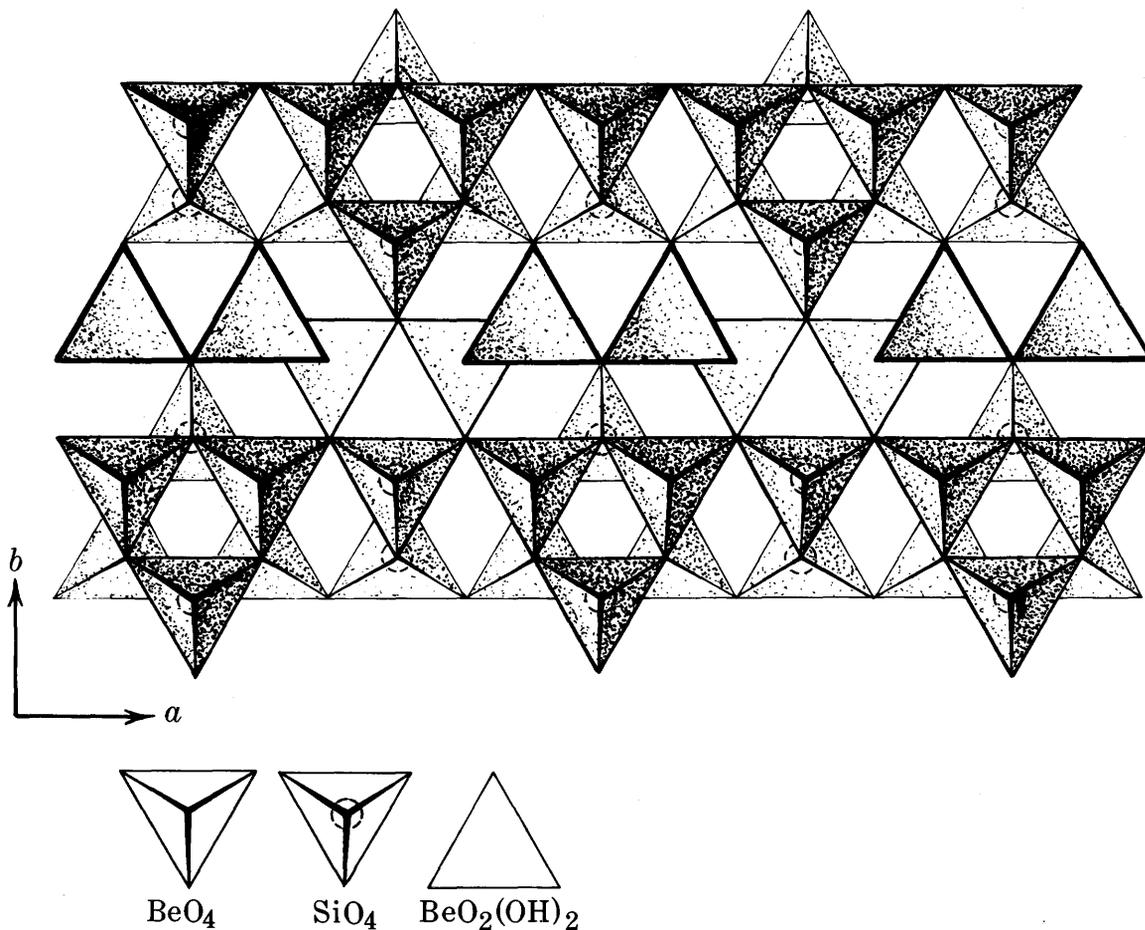


FIGURE 2.—The bertrandite, $\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$, structure as postulated by Ito and West (1932).

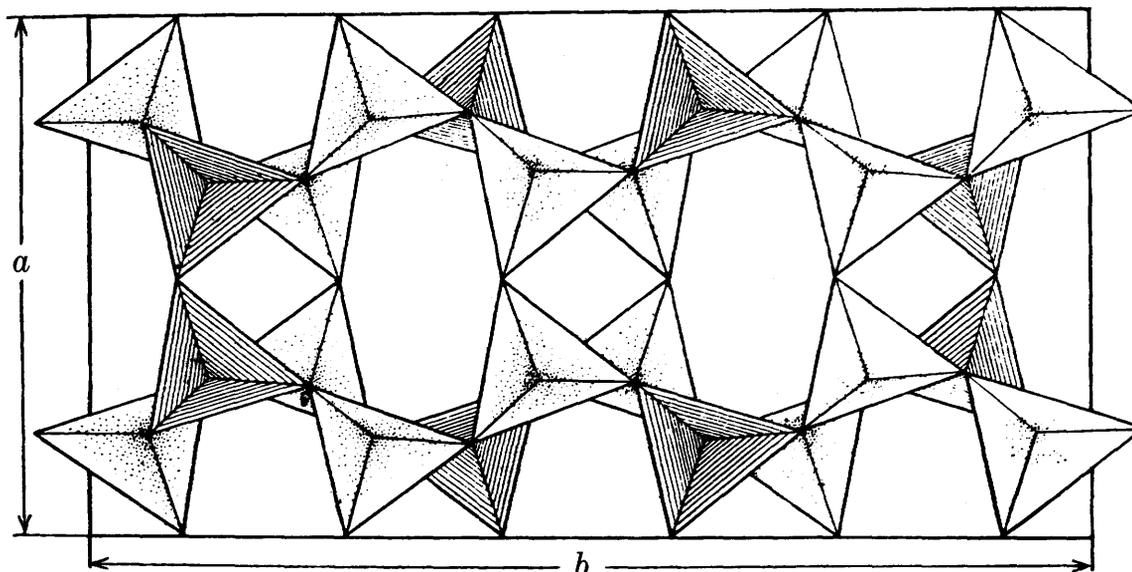


FIGURE 3.—Bertrandite, $\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$. Reprinted from Solovieva and Belov, 1961. BeO_4 tetrahedra, unshaded; SiO_4 tetrahedra shaded.

the $\text{BeO}_2(\text{OH})_2$ tetrahedra also coordinate one Si and two Be atoms. The two (OH) groups coordinate two beryllium atoms only.

Ito and West's structure is a model only and probably, in view of the work of Solovieva and Belov (1961), is not correct.

Solovieva and Belov (1961) recently determined the crystal structure of bertrandite from analysis of hkl and $0kl$ intensity data. Their structure is different from that given by Ito and West as can be seen in figure 3 which shows a projection of the structure on (001). Each $\text{BeO}_3(\text{OH})$ tetrahedron shares the (OH) corner with another $\text{BeO}_3(\text{OH})$ tetrahedron, and each of the oxygen corners with one SiO_4 tetrahedron and one $\text{BeO}_3(\text{OH})$ tetrahedron. The SiO_4 tetrahedra share one corner with another SiO_4 tetrahedron and each of the other three corners with two $\text{BeO}_3(\text{OH})$ groups. In this way a three-dimensional framework structure is formed. The structure may be also viewed as being formed of linked double Si_2O_7 and $\text{Be}_2\text{O}_6(\text{OH})$ tetrahedra.

BERYL



CRYSTALLOGRAPHY

[Bragg and West, 1926]

Hexagonal:

a ----- 9.21 kX
 c ----- 9.17 kX
 V ----- 673.6 kX³

Z ----- 2
 D_x ----- 2.63 g/cm³

Space group: $P6/mcc$

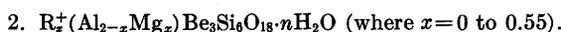
CHEMICAL COMPOSITION

Beus (1960, p. 66-90) gives a very complete description of the chemistry of beryl including 38 chemical analyses. Schaller, Stevens, and Jahns (1962) have

proposed two main solid-solution series for the beryls. They are given as follows:



and



If $x=0$ we have the ideal end-member $\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$ which is never found in nature. R^+ may be Cs, Rb, Na, or K. Fe^{3+} may replace Al in the octahedral sites, and Mn^{2+} and Fe^{2+} may replace Mg in the octahedral sites. Only small amounts (0 to 2.5 percent) of H_2O appear in the beryl analyses.

CRYSTAL STRUCTURE

[Bragg and West, 1926; Belov and Matveeva, 1951; Schaller, Stevens, and Jahns, 1962]

The beryl structure contains rings of the composition Si_6O_{18} and are composed of six SiO_4 tetrahedra sharing corners. Figure 4 shows these rings projected on (0001). Figure 17 shows a projection of the beryl structure perpendicular to c . The Si_6O_{18} rings are linked together into a three-dimensional structure by Al octahedra and BeO_4 tetrahedra as shown in figures 4 and 17. In the solid solution series described above Al, Li, Mg, Mn^{2+} , Fe^{2+} , and Fe^{3+} can appear in the octahedral sites. In the tetrahedral sites outside the Si_6O_{18} rings, Be and Al can appear. There appears to be no substitution of other cations for silicon.

The cesium, rubidium, sodium, and potassium ions and also the water molecules are probably situated within the tunnels running through the center of the Si_6O_{18} rings. The openings in the rings are shown in figures 4 and 5. In figure 5 the possible location of a cesium ion is shown. The role of Na^+ , K^+ , Rb^+ , and Cs^+

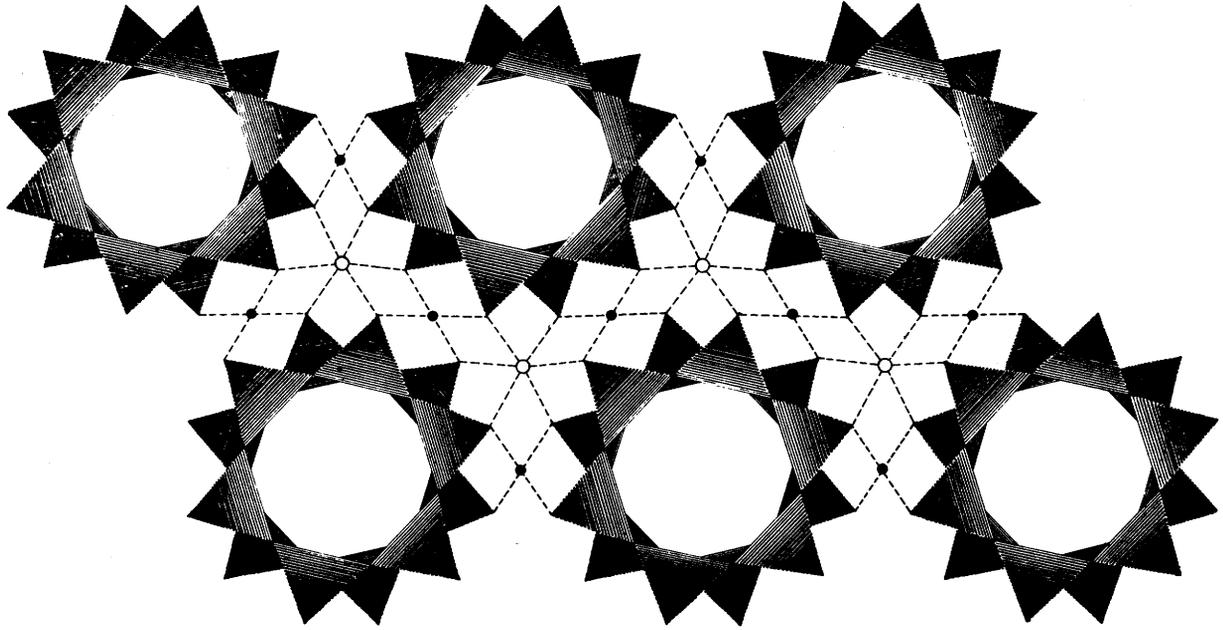


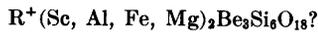
FIGURE 4.—The beryl, $Al_2Be_3Si_6O_{18}$, structure projected on (0001). Each ring of shaded tetrahedra represents an $Si_6O_{18}^{12-}$ group. The solid black circles represent Be^{2+} ions, and the open circles Al^{3+} ions. Reprinted from Schaller, Stevens, and Jahns, 1962.

in the beryl structure is much disputed and we must wait for an accurate structure determination of a beryl containing a large amount of these alkalis before we can be sure of their true position in the lattice. It is interesting to note that the presence of appreciable amounts of the alkali metals, particularly the large cesium ions, causes an increase in the c dimension. The a -dimension is apparently not affected by the alkali content.

Belov and Matveeva (1951) found the following bond lengths in beryl:

	<i>Angstroms</i>
Be-O	1.64
Si-O	1.60
Al-O	1.95

BAZZITE



CRYSTALLOGRAPHY

[Peyronel, 1956]

Hexagonal:

a	9.51 A
c	9.11
V	713.5 A ³
D_m	2.819 g/cm ³
Z	2
D_z	2.809–2.825 g/cm ³

Space group: $P6/mcc$

CHEMICAL COMPOSITION

Bazzite is a rare mineral and has only been analyzed

spectrographically. The major constituents appear to be Be, Si, Al, Mg, and Sc. Lesser amounts of Fe, Na, and Ba are present. Minor amounts of Cu, Ga, V, Sn, Y, Yb, and Ag have been found (Huttenlocher, Hugi, and Nowacki, 1954).

CRYSTAL STRUCTURE

[Peyronel, 1956]

Peyronel (1956) worked out the crystal structure of a bazzite containing Sc, Fe, Na, Y, Yb, Al and Si. He found the mineral to be isostructural with beryl. Scandium appears to occupy the octahedral sites.

BERYLLITE



CRYSTALLOGRAPHY

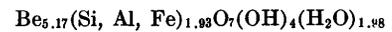
[Kuz'menko, 1954]

$D_m = 2.196$ g/cm³
X-ray powder data given

CHEMICAL COMPOSITION

[Beus, 1960, p. 103. Numbers of ions on the basis of 7.00 oxygens and 4.00 OH]

	<i>Weight percent</i>	<i>Ratios</i>		<i>Weight percent</i>	<i>Ratios</i>
SiO ₂	34.10	1.83	CaO	.50	
Al ₂ O ₃	1.63	.05	Na ₂ O	2.42	
Fe ₂ O ₃	.12		H ₂ O ⁺	18.95	} 3.98
TiO ₂	Tr.		H ₂ O ⁻	3.25	
MgO	Tr.				
BeO	40.00	5.17		100.97	



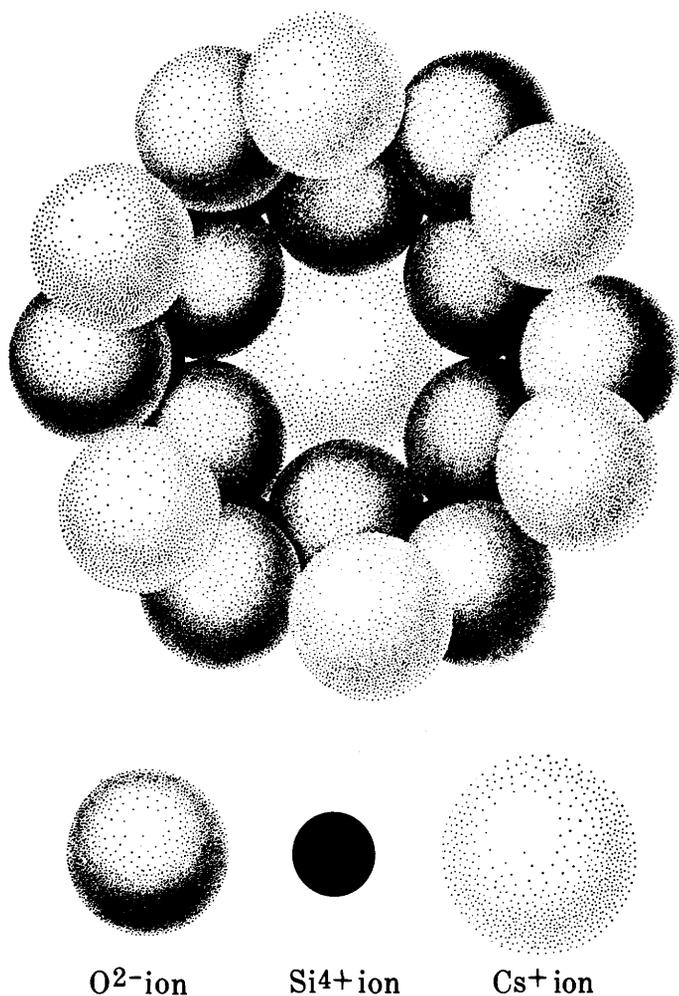


FIGURE 5.—The structure of the $\text{Si}_5\text{O}_{18}^{2-}$ ring in beryl projected on (0001). The opening in the center of the ring is apparently sufficiently large to accommodate a Cs^+ ion, one of which is shown in the center of the diagram. Reprinted from Schaller, Stevens, and Jahns, 1962.

