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Abstract. A complete set of new optical and x-ray data is given for eleven analyzed alkali amphiboles $[Na_2(Mg, Fe'')_3(Al, Fe'')_2Si_8O_{22}(OH)_2]$. Nine new wet chemical analyses are reported. Using additional selected data from the literature, variation in refractive indices, extinction angles $(\gamma - \alpha)$, optic angles, density, lattice constants and cell volume are expressed graphically as a function of composition in the glaucophane-riebeckite and magnesioriebeckite-ferroglaucophane series. Four orientations (G, C, O, and R) of the optical indicatrix within the structure are described and shown to be characteristic of the chemical species glaucophane (G), crossite (C), magnesioriebeckite (O), riebeckite (O), and riebeckite-arfvedsonite (R and O).

Optical properties of the pure end members by extrapolation are:

	α	β	γ	(γ—α)		$c \wedge n$	ę
Glaucophane Riebeckite Magnesioriebeckite	$1.594 \\ 1.702 \\ 1.65_5$	$1.612 \\ 1.712 \\ 1.67_1$	$1.618 \\ 1.719 \\ 1.67_2$	$\begin{array}{c} 0.025 \\ 0.015 \\ 0.02 \end{array}$	$b = \beta$ $b = \gamma$ $b = \gamma$	$egin{array}{lll} c \wedge \gamma &=& 6^\circ \ c \wedge lpha &=& 6^\circ \ c \wedge lpha &=& 32^\circ \end{array}$	$3.03 \\ 3.40 \\ 3.15$

	$a_0(\text{\AA})$	$b_0(\text{\AA})$	$c_0({\rm \AA})$	β(°)	$V({ m \AA}^3)$
Glaucophane	9.50	17.67	5.29	103.7	864
Riebeckite	9.78	18.08	5.34	103.5	918
Magnesioriebeckite	9.76	17.97	5.31	103.9	904

X-ray parameters of the end members referred to the C 2/m space group are:

These show very good agreement with comparable measurements on synthetic counterparts. There is some indication that the two proposed synthetic polymorphs of glaucophane (EENST, 1963) are both more disordered than the natural end member.

Introduction

The chemical and physical properties of the glaucophane-riebeckite-magnesioriebeckite group of alkali amphiboles are imperfectly known, despite a large pertinent literature and numerous surveys beginning with MURGOCI (1906). RECENTLY, MIYASHIRO (1957) and DEER *et al.* (1963) have written excellent summaries of the properties of the group from data in the literature. The reason for the imperfect knowledge lies in the incompleteness of most amphibole descriptions. Good chemical analyses, e.g., KUNITZ' (1930) are available over most of the composition span, but optical data are sparse and in some instances unreliable. Contributing factors to the paucity of optical data are the difficulties

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in making measurements on highly opaque iron-rich minerals which characteristically show extreme dispersion of optic directions as well as optic axes. Fibrosity of some members (Mg-crocidolites and crocidolites proper) has also hindered investigation. There are, for example, forty or more chemical analyses of fibrous types in the literature, but fewer than six are accompanied by even a partial description of their optical properties. The large number of analyses of fibrous varieties is doubtless related to the relatively pure state in which they occur naturally, as well as to their commercial importance as asbestiform minerals.

The present study was undertaken to establish the elusive relations between optical, chemical, and x-ray parameters. To this end the author has selected eleven representative samples, which were chosen so as to span the composition range of the glaucophane-riebeckite series, and she has supplied a complete set of data for each. Included in the group are the type *crossite*, first described by PALACHE (1894) from Berkeley, California; the type *osannite* from pegmatites from Alter Pedroso, Portugal, named by HLAWATSCH (1906) for its distinctive optic orientation; and the *riebeckite* from St. Peters Dome, Colorado, early descriptions of which [optic plane parallel to (010), LACROIX, 1889; MURGOCI, 1906; JOHNSEN, 1910], strongly influenced optical criteria for recognition of the species. By current chemical and structural criteria, the latter two amphiboles are riebeckite-arfvedsonites. True riebeckites, meaning amphiboles near to the composition of the end member $Na_2Fe''_{3'}Fe''_{2''}Si_8O_{22}(OH)_2$ are rare; however, one was located and included in the study.

Finally, the new data have been combined with *selected values* chosen from previous investigations to provide graphical descriptions of minerals representing solid solutions between either glaucophane and riebeckite or magnesioriebeckite and ferroglaucophane.

The optical indicatrix can have one of four orientations with respect to the crystallography of these alkali amphiboles. Very small variations in refractive indices within grains of a single thin section can produce a dramatic variation in optical properties (orientation). Since the different orientations have been a source of confusion, an indication of which compositions they are associated with is given, as well as an explanation of how they come about.

Although some new optical data are presented here for the fibrous varieties, they have not been the subject of systematic study. No attempt has been made to explain their fibrous habit except to note that both Mg-crocidolites and crocidolites proper are included within very limited ranges of composition. The clearly merit more study, as do the members of the magnesioriebeckite-crossite-ferroglaucophane series, whose properties are only generally outlined here.

Nomenclature

Substitutions into the general amphibole formula $AX_2Y_5Z_8O_{22}(OH)_2$ are the basis of the nomenclature proposed by MIYASHIRO (1957) and adopted here with minor modifications. The formula units (X, Y and Z) for one-half the unit cell content and corresponding cation sites (A, M₁, M₂, M₃, M₄ and Si) (WARREN, 1930; PHILLIPS, 1963; GHOSE, 1965):

X = Na and Ca in M_4 cation site (6-8 fold coordination) with K and excess Na when (Na+Ca) > 2.00 accommodated at A (10 fold coordination).

Y = R''' + R'' where $R''' = Al^{VI}$, Fe''', Ti in the M_2 site and R'' = Mg, Fe'', Li, Zn and Cu in the M_1 and M_3 sites (all six-fold coordination). Z = Si and tetrahedrally coordinated Al^{IV} . (OH)=OH+F+Cl.



Fig. 1. Chemical variation in the glaucophane-riebeckite-magnesioriebeckite-ferroglaucophane group. Formulas of 109 amphiboles are calculated and plotted from chemical analyses on the basis of 24 (O, OH, F, Cl) per half-unit cell. Open circles numbered 1—11 are amphiboles for which new chemical, optical and/or x-ray data are presented; filled circles lettered a - o are from the literature and are identified in the captions to Figs. 3, 4, 5 and 6. Crosses indicate fibrous varieties

The end members in the series (Fig. 1) are represented by the following formulae:

Glaucophane	$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$
Riebeckite	$Na_{2}Fe_{3}''Fe_{2}''Si_{8}O_{22}(OH)_{2}$
Magnesioriebeckite	$Na_2Mg_3Fe_2^{\prime\prime\prime}Si_8O_{22}(OH)_2$
Ferroglaucophane	Na ₂ Fe''Al ₂ Si ₂ O ₂ (OH)

The formula for the related arfvedsonite end member is $(Na_{2.5}Ca_{0.5})_{3.0}(Fe'', Mg, Fe''', Al)_5(Si, Al)_8O_{22}(OH, F)_2$ after DEER *et al.* (1963), where $R'' \simeq 3.5$ and $R''' \simeq 1.5$. Riebeckite-arfvedsonites, $(Na, Ca)_{2.0-3.0}Fe''_{3.5-3.0}Fe''_{1.5-2.0}Si_8O_{22}(OH, F)_2$, are far more common among natural amphiboles than either pure end member. Riebeckite-arfvedsonite typically contains appreciable amounts of F and unusual elements such as Zn, Cu and Pb, which suggests that they behave as "scavengers" during crystallization [see analyses No. 9, riebeckite and No. 10, No. 11, riebeckite-arfvedsonite, Table 1 this work; BORLEY (1963)].

