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Subcalcic, Fe-rich amphiboles in meta-dolerites, Glenrock Station, NSW, Australia

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ABSTRACT. Sub-greenschist facies metamorphism has produced unusual subcalcic, Fe-rich actinolitic amphiboles in meta-dolerites from the Glenrock Station area, NSW. They show edenite, riebeckite, ferri-tschermakite and Ti-tschermakite coupled substitutions. Their high Fe content is attributed to high $a_{Fe^{2+}}$ and $a_{Fe^{3+}}$ in the fluid phase produced during the breakdown of clinopyroxene, hornblende, magnetite, and ilmenite. The high $a_{Fe^{2+}}$ led to Fe^{2-} occupying the *B* site, resulting in the formation of subcalcic amphiboles. Variation in $a_{Fe^{2+}}$, $a_{Fe^{3+}}$, a_{Mg}, a_{Si}, a_{Al}, a_{Ti}, and a_{Ca} in different domains resulted in the crystallization of chemically inhomogeneous amphiboles.

IN the Glenrock Station area, approximately 300 km north of Sydney, NSW, rocks of varying age, lithology, and structure occur in fault slices of the Peel–Manning Fault System (Offler, 1979, 1982). Those examined in this study are dolerites which intrude middle Devonian volcanogenic sediments of the Tamworth Group (Crook, 1961), Ordovician–early Devonian(?) cherts and jaspers of the Woolomin Beds (Crook, 1961), volcanogenic sediments of unknown age in the north-eastern part of the area, and serpentinites. They are tholeiitic or chemically transitional between tholeiitic and alkaline magmas according to their pyroxene chemistry, and are extensively replaced by metamorphic assemblages transitional between the prehnite–pumpellyite and pumpellyite–actinolite facies (Table I).

In the course of a detailed chemical study of the metamorphic and igneous minerals in rocks from this area, unusually Fe-rich amphiboles were noted which differed in composition from those previously reported in other low-grade metamorphic terrains (Kawachi, 1975; Coombs *et al.*, 1976; Watanabe, 1977; and others). Further studies revealed that these amphiboles are widespread and that particular substitutions were responsible for their unusual subcalcic, Fe-rich nature. In addition, they showed that their compositions were controlled by local variations in $a_{Fe^{2+}}$, $a_{Fe^{3+}}$, a_{Si}, a_{Mg}, a_{Al}, a_{Ti}, and a_{Ca}. The results of these studies are the subject of this paper.

Petrography

All the dolerites show well-preserved igneous textures but the igneous minerals are partly or completely replaced by low-grade metamorphic minerals (Table I). Their textures and mineralogy are similar to those previously described in earlier investigations of rocks in the Glenrock Station area (Offler, 1979, 1982). The amphiboles epitaxially replace clinopyroxene and also occur as isolated, idioblastic, acicular crystals or in aggregates intimately associated with prehnite (0–6.9% Fe_2O_3), Fe-rich chlorite (magnesio-chamosite; Bayliss, 1975), and less commonly with quartz and pumpellyite (1.0–21.3% Fe_2O_3). These aggregates replace clinopyroxene and hornblende, and form in interstices. The *Z* absorption colour of these amphiboles varies from very pale green to apple green.

Methods

The analyses were carried out on a JEOL JXA-50A electron microprobe by energy dispersive methods using a program modified from Reed and Ware (1975).

The amphiboles have been calculated on the basis of an 'anhydrous' total of 98.00% and 23(O).

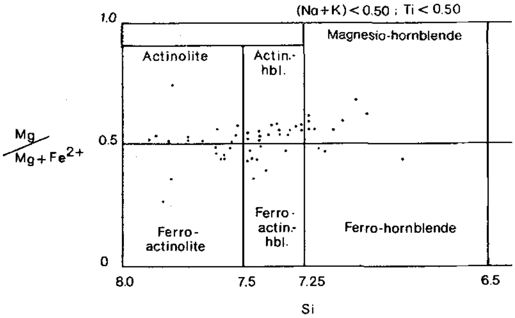


FIG. 1. Composition of amphiboles $Mg/(Mg+Fe^{2+})$ *vs.* Si, atoms in structural formula. Classification after Leake (1978).

