

THE CRYSTAL STRUCTURE AND CATION DISTRIBUTION OF GLAUCOPHANE¹J. J. PAPIKE AND JOAN R. CLARK, *U. S. Geological Survey, Washington, D. C. 20242.*

ABSTRACT

Three-dimensional, scintillation-counter measured, X-ray diffraction data have been used in least-squares refinement of the atomic parameters and cation-site occupancy factors for the crystal-structure of glaucophane from Tiburon Peninsula, California. By assuming that each of the four cation sites in amphiboles is fully occupied by no more than two atomic species, preferably of the same valence state, occupancy factors are obtained from the X-ray diffraction data refinement as follows: M(1), 0.84Mg+0.16Fe²⁺; M(2), 0.91Al+0.09Fe³⁺; M(3), 0.71Mg+0.29Fe²⁺; M(4), 0.98Na+0.02Ca. These values lead to the chemical composition (Na_{1.96}Ca_{0.04})(Mg_{2.39}Fe_{0.61}²⁺Fe_{0.18}³⁺Al_{1.52})Si₅O₂₂(OH)₂, comparing reasonably well with the composition obtained from the bulk chemical analysis, (Na_{1.84}Ca_{0.20})(Mg_{2.38}Fe_{0.70}²⁺Fe_{0.30}³⁺Al_{1.58}Ti_{0.96}Mn_{0.01})(Si_{7.92}Al_{0.08})(O²⁻,OH⁻,F⁻,Cl⁻)₂₄. The location of the atomic species in the four sites agrees with the crystal-chemical proposal by Whittaker that trivalent cations would occupy M(2) when univalent cations are located in M(4). The ordered occupancies are in accord with the suggestion by Ernst that the natural material, which he called the high-pressure, low-temperature polymorph, glaucophane II, would have an ordered cation distribution.

INTRODUCTION

The petrogenesis of glaucophane schists has intrigued geologists for some time and much work concerned with the mapping, microscopic description, chemistry, and stability of glaucophane schist minerals has been carried out. Despite this wealth of experimental and field work, the crystal structure of glaucophane itself has not previously been refined. The literature up to 1963 has been summarized by Deer, Howie and Zussman (1963), who emphasize that pure natural glaucophanes are rare. The variation of unit-cell parameters with composition in the series glaucophane-ferroglaucophane-riebeckite-magnesioriebeckite has been studied recently by Borg (1967) and Coleman and Papike (1968). Some general considerations concerning cation substitutions in amphiboles were described by Whittaker (1949, 1960), and Ghose (1965a). Colville, Ernst and Gilbert (1966) also examined these problems, with particular reference to glaucophane. The crystal structure of riebeckite has been reported in a preliminary account by Colville and Gibbs (1964).

The possibility of polymorphism in the alkali amphiboles was proposed by Ernst (1963), who suggested the polymorphism might be related to order-disorder relationships among sixfold coordinated cations. Ernst designated the high-pressure, low-temperature polymorph as glaucophane II.

¹ Studies of Silicate Minerals (9). Publication authorized by the Director, U. S. Geological Survey.

phane II, and the low-pressure, high-temperature polymorph as glaucophane I, and suggested that the two polymorphs can be distinguished by their unit-cell parameters. Glaucophane I has been synthesized (Ernst, 1961) but to the present has not been reported as a naturally occurring mineral.

The purpose of the present investigation is to characterize the basic features of the glaucophane crystal structure, to determine the actual cation distribution within the crystal structure, and to discuss the crystal chemistry and the proposed polymorphism of glaucophane in the light of these results.

UNIT CELL AND SPACE GROUP

The glaucophane used in the present investigation is from a glaucophane schist inclusion in serpentinite located on the Tiburon Peninsula, Marin County, California. Chemically analyzed material was supplied by W. G. Ernst, University of California, Los Angeles (analyst, Shirou

TABLE 1. CHEMICAL ANALYSIS AND UNIT-CELL CONTENTS FOR
GLAUCOPHANE FROM TIBURON PENINSULA, CALIFORNIA

Chemical analysis ^a		Unit-cell contents ^b	
Oxide	Weight per cent	Ion	Number of ions per formula unit
SiO ₂	58.04	Si	7.92
TiO ₂	0.66	Al	0.08
Al ₂ O ₃	10.31	Σ tetrahedral cations	8.00
Fe ₂ O ₃	2.89	Al	1.58
FeO	6.12	Ti	0.06
MnO	0.07	Fe ³⁺	0.30
MgO	11.71	Mg	2.38
CaO	1.37	Fe ²⁺	0.70
BaO	—	Mn	0.01
Na ₂ O	6.97	Σ octahedral cations	5.03
K ₂ O	0.02	Na	1.84
H ₂ O ⁺	1.98	Ca	0.20
H ₂ O ⁻	0.00	Σ large cations	2.04
CO ₂	0.00	OH ⁻	1.80
F	0.02		
Cl	0.01		
Total	100.17		

^a Analysis by Shirou Imai, Japan Analytical Chemistry Research Institute; data from W. G. Ernst (written communication, 1966).

^b Calculated by present authors on the basis of 24(O²⁻+OH⁻+F⁻+Cl⁻) per formula unit.

