

Significance of clinopyroxene compositions from the Cudgegong Volcanics and Toolamanang Volcanics; Cudgegong-Mudgee district, NSW, Australia

J. W. PEMBERTON

Department of Geology, University of Wollongong, Wollongong, NSW, Australia, 2500

AND

R. OFFLER

Department of Geology, University of Newcastle, Newcastle, NSW, Australia, 2308

SYNOPSIS

CLINOPYROXENE phenocrysts and groundmass crystals are relict phases in altered basalt and basaltic andesite lavas, and arenites of the Cudgegong Volcanics and Toolamanang Volcanics, Cudgegong-Mudgee district, New South Wales. Petrography, field relationships and clinopyroxene compositions indicate that basaltic blocks in the latter unit are reworked from the Cudgegong Volcanics. Clinopyroxene phenocrysts show a restricted compositional range and minor Fe-enrichment from core to rim, features considered indicative of a calc-alkaline parent magma. It is proposed that the Cudgegong Volcanics crystallized under hydrous conditions, at least in the later stages, with rising f_{O_2} , resulting in a Fe-Ti oxide crystallizing as a primary phase. The clinopyroxenes are considered to have crystallized at moderate (5-6 kbar) and falling pressures and at

minimum temperatures in the range 900 to 1000 °C. Coupled substitutions affecting the 'other' components in the clinopyroxene structural formula indicate that the ${}^{iv}Al-{}^{vi}Fe^{3+}$, ${}^{iv}Al-{}^{vi}Al$ and ${}^{iv}Al-{}^{vi}Ti^{4+}$ couples are important. The Sofala Volcanics, south of the study area, and the Cudgegong Volcanics are similar in age, petrography and stratigraphic position, and contain relict clinopyroxenes which are chemically similar. This suggests that the units are laterally equivalent and adds further evidence to the proposal that an oceanic island arc system was active in central western New South Wales during the Late Ordovician.

KEYWORDS: clinopyroxene, basalts, arenites, Cudgegong Volcanics, Toolamanang Volcanics, New South Wales, Australia.

Introduction. Cudgegong is located approximately 200 km northwest of Sydney and approximately 40 km southeast of Mudgee (fig. 1). The Cudgegong-Mudgee district is situated on the northeastern margin of the Lachlan Fold Belt and incorporates volcanic and sedimentary rocks deposited in the Hill End Trough and on the Capertee High (Packham, 1968). Rocks of the study area are of Ordovician and Silurian age and crop out in a northwest-plunging anticline, flanked by Devonian sedimentary sequences (Pemberton, 1980).

The oldest rocks are the Late Ordovician Cudgegong Volcanics, consisting of basalt and basaltic andesite lavas and immature, fine- to coarse-grained volcanarenites. The Volcanics are overlain unconformably by the Wenlockian to Ludlovian Willow Glen Formation (principally conglomerates and shales with limestone horizons) which is conformably overlain by the Windamere Volcanics, a sequence of dacitic and rhyolitic lavas associated with dacite breccias and minor fine- to coarse-grained volcanarenites. They are in turn conformably overlain by the Ludlovian Millsville Beds consisting of coarse breccias (containing limestone, dacite and rhyolite clasts) and minor limestone and shale lenses. At Cudgegong, the

Willow Glen Formation appears to be conformably overlain by the Toolamanang Volcanics. The Volcanics are dominantly massive, immature arenites which are thought to be derived from, or laterally equivalent to, the Windamere Volcanics. In addition, the Toolamanang Volcanics include basaltic blocks which may have been reworked from the Cudgegong Volcanics.

The rocks show the imprint of prehnite-pumpellyite to lower greenschist facies metamorphism (Offler and Pemberton, 1983). Although the alteration has masked many of the mineralogical and geochemical characteristics of the original volcanic rocks, igneous textures are generally well-preserved and clinopyroxene and amphibole are relict phases in the Cudgegong Volcanics.

Previous studies on Ordovician volcanic rocks in the northeastern part of the Lachlan Fold Belt have been concerned with their metamorphism (Smith, 1969; Barron and Barron, 1976); the mobility of trace elements during their alteration (Smith and Smith, 1976; Hellman *et al.*, 1977) and the recognition of their magmatic affinity from clinopyroxene chemistry (Barron, 1976). The present study has been carried out to ascertain