Table I. Mineral assemblages of amphibole bearing rocks.

	10950#	10951	10952	10955	10953	10949	7429	10663	4562	1852	7494
Metamorphic phases											
Prehnite	x	x	x	x	x	x	x	(x)	(x)	(x)	
Chlorite	x	x	x	x	x	x	x	x	x	x	
Pumpellyite	x	x	x	x			x	(x)		x	x
Actinolite	x	x	x	x	x	x	x	x	x	x	x
Albite	x	x	x	x	x	x	x	x	x	x	x
Calcite			(x)	(x)				(x)		x	
Epidote	(x)	(x)							x		x
Sphene	x	x	x	x	x		x			x	x
Rutile	x	x		x	x		x			x	
Quartz							x				
White mica	x	x	x								
Relict igneous phases											
Clinopyroxene	x	x	x	x	x	x	x	x		x	x
Hornblende			x	x	x		(x)	x	x	x	x
Biotite					x	(x)		(x)		(x)	
Quartz									x		
Plagioclase	x	x	x	x	x	x	x	x	x	x	x
Ilmenite	x	x	x	x	x	x				x	x
Magnetite	x	x	x	x	x	x	x	x		x	
Pyrite	x			x		x		x			
Apatite	x			x	x	x	x	x		x	x

(x) Uncommon.

\# Specimen numbers refer to those in the collection of the Department of Geology, The University of Newcastle.

Table II. Representative electron microprobe analyses of amphiboles.

	c10949°	r10949	10950°	10951	10953°	10953	10955°	10952	10663
SiO_2	49.92	49.70	49.80	45.00	51.10	50.92	50.92	48.68	51.91
Al_2O_3	1.55	1.94	2.37	4.18	0.89	2.58	2.41	3.41	2.63
TiO_2	0.42	0.47	0.47	0.74	0.35	0.79	0.30	0.80	0.71
FeO^*	28.17	23.03	23.62	29.28	32.25	23.29	25.82	24.06	19.00
MnO	0.87	0.55	0.44	0.62	0.66	0.54	0.50	0.38	0.34
MgO	10.36	10.04	9.87	5.64	9.37	10.02	8.38	9.21	11.61
CaO	5.80	9.88	10.14	9.14	3.04	9.84	10.57	10.51	10.92
Na_2O	1.05	0.94	1.25	1.95	0.54	1.16	1.08	1.44	0.68
K_2O	0.09	0.09	0.18	0.77	-	0.30	0.10	0.31	0.20
Total	98.23	96.64	98.14	97.32	98.20	99.44	100.08	98.80	98.00
	Formula on the basis of 23(0)								
Si	7.476	7.488	7.374	6.856	7.804	7.445	7.485	7.165	7.611
Al_{iv}	0.274	0.345	0.413	0.751	0.161	0.445	0.418	0.591	0.389
Al_{vi}	-	-		-		-	-	-	0.065
Ti	0.047	0.053	0.414	0.085	0.041	0.087	0.033	0.089	0.079
Fe^{3+}	1.002	0.864	1.127	2.094	0.308	0.878	0.872	1.371	0.399
Mg	2.313	2.255	2.178	1.281	2.133	2.184	1.836	2.020	2.538
Fe^{2+}	2.525	2.038	1.798	1.637	3.811	1.970	2.302	1.590	1.930
Mn	0.110	0.070	0.055	0.080	0.085	0.067	0.062	0.047	0.042
Ca	0.931	1.595	1.609	1.492	0.498	1.541	1.665	1.657	1.715
Na	0.305	0.275	0.359	0.576	0.159	0.329	0.308	0.411	0.194
K	0.017	0.017	0.034	0.150	-	0.056	0.019	0.058	0.038

*Total Iron as FeO. ° V detected in these amphiboles.

c = core; r = rim.

