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Pyroxenes in altered volcanic rocks, Glenrock Station, NSW, Australia

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SUMMARY. Microprobe analyses of relict pyroxenes in meta-basalts from thrust slices of the Peel fault zone, Glenrock Station, NSW, demonstrate that the majority of these rocks have a tholeiitic affinity. Those of Ordovician to L. Devonian(?) age in the upper thrust slices show a greater Fe-enrichment, and lower wollastonite, Al and Ti contents than their Devonian counterparts in the lowest thrust sheet. The pyroxene data also indicate that some rocks are geochemically transitional between tholeiitic and alkaline magmas. The relict pyroxenes in meta-dolerites emplaced in the Devonian sequence show that these rocks are transitional to tholeiitic in character and that they appear not to be consanguineous with the meta-basalts.

ALTERED volcanic rocks are exposed within thrust slices of the Peel fault zone, in the Glenrock Station area, approximately 300 km north of Sydney, NSW (fig. 1). Those examined in this study vary in age from Ordovician or early Devonian(?) to Middle Devonian (N. Morris, A. Wright pers. comm.); the former belong to the Woolomin Beds, the latter to the Tamworth Group (Crook, 1961). They are of basic composition and are associated with volcanogenic sediments, tuffs, less common silicic volcanic rocks, and limestones, or with pelagic cherts. Intrusive into these rocks are concordant and discordant bodies of dolerite (fig. 1).

Some studies have been done on the geochemistry of the altered volcanic rocks in the Peel fault zone (Benson, 1913, 1915*a*, *b*; Cross, 1974; Vallance, 1969*a*, 1974; Herbert, 1978; Offler, 1978) but only one other on the pyroxenes which occur in them as relict phases (Vallance, 1969*b*, 1974). This study was undertaken to complement Vallance's preliminary work in the Nundle area and to determine the magmatic affinity of the volcanic rocks in the Glenrock Station area from the chemistry of the pyroxenes. Such minerals have been successfully used in other studies for the identification of magma type (Hynes, 1976; Garcia, 1978). Further, pyroxenes from the intrusive dolerites were examined to ascertain whether they are consanguineous with the basic lavas as suggested by Vallance (1969*b*) for similar rocks in the Nundle area.

Petrography. All the rocks examined show, to varying degrees, the effects of low grade metamorphism which has produced, in most specimens, assemblages typical of the prehnite-pumpellyite and the transitional facies of Coombs *et al*. (1970). However, igneous textures are generally well preserved and, in many instances, remnants of the primary igneous mineralogy remain.

The altered lavas are porphyritic or aphyric and show intergranular and subvariolitic groundmass textures. In the porphyritic varieties, phenocrysts and, or, glomeroporphyritic aggregates of clinopyroxene and plagioclase are present. Hourglass structures occur in the pyroxenes and are particularly well developed in those from the Devonian rocks. Complex zoning is a feature of many of the pyroxenes (fig. 2) and, in deformed specimens undulose extinction, fracturing, and rare kinking also appear. A red-brown spinel occurs as inclusions in some phenocrysts.

The groundmass in the least altered rocks consists of intergranular, stubby, clinopyroxene crystals, laths of plagioclase, and titanomagnetite which may be irregular, skeletal or subhedral in form. Associated with the titanomagnetite may be pyrite and, or, chalcopyrite; subhedral or euhedral ilmenite crystals appear in place of, or coexist with, titanomagnetite in the meta-volcanic rocks from the Woolomin Beds. In the more rapidly chilled rocks the plagioclase exhibits swallow tail terminations and forms microlites. The titanomagnetite, on the other hand, shows dendritic growth forms.

The dolerites are typically massive rocks showing a poikilitic texture in which plagioclase encloses clinopyroxene crystals; less common is a subophitic texture where pyroxene is moulded on to plagioclase. Brown or green hornblende is a typical late stage crystallization product which may be a major or minor phase in the meta-dolerites. It rims or replaces clinopyroxene and appears as euhedral

