

POLYMORPHISM IN ALKALI AMPHIBOLES<sup>1</sup>

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## ABSTRACT

Unit cell dimensions of synthetic glaucophane,  $\text{Na}_2\text{Mg}_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$ , magnesioriebeckite,  $\text{Na}_2\text{Mg}_3\text{Fe}_2^{3+}\text{Si}_8\text{O}_{22}(\text{OH})_2$ , riebeckite,  $\text{Ma}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_8\text{O}_{22}(\text{OH})_2$ , and three intermediate members of the glaucophane-riebeckite series have been investigated as a function of temperature and total pressure. Oxidation state was controlled by hematite-magnetite buffers.

Cell volumes of magnesioriebeckite,  $901 \pm 3 \text{ \AA}^3$ , and riebeckite,  $913 \pm 2 \text{ \AA}^3$ , are constant in the region 400–800° C. and up to 40 kb. The cell volume of glaucophane is  $897 \pm 4 \text{ \AA}^3$  at 800° C., 1 kb, and  $877 \pm 4 \text{ \AA}^3$  at 800° C., 20 kb. Both low-pressure and high-pressure forms, designated I and II respectively, have diffractometer patterns indexable on the basis of  $C2/m$  space group extinction criteria. The transition between the two glaucophane polymorphs appears to be gradational with intermediate cell volumes restricted to a zone about 3 kb wide and passing through the PT points 300° C., 2.5 kb and 800° C., 17.5 kb. Synthetic members of the glaucophane-riebeckite series exhibit similar polymorphism; magnitude of  $\Delta V$  for the transition is proportional to the mole fraction Al ( $\text{Fe}^{3+} + \text{Al}$ ). The I-II transition is second order. Aluminum is thought to be concentrated in the  $M_2$  structural site in the high-pressure polymorph, and is more randomly distributed among all octahedral positions in the low-pressure polymorph.

Natural alkali amphiboles thus far examined are similar to the high-pressure, low-temperature series produced in this study.

## INTRODUCTION AND ACKNOWLEDGMENTS

Amphibole structures have been studied by a number of investigators and the principal variations are well known. Warren (1929) determined the crystal structure of tremolite, and Warren and Modell (1930) elucidated the atomic arrangement of anthophyllite. More recently Whittaker (1949), Zussman (1955, 1959), Heritsch *et al.* (1957, 1959) Heritsch and Kahler (1959), Heritsch and Riechert (1959), Ghose and Hellner (1959) and Ghose (1961) have performed refined structural analyses of magnesioriebeckite (crocidolite), actinolite, tremolite, six hornblendes, grunerite and cummingtonite. All investigators were able to index  $x$ -ray reflections for the monoclinic amphiboles on the basis of a  $C2/m$  (or symmetrically equivalent  $I2/m$ ) space group.

$X$ -ray properties of synthetic fluortremolite (Comeforo and Kohn, 1954), tremolite and pargasite (Boyd, 1959) and magnesioriebeckite and riebeckite-arfvedsonite (Ernst, 1960, 1962) closely resemble those of the natural minerals. However, synthetic glaucophane produced under the conditions of approximately 800° C. and 1000 bars fluid pressure (Ernst, 1961) has a unit cell volume more than two per cent greater than that of

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the natural material. Preliminary investigation at about 800° C. and 20 kb pressure yielded glaucophane with a cell volume comparable to naturally occurring analogues, and it was suggested that two polymorphs might exist. In this paper, the large-volume polymorph will be designated as I, the small-volume polymorph as II. Indexed powder patterns for the two synthetic polymorphs of glaucophane are compared in Table 1. Existence of a structural transformation in glaucophane is of petrologic significance in delineating PT conditions of crystallization for glaucophane-bearing rocks.

The present investigation was undertaken in order to determine the

TABLE 1. COMPARISON OF LOW-PRESSURE SYNTHETIC GLAUCOPHANE I WITH HIGH-PRESSURE SYNTHETIC GLAUCOPHANE II. (SPACE GROUP  $C^2/m$ )

| (hkl)       | Glaucophane I                   |          | Glaucophane II                  |          |
|-------------|---------------------------------|----------|---------------------------------|----------|
|             | $2\theta$ obs. <sup>1</sup> in° | d obs. Å | $2\theta$ obs. <sup>1</sup> in° | d obs. Å |
| 020         | 9.82                            | 9.00     | 9.98                            | 8.86     |
| 110         | 10.56                           | 8.38     | 10.68                           | 8.28     |
| $\bar{1}11$ | 18.42                           | 4.818    | 18.34                           | 4.837    |
| 200         | —                               | —        | 18.94                           | 4.686    |
| 040         | 19.814                          | 4.481    | 20.058                          | 4.427    |
| 111         | 21.95                           | 4.049    | 22.09                           | 4.024    |
| $\bar{1}31$ | 23.19                           | 3.885    | 23.25                           | 3.827    |
| 131         | 26.114                          | 3.412    | 26.39                           | 3.378    |
| 240         | 27.38                           | 3.257    | 27.82                           | 3.208    |
| 310         | 28.691                          | 3.120    | 29.050                          | 3.074    |
| 221         | 29.99                           | 2.980    | 30.454                          | 2.935    |
| $\bar{1}51$ | 30.69                           | 2.913    | 30.91                           | 2.893    |
| 330         | 32.04                           | 2.794    | 32.53                           | 2.753    |
| 151         | 33.000                          | 2.714    | 33.422                          | 2.681    |
| 331         | 33.40                           | 2.683    | —                               | —        |
| 241         | 34.76                           | 2.581    | —                               | —        |
| 061         | —                               | —        | 35.06                           | 2.560    |
| $\bar{2}02$ | 35.894                          | 2.502    | 35.708                          | 2.514    |
| $\bar{3}51$ | 39.14                           | 2.301    | 39.41                           | 2.286    |
| $\bar{1}71$ | —                               | —        | 39.88                           | 2.260    |
| 331         | 33.79                           | 2.265    | —                               | —        |
| 080         | —                               | —        | —                               | —        |
| 261         | 41.56                           | 2.173    | 42.29                           | 2.137    |
| 202         | 43.49                           | 2.081    | —                               | —        |
| 351         | 44.63                           | 2.031    | —                               | —        |
| $\bar{4}02$ | —                               | —        | 45.90                           | 1.977    |
| 242         | 48.23                           | 1.887    | —                               | —        |

<sup>1</sup> CuK $\alpha$ .

variation of unit cell parameters of alkali amphiboles as a function of temperature, pressure and composition. Initial experiments were carried out at the Geophysical Laboratory, Carnegie Institution of Washington, and the study was concluded at the Department of Geology and Institute of Geophysics, University of California, Los Angeles. F. R. Boyd of the former institution and G. C. Kennedy of the latter provided high-pressure equipment utilized in the investigation. C. E. Corbato, Department of Geology, University of California, Los Angeles, advised the author on statistical treatment of the data. The manuscript was critically reviewed by Boyd, Kennedy, and George Tunell and Joseph Murdoch, Department of Geology, University of California, Los Angeles. The author wishes to thank the above-named institutions and individuals for their support and constructive criticism.

#### EXPERIMENTAL TECHNIQUES

Equipment employed for synthesis of amphiboles was of three different types.

(1) Conventional hydrothermal apparatus as described in previous reports was used at pressures below 5000 bars. Charges+excess H<sub>2</sub>O were sealed in silver capsules and subjected to the desired PT conditions. Fluid pressure is equal to total pressure in these experiments. Cold seal pressure vessels (Tuttle, 1949) were calibrated for temperature gradient against the melting points of LiCl (605° C.) or NaCl (800.5° C.). Hydrostatic run pressure was measured continuously on a variety of gauges calibrated against 14 inch standard Heise gauges (1400 and 3000 bar bourdon tube gauges). Observed temperature fluctuations in all cases were within  $\pm 3^\circ$  C.; observed pressure fluctuations were within  $\pm 10$  bars.

(2) Experiments at high temperatures and high pressures were performed in the apparatus described and calibrated by Boyd and England (1960a). As with hydrothermal equipment, the use of sealed capsules+excess H<sub>2</sub>O meant that fluid pressure on the charge was equal to the computed confining pressure. Errors and gradients estimated by Boyd and England (1960b) for the investigated PT range are  $\pm 10^\circ$  C. and  $\pm 0.5$  kb.