Table III. Representative analyses of amphibole-bearing rocks.

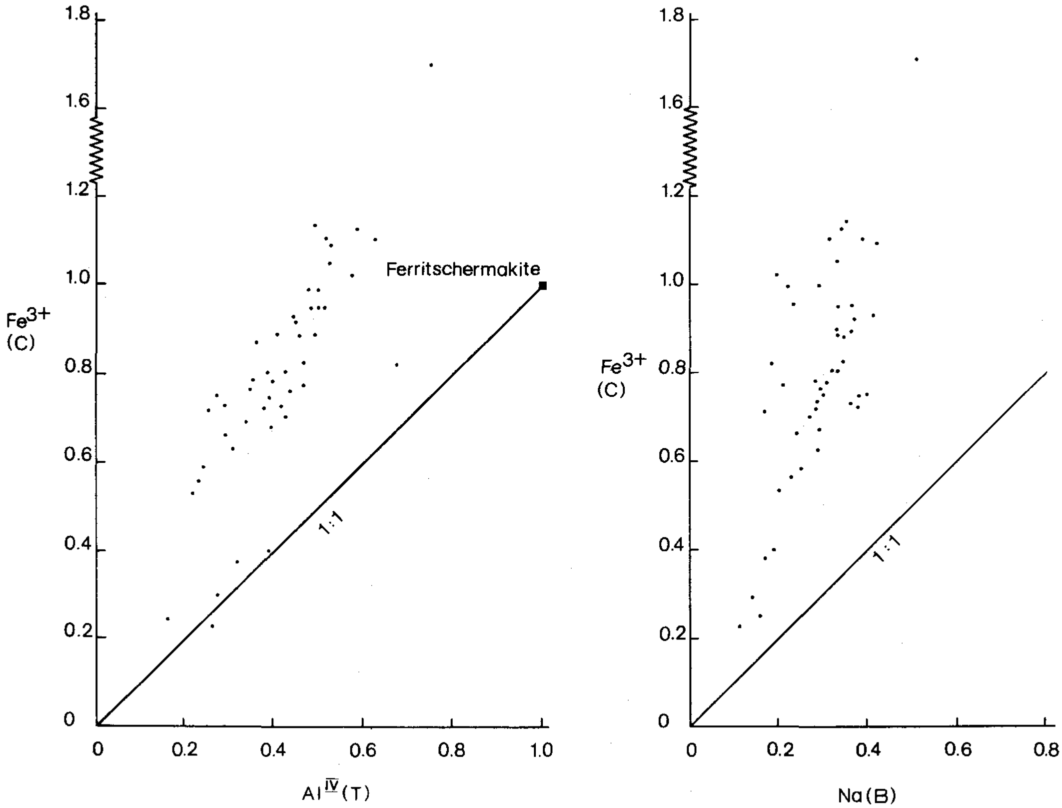
	10949	10950	10951	10952	10955	10953	10663	1852
SiO_2	49.96	47.15	49.49	55.11	51.72	45.23	49.57	55.46
TiO_2	2.40	3.05	2.77	1.75	1.82	3.49	1.87	1.59
Al_2O_3	14.09	13.39	14.81	15.28	14.75	12.63	14.44	14.69
FeO	9.47	4.81	2.95	4.77	7.10	9.60	7.90	6.93
Fe_2O_3	2.79	9.50	10.47	3.89	3.64	6.76	3.80	3.98
MnO	0.26	0.27	0.14	0.15	0.18	0.23	0.22	0.18
MgO	2.57	3.38	1.23	1.85	3.22	3.68	5.24	2.94
CaO	6.64	7.86	9.07	7.08	7.88	7.82	7.64	5.00
Na_2O	4.49	4.39	4.80	6.52	4.98	3.88	4.85	5.92
K_2O	0.71	0.54	0.22	0.26	0.42	0.49	0.42	0.14
P_2O_5	1.22	0.41	0.69	0.53	0.40	0.36	0.23	0.21
L.O.I.	2.94	5.94	2.53	1.92	2.45	3.30	2.88	2.12
	97.54	100.69	99.17	99.11	98.56	97.47	99.06	99.16
$\frac{Fe_2O_3+FeO}{Fe_2O_3+FeO+MgO}$ (Mol. Prop.)	0.670	0.600	0.775	0.662	0.603	0.659	0.506	0.624