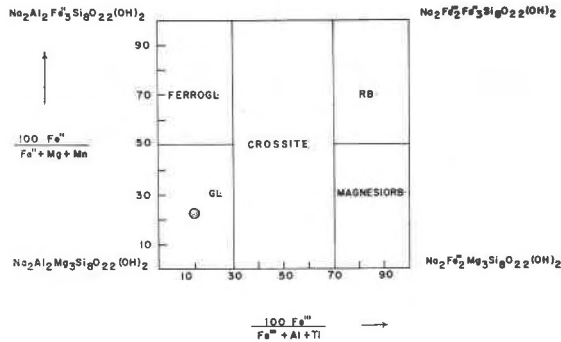


FIG. 1. Compositional diagram after Miyashiro (1957); circle indicates the composition of the glaucophane used for the crystal structure study. GL = glaucophane; FERROGL = ferroglaucophane; RB = riebeckite; MAGNESIORB = magnesioriebeckite.

Imai, Japan Analytical Chemistry Research Institute). The analysis of the material is presented in Table 1 and located in Figure 1 according to the classification of Miyashiro (1957) and Deer, Howie and Zussman (1963).

Single crystals display diffraction symmetry $2/m C/-$ consistent with space groups Cm , $C2$, and $C2/m$. Because there was no indication of a noncentric nature of these crystals either from piezoelectric tests or intensity distributions, the centric space group $C2/m$ was used throughout the refinement.

Unit-cell parameters were obtained from refinement by a least-squares method (Evans, Appleman and Handwerker, 1963) of X-ray diffractometer pattern measurements ($\text{CuK}\alpha_1$, $\lambda = 1.5405 \text{ \AA}$, NaF internal standard), and are: $a 9.541 \pm 0.002 \text{ \AA}$, $b 17.740 \pm 0.003 \text{ \AA}$, $c 5.295 \pm 0.002 \text{ \AA}$, $\beta 103^\circ 40' \pm 1'$, $V 870.9 \pm 0.3 \text{ \AA}^3$. One cell contains two formula units of the composition $(\text{Na}_{1.84}\text{Ca}_{0.20}) (\text{Mg}_{2.38}\text{Fe}_{0.70}^{2+}\text{Fe}_{0.30}^{3+}\text{Al}_{1.58}\text{Ti}_{0.06}\text{Mn}_{0.01}) (\text{Si}_{7.92}\text{Al}_{0.08}) (\text{O}^{2-}, \text{OH}^-, \text{F}^-, \text{Cl}^-)_{24}$, obtained from bulk chemical analysis (Table 1). The density calculated on this basis is 3.127 g/cm^3 .

INTENSITY DATA

X-ray diffraction data were collected manually with the single-crystal diffractometer (goniostat) which was equipped with a scintillation counter. The crystal used was a pale-blue (110) cleavage fragment, about $0.16 \times 0.04 \times 0.03 \text{ mm}$. All non-equivalent reflections having $2\theta \leq 60^\circ$ were measured using Nb-filtered Mo radiation and the 2θ -scan technique, for which the scan range was calculated according to the method described by Alexander and Smith (1964). The background intensities were counted for 20 seconds at both the initial and final 2θ points of the scan.

Out of the total 1,389 reflections measured, 986 had scan counts greater than twice the total background intensity, and these reflections were used initially in the refinement. Later on, errors in recording measurements were discovered for 23 of these reflections, which were therefore removed from the refinement, leaving 963 reflections for the final least-squares processing. The intensities were corrected for Lorentz and polarization effects, and for absorption ($\mu = 17.82 \text{ cm}^{-1}$) using the numerical integration method (Burnham, 1966) incorporated into the program system by Stewart and High¹ that was used with the IBM 7094 for the least-squares refinement and other calculations.

REFINEMENT OF THE CRYSTAL STRUCTURE

The monoclinic amphibole crystal structure was initially solved for tremolite by Warren (1930), and a refinement of the tremolite structure is in progress (M. Ross, U. S. Geological Survey, oral communication, 1967). The $C2/m$ structure of glaucophane follows the general description of the tremolite structure. The amphibole A site is located at a special position of twofold multiplicity ($2b$) in $C2/m$; the results obtained from difference Fourier syntheses calculated at the end of the present refinement show that this site is vacant in glaucophane.

Using 986 observed reflections and assigning atomic positional parameters from the refinement of cummingtonite (Ghose, 1961), four cycles of least-squares refinement were executed for glaucophane utilizing the full matrix of the normal equations. During this treatment the individual isotropic temperature factors B were fixed at 0.8 \AA^2 for (O) and (OH), 0.4 \AA^2 for Si, 0.6 \AA^2 for Na, and 0.4 \AA^2 for the M(1), M(2), and M(3) octahedral cations. The scattering factors used at this stage of the refinement were those for O^0 , Na^0 , Si^0 , and $0.8\text{Mg}^0 + 0.2\text{Fe}^0$ taken from Macgillavry *et al.*, (1962), p. 202–205. The residual R ($R_o \Sigma | | F_c | - | F_o | | / \Sigma | F_o |$) was 0.30 after one cycle of refinement and dropped to 0.11 after three additional cycles in which only the scale factor and positional parameters were allowed to vary. Four additional refinement cycles were then executed with the isotropic temperature factors being allowed to vary (R , 0.10).