(3) Experiments at moderate temperatures and moderate to high pressures were conducted using a redesigned piston anvil device as described by Griggs and Kennedy (1956). The apparatus was calibrated for temperature gradient at one atmosphere total pressure against the melting points of LiCl and NaCl; the pressure at 9.8 kb was determined by calibration using LiCl and the PT data of Clark (1959). Run temperatures and pressures are considered accurate to about  $\pm 10^\circ$  C. and  $\pm 1$  kb respectively. Departure of  $P_{\text{fluid}}$  from  $P_{\text{total}}$  may be significant in this type of apparatus. However, assuming the different amphibole structural types have the same mole proportion of H<sub>2</sub>O, water does not enter into the investigated reactions (*i.e.*, it is an indifferent phase), and variance of the ratio  $P_{\text{fluid}}/P_{\text{total}}$  does not affect the determined polymorphic stability relations. Run data employing the three different types of equipment are consistent and are equivalent in areas of PT overlap.

Mixtures of oxides in stoichiometric proportions of the desired amphibole were used as starting material in most experiments. Six different bulk compositions were investigated:

(1) glaucophane+water,  $\text{Na}_2\text{O}\cdot 3\text{MgO}\cdot \text{Al}_2\text{O}_3\cdot 8\text{SiO}_2+\text{H}_2\text{O}$ ; (2) magnesioriebeckite+water,  $\text{Na}_2\text{O}\cdot 3\text{MgO}\cdot \text{Fe}_2\text{O}_3\cdot 8\text{SiO}_2+\text{H}_2\text{O}$ ; (3) riebeckite+water,  $\text{Na}_2\text{O}\cdot 3\text{FeO}\cdot \text{Fe}_2\text{O}_3\cdot 8\text{SiO}_2+\text{H}_2\text{O}$ ; (4) 75 mole per cent glaucophane+25 mole per cent riebeckite+ $\text{H}_2\text{O}$ ; (5) crossite+water, 50 mole per cent glaucophane+50 mole per cent riebeckite+ $\text{H}_2\text{O}$ ; and (6) 25 mole per cent glaucophane+75 mole per cent riebeckite+ $\text{H}_2\text{O}$ .

The charges commonly crystallized only partly to amphiboles, variable amounts of the high-temperature anhydrous assemblages of equivalent bulk compositions being present; higher temperature, higher  $P_{\text{fluid}}$  and longer run duration favored increased proportions of amphibole. Micro-metric analyses have demonstrated that relative proportions among high-temperature phases are the same regardless of whether these phases crystallized without amphibole or in metastable association with amphibole. This indicates that the composition of the amphibole is the same as the bulk composition. An attempt was made to analyze individual crystals of glaucophane I and glaucophane II using an electron microprobe through the courtesy of G. O. S. Arrhenius and R. W. Fitzgerald, University of California, San Diego, However, difficulty was experienced in identifying grains of glaucophane in the absence of refractive index oils. Furthermore, precision of the data was diminished owing to the small size of the glaucophane crystals (fibrous individuals averaged 10–30 microns in length, and up to 2 microns in thickness) and large number of inclusions, and because of strong electron beam penetration and  $x$ -ray absorption for the elements of low atomic number being analyzed.

Experiments were performed starting with synthetic amphibole-bearing charges previously crystallized from oxide mixtures. Glaucophanes and crossites with small unit cell volumes were recrystallized to large cell volume polymorphs, and *vice versa* (see Table 2, runs at 800° C.-500 bars, 713° C.-20,300 bars, 350° C.-2990 bars, 296° C.-2990 bars; Table 6, runs at 515° C.-20,400 bars, 509° C.-1000 bars).

Oxidation state was controlled by the hematite-magnetite buffer pair on all runs where iron was present in the sample. These are the iron oxides most commonly associated with alkali amphiboles in low and medium-grade metamorphic rocks and in pegmatites (*e.g.*, Ernst, 1962). The double capsule method described by Eugster (1957) was employed on hydrothermal experiments. Excess  $\text{Fe}_2\text{O}_3+\text{Fe}_3\text{O}_4$  were added to the charge which was surrounded by gold foil on runs performed using the piston anvil device.

Run products were examined with a petrographic microscope and index oils. Norelco  $x$ -ray diffractometer patterns were obtained using copper or iron radiation; several samples were examined using powder cameras. Unit cell dimensions of amphiboles were determined in the following manner.  $2\theta$  values for 6 or 7 reflections were measured using

quartz or NaCl as an internal standard. From 3 to 5 complete oscillations were performed on each sample depending on the resolution of individual reflections. Peak locations were measured to  $0.005^\circ 2\theta$  and averaged. Cell parameters were calculated to three decimal places using a least squares treatment programmed for an IBM 7090 computer (University of California, Los Angeles, Computing Facility) by W. E. Sharp, Department of Geology, University of California, Los Angeles. Values were subsequently rounded off to  $0.01 \text{ \AA}$ ,  $0.1^\circ$  and  $1 \text{ \AA}^3$ .

## RUN DATA

Unit cell dimensions of synthetic glaucophane, magnesioriebeckite, riebeckite, and intermediate members  $\text{Gl}_{75}\text{R}_{25}$ ,  $\text{Gl}_{50}\text{R}_{50}$  (crossite) and  $\text{Gl}_{25}\text{R}_{75}$  produced at various temperatures and pressures are presented in Tables 2-7 respectively. It should be pointed out that cell dimensions of magnesioriebeckite given previously (Ernst, 1960, Table 15) were deter-

TABLE 2. RESULTS OF INVESTIGATION OF THE COMPOSITION  
 $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2 + \text{H}_2\text{O}$

| Starting material | Temp (° C.) | Pressure (bars) | Duration (hrs) | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | $\beta$ (°) | Cell vol (Å <sup>3</sup> ) |
|-------------------|-------------|-----------------|----------------|--------------|--------------|--------------|-------------|----------------------------|
| Gl I              | 713         | 20,300          | 5              | 9.61         | 17.71        | 5.28         | 103.8       | 873                        |
| Mix               | 700         | 20,000          | 21             | 9.64         | 17.70        | 5.28         | 103.7       | 875                        |
| Mix               | 800         | 20,000          | 20             | 9.66         | 17.70        | 5.28         | 103.7       | 877                        |
| Glass             | 599         | 30,000          | 6              | 9.61         | 17.75        | 5.29         | 103.6       | 877                        |
| Mix               | 294         | 4,600           | 1460           | 9.66         | 17.74        | 5.28         | 103.7       | 878                        |
| Gl I              | 296         | 2,990           | 1096           | 9.59         | 17.77        | 5.30         | 103.4       | 878                        |
| Mix               | 600         | 12,400          | 72             | 9.66         | 17.83        | 5.25         | 103.6       | 878                        |
| Mix               | 700         | 25,000          | 13             | 9.69         | 17.72        | 5.27         | 103.7       | 879                        |
| Mix               | 690         | 17,000          | 13             | 9.69         | 17.74        | 5.28         | 103.7       | 882                        |
| Glass             | 697         | 13,800          | 4              | 9.67         | 17.83        | 5.26         | 103.0       | 883                        |
| Mix               | 750         | 16,700          | 20             | 9.71         | 17.73        | 5.28         | 103.7       | 883                        |
| Mix               | 800         | 16,700          | 18             | 9.73         | 17.80        | 5.27         | 103.7       | 888                        |
| Glass             | 797         | 12,800          | 6              | 9.70         | 17.86        | 5.27         | 102.7       | 891                        |
| Glass             | 521         | 11,100          | 4              | 9.69         | 17.90        | 5.27         | 103.1       | 891                        |
| Gl II             | 350         | 2,990           | 1097           | 9.72         | 17.98        | 5.25         | 103.4       | 893                        |
| Glass             | 631         | 10,400          | 15             | 9.74         | 17.83        | 5.28         | 102.6       | 895                        |
| Mix               | 835         | 1,190           | 37             | 9.71         | 17.92        | 5.27         | 102.6       | 896                        |
| Gl II             | 800         | 500             | 241            | 9.73         | 17.90        | 5.27         | 102.8       | 896                        |
| Glass             | 815         | 1,000           | 1920           | 9.73         | 17.91        | 5.27         | 102.8       | 896                        |
| Mix               | 403         | 4,750           | 1414           | 9.76         | 18.01        | 5.25         | 103.5       | 896                        |
| Glass             | 603         | 4,600           | 1082           | 9.78         | 17.82        | 5.29         | 103.6       | 897                        |
| Glass             | 760         | 2,000           | 221            | 9.75         | 17.91        | 5.27         | 102.8       | 898                        |
| Mix               | 680         | 10,000          | 52             | 9.77         | 17.92        | 5.27         | 103.0       | 898                        |
| Mix               | 750         | 15,000          | 47             | 9.76         | 17.90        | 5.28         | 102.5       | 899                        |
| Glass             | 796         | 10,000          | 8              | 9.81         | 17.93        | 5.25         | 103.1       | 899                        |