Table 1. Chem	vical analyses of glaucor	oahne-riebeckites				
	1	2	eo	4	5	6
SiO_2 TiO_2	57.73 n.d.	57.48 0.15	57.93 0.26	56.72 0.08	56.38 0.11	50.41 1.66
Al_2O_3 Fe.O.	12.04 1.16	12.39 2.25	11.92 1.31	9.52 4.17	8.45 4.98	7.82 8.73
FeO	5.41	4.91	10.78	8.61	9.40	10.81
MnO MeO	n.d. 12.09	0.02	0.11 8 05	0.19	0.19 0.80	0.14 7 30
Li,0	n.d.	n.d.	trace	n.d.	trace	n.d.
CaO	1.04	0.43	0.29	1.16	1.29	3.99
	6.98 0.68	0.00	0.11	0.06	0.08	0.57
H.0+	2.27	2.17	2.24	2.19	1.86	1.17
H_2^{-0} -		0.00	0.00	0.03	0.04	0.10
H D	n.d. n.d.	$0.02 \\ 0.04$	0.05 n.d.	0.03	0.010.0	n.d. n.d.
Less	100.33	99.52	99.75	99.89	99.46	99.83
0 = F and CI		0.02	0.02	0.02	0.01	
		99.50	99.73	99.87	99.45	
Analyst	W. KUNITZ	D. THAEMLITZ	C. O. INGAMELLS	C. O. INGAMELLS	C. O. INGAMELLS	N. HOLGATE
Si Aliv Aliv Fe Ci F G H O H Ci S Si Si Si Si Si Si Si Si Si Si Si Si	$\left.\begin{array}{c} 7.789\\ 0.211\\ 1.705\\ \hline 1.705\\ \hline 0.2118\\ 0.118\\ \hline 0.118\\ 2.617\\ \hline 2.617\\ \hline 2.617\\ \hline 2.617\\ \hline 3.227\\ \hline 0.1160\\ \hline 1.825\\ 0.117\\ \hline 2.042\\ 2.042\\ 2.042\\ \hline 2.042\\ \hline 2.042\\ \hline 2.042\\ \hline \end{array}\right\} 5.050$	$\left.\begin{array}{c} 7.780\\ 0.220\\ 1.757\\ 0.229\\ 0.015\\ 0.015\\ 0.0229\\ 0.022\\$	$\left.\begin{array}{c} 7.975\\ 0.025\\ 1.909\\ 1.909\\ 0.027\\ 0.136\\ 0.136\\ 0.136\\ 1.241\\ 0.013\\ 1.622\\ 0.013\\ 1.652\\ 1.851\\ 0.043\\ 1.851\\ 0.043\\ 1.851\\ 0.020\\ 0.020\\ 0.022\\ 2.078\end{array}\right\}$	$\left.\begin{array}{c} 7.861\\ 0.139\\ 0.139\\ 1.416\\ 0.008\\ 0.435\\ 0.097\\ 0.097\\ 0.097\\ 0.097\\ 0.022\\ 2.180\\ 0.022\\ 3.199\\ 0.022\\ 3.199\\ 0.022\\ 3.199\\ 1.942\\ 0.058\\ 0.013\\ 0.013\\ 2.039\\ 0.005\\ 0.005\\ 0.005\\ 0.005\\ 0.005\\ 0.005\\ 0.003\\ 0.005\\ 0.003\\ $	$\left. \begin{array}{c} 7.937\\ 0.063\\ 0.063\\ 1.340\\ 0.012\\ 0.012\\ 0.023\\ 0.023\\ 0.025\\ 0.023\\ 0.025\\ 0.025\\ 0.025\\ 0.014\\ 1.746\\ 0.014\\ 1.753\\ 0.004\\ 1.753\\ 0.004\\ 1.753\\ 0.004\\ 1.753\\ 0.004\\ 1.753\\ 0.003\\ 0.004\\ 1.753\\ 0.004\\ 1.753\\ 0.003\\ 0.004\\ 1.753\\ 0.003\\ 0.004\\ 1.753\\ 0.003\\ 0.004\\ 1.753\\ 0.003\\ 0.003\\ 0.004\\ 1.753\\ 0.003\\$	$\left.\begin{array}{c} 7.443\\ 0.557\\ 0.557\\ 0.805\\ 0.805\\ 0.0869\\ 0.048\\ 1.938\\ 0.018\\ 1.335\\ 0.018\\ 1.626\\ 1.626\\ 1.626\\ 1.626\\ 1.626\\ 1.153\\ 1.153\end{array}\right\} 4.938$
0	21.958	22.023	21.922	21.961	22.247	22.847

70

I. Y. Borg:

	7	8	6	10	11
\mathbb{R}^{200}_{100} $\mathbb{R}^{200}_$	55.38 0.36 5.29 9.74 13.07 13.07 0.18 6.31 n.d. n.d. 1.10 0.05 0.09 0.09 0.01 0.01	55.10 0.68 0.68 9.78 9.78 9.78 0.48 8.86 n.d. trace n.d. 1.43 0.09 0.09 0.03 0.03	$\begin{array}{c} 51.17\\ 0.63\\ 1.11\\ 15.18\\ 15.18\\ 18.48\\ 18.48\\ 0.29\\ 0.13\\ 0.29\\ 0.13\\ 0.13\\ 0.13\\ 0.13\\ 0.13\\ 0.13\\ 0.28\\ 0.28\\ 0.04\\ 0.04\end{array}$	49.87 0.34 1.04 1.04 20.19 20.19 0.03 0.44 0.67 0.44 0.44 0.44 0.16 0.84 0.16 0.84 0.84 0.84 0.84 0.84 0.84 0.84 0.84	48.30 0.38 2.66 13.41 20.40 1.17 0.14 0.02 1.40 6.91 1.41 1.24 1.24 1.24 0.03 1.12 0.03 1.12 1.12 n.d.
$\frac{\text{Less}}{0=\text{Fand Cl}}$	99.99 0.01 99.98	99.75 0.02 99.73	100.35 0.26 100.09	100.86 1.03 99.83	100.17 0.47 99.70
Analyst Si Alvi Fe Mn Mg Cu Cu Cu Cu Cu Cu Cu Cu Cu Cu Cu Cu Cu	C. O. INGAMELLS 7.997 0.003 0.003 0.897 0.039 1.994 1.578 1.994 1.578 1.994 1.578 1.994 1.578 1.994 1.970 0.029 1.970 0.029 1.994 1.995 1.994 1.957 1.994 1.995 1.994 1.957 1.992 1.970 0.003 1.970 1.970 1.970 1.970 1.957 1.994 1.995 1.994 1.995 1.994 1.995 1.994 1.995 1.994 1.995 1.994 1.995 1.992	$\begin{array}{c} \text{D. THAEMLITZ} \\ \hline 7.925 \\ 0.075 \\ 0.075 \\ 0.073 \\ 1.147 \\ 1.147 \\ 1.147 \\ 1.166 \\ 1.168 \\ 1.1766 \\ 3.133 \\ 1.898 \\ 1.898 \\ 1.898 \\ 1.897 \\ 0.016 \\ 1.897 \\ 0.008 \\ 0.008 \\ 0.$	$\left.\begin{array}{c} \text{C. O. INGAMELLS} \\ 7.926 \\ 0.074 \\ 0.074 \\ 1.768 \\ 0.074 \\ 0.074 \\ 2.393 \\ 0.074 \\ 2.3976 \\ 0.033 \\ 0.074 \\ 2.976 \\ 0.033 \\ 0.033 \\ 0.074 \\ 2.976 \\ 0.033 \\ 0.015 \\ 0.033 \\ 0.015 \\ 0.015 \\ 0.015 \\ 0.015 \\ 0.015 \\ 0.015 \\ 0.016 \\ 0.010 \\ 0.000 \\$	$\left.\begin{array}{c} \text{C. O. INGAMELLS}\\ 7.826\\ 0.174\\ 0.174\\ 0.040\\ 1.683\\ 1.683\\ 1.683\\ 1.683\\ 1.683\\ 1.683\\ 1.683\\ 1.683\\ 1.683\\ 0.001\\ 0.007\\ 0.078\\ 0.078\\ 0.078\\ 0.078\\ 0.078\\ 0.078\\ 0.078\\ 0.078\\ 0.078\\ 0.078\\ 0.078\\ 0.078\\ 0.078\\ 0.001\\ 0.001\\ 0.000\\ 0$	$ \begin{array}{c} \textbf{E. H. OSLUND} \\ \hline 7.605 \\ 0.395 \\ 0.045 \\ 1.589 \\ 1.589 \\ 1.589 \\ 0.045 \\ 1.589 \\ 0.045 \\ 1.589 \\ 0.029 \\ 0.029 \\ 0.029 \\ 0.029 \\ 0.029 \\ 0.029 \\ 0.029 \\ 0.029 \\ 0.029 \\ 0.029 \\ 1.859 \\ 0.000 \\ 1.859 \\ 0.000 \\ 1.859 \\ 0.000 \\ 0.000 \\ 1.859 \\ 0.000 \\ 0.000 \\ 0.000 \\ 1.859 \\ 0.000 \\ 0.$
Explanation of	f Table 1 see p. 72.				