At this point in the refinement bond lengths were calculated with particular attention being paid to the mean metal-oxygen distances of the M(1), M(2), and M(3) octahedra. These metal-oxygen distances were found to be 1.95 \AA for M(2), and 2.09 \AA for M(1) and M(3). Comparison of these distances with others for refined silicate structures

¹ Stewart, James M. and Darrell High. "X-Ray 63"; Program system for X-ray crystallography. April, 1965. Departments of Chemistry, University of Washington, Seattle, and University of Maryland, College Park.

(Ghose, 1961, 1965b; Prewitt and Burnham, 1966; Macgillavry *et al.*, 1962, p. 260–269) indicated that the M(2) site was occupied by Al and Fe³⁺ and M(1) and M(3) sites were occupied by Fe²⁺ and Mg. These occupancies are consistent with the results of Whittaker (1949), who found that the M(2) site in magnesioriebeckite (crocidolite) was occupied preferentially by Fe³⁺ and Al. A nonrandom distribution of Fe²⁺ and Mg over the M(1) and M(3) sites in glaucophane was also indicated by significant differences in the isotropic temperature factors at this stage of refinement, $B(M1) = 0.61 \text{ \AA}^2$ and $B(M3) = 0.02 \text{ \AA}^2$. These temperature factors were interpreted as resulting for enrichment of Fe in the M3 site, and this interpretation was later confirmed by the results from a site-occupancy refinement, using a program written by Dr. C. T. Prewitt, E. I. duPont de Nemours Co., Wilmington, Delaware, and Professor C. W. Burnham, Harvard University, Cambridge, Massachusetts.

In the last stages of refinement, 963 observed data were used, and during four least-squares cycles the isotropic temperature factors, positional parameters, and site occupancies for the M(4), (Na,Ca), M(2), (Al,Fe), M(3), (Mg,Fe), and M(1),(Mg,Fe), sites were allowed to vary, assuming each site to be fully occupied. Scattering factors for fully ionized atoms were represented by an analytical expression (Prewitt and Burnham, 1966). Because of strong mathematical interactions between the isotropic temperature factors and site occupancies (correlation coefficients 0.82–0.90), the site-occupancy refinement was carried out in two additional ways: first, with four cycles in which the isotropic temperature factors were fixed at reasonable values and the occupancies were allowed to vary; and second, with ten cycles in which the temperature factors and occupancies were allowed to vary on alternate cycles. The R value after each of the three different treatments of the data was 0.08, and the resulting site occupancies are presented in Table 2. The values for the site occupancy (1), Table 2, were selected and fixed for three final cycles of least-squares refinement. The R value and positional parameters remained the same but temperature factors shifted slightly and are reported in Table 3. Unit weights were used throughout the refinement.

The three refinement methods converged on identical positional parameters and gave very similar results for the site occupancies (Table 2). The method of alternating temperature-factor and site-occupancy refinement converged more slowly, but the values were approaching those obtained by the other two methods. The cation contents per formula unit derived from the final site refinement are given in Table 3, and lead to the following chemical formula:

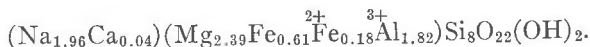


TABLE 2. PROGRESS OF CATION SITE-OCCUPANCY REFINEMENTS FOR GLAUCOPHANE

Refinement ^a	Cation sites ^b											
	M(1)			M(3)			M(2)			M(4)		
	Cations		<i>B</i> (Å ²)	Cations		<i>B</i> (Å ²)	Cations		<i>B</i> (Å ²)	Cations		<i>B</i> (Å ²)
	Mg	Fe ²⁺		Mg	Fe ²⁺		Al	Fe ³⁺		Na ⁺	Ca ²⁺	
1	0.84	0.16	0.45	0.71	0.29	0.34	0.91	0.09	0.30	0.98	0.02	0.85
2	0.83	0.17	0.49	0.74	0.26	0.25	0.90	0.10	0.33	0.99	0.01	0.84
3	0.85	0.15	(0.40)	0.70	0.30	(0.40)	0.91	0.09	(0.30)	0.98	0.02	(0.85)

^a Refinements as follows: 1. Site-occupancy, *B* refined together for 4 least-squares cycles; occupancy values chosen as final (Table 3). 2. Site-occupancy, *B* refined alternately during 10 least-squares cycles. 3. *B* values fixed, site-occupancies refined during 4 least-squares cycles.

^b Total occupancy of 1.00 assumed in each site.

The density calculated using this formula is 3.083 g/cm³. The formula is in good agreement with the one already given that was derived from the chemical analysis, except that the X-ray results indicate the presence of slightly more Al, somewhat less total Fe and less Ca than does the chemical analysis. Because the composition of the particular crystal selected for X-ray examination need not be identical to the bulk composition de-