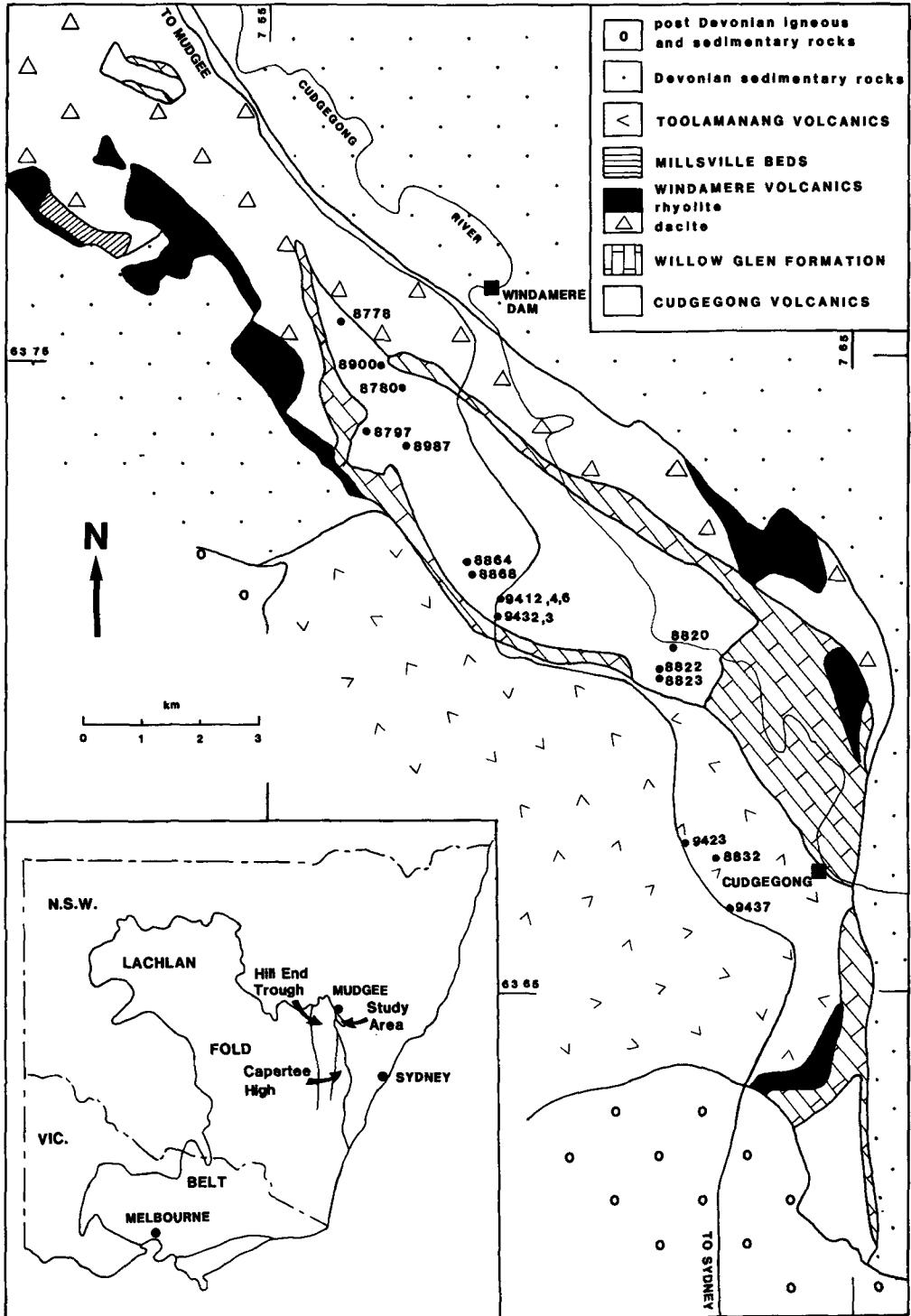


FIG. 1. The geology of the Cudgong-Mudgee district and specimen localities. Australian map grid (last three zero's deleted) taken from the Mudgee and Rylstone 1:50,000 topographic sheets.

whether the Cudjegong Volcanics have a similar magmatic affinity to other Ordovician basic volcanic rocks in this region, using the chemistry of the relict clinopyroxenes. A further aim has been to determine the substitutions that occur in the clinopyroxenes and possible pressure and temperature conditions at which they have crystallised.

Cudjegong Volcanics. The basalt and basaltic andesite lavas are porphyritic containing abundant phenocrysts of plagioclase (commonly altered to albite, chlorite, calcite, white mica and epidote) and clinopyroxene, often in glomeroporphyritic aggregates; amphibole is rare. The phenocrysts are set in a pilotaxitic groundmass of relict clinopyroxene and amphibole together with the alteration phases albite, chlorite, calcite, epidote, sphene, actinolite, pyrite. Chlorite, calcite, prehnite, pumpellyite and quartz are common in amygdules and veins.

Clinopyroxene occurs as subhedral to euhedral phenocrysts, up to 6 mm across, often with strong zoning, and as subhedral grains in the groundmass of the lavas; in the arenites it appears as phenoclasts. Many grains are unaltered yet others are replaced by calcite, chlorite, actinolite and epidote.

Pargasitic amphibole occurs as anhedral grains up to 2 mm in width in the arenites and as rare euhedral phenocrysts and subhedral grains in the groundmass of the lavas. The grains are pleochroic (X = colourless, Y = light green, Z = green/brown) and show no zonation.

Toolamanang Volcanics. The fine- to medium-grained, grey to brown volcanics of the Toolamanang Volcanics commonly contain broken albitised plagioclase and quartz crystals together with fine-grained siliceous clasts, some of which contain albitised plagioclase phenocrysts. In addition, minor subhedral hornblende crystals and more common pseudomorphs after amphibole occur in some clasts. Rock types identified from this detritus are comparable to those in the Windamer Volcanics and suggest a dacitic parentage for the Toolamanang Volcanics. However, the volcanics enclose basaltic blocks of variable size. The basalts and basaltic andesites contain relict clinopyroxene and amphibole and are petrographically similar to rocks of the Cudjegong Volcanics.

Methods. The analyses were carried out on a JEOL JXA-50A electron microprobe 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.

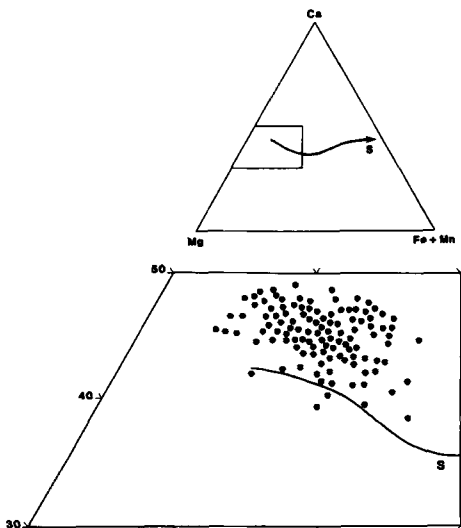


FIG. 2. Compositions of clinopyroxene phenocrysts (atomic %) from the Cudjegong Volcanics. The Skaergaard differentiation trend (S) is included (Wager and Brown, 1968).

Clinopyroxene phenocrysts were analysed at several points along traverses from core to rim to determine whether they were chemically heterogeneous. In addition, unaltered groundmass crystals were analysed to ascertain their compositional variation.

Results

Phenocrysts and groundmass crystals of clinopyroxene from the Cudjegong Volcanics and Toolamanang Volcanics have been analysed by electron microprobe. Representative analyses are shown in Table 1. The compositions of the clinopyroxene phenocrysts from the Cudjegong Volcanics are plotted on the Ca-Mg-Fe+Mn quadrilateral (fig. 2) which indicates that they are diopsides, salites and augites according to the classification of Poldervaart and Hess (1951). The analyses also reveal minor MgO enrichment in the cores as well as minor FeO and Al_2O_3 enrichment in the rims. The groundmass clinopyroxenes show greater MgO depletion and FeO and Al_2O_3 enrichment, however, they are noticeably more variable in composition than the phenocrysts.

The compositions of clinopyroxene phenocrysts from basaltic blocks in the Toolamanang Volcanics are similar to those in the Cudjegong Volcanics (fig. 3). Further, the basalts and basaltic andesites in the two sequences

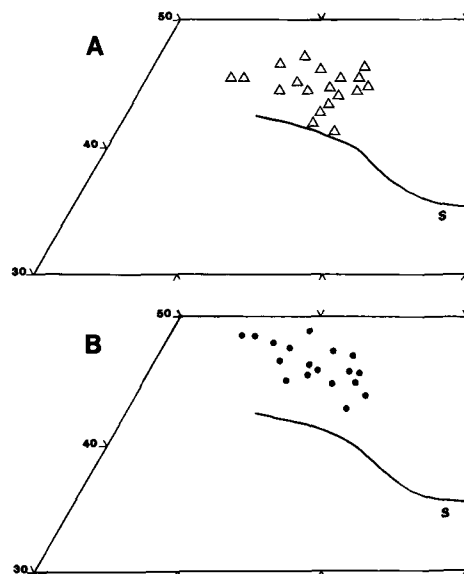


FIG. 3. Compositions of clinopyroxene phenocrysts (atomic %) from A, the Toolamanang Volcanics and B, the Sofala Volcanics (Barron, 1976).

are petrographically similar and together with the field relationships, this suggests that these blocks in the Toolamanang Volcanics are reworked from the Cudjegong Volcanics.

