

*The mineralogy of metamorphosed basic rocks from the Willyama Complex, Broken Hill district, New South Wales. PART I. Hornblendes*

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*Summary.* The typical hornblendes of metabasic rocks in the Willyama Complex change from bluish-green to deeply coloured brownish varieties with increase in metamorphic grade. Chemical analyses and optical properties of 23 representative hornblendes are interpreted as showing this colour change to reflect steady increase in titanium content of the hornblendes with increase in grade. High-grade hornblendes also differ from those of lower grade in that tetrahedral aluminium in the Z sites is balanced to an increased extent by alkalis entering the A site rather than by octahedral aluminium entering the Y site. Comparison between theoretical and measured densities of Willyama hornblendes suggest that a calculation based on 23 oxygen anion provides closer approximations than a 24 (O, OH, F) calculation to their structural formulae.

THIS paper discusses common hornblendes formed in metamorphosed basic rocks during the Willyama Metamorphism, the major period of recrystallization in the Willyama Complex of the Barrier Ranges, far-western New South Wales.

Three zones of progressive regional metamorphism have been recognized in the Willyama Complex (Binns, 1962, 1964). *Zone A* is characterized by amphibolites containing bluish-green hornblende and by sillimanite-bearing muscovite-biotite pelitic schists. In *Zone B* the hornblendes of basic amphibolites are typically brown-green in colour, and the pelitic lithology is orthoclase-bearing sillimanite gneiss. *Zone C*, the highest grade zone, is marked by orthopyroxene-bearing basic gneisses containing very deeply coloured hornblendes and by pelitic gneisses similar to those in *Zone B*. *Zone C* has been divided into *Subzone Ci* (2-3 miles wide), the lower-grade portion lying close to the *orthopyroxene isograd* dividing *Zone C* from *Zone B*, and *Subzone Cii*, the higher-grade portion lying further to the south-east (see Binns, 1962, fig. 1).

Twenty hornblendes from metabasic rocks or their garnet-bearing

associates have been analysed with the dual aim of investigating possible grade-dependent changes in their chemical composition and of evaluating factors underlying variation in their colours. Two additional analysed specimens (H39, H40, data previously unpublished) were generously provided for this study by Dr. T. G. Vallance; Brown (1922) listed a further analysed specimen (H25). Dr. I. A. Brown kindly supplied a sample of the latter on which the writer has determined the optical properties quoted in table I.<sup>1</sup>

Petrographical notes and chemical analyses for the host rocks are given by Binns (1964).

### *Optical and Physical Properties*

*Colour.* Increase in metamorphic grade is reflected by a progressive deepening in absorption colours of the Willyama hornblendes and by a change in their colour along  $\gamma$  from blue-green to brown.

Variation in colour exists within each metamorphic zone. Although the typical  $\gamma$  absorption colour of Zone A hornblendes is either blue-green or green with a distinctly bluish tint, some greyish-green, green, and rare brownish-green varieties also occur. In Zone B, most hornblendes are brown-green along  $\gamma$  but occasional green and very rare bluish-green types are found. The colour of Zone B hornblendes tends to deepen as the orthopyroxene isograd is approached. Deep brown-green, olive-green and reddish-brown are the usual  $\gamma$  colours in Zone C, but a slight bluish tint may be detected in hornblendes from certain magnetite-bearing basic gneisses. Most hornblendes from all three zones show a brown-green absorption colour along  $\beta$  and a pale yellow-green along  $\alpha$ . The variations in absorption colours are illustrated by those of the analysed hornblendes given in table I. Tungsten light with a blue 'sunlight' filter has been used when observing these colours.

Many workers have examined relationships between colour and composition of hornblendes. By heating common green hornblende at about

<sup>1</sup> Edwards (1958) listed an analysis of a hornblende from Broken Hill (Subzone Ci) containing 1.40 wt. %  $P_2O_5$ . The high phosphorus content is accompanied by relatively low alumina (8.29 wt. %  $Al_2O_3$ ). In similar hornblendes analysed by the writer and by W. H. Herdsman, phosphorus is present in trace proportions only; consequently the analysis quoted by Edwards must be held suspect. If it is assumed that phosphorus has been grossly overestimated, and a correction is applied to the figure for alumina, the chemical composition obtained for Edwards' hornblende compares favourably with others quoted in the present work. When the modified analysis is expressed as a structural formula, it conforms to the relationships for Subzone Ci hornblendes discussed below. However, in view of the uncertainty attached to this analysis, it has not been incorporated in the following discussion

TABLE I. Chemical analyses, atomic ratios to 23 oxygen (anhydrous basis), and physical properties of Wilyama hornblendes