TABLE 3. FINAL ATOMIC POSITIONAL PARAMETERS, TEMPERATURE FACTORS, AND SITE-OCCUPANCIES FOR GLAUCOPHANE

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	Occupancy, atoms per site
O(1)	0.1092 ± 0.0006	0.0927 ± 0.0003	0.2037 ± 0.0011	0.50 ± 0.08	1.0
O(2)	0.1177 ± 0.0006	0.1714 ± 0.0003	0.7480 ± 0.0011	0.50 ± 0.08	
O(3) (OH)	0.1126 ± 0.0009	0	0.7088 ± 0.0016	0.65 ± 0.12	
O(4)	0.3679 ± 0.0006	0.2529 ± 0.0003	0.8058 ± 0.0011	0.61 ± 0.08	
O(5)	0.3548 ± 0.0006	0.1318 ± 0.0003	0.0893 ± 0.0011	0.64 ± 0.08	
O(6)	0.3407 ± 0.0006	0.1224 ± 0.0003	0.5814 ± 0.0011	0.68 ± 0.08	
O(7)	0.3317 ± 0.0009	0	0.3018 ± 0.0016	0.66 ± 0.11	
Si(1)	0.2831 ± 0.0002	0.0871 ± 0.0001	0.2931 ± 0.0004	0.31 ± 0.03	1.0
Si(2)	0.2920 ± 0.0002	0.1730 ± 0.0001	0.8087 ± 0.0004	0.29 ± 0.03	
M(1)	0	0.0908 ± 0.0002	0.50	0.38 ± 0.05	0.16 ± 0.02 Fe 0.84 ± 0.02 Mg
M(2)	0	0.1807 ± 0.0002	0	0.26 ± 0.04	0.09 ± 0.02 Fe 0.91 ± 0.02 Al
M(3)	0	0	0	0.24 ± 0.03	0.29 ± 0.02 Fe 0.71 ± 0.02 Mg
M(4)	0	0.2772 ± 0.0003	0.50	0.80 ± 0.07	0.98 ± 0.04 Na 0.02 ± 0.04 Ca

TABLE 5. BOND DISTANCES IN THE SILICATE TETRAHEDRA COMPARED FOR GLAUCOPHANE AND CUMMINGTONITE

Atoms	Si-O distances (Å) Glaucophane present study	Cummingtonite Ghose (1961)
Si(1)-O(1)	1.618 ± 0.006	1.63 ₁
Si(1)-O(5)	1.616 ± 0.007	1.61 ₉
Si(1)-O(6)	1.621 ± 0.006	1.64 ₂
Si(1)-O(7)	1.611 ± 0.003	1.61 ₉
Average	1.616	1.62 ₈
Si(2)-O(2)	1.618 ± 0.006	1.62 ₇
Si(2)-O(4)	1.594 ± 0.006	1.61 ₇
Si(2)-O(5)	1.637 ± 0.007	1.64 ₆
Si(2)-O(6)	1.654 ± 0.007	1.63 ₈
Average	1.626	1.63 ₂
	O-O distances (Å)	
Si(1) tetrahedron		
O(1)-O(5)	2.648 ± 0.008	2.65 ₈
O(1)-O(6)	2.659 ± 0.007	2.67 ₉
O(1)-O(7)	2.638 ± 0.008	2.67 ₀
O(5)-O(6)	2.646 ± 0.009	2.66 ₀
O(5)-O(7)	2.627 ± 0.007	2.63 ₁
O(6)-O(7)	2.617 ± 0.008	2.65 ₈
Average	2.639	2.65 ₈
Si(2) tetrahedron		
O(2)-O(4)	2.745 ± 0.008	2.75 ₅
O(2)-O(5)	2.635 ± 0.008	2.66 ₃
O(2)-O(6)	2.636 ± 0.009	2.63 ₆
O(4)-O(5)	2.640 ± 0.008	2.65 ₆
O(4)-O(6)	2.588 ± 0.008	2.57 ₉
O(5)-O(6)	2.666 ± 0.008	2.69 ₁
Average	2.652	2.66 ₃
	Si-Si distances (Å)	
Si(1)-Si(2)	3.110 ± 0.003	3.09 ₆
Si(1)-Si(2) (at $z-1$)	3.003 ± 0.003	3.06 ₂
Si(1)-Si(1') (at $-y$)	3.090 ± 0.003	3.06 ₃

terminated by chemical analysis, this difference may be real. However, no confirming evidence, such as the results of electron-probe scans for the same crystal or even for several individual crystals, has been obtained.

The final atomic positional parameters, temperature factors, and site occupancies for the glaucophane structure are presented in Table 3, and a comparison of the observed and calculated structure factors is given in

TABLE 6. BOND ANGLES IN THE SILICATE TETRAHEDRA COMPARED FOR GLAUCOPHANE AND CUMMINGTONITE

Atoms	Glaucothane Present study	Cummingtonite Ghose (1961)
O(1)-Si(1)-O(5)	110.0±0.3°	109.8°
O(1)-Si(1)-O(6)	110.4±0.3°	109.9°
O(1)-Si(1)-O(7)	109.6±0.4°	110.5°
O(5)-Si(1)-O(6)	109.7±0.3°	109.3°
O(5)-Si(1)-O(7)	109.0±0.4°	108.6°
O(6)-Si(1)-O(7)	108.2±0.4°	108.8°
Average	109.5°	109.5°
O(2)-Si(2)-O(4)	117.5±0.3°	116.3°
O(2)-Si(2)-O(5)	108.1±0.3°	109.0°
O(2)-Si(2)-O(6)	107.4±0.3°	107.7°
O(4)-Si(2)-O(5)	109.6±0.3°	109.0°
O(4)-Si(2)-O(6)	105.6±0.3°	104.7°
O(5)-Si(2)-O(6)	108.2±0.3°	110.3°
Average	109.4°	109.5°
Si(1)-O(5)-Si(2)	134.7±0.5°	139.4°
Si(1)-O(6)-Si(2)	143.5±0.4°	141.4°
Si(1)-O(7)-Si(1')	147.2±0.6°	142.2°

Table 4.¹ Selected interatomic distances and angles are listed in Tables 5-7, and some of these are illustrated in Figures 2-5.