TABLE 3. RESULTS OF INVESTIGATION OF THE COMPOSITION  $\text{Na}_2\text{O}\cdot 3\text{MgO}\cdot \text{Fe}_2\text{O}_3\cdot 8\text{SiO}_2 + \text{H}_2\text{O}$  AND WITH OXYGEN FUGACITY DEFINED BY THE HEMATITE-MAGNETITE BUFFER

| Starting material | Temp (° C.) | Pressure (bars) | Duration (hrs) | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | $\beta$ (°) | Cell vol (Å <sup>3</sup> ) |
|-------------------|-------------|-----------------|----------------|--------------|--------------|--------------|-------------|----------------------------|
| Mr                | 639         | 3,025           | 233            | 9.70         | 17.94        | 5.30         | 103.4       | 897                        |
| Mix               | 554         | 30,200          | 40             | 9.70         | 17.98        | 5.29         | 103.0       | 899                        |
| Mr                | 879         | 1,010           | 23             | 9.77         | 17.91        | 5.29         | 103.4       | 901                        |
| Mix               | 553         | 39,600          | 18             | 9.72         | 17.93        | 5.31         | 103.2       | 901                        |
| Mix               | 853         | 1,000           | 34             | 9.75         | 17.92        | 5.31         | 103.5       | 902                        |
| Mr                | 864         | 1,500           | 2              | 9.75         | 17.95        | 5.30         | 103.4       | 902                        |
| Mix               | 552         | 17,800          | 16             | 9.74         | 17.99        | 5.29         | 103.2       | 902                        |

mined for a sample crystallized at a low oxidation state defined by the magnetite-wüstite buffer. Comparing the earlier data with those presented in Table 3, the unit cell volume of magnesioriebeckite apparently increases slightly with decreasing oxygen fugacity (although in the original publication diffractometer patterns were said to be identical for amphiboles crystallized at different oxidation states). Similar variation in cell volume was observed in an investigation of the riebeckite bulk composition (Ernst, 1962); through micrometric analyses it was demonstrated that at low oxidation states, riebeckite-arfvedsonite solid solutions were obtained; pure riebeckite was synthesized only at relatively high oxygen fugacities defined by the pair hematite+magnetite. By analogy it seems

TABLE 4. RESULTS OF INVESTIGATION OF THE COMPOSITION  $\text{Na}_2\text{O}\cdot 3\text{FeO}\cdot \text{Fe}_2\text{O}_3\cdot 8\text{SiO}_2 + \text{H}_2\text{O}$  AND WITH OXYGEN FUGACITY DEFINED BY THE HEMATITE-MAGNETITE BUFFER

| Starting material | Temp (° C.) | Pressure (bars) | Duration (hrs) | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | $\beta$ (°) | Cell vol (Å <sup>3</sup> ) |
|-------------------|-------------|-----------------|----------------|--------------|--------------|--------------|-------------|----------------------------|
| Mix               | 489         | 1,960           | 619            | 9.72         | 18.05        | 5.33         | 103.3       | 911                        |
| R                 | 545         | 30,200          | 41             | 9.71         | 18.06        | 5.33         | 103.1       | 911                        |
| R                 | 546         | 39,300          | 22             | 9.72         | 18.03        | 5.34         | 103.0       | 912                        |
| Mix               | 514         | 2,000           | 143            | 9.73         | 18.07        | 5.33         | 103.2       | 912                        |
| R                 | 487         | 990             | 177            | 9.73         | 18.05        | 5.33         | 103.4       | 912                        |
| Mix               | 473         | 1,000           | 711            | 9.73         | 18.07        | 5.33         | 103.4       | 912                        |
| R                 | 478         | 2,000           | 309            | 9.71         | 18.06        | 5.34         | 103.2       | 912                        |
| R                 | 450         | 1,965           | 239            | 9.73         | 18.04        | 5.34         | 103.5       | 912                        |
| R                 | 455         | 2,000           | 263            | 9.73         | 18.08        | 5.33         | 103.4       | 913                        |
| R                 | 408         | 2,000           | 161            | 9.74         | 18.06        | 5.33         | 103.3       | 913                        |
| R                 | 470         | 2,010           | 358            | 9.74         | 18.09        | 5.33         | 103.4       | 913                        |
| R                 | 502         | 2,000           | 724            | 9.72         | 18.08        | 5.34         | 103.2       | 914                        |
| R                 | 411         | 2,000           | 399            | 9.75         | 18.08        | 5.33         | 103.4       | 914                        |
| R                 | 418         | 1,000           | 338            | 9.74         | 18.09        | 5.33         | 103.4       | 914                        |
| R                 | 551         | 20,500          | 21             | 9.73         | 18.06        | 5.35         | 103.4       | 915                        |

TABLE 5. RESULTS OF INVESTIGATION OF THE COMPOSITION  $\text{Na}_2\text{O} \cdot (\text{Mg}_{2.25}\text{Fe}_{0.75})\text{O} \cdot (\text{Al}_{1.5}\text{Fe}_{0.5})\text{O}_3 \cdot 8\text{SiO}_2 + \text{H}_2\text{O}$  AND WITH OXYGEN FUGACITY DEFINED BY THE HEMATITE-MAGNETITE BUFFER

| Starting material                  | Temp (° C.) | Pressure (bars) | Duration (hrs) | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | $\beta$ (°) | Cell vol (Å <sup>3</sup> ) |
|------------------------------------|-------------|-----------------|----------------|--------------|--------------|--------------|-------------|----------------------------|
| Gl <sub>75</sub> R <sub>25</sub> I | 508         | 30,900          | 7              | 9.66         | 17.75        | 5.30         | 103.3       | 884                        |
| Mix                                | 504         | 3,000           | 806            | 9.70         | 17.93        | 5.29         | 103.6       | 895                        |
| Mix                                | 543         | 2,010           | 547            | 9.76         | 17.93        | 5.29         | 103.6       | 900                        |
| Gl <sub>75</sub> R <sub>25</sub> I | 604         | 990             | 399            | 9.72         | 17.99        | 5.32         | 103.6       | 905                        |

probable that, for the magnesioriebeckite bulk composition, the pure end member is stable at high oxidation states (Table 3), and at lower oxidation states, magnesioriebeckite-magnesiorarfvedsonite solid solutions were produced. Synthetic amphibole cell volumes at fixed oxidation state (Tables 2-4, 6) are plotted as a function of P and T in Figures 1-4 respectively. Variation of unit cell parameters is shown as a function of composition in Figure 5. Aluminum-bearing amphiboles exhibit a decrease in cell volume at constant composition with increased pressure. The magnitude of the transition volume change is proportional to the mole fraction  $\text{Al}/(\text{Fe}^{3+} + \text{Al})$ .