Zone	H1 Cl	H2 Cl	H3 Cl	H4 Cl	H6 Cl	H10 Cl*	H11 Cl	H12 Cl	H17 Cl*	H18 Cl	H25 Cl	H26 B*
SiO <sub>2</sub>	44.75	44.76	40.79	44.73	43.16	40.85	44.38	42.21	40.88	42.62	44.27	42.25
TiO <sub>2</sub>	1.77	1.51	2.03	2.16	1.90	1.95	1.84	2.20	1.84	2.04	2.36	1.79
AlO <sub>3</sub>	9.76	9.84	10.97	10.67	11.25	11.81	9.96	10.75	11.69	11.32	9.56	11.47
Fe <sub>2</sub> O <sub>3</sub>	1.58	1.53	3.38	2.37	2.08	3.61	2.24	3.01	4.85	2.43	0.11	2.04
FeO	17.88	19.16	22.62	13.53	15.70	21.56	16.55	18.96	18.88	15.52	17.41	20.29
MnO	0.32	0.25	0.46	0.26	0.15	0.18	0.29	0.35	0.33	0.20	n.d.	0.66
MgO	9.42	8.95	5.13	11.74	10.24	5.12	10.13	7.64	6.45	10.17	10.83	6.08
CaO	11.16	11.00	10.46	10.92	11.27	10.90	10.93	10.70	11.79	11.42	11.30	11.73
Ni <sub>2</sub> O	1.44	1.37	1.91	1.86	1.47	1.64	1.58	1.69	0.95	1.55	1.19	1.29
K <sub>2</sub> O	0.42	0.21	0.77	0.14	0.72	0.47	0.21	0.90	1.49	1.69	0.75	1.00
H <sub>3</sub> O+	1.59	1.60	1.30	1.49	1.70	1.72	1.56	1.53	1.61	1.16	2.19	1.49
H <sub>2</sub> O-	0.02	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.04	0.04	0.04
P <sub>2</sub> O <sub>5</sub>	0.02	0.02	n.d.	0.02	n.d.	n.d.	0.02	n.d.	n.d.	0.00	n.d.	n.d.
Total	99.63	100.20	99.82	99.89	99.64	99.81	99.70	99.94	100.26	100.16	100.01	100.13
F (wt. %) <sup>†</sup>	0.2	0.5	—	nil	0.08	—	0.05	0.1	0.8	—	—	0.15
Si	6.71	6.70	6.33	6.56	6.45	6.30	6.62	6.42	6.25	6.36	6.65	6.45
Al <sup>IV</sup>	1.29	1.30	1.67	1.44	1.55	1.70	1.38	1.58	1.75	1.64	1.85	1.55
Al <sup>VI</sup>	0.43	0.43	0.33	0.40	0.43	0.45	0.36	0.34	0.37	0.35	0.33	0.51
Ti	0.20	0.17	0.23	0.24	0.22	0.23	0.21	0.25	0.21	0.23	0.25	0.20
Fe <sup>+++</sup>	0.18	0.17	0.39	0.26	0.23	0.43	0.25	0.35	0.50	0.27	0.02	0.24
Fe <sup>++</sup>	2.17	2.40	2.94	1.66	1.95	2.78	2.06	2.41	2.42	1.94	2.18	2.58
Mg	0.04	0.03	0.06	0.03	0.02	0.02	0.04	0.05	0.05	0.03	—	0.08
Mn	2.10	1.99	1.18	2.56	2.28	1.17	2.25	1.73	1.47	2.26	2.44	1.38
Ca	1.79	1.76	1.73	1.72	1.80	1.80	1.75	1.75	1.94	1.83	1.82	1.92
Na	0.41	0.40	0.58	0.53	0.43	0.30	0.47	0.49	0.29	0.45	0.84	0.38
K	0.07	0.04	0.15	0.03	0.14	0.09	0.04	0.17	0.29	0.32	0.14	0.19
ΣV	5.12	5.19	5.13	5.15	5.13	5.08	5.17	5.13	5.02	5.08	5.22	4.99
ΣX	2.27	2.20	2.46	2.28	2.37	2.33	2.26	2.41	2.33	2.60	2.30	2.49
Σ <sup>††</sup>	0.30	0.34	0.45	0.30	0.43	0.35	0.35	0.42	0.51	0.59	0.48	0.39

HORNBLENDES FROM NEW SOUTH WALES

No.	H27	H28	H29	H30	H34	H35	H36	H37	H38	H39	H40
Zone	B	B*	B	B	A	A	A*	A	A*	A	A*
SiO <sub>2</sub>	44.55	42.97	45.24	44.28	45.53	41.78	40.43	42.60	40.85	44.06	39.62
TiO <sub>2</sub>	1.39	1.70	1.26	1.53	0.90	1.26	1.25	1.24	0.65	1.44	1.08
Al <sub>2</sub> O <sub>3</sub>	10.52	11.43	10.77	10.24	11.06	12.50	12.62	11.84	14.45	11.03	14.64
Fe <sub>2</sub> O <sub>3</sub>	1.67	1.74	0.41	2.22	2.63	2.30	4.24	4.89	5.59	1.68	4.33
FeO	18.75	19.67	19.33	19.53	13.96	21.99	22.15	17.03	18.53	17.27	18.73
MnO	0.33	0.46	0.75	0.37	0.34	0.70	0.28	0.64	0.35	0.18	0.32
MgO	8.73	7.20	8.90	8.18	9.52	4.51	3.80	6.65	5.11	9.03	5.08
CaO	10.60	11.17	10.21	10.40	10.98	11.33	11.60	11.30	10.86	11.02	11.26
Na <sub>2</sub> O	1.05	1.24	1.34	1.37	0.92	1.17	0.89	0.93	1.48	1.68	1.53
K <sub>2</sub> O	0.39	0.59	0.42	0.24	0.39	0.97	1.01	0.57	0.61	0.44	1.10
H <sub>2</sub> O <sup>+</sup>	2.02	1.74	1.50	1.45	1.82	1.57	1.76	1.78	1.60	2.18	2.09
H <sub>2</sub> O <sup>-</sup>	0.05	0.02	0.00	0.00	0.00	0.00	0.05	0.00	0.02	0.16	0.12
P <sub>2</sub> O <sub>5</sub>	0.02	n.d.	0.00	n.d.	n.d.	0.06	n.d.	0.05	0.00	tr.	tr.
Total	100.07	99.93	100.13	99.81	100.05	100.14	100.08	99.52	100.10	100.17†	99.90†
F (wt.%)†	—	—	—	—	—	—	0.9	0.4	—	0.8	1.0
Si	6.70	6.51	6.74	6.66	6.73	6.42	6.27	6.46	6.21	6.60	6.10
Aliv	1.30	1.49	1.26	1.34	1.27	1.58	1.73	1.54	1.79	1.40	1.90
Alvi	0.56	0.55	0.63	0.47	0.66	0.68	0.58	0.57	0.80	0.54	0.75
Ti	0.16	0.19	0.14	0.17	0.10	0.15	0.15	0.15	0.07	0.16	0.12
Fe+++	0.19	0.20	0.05	0.25	0.29	0.27	0.49	0.56	0.64	0.19	0.50
Fe++	2.35	2.49	2.41	2.46	1.97	2.82	2.87	2.16	2.35	2.16	2.41
Mn	0.05	0.06	0.10	0.05	0.04	0.09	0.04	0.08	0.04	0.02	0.04
Mg	1.95	1.62	1.97	1.83	2.10	1.86	1.88	1.50	1.16	2.01	1.17
Ca	1.70	1.81	1.63	1.68	1.74	1.86	1.93	1.84	1.77	1.77	1.86
Na	0.31	0.37	0.39	0.40	0.27	0.35	0.27	0.27	0.44	0.48	0.48
K	0.07	0.12	0.08	0.04	0.07	0.19	0.21	0.11	0.12	0.09	0.22
ΣY	5.26	5.11	5.30	5.23	5.16	5.04	5.01	5.02	5.06	5.08	4.99
ΣX	2.08	2.10	2.10	2.12	2.08	2.40	2.41	2.22	2.33	2.34	2.54
F	0.30	0.33	0.33	0.26	0.14	0.34	0.36	0.10	0.22	0.27	0.40

TABLE I (cont.)