DISCUSSION OF THE CRYSTAL STRUCTURE

General features and the A site coordination. The general features of the crystal structure of glaucophane are similar to those of other clin amphiboles, *i.e.*, tremolite (Warren, 1930; Zussman, 1959), crocidolite (Whittaker, 1949), actinolite (Zussman, 1955), grunerite (Ghose and Hellner, 1959), cummingtonite (Ghose, 1961; Fischer, 1966), and riebeckite (Colville and Gibbs, 1964). Strips of octahedra running parallel to the *c*-axis are cross-linked by double chains of SiO₄ tetrahedra (Fig. 2*a*). Viewed along the *c* direction (Fig. 2*b*) the structure can be described in terms of alternating tetrahedral and octahedral layers. In this view, the marked

¹ Table 4 has been deposited as Document No. 9895 with the ADI Auxiliary Publications Project, Library of Congress, Washington, D.C. 20540. A copy may be secured by citing the document number and remitting in advance \$2.50 for photoprints or \$1.75 for 35 mm microfilm. Make checks or money orders payable to: Chief, Photoduplications Service, Library of Congress.

TABLE 7. CATION-OXYGEN COORDINATION AND CATION-CATION SEPARATIONS COMPARED FOR GLAUCOPHANE AND CUMMINGTONITE

Atoms	Glauconephane present study		Cummingtonite	
			Fischer (1966)	Ghose (1961)
	Cation site occupancy, ions per site	Distance (Å)	Cation site occupancy, ions per site	Distance (Å)
(2) M(1)-O(1)	0.84 Mg ²⁺ ,	2.078 ± 0.006	0.84 Mg ²⁺ ,	2.07 ₇
(2) M(1)-O(2)	0.16 Fe ²⁺	2.082 ± 0.006	0.16 Fe ²⁺	2.11 ₆
(2) M(1)-O(3)		2.100 ± 0.005		2.10 ₄
Average		2.087		2.09 ₉
(2) M(2)-O(1)	0.91 Al ³⁺ ,	2.038 ± 0.006	0.95 Mg ²⁺ ,	2.12 ₉
(2) M(2)-O(2)	0.09 Fe ³⁺	1.943 ± 0.006	0.05 Fe ²⁺	2.09 ₄
(2) M(2)-O(4)		1.849 ± 0.006		2.02 ₉
Average		1.943		2.08 ₁
(4) M(3)-O(1)	0.71 Mg ²⁺ ,	2.103 ± 0.005	0.84 Mg ²⁺ ,	2.10 ₂
(2) M(3)-O(3)	0.29 Fe ²⁺	2.077 ± 0.005	0.16 Fe ²⁺	2.07 ₂
Average		2.094		2.09 ₂
(2) M(4)-O(2)	0.98 Na ⁺ ,	2.411 ± 0.006	0.13 Mg ²⁺ ,	2.17 ₇
(2) M(4)-O(4)	0.02 Ca ²⁺	2.337 ± 0.006	0.87 Fe ²⁺	2.04 ₂
(2) M(4)-O(6)		2.446 ± 0.006		2.69 ₉
(2) M(4)-O(5)		2.798 ± 0.006		
Average of 8		2.498		
Average of 6 shortest		2.398		2.30 ₆
(4) A-O(5)	Vacant	2.814 ± 0.006	Vacant	(2.83)
(4) A-O(6)		3.216 ± 0.006		(3.34)
(2) A-O(7)		2.519 ± 0.009		(2.28)
(2) A-O(7)		3.666 ± 0.008		(3.87)
M(1)-M(1')		3.221 ± 0.004		
M(1)-M(2)		3.091 ± 0.002		
M(1)-M(3)		3.099 ± 0.002		
M(1)-M(4)		3.307 ± 0.006		
M(2)-M(3)		3.206 ± 0.003		
M(2)-M(4)		3.153 ± 0.003		

kink in the tetrahedral chains is clearly visible. This feature has been noted in other clinoamphibole structures and appears to be necessary in order to fit together the tetrahedral chains and the slightly undersized octahedral strips.

The amphibole A site previously mentioned can be located in Figure 2a at 0, 1/2, 0. The distances of nearby oxygen atoms to this location are

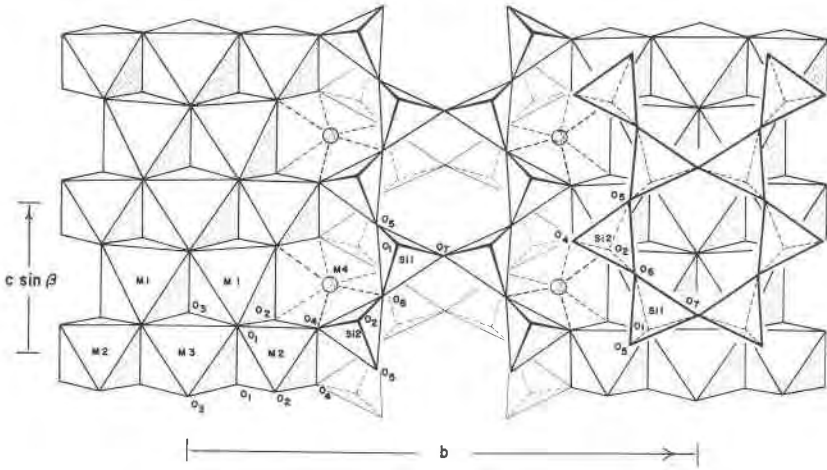


FIG. 2a. View of the glaucophane structure along a , showing selected portions of the cell contents. Dashed lines indicate the six shortest oxygen bonds to M4(N a).