BERYLLONITE**CRYSTALLOGRAPHY**
[Wehrenberg, 1964]

Monoclinic:

a -----	8.16 Å	V ---	895 Å ³
b -----	7.79 Å	D_m ---	2.81 g/cm ³
c -----	14.08 Å	Z ---	12
β -----	90°	D_z ---	2.831 g/cm _z

Space group: $P2_1/n$

X-ray powder data (Mrose, 1952, p. 938)

CHEMICAL COMPOSITION

[Beus, 1960, p. 111]

CRYSTAL STRUCTURE

[Golovastikov, 1961]

Golovastikov, 1961, using the unit-cell data of Wehrenberg, 1954, solved the crystal structure of beryllonite by three-dimensional Patterson techniques. Each BeO_4 tetrahedron shares corners with four PO_4 tetrahedra and likewise each PO_4 tetrahedron shares corners with four BeO_4 tetrahedra. The BeO_4 and PO_4 tetra-

hedra link-up to form pseudo-hexagonal rings as shown in figure 6. The rings are joined to similar rings above and below through the sharing of six apical oxygens, three of which point up and three of which point down. Within the rings are found channels running parallel to the b axis. The rings link together as shown in figure 6 to form a continuous three-dimensional network. The sodium atoms lie within the channels. Na_1 is found to be in ninefold coordination; Na_2 and Na_3 in octahedral coordination.

The range of values for the various bond lengths were found to be as follows:

P-O-----	Angstroms
Be-O-----	1.48-1.56
Na ₁ -O-----	1.58-1.66
Na ₂ , Na ₃ -O-----	2.51-2.82
	2.22-2.68

BERYLLOSODALITE**CRYSTALLOGRAPHY**

[Semenov and Bykova, 1960]

Pseudocubic:

a -----	$\cong 8.7$ Å
D_m -----	2.28 g/cm ³
D_z -----	2.36 g/cm ³ (for $Z=2$ and $V=658.5$ Å ³)

Anisotropic

X-ray powder data given

CHEMICAL COMPOSITION

[Semenov and Bykova, 1960]

	Weight percent	Theoretical
SiO_2 -----	50.45	51.33
Al_2O_3 -----	12.56	10.92
Ga_2O_3 -----	.04	-----
BeO -----	5.30	5.35
CaO -----	.50	-----
Na_2O -----	23.26	26.52
K_2O -----	.40	-----
H_2O^+ -----	1.50	-----
H_2O^- -----	1.51	-----
Cl -----	6.04	7.59
	101.56	101.71
Less O = Cl/2-----	1.40	1.71
Total-----	100.16	100.00

CRYSTAL STRUCTURE

This mineral is probably isostructural with sodalite, $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$, with (BeSi) replacing (2Al). In the well-known sodalite structure (Pauling, 1930), each oxygen atom is coordinated by one silicon, one aluminum, and one sodium atom. Each sodium atom is coordinated by three oxygens and one chlorine atom. The chlorine atoms are coordinated by four sodium atoms. The aluminum and silicon atoms are coordinated tetrahedrally by four oxygens. The aluminum and silicon atoms are ordered.

Semenov and Bykova state that the X-ray powder pattern cannot be indexed with a cubic unit cell. The deviation of beryllsodalite from cubic symmetry is perhaps due to the ordering of Be, Al, and Si, which requires lower symmetry than that of sodalite ($P43n$).

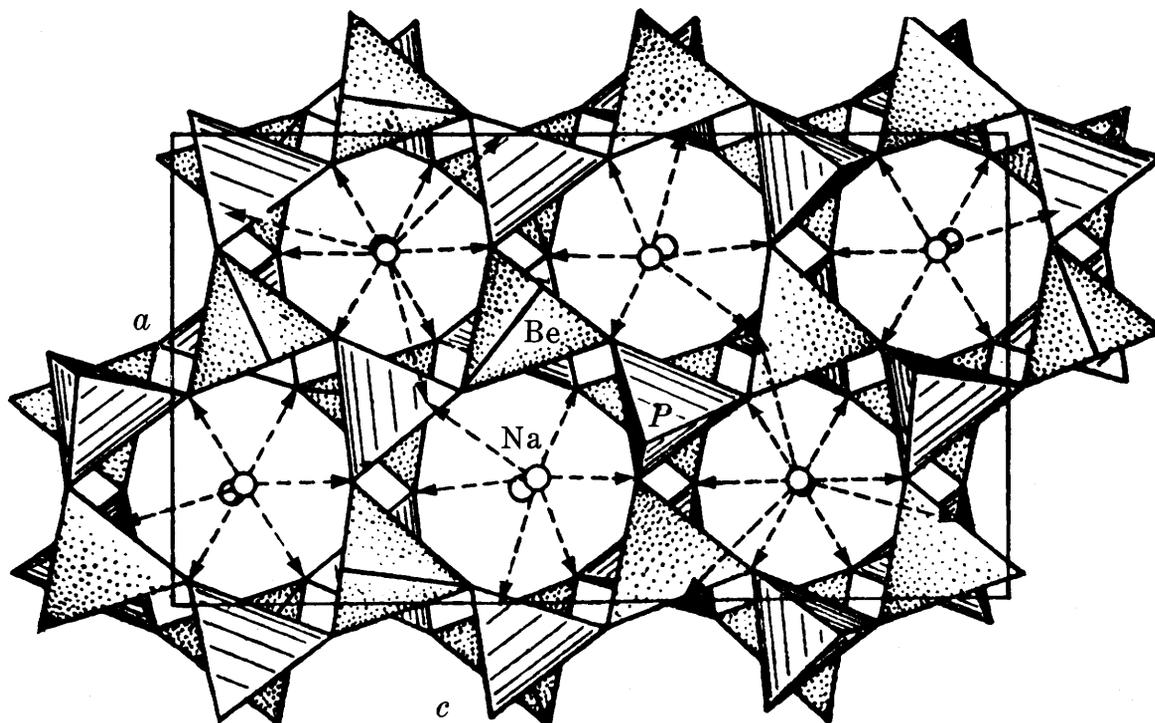
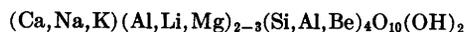


FIGURE 6.—The crystal structure of beryllonite, NaBePO_4 , showing the arrangement of the BeO_4 (stippled) and PO_4 (lined) tetrahedra. The sodium atoms are shown as circles. Reprinted from Golovastikov, 1961.

If in this mineral we retain the $P\bar{4}3n$ symmetry with one Be, Si, and Al atom statistically distributed in the six-fold aluminum position (6d), the bond strengths about each oxygen atom will vary between $1\frac{3}{4}$ and $2\frac{1}{4}$. This leads, probably, to an unstable structure.

BITYITE



CRYSTALLOGRAPHY

[Strunz, 1956]

Monoclinic:

a -----	4.98 Å	V -----	809.1 Å ³
b -----	8.67 Å	D_m -----	3.07 g/cm ³
c -----	18.74 Å	Z -----	4
β -----	$\cong 90^\circ$	D_z -----	3.14 g/cm ³

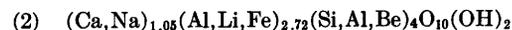
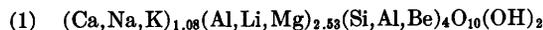
Probable space group: $C2/c$

X-ray powder data given

CHEMICAL COMPOSITION

[Strunz, 1956. Numbers of ions on the basis of 10.00 oxygens and 2.00 OH]

	Weight percent		Ratios	
	(1)	(2)	(1)	(2)
SiO_2 -----	31.95	33.37	2.14	2.17
BeO -----	2.27	7.30	.36	1.14
Al_2O_3 -----	41.75	36.24	1.64	1.39
FeO -----	-----	.17	-----	.01
MgO -----	.13	.04	.01	-----
Li_2O -----	2.73	2.39	.37	.31
Na_2O -----	.40	.29	.02	.02
K_2O -----	.16	.04	.01	-----
CaO -----	14.30	14.42	1.02	1.01
H_2O -----	6.50	5.72	1.45	1.24
	100.19	99.98	-----	-----



In calculating the formulas from these analyses I assume that (1) the tetrahedral positions are completely filled (4 atoms per formula unit); (2) all Si and Be atoms go into the tetrahedral positions; (3) the remaining vacancies in the tetrahedral positions are filled by aluminum; (4) the excess aluminum plus all lithium, iron, and magnesium go into the octahedral positions; (5) calcium, sodium, and potassium go into the interlayer sites; and (6) no water in the form of oxonium ions replaces the interlayer cations.

CRYSTAL STRUCTURE

Bityite is a beryllium margarite. The beryllium replaces some of the aluminum and silicon in the tetrahedral sites. To balance the charges lithium goes into some of the vacant octahedral sites.

BROMELLITE



CRYSTALLOGRAPHY

[Aminoff, 1925]

Hexagonal:

a -----	2.68 kX	D_m -----	3.02 g/cm ³
c -----	4.36 kX	Z -----	2
V -----	27.12 kX ³	D_z -----	3.04 g/cm ³

Space group: $P6_3mc$

CHEMICAL COMPOSITION

[Aminoff, 1925]

	Weight percent		Weight percent
BeO	98.02	Sb ₂ O ₅	.29
CaO	1.03	Al ₂ O ₃	.14
BaO	.55	Loss	.85
MgO	.07		
MnO	Tr.		100.95

CRYSTAL STRUCTURE

Bromellite has the wurtzite structure. Pure synthetic bromellite gives Be-O bond lengths of 1.655 and 1.647 Å, and O-Be-O bond angles of 109.0° and 110.0° (Jeffrey, Parry, and Mozzi, 1956). The unit-cell size of pure BeO is

Angstroms

$$a = 2.698$$

$$c = 4.379$$

CHKALOVITE



CRYSTALLOGRAPHY

[Pyatenko, Bokil, and Belov, 1956]

Orthorhombic:

<i>a</i>	21.1 Å	<i>V</i>	3059 Å ³
<i>b</i>	21.1 Å	<i>Z</i>	24
<i>c</i>	6.87 Å	<i>D_x</i>	2.66 g/cm ³

Space group: *Fddd*

CHEMICAL COMPOSITION

[Beus, 1960, p. 38. Numbers of ions on the basis of 6.00 oxygens]

	Weight percent	Ratios		Weight percent	Ratios
SiO ₂	56.81	1.98	K ₂ O	0.13	-----
Al ₂ O ₃	-----	-----	H ₂ O+	-----	-----
Fe ₂ O ₃	.30	-----	H ₂ O-	.23	-----
FeO	.12	-----	F	-----	-----
BeO	12.67	1.06	SO ₃	.22	-----
CaO	.37	-----			
Na ₂ O	28.93	0.98		99.78	-----



CRYSTAL STRUCTURE

[Pyatenko, Bokil, and Belov, 1956]

Chkalovite has the high cristobalite structure with beryllium substituting for one out of three silicon atoms in the SiO₂ framework. The sodium atoms occupy two-thirds of the large voids in the structure. A structure similar to this was predicted by Buerger (1954) for the compound Na₂BeSiO₄ which represents the fully "stuffed" Na-Be derivative of cristobalite. The formulas of chkalovite and Na₂BeSiO₄ expressed as dioxides are Na_{2/3}(Be_{1/3}Si_{2/3})O₂ and Na(Be_{1/2}Si_{1/2})O₂, respectively. In chkalovite sodium possesses a somewhat irregular coordination, one sodium being in tenfold coordination, the other in elevenfold coordination. Ideally the sodium atom in an undistorted high cristobalite structure would have twelfold coordination.

The unit cell of chkalovite (chk) is related to that of high cristobalite (crist) by:

$$a_{\text{chk}} = b_{\text{chk}} \cong 3a_{\text{crist}}$$

$$c_{\text{chk}} \cong a_{\text{crist}}$$

CHRYSOBERYL



CRYSTALLOGRAPHY

[Bragg and Brown, 1926]

Orthorhombic:

<i>a</i>	5.47 kX	<i>V</i>	227.0 kX ³
<i>b</i>	9.39 kX	<i>Z</i>	4
<i>c</i>	4.42 kX	<i>D_x</i>	3.69 g/cm ³

Space group: *Pbnm*

CRYSTAL STRUCTURE

[Bragg and Brown, 1926]

The oxygen atoms in this structure are approximately in positions of hexagonal close packing, with the two layers perpendicular to (001) repeating every 4.42 kX. The beryllium and aluminum atoms fill, respectively, certain tetrahedral and octahedral holes. Figure 7 shows the linked polyhedra of the two layers of the hexagonal close-packed repeat unit. The structure may be visualized by superimposing figure 7A on figure 7B.

Chrysoberyl is isostructural with olivine and also with the compounds AlGaBeO₄, AlFeBeO₄, and AlCrBeO₄ (Gjessing, Larsson, and Major, 1942).

EPIDIDYMITE



CRYSTALLOGRAPHY

[Ito, 1934; see also Pobedimskaya and Belov, 1960]

Orthorhombic:

<i>a</i>	12.63 kX	<i>V</i>	1255 kX ³
<i>b</i>	7.32 kX	<i>Z</i>	8
<i>c</i>	13.58 kX	<i>D_x</i>	2.58 g/cm ³

Space group: *Pnam*

CHEMICAL COMPOSITION

Beus (1960, p. 37) gives seven chemical analyses of epididymite and its polymorph eudidymite. The composition of these minerals is close to the theoretical composition NaBeSi₃O₇(OH). Minor amounts of aluminum and ferric iron appear to substitute for Be or Si. Also, minor amounts of Ca and Mg probably substitute for Na. Epididymite loses water at 700° to 800° C indicating that hydroxyl groups are present in the structure.

CRYSTAL STRUCTURE

[Ito, 1934; Pobedimskaya and Belov, 1960]

The structure proposed by Ito (1934) has been contradicted by Pobedimskaya and Belov (1960). The

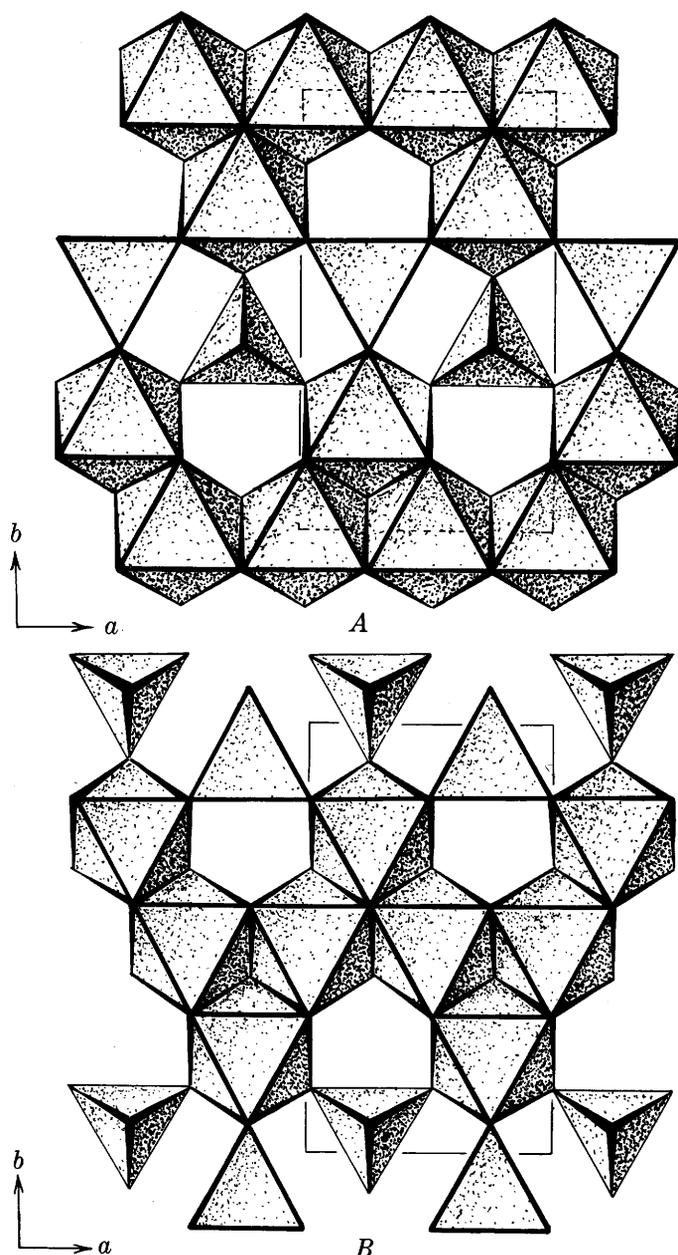


FIGURE 7.—The arrangement of tetrahedra and octahedra in (A) layer I of chrysoberyl, Al_2BeO_4 , and (B) layer II of chrysoberyl.

atomic parameters proposed by Ito give unusually poor Be-O and Si-O bond lengths which led the Russian workers to reexamine the structure. The atomic parameters proposed by these workers give plausible bond lengths. Their structure cannot, however, be accepted at this time. The epididymite unit cell contains 56 oxygen atoms and 8 (OH) groups. Pobedinskaya and Belov list coordinates for 60 oxygen atoms and 8 (OH) groups.

