

Relict clinopyroxenes from within-plate metadolerites of the Petroi Metabasalt, the New England fold belt, Australia

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Abstract

Relict clinopyroxenes from metadolerites of the Early Permian Petroi Metabasalt formation, studied by electron microprobe, show a limited compositional range near the diopside–augite boundary in the pyroxene quadrilateral. Clinopyroxene analyses from three metadolerites, grouped in approximately equal Fs contents, define an overall smooth trend between Fs_{10} and Fs_{16} . This is typical of clinopyroxenes from mildly alkaline basic magmas. Pyroxene stoichiometry suggests high Fe^{3+} contents (0.04 to 0.20 a.f.u.), which with high Al (0.10 to 0.31 a.f.u.) and Ti (0.03 to 0.08 a.f.u.) implies that $CaTiAl_2O_6$ and $CaFe^{3+}AlSiO_6$ are important 'other components'. Relative Al_z in $CaFe^{3+}AlSiO_6$ decreases and consequently $CaTiAl_2O_6$ increases with progressive fractionation. This, with the $Fe^{2+}:Fe^{3+}$ ratios in the Petroi clinopyroxenes, suggests falling f_{O_2} in the magma with fractionation. The f_{O_2} controlled entry of Al_z , Ti_y and Na_x into the clinopyroxenes and hence the Petroi clinopyroxene trend.

KEYWORDS: clinopyroxenes, metadolerite, New England fold belt, Australia.

Introduction

THE classic works of Kushiro (1960), LeBas (1962), Verhoogen (1962) and Coombs (1963) established that chemical differences observed among clinopyroxenes in mafic rocks are primarily related to their magma compositions, physico-chemical environments and (vis-a-vis) tectonic settings. Different cationic proportions of major and trace elements among clinopyroxenes (e.g. Schweitzer *et al.*, 1979; Papike, 1980; BVSP, 1981; Leterrier *et al.*, 1982) produce distinct pyroxene fractionation trends on the pyroxene quadrilateral (e.g. Gibb, 1973; Fodor *et al.*, 1975; Garcia, 1978). These trends reflect the equilibrium (or near equilibrium) between pyroxene and the melt, during crystallisation differentiation.

Statistical studies on elemental variations of relict clinopyroxene grains from altered mafic rocks include those of Nisbet and Pearce (1977), Schweitzer *et al.* (1979), Leterrier *et al.* (1982) and Morris (1988). However, interpretation of the clinopyroxene fractionation trends presents problems including the frequently large scatter shown by the analyses on the pyroxene quadrilateral

(e.g. Schweitzer *et al.*, 1979, Fig. 14), and the often limited iron enrichment exhibited by the relict clinopyroxene grains. The latter is probably due to: (a) the inability to study zoning phenomena as grain margins are frequently altered and (b) the groundmass clinopyroxenes are too fine grained for reliable microprobe analyses.

This paper deals with the second-order variations of microprobe analyses of 'unaltered' clinopyroxene grains from metadolerite sills of the Petroi Metabasalt and establishes the overall clinopyroxene fractionation trend. This trend, and its elemental and interelemental variations with fractionation, are related to the petrogenesis of the Petroi magma.

Petroi metadolerites

Metadolerites and altered basalt flows of the Petroi Metabasalt formation occur along Branch Creek, a tributary of Lower Creek, in the Upper Macleay District of New South Wales, Australia¹ (Fig. 1 of Asthana and Leitch, 1985). They lie in a major structural block, the 'Nambucca Slate

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¹ The superscripts refer to notes at the end of the paper.

Belt', of the Southern New England Fold Belt. The geological evolution of the Petroi Metabasalt and Numbucca Slate Belt is detailed elsewhere (Leitch, 1976, 1978; Asthana, 1984; Asthana and Leitch, 1985; Leitch and Asthana, 1986).

Two to thirty metre thick metadolerite sills are common in the thicker upper part of the formation. Dark green and aphanitic chilled contacts pass inwards into pale green rocks of fine to medium grain size (0.1 to 1.0 mm). Small vesicles appear along some margins, but they generally lack internal structures. The metadolerites and host rocks, show sea-floor alteration and two earlier deformation episodes recognised in the Nambucca Slate Belt (Leitch, 1978). This accompanied regional metamorphism at about 255 Ma (Leitch and McDougall, 1979), suggesting an Early Permian age for these rocks. (Asthana, 1984; Asthana and Leitch, 1985; Leitch and Scheibner, 1987).