71

Explanation of Table 1. See Table 2 for description of samples. All analyses new except 1 and 6. 1 = Glaucophane (KUNITZ, 1930). 2 = Glaucophane. 3 = Glaucophane. 4 = Glaucophane. 5 = Glaucophane. 6 = Crossite (HOLGATE, 1951). 7 = Crossite. 8 = Crossite; Cr₂O₃ and V₂O₃ absent. 9=Riebeckite; Cr₂O₃, trace, PbO, V₂O₃ absent; Al₂O₃ has been reduced by the wt % ZnO/2 on assumption that part of ZnO was included in gravimetrically determined Al₂O₃, 10 = Riebeckite-arfvedsonite; Zr = 450 ppm (ZrO₂ = 0.05); Ni, V, Cr and Pb < 10 ppm; reported Al₂O₃ treated as in 9. 11 = Riebeckite-arfvedsonite; Cr₂O trace; PbO, V₂O₃ absent reported Al₂O₃ treated as in 9. H₂O(+) may be low (S. GOLDICH, personal communication). — Key: n.d. = not determined; trace = less than 0.02%.

Widely differing optical orientations and crystal habits have encouraged a plethora of mineral names in this group of alkali amphiboles. Intermediate members of the series, whose names have gained currency, are listed below together with the usage in the present text. History of these names and others that have been suggested is given by HINTZE (1897), HINTZE (1938); and MIYASHIRO (1957).

Crossite — $Na_2(Mg, Fe^{\prime\prime})_3(Al, Fe^{\prime\prime\prime})_2Si_8O_{22}(OH)_2$

— initially intended to set apart those members of the glaucophane-riebeckite series having crossed axial planes, viz. optic planes normal to c, $(\gamma = b)$. This restriction is no longer useful, but the many commonly occuring intermediate members are conveniently described by the name.

Mg-crocidolite — (including rhodusite) — $Na_2(Mg_{2.6}Fe_{.6}'')_{3.2}Fe_{1.8}'''(Si, Al)_8O_{22}(OH)_2$ — fibrous variety whose composition is closely limited near the magnesioriebeckite end member (× of Fig. 1).

Crocidolite — $Na_2(Fe_{2,6}^{''}Mg_{,4})_{3,0}Fe_{2,0}^{'''}Si_8O_{22}(OH)_2$

— fibrous variety of riebeckite which closely approaches theoretical composition when fresh (Hodgson, 1965; Hodgson *et al.*, 1965). Most published analyses when calculated (× of Fig. 1) give a composition near Na_{2.0}(Fe_{2.0}Mg_{.7})_{2.7}Fe_{2.3}'Si₈O₂₂(OH)₂ presumably due to oxidation of Fe''. (Si+Al^{IV}) in tetrahedral coordination is characteristically low in these, i.e., <8.00.

$$Osannite - Na_{2,0-3,0} Fe_{3,5-3,0}^{\prime\prime} Fe_{1,5-2,0}^{\prime\prime\prime} Si_8 O_{22}(OH, F)_2$$

— a riebeckite-arfvedsonite named by HLAWATSCH (1906) who demonstrated that its optical orientation [optic plane \perp to (010), $b = \gamma$, (—) sign of elongation] was distinct from what was then called riebeckite. The latter are now also considered to be riebeckite-arfvedsonites (e.g., No. 10, Table 2). The name osannite is used here to designate an orientation of the indicatrix rather thancomposition.

A total of 109 analyses of alkali amphiboles are plotted in Fig. 1. The grouping of Fe''+Mn and Fe'''+Ti on the ordinate and abscissa, respectively, is in consideration of their similar ionic radii and comparable influence on optical properties. Amphiboles for which new data are presented (Tables 1, 2 and 3) are indicated by numbered open circles; fibrous amphiboles are marked by crosses. Amphiboles whose published descriptions are included in plots of variation of physical properties with composition (Figs. 3, 4, 5 and 6) are indicated by lettered dots; the literature reference for these analyses are given in the text. While Fig. 1 expresses the gross variation found in natural amphiboles, the method of normalizing all variation to 1.00 obscures large departures from the usual R'''=3.0 and R'''=2.0 totals. Many of the so-called riebeckites plotted are in fact riebeckite-arfvedsonites since X is >2.00 and R'''<2.00. Many also contain large quantities of F+Cl. No. 9 (Fig. 1 and Table 1) closely approaches the theoretical composition of riebeckite. Pure glaucophane and ferroglaucophane have no natural representatives.

72

The general distribution of points along diagonals attests to the common solid solution between two end members. The substitutions are $Fe'_{3}Fe''_{2}$ for $Mg_{3}Al_{2}$ and a more limited substitution of $Fe''Al_{2}$ for $Mg_{3}Fe''_{2}$. It is possible that many of the compositions displayed in Fig. 1 which do not fall exactly on the diagonals would do so if the analyses were accurate or if the samples were free of all impurities.

Experimental Method

Separation and Chemical Analysis

Separation of the amphiboles was obtained by repeatedly centrifuging samples finer than 100 mesh in heavy liquids (methylene iodide, $\rho = 3.32$ and tetrabromoethane, $\rho = 2.96$) and by using the Frantz isodynamic separator on material previously washed with alcohol to remove ultra-fine particles.

Separation of several ultimately had to be abandoned because they could not be adequately purified. Single crystals of riebeckite-arfvedsonite (No. 10 and No. 11) were crushed and put through the Frantz separator to remove adhering oxides and inclusions.

The analyses recorded in Table 2 have been corrected for the following contaminants: No. 2, 1% chlorotoid; No. 3, 0.14% C, gravimetrically determined; No. 4, 0.45% CO₂, gravimetrically determined, and 0.72% Ca present as calcite; No. 8, 1% albite. These and remaining samples contain impurities less than 0.5 weight per cent (see Table 2).

The analyses were done at the Rock Analysis Laboratory, University of Minnesota, by routine gravimetric methods. Spectra of iron-rich members of the series were examined by x-ray fluoresence techniques to detect presence of elements, such as Zn, Cu, Cr, Pb, etc., which are common in these amphiboles. If zinc and/or copper were present, the amounts were determined colormetrically at the University of California, Lawrence Radiation Laboratory, by methods outlined by RADER and GRIMALDI (1961). On the assumption that some part of the ZnO was erroneously reported as Al_2O_3 in the gravimetric analysis, the latter was reduced by one-half the weight per cent of ZnO (FURMAN, 1939; p. 9; BORLEY, 1963).

Density

All densities were measured by using a flotation technique. The powdered sample was centrifuged in Clerici solutions whose density could be varied by dilution with water until all or most of the powder remained in suspension after the method of BASS (1957) and HESS (1960, p. 19). The density of the solution was measured on a Christian Becker liquid-density balance. The method is inherently very accurate (± 0.003 g/cc). It can be very rapid if a calibration of the $\triangle \varrho$ associated with the addition of a drop of water (or Clerici) is made on the centrifuge liquid once the approximate ϱ has been reached.

The method has the added advantage of allowing an estimate to be made of the variation in ϱ within a powder because ϱ like other properties of the silicates shows variation within the same specimen (HAGNER *et al.*, 1965; WILSON, 1960). The data reported here are mean densities. The variation is judged by the densities of the solutions in which 95% and 5% of the sample is suspended after centrifuging.

Refractive Indices

The Becke line method was used to determine the refractive indices of the minerals. The approximate range of the R.I. were first determined in white light on grains giving centered or off-centered interference figures by taking advantage of the dispersion of the oils. The final values were determined after appropriately orienting the grains with a universal stage (hemispheres n = 1.649) in Na_D-light ($\lambda = 590 \text{ m}\mu$). The R.I. of the oils were measured with an Abbé refractometer in Na light under carefully controlled temperature conditions. Before and after each determination of a R.I. of a mineral, the ambient temperature above the stage was measured and the appropriate corrections made to the R.I. of the oils under the tacit assumption that the sample was in thermal equilibrium with the surrounding air. The largest source of error is the uncertainty in the temperature. In the course of a 4-hour deter-

Table	2. Description	of samples					
Am- phi- bole No.	Original No.	Type (given name)	Locale	Rock type	Impurities in analyzed sample	Source	Pertinent literature references
1	A.M.N.H. 10120	Glauco- phane	Zermatt, Switz.	Garnet-chlorite-muscovite glaucophane schist	Not reported	MASON and SEA- MAN, American Museum Nat'l Histo	Воръчие (1876); КUNITZ (1930) rry
61	A.M.N.H. 10121	Glauco- phane (gastaldite)	Piedmont Prov., Italy (Probably St. Marcel or Val de Chisone)	Chlorotoid-chlorite-glauco- phane rock (with minor quartz)	None	Mason and SEA- Man, American Museum Nat'l History	ZAMBONINI (1906); Iddings (1911, p. 468)
ಣ	331-M-121	Glauco- phane	Junction School Area, Healdsburg Quad., Calif.	Quartz-lawsonite glauco- phane schist with minor chlorite	Quartz inclu- sions (<0.5%)	U.C., Berkeley	Borg (1956) including rock analysis (Table 1f)
Ŧ	SE-1	Glauco- phane	Sebastopol Quad., Calif.	Glaucophane in altered eclogite	Chlorite $(<0.5\%)$	U.C., Berkeley	TRAVIS (1952)
20	331-M-19B	Glauco- phane	Junction School Area, Healdsburg Quad., Calif.	Glaucophane-chlorite rock with remnant garnet, pyroxene and rutile and minor sphene and apatite	Chlorite $(<0.5\%)$	U.C., Berkeley	Вока (1956)
9	47972	Crossite	Monument Hill, Anglesy, Wales	Crossite-epidote quartz- albite schist with minor muscovite, chlorite sphene, hematite and apatite	Epidote (<1%) (see footnote p. 84)	S. AGRELL, Cambridge	Но цатв (1951)
5	331-M-56	Crossite	Junction School Area, Healdsburg Quad., Calif.	Quartz-crossite schist with minor pyrhotite and hema- tite (?)	Quartz (<0.5%)	U.C., Berkeley	Вока (1956)