EPIDIDYMITE



CRYSTALLOGRAPHY

[Ito, 1947; see also Pobedinskaya and Belov, 1961]

Monoclinic:

a -----	12.62 kX	V -----	1264 kX ³
b -----	7.37 kX	D_m -----	2.553 g/cm ³
c -----	13.99 kX	Z -----	8
β -----	103°43'	D_x -----	2.561 g/cm ³

Space group: $C2/c$

CHEMICAL COMPOSITION

[See the discussion of the chemistry of epididymite]

CRYSTAL STRUCTURE

[Ito, 1947; Pobedinskaya and Belov, 1961]

Ito (1947) has proposed a structure for this mineral. The bond distances are, however, so grossly in error that the structure cannot be considered correct. Pobedinskaya and Belov (1961), as they did with epididymite, proposed a structure with 60 oxygen atoms and 8 (OH) groups in the unit cell.

FAHEYITE



CRYSTALLOGRAPHY

[Lindberg and Murata, 1953]

Hexagonal?:

a -----	9.43 Å	D_m -----	2.660 g/cm ³
c -----	16.00 Å	Z -----	3
V -----	1232 Å ³	D_x -----	2.670 g/cm ³

X-ray powder data given

CHEMICAL COMPOSITION

[Lindberg and Murata, 1953. Numbers of ions on the basis of 16.00 oxygens]

	Weight percent	Ratios		Weight percent	Ratios
P_2O_5 -----	38.11	1.99	K_2O -----	Tr.	-----
Fe_2O_3 -----	21.42	.99	F-----	Tr.	-----
Al_2O_3 -----	.10	.01	H_2O -----	14.90	6.11
BeO -----	7.26	2.15	Insol-----	9.44	-----
MnO -----	5.99	.62			
MgO -----	1.14	.21		99.20	-----
Na_2O -----	.84	.10			



GELBERTRANDITE



CRYSTALLOGRAPHY

[Semenov, 1957]

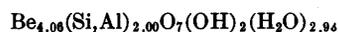
$D_m = 2.176 \text{ g/cm}^3$

X-ray powder data given

CHEMICAL COMPOSITION

[Semenov, 1957. Numbers of ions on the basis of 7.00 oxygens and 2.00 OH]

	Weight percent	Ratios		Weight percent	Ratios
SiO_2 -----	38.70	1.92	$\text{H}_2\text{O} +$ -----	15.62	} 3.93
Al_2O_3 -----	1.20	.04	$\text{H}_2\text{O} -$ -----	8.17	
BeO -----	34.16	4.06			
CaO -----	1.93	-----		100.11	-----
$(\text{Na}, \text{K})_2\text{O}$ ---	.33	-----			



This mineral may be a poorly crystallized bertrandite (Fleischer, 1958).

HAMBERGITE**CRYSTALLOGRAPHY**

[Zachariasen, 1931b; Zachariasen and Plettinger, 1958]

Orthorhombic:

a.....	9.755 ± 0.002A
b.....	12.201 ± 0.002A
c.....	4.426 ± 0.001A
V.....	526.79 Å ³
Z.....	8
D _z	2.34 g/cm ³

Space group: *Pbca***CRYSTAL STRUCTURE**

[Zachariasen and Plettinger, 1958]

The beryllium atoms are coordinated tetrahedrally by three oxygen atoms and one (OH) group. Each oxygen atom of the $\text{BeO}_3(\text{OH})$ tetrahedra is shared with another $\text{BeO}_3(\text{OH})$ group and a BO_3 triangle. The (OH) group is shared between two $\text{BeO}_3(\text{OH})$ tetrahedra. The boron atoms are in triangular coordination by three oxygens at distances of 1.33 ± 0.02 Å. Each of these oxygens is also shared with two $\text{BeO}_3(\text{OH})$ tetrahedra. The triangles lie in a plane parallel to the *c*-axis. Figure 8 shows a portion of the hambergite structure projected on (001). The $\text{BeO}_3(\text{OH})$ groups are shown as shaded polyhedra in this figure. As can be seen the structure is a three-dimensional one formed by the linking of tetrahedra in infinite spirals parallel to *c*. There appears to be a hydrogen bond of 2.89 Å between the (OH) groups (shown as dashed lines in fig. 8).

Zachariasen found Be-O bond lengths of 1.655, 1.639, 1.657, 1.636, 1.663, and 1.667 Å. Be-(OH) lengths of 1.637 and 1.645 Å were observed. The average Be-O (OH) lengths is 1.650 Å.

HARSTIGITE**CRYSTALLOGRAPHY**

[Flink, 1917]

Orthorhombic

CHEMICAL COMPOSITION

[Flink, 1917. Numbers of ions on the basis of Si=6.00]

	(1)		(2)	
	Weight percent	Ratios	Weight percent	Ratios
SiO ₂	39.92	6.00	40.70	6.00
BeO.....	11.57	4.18	11.40	4.10
FeO.....	Tr.	---	Tr.	---
MnO.....	7.07	.90	7.03	.89
MgO.....	.94	.21	.93	.21
CaO.....	37.78	6.08	37.86	6.08
H ₂ O.....	2.48	.13	---	---
F.....	---	---	.15	.07
Less O = F/2.....	99.76	---	97.44	---
Total.....	---	---	97.38	---

(1) $(\text{Ca}, \text{Mn}, \text{Mg})_{7.19}\text{Be}_{4.16}\text{Si}_{6.00}(\text{O}, \text{OH}, \text{F})_{23.60}$ (2) $(\text{Ca}, \text{Mn}, \text{Mg})_{7.18}\text{Be}_{4.10}\text{Si}_{6.00}(\text{O}, \text{OH}, \text{F})_{23.35}$ **HELVITE****DANALITE****GENTHELVITE****CRYSTALLOGRAPHY**

[Glass, Jahns, and Stevens, 1944; Pauling, 1930]

Extrapolated X-ray data for the Mn, Fe, and Zn end members are given as follows:

	a (kX)	V (kX ³)	Z	D (g/cm ³)	Space group (cubic)
Helvite.....	8.27	565.6	2	3.20	$\overline{P}43n$
Danalite.....	8.18	547.3	2	3.35	$\overline{P}43n$ (probable)
Genthelvite.....	8.10	531.4	2	3.70	$\overline{P}43n$ (probable)

CHEMICAL COMPOSITION

[Glass and others 1944; Beus, 1960]

Helvite, danalite, and genthelvite are names designating the manganese, iron, and zinc end members, respectively. There is apparently a complete solid solution formed between these end members. Inspection of the chemical analyses given by Beus (1960, p. 43) indicates that some aluminum substitutes for beryllium with a concomitant substitution of Na for Mn, Fe, or Zn. A limited solid solution towards the $(\text{R}_3^{2+}\text{Na})(\text{Be}_2\text{Al})\text{Si}_3\text{O}_{12}\cdot\text{S}$ end member may thus exist.

CRYSTAL STRUCTURE

[Pauling, 1930]

Helvite has the sodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$) structure with Mn replacing sodium, Be replacing Al, and S replacing Cl. Helvite, by analogy to sodalite, possesses a framework structure with each SiO_4 tetrahedron sharing corners with four BeO_4 tetrahedra and with each BeO_4 tetrahedron similarly sharing all corners with SiO_4 tetrahedra. The two types of tetrahedra link into a three-dimensional network in which there appear large cages. In these cages, composed of 24 tetrahedra, lie the sulfur atoms. In helvite the Mn atoms lie within six-sided orifices and according to Pauling are coordinated by one sulfur and three oxygen atoms in a tetrahedral arrangement. The electrostatic valence rule is satisfied. The bond strength from Si, Be, and Mn is 1, $1/2$, and $1/2$, respectively. Each oxygen atom is in contact with one Si, one Be, and one Mn atom to give a charge balance of two. Each sulfur atom is in contact with four Mn atoms to give a charge balance of two.

Danalite and genthelvite are isostructural with helvite.

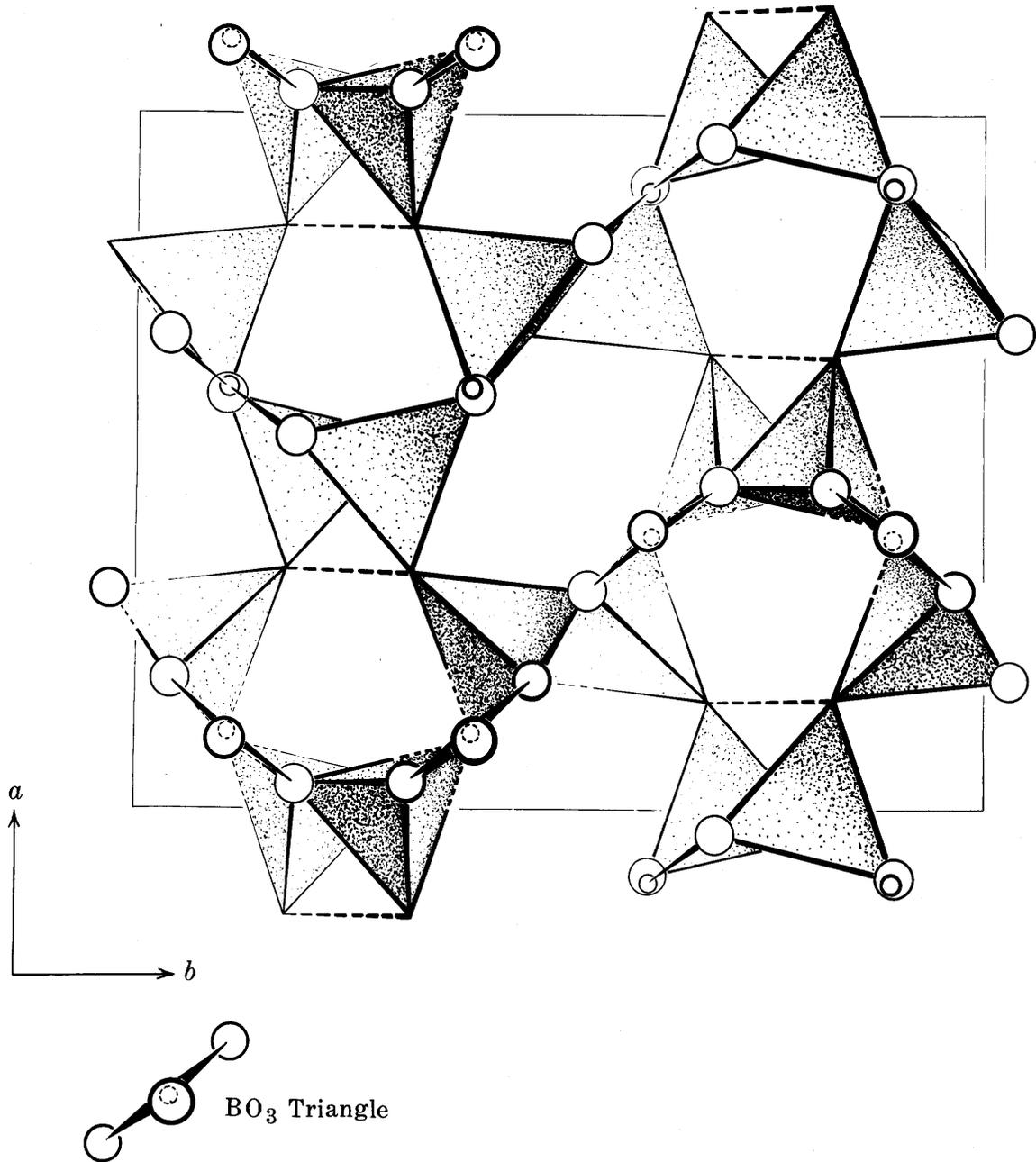


FIGURE 8.—The crystal structure of hambergite, $\text{Be}_2(\text{BO}_3)(\text{OH})$. The $\text{BeO}_3(\text{OH})$ tetrahedra link to form spirals parallel to the c -axis.

HERDERITE**CRYSTALLOGRAPHY**

[Pavlov and Belov, 1960]

Monoclinic:

<i>a</i>	9.80 Å	<i>V</i>	361.3 Å ³
<i>b</i>	7.68 Å	<i>D_m</i>	3.00 g/cm ³
<i>c</i>	4.80 Å	<i>Z</i>	4
<i>β</i>	90°6'	<i>D_z</i>	2.98 g/cm ³

Space group: *P2₁/a*

X-ray powder data (Mrose, 1952, p. 938)

CHEMICAL COMPOSITION

There is apparently a complete solid solution between herderite, CaBePO₄F, and hydroxyl-herderite, CaBePO₄(OH).

CRYSTAL STRUCTURE

[Pavlov and Belov, 1960]

The herderite structure consists of infinite sheets of linked PO₄ and BeO₃F tetrahedra. Each BeO₃F tetrahedron shares three oxygens with three adjacent PO₄ tetrahedra. The PO₄ tetrahedra share three corners with three adjacent BeO₃F tetrahedra. Between the (BePO₄F)_n sheets lie the calcium atoms. These atoms are coordinated by six oxygen atoms and two fluorine atoms; F, O₁, O₂, and O₃ of one sheet and by F, O₁, O₃, and O₄ of the second sheet. The structure of the sheets is shown in figure 9. The arrangement of the calcium polyhedra is shown in figure 10.

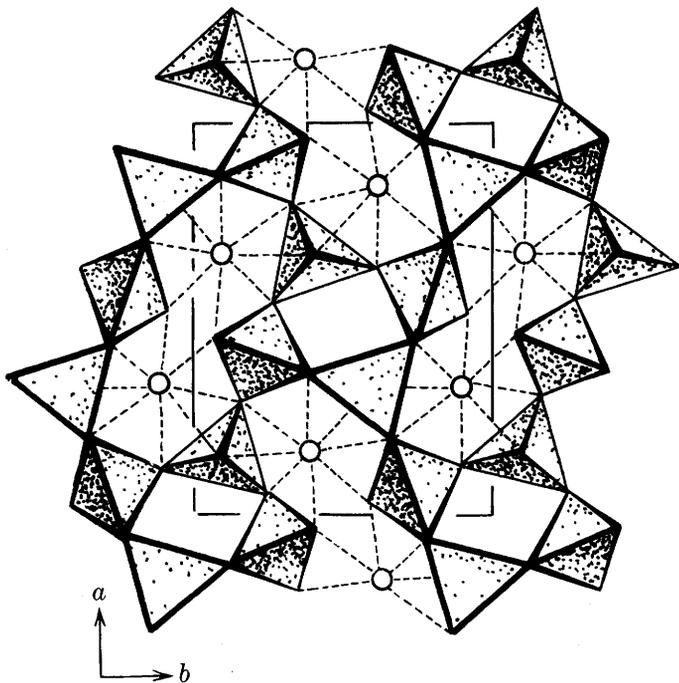


FIGURE 9.—Herderite, CaBePO₄(F,OH), showing the structure of the infinite (BePO₄F)_n sheets. Dashed lines denote the calcium-oxygen (fluorine) bonds. The PO₄ tetrahedra have their 4 axes approximately perpendicular to the *a-b* plane; the BeO₃F tetrahedra have their threefold axes approximately perpendicular to the *a-b* plane.

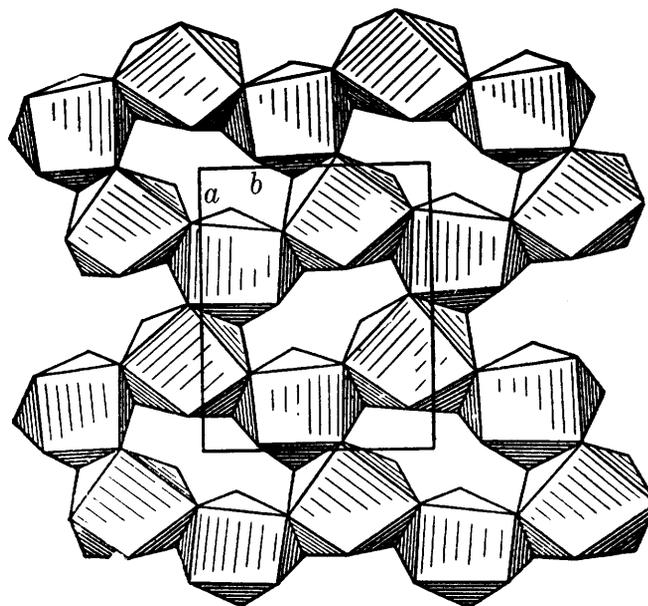


FIGURE 10.—Herderite, CaBePO₄(F,OH), showing the arrangement of the calcium polyhedra. Reprinted from Pavlov and Belov, 1960.

The bond lengths are given as follows:

	Angstroms		Angstroms
P-O ₁	1.51	Be-F.....	1.67
P-O ₂	1.52	Ca-O ₁	2.40, 2.40
P-O ₃	1.57	Ca-O ₂	2.44
P-O ₄	1.51	Ca-O ₃	2.61, 2.70
Be-O ₂	1.64	Ca-O ₄	2.44
Be-O ₃	1.55	Ca-F.....	2.71, 2.58
Be-O ₄	1.67		

Herderite is isostructural with datolite, CaBSiO₄(OH) (Ito and Mori, 1953). In datolite Be²⁺P⁵⁺ is replaced by B³⁺Si⁴⁺. Herderite is also structurally related to gadolinite, Fe_{1/2}YBeSiO₄.O, which will be described next.