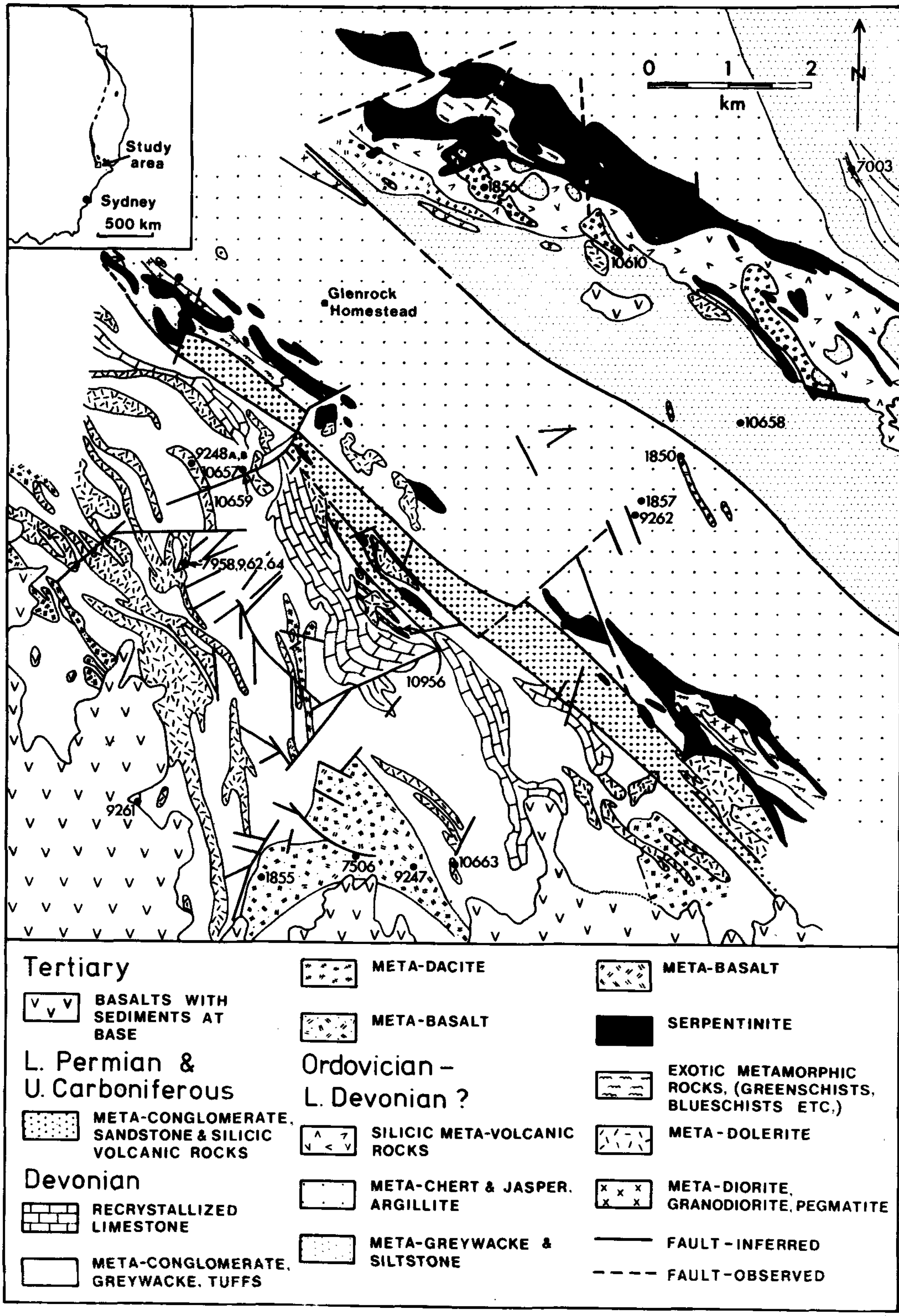

FIG. 1. Geology of the Glenrock Station area and location of samples. Modified from Williams (1979).

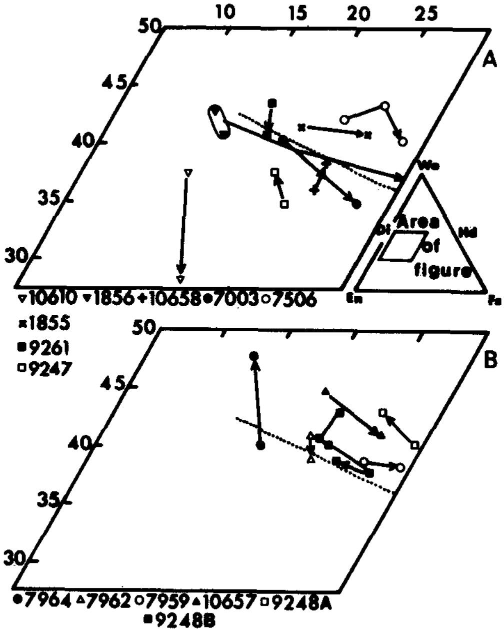

FIG. 2. Composition of some zoned clinopyroxenes with arrows indicating change in composition from core to rim. (A) Meta-volcanic rocks, (B) Meta-dolerites. Part of the crystallization trend for pyroxenes from the Skaergaard intrusion (Brown, 1957) is shown.