74

I. Y. Borg:

PALACHE (1894); BROTHERS (1954) also SWITZER (1951) and KUNTZ (1930)	-	LACROIX (1889); COLE- MAN (1951); SHODA (1958); GROSS and HEINRICH (1966)	OSANN and UMHAUER 1 (1914); VENDL (1924); JACOB and BRANDEN- BERGER (1931)
U.C., Berkeley	H.M.E. Schür. Mann and R. Suringa	Wards Nat'l Sci. Est.	Mason and SEA- MAN, Am. Museur Nat'l History
None	Unidentified inclusions $(<0.5\%)$	Altered rie- beckite (minor)	Unidentified oxide (<0.5%)
Crossite-quartz-albite schist with minor acmitic pyroxene, sphene and apatite	Riebeckite granite with perthitic plagioclase, and minor allanite, fluorite, biotite and magnetite	Single crystal from peg- matite	Single crystal from um- ptekite pegmatite
N. Saddle Peak, Berkeley Hills, Calif.	Doubrutscha, Roumania	St. Peters Dome, Colo.	Alter Pedrozo, Alemejo Pro- vince, Portugal
Crossite	Riebeckite	Riebeckite- arfvedsonite (riebeckite)	Riebeckite- arfvedsonite (osannite)
307-M-9	RDR-1	SP.1	A.M.N.H. 10123
x	6	0	Ξ

mination the ambient temperature may change by 3° C, which is equivalent to 0.0018 in some of the high index oils. However, the R.I. are believed accurate to + 0.001.

The optical properties of iron-rich members of the series are particularly troublesome to measure. In addition to the well known incomplete extinction on (010) in monchromatic light (VENDL, 1924; ESKOLA and SAHLSTEIN, 1930; YAGI, 1953; SHODA, 1954), two Becke lines move in opposite directions when the R. I. of the immersion oil is near to that of the transmitted ray. An additional complication is extreme opacity of these materials, particularly to Na-light.

Extinction Angle

The extinction angle was determined graphically by measuring the angle between the appropriate optic direction $(\alpha, \beta \text{ or } \gamma)$ and the *c* axis on a stereogram. The *c* axis was located by plotting the positions of the poles of one or more (110) cleavages and pole of $(010) = b = \beta$ or γ as measured with a universal stage. The cleavage angle, ca. 55.5° (see Table 3) and the angle between α, β and γ were also graphically determined and used as a check on the accuracy of location. The extinction angle is accurate to 1°-1.5°.

It was possible to determine the sign of the extinction angle for three single crystals which were photographed with an x-ray precession camera. SCHUSTER'S rule was followed (WINCHELL and WINCHELL, 1951, p. XV), viz, the sign is considered positive if the extinction direction lies in the acute angle between a and c and negative if it is the obtuse angle. The signs given in Table 3 are for optical extinctions in a structure described as C 2/m.

The suggestion that extinction angles on (110) cleavage flakes be used for diagnostic purposes has been recently made by PARKER (1961) and GAZZI (1963). On this account these data $(c \wedge \gamma'_{110}, \text{ etc.})$ are presented, together with comparable values calculated from extinction angles $(c \wedge \lambda, \text{ etc.})$ and 2V from equations modified from GAZZI (1963). In practice, accurate measured values of $c \wedge \lambda'_{(110)}$ or $c \wedge a'_{(110)}$ are as hard to obtain as values of $c \wedge \lambda$ and $c \wedge \alpha$. Gross errors result if (110) is not strictly parallel to the slide. Yet despite the large scattering of the data, good to very good agreement was had between the average measured and calculated values. This suggests that while the perfect (110) cleavage flake is not common, data measured on flakes that depart

Table 3. Phys	sical properties of glau	cophane-riebeckites				:	
		1	2	n	4	5	9
Pleochroism	α n	colorless v. lt. purple v. lt. blue	colorless v. lt. purple v. lt. blue	colorless lt. purple lt. blue	nearly colorless lt. purple lt. blue	nearly colorless violet blue	colorless pale violet blue
Orientation		$\mathbf{G} \begin{cases} b = \beta \\ \mathbf{T.O.P.} \ (010) \end{cases}$	G $\begin{cases} b = \beta \\ T.0.P. \ (010) \end{cases}$	$_{\mathrm{G}} \left\{ \begin{smallmatrix} b = eta \\ \mathrm{T.O.P.} \ (010) \end{smallmatrix} ight.$	$\mathrm{G}\left\{ \substack{b=eta\ \mathrm{T.O.P.}\ (010)} ight.$	$\mathbf{G} \begin{cases} b = \beta \\ \mathbf{T.O.P.} \ (010) \end{cases}$	$\mathbf{G} \begin{cases} b = \beta \\ \mathbf{T.0.P.} \ (010) \end{cases}$
Absorption		$\gamma\!=\!eta\!>\!lpha$	$\gamma\!=\!eta\!>\!lpha$	$eta\!=\!\gamma\!>\!lpha$	$eta\!=\!\gamma\!>\!lpha$	$\gamma = eta > lpha$	$\gamma = eta > lpha$
Refractive indices $(\lambda = 590 \text{ m}\mu)$	8 A V	1.611 1.630 1.633	$1.610 \\ 1.630 \\ 1.632$	1.613 1.638 1.642	$\begin{array}{c} 1.626 \\ 1.644 \\ 1.646 \end{array}$	1.632 1.645^{5} 1.646	1.646 1.658 1.658
Birefringence	ya	0.022	0.022	0.029	0.020	0.014	0.012
Dispersion			$\lim_{r < v \text{ weak}}$	$ \begin{cases} \text{inclined} \\ \mathbf{r} < \mathbf{v} \text{ weak} \end{cases} .$		$ \begin{cases} inclined \\ r < v \text{ weak} \end{cases} $	$ \begin{cases} \text{inclined} \\ \mathbf{r} < \mathbf{v} \text{ weak} \end{cases} \end{cases} $
Extinction angle $(\lambda = 590 \text{ m}\mu)$	$\stackrel{c}{c} \bigwedge \stackrel{\gamma}{\gamma_{110}} \stackrel{c}{(c} \bigwedge \stackrel{\gamma'_{110}}{\gamma_{110}} \stackrel{c}{ m calc}$	6° 7.5 $^{\circ}$ (8.5 $^{\circ}$)	$6.25^{\circ} \\ 8^{\circ} (9^{\circ})$	$\begin{array}{c} 4^{\circ} \\ 7^{\circ} \end{array} (7^{\circ}) \end{array}$	6° 10° (10°)	7° 1 3° (1 3°)	7.5° 11° (15°)
Sign of extin	otion angle				(+)		
$\begin{array}{c} \text{Optic angle} \\ (\lambda {=}590 \text{ m}\mu) \end{array}$	$\frac{2V}{2V_{(calc.)}}$	-43.6° -42.4°	-41.8° -36.5°	-48.9°	-38.1° -35.0°	-21.5° -21.3°	-5°
Density	φ (median) φ (obs. variation) φ (calc)	$\pm 0.030 \pm 3.088$	± 0.009 ± 3.077	± 0.016 ± 3.138	± 0.011 ± 0.011 3.132	${}^{3.149}_{-0.005}$	3.206* **
Cleavage angle	(110) A (110)(calc.)	55° 13′	55° 13′	55° 10'	55° 26′	55° 20'	55° 10'
Unit cell $C \frac{2}{m}$ Z = 2	$egin{array}{l} a_0 \left(ec{\mathrm{A}} ight) \ b_0 \left(ec{\mathrm{A}} ight) \ c^0 \left(ec{\mathrm{A}} ight) \ c^0 \left(ec{\mathrm{A}} ight) \ eta \ c^0$	$\begin{array}{c} 9.550\pm0.001\\ 17.842\pm0.003\\ 5.296\pm0.001\\ 103.70\pm0.01\\ 9.278\\ 871.9\end{array}$	$\begin{array}{c} 9.547\pm0.001\\ 17.738\pm0.002\\ 5.298\pm0.001\\ 103.68\pm0.001\\ 9.276\\ 871.7\end{array}$	$\begin{array}{c} 9.535\pm 0.001\\ 17.745\pm 0.002\\ 5.306\pm 0.001\\ 103.54\pm 0.01\\ 9.270\\ 872.7\end{array}$	$\begin{array}{c} 9.595\pm0.002\\ 17.798\pm0.003\\ 5.307\pm0.001\\ 103.66\pm0.01\\ 9.324\\ 880.6\end{array}$	$\begin{array}{c} 9.609 \pm 0.002 \\ 17.813 \pm 0.004 \\ 5.311 \pm 0.002 \\ 103.61 \pm 0.02 \\ 9.339 \\ 883.5 \end{array}$	$\begin{array}{c} 9.614 \pm 0.002 \\ 17.882 \pm 0.003 \\ 5.312 \pm 0.001 \\ 103.71 \pm 0.01 \\ 9.339 \\ 887.2 \end{array}$
с, <u> </u>			1				

76

* HOLGATE (1951). ** Accurate calculation not possible.