GADOLINITE**CRYSTALLOGRAPHY**

[Ito and Mori, 1953; Pavlov and Belov, 1960]

Monoclinic:

<i>a</i>	9.89 ± 0.01 Å	<i>β</i>	90°33'
<i>b</i>	7.52 ± 0.01 Å	<i>V</i>	350.3 Å ³
<i>c</i>	4.71 ± 0.01 Å	<i>Z</i>	4

Space group: *P2₁/a***CHEMICAL COMPOSITION**

Gadolinite is a complex rare earth silicate; it is often in the metamict state owing to the presence of radioactive thorium and uranium in the structure. Fe²⁺, Be,

and Si are apparently essential constituents although small amounts of Fe^{3+} , Al, and Mn^{2+} may substitute for these ions. Yttrium and the yttrium earths are usually present to the extent of 22 to 46 percent by weight (Dana, 1892, p. 511). Other elements including the cerium earths, thorium, uranium, calcium, magnesium, sodium, and potassium may substitute for yttrium and the yttrium earths. Nakai (1938) reports a calcium-lanthanum gadolinite containing 11.93 percent Ca (see also Beus, 1960, p. 59).

CRYSTAL STRUCTURE

[Ito and Mori, 1953; Pavlov and Belov, 1960]

The formula of gadolinite is derived from that of herderite, CaBePO_4F , by replacing Ca with Y^{3+} , PO_4 with SiO_4 and F with O^{2-} to give the radical $(\text{YBeSiO}_4\text{O})^-$. Fe^{2+} is placed in the special positions $2a$ ($000, \frac{1}{2}, 0$) of space group $P2_1/a$ which are unoccupied in the herderite structure. The other atoms are in the general positions ($4e$) so that we have one Fe atom for every two Y, Be, and Si atoms. The formula can thus be written $\text{Fe}\frac{1}{2}\text{YBeSiO}_4\text{O}$. The iron atoms occupy a position within the rings of six YO_6 polyhedra as shown in figure 11.

HSIANGUALITE



CRYSTALLOGRAPHY

[Huang, Tu, Wang, Chao, and Yu, 1958; Fleischer, 1959; Beus, 1960, p. 60-61]

Cubic:

a	12.879 \pm 0.004 A
V	2136 A ³
D_m	2.97-3.00 g/cm ³
Z	8
D_x	2.95 g/cm ³

Space group: $I4_32$

CHEMICAL COMPOSITION

[Huang and others, 1958; Beus, 1960, p. 60-61. Numbers of ions on the basis of 12.00 oxygens and 2.00 F]

	(1)		(2)	
	Weight percent	Ratios	Weight percent	Ratios
SiO_2	35.66	2.93	36.64	2.95
CaO	34.60	3.05	35.18	3.04
BeO	15.78	3.12	16.30	3.16
Li_2O	5.85	.97	5.60	.90
Al_2O_350	-----	-----	-----
Fe_2O_322	-----	.06	-----
MgO18	-----	.17	-----
Na_2O13	-----	.03	-----
K_2O06	-----	.03	-----
F.....	7.81	2.03	7.27	1.85
Loss.....	1.28	-----	-----	-----
	102.07	-----	101.28	-----
Less $\text{O} = \text{F}/2$	3.29	-----	3.06	-----
Total.....	98.78	-----	98.22	-----

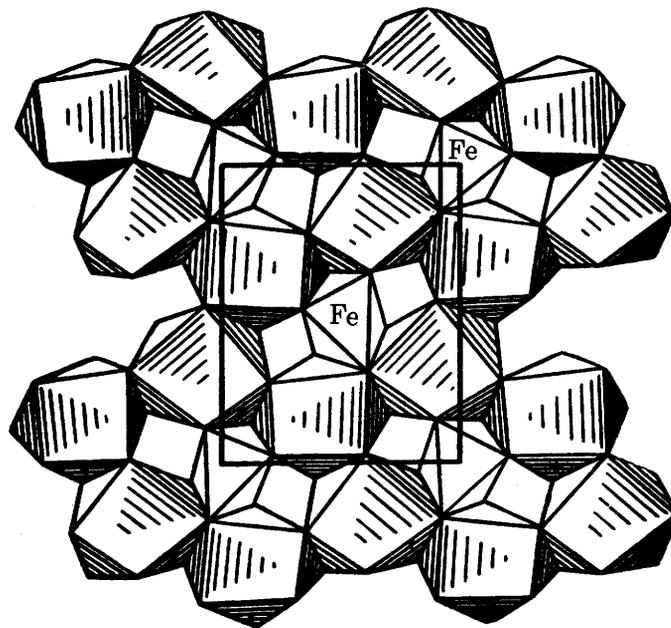
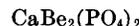


FIGURE 11.—Gadolinite, $\text{Fe}\frac{1}{2}\text{YBeSiO}_4\text{O}$, showing the arrangement of the YO_6 and FeO_6 polyhedra. Reprinted from Pavlov and Belov, 1960.

HURLBUTITE



CRYSTALLOGRAPHY

[Bakakin and Belov, 1960]

Monoclinic:

a	8.29 A	V	569.8 A ³
b	8.80 A	Z	4
c	7.81 A	D_x	2.89 g/cm ³
β	$\cong 90^\circ$		

Space group: $P2_1/a$

X-ray powder data (Mrose, 1952, p. 937-938)

CRYSTAL STRUCTURE

Hurlbutite is isostructural with danburite, $\text{CaB}_2(\text{SiO}_4)_2$ (Dunbar and Machatschki, 1931; Bakakin, Krauchenko, and Belov, 1959; Bakakin and Belov, 1960). The hurlbutite structure is also related to that of the feldspars. Compare the hurlbutite structure (fig. 12) with that of sanidine (Eitel, 1958, fig. 56, p. 85).

For convenience of presentation a sheet of the composition $(\text{BePO}_5)_n^{3n-}$ is isolated from the three-dimensional structure and is shown in figure 12. This sheet is connected above and below through sharing of apical oxygens to two nearly identical $(\text{BePO}_5)_n^{3n-}$ sheets. Each BeO_4 tetrahedron is linked by sharing corners to four PO_4 tetrahedra. Likewise, each PO_4 tetrahedron is linked to four BeO_4 tetrahedra. The phosphorus and beryllium atoms in adjacent sheets are interchanged so

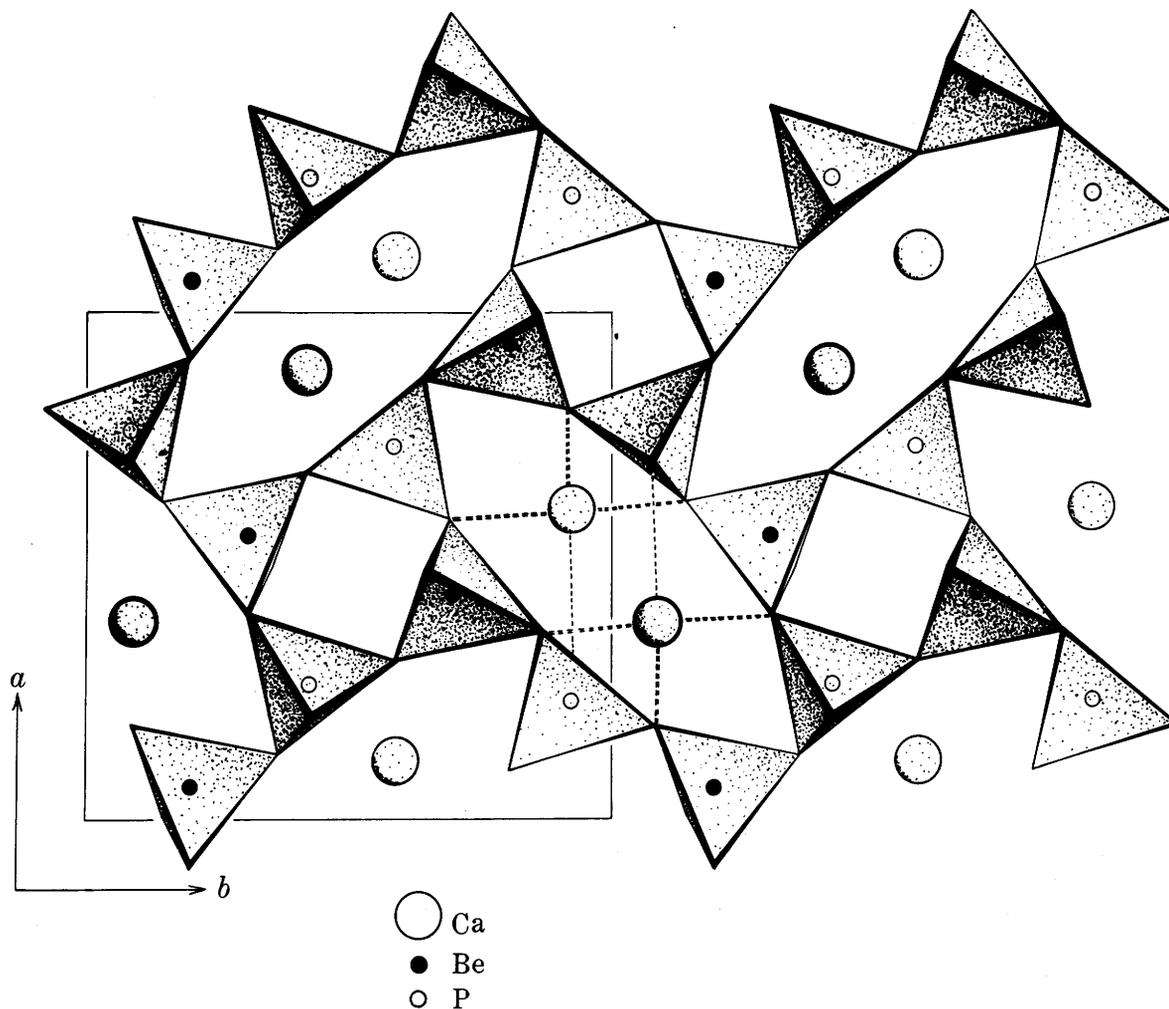


FIGURE 12.—The hurlbutite, $\text{CaBe}_2(\text{PO}_4)_2$, structure showing the arrangement of the infinite $(\text{BePO}_5)_n^{2n-}$ sheets.

that only beryllium atoms are adjacent to phosphorus atoms. The calcium atoms lie between the $(\text{BePO}_5)_n^{2n-}$ sheets and are in sevenfold coordination. The Ca-O bonds are shown as dashed lines in figure 12.

In danburite, the SiO_4 and BO_4 tetrahedra link up in much the same manner as in hurlbutite. In danburite, however, each SiO_4 tetrahedron is linked to three BO_4 tetrahedra and one SiO_4 tetrahedron. Each BO_4 tetrahedron is linked to three SiO_4 tetrahedra and one BO_4 tetrahedron. The two different distributions of tetrahedrally coordinated cations in hurlbutite and danburite are necessary in order to balance charges on the oxygen atoms. The charge distribution on the oxygen atoms is given in table 3. Although danburite is orthorhombic, it has a unit cell similar in size and shape to that of hurlbutite ($a=8.01\text{A}$, $b=8.75\text{A}$, and $c=7.71\text{A}$). The calcium atom in danburite is also in sevenfold coordination.

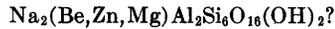
TABLE 3.—Charge distribution on the oxygen atoms in hurlbutite and danburite

HURLBUTITE		DANBURITE	
(4) O_1 -----	2.036	(8) O_1 -----	2.036
(4) O_2 -----	2.036	(8) O_2 -----	2.036
(4) O_3 -----	2.036	(8) O_3 -----	2.036
(4) O_4 -----	2.036	(4) O_4 -----	2.000
(4) O_5 -----	2.036	(4) O_5 -----	1.784
(4) O_6 -----	2.036		
(4) O_7 -----	1.750		
(4) O_8 -----	2.036		

TABLE 4.—Bond lengths in the hurlbutite structure

	Angstroms		Angstroms
P_1-O_1 -----	1.60	Be_2-O_2 -----	1.60
P_1-O_3 -----	1.58	Be_2-O_4 -----	1.58
P_1-O_5 -----	1.56	Be_2-O_6 -----	1.59
P_1-O_8 -----	1.59	Be_2-O_8 -----	1.61
P_2-O_2 -----	1.55	$\text{Ca}-\text{O}_1$ -----	2.52
P_2-O_4 -----	1.57	$\text{Ca}-\text{O}_2$ -----	2.49
P_2-O_6 -----	1.56	$\text{Ca}-\text{O}_3$ -----	2.46
P_2-O_7 -----	1.58	$\text{Ca}-\text{O}_4$ -----	2.42
Be_1-O_1 -----	1.57	$\text{Ca}-\text{O}_5$ -----	2.43
Be_1-O_3 -----	1.59	$\text{Ca}-\text{O}_6$ -----	2.46
Be_1-O_5 -----	1.59	$\text{Ca}-\text{O}_7$ -----	2.47
Be_1-O_7 -----	1.59		

Table 4 gives the bond lengths found in hurlbutite by (Bakakin and Belov, 1960). The average phosphorus-phosphate oxygen distance is 1.57Å. The average beryllium-beryllium oxygen distance is 1.59Å. It appears that this structure needs further refinement for we should expect the average P-O and Be-O bond distances to be 1.52 and 1.64Å respectively.

KARPINSKYITE**CRYSTALLOGRAPHY**

(Shilin, 1956)

Trigonal:		D_m -----	2.545 g/cm ³
a -----	14.24 Å	Z -----	6
c -----	4.83 Å		
V -----	848.2 Å ³		
Diffraction symbol:	$P \dots$		
X-ray powder data given			

CHEMICAL COMPOSITION

(Shilin, 1956. Numbers of ions on the basis of 16.00 oxygens and 2.00 OH)

	Weight percent	Ratios		Weight percent	Ratios
SiO ₂ -----	56.68	5.94	Na ₂ O-----	9.18	1.04
Al ₂ O ₃ -----	16.40	1.02	K ₂ O-----	1.55	1.75
Fe ₂ O ₃ -----	.06		H ₂ O+-----	5.00	.87
BeO-----	2.58	.65	H ₂ O-----	2.50	
ZnO-----	3.26	.25			
MgO-----	.78	.12		97.99	-----

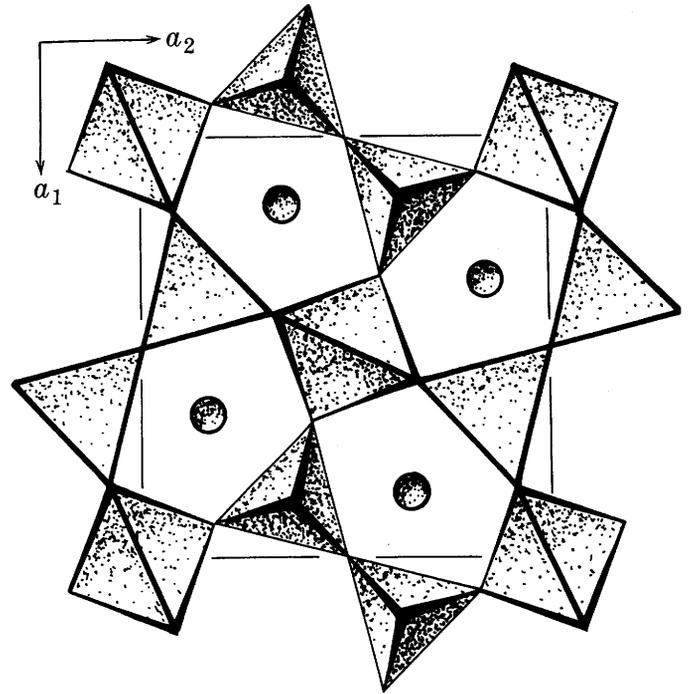
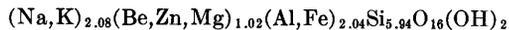


FIGURE 13.—Melilite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$). The MgO_4 tetrahedra are located at 0,0 and $\frac{1}{2}, \frac{1}{2}$ along the x and y (a_1 and a_2) axes. About the MgO_4 tetrahedra are arranged four Si_2O_7 groups. The calcium atoms are depicted by circles.

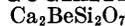
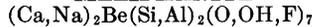
GUGIAITE**LEUCOPHANITE****MELIPHANITE**

Table 5.—Crystallography of gugiaite, leucophanite, meliphanite, and the related minerals melilite and hardystonite

	(1)	(2)	(3)	(4)	(5)
	Gugiaite, tetragonal	Leucophanite, orthorhombic ¹	Meliphanite, tetragonal ¹	Melilite, tetragonal	Hardystonite, tetragonal ¹
a -----	7.48±0.02	7.40±0.02	10.62±0.02	7.789±0.005	7.87
b -----		7.40±0.02			
c -----	5.044±0.003	10.0±0.02	9.92±0.02	5.018±0.005	5.01
V -----	282.2	548	1119	304.4	310
Z -----	2	4	8	2	2
Space group	$P4_2/m$			$P4_2/m$	$P4_2/m$
Pseudocell:					
a -----		7.39	7.50		
c -----		5.0	4.96		
Reference	Peng and others, 1962	Zachariasen, 1930, 1931a	Zachariasen, 1930, 1931a	Smith, 1953, 1954	Warren and Trautz, 1930
Chemical composition ² -----	See analysis (8)	See analysis (4)	See analysis (5)	From Smith, 1953	From Palache, 1935, p. 94

¹ Unit cell edges have been converted from kX units to angstrom units.