The total cations were adjusted to 15 by varying the Fe^{2+}/Fe^{3+} ratio. A cation total of 13, excluding (Na+K+Ca), as recommended by Leake (1978), was found to be unsuitable because these amphiboles are unusually Fe-rich resulting in an overestimation of their Fe^{3+} contents.

Results

Representative analyses of the amphiboles are shown in Table II. The microprobe study revealed that:

1. Most amphiboles are actinolites and actinolitic-hornblendes or their Fe-rich equivalents (fig. 1) according to the classification of Leake (1978). Some of the Fe-rich amphiboles contain more than 1.0 Fe^{3+} and are ferri-actinolites assuming that the Fe^{2+} and Fe^{3+} contents have been calculated correctly. This cannot be proven but the occurrence of Al only in the *T* site (terminology after Leake, 1978) in many amphiboles, suggests that Fe^{3+} is a dominant R^{3+} cation in the *C* site.
2. Many are strongly subcalcic with CaO contents as low as 2.59 % (e.g. 10949). Such amphiboles are more subcalcic than those reported in Leake (1968). Further, in the strongly subcalcic varieties, K_2O is absent and MnO higher than in the calciferous amphiboles.
3. FeO* contents are high in many amphiboles (up to 32.25 %, 10953°, Table II).
4. Na_2O and TiO_2 contents are higher than in amphiboles from other sub-greenschist, regional metamorphic terrains (e.g. Glenrock Station: $n = 49$, $Na_2O = 0\text{–}1.95\,\%$, $\bar{x} = 1.0\,\%$, $\sigma n = 0.47$, $Al_2O_3 = 1.21\text{–}4.31\,\%$, $\bar{x} = 2.50\,\%$, $\sigma n = 0.78$, $TiO_2 = 0\text{–}1.06\,\%$, $\bar{x} = 0.46\,\%$, $\sigma n = 0.25$; Loèche, Coombs *et al.* (1976): $Na_2O = 0.1\text{–}0.2\,\%$, $Al_2O_3 < 2\,\%$, $TiO_2 < 0.05\,\%$; Upper Wakatipu, Kawachi (1975): $Na_2O = 0.14\text{–}1.98\,\%$, $Al_2O_3 = 0.38\text{–}1.91$, $TiO_2 = 0\text{–}0.17\,\%$).
5. Considerable intraspecimen and to a lesser degree, intragranular variation in composition is apparent in many samples (Table II).
6. In addition to simple $Fe^{2+} \rightleftharpoons Mg$ exchange,



FIGS. 2 and 3. FIG. 2 (*left*). Fe^{3+} in *C* site *vs.* Al(IV) in *T* site. Ferri-tschermakite substitution. FIG. 3 (*right*). Fe^{3+} in *C* site *vs.* Na in *B* site. Riebeckite substitution.

ferri-tschermakite Fe^{3+}(vi)+Al(iv)$\rightleftharpoons$Si(iv)+Mg(vi), riebeckite Na(*M*4)+Fe^{3+}(vi)$\rightleftharpoons$Ca(*M*4)+Mg(vi), and edenite Na(*A*)+Al(iv)$\rightleftharpoons$$\square$(*A*)+Si(iv) coupled substitutions have occurred (figs. 2, 3, 4). The Ti-tschermakite Al(iv)+Ti(vi)$\rightleftharpoons$Si(iv)+Mg(vi) substitution appears to have taken place since there is a moderate correlation between Al$^{\mathrm{IV}}$ and Ti.