		7	8	6	10	11
Pleochroism	r B R	pale yellow blue purple	pale yellow deep blue deep purple	deep blue yellow dark grey blue	dk. sky blue It. grey blue It. greenish yellow	deep blue yellow dk. grey blue
Orientation		$\subset \begin{cases} b = \gamma \\ T.0.P. \bot (010) \end{cases}$	C $\begin{cases} b = \gamma \\ \text{T.O.P.} \perp (010) \end{cases}$	$0 \left\{ \substack{b=\gamma \ \mathrm{T.0.P.} \perp (010)} ight.$	$\mathbf{R} \begin{cases} b = \beta \\ [\text{T.O.P.}] \\ (010) \end{cases}$	$\mathrm{O}\left\{ \substack{b=\gamma\ \mathrm{T.0.P.}, \perp(010)} ight.$
Absorption		$\beta = \gamma > \alpha$	$\beta = \gamma > \alpha$	$lpha > \gamma > eta$	$\alpha > \beta > \gamma$	$lpha > \gamma > eta$
Refractive indices $(\lambda = 590 \text{ m}\mu)$	8 0 2 X	1.659 1.670 1.674	1.663 1.666 1.669	1.693 1.701 1.709	1.686 1.694 1.700 ₅	1.69 3 1.700 1.709
Birefringence	, γ—α	0.015	0.006	0.016	0.014_{5}	0.015
Dispersion		$\left\{ r < v \text{ moderate} \right\}$	{crossed or horizontal r≷v strong	$\{r < v \text{ strong}$	∫inclined [r≶v extreme	r < v
Extinction angle $(\lambda = 590 \mathrm{m}\mu)$	$c \land \gamma$, etc. $c \land \gamma_{110} (c \land \gamma_{110})$ (cate), etc.	$c \wedge \beta 2^{\circ}$, $3^{\circ} (1^{\circ})$	$c \land \beta 11^{\circ}$ 10° (11°)	$c \wedge \alpha 4^{\circ}$ $4^{\circ} (2^{\circ})$	$c \land \alpha \ \theta^{\circ}$ 7° (5°)	$c \land \alpha 11^{\circ}$ $2^{\circ} (2^{\circ})$
Sign of extin Optic angle	ction angle $2V$	59.8°	(+) 91°	$\begin{cases} -94^{\circ} \text{ at 591 m} \mu \\ 000 & 0.4 & 407 \\ 000 & 0.4 & 407 \\ 000 & 0.4 & 0.7 \\ 0.00 & 0.4 & 0.7 \\ 0.00 & 0.4 & 0.7 \\ 0.00 & 0.4 \\ 0$	(-) 87°	$\left\{-102^{\circ} \text{ at 591 m}, 02^{\circ} \text{ at 467 m}, 02^{\circ} \text{ at 467 m} \right\}$
$(\lambda = 590 \mathrm{mp})$	$2 V_{ m (calc)}$	-61.5°	90°	90°	-84°	
Density	φ (median) φ (obs. variation) φ (calc)	$\pm 0.020 \pm 0.020$	${3.189 \atop 3.196} \pm 0.022$	± 0.011 ± 0.011 3.380	${3.414 \atop 3.406}$	$\pm 3.406 \pm 0.020 \pm 3.405$
Cleavage angle	(110 Å (110) (calc)	55° 17′	55° 20′	55° 30′	55° 48′	55° 46′
Unit cell $C \frac{2}{m}$ Z = 2	$egin{array}{l} a_0 \left(ec{\mathrm{A}} ight) \ b_0 \left(ec{\mathrm{A}} ight) \ c_0 \left(ec{\mathrm{A}} ight) \ eta \left$	$\begin{array}{c} 9.647\pm0.001\\ 17.905\pm0.003\\ 5.316\pm0.001\\ 103.60\pm0.01\\ 9.377\\ 892.5\end{array}$	$\begin{array}{c} 9.673 \pm 0.002 \\ 17.923 \pm 0.003 \\ 5.316 \pm 0.001 \\ 103.68 \pm 0.01 \\ 9.398 \\ 894.4 \end{array}$	$\begin{array}{c}9.769\pm0.002\\18.048\pm0.003\\5.335\pm0.001\\103.59\pm0.01\\9.495\\914.3\end{array}$	$\begin{array}{c} 9.823 \pm 0.002 \\ 18.021 \pm 0.004 \\ 5.328 \pm 0.002 \\ 103.70 \pm 0.01 \\ 9.544 \\ 916.4 \end{array}$	$egin{array}{c} 9.846 \pm 0.001 \\ 18.068 \pm 0.002 \\ 5.334 \pm 0.001 \\ 103.81 \pm 0.01 \\ 9.562 \\ 921.4 \end{array}$

77

from this position form an approximately gaussian distribution. Additional complications in measuring extinction occur in amphiboles with fibrous habit, small grain size and/or low birefringence; a universal stage must be used to orient the grains so as to obtain acceptable results.

Optic Angle

Standard orthoscopic procedures were used with sodium light to measure 2V (or actually 2H before appropriate corrections are made for the difference between R.I. of the mineral and that of the hemispheres). Thin sections were mounted on a standard Leitz-4-axis universal stage with hemispheres of n = 1.649 and a central plate of n = 1.520. Choice of objective (U.M.2) and a fully opened substage diaphragm minimized the potentially large errors in the method described by MUNRO (1963 and 1964). It is likely that optic angles smaller than 65° are accurate to within a degree while angles between 80° — 90° , which are readily determined to within 2° under good circumstances, are $\pm 3^{\circ}$ — 5° . These large angles are associated with iron-rich members in which optical anomalies and strong absorption are the rule.

The optic angle given for each amphibole analyzed is the average of the results from six or more grains, each measured four times. The angle varies from $3^{\circ}-8^{\circ}$ (average 4°) in any sample.

Especially thin sections were cut normal to (001) and hence subnormal to the acute or obtuse bisectrix in the single crystals of riebeckite-arfvedsonite. In these the optic angle was determined by using the method of KAMB (1958) for slightly off-centered figures viewed with an objective of N.A. 0.85. The precision of these determinations is not high because of the diffuse nature of the isogyres, even in monochromatic light.

2V's were checked against values calculated from refractive indices with the equation

$$\cos^2 V_{\alpha} = \frac{\gamma^2 \left(\beta^2 - \alpha^2\right)}{\beta^2 \left(\gamma^2 - \alpha^2\right)}$$

or approximate values read from the charts of MCANDREW (1963, Figs. 1 and 2).

X-Ray Data

Cell parameters were measured by the powder method with a camera of 114.6 mm diameter, 0.02 mm capillaries made from low-absorbing glass, and manganese filtered, Fe radiation. Eccentricity and absorption errors were corrected by BACON'S (1948) extrapolation method used in conjunction with a silicon internal standard. All data had been previously corrected for film shrinkage. On the average, 50 diffraction lines from $2\Theta = 12^{\circ}-164^{\circ}$ from each amphibole were measured; of these an average of 39 could be unambiguously indexed and used in a least-squares code (MAST), which was run on an IBM 7094 computer.

Indexing was accomplished with visually estimated intensities from a series of precession and Weissenberg films of glaucophane, crossite and riebeckite-arfvedsonite (No. 4, No. 8, No. 10, Table 2, respectively) taken with Mo and Fe radiations, respectively.

Strong high-index diffraction lines not included in the Weissenberg and precession films (e.g., 355, 465, and 804 of iron-rich members in a C 2/m cell) were indexed on the powder films by comparison with theoretical patterns computed from the chemical analyses, likely site occupation, and atomic coordinates from a refinement of the riebeckite structure (COL-VILLE and GIBBS, 1964; GIBBS, personal communication) with SMITH's program (SMITH, 1963). Use of the WHITTAKER (1949, p. 315) atomic coordinates for "crocidolite" transformed to a C 2/m cell (WYCKOFF, 1953, pp. 49-50) were less successful in this connection.