It was thought that intermediate cell dimensions (Tables 2, 5-7) might represent mixtures of the two distinct polymorphs. In this case, individual x-ray peaks measured would be the composite result of two separate reflections. In an effort to resolve possible doublets, 3 samples of glaucophane of intermediate cell volume were examined with both dif-

TABLE 6. RESULTS OF INVESTIGATION OF THE COMPOSITION  $\text{Na}_2\text{O} \cdot (\text{Mg}_{1.5}\text{Fe}_{1.5})\text{O} \cdot (\text{Al}_{1.0}\text{Fe}_{1.0})\text{O}_3 \cdot 8\text{SiO}_2 + \text{H}_2\text{O}$  AND WITH OXYGEN FUGACITY DEFINED BY THE HEMATITE-MAGNETITE BUFFER

| Starting material                   | Temp. (° C.) | Pressure (bars) | Duration (hrs) | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | $\beta$ (°) | Cell vol (Å <sup>3</sup> ) |
|-------------------------------------|--------------|-----------------|----------------|--------------|--------------|--------------|-------------|----------------------------|
| Gl <sub>50</sub> R <sub>50</sub> I  | 515          | 20,400          | 22             | 9.72         | 17.83        | 5.29         | 103.4       | 891                        |
| Gl <sub>50</sub> R <sub>50</sub> I  | 603          | 30,000          | 8              | 9.68         | 17.91        | 5.30         | 103.4       | 893                        |
| Gl <sub>50</sub> R <sub>50</sub> I  | 542          | 36,100          | 6              | 9.69         | 17.93        | 5.29         | 103.4       | 895                        |
| Gl <sub>50</sub> R <sub>50</sub> I  | 517          | 14,800          | 4              | 9.70         | 18.04        | 5.28         | 103.2       | 900                        |
| Mix                                 | 351          | 3,000           | 807            | 9.70         | 17.95        | 5.32         | 103.4       | 902                        |
| Gl <sub>50</sub> R <sub>50</sub> I  | 500          | 7,800           | 5              | 9.69         | 18.02        | 5.30         | 103.0       | 903                        |
| Mix                                 | 260          | 3,000           | 829            | 9.75         | 17.91        | 5.32         | 103.2       | 905                        |
| Mix                                 | 503          | 3,000           | 449            | 9.70         | 18.00        | 5.32         | 103.4       | 905                        |
| Mix                                 | 300          | 2,990           | 830            | 9.74         | 17.93        | 5.32         | 103.2       | 905                        |
| Gl <sub>50</sub> R <sub>50</sub> II | 509          | 1,000           | 477            | 9.72         | 17.99        | 5.32         | 103.3       | 906                        |
| Mix                                 | 385          | 3,005           | 766            | 9.74         | 17.97        | 5.32         | 103.3       | 907                        |

fractometer and powder camera employing copper and iron radiation under various exposure conditions. No doublets were detected. Efforts to grow crystals large enough for single-crystal x-ray work failed completely, even where fluxes were employed.

Evaluation of precision of unit cell parameter determination was necessary in order to specify limits of confidence in specific values. Replicate measurements of remounted fractions of the same sample always

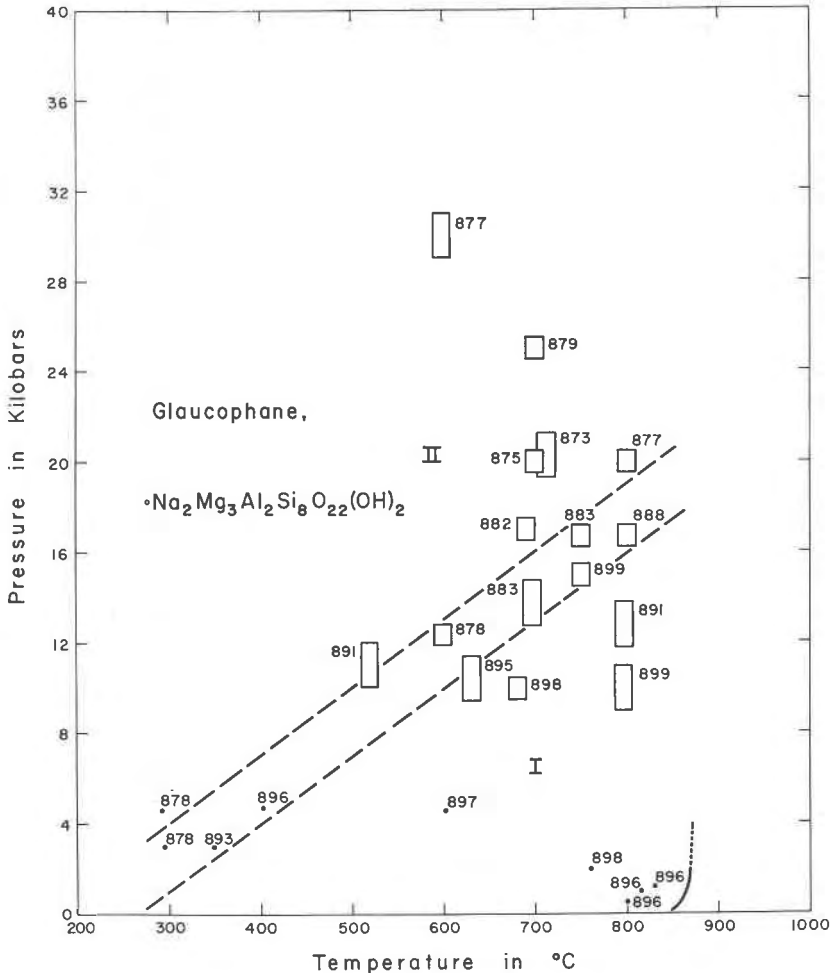


FIG. 1. Unit cell volumes of synthetic amphibole for the bulk composition  $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2 + \text{H}_2\text{O}$  as a function of P and T. Dashed curves define PT region of intermediate cell volumes. High-temperature stability limit of glaucoephane I shown at 800–870° C., 0–4 kb (Ernst, 1961, Fig. 3).



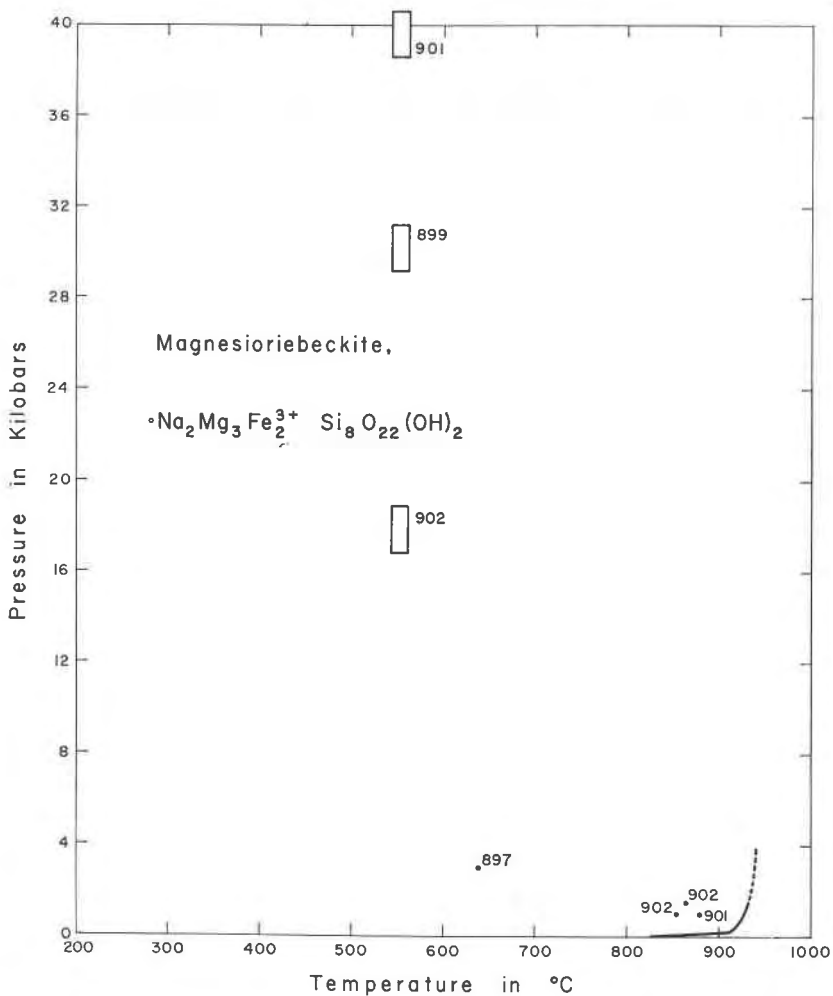


FIG. 2. Unit cell volumes of synthetic amphibole for the bulk composition  $\text{Na}_2\text{O} \cdot 3\text{MgO} \cdot \text{Fe}_2\text{O}_3 \cdot 8\text{SiO}_2 + \text{H}_2\text{O}$  as a function of P and T. Oxygen fugacity defined by the hematite-magnetite buffer. High-temperature stability limit of magnesioriebeckite shown at 800–950° C., 0–4 kb (Ernst, 1960, Fig. 3a).

yielded deviations of less than  $\pm 0.01 \text{ \AA}$  for axial lengths (variation in  $b$  closely approached  $\pm 0.01 \text{ \AA}$ , however),  $\Delta\beta$  of less than  $\pm 0.1^\circ$ . Replicate cell volumes were generally within  $\pm 2 \text{ \AA}^3$ . The products of different experiments under closely similar physical conditions vary more widely: cell volumes differ by as much as  $\pm 4 \text{ \AA}^3$ . Such deviations in all parameters may represent real differences, but might also be explained as re-

sulting from vagaries of mounting the sample for  $x$ -ray investigation, or due to interference from adjacent peaks of other phases. Accordingly, a sample of low-pressure glaucophane I and a sample of high-pressure glaucophane II were mixed in approximately equal proportions by grinding the synthetic amphiboles together in an agate mortar under acetone for five minutes.  $2\theta$  values, standard (chart) errors of the mean and cell dimensions for the pure and mixed amphiboles are compared in Table 8.