García (1978) emphasises the commonly accepted view that differentiation of tholeiitic magmas produces a distinct to strong Fe-enrichment in the clinopyroxenes (for example, the Skaergaard intrusion (Wager and Brown, 1968)) whereas clinopyroxenes from calc-alkaline magmas show little or no Fe-enrichment. Fig. 2 reflects the restricted compositional range of the clinopyroxenes of the Cudjegong Volcanics and shows that the minor Fe-enrichment noted from core to rim is not nearly as marked as the intra-granular Fe-enrichment described for individual clinopyroxenes of some tholeiitic suites (Fodor *et al.*, 1975; Marcelot *et al.*, 1983). Thus a calc-alkaline parentage is suggested for the Cudjegong Volcanics.

The Sofala Volcanics, which are similar in age and petrography to the Cudjegong Volcanics (Pemberton, 1980; Pickert, 1982), crop out approximately 40 km south of Cudjegong on the eastern margin of the Hill End Trough (Packham, 1968). They contain clinopyroxenes with Ca, Mg, Fe and Mn contents comparable to those in the Cudjegong Volcanics (fig. 3). Barron (1976) noted that clinopyroxenes of the Sofala Volcanics contained appreciable Cr_2O_3 and low TiO_2 and MnO, together with a trend towards MgO

Table 1.A. Representative electron microprobe analyses and structural formulae for clinopyroxene phenocrysts in the Cudjegong Volcanics.

	8778	8780	8797	8820	8822	8823	8864	8868	8900	8987	9412	9414	9416	9432	9433	
+																
SiO ₂	52.01	50.41	51.24	52.19	50.84	51.77	50.27	51.12	50.79	52.28	52.51	51.97	49.81	50.30	50.72	
Al ₂ O ₃	2.57	3.52	3.56	2.34	3.12	2.86	3.34	2.34	3.71	2.26	1.90	1.98	3.06	4.32	3.09	
TiO ₂	0.13	0.44	0.32	0.21	0.37	0.30	0.51	0.32	0.26	0.14	0.15	0.31	0.73	0.32	0.36	
Cr ₂ O ₃	0.57	0.17	0.24	0.55	0.18	0.53	0.13	0.13	0.54	0.39	—	—	—	0.13	—	
FeO*	6.01	9.15	6.95	6.43	8.84	5.87	8.50	9.15	7.26	6.43	8.99	9.04	12.19	7.61	8.75	
MnO	—	0.31	—	0.16	0.25	—	0.20	0.46	—	—	0.53	0.34	0.35	0.13	0.21	
MgO	15.70	13.78	15.60	15.77	14.94	15.75	14.06	15.53	15.29	14.68	15.15	15.01	13.40	14.86	14.14	
CaO	23.01	21.79	22.09	22.35	21.45	22.93	22.99	22.13	21.42	23.22	20.68	21.26	19.72	22.05	22.02	
Na ₂ O	—	0.33	—	—	—	—	—	0.70	0.42	0.51	—	—	0.60	0.27	0.65	
Total	100.97	99.96	99.88	100.94	99.07	100.67	100.07	100.64	99.17	99.17	99.75	100.59	100.40	100.34	100.21	
Ionic ratios per 6 oxygens																
Si	1.920	1.890	1.895	1.928	1.897	1.910	1.883	1.921	1.884	1.938	1.952	1.937	1.882	1.870	1.890	
Al ^{iv}	0.080	0.110	0.105	0.072	0.103	0.090	0.117	0.079	0.116	0.062	0.048	0.063	0.118	0.130	0.100	
Al ^{vi}	0.032	0.046	0.050	0.030	0.034	0.034	0.030	0.024	0.047	0.036	0.036	0.024	0.019	0.060	0.036	
Ti	0.004	0.012	0.009	0.006	0.010	0.008	0.014	0.009	0.007	0.004	0.004	0.009	0.021	0.009	0.010	
Cr	0.016	0.005	0.007	0.016	0.005	0.015	0.004	0.004	0.016	0.012	—	—	—	0.004	—	
Fe	0.185	0.288	0.215	0.199	0.276	0.181	0.266	0.287	0.225	0.199	0.280	0.282	0.386	0.237	0.274	
Mn	—	0.010	—	0.005	0.008	—	0.006	0.014	—	—	0.017	0.011	0.011	0.004	0.007	
Mg	0.864	0.768	0.860	0.868	0.831	0.866	0.785	0.758	0.845	0.811	0.840	0.834	0.757	0.824	0.784	
Ca	0.910	0.875	0.875	0.884	0.857	0.906	0.923	0.891	0.864	0.922	0.824	0.849	0.801	0.878	0.888	
Na	—	0.024	—	—	—	—	—	0.051	0.030	0.037	—	—	0.044	0.020	0.047	
Cations — atomic percent																
Ca	46.65	45.31	44.88	45.33	43.65	46.40	46.74	46.02	44.64	47.71	42.39	43.22	41.18	45.31	45.63	
Mg	44.08	39.84	44.08	44.49	42.31	44.33	39.77	39.14	43.71	41.97	43.22	42.44	38.95	42.48	40.28	
Fe	9.47	14.85	11.03	10.18	14.04	9.27	13.49	14.84	11.65	10.32	14.39	14.34	19.87	12.21	14.09	

Table 1.B. Representative electron microprobe analyses and structural formulae for groundmass clinopyroxenes in the Cudjegong Volcanics.