² For analyses see table 6.

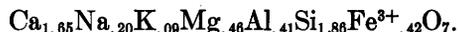
CRYSTAL STRUCTURE

Zachariasen (1930, 1931a) has shown that there is a close structural relationship between leucophanite, meliphanite, and the melilites. Peng and others (1962) demonstrated that gugiaite is a beryllium melilite. Before discussing the structure of leucophanite, meliphanite, and gugiaite it will be useful to first consider the structure of the melilites.

Warren (1930) found the structure of a melilite, of

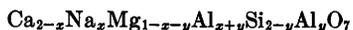
the composition $(\text{Ca,Na})_2(\text{Mg,Al})(\text{Si,Al})_2\text{O}_7$, to consist of sheets composed of Si_2O_7 groups linked to MgO_4 tetrahedra through the sharing of the oxygen atoms. Figure 13 shows a sheet of this type projected on (001). These sheets, of the ideal composition $(\text{MgSi}_2\text{O}_7)_n^{4n-}$, are held together by calcium and sodium atoms. The calcium (and sodium) polyhedra are in the form of square Archimedean antiprisms and are shown in figure 14.

Smith (1953) has accurately determined the structure of a melilite of the composition



He finds that sodium and potassium may substitute for calcium; Mn^{2+} , Fe^{2+} , Fe^{3+} , and Al for Mg; and Al and Fe^{3+} for Si.

A review of the papers discussing the melilite mineral group, for example, Berman (1929), Goldsmith (1948), Andrews (1948), Smith (1953), and Neuvonen (1955), gives a fairly good picture of the cationic substitution found in these minerals. We may give the following general formula for the melilites:



where small amounts of K may substitute for Na, small amounts of MnO and FeO for MgO, and moderate amounts of Fe_2O_3 for Al_2O_3 . From the analyses given by Berman (1929) we find that as much as 0.52 atom of Na may substitute for Ca, up to 1.00 atom of Al may substitute for Mg, and as much as 0.78 atom of Al may substitute for Si. The theoretical end members in this mineral group are gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$, and akermanite, $\text{Ca}_2\text{MgSi}_2\text{O}_7$. Hardystonit \acute{e} , $\text{Ca}_2\text{ZnSi}_2\text{O}_7$, is the rare zinc-containing end member (Palache, 1935, p. 94).

We have already compared the unit cell dimensions of melilite and hardystonite to those of leucophanite, meliphanite, and gugiaite. We see that the minerals of the leucophanite group have unit cells or pseudo-unit cells similar in size to those of the melilites.

Leucophanite, meliphanite, and gugiaite may be considered to be calcium-sodium beryllium melilites.

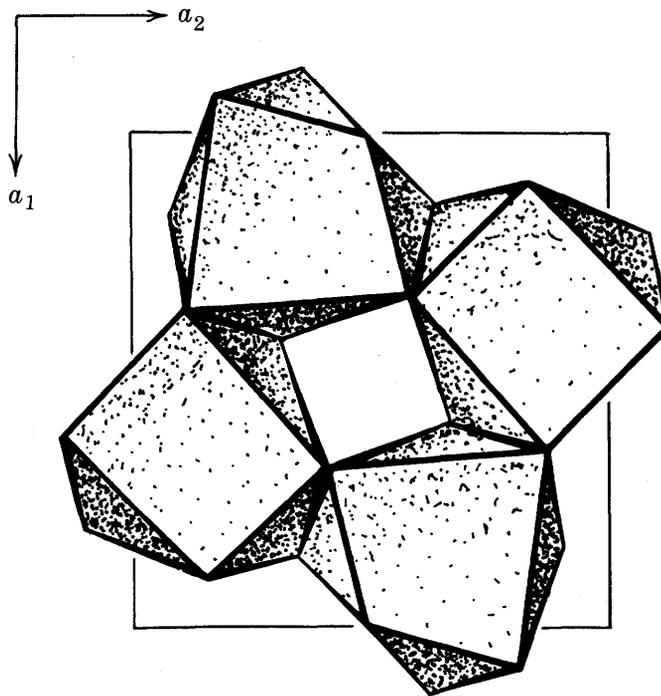


FIGURE 14.—The arrangement of the CaO polyhedra in melilite, $\text{Ca}_2\text{MgSi}_2\text{O}_7$

Some aluminium replaces silicon and some fluorine and (or) chlorine replaces oxygen in the structure. The H_2O reported in the analyses probably occurs as (OH) groups substituting for oxygen. If we examine figure 13 we see that four of the 14 oxygen atoms within the unit cell are not shared between two tetrahedra. It is

TABLE 6.—Chemical composition of gugiaite, leucophanite, and meliphanite

(Samples 1-6, Dana, 1892, p. 418; 7, Semenov, 1957; 8, Peng and others, 1962. Numbers of ions on the basis of $\text{O}+\text{F}+\text{OH}=7.00$)

	1		2		3		4		5		6		7		8	
	Weight percent	Ratios														
SiO_2	47.82	1.96	47.03	1.96	48.38	1.98	48.50	1.98	43.60	1.82	43.66	1.84	45.98	1.85	44.90	1.91
Fe_2O_3															2.17	.05
Al_2O_3			1.03	.02			.45	.01	4.61	.12	1.57	.04	2.32	.06	9.49	.97
BeO.....	11.51	1.13	10.70	1.07	11.97	1.17	10.03	.98	9.80	.99	11.74	1.19	11.52	1.11	40.09	1.82
CaO.....	25.00	1.10	23.37	1.04	23.37	1.02	22.94	1.00	29.56	1.33	26.74	1.21	23.65	1.02	72	.03
Na_2O	10.20	.40	11.26	.45	10.27	.40	12.42	.49	7.96	.33	8.55	.35	10.79	.42	.20	.01
K_2O31	.01	.30	.01	.30	.01			.23		1.40	.04	.70	.01	.38	.02
MgO.....			.17	.01			.27	.01	.16	.01	.11	.01	.30	.02	.07	
MnO.....	1.01	.04													.25	.03
F.....	6.17	.80	6.75	.86	6.77	.87	5.94	.76	5.43	.72	5.73	.76	7.04	.89	.90	.13
H_2O^+							1.08	.15			.30	.04	.83	.11	.36	
H_2O^-18	.01
Cl.....															.08	
P_2O_5															Tr.	
TiO_204	
Volatiles.....																
Less $\text{O}=\text{F}+\text{Cl}/2$	102.02		100.61		101.06		101.63		101.37		99.80		103.35		99.94	
	2.58		2.84		2.85		2.50		2.29		2.40		2.95		1.15	
	99.44		97.77		98.21		99.13		99.08		97.40		100.40		99.79	

FORMULAS OF SAMPLES

- $(\text{Ca}, \text{Na}, \text{K})_{1.96}(\text{Be}, \text{Mn})_{1.17}\text{Si}_{1.96}\text{O}_{6.20}\text{F}_{.80}$
- $(\text{Ca}, \text{Na}, \text{K})_{1.96}(\text{Be}, \text{Mg})_{1.03}(\text{Si}, \text{Al})_{2.00}\text{O}_{6.14}\text{F}_{.86}$
- $(\text{Ca}, \text{Na}, \text{K})_{1.94}\text{Be}_{1.17}\text{Si}_{1.95}\text{O}_{6.12}\text{F}_{.87}$
- $(\text{Ca}, \text{Na})_{1.93}(\text{Be}, \text{Mg})_{.99}(\text{Si}, \text{Al})_{2.00}\text{O}_{6.91}(\text{F}, \text{OH})_{.09}$
- $(\text{Ca}, \text{Na})_{1.99}(\text{Be}, \text{Mg})_{1.00}(\text{Si}, \text{Al})_{2.00}\text{O}_{6.23}\text{F}_{.72}$
- $(\text{Ca}, \text{Na}, \text{K})_{1.99}(\text{Be}, \text{Mg})_{1.20}(\text{Si}, \text{Al})_{1.92}\text{O}_{6.15}(\text{F}, \text{OH})_{.34}$
- $(\text{Ca}, \text{Na}, \text{K})_{1.88}(\text{Be}, \text{Mg})_{1.13}(\text{Si}, \text{Al}, \text{Fe})_{1.97}\text{O}_{6.90}(\text{F}, \text{OH})_{1.11}$
- $(\text{Ca}, \text{Na}, \text{K})_{1.90}(\text{Be}, \text{Mg})_{.99}(\text{Si}, \text{Al})_{2.01}\text{O}_{6.70}(\text{F}, \text{Cl}, \text{OH})_{.30}$

these oxygen atoms that are probably replaced by F, Cl, and (OH).

Examination of the chemical compositions of various minerals belonging to the leucophanite group given previously suggests the following general chemical formula:



where

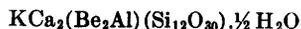
$$0 \leq (x+y) \leq 2.$$

Small amounts of K substitute for Na, and Mg and Mn for Be. The substitution of (OH) groups for oxygen atoms in the melilites has been postulated by Goldsmith (1948). Smith (1953, 1954) also discussed this but did not consider the mechanism important.

The names leucophanite, meliphanite, and gugiaite are synonymous. The mineral aminoffite is probably a member of the leucophanite group, perhaps having a formula similar to that of gugiaite.

A synthetic beryllium melilite ($\text{Ca}_2\text{BeSi}_2\text{O}_7$) close to gugiaite in composition, has been reported by Gorja (1953-54). The compound is tetragonal with $a=7.501$ Å and $c=4.931$ Å ($Z=2$). The probable space group is $P4_2/m$. The synthetic compound $\text{Na}_2\text{LiBe}_2\text{F}_7$, reported by O'Daniel and Tscheischwili (1948) is tetragonal with $a=7.5$ Å and $c=5.03$ Å ($Z=2$). From a comparison of X-ray powder patterns $\text{Na}_2\text{LiBe}_2\text{F}_7$ was found to be isostructural with the melilites. Here Na plays the role of calcium, Li that of Mg, Be that of Si, and F that of oxygen.

MILARITE



CRYSTALLOGRAPHY

[Belov and Tarkhova (1951)]

Hexagonal:

a	10.43 Å	D_m	2.57 g/cm ³
c	13.85 Å	Z	2
V	1304 Å ³	D_x	2.52 g/cm ³

Space group: $P6/mcc$

[Ito, Morimoto, and Sadanaga (1952)]

Hexagonal:

a	10.54 Å	D_m	2.55 g/cm ³
c	13.96 Å	Z	2
V	1343 Å ³	D_x	2.45 g/cm ³

Space group: $P6/mcc$

CHEMICAL COMPOSITION

[Palache, 1931. Numbers of ions on the basis of 30.00 oxygens]

	Weight percent	Ratios		Weight percent	Ratios
SiO_2	71.66	11.93	Na_2O	0.46	0.07
Al_2O_3	4.68	.46	H_2O^+	1.02	.57
BeO	5.24	2.10	H_2O^-05	----
CaO	11.70	2.09			
K_2O	4.91	.52		99.72	----

CRYSTAL STRUCTURE

[Belov and Tarkhova, 1951; Ito, Morimoto, and Sadanaga, 1952]

The milarite structure is composed of double hexagonal rings of the composition $(\text{Si}_{12}\text{O}_{30})$. These rings are shown in figure 15 and 16. The rings are joined to-

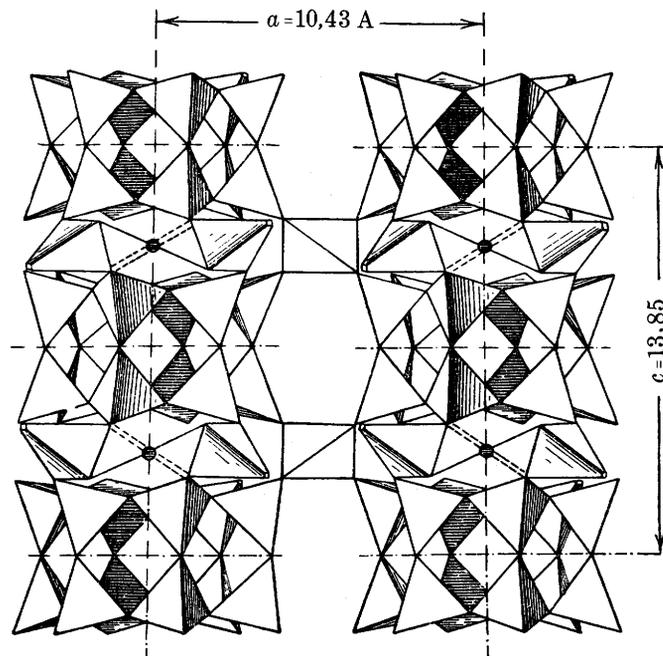


FIGURE 15.—The crystal structure of milarite, $\text{KCa}_2(\text{Be}_2\text{Al})(\text{Si}_{12}\text{O}_{30}) \cdot \frac{1}{2} \text{H}_2\text{O}$ projected on (100). The double $\text{Si}_{12}\text{O}_{30}^{12-}$ rings are shown linked together by BeO_4 and AlO_4 tetrahedra and by CaO_6 octahedra. Solid circles represent the calcium atoms. Reprinted from Belov and Tarkhova, 1951.

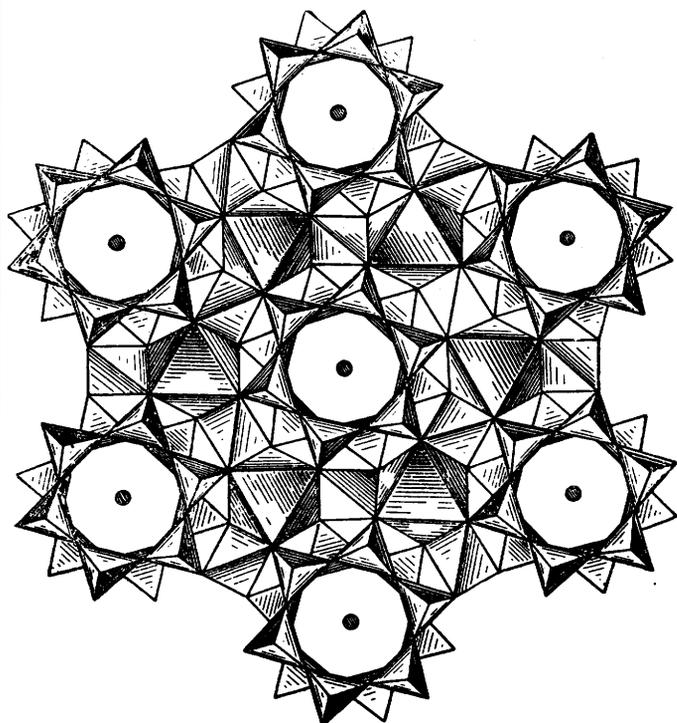


FIGURE 16.—The crystal structure of milarite, $\text{KCa}_2(\text{Be}_2\text{Al})(\text{Si}_{12}\text{O}_{30}) \cdot \frac{1}{2} \text{H}_2\text{O}$ projected on (0001). The $\text{Si}_{12}\text{O}_{30}^{12-}$ groups are shown linked together by $(\text{Be}, \text{Al})\text{O}_4$ tetrahedra and CaO_6 octahedra. The circles represent potassium atoms lying between the $\text{Si}_{12}\text{O}_{30}^{12-}$ groups. Reprinted from Belov and Tarkhova, 1951.