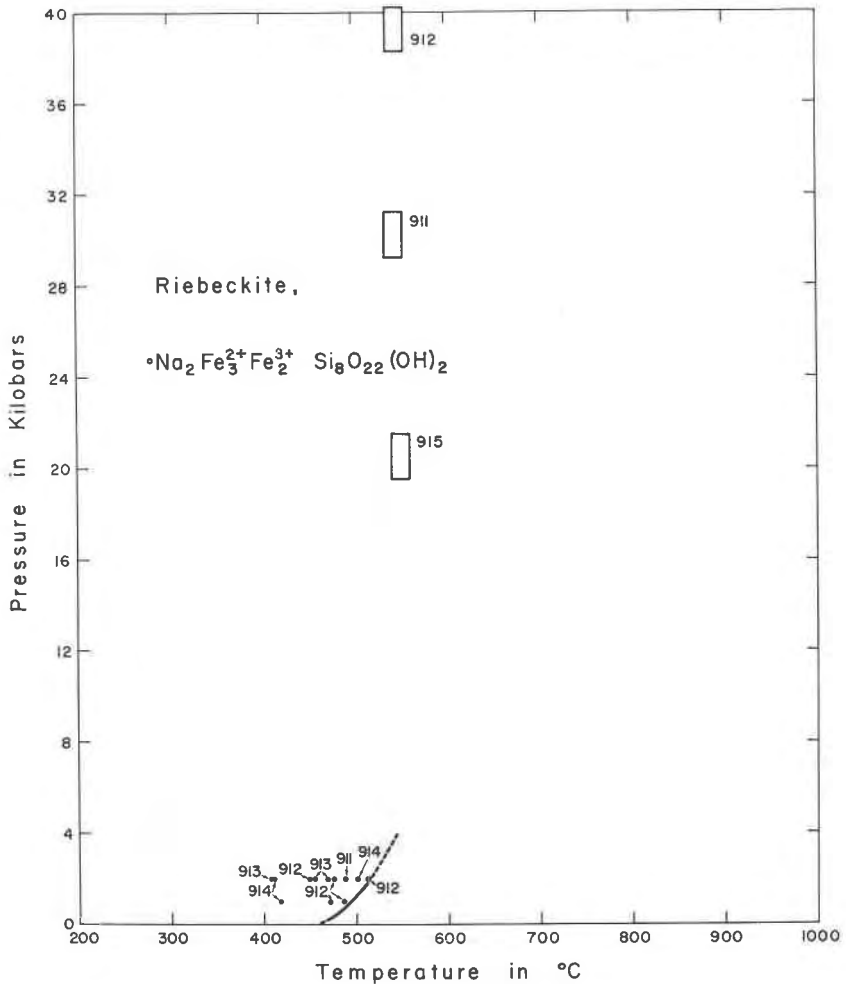


FIG. 3. Unit cell volumes of synthetic amphibole for the bulk composition  $\text{Na}_2\text{O} \cdot 3\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 8\text{SiO}_2 + \text{H}_2\text{O}$  as a function of P and T. Oxygen fugacity defined by the hematite-magnetite buffer. High-temperature stability limit of riebeckite shown at 450–540° C., 0–4 kb (Ernst, 1962, Fig. 6).

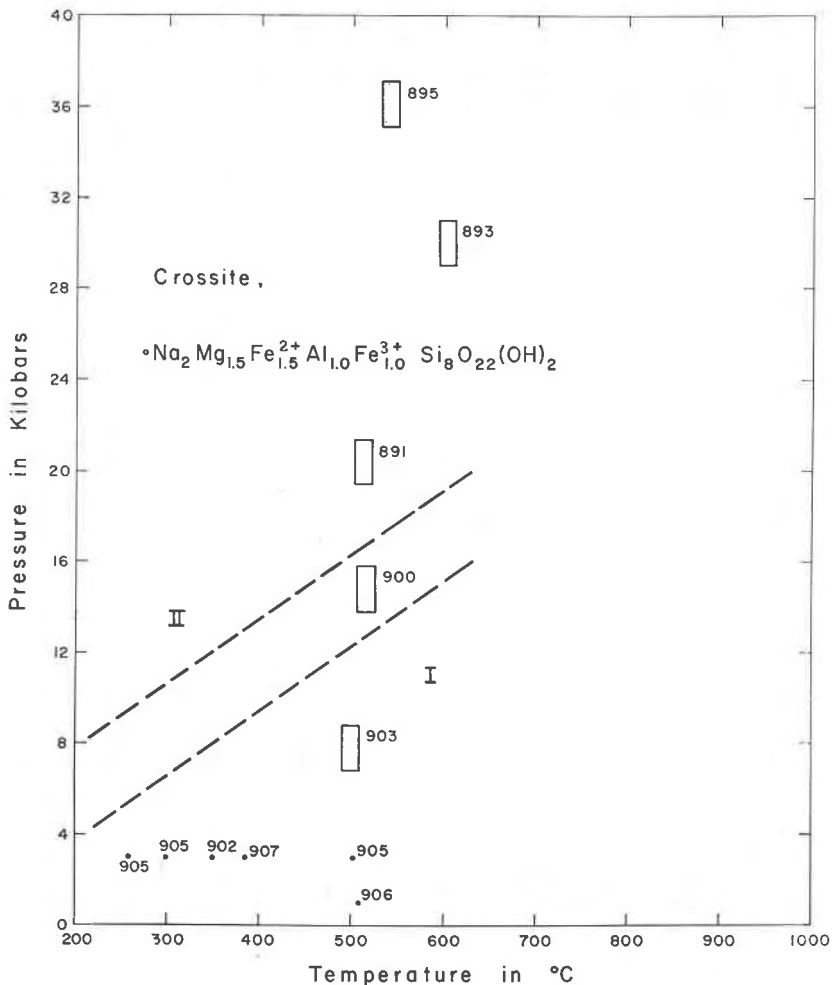


FIG. 4. Unit cell volumes of synthetic amphibole for the bulk composition  $\text{Na}_2\text{O} \cdot (\text{Mg}_{1.5}\text{Fe}_{1.5})\text{O} \cdot (\text{Al Fe}) \text{O}_3 \cdot 8\text{SiO}_2 + \text{H}_2\text{O}$  as a function of P and T. Oxygen fugacity defined by the hematite-magnetite buffer. Dashed curves define PT region of intermediate cell volumes.