	8780	8797	8823	8900	8987
+					
SiO ₂	50.86	50.26	50.79	49.42	48.78
Al ₂ O ₃	2.89	4.07	2.91	0.99	5.16
TiO ₂	0.44	0.52	0.46	—	0.58
Cr ₂ O ₃	—	—	—	—	0.17
FeO*	9.61	9.50	10.32	16.88	9.17
MnO	0.38	0.16	0.37	0.16	0.18
MgO	14.40	14.10	14.83	7.39	13.07
CaO	20.38	21.67	20.07	22.39	22.19
Na ₂ O	0.82	0.32	0.25	0.91	0.55
Total	100.11	99.07	99.87	101.16	100.22
Ionic ratios per 6 oxygens					
Si	1.907	1.871	1.902	1.960	1.837
Al ^{iv}	0.093	0.129	0.098	0.041	0.164
Al ^{vi}	0.035	0.051	0.031	0.005	0.066
Ti	0.012	0.015	0.013	—	0.017
Cr	—	—	—	—	0.005
Fe	0.302	0.297	0.323	0.554	0.289
Mn	0.012	0.005	0.012	0.039	0.006
Mg	0.805	0.786	0.828	0.433	0.734
Ca	0.819	0.844	0.805	0.942	0.895
Na	0.593	0.023	0.018	0.070	0.040
Cations — atomic percent					
Ca	42.52	43.81	41.17	48.84	46.68
Mg	41.80	40.78	42.31	22.43	38.26
Fe	15.68	15.41	16.52	28.73	15.06

Table 1.C. Representative electron microprobe analyses and structural formulae for clinopyroxene phenocrysts in the Toolamanang Volcanics.

	8832	9423	9423 ^o	9437
+				
SiO ₂	49.99	50.70	44.75	51.52
Al ₂ O ₃	4.06	3.32	8.05	2.81
TiO ₂	0.55	0.39	1.16	0.34
Cr ₂ O ₃	0.14	0.39	—	0.23
FeO*	8.72	7.62	13.34	7.24
MnO	0.20	0.20	0.22	0.21
MgO	14.32	14.60	10.52	15.57
CaO	21.45	22.68	21.82	21.99
Na ₂ O	0.48	—	—	—
Total	100.00	100.00	100.83	100.95
Ionic ratios per 6 oxygens				
Si	1.870	1.887	1.721	1.910
Al ^{iv}	0.130	0.113	0.278	0.090
Al ^{vi}	0.049	0.033	0.086	0.033
Ti	0.016	0.011	0.034	0.010
Cr	0.004	0.012	—	0.007
Fe	0.275	0.237	0.429	0.225
Mn	0.006	0.006	0.007	0.007
Mg	0.798	0.811	0.603	0.866
Ca	0.860	0.806	0.900	0.873
Na	0.035	—	—	—
Cations — atomic percent				
Ca	44.48	46.35	46.57	44.47
Mg	41.31	41.49	31.22	44.10
Fe	14.21	12.16	22.21	11.43

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

* Total iron as FeO.

^o Groundmass clinopyroxene.

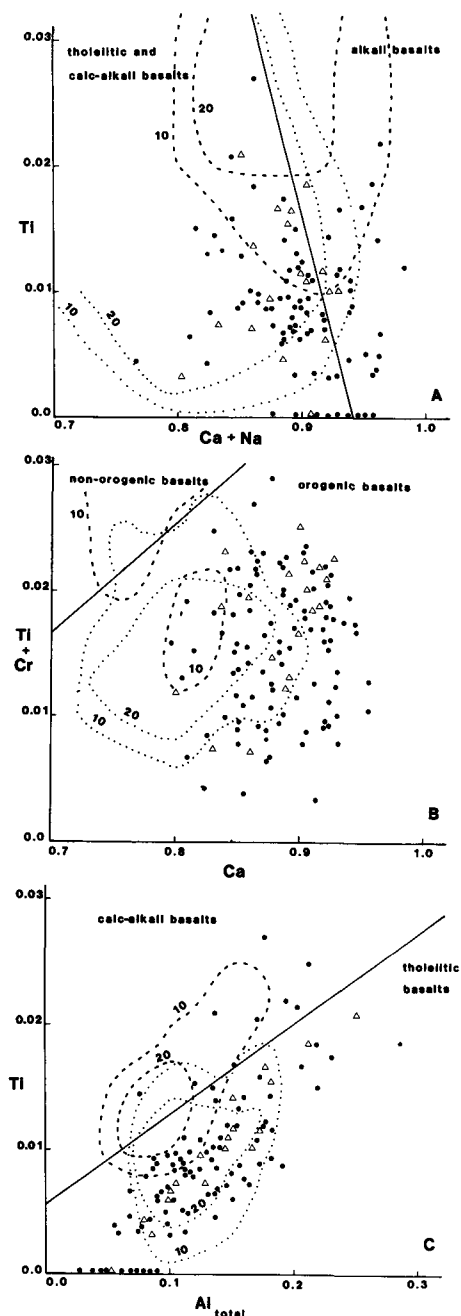


FIG. 4. Compositions of clinopyroxene phenocrysts (cations per structural formula unit; $O = 6$) from the Cudjegong Volcanics and Toolamanang Volcanics. Symbols are the same as in figs 2 and 3A. Discriminant diagrams are after Leterrier *et al.* (1982); 10% and 20% frequency curves are included.

depletion and FeO enrichment in crystal rims. The clinopyroxenes of the Cudjegong Volcanics have similar compositions. Further, the stratigraphic position of the two units is considered similar (Pemberton, 1980) suggesting that the Cudjegong Volcanics and Sofala Volcanics are laterally equivalent.

Leterrier *et al.* (1982) distinguish between three magma types on the basis of Ca, Ti and Al_{total} contents (and to a lesser degree Cr and Na) of clinopyroxenes from basalts and basaltic andesites. Fig. 4 incorporates data from the Cudjegong Volcanics and Toolamanang Volcanics in the diagrams of Leterrier *et al.* (1982). The majority of clinopyroxenes plot in the tholeiitic and calc-alkali field (fig. 4A) and in the orogenic basalt field (fig. 4B); fig. 4C indicates that the clinopyroxenes are tholeiitic rather than calc-alkaline in nature. However, the usefulness of the latter discriminant diagram may be questioned. Clinopyroxene data from documented island arc suites of known calc-alkaline affinity commonly plot within the "tholeiitic" field; as does Leterrier *et al.*'s data (Table 1, p. 141) for calc-alkaline rocks of island arcs.

The reason for this apparently anomalous behaviour may be due to the crystallisation of Fe-Ti oxides, thus restricting the Fe and Ti available for clinopyroxene. This results in the crystallisation of clinopyroxene low in Ti and thus clinopyroxenes from calc-alkaline lavas could plot in either the calc-alkali or tholeiitic field of Leterrier *et al.*'s Ti-Al_{total} diagram. This aspect will be discussed later in the paper.