crystals in the interstices. Additional phases which occur interstitially, are euhedral to subhedral, red-brown biotite, skeletal, irregular aggregates or subhedral crystals of titanomagnetite, pyrite and minor chalcopyrite, and slender prisms of apatite. Quartz is a minor intersertal phase in some rocks and orthopyroxene is rare.

Methods. The analyses were carried out on a JEOL JXA-50A microprobe fitted with an EDAX 183 detector and a 707 multi-channel analyser interfaced to a Data General Nova 2-10 mini computer. A program developed by Reed and Ware (1975) and modified for this equipment, was used to calculate the results. The analytical conditions were: an accelerating voltage of 15 kV, an electron beam diameter of 0.15 microns and a specimen current of 1.80 nanoamps.

Most analyses were of phenocrysts since groundmass pyroxenes were normally replaced by metamorphic minerals. In each specimen, phenocrysts were analysed at several points along traverses from core to rim to determine any chemical inhomogeneity that may exist. Pyroxenes exhibiting a sector zoning were avoided since they may show variation in composition from sector to sector (Nakamura and Coombs, 1973). Similarly, pyroxenes which show textures indicative of rapid chilling were also avoided since it has been demonstrated that cooling rates can affect the Ti/Al ratios of these minerals (Mevel and Velde, 1976; Coish and Taylor, 1978).

Results. Representative analyses showing the variation in chemical composition of pyroxenes in meta-volcanic rocks from the Tamworth Group and Woolomin Beds are shown in Tables I-IV.

To determine the magmatic affinity of the various rock suites in the area, the analyses have been plotted on a series of En-Fs-Di-Hd diagrams (fig. 3) and on $Ca+Na+K$:Mg:$Fe^{II}+Fe^{III}+Mn$ diagrams (fig. 4; Le Bas, 1962). The SiO_2-Al_2O_3 diagram of Le Bas (1962) has not been employed to discriminate between magma types since it has been shown that pyroxenes with apparent non alkaline to peralkaline SiO_2-Al_2O_3 values can occur within a single magmatic body (Gibb, 1973). An examination of the diagrams indicates that:

1. Most volcanic rocks from the Tamworth Group and Woolomin Beds have a tholeiitic parentage since the pyroxene compositions plot within the non-alkaline field of Le Bas (1962) and adjacent to or on the Skaergaard Fe-enrichment trend (figs. 3A, B, C; 4A, B, C). However, those pyroxenes in lavas associated with volcanogenic sediments from the Woolomin Beds in the upper thrust slice show a slightly greater Fe-enrichment and lower wollastonite content than their counterparts in the other suites of volcanic rocks.

2. Some volcanic rocks are geochemically transitional between tholeiitic and alkaline magmas since pyroxenes with moderately high Ca contents (e.g. 7506, 9262) have been noted. These are comparable with the pyroxenes in spilites from a Devonian marine succession in the Nundle region (fig. 3A; Vallance, 1974).

3. The dolerites which intrude the Tamworth Group sequence appear to have either a tholeiitic affinity or are geochemically transitional between tholeiitic and alkaline magmas (e.g. 10657, 9248A, B; figs. 3D; 4D). The tholeiitic affinity is clearly shown by one of the differentiated dolerites (fig. 3E).

4. Specimen 1857, a dolerite intrusive into the cherts of the Woolomin Beds is of alkaline affinity.

To investigate further the compositional differences between the volcanic rock suites, the analyses have been plotted on Ti:$Al_{Tot.}$ diagrams (fig. 5). Examination of these diagrams reveals that the pyroxenes in the Tamworth Group meta-volcanic rocks are more enriched in Al and Ti than those in the Woolomin Beds. A similar enrichment in Ti has been noted in the rocks.

The differences revealed by these diagrams are considered to be real as the paragenetic sequence in

Table I. Representative electron microprobe analyses and structural formulae of pyroxenes in the Devonian meta-volcanic rocks.