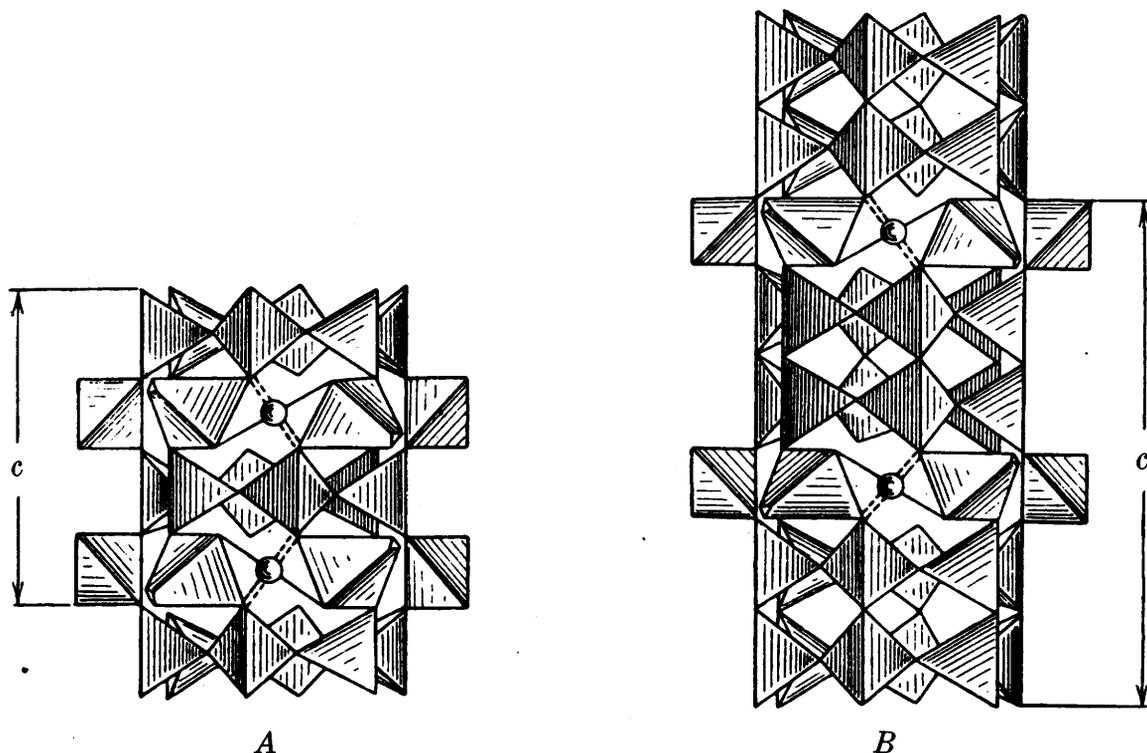


FIGURE 17.—Comparison of the beryl structure (A) with the milarite structure (B), reprinted from Belov and Tarkhova, 1951.

gether into a three-dimensional network by BeO_4 and AlO_4 tetrahedra. The Be and Al atoms appear to substitute randomly for one another. This structure bears some resemblance to beryl, $\text{Al}_2\text{Be}_3\text{Si}_6\text{O}_{18}$, in which single hexagonal rings of the composition $(\text{Si}_6\text{O}_{18})$ are linked into a three-dimensional structure by BeO_4 tetrahedra and AlO_6 octahedra. Figure 17 compares the milarite and beryl structures.

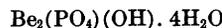
In milarite the calcium atoms are in octahedral coordination surrounded by six oxygen atoms, one from each of six neighboring rings. The potassium atoms lie on the sixfold axis between the double $(\text{Si}_{12}\text{O}_{30})$ rings (fig. 16). These atoms have twelvefold coordination and lie in positions similar to the K^+ position in the micas. The water molecules appear to lie within the cages formed by the double rings.

The bond lengths as determined by Belov and Tarkhova (1951), and Ito, and others (1952) are given in table 7.

TABLE 7.—Bond lengths in milarite

BELOV AND TARKHOVA, 1951		ITO, MORIMOTO, AND SADANAGA, 1952	
	Angstroms		Angstroms
Si-O ₁	1. 60	Si-O ₁	1. 64
Si-O ₂	1. 60, 1. 59	Si-O ₂	1. 59
Si-O ₃	1. 61	Si-O ₃	1. 63
(4) Be(Al)-O.....	1. 65	(4) Be(Al)-O.....	1. 75
(6) Ca-O ₃	2. 42	(6) Ca-O ₃	2. 35
(12) K-O ₂	3. 04	(12) K-O ₂	3. 14

MORAESITE



CRYSTALLOGRAPHY

[Lindberg, Pecora, and Barbosa, 1953]

Monoclinic:

a	$8.55 \pm 0.04 \text{ \AA}$	V	2229 \AA^3
b	$36.90 \pm 0.18 \text{ \AA}$	D_m	1.805 g/cm^3
c	$7.13 \pm 0.04 \text{ \AA}$	Z	12
β	$97^\circ 41'$	D_x	1.806 g/cm^3

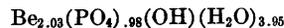
Space group: $C2/c$ or Cc

X-ray powder data given

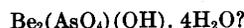
CHEMICAL COMPOSITION

[Lindberg and others 1953. Numbers of ions on the basis of 4.00 oxygens and 1.00 OH]

	Weight percent	Ratios		Weight percent	Ratios	
P_2O_5	34. 76	0. 49	Insol.....	0. 30	-----	
BeO	25. 28	2. 03			100. 25	-----
Fe_2O_3 11	-----				-----
H_2O	39. 80	4. 45				-----



BEARSITE



CRYSTALLOGRAPHY

Kopchenova and Sidorenko, 1962]

Monoclinic:

a	$8.55 \pm 0.02 \text{ \AA}$
b	$36.90 \pm 0.02 \text{ \AA}$
c	$7.13 \pm 0.02 \text{ \AA}$
β	$97^\circ 49' \pm 30'$
V	2229 \AA^3
D_m	$> 1.8 < 2.0 \text{ g/cm}^3$
Z	12
D_x	2.20 g/cm^3 (unit-cell constants determined from X-ray powder data)

X-ray powder data given

CHEMICAL COMPOSITION

[Kopchenova and Sidorenko, 1962]

	Weight percent	Theoretical composition bearsite		Weight percent	Theoretical composition bearsite
BeO	16.75	20.35	SiO ₂	1.64	
Al ₂ O ₃	6.06		As ₂ O ₅	>25.5	46.72
Fe ₂ O ₃	1.08		H ₂ O	>29.0	32.93
CaO	1.40				100.00
MgO	.61				

The close similarity of the X-ray powder patterns led Kopchenova and Sidorenko to propose that bearsite is the arsenate analogue of moraesite, Be₂(PO₄)(OH)·4H₂O. Further work is needed to verify the unit cell and chemical composition of bearsite.

PHENAKITE



CRYSTALLOGRAPHY

[Bragg and Zachariasen, 1929]

Rhombohedral:

<i>a</i>	7.68 kX	<i>Z</i>	6
<i>α</i>	108°01'	<i>D_x</i>	2.99 g/cm ³
<i>V</i>	367.5 kX ³		

Space group: *R* $\bar{3}$

CHEMICAL COMPOSITION

[Dana, 1892, p. 463]

Unessential amounts of Al₂O₃, Fe₂O₃, Na₂O, CaO, and MgO are present in the chemical analyses of phenakite.

CRYSTAL STRUCTURE

[Bragg and Zachariasen, 1929]

The beryllium and silicon atoms are in tetrahedral coordination. The SiO₄ tetrahedra share each of all four corners with two BeO₄ tetrahedra. The BeO₄ tetrahedra share each corner with one SiO₄ tetrahedron and one BeO₄ tetrahedron. The two types of tetrahedra link to form a complex three-dimensional network. The Be-O distance in phenakite is 1.65 Å; the Si-O distance is 1.62 Å.

RHODIZITE



CRYSTALLOGRAPHY

[Strunz, 1943]

Cubic:

<i>a</i>	7.303 ± 0.025 kX	<i>Z</i>	1
<i>V</i>	390 kX ³	<i>D_x</i>	3.25 g/cm ³

Space group: *P* $\bar{4}3m$

CHEMICAL COMPOSITION

[Palache, Berman and Frondel, 1951, p. 330]

	(1) Weight percent	(2) Weight percent	(3) Weight percent
Li ₂ O	7.81	7.30	0.68
Na ₂ O	4.05	3.30	1.78
K ₂ O			1.41
Rb ₂ O	6.16	5.90	2.29
Cs ₂ O			3.47
Al ₂ O ₃	26.65	30.50	27.40
BeO	9.81	10.10	14.93
B ₂ O ₃	45.52	40.60	[43.33]
Rem		1.81	1.71
<i>D_m</i>	100.00	99.51	[100.00]
		3.305	3.344

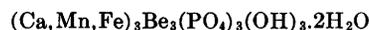
1. NaKLi₄Al₄Be₃B₁₀O₂₇.
2. Antandrokomby, Madagascar.
3. Sahatany Valley, Madagascar.

CRYSTAL STRUCTURE

[Strunz, 1943]

Strunz gives a partial description of the structure. The structure cannot be considered solved on the basis of this work alone.

ROSCHÉRITE



CRYSTALLOGRAPHY

[Lindberg, 1958]

	(1)	(2)	(3)
<i>a</i>	15.95 ± 0.06	15.88 ± 0.04	15.89 ± 0.04
<i>b</i>	11.95 ± 0.04	11.90 ± 0.03	11.90 ± 0.03
<i>c</i>	6.62 ± 0.04	6.66 ± 0.03	6.59 ± 0.03
<i>β</i>	94°30' ± 15'	94°30' ± 15'	94°50' (assumed)
<i>V</i>	1257	1254	1242
<i>D_m</i>	2.934	2.916	2.936
<i>Z</i>	4	4	4
<i>D_x</i>	2.93	2.90	2.94
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>

X-ray powder data given.

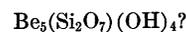
CHEMICAL COMPOSITION

[Lindberg, 1958. Numbers of ions on the basis of 12.00 oxygens and 3.00 OH]

	Weight-percent			Ratios		
	(1)	(2)	(3)	(1)	(2)	(3)
CaO	7.60	11.48	10.11	0.75	1.13	1.00
MnO	10.04	14.47	8.66	.78	1.13	.68
FeO	6.26	10.13	16.49	.48	.75	1.27
Fe ₂ O ₃	13.36		.90	.46		.03
BeO	12.58	13.74	13.01	2.78	3.04	2.89
P ₂ O ₅	37.60	38.01	38.74	1.46	1.48	1.51
H ₂ O	11.56	12.17	12.09	3.55	3.74	3.72
Insol	.80					
	99.80	100.00	100.00			

- (1) (Ca, Mn, Fe²⁺, Fe³⁺)_{2.93}Be_{2.73}P_{2.92}O₁₂(OH)₃(H₂O)_{2.05}, Sapucaia pegmatite mine, Minas Gerais, Brazil.
- (2) (Ca, Mn, Fe²⁺)_{3.01}Be_{3.01}P_{2.96}O₁₂(OH)₃(H₂O)_{2.21}, Greifenstein, Saxony.
- (3) (Ca, Mn, Fe²⁺, Fe³⁺)_{3.01}Be_{2.89}P_{3.02}O₁₂(OH)₃(H₂O)_{2.22}, Nevel Quarry, Newry Maine.

SPHEROBERTRANDITE



CRYSTALLOGRAPHY

[Semenov, 1957]

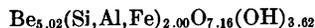
X-ray powder data given

CHEMICAL COMPOSITION

[Semenov, 1957]

[Numbers of ions on the basis of Si+Al+Fe=2.00]

	Weight percent	Ratios		Weight percent	Ratios
SiO ₂ -----	41.03	1.90	H ₂ O+-----	11.70	1.81
Al ₂ O ₃ -----	1.40	.04	H ₂ O-----	.30	
Fe ₂ O ₃ -----	.07	.01			
BeO-----	45.20	5.02		99.70	



The X-ray powder data of this mineral indicates that it is closely related to bertrandite (Fleischer, 1958).

SWEDENBORGITE



CRYSTALLOGRAPHY

[Pauling, Klug, and Winchell, 1935]

Hexagonal:	Z-----	2
a-----	D _z -----	4.18 g/cm ³
c-----		
V-----		
Space group: P6 ₃ mc		

CHEMICAL COMPOSITION

[Palache, Berman, and Frondel, 1951, p. 1028]

CRYSTAL STRUCTURE

[Pauling, Klug, and Winchell, 1935]

In this structure each beryllium atom is coordinated tetrahedrally by four oxygen atoms at approximately 1.63 Å. Each antimony atom is coordinated octahedrally by six oxygen atoms at approximately 1.93 Å.

The swedenborgite structure is based on a four-layer closest packing of the form . . . ABAC . . . such as is found in the mineral topaz. This is referred to by Pauling as double-hexagonal closest packing. Of the 16 close-packed oxygen positions in the unit cell, only 14 are occupied by oxygens; the other two positions are occupied by sodium atoms. The sodium atoms are thus coordinated by 12 oxygen atoms. The antimony atoms occupy 1/4 of the octahedral holes of alternate double layers. The beryllium atoms occupy 1/8 of the tetrahedral holes within the double layer holding the antimony atoms. Within the double layers not occupied by antimony the beryllium atoms occupy 3/8 of the tetrahedral holes. Each O₁ atom is shared with four BeO₄ tetrahedra. The unusual sharing of four tetrahedra with a common oxygen atom is also found in the basic beryllium acetate, Be₄O(CH₃COO)₆, structure. Each O₂ and O₃ oxygen atom of swedenborgite is coordinated by one antimony atom, two beryllium atoms, and two sodium atoms. The arrangement of the various polyhedra of the swedenborgite structure is shown in figure 18.

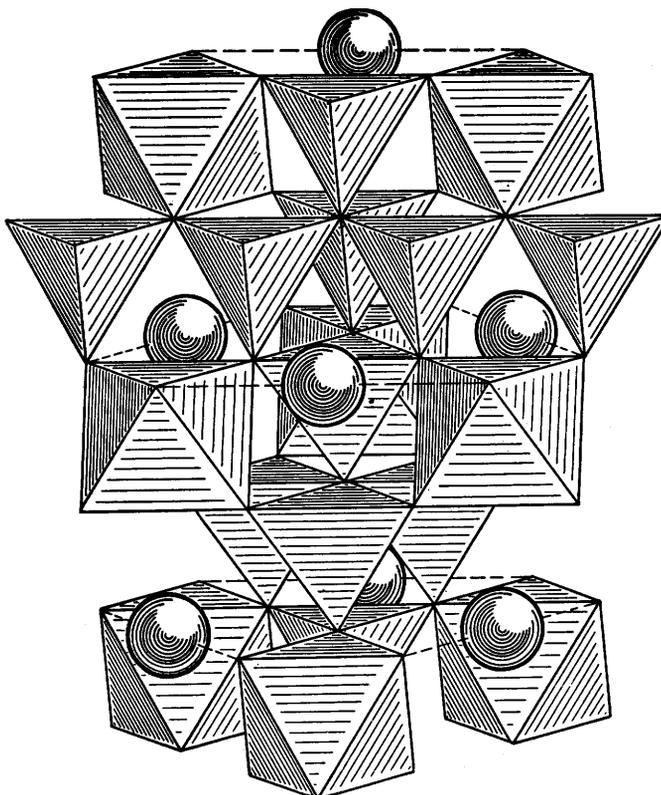
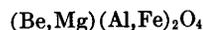


FIGURE 18.—The crystal structure of swedenborgite, NaBe₄SbO₇, showing the SbO₆ octahedra, the groups of four BeO₄ tetrahedra, and the sodium ions (spheres). The oxygen and sodium ions together form a double hexagonal close-packed aggregate. Reprinted from Pauling, Klug, and Winchell, 1935.

TAAFFEITE



CRYSTALLOGRAPHY

[Anderson, Payne, and Claringbull, 1951]

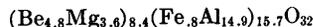
Hexagonal:	D _m -----	3.613 g/cm ³
a-----	Z-----	8
c-----		
V-----		
Space group: P6 ₃ 22		
X-ray powder data given		

CHEMICAL COMPOSITION

[Anderson and others, 1951].

[Numbers of ions on the basis of 32.00 oxygens]

	Weight percent	Ratios		Weight percent	Ratios
Al ₂ O ₃ -----	70.0	7.47	BeO-----	11.0	4.79
Fe ₂ O ₃ -----	5.9	0.39			
MgO-----	13.4	3.64		100.3	



CRYSTAL STRUCTURE

[Anderson and others, 1951]

The structure of taaffeite appears to be based on a close-packed oxygen framework with eight close-packed oxygen sheets in hexagonal stacking. The distance between adjacent sheets (18.38/8=2.30 Å) agrees closely with the corresponding dimensions for spinel, MgAl₂O₄, where the sheets are 2.32 Å apart. In spinel, however,

the oxygen atoms are in a cubic close-packed arrangement. The oxygen atoms within the sheets of taaffeite are 2.86 Å apart; in spinel they are 2.85 Å apart.

The data given by Anderson, Payne, and Claringbull indicate that one of the following structures is the correct one for the oxygen framework of taaffeite. The oxygen atoms appear to form a subcell with $a=2.86$ Å and $c=18.38/n$ Å, where $n=1, 2, \text{ or } 4$ (eight, four, or two oxygens per subcell). There are six possible hexagonal eight-layer stacking sequences for a subcell with $c=18.38$ Å but only two are compatible with space group $P6_322$. These two sequences are $\dots ABABACAC \dots$ and $\dots ABCABACB \dots$. The only possible hexagonal four and two layer stacking sequences for subcells with $c=9.2$ Å and 4.6 Å are $\dots ABCB \dots$ and $\dots AB \dots$, respectively. These structures require the oxygen atoms to lie on or near the $\bar{6}$ and 6_3 axes of the subcell in a close-packed array. The cations must lie in the tetrahedral and octahedral voids of the oxygen framework.

TENGERITE



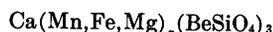
CHEMICAL COMPOSITION

[Hidden, 1905. Numbers of ions on the basis of $Y+Ce+Fe=1.00$]

	Weight percent	Ratios		Weight percent	Ratios
Y_2O_3 -----	40.8	} 0.500	H_2O+ -----	14.1	1.82
Ce_2O_3 -----	7.0		H_2O- -----	3.2	-----
Fe_2O_3 -----	4.0		$MgO, \text{ loss}$ -----	1.2	-----
BeO -----	9.7				
CO_2 -----	19.6	1.04		100.0	-----
SiO_2 -----	.4	-----			

Tengerite is also reported as having approximately the composition $CaY_3(CO_3)_4(OH)_3 \cdot 3H_2O$ and apparently is not the same as Hidden's material which contains beryllium (Iimori, 1938).