Zone	H1	H2	H3	H4	H6	H10	H11	H12	H17	H18	H25	H26
CI	CI	CI	CI	CI	CI	CI*	CI	CI	CI*	CI	CI	B*
$\alpha$	PYG	PYG	PYG	PS	PYG	YG	PYG	YG	PG	YG	PS	PYG
$\beta$	DBrG	DBrG	VDGBr	DRBr	DOG	DBrshG	MGBr	VDGishBr	MG	DBrG	DRBr	DGishBr
$\gamma$	DBrshG	DOG	VDBrshG	DRishBr	DG	DG (BT)	MBrshG	VDG	DG (BT)	DBrshG	DRishBr	DBrG
$\alpha$	1.661	1.663	1.685	1.658	1.669	1.679	1.661	1.677	1.679	1.666	1.663	1.672
$\beta$	1.675	1.678	1.700	1.671	1.683	1.694	1.675	1.682	1.694	1.682	1.676	1.685
$\gamma$	1.686	1.689	1.711	1.683	1.694	1.704	1.686	1.702	1.704	1.692	1.688	1.696
$\Delta$	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.025	0.026	0.025	0.024
$2V_x^\circ$	78	77	67	84	72	64	81	70	65	73	82	75
$\gamma \cdot c^\circ$	12	14	12	14	11	14	12	12	13	12	13	11
Dispersion	weak	weak	strong	mod.	weak	mod.	weak	mod.	mod.	strong	mod.	weak
( $t > v$ )	—	3.293¶	3.364	3.230	3.245††	3.353**	3.260¶	3.316	—	—	—	3.324¶
D(gm/cc)	9.836	9.821	9.857	9.823	9.858	9.845	9.825	9.864	9.880	—	—	9.876
$a$ (Å)	18.098	18.094	18.130	18.050	18.109	18.113	18.082	18.119	18.115	—	—	18.107
$b$	5.308	5.309	5.321	5.303	5.318	5.320	5.308	5.319	5.322	—	—	5.320
$c$	104.86	104.82	104.84	104.85	104.88	104.88	104.83	104.92	105.00	—	—	105.05
$\beta^\circ$	9.507	9.501	9.529	9.495	9.527	9.514	9.498	9.532	9.544	—	—	9.537
$\alpha \sin \beta$	913.3	912.6	919.2	908.8	917.5	916.8	911.6	918.6	920.0	—	—	918.6
$V$ (Å <sup>3</sup> )	100ΣFe/	(Mg+ΣFe)	53.2	74.2	49.1	73.4	51.1	61.9	66.9	49.8	47.4	67.8

No.	H27	H28	H29	H30	H34	H35	H36	H37	H38	H39	H40
Zone	B	B*	B	B	A	A	A*	A	A*	A	A*
Absorption colours											
$\alpha$	PYG	PYG	PYG	PYG	PYG	PYG	PYG	PYG	PYG	PYG	YG
$\beta$	GishBr	DBr	GishBr	DBr	BrshG	DBrG	DOG	DG	DOG	DBrshG	DG
$\gamma$	BrG	DGBr	BrG	DGishB	G (BT)	DBIG	DBIG	DBIG	DBIG	DG (BT)	DBIG
$\alpha$	1-659	1-661	1-660	1-665	1-653	1-676	1-683	1-673	1-677	1-664	1-685
$\beta$	1-873	1-875	1-873	1-880	1-666	1-693	1-699	1-688	1-691	1-678	1-701
$\gamma$	1-684	1-687	1-685	1-691	1-678	1-701	1-708	1-697	1-702	1-689	1-710
$\lambda$	0-025	0-026	0-025	0-026	0-025	0-025	0-025	0-024	0-025	0-025	0-025
$2V_x^\circ$	80	78	79	77	85	65	64	67	75	78	61
$\gamma_x^\circ$	14	14	14	13	15	13	14	14	13	14	13
Dispersion	weak	weak	v. weak	weak	mod.	mod.	strong	strong	mod.	mod.	strong
( $r < v$ )	3-268	3-304	—	—	3-234¶	—	3-372¶	—	—	—	—
D(gm/cc)	9-835	9-845	—	9-825	9-822	—	9-864	9-827	—	9-832	9-844
$a$ (Å)	19-085	18-081	—	18-076	18-072	—	18-130	18-081	—	18-065	18-091
$b$	5-312	5-312	—	5-312	5-331	—	5-324	5-324	—	5-314	5-325]
$c$	104-85	104-85	—	104-83	104-85	—	104-95	104-96	—	104-84	105-03]
$\alpha \sin \beta$	9-506	9-516	—	9-497	9-494	—	9-530	9-494	—	9-504	9-507
$V$ (Å <sup>3</sup> )	913-2	914-0	—	912-0	912-2	—	921-0	913-8	—	912-2	915-9
100 $\Sigma Fe$ / (Mg + $\Sigma Fe$ )	57-1	65-9	56-4	60-1	52-3	75-5	79-4	65-1	72-3	54-1	71-7

\* Indicates hornblendes that coexist with garnet. † CO<sub>2</sub> nil. ‡ Semiquantitative spectrographic analysis by R. S. Allen, Cambridge.  
 § Abbreviations: P, Pale; D, deep; M, moderately deep; YD, very deep; S, straw; Y, yellow; G, green; O, olive; R, red; Br, brown; Bl, blue; (BT), bluish tinge; Brsh, brownish, &c. \*\*  $\pm 0-002$ . †† 'Edenite alkalis', as defined in text. ¶  $\pm 0-003$ . ††  $\pm 0-006$ .

Analyses: H25; I. A. Brown (Brown, 1922). H39, H40; W. H. Herdsman, Glasgow (1954). H18, H29, H35, H38; W. H. Herdsman, Glasgow (1962), total iron redetermined by R. A. B.; remainder, R. A. Binns. Notes on host rocks given by Binns (1964).

800° C, Barnes (1930) produced a brown hornblende in which much iron had been oxidized to the ferric state and hydrogen was lost from the hydroxyl group. His products have natural analogues in the oxyhornblendes of certain lavas and scoriae that appear to have undergone exothermic oxidation reactions during extrusion. However, it is doubtful whether oxidation of this type has taken place in the majority of igneous and metamorphic hornblendes (see discussion below). In hydroxyl-rich metamorphic amphiboles Seitsaari (1953) correlated high ferric iron contents with blue-green coloration along  $\gamma$ . Many kaersutites possess relatively little ferric iron (*cf.* Wilkinson, 1961, table 3), and their deep red-brown colour consequently appears related to their high titanium content. Goldschmidt (1958) suggested that red-brown colours indicate presence of trivalent titanium. Similar relationships between colour and the content of ferric iron and titanium are suggested for the Willyama hornblendes by the data presented in fig. 1. High titanium contents accompanied by low ferric iron correlate with red-brown colours along  $\gamma$  while the reverse situation results in a blue-green colour in that direction. Hornblendes with intermediate contents of these two components vary in colour through green and brown-green depending on the balance between titanium and ferric iron. Fig. 1 also shows that, although ferric iron content is highest in certain Zone A hornblendes, the colour trend in Willyama hornblendes is influenced principally by a steady increase in content of titanium with increase in metamorphic grade.