	9247#	9247	9261	9261	1855	1855	7506
SiO_2†	50.66	49.51	51.19	50.84	49.83	48.52	47.12
Al_2O_3	2.32	3.40	2.37	2.75	3.16	4.41	4.97
TiO_2	0.59	1.04	0.45	0.61	0.76	1.03	0.93
Cr_2O_3	0.18	0.16	0.25	0.18	0.14	0.12	0.22
FeO*	9.68	9.75	8.76	7.77	9.17	10.70	9.70
MnO	0.20	0.22	0.24	0.13	0.25	0.16	0.23
MgO	16.64	15.68	19.04	16.94	15.64	14.97	13.87
CaO	19.72	20.25	17.68	20.77	21.05	20.09	20.04
Na_2O	-	-	-	-	-	-	0.44
Total	100.85	99.97	100.00	98.83	99.00	99.20	97.52
Ionic ratios to 6 oxygens							
Si	1.891	1.855	1.891	1.885	1.865	1.826	1.818
Al^{IV}	0.102	0.150	0.103	0.115	0.135	0.174	0.182
Al^{VI}	-	-	-	0.006	0.005	0.021	0.046
Ti	0.017	0.029	0.013	0.017	0.021	0.029	0.028
Cr	0.005	0.005	0.007	0.005	0.004	0.004	0.005
Fe^{2+}	0.302	0.305	0.271	0.241	0.287	0.337	0.313
Mn	0.006	0.007	0.008	0.004	0.008	0.005	0.007
Mg	0.926	0.875	1.049	0.936	0.873	0.840	0.797
Ca	0.789	0.813	0.700	0.825	0.844	0.810	0.828
Na	-	-	-	-	-	-	0.032
Cations - atomic percent							
Mg	45.9	43.9	51.9	46.8	43.6	42.3	41.1
Fe	15.0	15.3	13.4	12.0	14.3	17.0	16.2
Ca	39.1	40.8	34.7	41.2	42.1	40.7	42.7

†All values in weight percent normalised to 100% total; original total is also listed.

*Total iron as FeO.

#Specimen numbers refer to those in the collection of the Department of Geology, The University of Newcastle. The location of these specimens is shown in fig.1.

Table II. Representative electron microprobe analyses and structural formulae of pyroxenes in meta-volcanic rocks associated with sediments from the Woolomin Beds.

	10610	10610	10610#	1856	1856	10658	7003
SiO_2†	52.05	51.60	52.19	51.34	49.63	51.67	49.45
Al_2O_3	2.33	2.60	2.69	2.85	1.52	2.96	2.90
TiO_2	-	-	-	-	0.48	0.18	0.67
Cr_2O_3	1.17	0.65	-	0.82	-	0.46	-
FeO*	5.09	6.29	8.69	4.92	17.41	5.58	10.69
MnO	-	0.23	-	-	0.45	0.16	0.30
MgO	19.06	20.20	21.28	18.01	12.36	16.47	14.59
CaO	20.29	18.43	21.28	22.06	18.14	22.51	19.36
Total	99.64	101.62	99.63	98.25	98.43	97.85	97.96
Ionic ratios to 6 oxygens							
Si	1.904	1.889	1.905	1.886	1.915	1.904	1.895
Al^{IV}	0.096	0.111	0.095	0.123	0.069	0.096	0.129
Al^{VI}	0.005	0.002	0.021	0.010	-	0.032	-
Ti	-	-	-	-	0.014	0.005	0.019
Cr	0.034	0.019	-	0.024	-	0.013	-
Fe^{2+}	0.156	0.193	0.265	0.151	0.562	0.172	0.343
Mn	-	0.007	-	-	0.015	0.005	0.009
Mg	1.039	1.103	1.158	0.987	0.711	0.905	0.833
Ca	0.795	0.723	0.593	0.868	0.750	0.888	0.794
Na	-	-	-	-	-	-	-
Cations - atomic percent							
Mg	52.2	54.6	57.4	49.2	35.1	46.1	42.3
Fe	7.8	9.6	13.2	7.5	27.8	8.8	17.4
Ca	40.0	35.8	29.4	43.3	37.1	45.1	40.3

†All values in weight percent normalised to 100% total; original total is also listed.

*Total iron as FeO.

#Groundmass clinopyroxene.

Table III. Representative electron microprobe analyses and structural formulae of pyroxenes in meta-dolerites.