Discussion

Fe-enrichment trends. The composition of clinopyroxenes depends largely on the chemistry of the host magma. The subsequent crystallisation trend is controlled by the conditions under which fractionation occurs (Gibb, 1973). Tholeiitic complexes generally preserve their crystallisation history as orderly differentiated layers, a characteristic of the tectonically stable environment in which they are normally emplaced (Mueller and Saxena, 1977). Clinopyroxene phenocrysts reflect the whole rock trend towards Fe-enrichment with differentiation (Kay *et al.*, 1983). It is considered that in this environment a closed system prevails whereby fO_2 is low and anhydrous conditions exist (Best and Mercy, 1967; Gibb, 1973; Kay *et al.*, 1983). Under these conditions, Fe is partitioned into the crystallising silicate phases (of which clinopyroxene is dominant) and results in the Fe-enrichment trend observed for clinopyroxenes of tholeiitic magmas (Crove *et al.*, 1982).

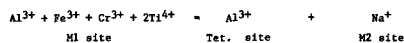
Calc-alkaline magmas, on the other hand, are restricted to orogenic settings and rarely display complete differentiation suites (Mueller and Saxena, 1977). Clinopyroxene phenocrysts commonly exhibit a restricted compositional range with little or no Fe-enrichment. It has been suggested that calc-alkaline magmas crystallise in an open system where the tectonic setting produces hydrous conditions providing an abundance of oxygen in the system thus maintaining a constant or rising fO_2 (Best and Mercy, 1967; Morse, 1980; Kay *et al.*, 1983). Oxygen fugacity is of critical importance in magmatic differentiation as it controls the partitioning of Fe in the magma (Osborn, 1959; Gibb, 1973). Under oxidising conditions, Fe is partitioned into oxide phases such as magnetite and titaniferous magnetite at the expense of the crystallising silicates, thus limiting the Fe, and perhaps Ti, available to the clinopyroxenes and producing the restricted compositional variation observed for clinopyroxenes in calc-alkaline rocks (Fodor, 1971; Nisbet and Pearce, 1977; Gill, 1981; Kay *et al.*, 1983; Marcelot *et al.*, 1983; Mullen, 1983). In addition, hydrous conditions result in the fractionating magma leaving the clinopyroxene stability field with only moderate Fe content as hornblende and biotite take over as the dominant Fe/Mg crystallising phases (Best and Mercy, 1967; Fodor, 1971).

The following discussion examines these suggested conditions with respect to the clinopyroxenes of the Cudjegong Volcanics and Toolamanang Volcanics.

Fe^{3+}/Fe^{2+} contents in clinopyroxenes. Oxygen fugacity varies with the temperature of the magma (Osborn, 1959; Nash and Wilkinson, 1970). However, the ferric/ferrous iron ratio of a magma is considered an indicator of its potential for oxidation and reduction (Morse, 1980). Best and Mercy (1967) suggest that fO_2 can be evaluated from the Fe^{3+}/Fe^{2+} ratio of the Fe-bearing crystallising phases. Vieten (1980) proposed that, with increasing fO_2 , Fe^{3+} is partitioned into the clinopyroxene M1 site to compensate for Al^{3+} replacing Si^{4+} in the tetrahedral site. This increasing fO_2 can be reflected by an increase in the Fe^{3+}/Fe^{2+} ratio in clinopyroxene phenocrysts analysed from core to rim.

The majority of recent clinopyroxene analyses have been produced by electron microprobe, from which there is no direct measure of the oxidation state of Fe. However, the importance of Fe^{3+} has been shown by wet chemical analytical methods. Several methods have been proposed to calculate the Fe^{3+} content of clinopyroxenes from electron microprobe analyses. For example, Papke *et al.* (1974) calculate Fe^{3+} by use of the charge balancing equation produced from the coupled substitutions in the 'other' components of the clinopyroxene structural formula. According to

these authors, charge excess cations should balance with charge deficiency cations to produce the following:



Cameron and Papike (1981) consider a clinopyroxene analysis is of acceptable quality if the above equation balances ± 0.03 structural formula units. The significance of this value in calculating Fe^{3+} must be noted.

Methods involving the stoichiometry of the clinopyroxene structural formula (ie: four cations and six oxygens) have been used by Robinson (1980) and D. French (pers comm). Robinson (1980) recalculates the analysis to 4.0 cation total and assigns each cation a proportion of oxygen dependent on the cation charge (at this stage, Fe is calculated as Fe^{2+}). If any oxygen remains, it is referred to Fe_2O_3 and the Fe^{3+} value is calculated. D. French (pers comm) computes the clinopyroxene structural formula initially with Fe as Fe^{2+} . He adjusts the proportions of Fe^{2+} and Fe^{3+} in the formula until the ratio of stoichiometric cation total (4.0) to the total of computed cation proportions is near unity.

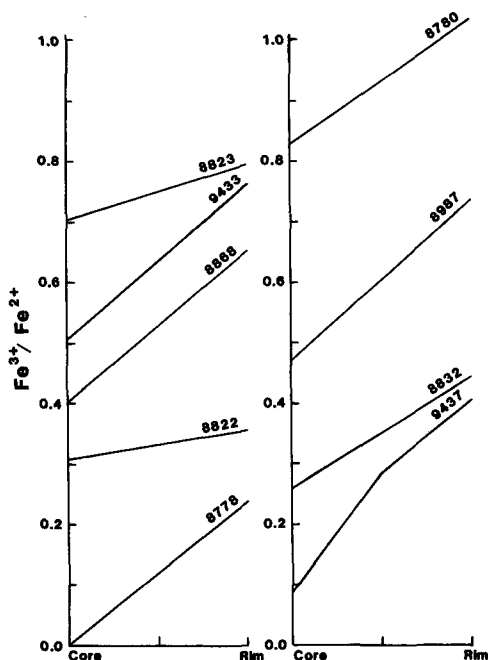


FIG. 5. $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios determined from the method of Robinson (1980) for clinopyroxene phenocrysts from the Cudgegong Volcanics (8778, 8780, 8822, 8823, 8868, 8987, 9433) and Toolamanang Volcanics (8832, 9437).

Each of the methods was used to estimate Fe^{3+} , Fe^{2+} and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio for the clinopyroxenes of the Cudgegong Volcanics and Toolamanang Volcanics. The sensitivity of each method to analytical error must be emphasised, in particular the impact of inaccurately determined SiO_2 . The methods of Robinson and French produced similar results whereas Papike *et al.*'s values differed substantially. In general, stoichiometric methods produced relatively higher Fe^{3+} and lower Fe^{2+} . Plots of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio for clinopyroxene phenocrysts (eg: fig. 5) show a consistent increase towards phenocryst rims regardless of which method was used to calculate Fe^{3+} . Similar plots for groundmass clinopyroxene grains show greater variation and a less discernable trend. The increasing $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio suggests that $f\text{O}_2$ increased during crystallisation of the clinopyroxene phenocrysts of the Cudgegong Volcanics.