given in Table 7 for both cummingtonite and glaucophane and the atomic array surrounding this site in glaucophane is illustrated in Figure 3. The A site is assumed to be occupied by potassium in the hornblendes, and Heritsch, Paulitsch and Walitzi (1957) have tabulated the distances of nearby oxygen atoms to this site for various amphiboles in connection with their two-dimensional refinement of the structures of two hornblendes. The A-O distances for the hornblendes range from 2.7 to 3.4 Å, and are more evenly balanced for coordination purposes than are the corresponding bonds to the vacant site in glaucophane and cummingtonite

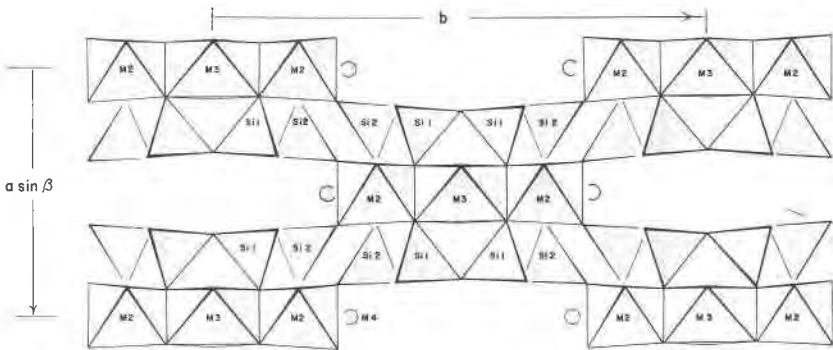


FIG. 2b. View of the glaucophane structure along c , showing the arrangement of the octahedral and tetrahedral layers. The kinking effect is apparent in this view. M(1) octahedra are omitted.

(Table 7). Further information about this structural feature should be obtained by a study in progress of the crystal structure of a hornblende with high potassium content (Mason, 1966; Papike and Clark, 1967).

Unfortunately, of all the clinoamphibole structures noted above, only cummingtonite has been refined by modern three-dimensional methods and completely reported in the literature. Therefore detailed comparison is limited in the following discussion to the cummingtonite structure.

Geometry of the SiO_4 tetrahedra. The two crystallographically distinct tetrahedral sites, T(1) and T(2), in the $C2/m$ clinoamphibole structure are also distinct structurally. The T(1) tetrahedra are comparable to

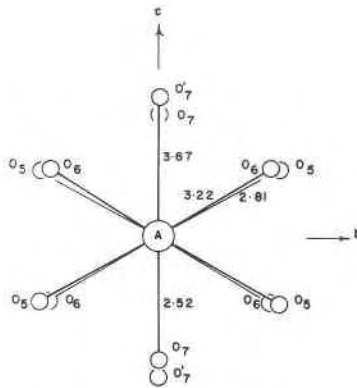


Fig. 3. Projection on (100) showing details of coordination around the vacant amphibole A site in glaucophane (Table 7).

those in sheet-silicate structures (Pauling, 1930; Jackson and West, 1930, 1933), having three oxygen atoms, each of which bridges between two tetrahedral cations, and only one oxygen atom that may be called non-bridging or external, because it links to only one tetrahedral cation. The T(2) tetrahedra closely resemble the tetrahedra in single-chain silicate structures (Warren and Bragg, 1928), having two bridging and two non-bridging oxygen atoms. Recent refinements of several single-chain silicate structures (clinoenstatite and pigeonite, Morimoto, Appleman and Evans, 1960; hypersthene, Ghose, 1965b; jadeite, Prewitt and Burnham, 1966; orthoenstatite, Koto, 1967; johannsenite, Freed and Peacor, 1967; omphacite, Clark and Papike, 1968) demonstrate that such tetrahedra are characterized by long Si-O bonds for the bridging oxygens, and short Si-O bonds for the external oxygens (Clark and Papike, 1968). For example, in omphacite the averages are 1.66 Å for bridging Si-O and 1.60 Å for nonbridging Si-O. The O-Si-O angles also depart from the tetrahedral

value for the pairs of bridging oxygens (around 107°) and nonbridging oxygens (around 117°). Cruickshank (1961) and Noll (1961) suggested that such differences might occur, and some of the reasons for these differences are discussed by McDonald and Cruickshank (1967).

The T(2) tetrahedra in glaucophane and cummingtonite exhibit similar tendencies, although the range of values appears to be smaller, 1.637 to 1.654 Å (Table 5; O(5) and O(6), bridging oxygen atoms). The O(2)-Si(2)-O(4) angle for the pair of external oxygen atoms is 117.5° in glaucophane, 116.3° in cummingtonite, and 116.8° in riebeckite (Colville and Gibbs, 1964), values close to those observed for the O-Si-O angles involving external oxygen atoms in the single-chain silicates. However, the O(5)-Si(2)-O(6) angle for the pair of bridging oxygens in the amphiboles discussed here approaches the tetrahedral value more closely than do the corresponding angles in the single-chain structures.