	7959	7959	10663	10663	7958	10657	10657
SiO_2†	50.30	50.27	50.95	51.09	50.56	51.83	52.63
Al_2O_3	1.59	1.21	1.77	0.71	1.71	0.33	0.30
TiO_2	0.58	0.50	0.63	0.38	0.69	0.12	-
Cr_2O_3	-	-	-	-	0.13	0.11	-
FeO*	13.31	15.13	10.55	14.93	12.16	10.44	9.40
MnO	0.50	0.56	0.23	0.57	0.49	0.48	0.40
MgO	14.42	13.35	15.81	12.94	14.78	14.40	14.78
CaO	19.30	18.98	20.06	19.39	19.48	22.28	22.48
Total	98.34	99.46	101.87	100.89	99.63	98.21	99.06
Ionic ratios to 6 oxygens							
Si	1.910	1.924	1.910	1.952	1.910	1.955	1.972
Al^{IV}	0.071	0.055	0.078	0.032	0.076	0.015	0.013
Al^{VI}	-	-	-	-	-	-	-
Ti	0.017	0.014	0.018	0.011	0.020	0.003	-
Cr	-	-	-	-	0.004	0.003	-
Fe^{2+}	0.423	0.484	0.331	0.477	0.384	0.329	0.295
Mn	0.016	0.018	0.007	0.018	0.016	0.015	0.013
Mg	0.816	0.762	0.883	0.737	0.833	0.810	0.825
Ca	0.785	0.778	0.806	0.794	0.789	0.901	0.902
Na	-	-	-	-	-	-	-
Cations - atomic percent							
Mg	40.3	37.6	43.7	36.7	41.5	39.7	40.8
Fe	20.9	23.9	16.4	23.8	19.2	16.1	14.6
Ca	38.8	38.5	39.9	39.5	39.3	44.2	44.6

†All values in weight percent normalised to 100% total; original total is also listed.

*Total iron as FeO.

Table IV. Representative electron microprobe analyses and structural formulae of pyroxenes in meta-volcanic rocks and a meta-dolerite associated with cherts from the Woolomin Beds.

	9262	1850	1857
SiO_2†	51.80	50.71	45.16
Al_2O_3	1.01	1.59	6.52
TiO_2	0.21	0.65	4.23
Cr_2O_3	-	-	-
FeO*	7.54	11.93	8.84
MnO	0.25	0.41	-
MgO	15.54	11.93	12.64
CaO	23.64	20.36	22.61
Total	100.00	99.85	100.88
Ionic ratios to 6 oxygens			
Si	1.934	1.917	1.708
Al^{IV}	0.044	0.071	0.290
Al^{VI}	-	-	-
Ti	0.006	0.019	0.120
Cr	-	-	-
Fe^{2+}	0.236	0.377	0.280
Mn	0.008	0.013	-
Mg	0.865	0.808	0.712
Ca	0.946	0.824	0.916
Na	-	-	-
Cations atomic percent			
Mg	42.3	40.2	37.3
Fe	11.5	18.8	14.7
Ca	46.2	41.0	48.0

†All values in weight percent normalised to 100% total; original total is also listed.

*Total iron as FeO.