The presence of Fe-bearing oxides. Neither Fe oxide nor Fe-Ti oxide have been observed in the Cudgegong Volcanics or the Toolamanang Volcanics. However, sphene is common as a secondary phase. In the more altered rocks, sphene occurs as very fine-grained disseminated masses whereas in less altered rocks, it occurs as aggregates, up to 0.2 mm across, of very fine grains forming rounded inclusions in clinopyroxene phenocrysts and as rounded to angular aggregates of similar size in the groundmass. It is possible that some of the coarser-grained sphene masses are pseudomorphs after Fe-Ti oxide. However, it must be considered that some of Ti for the production of sphene could have been generated by clinopyroxene breakdown. The latter is suggested particularly in the more altered basalts and basaltic andesites where groundmass clinopyroxene is commonly altered to actinolite and the sphene is very fine-grained and disseminated.

Calculations using the modal volume of phenocrystic and groundmass clinopyroxene together with the maximum recorded TiO_2 content for each show that the clinopyroxenes of the Cudgegong Volcanics would account for less than two-thirds of the whole rock TiO_2 recorded for the Cudgegong Volcanics and Toolamanang Volcanics, namely from 0.50 to 0.67%. Thus it appears that crystallising clinopyroxene could not accommodate the whole rock TiO_2 and the remainder must be partitioned into another primary phase. Pargasitic amphibole is present as a minor late-stage primary phase, however, it would accept only a minor amount of TiO_2 .

The modal volume of sphene, the major Ti-bearing secondary phase, proves difficult to calculate as it is commonly very fine-grained. If IX modal sphene, a conservative estimate of the volume, is present with the lowest recorded TiO_2 content for sphene in the Cudgegong Volcanics (ie: 30.76%), the amount of TiO_2 necessary to produce this sphene is much greater than that accounted for by clinopyroxene. Complete breakdown of clinopyroxene could not produce the amount of sphene observed in the Cudgegong Volcanics.

If IX modal Fe-Ti oxide with a 20% TiO_2 content (Deer *et al.*, 1971, p. 427) was present as a primary phase, it would account for approximately 0.35% whole rock TiO_2 . The breakdown of the Fe-Ti oxide and some groundmass clinopyroxene could produce the necessary TiO_2 to crystallise IX modal secondary sphene. Thus it is considered likely that a Fe-Ti oxide was a primary phase in the Cudgegong Volcanics.

Pargasitic amphibole. The presence of pargasitic amphibole as rare phenocrysts and more commonly as groundmass crystals suggests it is a late stage crystallisation product of the Cudgegong Volcanics and adds credence to the proposed hydrous nature of the magma. With amphibole crystallisation, Fe and Ti would partition between clinopyroxene and amphibole, thus providing another possible mechanism for limiting Fe-enrichment in clinopyroxenes.

Thus it is considered that the Cudgegong Volcanics crystallised under hydrous conditions, at least in the later stages, with rising $f\text{O}_2$ resulting in a Fe-Ti oxide crystallising as a primary phase. These conditions are consistent with those previously proposed to explain the restricted compositional range of clinopyroxenes from calc-alkaline magmas and would indicate a calc-alkaline magmatic affinity for the Cudgegong Volcanics.

Substitutions in the clinopyroxenes. The simplest clinopyroxene structural formula is that of diopside, $\text{CaMgSi}_2\text{O}_6$ where Ca occupies the M2 site; Mg is in the octahedral M1 site and Si is tetrahedrally co-ordinated. Substitution of divalent cations, Fe, Mn and Mg for Ca in the M2 site and Fe and Mn for Mg in the M1 site, produces the compositional variations observed in the pyroxene quadrilateral. However, clinopyroxene analyses indicate the presence of significant amounts of cations other than Ca^{2+} , Mg^{2+} , Fe^{2+} and Mn^{2+} (Cameron and Papike, 1981). Substitutions involving the "other or nonquadrilateral" cations may cause charge imbalance within each of the three occupancy sites (Papike *et al.*, 1974; Tracy and Robinson, 1977). These substitutions are coupled so that overall charge balance is preserved.

Substitution of Na^{+} for Ca^{2+} in the M2 site causes a charge deficiency of one in this site. In addition, Al^{3+} replacing Si^{4+} in the tetrahedral site produces a similar charge deficiency. Huckenholz *et al.* (1969) recognise the substitution of Fe^{3+} for Si^{4+} in the latter site. However, this substitution is considered of minor importance. The charge increasing substitutions involve trivalent cations (Al, Cr, Fe and Ti) replacing Mg in the M1 site creating a charge excess of one. In addition, Ti^{4+} may substitute in the M1 site producing a charge excess of two. To maintain charge balance in the structural formula, site charge excess must

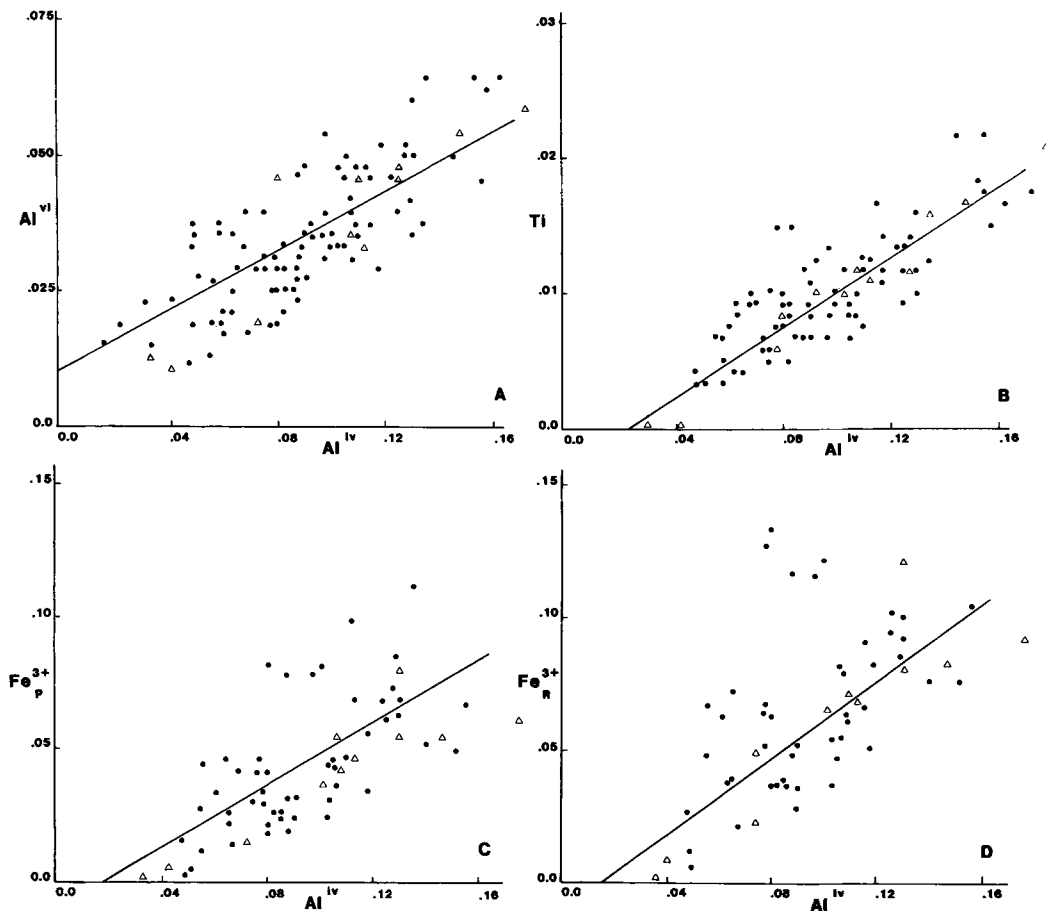
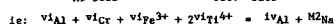
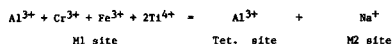