As the values in Tables 5 and 6 show, the Si-O distances for T(1) in glaucophane and cummingtonite have a smaller range than do those in T(2), and the O-T(1)-O angles are all close to the tetrahedral value. These tetrahedra are thus more nearly regular tetrahedra than are those of the T(2) type. Unfortunately, in sheet silicates pure SiO_4 tetrahedra are rare because there is usually appreciable Al in tetrahedral coordination, and no modern three-dimensional structural refinement of a sheet silicate with pure SiO_4 tetrahedra is available, to our knowledge. However, the values given for the SiO_4 tetrahedra in dickite (Newnham, 1961) do indicate a greater degree of regularity associated with tetrahedra of this type.

Because the bridging T(2)-O distances are long, the average T(2)-O values may normally range from 1.62 to 1.65 Å for pure SiO_4 tetrahedra, as in the pyroxene structures previously cited. The suggestion by Colville and Gibbs (1964) that an overall average T-O distance of 1.63 Å in riebeckite is larger than expected and therefore indicates the presence of a small amount of Fe replacing Si seems unwarranted on the basis of the present evidence. However, any observed lengthening of the T(2)-O(2) and T(2)-O(4) bonds should be a significant indicator of either Al or Fe substitution in the T(2) site.

The Si-O-Si angles in glaucophane are within the expected range; the amphibole bridging angle Si(1)-O(7)-Si(1') is 147.2° , appreciably larger than the two pyroxene-type bridging angles (134.7° and 143.5° , respectively) which are entirely comparable to the bridging angles reported in the previously cited references for pyroxenes.

Environment of the sodium cation. The M(4) site is occupied by Na in glaucophane, and is coordinated by six short bonds averaging 2.398 Å

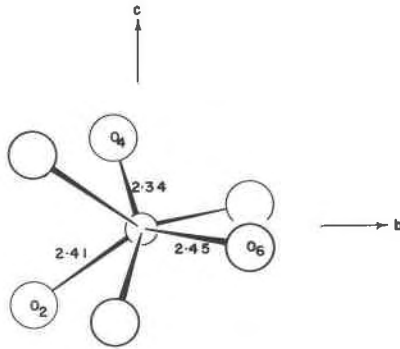


FIG. 4. Projection on (100) showing the six shortest bonds to the M(4) site, occupied by Na in glaucophane (Table 7). The two longer distances to symmetry-related O(5) atoms may be located on Fig. 2a.

(Table 7) and two longer bonds, each 2.798 Å. The coordination of the six closest oxygen atoms is illustrated in Figure 4 as projected on (100). The longer bonds are to O(5) symmetry-equivalent atoms and may be located in Figure 2a. Colville and Gibbs (written communication, 1965) find a similar coordination for the sodium cation in riebeckite, the average value for the six shortest bonds being 2.438 Å, slightly longer than for glaucophane. The six short, two long coordination pattern is normal for sodium in other structures, e.g. jadeite (Prewitt and Burnham, 1966) where the six short bonds average 2.377 Å, and the two longer ones are each 2.741 Å.

Octahedra M(1), M(2) and M(3), and charge balance considerations. The bond distances and site occupancies for these octahedra are compared in Table 7 with those found for cummingtonite; the coordination is illustrated for glaucophane in Figure 5. The M(1) and M(3) octahedra have very similar Mg-Fe²⁺ distribution in both structures, and the bond distances are correspondingly close in value. The effect of the Al-Fe³⁺ occupancy in M(2) for glaucophane is shown by the markedly smaller M(2)-O distances observed, the average M(2)-O being 1.943 Å for glaucophane, compared with 2.084 Å for cummingtonite which has largely Mg in the M(2) site.

The charge balance considerations governing location of the trivalent cations in the M(2) site when M(4) is occupied by a univalent cation were discussed by Whittaker (1949) in connection with crocidolite, and his remarks apply equally to the glaucophane structure. Assuming ionic bonding, with positive charges of two units each on M(1) and M(3), one

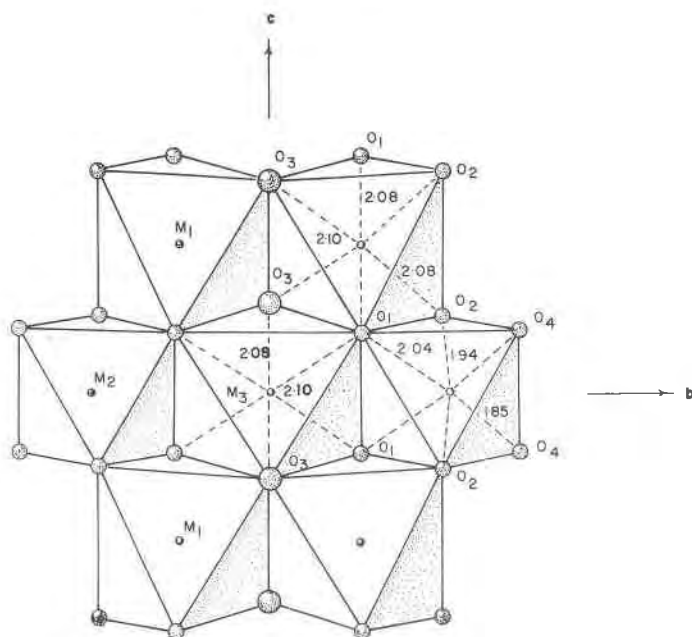


FIG. 5. Projection on (100) showing the octahedral coordination for M1(Mg,Fe²⁺), M2(Al, Fe³⁺) and M3(Mg,Fe²⁺) in glaucophane (Table 7).