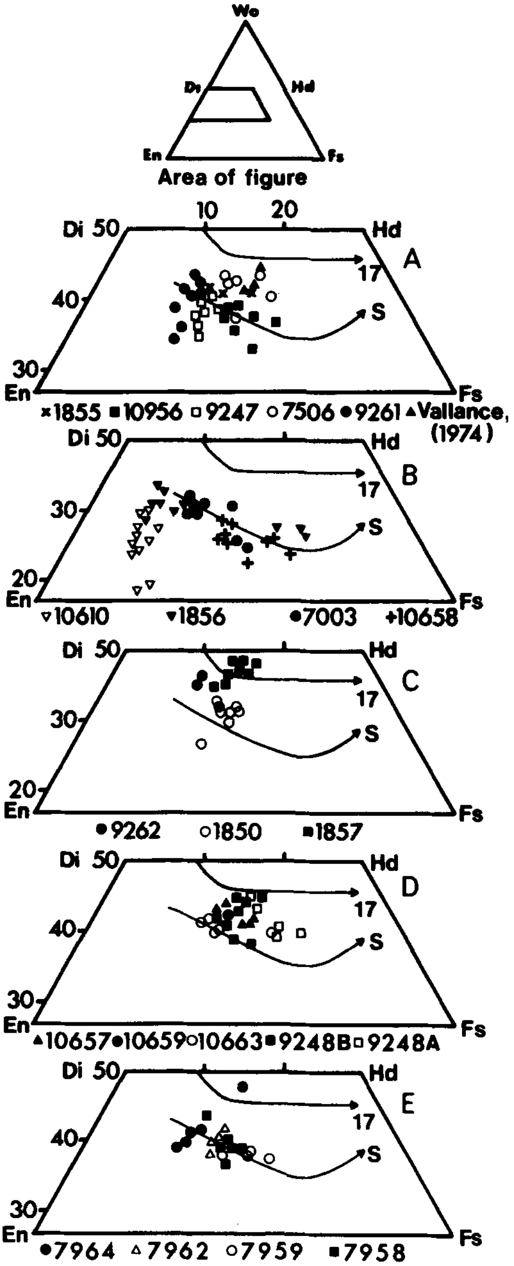

FIG. 3. Composition of clinopyroxenes (atomic per cent) in (A) Meta-basalts, Tamworth Group, (B) Meta-basalts associated with sediments of the Woolomin Beds, (C) Meta-basalts associated with cherts of the Woolomin Beds (1857, a dolerite is also included), (D) Meta-dolerites intrusive into the Tamworth Group sequence, (E) A differentiated meta-dolerite intrusive into the Devonian sequence. 7964 is from the chilled margin. Pyroxene crystallization trends for the Skaergaard intrusion (Brown, 1957), S, and the alkali basalt sill from site 169 of DSDP Leg 17 (Myers *et al.*, 1975), 17.

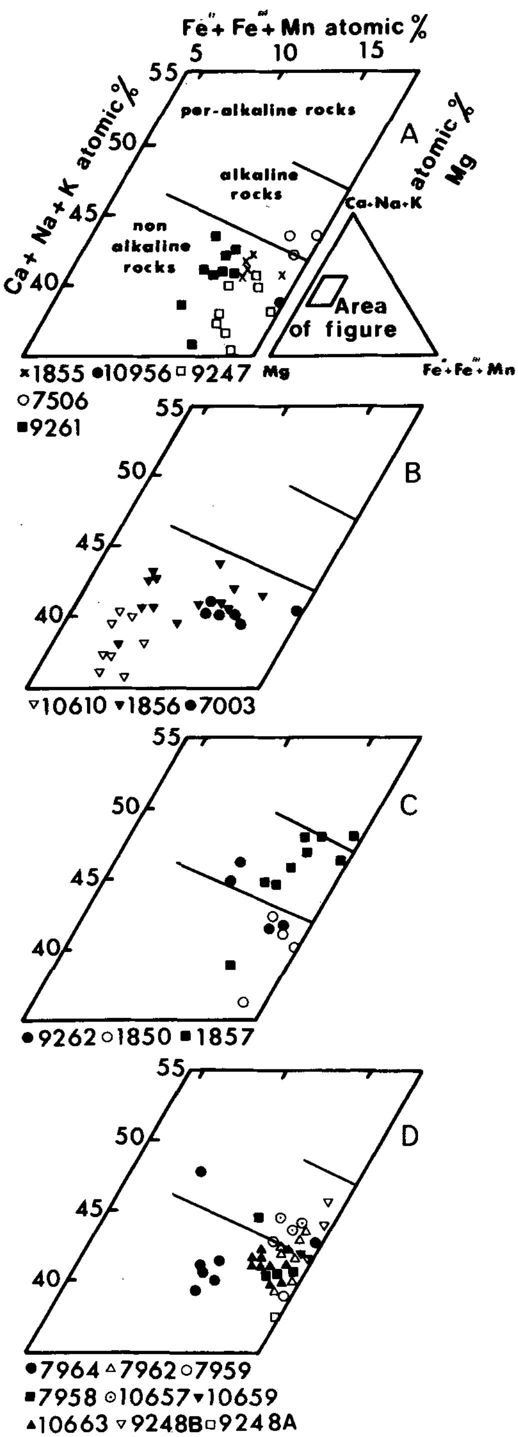

FIG. 4. Composition of clinopyroxenes plotted on the Ca + Na + K : Mg : Fe^{2+} + Fe^{3+} + Mn diagram of Le Bas (1962). Rock suites for (A), (B), (C), and (D) are the same as in fig. 3.

both suites of rocks is the same. There is no indication in any of the rocks that plagioclase or titanomagnetite are early phenocrystic phases, phases which are thought to affect the Al and Ti content of pyroxenes which crystallize later in the paragenetic sequence (Barberi *et al.*, 1971; Gibb, 1973).