Similar colour changes in the hornblendes of basic rocks undergoing progressive metamorphism have been reported from the Scottish Highlands, the Abukuma Plateau of Japan, the Lizard area of Cornwall, and the Adirondack Mountains, New York (Wiseman, 1934; Shidō and Miyashiro, 1959; Green, 1964; Engel and Engel, 1962), and also in some contact metamorphic aureoles (Flett, 1913; Binns, 1965).

There is no correlation between depth of colour and extent of iron-magnesium replacement. The more deeply coloured hornblendes are characterized by a higher total content of ferric iron and titanium, and also by higher occupation of the *A* site, particularly by potassium. However, although the latter feature would provide a better explanation of the trend towards deeper colours at higher grades (see below), it is uncertain whether alkalis in the *A* site can influence absorption colour. By way of comparison the very deeply coloured barkevikites of undersaturated alkaline igneous rocks deserve mention. Some barkevikites contain ferric iron and titanium in quantities comparable to

those in less deeply coloured common hornblendes, but they differ from the latter by the almost-complete occupation of their *A* site with alkali cations.

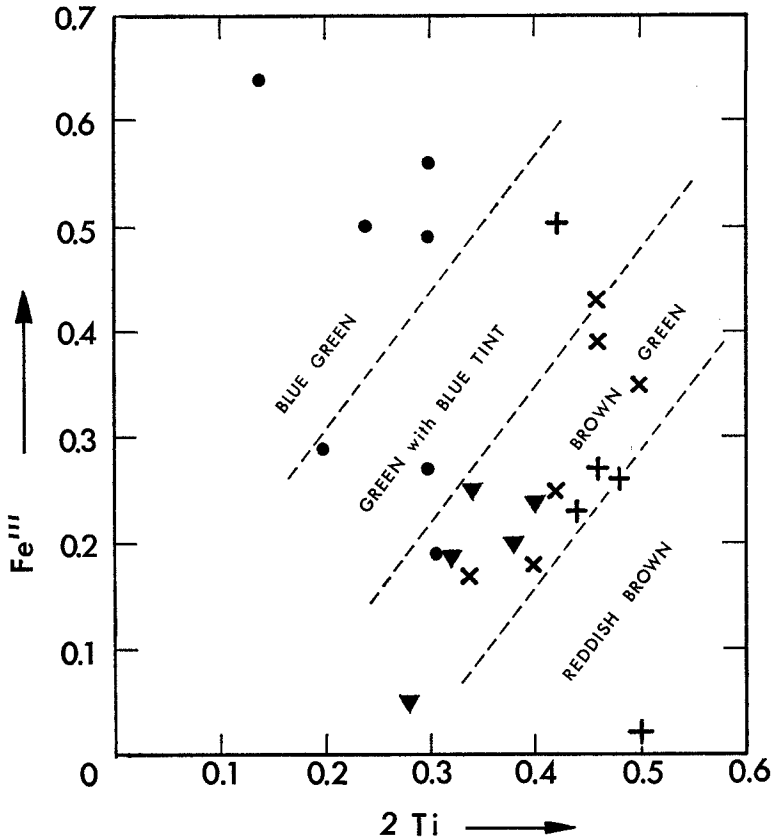


FIG. 1. Titanium content plotted against that of ferric iron in Willyama hornblendes, showing dependence of  $\gamma$  absorption colour upon composition and also the progressive increase in titanium content with increase of metamorphic grade.

Symbols: ● Zone A, ▼ Zone B, × Subzone Ci, + Subzone Cii.

*Optical properties* of the analysed hornblendes are listed in table I. Refractive indices and extinction angles were measured in sodium light on grains of the required orientation plucked from thin sections. The R.I. values are considered accurate to within  $\pm 0.002$ . Optic axial angles were measured in sodium light on a 4-axis Universal Stage,



using orthoscopic techniques on grains with both optic axes accessible. Several grains of each analysed hornblende were measured, the reproducibility of  $2V_\alpha$  being  $\pm 2^\circ$ . Degree of dispersion was estimated from the colour fringes in off-centred acute bisectrix figures.

Fig. 2 shows how refractive indices increase and optic axial angles decrease with increase in iron content of the hornblendes (expressed as  $\Sigma \text{Fe}/(\text{Mg} + \Sigma \text{Fe})$ ). There is considerable scatter of points on the diagram, due presumably to the complex composition of the hornblendes and the influence upon optical properties of components such as aluminium and titanium. The birefringence of Willyama hornblendes is constant at 0.025, and extinction angles are consistently low ( $11\text{--}15^\circ$ ). Dispersion is more marked in iron-rich specimens.

The following ranges observed in  $\beta$  indicate that within each metamorphic zone similar variations occur in iron content of the hornblendes: Zone A, 1.666–1.701; Zone B, 1.665–1.693; Zone C, 1.664–1.700.

*Density* was determined on samples of 90–150-mesh size by weighing between 1 and 8 grams immersed in distilled water under controlled temperature conditions in a calibrated 10 ml relative-density bottle. Corrections were applied for the density of water at the temperature of measurement. Accuracy of measurement depends largely upon the quantity of specimen used and the care taken to exclude trapped air. Several density measurements of hornblendes H4, H12, H34, and H36 were made, excellent consistency of results being obtained. Fig. 2 shows that density increases somewhat irregularly with iron content.

The *cell constants* of Willyama hornblendes quoted in table I were kindly determined by Mr. M. T. Frost at the University of Manchester. Details of technique and accuracy are given by Frost (1963). In accordance with Frost's observations on other amphiboles, *c* shows the expected tendency to increase with increased substitution of aluminium for silicon in the Z site of the amphibole chains. Cell volume, *b*, and *a* sin  $\beta$  increase with iron content, but the correlation is poor. The angle  $\beta$  is consistently higher in those hornblendes that have more calcium in their X group.