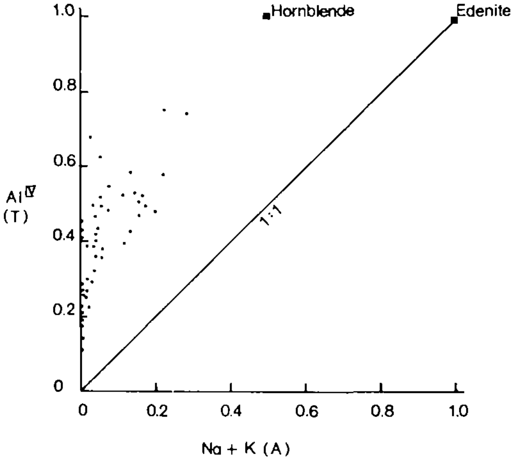


FIG. 4. Al(iv) in *T* site *vs.* (Na+K) in *A* site. Edenite substitution.

7. Small quantities of Fe^{3+} are required to fill the *T* site (Table II) in many amphiboles which may reflect a ferri-ferri-tschermakite substitution commonly noted in pyroxenes. However, as yet, no evidence has been found for tetrahedrally co-ordinated Fe^{3+} (Hawthorne, 1981).

Discussion

Bulk rock chemistry and composition of amphiboles. The unusual composition of these amphiboles deserves some comment. In other regional metamorphic terrains where sub-greenschist facies assemblages occur, actinolitic amphiboles are not as Fe-rich, nor are they as deficient in CaO (Coombs *et al.*, 1976; Watanabe, 1977). However, Fe-rich actinolites have been noted in low-grade, contact metamorphosed rocks from the Gunflint Iron Formation, Canada (Floran and Papike, 1978). This association of Fe-rich amphiboles with Fe-rich host rocks suggests that bulk rock chemistry may be an important factor in defining the chemistry of the amphiboles from the Glenrock Station area. To test this hypothesis, the (Fe_2O_3+FeO)/(Fe_2O_3+FeO+MgO) ratios in the host rock (Table III) and amphibole were compared (fig. 5).

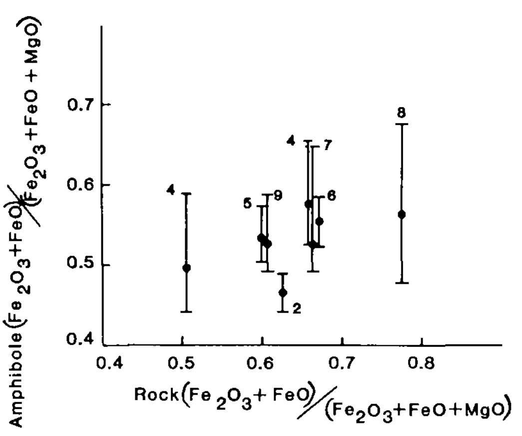


FIG. 5. Mol. prop. (Fe_2O_3+FeO)/(Fe_2O_3+FeO+MgO) amphibole *vs.* mol. prop. (Fe_2O_3+FeO)/(Fe_2O_3+FeO+MgO) rock. Number of amphibole analyses given besides each bar. Range in composition and mean also shown.

The plot shows in a gross way that the more Fe-rich amphiboles occur in rocks with high (Fe_2O_3+FeO)/(Fe_2O_3+FeO+MgO) ratios and that extreme variation in amphibole composition is apparent in many specimens. However, the relationship between bulk rock chemistry and amphibole composition is not well defined.