unit on M(4), and three units on M(2), there is perfect electrostatic balance for all oxygen atoms, including the hydroxyl O(3), except for three: O(1) and O(6) each receive an excess positive charge of 1/6, and O(4) is deficient by 1/3. The bond distances involving these oxygens are in the correct direction to balance the deviations (Tables 5, 7), namely, long for O(1) and O(6), and noticeably short for O(4), *i.e.* Si-O(4), 1.594 Å; M(2)-O(4), 1.849 Å; M(4)-O(4), 2.337 Å. Whittaker (1960) suggested that the magnitude of the β angle in clin amphiboles is controlled largely by the M(4)-O(4) distance, which he showed to be directly related to the tetrahedral chain packing. The suggestion is partially confirmed by comparison of the refined results for cummingtonite and glaucophane (Table 7), the β angles, respectively, being 101° 55' and 103° 40'. However, the nature of the atomic species occupying the M(2) site also affects the location of O(4), so a direct comparison of cummingtonite and a refinement of tremolite, with its β angle of 104° 39' (M. Ross, U. S. Geological Survey, written communication, 1967) and Mg occupancy of the M(2) site, will provide the best test of the prediction.

CATION DISTRIBUTION IN GLAUCOPHANE

Although the ordered cation distribution (Table 3) has been given in terms of Fe^{2+} and Fe^{3+} , the method used for the site-occupancy refinement cannot distinguish between these two. However, the M(3) site clearly is enriched in Fe relative to M(1), and assumption of Fe^{3+} together with Al in M(2) appears reasonable in view of the charge balance requirements and the observed bond distances (Table 7). In general, an average Fe^{3+} -O distance is about 2.03 Å, compared with 2.14 Å for an average Fe^{2+} -O distance.

On the basis of results obtained from infrared spectroscopic studies of amphiboles, Strens (1966) reported that in glaucophane the M(1) site is Fe^{2+} -enriched. This assignment was in conflict with the Fe-enrichment of M(3) found during the present refinement. However, R. G. J. Strens (The University, Leeds, England, written communication, 1967) later discovered that calculations based on peak areas rather than peak heights should be used in reducing the spectroscopic data. When such a correction is made, he reports that the agreement between the infrared and X-ray results is good, and therefore the Fe-enrichment of M(3) is confirmed by the results of both methods. These results are further supported by Mössbauer measurements on glaucophane of similar composition by Pritchard (Oxford University, written communication by R. G. J. Strens, 1967) who finds a very similar cation distribution to that arrived at from the X-ray data.

The observed cation distributions for glaucophane are applicable to crystalline solution models in the system glaucophane, $\text{Na}_2\text{Mg}_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ -ferroglaucophane, $\text{Na}_2\text{Fe}_3^{2+}\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ -riebeckite, $\text{Na}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_8\text{O}_{22}(\text{OH})_2$ -magnesioriebeckite, $\text{Na}_2\text{Mg}_3\text{Fe}_2^{3+}\text{Si}_8\text{O}_{22}(\text{OH})_2$. If we assume that Fe^{3+} and Al occupy the M(2) site and Fe^{2+} and Mg occupy the M(1) and M(3) sites throughout the series, then mixing of Fe^{3+} and Al over only one crystallographically distinct site occurs in crystalline solutions between glaucophane and riebeckite. However, in crystalline solutions between glaucophane and ferroglaucophane, and between riebeckite and magnesioriebeckite, mixing of Fe^{2+} and Mg over the two crystallographically distinct sites M(1) and M(3) would occur. Assuming ideal mixing for each site and an associated temperature of equilibration for the observed distribution, an interchange energy $\Delta^0G = -RT \ln K$ can be calculated (Mueller, 1962). For our glaucophane sample, the ΔG_i^0 for Mg and Fe^{2+} interchange between the M(1) and M(3) sites is 0.72 kcal/mole at 200°C and 1.02 kcal/mole at 400°C. These temperatures are of reasonable range for the glaucophane schist facies. Thus, if the observed ordering of Fe^{2+} and Mg took place at the last equilibration and is

not the result of slow cooling, nonideality in crystalline solutions between glaucophane and ferroglaucophane under blueschist facies conditions is indicated.

Ernst (1963) suggested that glaucophane II would have an ordered cation distribution with Al in the M(2) site, Mg in M(1) and M(3) sites, and that glaucophane I would have a disordered cation distribution with Al and Mg distributed over M(1), M(2) and M(3) sites. The I-II polymorphic transition would thus be one of order-disorder. The results of our study support Ernst's hypothesis to the extent that the ordered distribution he predicted does occur in the mineral, which is glaucophane II. However, validation of the hypothesis depends on the results of a structural refinement for glaucophane I. So far no crystals large enough for single crystal work have been obtained.

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