*Exsolution phenomena.* Those hornblendes with large excesses in their Y group cations ( $\Sigma Y = 5.15\text{--}5.30$ ) and calcium less than 1.75 cations per formula unit frequently show (001) exsolution plates of colourless or very pale-green cummingtonite, up to  $5\ \mu$  thick. These are accompanied in some specimens by very narrow (100) plates, visible only when normal to the plane of the thin section. Although they are too narrow to permit optical substantiation of their orthorhombic symmetry, analogy with

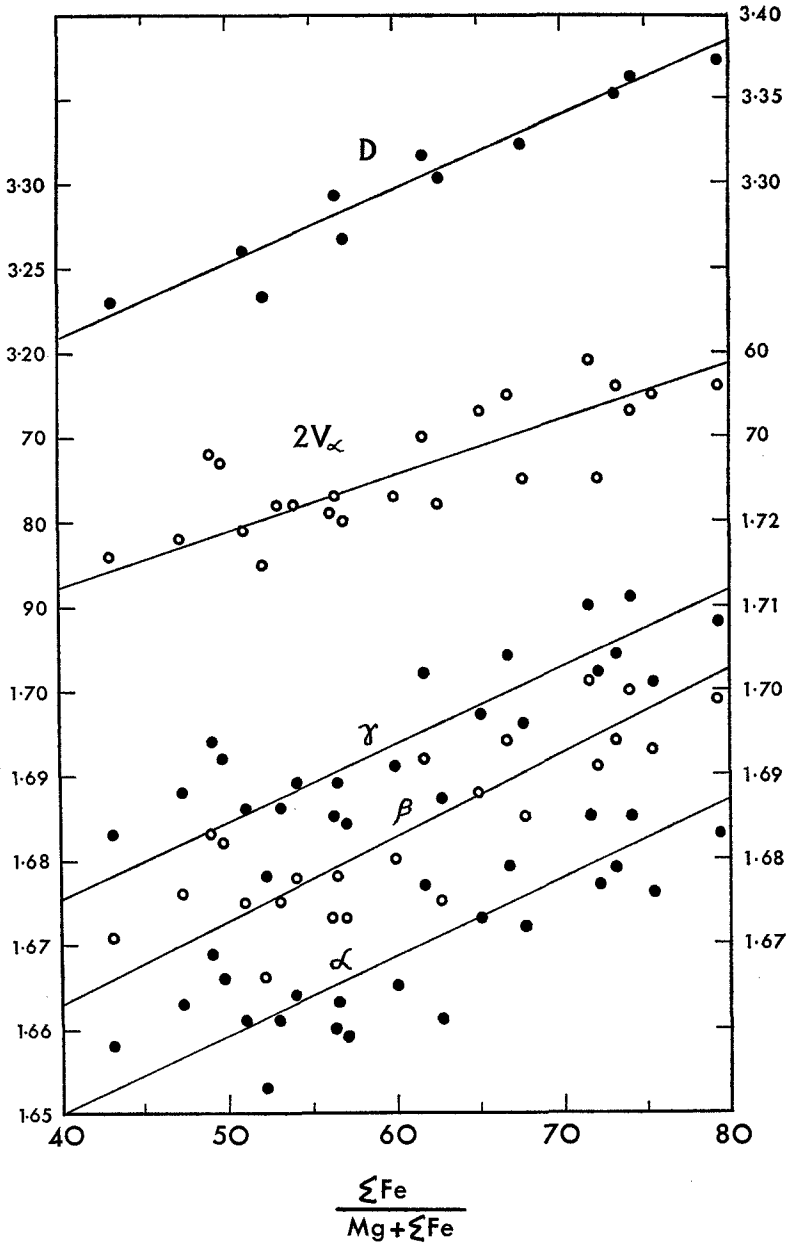
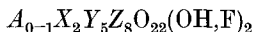


FIG. 2. Variation of refractive indices, optic axial angle, and density with iron content in the Willyama hornblendes.

exsolution phenomena in clinopyroxene suggests that the second group of lamellae may be anthophyllite. Hornblende H29 ( $\Sigma Y = 5.30$ ) shows particularly well-developed exsolution lamellae of both types.

#### *Chemical Variations*

*Calculation of structural formulae.* Inaccuracies in the determination of  $H_2O^+$  or the omission of fluorine from a chemical analysis can impart substantial errors to amphibole structural formulae calculated on the basis of 24 (O, OH, F, Cl). In a formula expressed as



such errors accumulate in the partly occupied *A* site. An error of 1 wt. %  $H_2O^+$  or neglect of its equivalent in fluorine in an average hornblende analysis can increase by some 10 % (to 5.5 or more) the sum of those cations normally expected to occupy the five *Y* sites, and as a consequence the number of cations in the *A* group of the formula may be almost doubled. Excess beyond five in the total of *Y* cations is commonly encountered in structural formulae of analysed hornblendes quoted in the literature, and in many examples there is insufficient space unoccupied by calcium in the *X* sites available to accommodate this excess as so-called 'cummingtonite solid solution'. Errors in the structural formulae arising from inaccurate water determinations might be suspected in such cases.

These difficulties are avoided by calculating amphibole structural formulae on the basis of 23 oxygen anions exclusive of those combined with hydrogen, while assuming that two hydroxyl plus halogen ions are really present. This procedure gives a formula independent of possible analytical errors in  $H_2O^+$  or non-determination of fluorine, &c. An example showing the differences between structural formulae calculated by the two alternative procedures is given in table II. Corresponding differences arise in theoretical densities computed from cell dimensions and the alternative structural formulae. The close similarity between observed densities of Willyama hornblendes and their theoretical densities calculated using the 23 oxygen formulae (table III) strongly favours the 23 oxygen method as the basis of calculating amphibole structural formulae.

The main objection to the 23 oxygen method is that it ignores the possibility of hydrogen deficiency such as occurs in the oxyhornblendes. However, oxyhornblende is a comparatively rare mineral requiring special conditions of formation (Wilkinson, 1961). Many metamorphic

hornblendes (e.g. H29, table I) do not contain sufficient ferric iron to balance their apparent hydrogen deficiency in the manner postulated for oxyhornblende. The high ferrous to ferric iron ratios of the host rocks of the Willyama hornblendes and of coexisting ferromagnesian minerals, and the presence in these rocks of ilmenite rather than magnetite as the typical opaque oxide do not conform with the highly oxidizing

TABLE II. Structural formulae of hornblende H3 calculated on two alternative bases

	24 (O, OH)	23 oxygen
Si	6.43	6.33
Al <sup>iv</sup>	1.57	1.67
Al <sup>vi</sup>	0.46	0.33
Ti	0.24	0.23
Fe <sup>+++</sup>	0.40	0.39
Fe <sup>++</sup>	2.98	2.94
Mn	0.06	0.06
Mg	1.20	1.18
Ca	1.77	1.73
Na	0.59	0.58
K	0.15	0.15
H	1.37	[2.00]
ΣY	5.34	5.13
Σ(X+A)	2.85	2.59

conditions apparently necessary for substantial hydrogen deficiency of the oxyhornblende type. That this is so for metamorphic hornblendes from other areas and also for many igneous hornblendes is suggested by the fact that the 23 oxygen method usually gives a structural formula in which, compared to formulae based on the 24 (O, OH, F) calculation, there is a closer approximation to the ideal five in the number of Y cations, and in which the sum of calcium and any excess in the Y cations rarely exceeds two, the number of X sites available.