The chief source of error in the cell dimensions is incorrect determination of the d-spacing of the planes in the sample and internal standard because of overlap, which is unavoidable in complex patterns. For this reason data from the generally more accurate back reflection region could not be used to the exclusion of data from the front reflection region.

Cell parameters and indexing are for the (001) centered cell (C 2/m) which was chosen following DONNAY'S rules (DONNAY and NOWACKI, 1954, p. 150). The data are given with pertinent probable errors. Volumes calculated therefrom have a maximum probable error of ± 0.56 Å³ (0.05%).

The cleavage angle $(110) \land (1\overline{1}0)$ was calculated from cell parameters using the relation

$$[(110) \land (1\bar{1}0)] = 2 \tan^{-1} \frac{a_0 \sin \beta}{b_0}$$

Optical Properties

Orientation of the Indicatrix

Within the amphibole group studied, there are four distinct orientations of the optical indicatrix. They have been called the "glaucophane", "crossite", "osannite" and "riebeckite" orientations (TRÖGER, 1956). To emphasize that they specify



Fig. 2. Orientation of the indicatrix with respect to the basal section of the amphiboles. Dashed lines are traces of the optic plane (T.O.P.). The cleavage angle $(110) \land (110)$ and pleochroism are indicated on the section normal to the *c* axis. Symbols (\bullet , \times , and \triangle) are associated with the refractive indices plotted in Figs. 3 and 4

particular optic orientations rather than chemical species, they are abbreviated to G, C, O, and R orientations respectively in subsequent discussion. A plot of composition versus refractive indices such as Fig. 3 shows that the orientation changes where substitutions cause any two of the three refractive indices to cross. R would also be represented if α , β and γ were extended until β and γ crossed e.g. beyond the bounds of either Fig. 3 on the riebeckite-rich side or Fig. 4 on the magnesioriebeckite-rich side.

For the sake of explanation it is convenient to assume that the absorption axes are parallel to the vibration directions within the crystal, although this is not necessarily true (SHODA, 1957). Then we may associate the vibration direction nearest to the *c* axis with a blue pleochroic color (\triangle in Figs. 2, 3, and 4), that nearest to the *a* axis with colorless, yellow or pale brown pleochroism (.), and that parallel to *b* with violet, purple or dark grey blue (x). Thus if the relative

Table 4. Opticat or	ventation						
Name of indi-	Chemical type	Pleochroi	sm*		Indicatrix	Extinction	Examples
catrix orientation (symbol)		8	β	γ	orientation	araus	
"Glaucophane" G	Glaucophane some crossites	yellow •	violet ×	blue ∆	$b = eta \parallel (010)$	$c \wedge \gamma$	 # 1, 2, this study # 6, this study; Ногоате (1951)
	Crossite						\pm 7 and 8, this study;
"Crossite" C	some Mg-riebeckites	yellow •	$^{\mathrm{blue}}$	violet ×	$b=\gamma$ \perp (010) and ca. \perp	$c \wedge \beta$	MIYASHIRO and IWASAKI (1957)
	Riebeckite	-					# 9, this study; Alnberg(1930); Рнемізтев <i>et al.</i> (1950)
"Osannite" O	some riebeckite- arfvedsonite	;	F			:	PALACHE and WARBEN (1911); VENDL (1924); # 11 this study
	Mg-riebeckites	blue to indigo △	yellow- brown	grey blue ×	$b = \gamma$ $\perp (010)$ and ca. $\ c\ $	c / c	WYMOND and WILSON (1951); McLachlan (1951)
	including Mg- crocidolites and rhodusites						DE VILLIERS (1948); King (1961)
"Riebeckite" R	Riebeckite- ar†vedsonites	dark blue △	dark grey- blue ×	yellow- brown	$b = \beta$ $\ (010) \text{ and }\ c$	cγα	 # 10, this study; MACKAY <i>et al.</i> (1949); BAIN (1934); COLEMAN (1951); LACROIX (1889); BORLEY (1963)
* Given for 0.03	mm sections; greenish	and blue-g	reen tints m	ay be conspico	us in thinner sections		

 \triangle Vibration direction nearest a axis. \times Vibration direction parallel to b axis. \bullet Vibration direction nearest c axis.

I. Y. BORG:

magnitudes of the refractive indices associated with these three absorption axes can be determined, the orientation of the indicatrix can be determined uniquely. In other words, the pleochroic scheme is distinct for each of the four orientations. Descriptions of the four orientations are given in Table 4 and in Fig. 2; the latter shows the basal section of amphiboles having each of the four orientations. Lacking measurements of R.I., the orientation of the optic plane can be used in conjunction with the sign of elongation to recognize the type of indicatrix orientation.

If one restricts the term riebeckite to alkali amphiboles in which $A+X \simeq 2.0-2.3$, i.e., the A position is either empty or only partially filled, most riebeckites have the O orientation. Riebeckite-arfvedsonites in which $A+X \simeq 2.5-3.0$ can have either R or O orientations, possibly depending on whether (F+Cl) is high ($\simeq 0.7-1.5$ formula units) or low ($\simeq 0-0.7$ formula units) respectively.

It is likely that β and γ indices do in fact intersect within the diagram (Fig. 4) and that the pure end member has the R orientation. However, most naturally occurring magnesioriebeckites including the fibrous varieties typically have the O orientation. A C orientation also is possible for intermediate types (*m*, Fig. 1; from MIYASHIRO and IWASAKI, 1957) because substitution of Fe₃''Al₂ for Mg₃Fe₂'' is associated with a more rapid increase in *n* associated with the yellow and violet absorption axes than the blue (Fig. 4).

Optical orientation of crocidolites is not well known because of their tendency to occur in bundles of fibers whose individual members are less than 1000 Å across and because coatings of iron oxide and quartz impurities which decorate external faces make them difficult to measure. MILES (1942) and SUZUKI (1939) describe the R orientation, while PEACOCK'S (1928) and the author's measurements below on crocidolite (from Malipsdrift, S. E. of Pietersburg, Transvaal, South Africa) indicate the orientation is O:

$$\alpha = \text{deep sky blue}$$
 $\beta = \text{pale yellow}$ $\gamma = \text{purple}$
 $b = \gamma, \text{ T. O. P. } \perp (010), c \land \alpha = 0^{\circ} - 3^{\circ}, 2 V = (--) \text{ large.}$

It is possible that the exact orientation of the indicatrix depends on the degree of weathering and hence on oxidation of Fe'', which commonly occurs in crocidolites (HODGSON, 1965).

The interpretation of the hollow fibers of Mg-crocidolites and crocidolites photographed by KING (1961) with an electron microscope remains elusive. Electron micrographs taken by the author of the crocidolite from South Africa described above also suggests that some fibers are hollow. These observations are reconciled with difficulty to WHITTAKER'S (1949) structural analysis of Mg-crocidolite. In all other respects the crocidolites resemble amphiboles, and the possibility that the tubular appearance is an artifact, e.g., a focusing effect, has not been eliminated.

Variation in Optical Parameters

Glaucophane-Riebeckite Series. Trends shown in Figs. 3 and 4 represent variation in optical properties of amphiboles which closely represent binary solid solutions. Ideally, the abscissa represents compositions along the diagonals of Fig. 1. As few amphiboles of this composition have been reported in the literature, Figs. 3 and 4 are constructed from amphiboles whose compositions only approach this ideal. Examples that deviate, especially iron-rich members (e.g., No. 6, Fig. 1) also depart from general trends in optical properties. The type crossite has been omitted altogether from Fig. 3 for the same reason. In addition to new data (numbered 1—11) Fig. 3 includes data from the literature (lettered). The amount of Ca in M_4 is on the order of 0.2 units per half-unit cell in all except No. 6, HOLGATE's crossite, and p, ERNST'S E4GL, in which it is higher.



Fig. 3. Variation in optical properties in the glaucophane-riebeckite series. Numbered points correspond to new data in Table 3; lettered points are form BANNO, 1959 (a and b), PHEMISTER *et al.*, 1950 (e); ERNST, 1964, E4 GL (p). Dashed lines indicate uncertainties in the curves because of lack of data; the dashed 2V and $(\gamma - \alpha)$ curves are computed from refractive indices extrapolated across the vacant area. Symbols (\bullet, \times , and \blacktriangle) represent *n* near or parallel to te *a*, *b* and *c* crystallographic axes respectively

Noteworthy features are:

1. The well known increase in R.I. with increased concentration of transition elements (Fe''', Ti, Fe'', and Mn).

2. Non-linear variation of n near to c (\blacktriangle) with composition. Natural riebeckites have lower indices than might be expected from a linear extrapolation from the crossite region of the diagram. This is due to the substitution of F and Cl in the OH position (BORLEY, 1963; COMEFORO and KOHN, 1954), which is a common and perhaps constant feature of natural riebeckites and riebeckite-arfvedsonites. 3. Insensitivity of extinction angle to change in composition. Higher values $(>10^\circ)$ occur in crossites (e.g., No. 8) which contain more of the magnesioriebeckite molecule.