TRIMERITE



CRYSTALLOGRAPHY

[Strunz, 1949, p. 223]

Monoclinic:

a -----	16.11 Å	V -----	3411 Å ³
b -----	7.60 Å	D_m -----	3.47 g/cm ³
c -----	27.86 Å	Z -----	16
β -----	90°09'	D_z -----	3.53 g/cm ³

(for $CaMn_2Be_3Si_3O_{12}$)

Space group: $P2_1/c$ (pseudohexagonal by twinning)

CHEMICAL COMPOSITION

[Dana, 1892, p. 460. Numbers of ions on the basis of 12.00 oxygens]

	Weight percent	Ratios		Weight percent	Ratios
SiO_2 -----	39.77	2.97	CaO -----	12.44	1.00
BeO -----	17.08	3.06			
MnO -----	26.86	} 2.01		100.63	-----
FeO -----	3.87				
MgO -----	.61				

CRYSTAL STRUCTURE

Trimerite may be structurally related to beryllonite, $NaBePO_4$.

VÄYRYNENITE



CRYSTALLOGRAPHY

[Mrose and Appleman, 1962]

Monoclinic:

a -----	5.411 ± 0.005 Å	V -----	361.7 Å ³
b -----	14.49 ± 0.02 Å	D_m -----	3.215 g/cm ³
c -----	4.730 ± 0.005 Å	Z -----	4
β -----	102°45' ± 05'	D_z -----	3.23 g/cm ³

Space group: $P2_1/a$

CHEMICAL COMPOSITION

[Mrose and von Knorring, 1959]

The two analyses of väyrynenite indicate that the ratio of Mn^{2+} to Fe^{2+} is about 85 to 15. A small amount of aluminum is present and probably substitutes for Be. Small amounts of Ca, K, and Na are also present and probably substitute for Mn^{2+} and Fe^{2+} .

CRYSTAL STRUCTURE

[Mrose and Appleman, 1962]

The väyrynenite structure consists of zigzag chains of the composition $[Be_2(OH)_2(PO_4)_2]_n^{4n-}$ (fig. 19A). The chains are linked together by the Mn atoms and also by hydrogen bonds. The manganese atoms are coordinated by two oxygen atoms and one hydroxyl group (O_1, O_2, OH) of one chain and by one oxygen atom (O'_1, O'_4, O_4) from each of three adjacent chains. Within the chain each beryllium atom is coordinated tetrahedrally by two oxygens (O_2, O'_3) and by two (OH) groups (OH, OH'). Each phosphorus atom is coordinated tetrahedrally by four oxygen atoms (O_1, O_2, O_3, O_4).

The $BeO_2(OH)_2$ tetrahedra share the two hydroxyl corners with like tetrahedra and the two oxygen corners with PO_4 tetrahedra. The PO_4 tetrahedra share two corners (O_2, O_3) with two adjacent $BeO_2(OH)_2$ tetrahedra. The remaining two oxygen atoms (O_1, O_4) of the PO_4 groups coordinate the manganese atoms.

A hydrogen bond exists between the (OH) group of one chain and the oxygen atom O_3 of an adjacent chain.

The bond lengths found in this structure are as follows:

	Ångstroms
Be-O-----	1.63, 1.65
Be-OH-----	1.69, 1.63
P-O-----	1.53, 1.53, 1.55, 1.51
Mn-O-----	2.08, 2.24, 2.14, 2.18, 2.23
Mn-OH-----	2.37

Väyrynenite bears an interesting relation to euclase which will be described next.

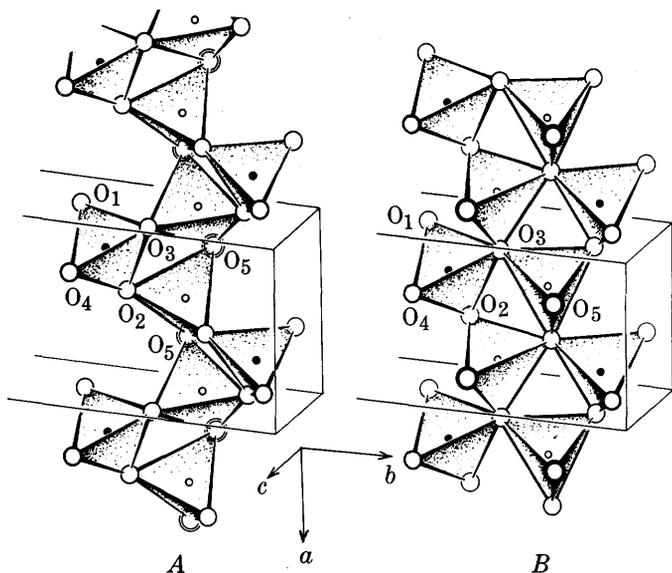


FIGURE 19.—A comparison of the $[\text{Be}_2(\text{OH})_2(\text{PO}_4)_2]_n^{4-}$ chain of väyrynenite (A) with the $[\text{Be}_2(\text{OH})_2(\text{SiO}_4)_2]_n^{6-}$ chain of euclase (B): large single circles, oxygen; large double circles, hydroxyl groups; small open circles, beryllium; and small solid circles, silicon or phosphorus. Reprinted from Mrose and Appleman (1962).

EUCLASE



CRYSTALLOGRAPHY

[Mrose and Appleman, 1962]

Monoclinic:

a -----	$4.763 \pm 0.005 \text{ \AA}$
b -----	$14.29 \pm 0.02 \text{ \AA}$
c -----	$4.618 \pm 0.005 \text{ \AA}$
β -----	$100^\circ 15' \pm 05'$

V -----	309.3 \AA^3
D_m -----	3.095 g/cm^3
Z -----	4
D_x -----	3.115 g/cm^3

Space group: $P2_1/a$

CRYSTAL STRUCTURE

[Mrose and Appleman, 1962]

The structure of euclase consists of zigzag chains of the composition $[\text{Be}_2(\text{OH})_2(\text{SiO}_4)_2]_n^{6-}$ (fig. 19B) cross-linked by aluminum atoms. These chains are oriented within the unit cell in the same manner as the chains in väyrynenite. The aluminum atoms are coordinated octahedrally by O_1 and O_2 of one chain, by O_4 and (OH) of a second chain, and by O_1 and O_4 of two additional chains. The SiO_4 tetrahedra share one corner (O_2) with an adjacent $\text{BeO}_2(\text{OH})_2$ tetrahedra and another corner (O_3) with two additional $\text{BeO}_2(\text{OH})_2$ tetrahedra. The two remaining corners are free to coordinate the aluminum atoms. The $\text{BeO}_2(\text{OH})_2$ tetrahedra share one corner (O_2) with an SiO_4 tetrahedra and each of two more corners (O_3, O'_3) with an SiO_4 group and a $\text{BeO}_2(\text{OH})_2$ group. The fourth corner (OH) coordinates aluminum. There appears to be no hydrogen bond in this structure.

The bond lengths are as follows:

	Angstroms
Be-O-----	1.60, 1.63, 1.64
Be-OH-----	1.68
Si-O-----	1.61, 1.62, 1.65, 1.62
Al-O-----	1.86, 1.98, 1.87, 1.93, 1.91
Al-OH-----	1.85

A comparison of the structures of väyrynenite and euclase shows that the arrangement of the PO_4 tetrahedra around Mn in väyrynenite is almost identical to the arrangement of the SiO_4 tetrahedra about Al in euclase. The difference in the two structures is due to the replacement of P^{5+} by Si^{4+} , and Mn^{2+} by Al^{3+} . Because $\text{O}_1, \text{O}_2,$ and O_4 coordinate both tetrahedral and octahedral sites, the sums of the bond strengths about these atoms is nearly the same in both minerals. The oxygen atom O_3 and the (OH) group, however, have a radically different coordination in the two structures. In order to maintain local charge balance, O_3 must form one Be-O bond in väyrynenite and two Be-O bonds in euclase; (OH) must form two Be-O bonds in väyrynenite and one Be-O bond in euclase. As a result, the configuration of the two chains must be quite different (fig. 19).

THE BERYLLIUM COMPOUNDS

The inorganic and organic compounds presented in the following pages are listed in table 8. Although this is not intended to be an exhaustive account of all the beryllium compounds, a large proportion of those with known crystal structures have been included. The beryllium intermetallic compounds have not been included in this study.

TABLE 8.—The beryllium compounds

$\text{Be}(\text{H}_2\text{O})_4\text{SO}_4$	BeSe
$\beta\text{-Be}(\text{OH})_2$	BeTe
BeSO_4	BeSiN_2
BeGeO_4	BeCl_2
BeS	$\text{Be}(\text{CH}_3)_2$
$\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$	$\text{BeC}_{22}\text{H}_{16}\text{N}_8$
The beryllium fluorides	

$\text{Be}(\text{H}_2\text{O})_4\text{SO}_4$

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

[Bevers and Lipson, 1932]

Tetragonal:

a -----	8.02 kX
c -----	10.75 kX
V -----	691 kX^3

Z -----	4
D_x -----	1.70 g/cm^3

Space group: $\bar{1}4c2$

This structure consists of tetrahedral $\text{Be}(\text{H}_2\text{O})_4^{2+}$ and SO_4^{2-} groups linked into a three-dimensional network through hydrogen bonds between the water molecules and the sulfate oxygen atoms. Each water molecule is hydrogen bonded to two oxygen atoms of two different SO_4^{2-} groups. The bond lengths are as follows:

	Angstroms
Be-H ₂ O-----	1.62
S-O-----	1.57
H ₂ O-O-----	2.56, 2.59

β -Be(OH)₂
CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE
[Seitz, Rösler, and Schubert, 1950]

Orthorhombic: <i>a</i> ... 4.620 ± 0.005 Å <i>b</i> ... 7.039 ± 0.008 Å <i>c</i> ... 4.535 ± 0.005 Å <i>V</i> ... 147.5 Å ³	 <i>D_m</i> ... 1.924 g/cm ³ <i>Z</i> ... 4 <i>D_x</i> ... 1.94 g/cm ³
--	---

Space group: *P*2₁2₁2₁

β -Be(OH)₂ has the ϵ -Zn(OH)₂ structure (Corey and Wyckoff, 1933). Beryllium is coordinated tetrahedrally by four (OH) groups. The distorted Be(OH)₄ tetrahedra link into a three-dimensional structure by sharing all four corners with other tetrahedra. Hydrogen bonds are formed between (OH) groups of adjacent tetrahedra. The bond lengths are:

Be-O ₁1.61, 1.69 Å	
Be-O ₂1.57, 1.68 Å	
O ₁ -O ₂2.85, 2.88 Å	

BeSO₄

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE
[Grund, 1955]

Tetragonal: <i>a</i> 4.49 Å <i>c</i> 6.90 Å <i>V</i> 139 Å ³	 <i>Z</i> 2 <i>D_x</i> 2.51 g/cm ³
--	---

Space group: *I*4

BeSO₄ possesses the low cristobalite structure with each BeO₄ tetrahedron sharing corners with four SO₄ tetrahedra and similarly each SO₄ tetrahedron sharing corners with four BeO₄ tetrahedra. The charge balance on each oxygen atom is thus 2. The bond lengths are as follows:

S-O..... 1.50 Å	
Be-O..... 1.56 Å	
O _s -O _s 2.46, 2.40 Å	
O _{Be} -O _{Be} 2.65, 2.50 Å	

BeGeO₄

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE
[Schütz, 1936]

Rhombohedral: <i>a</i> ... 7.89 ± 0.01 kX α ... 108°6' <i>V</i> ... 395.9 kX ³	 <i>Z</i> 6 <i>D_x</i> 3.64 g/cm ³
---	---

Space group: *R*3

BeGeO₄ is isostructural with phenakite (Be₂SiO₄) and willemite (Zn₂SiO₄).

BeS

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE
[Zachariasen, 1926a]

Cubic: <i>a</i> 4.853 kX <i>V</i> 114.3 kX ³ <i>D_m</i> 2.36 g/cm ³	 <i>Z</i> 4 <i>D_x</i> 2.37 g/cm ³
--	---

Space group: *F*43*m*

BeS possesses the sphalerite structure. The Be-S bond distance is 2.10 Å in length.

BeSe

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE
[Zachariasen, 1926b]

Cubic: <i>a</i> 5.139 ± 0.004 kX <i>V</i> 134.9 kX ³ <i>Z</i> 4 <i>D_x</i> 4.315 g/cm ³	
---	--

Space group: *F*43*m*

BeSe possesses the sphalerite structure and has a Be-Se bond distance of 2.18 Å.

BeTe

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE
[Zachariasen, 1926c]

Cubic: <i>a</i> 5.615 kX <i>V</i> 177.0 kX ³ <i>Z</i> 4 <i>D_x</i> 5.090 g/cm ³	
---	--

Space group: *F*43*m*

BeTe has the sphalerite structure. The Be-Te bond distance is 2.43 Å in length.

BeSiN₂

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE
[Rabenau and Eckerlin, 1959]

Hexagonal: <i>a</i> ... 2.872 ± 0.004 Å <i>c</i> ... 4.674 ± 0.004 Å <i>V</i> ... 33.39 Å ³	 <i>D_m</i> 3.12 g/cm ³ <i>Z</i> 1 <i>D_x</i> 3.24 g/cm ³
---	--

Space group: *P*6₃*m*c

BeSiN₂ possesses the wurtzite structure with Be and Si playing the role of S, and N the role of Zn.

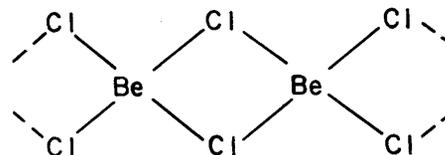
BeCl₂

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE
[Rundle and Lewis, 1952]

Orthorhombic: <i>a</i> 9.86 Å <i>b</i> 5.36 Å <i>c</i> 5.26 Å <i>V</i> 278 Å ³	 <i>D_m</i> 1.899 g/cm ³ <i>Z</i> 4 <i>D_x</i> 1.91 g/cm ³
---	---

Space group: *I*bam

The BeCl₂ structure is formed of chains of the type:



The chains consist of BeCl₄ tetrahedra linked through the sharing of two edges with adjacent tetrahedra. The Be-Cl bond distance is 2.04 Å. The Cl-Cl distance is 3.85 Å. This structure is similar to that of SiS₂.

Be(CH₃)₂**CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE**

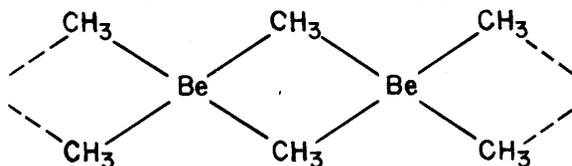
[Snow and Rundle, 1951]

Orthorhombic:

<i>a</i> 6.13 Å	<i>V</i> 294.4 Å ³
<i>b</i> 11.53 Å	<i>Z</i> 4
<i>c</i> 4.18 Å	<i>D_z</i> 0.881 g/cm ³

Space group: *Ibam*

Be(CH₃)₂ is isostructural with BeCl₂ and SiS₂. The structure is composed of chains of the type:



The CH₃ groups are arranged tetrahedrally about the beryllium atom. The packing of the chains is approximately close-packing of circular cylinders. The Be-C bond distance is 1.93±0.02 Å; the C-Be-C bond angle within the tetrahedron is 114°±1°.

BASIC BERYLLIUM ACETATE**CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE**

[Tullinsky and Worthington, 1959; see also Pauling and Sherman, 1934]

Cubic:

<i>a</i> 15.74±0.01 Å
<i>V</i> 3900 Å ³
<i>Z</i> 8
<i>D_z</i> 1.384 g/cm ³

Space group: *Fd3*

The structure of this compound bears an interesting relationship to swedenborgite (NaBe₄SbO₇). The central oxygen atom of the Be₄O(CH₃COO)₆ molecule is surrounded tetrahedrally by four beryllium atoms. Each Be atom is surrounded tetrahedrally by four oxygen atoms; the central oxygen and three oxygen atoms of three different (CH₃COO) groups. The four BeO₄ tetrahedra thus share a common corner (O₁). The Be-O₁ bond distance is 1.666±0.004 Å; the Be-O₂ distance is 1.624±0.010 Å.