Semiquantitative spectrographic analyses for fluorine quoted in table I and gravimetric determinations of chlorine in hornblendes H4 and H12 (0.01 and 0.03 wt. % respectively) show that the apparent water deficiency in the Willyama hornblendes is not as a rule compensated by abundance of halogen.<sup>1</sup> Evidently some structurally combined water escaped measurement in the Penfield tube method by which H<sub>2</sub>O<sup>+</sup> was determined. Table I reveals no correlation between apparent water deficiency and ferrous iron content, so reduction of expelled water in the

<sup>1</sup> Dr. J. A. Miller (pers. comm., 1961) noted that nitrogen was evolved from hornblende H12 during a mass spectrometer analysis for the purposes of age determination. Unfortunately it was not possible to determine the quantity of nitrogen present, or the form in which it was present.

Penfield tube by ferrous iron does not appear a satisfactory explanation of this deficiency. Temperatures attained in the Penfield tube were probably not sufficiently high to remove all the structurally combined water from hornblende. Dehydration experiments by Korzhinsky (1955, 1956) have shown that combined water is released at lower temperatures

TABLE III. Comparison of observed and theoretical densities of Willyama hornblendes

	Theoretical density		Observed density
	using 24 (O, OH) formula	using 23 oxygen formula	
<i>Group A</i>			<i>D</i> (gm/cc)
H4	3.251	3.230	3.230 ± 0.002
H12	3.328	3.314	3.316 ± 0.002
H34	3.246	3.234	3.234 ± 0.003
H36	3.374	3.368	3.372 ± 0.003
<i>Group B</i>			
H2	3.303	3.287	3.293 ± 0.003
H3	3.408	3.377	3.364 ± 0.002
H6	3.259	3.245	3.245 ± 0.006
H10	3.370	3.359	3.353 ± 0.004
H11	3.282	3.268	3.260 ± 0.003
H26	3.344	3.327	3.324 ± 0.003
H27	3.274	3.278	3.268 ± 0.002
H28	3.321	3.310	3.304 ± 0.002

Group A includes hornblendes for which repeated measurements gave consistent values for observed density.

Group B, those for which only one measurement of observed density was made.

from alkali-poor hornblendes than from varieties richer in alkalis. Inasmuch as alkali contents increase with grade (see below), this might explain the tendency for the more alkaline Willyama hornblendes to appear more deficient in water and hence for average figures for  $H_2O^+$  to decrease with increase in metamorphic grade.

*Chemical variations that depend mainly on chemistry of the parent rocks*

In the Willyama hornblendes, substitution of  $Fe^{++}$  and Mn for Mg in the Y sites is clearly dependent upon chemical composition of the host rocks. Refractive index measurements do not suggest any tendency for iron content to increase or become more limited with variation in metamorphic grade. In all three metamorphic zones the more iron-rich hornblendes coexist with garnet (e.g. those indicated by an asterisk in table I) or with iron-rich pyroxenes.

The distribution of divalent ions between the *X* and *Y* sites of the Willyama hornblendes also varies in accordance with host rock chemistry. There is usually a small excess over five in the number of *Y* group cations ( $\Sigma Y$  ranging up to 5.30) representing  $\text{Fe}^{++}$ , Mn, or Mg cations believed to occupy the *X* sites after the manner known in cummingtonite. The validity of the values for  $\Sigma Y$  quoted in table I is supported

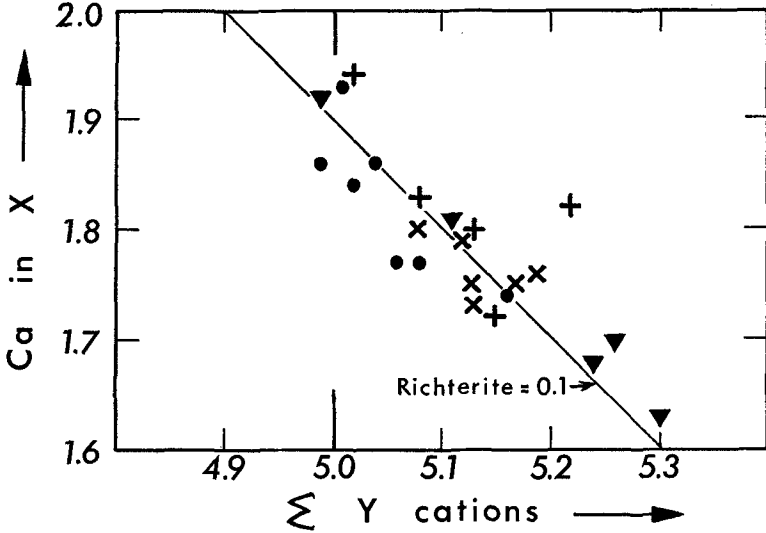


FIG. 3. Plot showing complementary relationship between amount of calcium in the *X* sites and the sum of the '*Y* group cations'. Hornblendes from all three zones of metamorphism fall close to a line denoting a richterite content of 0.10 (measured as atoms of sodium replacing calcium in *X*). Symbols as in Fig. 1.

by the exsolution phenomena discussed above. The largest excesses occur in hornblendes from rocks with a relatively low ratio of normative diopside to normative hypersthene (that is in rocks containing relatively less Ca available for substitution into hornblende) whereas the excess is small in hornblendes from rocks relatively rich in Ca (reflected modally by presence of particularly calcic plagioclase or abundance of calciferous clinopyroxene or both). Fig. 3 reveals complementary variation between the amount of calcium in the *X* sites and the excess in *Y* group cations (also believed to occupy the *X* sites) such that their sum is constantly 1.90. In hornblendes H26 and H40 there is a small deficiency in the *Y* group cations but calcium is correspondingly high. Although the quantities concerned are barely significant, it is possible that any

deficiency in  $\Sigma Y$  is made up by octahedrally co-ordinated calcium as in the calcium-rich amphibole istisuite (Kashkai and Mamedov, 1955).

Content of ferric iron also depends on host-rock chemistry (in this case reflecting oxidizing conditions during metamorphism). Almost all hornblendes with more than 0.30  $\text{Fe}^{3+}$  cations per formula unit coexist with magnetite and ilmenite, whereas those with less than this amount occur in rocks containing ilmenite as the only opaque oxide.

*Titanium content.* Colour variations in hornblendes from the three metamorphic zones have been shown to reflect a steady increase in titanium content with increase in metamorphic grade. This increase is illustrated by fig. 1 and by the following average figures for Ti cations per formula unit in the three zones: Zone A, 0.13; Zone B, 0.17; Zone C 0.21 (Ci, 0.20; Cii, 0.23). While these figures appear to indicate increased acceptance of titanium by the hornblende structure at higher metamorphic grades, a mineralogical control (viz. the crystallization in abundance of titanium-poor pyroxenes) may influence the relatively high Ti values in Zone C. The parent rocks show similar ranges in titanium content and in ilmenite content through all three metamorphic zones (cf. Binns, 1964, tables 2 and 3).