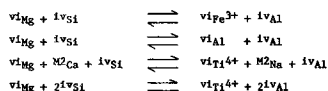
FIG. 6. Compositions of clinopyroxene phenocrysts (cations per structural formula unit; $O = 6$) from the Cudjegong Volcanics and Toolamanang Volcanics. Symbols are the same as in figs 2 and 3A. Explanation of lines is in the text.

be compensated by site charge deficiency. Thus the charge balancing equation should be obeyed (Cameron and Papke, 1981).



From the above, the relevant substitutional couples are: $v_{Al} - i_{Al}$; $v_{Cr} - i_{Al}$; $v_{Fe^{3+}} - i_{Al}$; $v_{Ti^{4+}} - 2i_{Al}$; $v_{Al} - Na$; $v_{Cr} - Na$; $v_{Fe^{3+}} - Na$; $v_{Ti^{4+}} - 2Na$; $v_{Ti^{4+}} - Na - i_{Al}$.

Cameron and Papke (1981) reviewed the clinopyroxene analyses in Deer *et al.* (1971) noting the most important substitutional couple in each analysis. They suggest the most important coupled substitutions are:



Analytical errors remain a problem. In particular, small errors in SiO_2 content will produce significantly different values of 'other' components (Tracy and Robinson, 1977).

Plots of the relevant substitutional couples for the clinopyroxenes of the Cudjegong Volcanics and Toolamanang Volcanics are presented in fig. 6. Anomalous high Na_2O values, owing to machine instability, were recorded during a later session on the electron microprobe. Clinopyroxenes analysed

earlier record little or no Na_2O and it is considered that Na plays a very minor role in the clinopyroxene composition. However, Na_2O directly affects the calculation of Fe^{3+} values. Thus in fig. 6C and 6D only the earlier analyses are plotted. Later analyses plot with a similar slope but with varying intercept on the Fe^{3+} axis.

Plots of i_{VAl} vs v_{Al} , i_{VAl} vs $v_{Ti^{4+}}$ and i_{VAl} vs $v_{Fe^{3+}}$ (determined by both Papke *et al.* (1974) and Robinson (1980) methods) are linear and emphasize the coupled nature of the pairs. No such trend was observed for i_{VAl} vs v_{Cr} . Slopes of the best fit lines were calculated and the relevant regression curves determined as follows:

$$\begin{array}{l} v_{Al} = .01 + .27 i_{VAl} \\ v_{Ti^{4+}} = -.003 + .13 i_{VAl} \\ v_{Fe^{3+}} \text{ (Papke)} = -.01 + .59 i_{VAl} \\ v_{Fe^{3+}} \text{ (Robinson)} = .72 i_{VAl} \end{array}$$

Marcelot *et al.* (1983) note that the slope of each line represents that amount of i_{VAl} coupled to each of v_{Al} , $v_{Ti^{4+}}$ and $v_{Fe^{3+}}$. Thus, for example, 27% of i_{VAl} is coupled with v_{Al} . Using the slopes of the regression curves above, the importance of the $i_{VAl} - v_{Fe^{3+}}$ couple is emphasised and the $i_{VAl} - v_{Al}$ and $i_{VAl} - v_{Ti^{4+}}$ couples are noted as significant.

Pressure of crystallisation. The relative amounts of tetrahedrally and octahedrally co-ordinated aluminium in clinopyroxenes are considered to reflect varying crystallisation pressure in the host magma (Velde and

Kushiro, 1978; Wass, 1979). Wass (1979) noted that with increasing pressure, aluminium would substitute in the octahedral M1 site instead of the tetrahedral site and thus the Al^{IV}/Al^{VI} ratio would decrease. Clinopyroxene phenocrysts from the Cudjegong Volcanics and Toolamanang Volcanics show a consistent increase in the Al^{IV}/Al^{VI} ratio from cores to rims which suggests that the rims crystallised at a lower pressure than the corresponding cores. Fig. 7B indicates that although both Al^{IV} and Al^{VI} increase from core to rim, Al^{IV} increases far more rapidly than emphasising the increasing Al^{IV}/Al^{VI} ratio. Groundmass clinopyroxene grains exhibit both similar and higher Al^{IV}/Al^{VI} ratios compared to phenocryst rims indicating lower crystallisation pressures. However the groundmass clinopyroxene values must be viewed with caution as it has been shown that rapid cooling rates affect the Ti and Al content in clinopyroxenes (Mevl and Velde, 1976; Coish and Taylor, 1978).

Further, the phenocrysts plot just above the low pressure field of Aoki and Kushiro (1968) and Wass (1979) (fig. 7A).

Comparison with the composition of clinopyroxenes produced under high pressure (Green, 1972 and unpublished data; Bender et al., 1978), in particular Al^{IV} and Al^{VI} , suggests that the clinopyroxenes of the Cudjegong Volcanics crystallised at pressures < 10 kbars. Marcelot et al. (1983) conclude that calc-alkaline and tholeiitic basaltic lavas in the New

Hebrides island arc suite crystallised at 5-6 kbars. Al^{IV} and Al^{VI} concentrations for the clinopyroxenes of both lava types are similar to those in the Cudjegong Volcanics and fall within the Cudjegong Volcanics field in fig. 7A. Thus it is considered that the Cudjegong Volcanics crystallised initially under moderate pressure (possibly 5-6 kbars) which fell during crystallisation as the magma ascended into the upper levels of the crust.