X-ray peaks of both amphiboles remain sharp and are displaced slightly by mutual reinforcement in the mixed sample. Cell parameter deviations of amphiboles in the mixed sample compared to corresponding pure single polymorph fractions are somewhat greater than replicate measurements on the same sample. Peak measurement in the mixed sample is less accurate because of (1) mutual reinforcement and apparent offset of x-ray reflections and (2) diminished amplitude resulting from dilution. Nevertheless, Table 8 shows that cell volume variations are on the order of

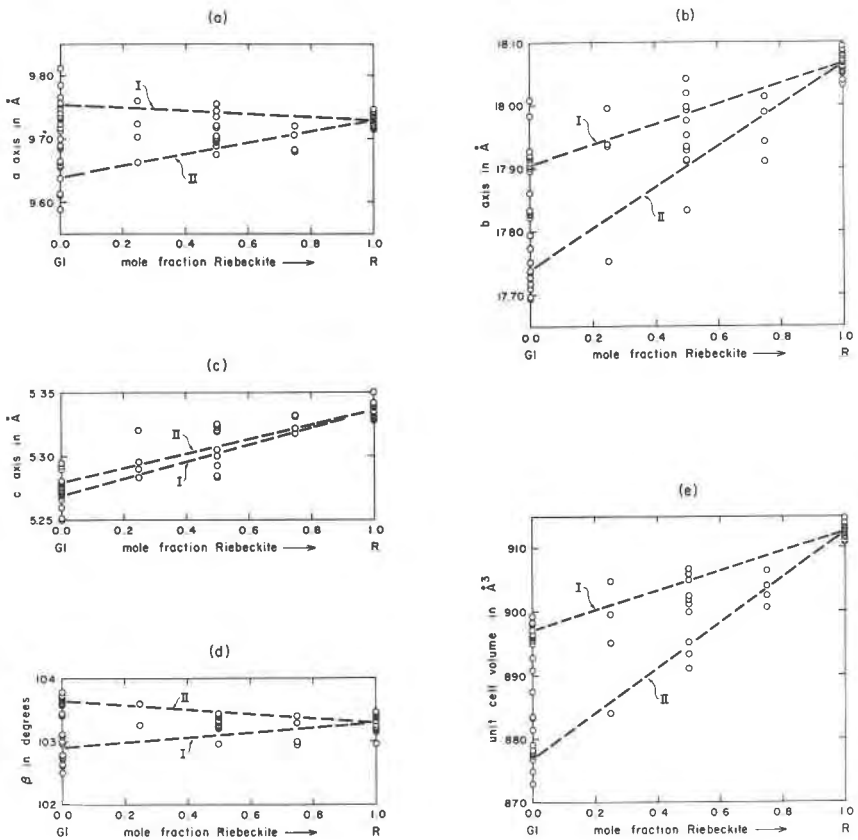


FIG. 5. Variation in unit cell parameters of synthetic members of the glaucophane-riebeckite series as a function of composition and structural state.

TABLE 7. RESULTS OF INVESTIGATION OF THE COMPOSITION  
 $\text{Na}_2\text{O} \cdot (\text{Mg}_{0.75}\text{Fe}_{2.25})\text{O} \cdot (\text{Al}_{0.5}\text{Fe}_{1.5})\text{O}_3 \cdot 8\text{SiO}_2 + \text{H}_2\text{O}$  AND  
 WITH OXYGEN FUGACITY DEFINED BY THE  
 HEMATITE-MAGNETITE BUFFER

| Starting material                  | Temp. (° C.) | Pressure (bars) | Duration (bars) | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | $\beta$ (°) | Cell vol (Å <sup>3</sup> ) |
|------------------------------------|--------------|-----------------|-----------------|--------------|--------------|--------------|-------------|----------------------------|
| Gl <sub>25</sub> R <sub>75</sub> I | 558          | 17,800          | 16              | 9.68         | 17.91        | 5.33         | 102.9       | 901                        |
| Gl <sub>25</sub> R <sub>75</sub> I | 521          | 30,900          | 7               | 9.68         | 17.94        | 5.33         | 103.0       | 902                        |
| Mix                                | 500          | 3,000           | 806             | 9.70         | 17.99        | 5.32         | 103.3       | 904                        |
| Mix                                | 540          | 2,010           | 547             | 9.71         | 18.01        | 5.32         | 103.4       | 906                        |

TABLE 8.  $2\theta$  VALUES FOR COPPER RADIATION AND DERIVED UNIT CELL DIMENSIONS FOR SYNTHETIC SAMPLES OF GLAUCOPHANE I AND GLAUCOPHANE II MEASURED IN SINGLE-AMPHIBOLE FRACTIONS AND IN A MECHANICALLY MIXED TWO-AMPHIBOLE FRACTION

| <i>(hkl)</i>                | Glaucophane I  |                            |                |                            | Glaucophane II |                            |                |                            |
|-----------------------------|----------------|----------------------------|----------------|----------------------------|----------------|----------------------------|----------------|----------------------------|
|                             | Pure           |                            | Mixed          |                            | Pure           |                            | Mixed          |                            |
|                             | $2\theta$ ave. | Standard error of the mean | $2\theta$ ave. | Standard error of the mean | $2\theta$ ave. | Standard error of the mean | $2\theta$ ave. | Standard error of the mean |
| 040                         | 19.814         | $\pm .010$                 | 19.796         | $\pm .008$                 | 20.059         | $\pm .006$                 | 20.035         | $\pm .007$                 |
| 131                         | 26.125         | $\pm .005$                 | 26.126         | $\pm .011$                 | 26.422         | $\pm .005$                 | 26.419         | $\pm .007$                 |
| 240                         | —              | —                          | —              | —                          | 27.709         | $\pm .008$                 | 27.776         | $\pm .006$                 |
| 310                         | 28.597         | $\pm .011$                 | 28.608         | $\pm .006$                 | 28.977         | $\pm .007$                 | 28.949         | $\pm .007$                 |
| 221                         | 29.989         | $\pm .008$                 | 29.969         | $\pm .015$                 | 30.418         | $\pm .005$                 | 30.379         | $\pm .009$                 |
| 330                         | 31.979         | $\pm .008$                 | 31.970         | $\pm .016$                 | —              | —                          | —              | —                          |
| 151                         | 33.014         | $\pm .009$                 | 32.997         | $\pm .006$                 | 33.414         | $\pm .008$                 | 33.359         | $\pm .005$                 |
| Cell dimensions             |                |                            |                |                            |                |                            |                |                            |
| <i>a</i> (Å)                | 9.748          |                            | 9.734          |                            | 9.663          |                            | 9.662          |                            |
| <i>b</i> (Å)                | 17.915         |                            | 17.936         |                            | 17.696         |                            | 17.689         |                            |
| <i>c</i> (Å)                | 5.273          |                            | 5.250          |                            | 5.277          |                            | 5.294          |                            |
| $\beta$ (°)                 | 102.78         |                            | 102.46         |                            | 103.67         |                            | 103.67         |                            |
| cell vol. (Å <sup>3</sup> ) | 898.1          |                            | 894.9          |                            | 876.8          |                            | 879.2          |                            |

about  $\pm 3 \text{ \AA}^3$ . Estimating *maximum* probable errors in crystallographic axial lengths, *a*, *b* and *c* of  $\pm 0.01 \text{ \AA}$  and  $\beta$  of  $\pm 0.1^\circ$ , the probable error in cell volumes of synthetic amphiboles measured in this study is about  $\pm 3.6 \text{ \AA}^3$  (for evaluation of probable error of a function of measured quantities given their probable errors, see Bomford, 1952). It may be concluded therefore that intermediate cell parameters calculated for Al-rich alkali amphiboles represent real variation.

Optical properties of synthetic glaucophane polymorphs are indistinguishable: glaucophane I has  $\alpha = 1.595$ ,  $\beta = 1.620$ ,  $\gamma \wedge c = 10^\circ$  (average of 20 different runs, Ernst, 1961, Table 3); glaucophane II has  $\alpha = 1.596$ ,  $\beta = 1.620$ ,  $\gamma \wedge c = 10^\circ$  (average of 7 different runs, this study). All values fall within the estimated errors of measurement,  $\pm 0.003$  for  $\alpha$  and  $\gamma$ ,  $\pm 4^\circ$  for extinction angle. The denser polymorph should have a mean index of refraction approximately 0.013 greater than glaucophane I, according to the rule of Gladstone and Dale (Larsen and Berman, 1934, p. 30–31). The lack of variation of optical properties of synthetic glaucophane with unit cell parameters is surprising and puzzling. Determination of optical constants for intermediate members of the glaucophane-riebeckite series proved to be imprecise because of fineness of grain and strong absorption among the synthetic amphiboles.

## DISCUSSION

Polymorphism among alkali amphiboles produced in this study apparently involves a second order transition as indicated by the lack of discontinuity in cell volumes. The phenomenon is most readily explained on the basis of increased ordering among cations in the high-pressure, low-temperature phase compared to the low-pressure, high-temperature polymorph. An order-disorder relationship is also suggested by the apparent identity of space group,  $C2/m$ , for both polymorphs. It should be mentioned, however, that extinction criteria do not allow distinction among the space groups  $C2/m$ ,  $C2$  and  $Cm$  (Donnay and Harker, 1940, Table 2). The exact nature of the substitution relations among the cations is not known. Reversibility of the transition has been demonstrated for glaucophane and crossite bulk compositions (Tables 2 and 6 respectively).