This result is not surprising because the host rocks show varying degrees of alteration. In the less altered specimens, unaltered to partially altered clinopyroxene, ilmenite and magnetite are abundant; thus Ca, Mg, Fe, Ti, and Si bound up in these minerals are not available for reaction. It follows therefore that the composition of the amphiboles cannot be defined by the bulk chemistry of the host rock. An alternative and more likely explanation is that their compositions have been controlled by the composition of the fluid phase. This phase contained ionic concentrations dependent on mineral–fluid interactions occurring in different parts of the rock at any one time.

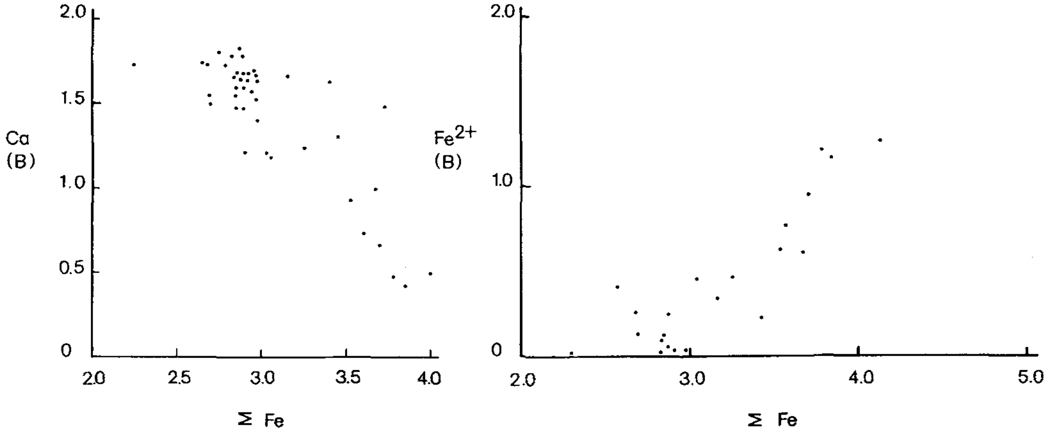
The type of ions that were released into the fluid were defined by the composition of the igneous minerals undergoing alteration, their susceptibility to breakdown, pH, and temperature. Fluctuation in $a_{\mathrm{Fe}^{2+}}$, $a_{\mathrm{Fe}^{3+}}$, a_{Mg}, a_{Si}, a_{Al}, a_{Ti}, and a_{Ca} in time and in different domains might have led to the formation of chemically inhomogeneous amphiboles. (Table II); high $a_{\mathrm{Fe}^{2+}}$ and $a_{\mathrm{Fe}^{3+}}$ resulted in the crystallization of Fe-rich amphiboles.

However, not all the variation in composition could have been fluid controlled. In some rocks the association of other Fe–Mg silicates with the amphiboles has had an effect. This is clearly shown by chlorite-actinolite pairs in which the Fe/Mg ratio of the actinolite is lower than in actinolites which have grown independently of other Fe–Mg silicates (e.g. Mg/Fe chlorite = 0.523–0.601, Mg/Fe actinolite = 0.693–0.761, 10950); preferential partitioning of Fe into chlorite appears to have taken place in this case (cf. Coombs *et al.*, 1976).