*Aluminium in the two co-ordination states.* A plot of aluminium in the Z group against that in Y (fig. 4) reveals the way in which this element is distributed between its two possible co-ordination states. Tetrahedrally co-ordinated aluminium in the Z group varies considerably but shows much the same range in each of the four zonal groups, its value (1.2 to 1.9) lying between those for amphibolite-facies hornblendes and magmatic hornblendes quoted by Harry (1950). On the other hand, octahedrally co-ordinated aluminium in the Y group is much more limited in its variation for each metamorphic zone, and decreases steadily as metamorphic grade rises.

Substitution of ferric iron or titanium into the Y sites results in an excess positive charge, which may be balanced either by aluminium occupying the Z sites or by sodium replacing calcium in the X site (balance by replacing  $(\text{OH})^-$  with  $\text{O}^{2-}$  is not considered likely, see above). A plot of  $\text{Fe}^{3+} + 2 \text{Ti}$  (i.e. the charge excess resulting from these substitutions) against  $\text{Al}^{\text{IV}}$  (fig. 5) shows hornblendes from all three metamorphic zones in the Willyama Complex falling very close to a line whose position and  $45^\circ$  slope indicate that titanium and ferric iron substitution in the Y sites are balanced entirely by aluminium replacing silicon in the Z site. Further, the amount of aluminium occupying the Z site other than that required to balance ferric iron and titanium is limited in its

variation. Average figures for this quantity, designated  $Al^*$ , show a slight decrease with increase in metamorphic grade (table IV).

*The balancing of tetrahedrally co-ordinated aluminium.* The available space in the  $X$  sites of the Willyama hornblendes not occupied by calcium or by excess of the  $Y$  group cations is presumably filled by monovalent alkali cations (possibly sodium only). As a simplification it may

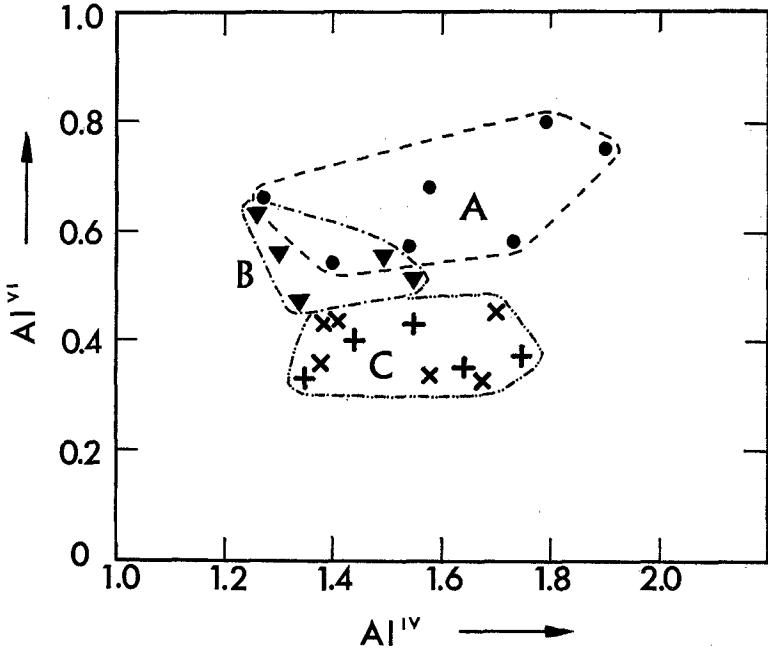


FIG. 4. Plot of octahedrally co-ordinated aluminium against tetrahedrally co-ordinated aluminium in Willyama hornblendes, showing fields for the three metamorphic zones.  $Al^{IV}$  displays similar variation over each zone but  $Al^{VI}$  decreases steadily with increase in metamorphic grade. Symbols as in Fig. 1.

be assumed (cf. Shidô, 1958) that entry of alkalis into the  $A$  site of the amphibole structure is the main mechanism by which the valency charge deficiency arising from alkali cations in the  $X$  sites is balanced. Since the number of alkali cations involved is relatively small and constant (fig. 3) this simplification will not substantially affect the conclusions that follow. Alkali cations, then, can be divided into those which fill, one for one, the  $X$  and  $A$  sites of the structure, and those additional cations that enter the  $A$  site and produce an overall charge



excess. These may be called *richterite alkalis* and *edenite alkalis* respectively after the two amphibole end-members in which they are dominant.

Corresponding to the decrease with increasing metamorphic grade in octahedrally co-ordinated aluminium (fig. 4) there is an increase in the

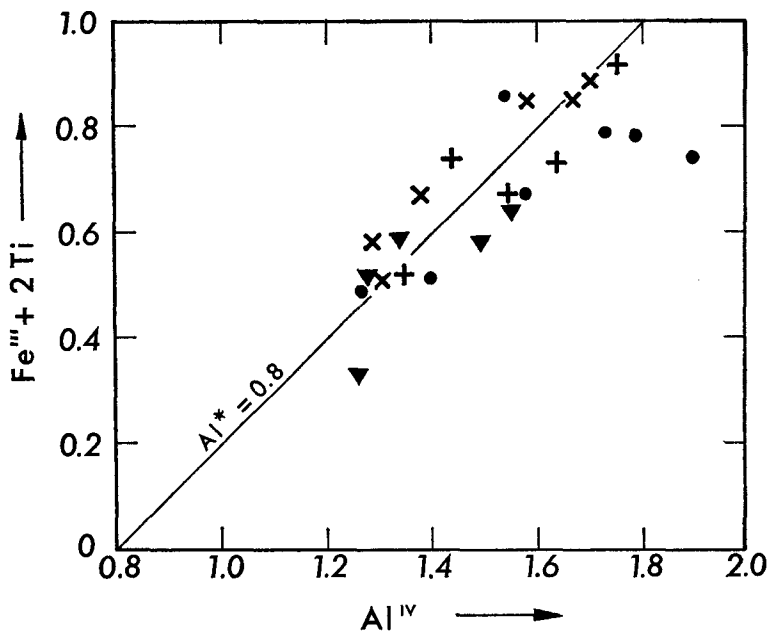


FIG. 5. Plot of tetrahedrally co-ordinated aluminium against the charge excess resulting from substitution of ferric iron and titanium into the *Y* sites. Hornblendes from all three metamorphic zones fall close to the line representing  $Al^* = 0.80$  (see text), indicating that the excess charge due to ferric iron and titanium is balanced by substitution of aluminium into the *Z* sites. Symbols as in Fig. 1.

alkali content of Willyama hornblendes, particularly in the edenite alkalis entering the *A* site. The manner whereby  $Al^*$  (that tetrahedrally co-ordinated aluminium not combined with ferric iron and titanium) is thus balanced is illustrated in fig. 6 and table IV. The increase in overall alkali content with metamorphic grade of the Willyama hornblendes agrees with the findings of Shidô (1958) in hornblendes from the Abukuma Plateau of Japan and of Engel and Engel (1962) in the Adirondack Mountains, New York.