In a structural investigation of magnesioriebeckite Whittaker (1949) determined that, among the metal positions,  $M_4$  (the calcium site in tremolite) was occupied by alkalis,  $M_2$  preferentially by ferric iron and minor aluminum over magnesium, and the  $M_1$  and  $M_3$  sites contained a greater proportion of magnesium (Fig. 6). No variations in synthetic magnesioriebeckite and riebeckite unit cell parameters are observable (Tables 3 and 4) even if, as is probable, disorder occurs between ferric iron and magnesium at low pressures and relatively high temperatures. In contrast, aluminum-bearing amphiboles do exhibit polymorphism, the

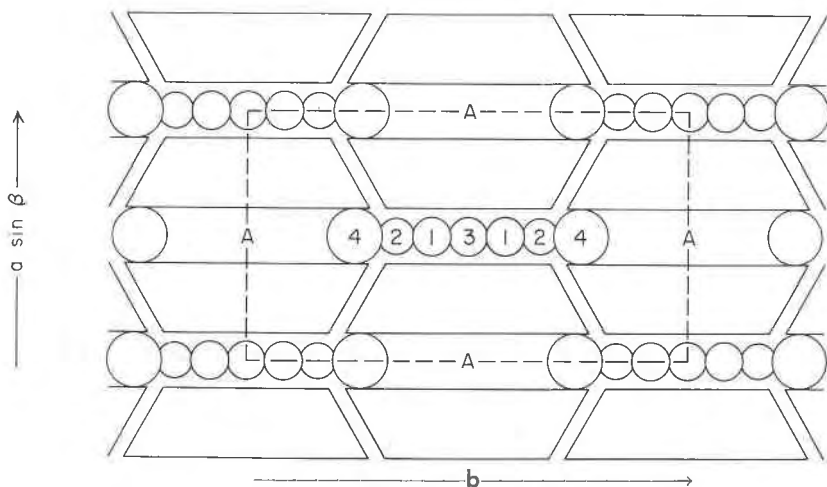


FIG. 6. Schematic projection of amphibole structure onto plane  $a \sin \beta - b$  ( $c$  axis normal to plane of projection). Coordination of cation sites are:  $M_1$ ,  $M_2$ ,  $M_3$ =6-fold;  $M_4$ =8-fold. A=10-12 fold. Double chains represented by trapezohedra.

$\Delta V$  of the transition being a direct function of the mole fraction  $\text{Al}/(\text{Fe}^{3+} + \text{Al})$  (Tables 2, 5-7, fig. 5). It therefore seems probable that aluminum is concentrated in the  $M_2$  position in polymorph II, but is more randomly distributed among all octahedral sites in form I.

The transition I $\rightarrow$ II involves decreases in lengths of  $a$  and  $b$  crystallographic axes and a negligible increase in  $c$ ; concomitantly the  $\beta$  angle becomes more obtuse. The distance between the  $\text{Si}_4\text{O}_{11}$  double chains ( $a \sin \beta$ ) thus decreases. Whittaker (1960) has called attention to the fact that  $M_4$ , the alkali position, is located at interchain contacts, and suggests that a close relationship exists between  $\beta$  and the mean Goldschmidt radius for ions occupying this site. The neighboring cation site,  $M_2$  is similarly situated: bonds from  $M_2$  link 4 adjacent Si-O double chains, and cation-oxygen bond distances are shorter than for  $M_4$ . Therefore, concentration of Al (smallest of the cations under consideration, with ionic radius of 0.51 Å) at  $M_2$  allows the silica chains to more closely approach one another normal to 100 (increasing obliquity of  $\beta$ , decreasing length of the  $a$  axis); in like fashion, adjacent chains more closely approach each other parallel to  $b$ , reducing the chain repeat in this direction (Fig. 6). No such readjustment is possible along the  $c$  crystallographic direction because the Si-O double chains are of fixed dimensions, and if anything, the transition I $\rightarrow$ II apparently involves a very slight increment in chain length. Absence of observable polymorphism in magnesioriebeckite and riebeckite apparently results from the fact that ionic radii of  $\text{Fe}^{3+}$  and Mg are nearly equal (0.64 Å and 0.66 Å respectively); hence order-disorder reactions would not significantly influence their unit cell dimensions. Perhaps other  $\text{Al}^{\text{VI}}$ -bearing amphiboles may show a second order transition such as that described in this paper for glaucophane and intermediate solid solutions.

Minor substitution of Al for Si in tetrahedral coordination would also favor volume increase in the low-pressure, high-temperature polymorph; however, an equivalent replacement of Al by Si in octahedral coordination would be necessitated for the amphibole to remain on composition. In many natural glaucophanes, minor amounts of alkali are accommodated in the A structural position; this substitution allows the minor replacement of tetrahedral silicon by aluminum. Cell volume variation due to this replacement,  $\text{Na} + \text{Al}^{\text{IV}}$  for  $\text{Si}^{\text{IV}}$ , is negligible as indicated by determinations of unit cell dimensions of natural glaucophanes (see section on geologic application). This behavior is similar to that observed for layer-lattice silicates by Radoslovich and Norrish (1962, p. 603-604) and Radoslovich (1962). These authors note that limited substitution of aluminum for silicon causes no significant change in  $b$  axis length; interlayer cations and the octahedral layer are thought to control the  $b$  crystal-

lographic dimension. Although similar replacement of  $\text{Si}^{\text{IV}}$  by  $\text{Al}^{\text{IV}}$  in alkali amphiboles may take place at constant cell volume, such behavior does not apply for the substitution of silicon by ferric iron, as in riebeckite-arfvedsonite solid solutions (Ernst, 1962). This latter variation in cell volume is not dependent on P and T, but rather reflects change in bulk composition of the amphibole (a function of oxidation state); hence it is not a polymorphic transition. In contrast, the transition observed among Al-bearing alkali amphiboles is a function of temperature and pressure, the magnitude of  $\Delta V$  depending on  $\text{Al}^{\text{VI}}$  content.

Ghose (1961, p. 624–625) has explained non-random distribution of Mg and  $\text{Fe}^{2+}$  in cummingtonite as a function of cation electronegativity; statistically  $M_2$  is occupied preferentially by a less electronegative ion, Mg, and  $M_1$  and  $M_3$  sites are occupied by the more electronegative  $\text{Fe}^{2+}$ ;

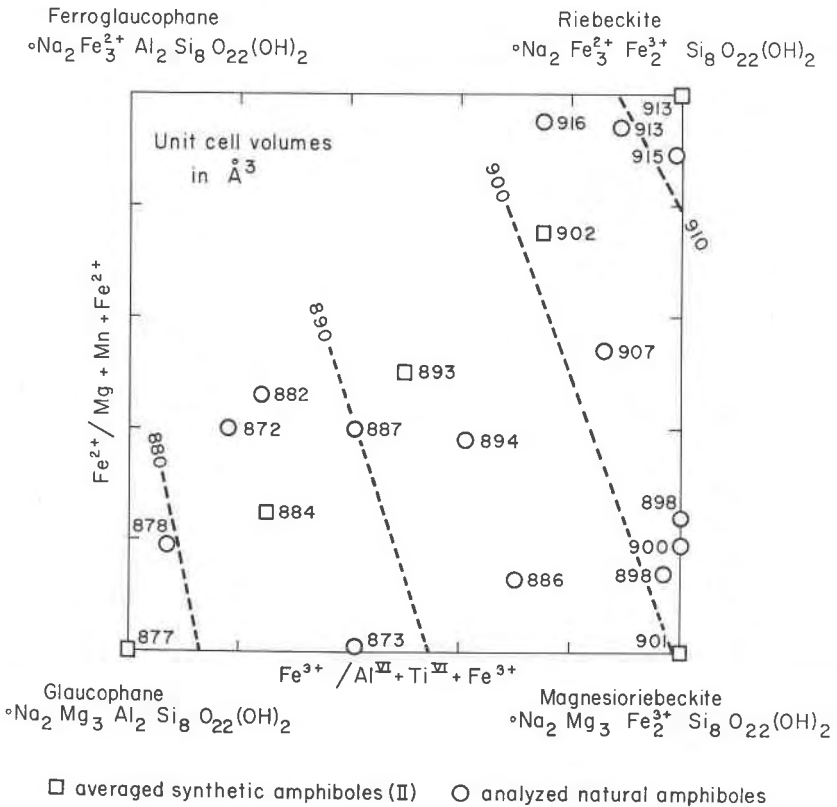


FIG. 7. Variation in unit cell volume of natural alkali amphiboles as a function of composition. Contours represent analogous variation of unit cell volume for synthetic high-pressure alkali amphiboles.