Precursor mineral chemistry and f_{O_2}. Other factors which also may have played a role are precursor mineral chemistry and f_{O_2}. Precursor mineral chemistry often defines the chemistry of the replacement product (Evarts, 1979; Offler *et al.*, 1981), but in these rocks this is not so since the amphibole is notable more Fe-rich than the clinopyroxene and hornblende it replaces (e.g. clinopyroxene $Na_{0.04}Ca_{0.79}Mg_{0.79}Fe_{0.34}Ti_{0.02}Mn_{0.01}Si_{1.94}Al_{0.08}O_6$ is replaced by actinolite $Na_{0.31}K_{0.03}Ca_{1.62}Mg_{2.33}Fe_{2.90}Ti_{0.07}Mn_{0.05}Si_{7.59}Al_{0.41}O_{23}$ in 10952). This suggests that some Fe has been derived from the opaque minerals. The role of f_{O_2} in defining amphibole chemistry is unclear because cation–cation plots carried out to test the importance of this variable, show contradictory results. For example, when $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ is plotted against Ti and $Mg/(Mg+Fe^{2+})$, positive correlations are obtained. Further, probe analyses of single crystals from core to rim indicate an increase in Ti and $Mg/(Mg+Fe^{2+})$ with increase in $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ in some specimens, in others a decrease. Since it has been shown in experimental studies on amphiboles that Ti and Fe^{2+} decrease and Mg and Fe^{3+} increase with increasing f_{O_2} at constant *P* and *T* (Spear, 1981), the chemistry of the amphiboles from the Glenrock Station area indicate that f_{O_2} has not been a major factor during their crystallization. However, it may well have been important in the early stages of alteration when the fluid first reacted with the igneous phases. At this time, extraction of O_2 from the fluid would result in the nucleation of phases more enriched in the cations Fe^{3+}, Mg, Si, and Mn^{2+} which are favoured by higher f_{O_2} (Spear, 1981). However, with further crystallization, variation in the activity of the cations may have been the main factor in defining amphibole composition. Evidence for this is indicated by the extreme variation in composition of adjacent crystals (e.g. MgO = 9.88–11.23 %, $\bar{x}$ = 10.42 %, FeO = 23.03–31.01 %, $\bar{x}$ = 27.05 %, CaO = 2.59–9.88 %, $\bar{x}$ = 6.35 %, n = 5, 10949) and by single crystals in many specimens which show a decrease in Fe^{2+} and Fe^{3+}, an increase in Ca and almost constant Mg, from core to rim.

Subcalcic nature of amphiboles. Low CaO contents are a distinctive feature of many of the amphiboles in these rocks. Examination of the analyses reveals that Ca contents fall with substitution of Na and in particular, Fe^{2+} in the *B* site. Moreover, the greatest decrease in Ca appears in those amphiboles which are extremely Fe-rich and in which substantial contents of Fe^{2+} occur in the *B* site (Table II; figs. 6, 7). This suggests that subcalcic amphiboles will form when sufficient Fe^{2+} is available to enter the *B* site. Such a condition may arise when the $a_{Fe^{2+}}$ in the fluid phase is high. However, Fe^{2+} will enter the *B* site only if the content of other cations in the *C* site is high enough to prevent all of the Fe^{2+} going into the latter site. Should this not occur, all Fe^{2+} will go into the *C* site, and Fe-rich calcic amphiboles such as those described by Floran and Papike (1978) will crystallize. In the amphiboles described by these authors and in some from the Glenrock Station area, MgO contents are low, allowing all the Fe^{2+} to enter the *C* site.

Na *and* Ti *contents.* The rocks in this area



FIGS. 6 and 7. Composition of amphiboles. FIG. 6 (*left*). Ca in *B* site *vs.* total Fe. FIG. 7 (*right*). Fe^{2+} in *B* site *vs.* total Fe.

contain amphiboles with variable and commonly high Ti and Na contents. Such variations are likely to be due to local fluctuations in a_{Ti} and a_{Na} in the fluid phase at the time of crystallization. However, the ready availability of a particular cation does not mean that excessive quantities of that cation will enter the amphibole lattice. Other variables such as P, T, and f_{O_2}, and mineral buffers will also define cation content. For example, Ti substitution in the C site is favoured by increase in T and decrease in P (Hynes, 1982). Therefore, the higher Ti contents of the amphiboles in the Glenrock Station area, relative to those in other areas, are probably a reflection of the low pressures of crystallization. This conclusion appears to be justified because assemblages characteristic of the higher P pumpellyite–actinolite facies are absent in the area. In contrast, the Na content appears to be controlled by f_{O_2} since the riebeckite substitution is responsible for most of the Na in the amphibole lattice; more Na goes into the lattice to balance increasing contents of Fe^{3+} in the C site.

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