4. Rapid and cyclic variation of 2V with increased (Fe''', Fe'' and Ti) beyond $Gl_{50}Ri_{50}$. The dashed line for 2V in Fig. 3 is constructed from the variation in refractive indices; the very few natural examples that have compositions between $Gl_{40}Ri_{60}$ and $Gl_{10}Ri_{90}$ are inadequately described in the literature or are represented by inferior chemical analyses.

5. Close agreement of indices for synthetic glaucopane and extrapolated values for the end member, viz:

$$\begin{aligned} \alpha &= 1.596 \pm 0.003 \quad \gamma = 1.620 \pm 0.003 \quad c \wedge \gamma = 10^{\circ} \pm 4^{\circ} \text{ (av. of 8)} \\ \text{(Ernst, 1961; Colville et al., 1966, Table 3)} \\ \alpha &= 1.594 \quad \beta = 1.612 \quad \gamma = 1.618 \quad c \wedge \gamma = 6^{\circ} \text{ (Fig. 3, this work)} \end{aligned}$$

$$\rho = 3.03 \quad 2V = (-) \quad 52^{\circ} \quad (\gamma - \alpha) = 0.025, \ b = \beta \text{ O. P.} \parallel (010)$$

For this composition the degree of disorder in the M_2 site does not appear to effect materially the refractive indices in contrast to its effect on lattice parameters (see p. 86).

6. There is similar close agreement of the indices for synthetic riebeckite with the extrapolated values for the end member although the latter presume minor F substitution for (OH).

 $\begin{array}{ll} \alpha = 1.709 \pm 0.004 \quad \gamma = 1.718 \pm 0.004 \quad c \wedge \beta = 3^{\circ} \pm 6^{\circ} \text{ (av. of 15)} \\ & (\text{ERNST, 1962, p. 704; COLVILLE et al., 1966, Table 3)} \\ \alpha = 1.702 \quad \beta = 1.712 \quad \gamma = 1.719 \ c \wedge \alpha = 6^{\circ} \text{ (Fig. 3, this work)} \\ \varrho = 3.40 \quad 2V = (-) 50^{\circ}, \quad (\gamma - \alpha) = 0.015, \ b = \gamma \text{ O.P. } \pm (010) \\ & \text{and ca.} \parallel c. \end{array}$

Optical data for both glaucophane and riebeckite end members show poor agreement with comparable data computed from linear regression equations (WINCHELL, 1963, Table 4).

7. The composition at which β and γ cross is approximately $\operatorname{Gl}_{56}\operatorname{Ri}_{44}$; α and β become equal at $\operatorname{Gl}_{17}\operatorname{Rie}_{83}$ where the C orientation gives away to O.

Magnesioriebeckite-Ferroglaucophane Series. Variation in optical properties of the magnesioriebeckite-ferroglaucophane series is indicated in Fig. 4. The detail is tentative, since accurate optical data for compositions which are simple solid solutions of the two end members, magnesioriebeckite and ferroglaucophane, are lacking. There is no reason to believe, for example, that refractive indices change linearly with composition. The composition at which the O orientation changes to C is poorly fixed at MgRi₇₀FeGl₃₀.

In addition to new analyses (indicated by number) data were compiled from the literature (indicated by letter). SWITZER'S crossite (1951) (d), Harvard collection No. 12873, was also included after the optical properties were reexamined and refined as follows:

$$\begin{array}{ll} \alpha=1.661 \quad \beta=1.666 \quad \gamma=1.668 \quad \mathrm{r}<\mathrm{v}, \ \mathrm{strong\ horizontal\ dispersion} \\ \alpha=\mathrm{pale\ yellow} \quad \beta=\mathrm{deep\ blue} \quad \gamma=\mathrm{deep\ purple} \quad \beta=\gamma>\alpha \quad b=\gamma \\ \mathrm{O.P.} \perp \ (010) \\ 2\mathrm{V} \ (--)=83^\circ, \ 86.5^\circ, \ 90^\circ, \ 91.8^\circ, \ 95^\circ; \ -- \ \mathrm{average\ } 89.0^\circ \\ c\wedge\beta=9.5^\circ, \ 9.5^\circ, \ 10^\circ, \ 10.5^\circ; \ -- \ \mathrm{average\ } 10.0. \end{array}$$

The magnesioriebeckite from Bizan (MIYASHIRO and IWASAKI, 1957) which has the C orientation could not be satisfactorily included in the group. As its x-ray

6*

parameters are also unusual (p. 87), it is likely that the zoning and colorless cores of the sample described by the authors have complicated correlation of composition with physical properties.

Refractive indices for several of the crossites in the group are lower than might be anticipated from the general trends of Fig. 4. Relevant observations are that two (No. 6* and i) contain more Ca and Al^{IV} than is typical of other members of the series, and the other (b) is not a simple binary solid solution.



Fig. 4. Variation in optical properties in the magnesioriebeckite-ferroglaucophane series. Curves compiled from numbered amphiboles in Table 3 and literature data as follows: (q) IWASAKI (1963); (f) POLOVINKA 1953), No. III; (g) DE VILLIERS (1948); (h) WYMOND and WILSON (1951); (b) BANNO (1959); (i) BLOXAM and ALLEN (1960); (c) LACROIX (1941); and (d) SWITZER (1951), a crossite with newly determined optical properties (see text). All chemical analyses are calculated on the basis of 24 (O, OH, Cl, F). Symbols ($\bullet, \times, \text{ and } \blacktriangle$) represent n near or parallel to the a, b and c axes, respectively. In order to recognize the trend in ρ with change in composition, the measured data have been augmented with a calculated density for the magnesioriebeckite end member (Fig. 6). Dashed lines indicate uncertain trends; as in Fig. 3, the dashed 2V and $(\gamma - \alpha)$ curves are calculated from the most likely values of α , β , and γ

Extrapolated values for the optical parameters of the pure magnesioriebeckite are in good agreement with measurements on synthetic counterparts, viz.,

 $\alpha = 1.654 \pm 0.003$ $\gamma = 1.672 \pm 0.003$ $c \land \alpha, \beta$ or $\gamma = 4^{\circ} - 13^{\circ} \pm 4^{\circ}$ (av. of 7) (ERNST, 1960, Table 10, runs with hematite-magnetite buffer only; ERNST, 1963, p. 245-247; COLVILLE et al., 1966, Table 3) $\begin{array}{ll} \beta = 1.67_1 & \gamma = 1.67_2 & c \wedge \alpha = 32^{\circ} \text{ (Fig. 4, also see p. 87 this work)} \\ 2 V = (+) & 0 - 20^{\circ} & (\gamma - \alpha) = 0.02 & b = \gamma \text{ O.P. } \perp (010) \text{ and } ca. \|c. \ \end{array}$ $\alpha = 1.65_{5}$

 $[\]rho = 3.15$

^{*} Microprobe analysis indicates a Na-poor and Ca-rich phase is strongly segregated within the amphibole suggesting presence of minute epidote inclusions.

There is only fair agreement with predictions from linear regression formulae (WINCHELL, 1963, Table 4).

HORI (1954) and WINCHELL (1961, Table 4) have shown that substitution of equal numbers of actions per unit volume into clinopyroxenes increases R.I. in the order of Mg, Mn, Fe'' and Ti. An analogous effect is observed in these amphiboles although the effect of Mn and Ti on R.I. cannot be confidently appraised relative to that of the other metals in the list. Recall that R.I. increases with increased total Fe''', Ti, Fe'' and Mn (Fig. 3). Note that a slight increase in n



Fig. 5. Variation in cell dimensions, cell volume and density in the glaucophane-riebeckite series. Solid numbered points correspond to new data in Table 3. Lettered points are ERNST's measurements (1963, Table 10) on amphiboles described by BANNO (1959) (a and b) and PHEMISTER *et al.* (1950) (e); PAPIKE and CLARK (1966) (n); and ERNST (1964, Table 4, E4 GL and E16 GL) (p and s). Open square is measured value rather than the calculated value. Chemical analysis of (s) was corrected for 4.2% epidote impurity and recalculated to 100.28 total. Chemical analyses and ϱ are calculated for 24 (O, OH, Cl, F) per half-unit cell

associated with the $a(\bullet)$ and $b(\times)$ axes results from substitution of Mg₃Fe₂^{''} for Fe₃^{''}Al₂ (Fig. 4). Thus, there is a greater increase from the substitution of Fe^{'''} for Al^{VI} than Fe^{''} for Mg. The situation is reversed for the index nearest the c axis (\blacktriangle).