BERYLLIUM PHTHALOCYANINE**CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE**

[Linstead and Robertson, 1936]

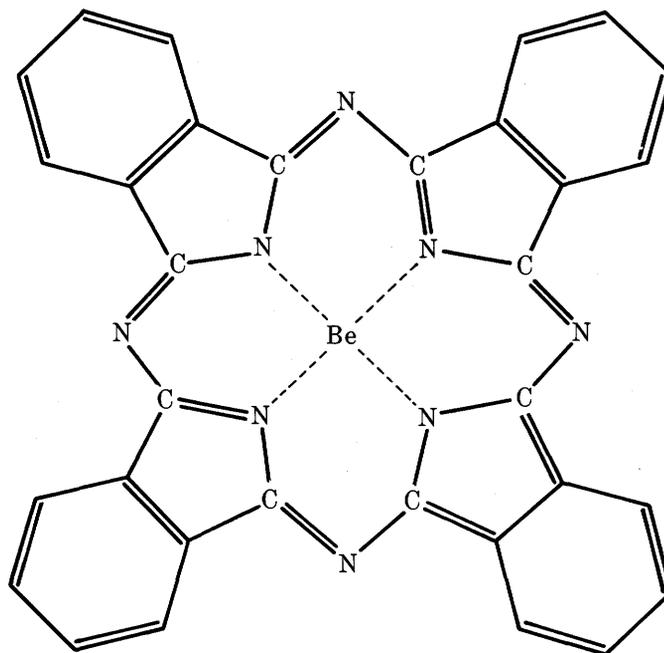
Monoclinic:

<i>a</i> 21.2 kX	<i>V</i> 1293 kX ³
<i>b</i> 4.84 kX	<i>Z</i> 2
<i>c</i> 14.7 kX	<i>D_z</i> 1.33 g/cm ³
<i>β</i> 121.0°	

Space group: *P2₁/a*

The beryllium phthalocyanine molecule is planar and is shown in figure 20. The compound is isostructural with Cu²⁺, Ni²⁺, Co²⁺, Pt²⁺, Fe²⁺, Mn²⁺ and Mg²⁺ phthalocyanine. The four Be-N bonds are apparently coplanar

by analogy to the nickel and platinum phthalocyanines which have been studied in detail. It is unusual to find Be, Co, Mn, Mg, and Fe in planar coordination for in no other types of compounds are these elements known to form four coplanar bonds. (Wells, 1962, p. 926-927.)

FIGURE 20.—The beryllium phthalocyanine, BeC₃₂H₁₆N₈ molecule.**THE BERYLLIUM FLUORIDES**

A large number of compounds have been studied which contain beryllium and fluorine as essential constituents. These compounds bear a close structural relationship to a number of common minerals and inorganic compounds. A compound isostructural with, say, a particular silicate mineral, may be derived by replacing Si with Be and O with F. An example is *α*-BeF₂ which is isostructural with *β*-cristobalite. Such beryllium fluorides are referred to as "model compounds." A number of these beryllium fluoride model compounds along with the common minerals and compounds that are thought to be isostructural with them are listed in table 9. The structural relationships are predicted by the similarity of the X-ray powder patterns, unit cell data, and chemical formulas. Inasmuch as the fluoride ion has a radius almost the same as that of O²⁻ (1.36 as compared with 1.40 Å; Green, 1959) and Be²⁺ a similar radius to that of Si⁴⁺ (0.33 as compared with 0.40 Å; Green, 1959) the fluorides should be expected to bear a crystal chemical similarity to the silicates. In all the beryllium fluorides listed in table 9 beryllium is coordinated tetrahedrally by four fluoride ions.

TABLE 9.—The beryllium fluoride model compounds and their structural analogs

Structure type	Compound	Unit cell				System	Space group	Z	Reference No.
		Edge ¹			Angle				
		a	b	c	$\beta(\alpha)$				
α - Na_2SiO_4	α - Na_2BeF_4	5.32	-----	7.09	-----	Hexagonal	P^{***}	2	3
	α - Na_2SO_4	5.38	-----	7.26	-----	do.	-----	2	2
	α - Ca_2SiO_4	5.45	-----	7.18	-----	do.	-----	2	1
	α - K_2SiO_4	5.71	-----	7.86	-----	do.	-----	2	2
	α - CaNaPO_4	5.23	-----	7.13	-----	do.	-----	2	2
β - K_2SiO_4	α' - Na_2BeF_4	5.22	9.40	6.72	-----	Orthorhombic	-----	4	1
	β - K_2SO_4 (arcanite)	5.73	10.01	7.42	-----	do.	$Pm\bar{c}n$	4	2
	Rb_2BeF_4	5.85	10.13	7.66	-----	do.	-----	4	6
	K_2BeF_4	5.693	9.896	7.27	-----	do.	$Pm\bar{c}n$	4	2
	Ti_2BeF_4	5.87	10.43	7.68	-----	do.	-----	4	6
	$(\text{NH}_4)_2\text{BeF}_4$	5.8	10.2	7.5	-----	do.	$Pm\bar{c}n$	4	2
	Sr_2SiO_4	5.59	9.66	7.262	-----	do.	$Pm\bar{c}n$	4	2
	Ba_2SiO_4	5.76	10.17	7.56	-----	do.	$Pm\bar{c}n$	4	2
	α' - Ca_2SiO_4	5.30	9.55	6.78	-----	do.	-----	4	1
	β - Ca_2SiO_4	β - Na_2BeF_4	5.50	6.75	9.30	95°	Monoclinic	-----	-----
β - Ca_2SiO_4		5.48	6.76	9.28	95°33'	do.	-----	-----	1
Olivine	γ - Na_2BeF_4	4.89	10.90	6.56	-----	Orthorhombic	-----	4	1
	NaLiBeF_4	4.64	10.72	6.20	-----	do.	$Pnma$	4	13
	γ - Ca_2SiO_4 (larnite)	5.06	11.28	6.78	-----	do.	$Pbnm$	4	2
	$(\text{Mg, Fe})_2\text{SiO}_4$ (olivine)	4.755	10.21	5.985	-----	do.	$Pbnm$	4	2
	CaMgSiO_4 (monticellite)	4.815	11.08	6.37	-----	do.	$Pbnm$	4	2
	Mn_2SiO_4 (tephroite)	4.862	10.62	6.221	-----	do.	$Pbnm$	4	2
	NaMnPO_4	4.97	10.52	6.32	-----	do.	$Pbnm$	4	2
	CaMnSiO_4 (glaucochroite)	4.92	11.19	6.51	-----	do.	$Pbnm$	4	2
	Mellilite	$\text{Na}_2\text{LiBe}_2\text{F}_7$	7.5	-----	5.03	-----	Tetragonal	-----	2
$\text{Ca}_2\text{Al}_2\text{SiO}_7$ (gehlenite)		7.69	-----	5.10	-----	do.	$P4_2/m$	2	2
$(\text{Ca, Na})_2(\text{Al, Fe}^{2+}, \text{Mg})(\text{Si, Al})_2\text{O}_7$ (mellilite)		7.789	-----	5.018	-----	do.	$P4_2/m$	2	10
β -Cristobalite	α - BeF_2	6.60	-----	6.74	-----	Tetragonal	-----	8	4, 5
	SiO_2 (β -cristobalite)	7.13	-----	-----	-----	Cubic	$Fd\bar{3}m?$	8	2
Quartz	γ - BeF_2	4.74	-----	5.15	-----	Hexagonal?	-----	3?	7
	SiO_2 (low-quartz)	4.910	-----	5.394	-----	Hexagonal	$P3_2$ or $P3_2$	3	2
Phenakite	α - Li_2BeF_4	8.120	-----	-----	107°36'	Rhombohedral	-----	6	7
	Be_2SiO_4 (phenakite)	7.68	-----	-----	108°1'	do.	$R\bar{3}$	6	8
	NaLiBeF_4	8.24	-----	-----	107°36'	do.	-----	6	1
	Zn_2SiO_4 (willemite)	8.63	-----	-----	107°45'	do.	$R\bar{3}$	6	2
	Be_2GeO_4	7.89	-----	-----	108°6'	do.	-----	6	2
Spinel	γ - Li_2BeF_4	6.08	-----	-----	-----	Cubic?	-----	-----	7
	Al_2MgO_4 (spinel)	8.106	-----	-----	-----	Cubic	$Fd\bar{3}m$	8	2
Barite	BaBeF_4	6.613	8.73	5.65	-----	Orthorhombic	-----	-----	11
	BaSO_4 (barite)	7.13	8.85	5.44	-----	do.	$Pbnm$	4	2
Wollastonite	NaBeF_3	15.25	7.17	6.9	95°	Monoclinic	-----	12	12
	β - CaSiO_3 (parawollastonite)	15.31	7.35	7.08	95°25'	do.	$P2_1/a$	12	2
Chrysoberyl	BeCr_2O_4	5.8	10.0	4.5	-----	Orthorhombic	-----	4	14
	BeAl_2O_4 (chrysoberyl)	5.47	9.39	4.42	-----	do.	$Pbnm$	4	15
Ca_2SiO_5	Na_2BeF_4	6.90	-----	24.36	-----	Rhombohedral	$R3m$	9	1
	Ca_2SiO_5	7.08	-----	24.94	-----	do.	$R3m$	9	1
Diopside	$\text{NaLiBe}_2\text{F}_6$	9.71	8.89	5.22	105°	Monoclinic	$P2_1/c$	4	1
	$\text{CaMgSi}_2\text{O}_6$ (diopside)	9.71	8.89	5.24	105°50'	do.	$C2/c$	4	2
Zircon	CaBeF_4	6.90	-----	6.07	-----	Tetragonal	-----	4	1
	ZrSiO_4 (zircon)	6.58	-----	5.93	-----	do.	$I4_1/amd$	4	2

¹ Measurements are assumed to be in kX units for references dated before 1949, and in angstrom units for references dated after 1948.

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CONCLUSIONS

Some of the beryllium minerals studied bear a close structural relationship to other well-known minerals. These are: (1) aminoffite, leucophanite, gugiaite, and meliphanite, which are closely related to melilite; (2) bazzite, which is isostructural with beryl; (3) beryll-sodalite, danalite, helvite, and genthelvite, which are isostructural with sodalite; (4) bromellite, which is isostructural with wurtzite; (5) bityite, which is isostructural with margarite; (6) chrysoberyl, which is isostructural with olivine; (7) herderite and gadolinite, which are isostructural with datolite; (8) hurlbutite, which is isostructural with danburite; (9) chkalovite, which is closely related to cristobalite; and (10) phenakite, which is isostructural with willemite.

In all but one of the structures examined, including a number of organic and inorganic compounds, beryllium occurs in tetrahedral coordination. In those structures that probably are accurately determined, the Be-O interatomic distances are approximately 1.64 Å, slightly longer than the average Si-O bond distance in the silicates. Only in a group of metallo-organic compounds known as the phthalocyanines of which beryllium phthalocyanine ($\text{BeC}_{32}\text{H}_{16}\text{N}_8$) is an example, does the beryllium atom occur in other than tetrahedral coordination. Here beryllium is coordinated by four nitrogen atoms in planar arrangement like that found commonly in the copper compounds.

Table 10 gives a summary of the bond distances between the beryllium ion and the tetrahedrally coordinating anions. In the accurately determined structures the average Be-O distance is 1.636 Å; the average Be-(OH) distance is 1.650 Å.

The beryllium tetrahedra usually link through the sharing of corners with one, two, or three additional tetrahedra. In the swedenborgite, bromellite, and $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$ structures four BeO_4 tetrahedra link to a single oxygen atom. In the BeS, BeSe, BeTe, and BeSiN_2 structures a similar configuration of four tetrahedra about one anion is found. Berylite, bertrandite, phenakite, and euclase possess structures in which the beryllium tetrahedra share one or more corners with two additional tetrahedra. In the bertrandite, hamburgite, väyrynenite, and $\beta\text{-Be}(\text{OH})_2$ structures Be-OH-Be linkages are found. The compounds BeCl_2 and $\text{Be}(\text{CH}_3)_2$ are unusual in that the BeCl_4 and $\text{Be}(\text{CH}_3)_4$ tetrahedra link by sharing edges instead of corners.

Kakihana and Sillén (1956) have studied the hydrolysis of the beryllium ion. They predict that the complexes $\text{Be}(\text{OH})_2(\text{H}_2\text{O})_2$, $\text{Be}_2(\text{OH})(\text{H}_2\text{O})_6^{3+}$, and

$\text{Be}_3(\text{OH})_3(\text{H}_2\text{O})_6^{3+}$ exist in aqueous solutions. It appears reasonable that the complex $\text{Be}(\text{OH})_2(\text{H}_2\text{O})_6$

TABLE 10.—The beryllium-anion bond lengths¹

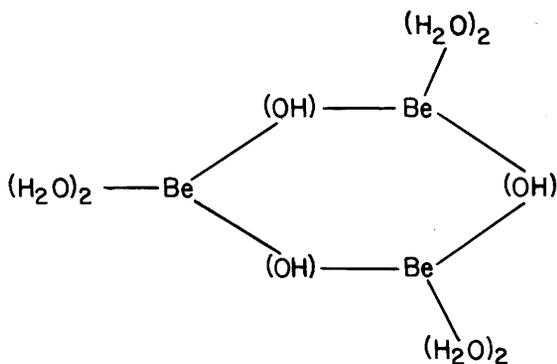
[An asterisk (*) indicates a compound in which the bond lengths are considered to be accurately determined]

Be-O	Angstroms
berylite.....	1.64-1.70
beryl.....	1.64
beryllonite.....	1.58-1.66
*hamburgite.....	1.655, 1.639, 1.657, 1.636, 1.663, 1.667
herderite.....	1.64, 1.55, 1.67
hurlbutite.....	1.60, 1.58, 1.59, 1.61, 1.57, 1.59, 1.59, 1.59
phenakite.....	1.65
swedenborgite.....	1.63
*väyrynenite.....	1.63, 1.65
*euclase.....	1.60, 1.63, 1.64
*BeO.....	1.655, 1.647
BeSO ₄	1.56
*Be ₄ O(CH ₃ COO) ₆	1.666, 1.624
Be-(OH)	
*hamburgite.....	1.637, 1.645
*väyrynenite.....	1.69, 1.63
*euclase.....	1.68
$\beta\text{-Be}(\text{OH})_2$	1.57, 1.68, 1.61, 1.69
Be-H ₂ O	
Be(H ₂ O) ₄ SO ₄	1.62
Be-F	
herderite.....	1.67
Be-S	
BeS.....	2.10
Be-Se	
BeSe.....	2.18
Be-Te	
BeTe.....	2.43
Be-Cl	
BeCl ₂	2.04
Be-C	
Be(CH ₃) ₂	1.93

¹ After this report went to press, two important papers describing refinements of the hamburgite and chrysoberyl structures came to my attention—Zachariasen, W. H. Plettinger, H. A., and Marezio, M., 1963. The structure and birefringence of hamburgite, $\text{Be}_2\text{BO}_3\text{-OH}$: Acta Cryst., v. 16, p. 1144-1146; Farrell, E. F., Fang, J. H., and Newnham, R. E., 1963. Refinement of the chrysoberyl structure: Am. Mineralogist, v. 48, p. 804-810. Be-O bond lengths of 1.629, 1.621, 1.673, 1.644, 1.612, and 1.638 Å, and Be-OH bond lengths of 1.619 and 1.629 Å were found in hamburgite. Be-O bond lengths of 1.579, 1.687, and 1.631 Å were found in chrysoberyl. If these values are included with others listed for the accurately determined structures in table 10, the average Be-O and Be-OH bond lengths would be 1.636 Å and 1.650 Å, respectively.

consists of two $\text{Be}(\text{OH})(\text{H}_2\text{O})_3$ tetrahedra sharing the (OH) corner. The complex $\text{Be}(\text{OH})_2(\text{H}_2\text{O})_2$ is probably also a tetrahedron.

The $\text{Be}_3(\text{OH})_3(\text{H}_2\text{O})_6^{3+}$ complex is the most stable of the three. Kakihana and Sillén find the most likely structure to be a six-membered ring, three tetrahedra being linked by sharing (OH) corners:



The compounds $\text{Be}(\text{OH})(\text{H}_2\text{O})_2\text{HgCl}_3$, $\text{Be}(\text{OH})(\text{H}_2\text{O})_2\text{HgBr}_3$ and $\text{Be}_3(\text{OH})_3(\text{H}_2\text{O})_6\text{Hg}_2\text{I}_7$ have been prepared and it appears that the ring-shaped complex described above may be found in them.

It may be asked in what other minerals beryllium may crystallize in moderate to trace amounts if available in the rock-forming magma or solution. The close similarity of beryllium and silicon in their crystal chemistry suggests that many of the silicates may crystallize with a certain amount of beryllium within the structure. Certain silicate minerals, owing to their structural resemblance to the beryllium minerals described above, appear to be possible sources of beryllium. These are olivine, the humites (closely related to olivine), the micas, sodalite, the melilites, cristobalite, tridymite, danburite, willemite, and datolite. The micas and the humites appear to be the only minerals among those reported by Fleischer and Cameron (1955) to contain abnormally large amounts of beryllium. Reports of high beryllium content in a number of minerals such as thorite, uraninite, and fergusonite, which appear to possess structures into which beryllium cannot readily substitute, suggest that the beryllium content may here be due to small amounts of an admixed beryllium mineral and not to solid-solution phenomenon. It is suggested by the present study that a greater effort should be made to analyze for beryllium the minerals that bear a close structural resemblance to the beryllium minerals and compounds described above.

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