Temperature of crystallisation. Lindsley and Andersen (1983) developed a graphical thermometer for coexisting high Ca - low Ca pyroxenes based on experimentally determined phase relations from 800°C to 1200°C and from pressures of 1 atmosphere to 15 kb. Single pyroxene compositions can be plotted and provide a minimum temperature of pyroxene formation. The thermometer is considered accurate $\pm 50^\circ C$, however appreciable contents of "other" components introduce additional inaccuracy and Lindsley (1983) concludes that this approach should be limited to pyroxenes with $Wo + En + Fs > 90X$.

The great majority of clinopyroxenes from the Cudjegong Volcanics and Toolamanang Volcanics have > 10% "other" components. For those analyses with < 10% "other" components, Wo, En and Fs values have been calculated from a program supplied by the above authors. The relevant values plot within a temperature range of approximately 900°C to 1000°C on the 5 kb pressure diagram (fig. 8). The Lindsley and Andersen (1983) program determines Fe^{3+} by Papke et al.'s (1974) method. However if stoichiometric methods are used, a similar pattern results on the 5 kb diagram but all temperatures are raised by approximately 50°C.

The affect of including clinopyroxene compositions with > 10% "other" components is to significantly alter the calculated temperatures. Rim analyses consistently show increased Fe^{3+} and Al^{VI} contents relative to clinopyroxene cores (figs 5 and 7B respectively). As well as increasing the amount of "other" components, these values significantly decrease the calculated Wo content whereas En is approximately constant and Fs increases. The overall effect on Lindsley and Andersen's (1983) 5 kb diagram is dominated by the decreasing Wo content and results in the rim analyses plotting with anomalously 100°C to 200°C higher temperatures than the corresponding cores.

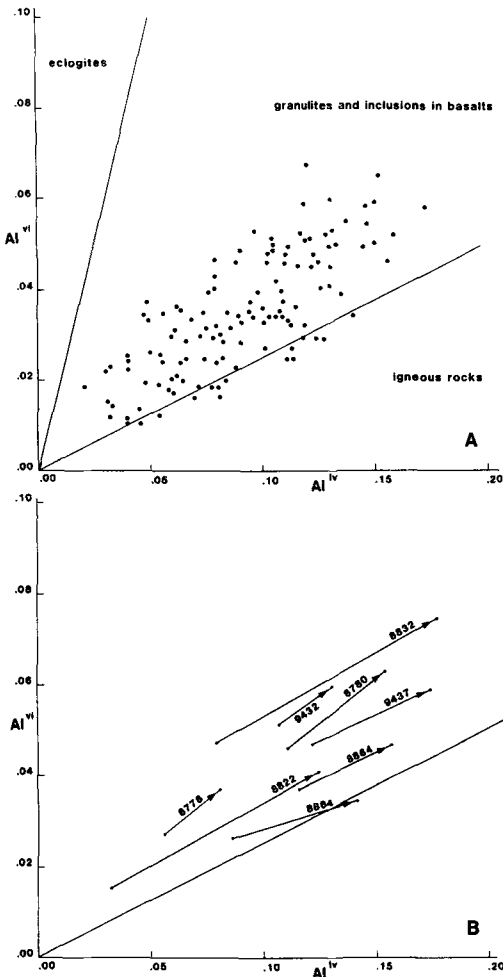


FIG. 7. Compositions of clinopyroxene phenocrysts (cations per structural formula unit: 0 = 6) for the Cudjegong Volcanics (8778, 8780, 8822, 8864, 9432) and Toolamanang Volcanics (8832, 9437). A. Pressure fields after Aoki and Kushiro (1968). B. Tie lines joining phenocryst cores to rims.

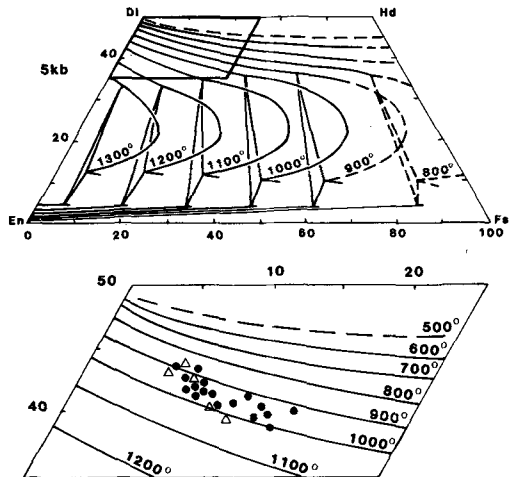


FIG. 8. Compositions of clinopyroxene phenocrysts (with < 10% "other" components) from the Cudjegong Volcanics and Toolamanang Volcanics. Symbols are the same as in figs 2 and 3A. Wo, En and Fs values were calculated using the method of Lindsley and Andersen (1983). The 500°C, 600°C and 700°C isotherms are excluded from the low Ca portion of the quadrilateral.

Tectonic setting. Barron (1976) considered that the volcanogenic sediments of the Sofala Volcanics, together with the associated radiolarian cherts and limestone lenses, were formed in a volcanic island radiolarian setting, the sides of which dipped steeply to the ocean floor. The laterally equivalent Cudjegong Volcanics, which are dominantly immature fine- to coarse-grained arenites containing basaltic and basaltic andesite

debris, are considered to be produced by high particle concentration debris flows as a result of explosive fragmentation or gravity collapse of a volcanic edifice. Associated limestone-bearing basaltic breccias indicate a nearby shallow marine source for at least these rocks. There is no apparent exposure of deep marine rocks in the Cudgong Volcanics, the finer-grained rocks representing probable ash fall deposits, and thus at Cudgong the volcanism was subaerial to shallow marine. The Ordovician rocks at Cudgong and Sofala suggest a setting in which a number of volcanic islands with fringing limestone reefs were in part adjacent to a deeper marine environment. This is consistent with present day oceanic island arc settings, the rocks of which include both calc-alkaline and tholeiitic types (Gill, 1981).

Thus the calc-alkaline nature of the Cudgong Volcanics and Sofala Volcanics (Barron, 1976) as suggested by the clinopyroxene chemistry, together with the proposed tectonic setting, adds credence to the hypothesis that an oceanic island arc system was active in central western New South Wales during the Late Ordovician (Scheibner, 1978; Cas, 1980; Powell, 1982).

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