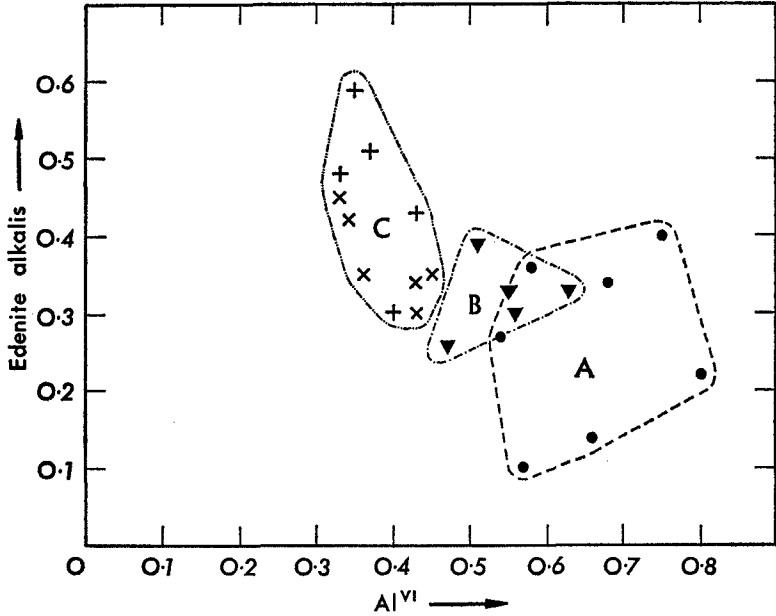


FIG. 6. Plot of 'edenite alkalis' (see text) against octahedrally co-ordinated aluminium in the Willyama hornblendes, showing the grade-dependent change in the way  $Al^*$  is balanced. Note that hornblendes from garnet-bearing rocks plot in the upper portions of the fields for each of the three metamorphic zones. Symbols as in Fig. 1.

TABLE IV. Average figures for the main chemical changes in hornblendes of the three metamorphic zones

Zone	Edenite alkalis	Octahedral aluminium	$Al^*$
A	0.26	0.65	0.91
B	0.32	0.54	0.86
C	0.40	0.39	0.79
Ci	0.35	0.40	0.75
Cii	0.46	0.38	0.84

$Al^*$  = aluminium in Z sites other than that required to balance titanium and ferric iron.

There is a certain amount of scatter and overlap in the fields representing the several zones on fig. 6. While this might be expected to result from the likely errors in a chemical analysis, the fact that hornblendes coexisting with garnet tend to lie in the upper right of each

field suggests that the scatter is not entirely random and that other chemical factors influence the position in which hornblendes fall on such a plot. High iron contents and also high potassium to sodium ratios in the alkali group appear to displace a hornblende towards the high alkali portion of each field. The composition of coexisting plagioclase has no detectable effect on position of plotting. Although Shidô (1958) concluded that hornblendes in metamorphic rocks free of quartz should be richer in alkalis than those coexisting with quartz, oversaturation with silica does not influence plotting on fig. 6. Indeed, the most alkaline hornblendes in Zones A and C occur in quartz-bearing rocks.

Any impurity in the mineral concentrates, particularly plagioclase or pyroxene, will alter the apparent formula of a hornblende and affect its position on fig. 6. However, all the Willyama hornblendes separated by the writer were better than 99.5% pure so that errors introduced in this way are insignificant.

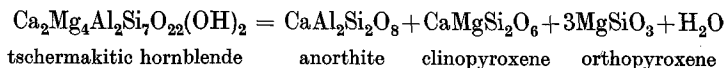
If the fields for Subzones Ci and Cii are separated on fig. 6, the general trend with increase of metamorphic grade can be seen to continue through Zone C. This verifies the subdivision of this Zone into these two subzones, a division that might equally well be based on cation distributional relationships in coexisting pyroxenes in the metamorphosed basic rocks (Binns, 1962).

#### *Conclusions*

Increasing grade of metamorphism has two main effects on the chemical composition of hornblendes in metamorphosed basic rocks from the Willyama Complex. The first is a progressive increase in content of titanium, a change that influences the colour of the typical hornblendes in each zone. The second, a more fundamental effect from the point of view of mineral reactions, is a change in the manner by which aluminium replacing silicon in the *Z* site is balanced. At higher grades the charge balance is maintained to a greater extent by alkali cations entering the *A* site, while the dominant compensating substitution at lower grades is the entry of aluminium into the *Y* sites.

In terms of end-member components, the second effect is essentially a progression from tschermakitic hornblende (a variety half-way between tremolite-actinolite and the tschermakite end-member of Sundius (1946),  $\text{Ca}_2\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$ ) towards edenite. In the lower grades of metamorphism this progression is accomplished with compensating changes in composition and amount of plagioclase, but at the boundary between Zones B and C in the Willyama Complex it is assisted by the selective

breakdown of the tschermakitic component to form calcic plagioclase and pyroxenes according to the equation:



In Zones A and B, hornblende typically makes up 60% of basic amphibolites, while in the pyroxene-bearing basic gneisses of similar bulk chemical composition from Zone C this proportion is reduced to about 30%. Thus approximately half the hornblende breaks down at the orthopyroxene isograd between Zones B and C. However, the average tschermakitic and edenite contents of hornblendes in each zone do not differ sufficiently to indicate that the above equation provides the only means of generating pyroxene. The edenite component is also involved, to a lesser extent, in the breakdown, yielding a soda-lime plagioclase rather than pure anorthite.

The data from the Willyama Complex indicate that composition of hornblende in metamorphosed basic rocks may be used as an indicator of metamorphic grade, the main limitation being analytical accuracy. Since temperature appears to be the principal physical variable in the Complex (Binns, 1964), the application of hornblende chemistry to estimation of metamorphic temperatures seems promising. Grade-dependent chemical changes similar to the Willyama trend occur in hornblendes from metabasic rocks in other metamorphic terrains, e.g. the Abukuma Plateau, Japan, and the Scottish Highlands (Shidô and Miyashiro, 1959) and the Adirondack Mountains (Engel and Engel, 1962). These will be discussed in a later publication.

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