The Ti and Al contents of the pyroxenes in the dolerites emplaced in the Devonian sequence are overall poorer in Ti and Al than the pyroxenes of the volcanic rocks, suggesting that they may not be related consanguineously to them. However, the results are inconclusive and additional probe analyses of pyroxenes from other dolerites are necessary before any conclusions can be made. Further, geochemical studies of these dolerites might also be fruitful as preliminary results indicate that at least some dolerites are of a different affinity to the volcanic rocks.

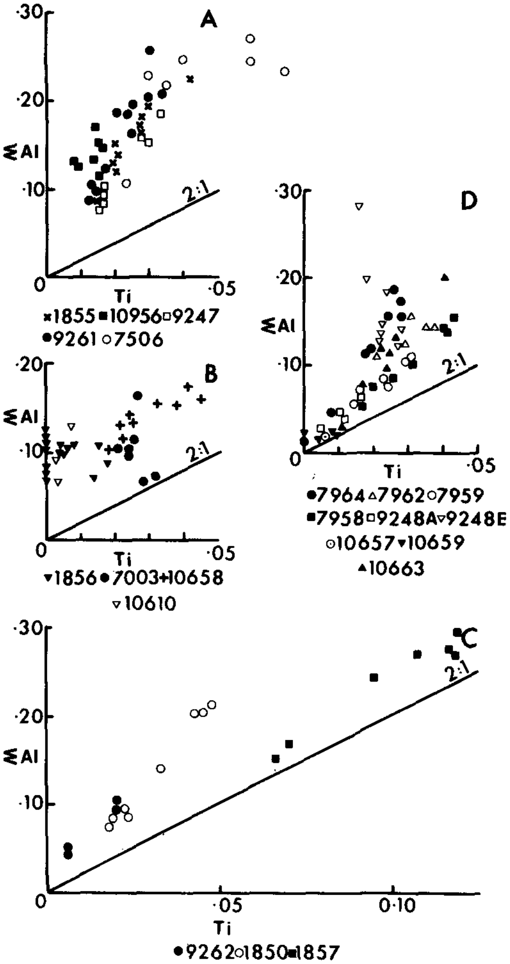

FIG. 5. Ti-Al plots for clinopyroxenes in meta-volcanic and meta-dolerites. Rock suites for (A), (B), (C), and (D) are the same as in fig. 3.

Finally, the pyroxenes in specimen 1857 contain high Al and also very high Ti which reflect their alkaline nature (Kushiro, 1960). In addition, they have Al/Ti ratios approaching 2, indicating that Al is present mostly as the $CaTiAl_2O_6$ component. This contrasts with many of the pyroxenes in the other rocks which have Al/Ti ratios of four or more. Since they contain no Al^{VI} and often insufficient Al^{IV} to fill the tetrahedral site, $CaFeAlSiO_6$ and $CaFeFeSiO_6$ are possible components of these pyroxenes.

Discussion. It might be argued that all the rocks are tholeiitic and that the more alkaline nature of 1857, 7506, 9248A and 9248B, is due to the metastable crystallization of the pyroxenes. Support for this argument can be found only for 9248B which contains pyroxenes with a wide range in wollastonite content (fig. 3D) and shows unusually low Ti/Al ratios (fig. 5D). Such ratios have been noted in pyroxenes from quenched tholeiitic to transitional lavas from the French Alps (Mevel and Velde, 1976). However, minor and trace element analyses of rocks (TiO_2, Zr, P_2O_5) indicates that 9248B is alkaline in nature (Offler, unpublished), so it would appear that the pyroxenes reveal the true magmatic affinity of this rock.

One further comment concerns the distinct compositional trend shown by the pyroxenes in 10610 (fig. 3B). The analyses which define a major portion of this trend represent groundmass clinopyroxenes or the rims of phenocrysts. Since this trend is typical of quench pyroxene trends (Evans and Moore, 1968), it would seem that metastable crystallization of pyroxenes took place after most phenocryst growth had been completed.

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[*Note added in proof*: Fig. 1. The symbols for 'FAULT INFERRED' and 'FAULT OBSERVED' should be reversed]

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