The optic angle varies widely with small changes in composition; its magnitude is not readily related to particular substitutions.

Variation in Cell Parameters

Glaucophane-Riebeckite. Cell dimensions, volumes and calculated densities of amphiboles are plotted versus composition in Fig. 5. Cell parameters indicated by open circles were measured by ERNST (1963, Table 10) on previously analyzed amphiboles (a and b), BANNO (1959); (e) PHEMISTER *et al.* (1950). Densities were calculated from these data; stoichiometry is based on 24 (O, OH, F, Cl) computations. The X site of all contains nearly 2.00 cations per half-unit cell and Ca is a minor constituent except in No. 6^* , p and s. Other amphiboles measured by ERNST but not included in Fig. 5 either contain large proportions of the other two end members or have analyses whose totals depart sufficiently from 100.0 to be suspect, e.g., E13 GL (ERNST, Table 4, 1964), PALACHE and WARREN'S No. 12 (PALACHE and WARREN, 1911) and SWITZER'S riebeckite No. 11 (ERNST'S numbers in Table 10, 1963). Amphiboles No. 10 and No. 11 (Table 3) are not included because AX = 2.66 and 2.63 respectively, and because their fluorine and chlorine contents are high. Both of these factors result in smaller cell dimensions, particularly b_0 and c_0 than would otherwise be measured (FROST, 1963). Comparison of the parameters of three iron-rich amphiboles included (Nos. 9, 10 and 11, Table 3) also tend to verify FROST'S observation (p. 381) that increased Ca and Fe'' is associated with increases in b_0 but not c_0 . Note for example that on the basis of F and Na contents (Table 2) it might be expected that amphiboles Nos. 9, 11 and 10 are in order of decreasing b_0 and c_0 dimensions. This in fact is true except for the b_0 dimension of No. 11, the amphibole which has the highest combined Ca and Fe" content.

Two crossites containing somewhat more Fe'' and Ti than required by a mixture of Gl and Ri end members depart slightly from the otherwise linear trends (Fig. 5). Extrapolated parameters for glaucophane and riebeckite end members are given in Table 5, together with ERNST'S data for synthetic counterparts (1962, 1963,

	End member glaucophane C 2/m	Synthetic g (ERNST, 19 COLVILLE e Table 2) C 2/m	glaucophane 63, Table 8; <i>t al.</i> , 1966,	End member riebeckite C 2/m	Synthetic riebeckite (ERNST, 1962, Table 10; COLVILLE <i>et al.</i> , 1966, Table 2) C 2/m
		I (av. of 10)	II (av. of 8)		(av. of 15)
a_{α} (Å)	9.50	9.75	9.64	9.78	9.73
b_0 (Å)	17.67	17.91	17.73	18.03	18.06
c_0 (Å)	5.29	5.27	5.28	5.34	5.33
β̈́́	103.7°	102.8°	103.6°	103.5°	103.3
$a_0 \sin \beta$	9.22	9.518	9.37	9.51	9.47
V (Å) ³	864	897	877	918	913
e (cale)	3.03	—	<u> </u>	3.39_{5}	—

Table 5. Comparison of cell dimensions of synthetic end members and extrapolated values for glaucophane and riebeckite

COLVILLE et al., 1966, Table 2). Agreement is very good in the case of riebeckite, but poor for glaucophane irrespective of which of ERNST's proposed polymorphs (I and II) is considered. The possibility of gross error in measurement of cell parameters is not likely since ERNST'S x-ray data for natural amphiboles (1963, p. 258) included in Fig. 5 (open circles) and the new data presented here (solid circles) are consistent.

The differences in parameters of the Gl end member and synthetic glaucophane lie primarily in the a_0 dimension and the related cell volume. If occupation of the M₂ site by Al to the exclusion of other cations produces minimum $a_0 \sin \beta$

* See footnote p. 84.

(the distance between silica chains) and a_0 dimensions (ERNST, 1963), then it is likely that the natural end member is a completely ordered form, whereas both the synthetic varieties (glaucophane I and II) are disordered counterparts that differ from each other in degree. Recent study of a natural glaucophane (Gl₈₀Ri₂₀) has in fact shown that the structure is ordered and that M_2 is occupied chiefly by Al (PAPIKE and CLARK, 1966).

A similar but less pronounced order-disorder relation might be expected in riebeckites. The average ionic radius at $M_2 = Fe^{\prime\prime\prime}$, $Fe^{\prime\prime}$ in a disordered structure is greater than that in an ordered structure $M_2 = Fe^{\prime\prime\prime}$ (Fe^{\prime\prime\prime} is 0.64 Å; Fe^{\prime\prime} is 0.74 Å); hence $a_0 \sin \beta$ should vary depending on the occupancy of the site.

Magnesioriebeckite-Ferroglaucophane. Parameters for members of the magnesioriebeckite-ferroglaucophane group are shown in Fig. 6. In addition to new data (solid circles) ERNST'S x-ray data (1963, Table 10) (open cricles) are plotted against compositions which were calculated on the basis of 24 (O, OH, Cl, F) from analyses in the literature. Calculated densities have been excluded for those amphiboles whose reported water content departs appreciably from the ideal. Unaccountably, one magnesioriebeckite for which data are available [MIYASHIRO and IWASAKI, 1957 (m, see Fig. 1); ERNST, 1963, Table 10, No. 5] does not fit into this scheme although the analysis is good and its composition indicates it is nearly a binary solid solution (also see p. 83).

Agreement between parameters measured on synthetic magnesioriebeckite and extrapolated values for the end member (Table 6) is very good.

	End member magnesio- riebeckite C 2/m	Synthetic magnesioriebeckite (ERNST, 1963, Table 3; COLVILLE <i>et al.</i> , 1966, Table 2) C 2/m
		(av. of 7)
a_0 (Å)	9.76	9.73
b_0 (Å)	17.97	17.95
c_0 (Å)	5.31	5.30
β	103.9°	103.3°
$a_0 \sin \beta$ (Å)	9.47	9.47
V (Å ³)	904	901
ę (calc)	3.15 (?)	

Effect of Cation Substitutions on Cell Parameters

Inspection of Figs. 5 and 6 indicates the following:

1. Cell dimensions increase as per cent of the riebeckite molecule increases, i.e., as $Fe_3''Fe_2'''$ substitutes for Mg_3Al_2 .

2. The increase in parameters associated with Fe'' substitution for Al^{VI} is much greater than the increase associated with Fe'' substitution for Mg; otherwise the magnitude of slopes in Figs. 5 and 6 would not be similar. [Slopes of a_0 , b_0 , and c_0 $a_0 \sin\beta$ are slightly greater for data in Fig. 5 than in Fig. 6, whereas slope of β angle is less in Fig. 5 than in Fig. 6. This might be anticipated from consideration

of ionic radii, viz., the difference betweel Al''' (0.52 Å) and Fe''' (0.64 Å) is greater than between Mg (0.67 Å) and Fe'' (0.74 Å).]

3. Fe'' substitution for Mg increases the b_0 dimension more than a_0 and $a_0 \sin \beta$. The effect can be seen in the greater difference in slopes associated with $Mg_3Al_2 \Leftrightarrow Fe'_3Fe''_2$ and $Fe''_3Al_2 \Leftrightarrow Mg_3Fe''_2$ in the case of b_0 , than a_0 and $a_0 \sin \beta$. Analogous effects on b_0 , a_0 and $a_0 \sin \beta$ have been observed for clinopyroxenes in which the Ca content is similar (BROWN, 1960, p. 24; WINCHELL and Tilling, 1960, Table 3—5; and especially VISWANATHAN, 1966, p. 433—435).



Fig. 6. Variation in cell dimensions, cell volume and density in magnesioriebeckite-ferroglaucophane series. Solid numbered points correspond to new data in Table 3. Lettered points are ERNST'S (1963) measurements on amphiboles described in the literature as follows: (j) WHITTAKER (1949); (k) ERNST (1960); (l) ERNST (1963); (d) SWITZER (1951); (b) crossite, BANNO (1959). Formula and ρ calculated from chemical analyses on the basis of 24 (O, OH, Cl, F)

4. The negligible change in the c_0 dimension in both series is to be expected since the length of the silica chain is not greatly influenced by cation substitution in M_4 , $M_1+M_3+M_2$ in either amphiboles or pyroxenes. Substitutions of Al^{IV} for Si has small effect contrary to observations on hornblendes (BINNS, 1965, p. 314).

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