TABLE 9. NEW ANALYSIS OF MAGNESIORIEBECKITE FROM SHEEP CREEK, MONTANA  
(FOR PETROGRAPHY, SEE HEINRICH AND LEVINSON, 1961, P. 1437-1438)

| Oxide                          | Weight % | Atomic Proportions <sup>1</sup> |        |
|--------------------------------|----------|---------------------------------|--------|
| SiO <sub>2</sub>               | 53.5     | Si                              | 7.71   |
| TiO <sub>2</sub>               | 0.25     | Ti                              | 0.03   |
| Al <sub>2</sub> O <sub>3</sub> | 1.3      | Al                              | 0.22   |
| Fe <sub>2</sub> O <sub>3</sub> | 14.5     | Fe <sup>3+IV</sup>              | 0.04   |
| FeO                            | 6.99     | Fe <sup>3+VI</sup>              | 1.53   |
| MnO                            | 0.13     | Fe <sup>2+</sup>                | 0.84   |
| MgO                            | 12.5     | Mn                              | 0.02   |
| CaO                            | 2.25     | Mg                              | 2.68   |
| Na <sub>2</sub> O              | 6.42     | Ca                              | 0.35   |
| K <sub>2</sub> O               | 0.08     | Na                              | 1.79   |
| H <sub>2</sub> O+              | 2.57     | K                               | 0.02   |
| Total                          | 100.49   | OH                              | (2.47) |

Chemical analysis by E. Szentvari, Department of Geology, University of California, Los Angeles.

<sup>1</sup> Atomic proportions calculated on the anhydrous basis of 23 oxygens, assuming OH=2.00 per formula unit (Miyashiro, 1957, p. 59).

M<sub>4</sub> appears to control this distribution as it contains a large proportion of ferrous iron. In contrast, in the present study of synthetic alkali amphiboles, the observed ordering of cations appears to be a function of ionic radius as discussed above. Electronegativity of aluminum is greater than that of magnesium and ferrous iron (Green, 1959, Table 2), yet this relationship does not appear to prohibit occupancy of M<sub>2</sub> by Al. However, for the alkali amphiboles, M<sub>4</sub> contains principally sodium, a weakly electronegative cation; this phenomenon should favor preferential occupancy of the adjacent M<sub>2</sub> site by the highly electronegative cations of iron and aluminum. Thus if the electronegativity of ions occupying M<sub>4</sub> controls distribution in M<sub>2</sub>, the proposed cation distribution appears to be explicable on the basis of electronegativity as well as on the basis of ionic size.

GEOLOGIC APPLICATION

Chemically analyzed natural members of the glaucophane-magnesioriebeckite-riebeckite series have been obtained from a number of sources and studied. A new chemical analysis of magnesioriebeckite is presented in Table 9. The maximum amount of tetrahedral aluminum computed for any of the samples is 0.45 ion per 8.00 four-fold structural sites; the investigated glaucophanes average about 0.20 Al<sup>IV</sup>. Unit cell parameters were determined and results are presented in Table 10 and in Fig. 7. All

TABLE 10. CELL DIMENSIONS OF NATURAL MEMBERS OF THE GLAUCOPHANE-MAGNESIORIEBECKITE-RIEBECKITE SERIES (SPACE GROUP  $C2/m$ )

| No. | Fe <sup>2+</sup>       | Fe <sup>3+</sup>                                     | <i>a</i><br>(Å) | <i>b</i><br>(Å) | <i>c</i><br>(Å) | $\beta$<br>(°) | Cell<br>vol<br>(Å <sup>3</sup> ) |
|-----|------------------------|--|-----------------|-----------------|-----------------|----------------|----------------------------------|
|     | Mg+Mn+Fe <sup>2+</sup> | Al <sup>VI</sup> +Ti <sup>VI</sup> +Fe <sup>3+</sup> |                 |                 |                 |                |                                  |
| 1   | 0.40                   | 0.18   | 9.55            | 17.81           | 5.27            | 103.0          | 872                              |
| 2   | 0.01                   | 0.41   | 9.59            | 17.74           | 5.28            | 103.9          | 873                              |
| 3   | 0.19                   | 0.07   | 9.58            | 17.80           | 5.30            | 103.8          | 878                              |
| 4   | 0.46                   | 0.24   | 9.59            | 17.83           | 5.31            | 103.7          | 882                              |
| 5   | 0.13                   | 0.70   | 9.65            | 17.81           | 5.30            | 103.3          | 886                              |
| 6   | 0.40                   | 0.41   | 9.62            | 17.86           | 5.31            | 103.7          | 887                              |
| 7   | 0.38                   | 0.61   | 9.67            | 17.92           | 5.31            | 103.7          | 894                              |
| 8   | 0.14                   | 0.97   | 9.74            | 17.95           | 5.30            | 103.9          | 898                              |
| 9   | 0.24                   | 1.00   | 9.74            | 17.96           | 5.29            | 104.0          | 898                              |
| 10  | 0.19                   | 1.00   | 9.73            | 17.95           | 5.31            | 103.7          | 900                              |
| 11  | 0.54                   | 0.86   | 9.72            | 18.02           | 5.33            | 103.6          | 907                              |
| 12  | 0.94                   | 0.89   | 9.75            | 18.06           | 5.34            | 103.6          | 913                              |
| 13  | 0.89                   | 0.99   | 9.76            | 18.07           | 5.34            | 103.7          | 915                              |
| 14  | 0.95                   | 0.75   | 9.80            | 18.00           | 5.34            | 103.4          | 916                              |

1. Glaucophane, California (Coleman and Lee, unpublished).
2. Glaucophane, Japan (Iwasaki, 1960, Table 1).
3. Glaucophane, Switzerland (Kunitz, 1930, p. 244).
4. Glaucophane, Japan (Banno, 1959, p. 659).
5. Magnesioriebeckite, Japan (Miyashiro and Iwasaki, 1957, Table 3).
6. Glaucophane, Japan (Banno, 1959, p. 659).
7. Crossite, California (Switzer, 1951, Table 3).
8. Magnesioriebeckite, Bolivia (Whittaker, 1949, p. 313).
9. Magnesioriebeckite, Montana (Table 9, this report).
10. Magnesioriebeckite, Bolivia (Ernst, 1960, Table 12).
11. Riebeckite, California (Switzer, 1951, Table 3).
12. Riebeckite, Massachusetts (Palache and Warren, 1911, p. 549).
13. Riebeckite, South Africa (Peacock, 1928, p. 256).
14. Riebeckite, Shetland (Phemister, *et al.*, 1950, Table 2).

specimens studied belong to the high-pressure, low-temperature series. In addition, 9 samples of glaucophane and crossite from various localities (California, Greece, Italy, Japan and Switzerland) have been examined with x-ray diffraction; the approximate compositions of these amphiboles were determined using refractive index liquids and the refringence diagram published by Miyashiro (1957). These samples also appear to be polymorph II.

Turner and Verhoogen (1960, p. 544) suggest that physical conditions of the glaucophane schist facies include very high lithostatic and fluid pressures, and temperatures of the order 300–400° C. Pressures must have reached a minimum of 3–6 kb by analogy with the experimentally

determined transition alkali amphibole I→alkali amphibole II. Such pressure corresponds to a depth of burial of roughly 10–20 kilometers, assuming hydrostatic stress. Other dense metamorphic phases, in particular, jadeitic pyroxene, lawsonite and aragonite occur in glaucophane schists and associated rocks. Experimental investigations (Birch and LeComte, 1960; Pistorius *et al.* 1961; Clark, 1957) indicate these minerals all require pressures in excess of the alkali amphibole I–II transition for their stable formation. It is therefore not surprising that the large-volume alkali amphibole polymorph is not encountered in rocks of the glaucophane or blueschist facies.

Polymorph I should be stable at high temperatures and low pressures under appropriate chemical conditions, but thus far no natural occurrence has been found.

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