The metadolerites are dominated by low-grade metamorphic minerals (pumpellyite-actinolite grade) and primary structures are difficult to discern. Of the magmatic phases, only clinopyroxene has survived metamorphism and it is commonly replaced, partially by fibrous aggregate of actinolite, opaque oxide minerals and dusty titanite. This alteration is greatest along grain boundaries, but is also found along cracks and cleavage surfaces extending into the centre of grains. Some relict morphology of the clinopyroxene grains can be established.

Clinopyroxenes appear subhedral in samples with modest amounts (*ca.* 15 to 25%), but where abundant (e.g. 59610, *ca.* 35%)² the grains are equant and well defined. An ophitic relationship is indicated in some samples (59609, 59611). In these, clusters of angular clinopyroxene grains, having common optical orientation, are separated by zones, now filled by secondary aggregates of albite, epidote and chlorite, which represent degraded plagioclase laths. Angular leucoxene masses are pseudomorphs after titanium-bearing oxide phases, whereas ill-defined aggregates of dusty titanite represent their non-pseudomorphous degradation. Irregular patches of chlorite, up to 1.0 mm across, represent alteration products of ferromagnesian phases (Asthana, 1984).

The major and trace element chemistry of the mafic suite of the Petroi Metabasalt is detailed by Asthana (1984) and Asthana and Leitch (1985). Metamorphism and earlier sea-floor alteration led to hydration, oxidation, carbonation (particularly in pillow lavas) and considerable redistribution of the major elements and the more labile trace elements, notably Rb, Sr, and Ba. However, 'the relatively immobile' trace elements

have near identical concentrations in the cores and margins of pillow lavas and show systematic variations in plots against fractionation indices (e.g. Zr) that are consistent with well established patterns resulting from crystallisation of basaltic liquids (Fig. 6 of Asthana and Leitch, 1985). These trace elements show an overall geochemical coherence and suggest a mildly alkaline within-plate basaltic parentage (Asthana, 1984; Figs. 7 and 8 of Asthana and Leitch, 1985).

Analytical procedure

Relict clinopyroxenes were analysed on an automated Siemens ETEC autoprobe in the Electron Microscope Unit of the University of Sydney. All machine functions for routine analysis, including matrix corrections to the raw data, were performed during on-line analysis by the computer programme 'MACH'. An accelerating voltage of 15 kV, a specimen current of 30 na and a beam spot diameter usually about 1 to 2 μm were used. Standards used were as follows: Fe—hematite; Si, Mn—rhodonite; Cr, Al, Mg—chromite; Na—albite; K—orthoclase; Ca—wollastonite and Ti—rutile. Reproducibility was checked by analysing the standards at different times. The precision of the analyses, expressed as two standard deviations is better than $\pm 5\%$ for all elements, except for Mn, Ti and Na, which is around 10%. The accuracy of the analyses, expressed as percentage deviation is better than $\pm 4\%$ for all elements, except for Mn and Na, for which it is around 7%. Ferric iron contents of the clinopyroxenes were estimated after the method of Papike *et al.* (1974).

Composition of the Petroi clinopyroxenes

Thirty four analyses of unaltered and clear clinopyroxene grains from three metadolerite sills are given by Asthana (1984, Table 5-1). Average compositions of Petroi clinopyroxene groups of approximately equal Fs contents (at 0.5 Fs intervals), along with their ideal site occupancy (e.g. Morimoto *et al.*, 1988) and end-member components are presented in the Table. The clinopyroxenes span a restricted compositional range, being rich in Mg, Al and Ti and poor in Si. Grains show appreciable differences in Si, Al and Ti contents. Compositional zoning was not studied due to the lack of optical zoning and altered margins, but central portions of grains tend to be richer in Al and Mg.

Most of the clinopyroxene analyses plot close to the diopside-augite boundary on the pyroxene quadrilateral (Fig. 1), largely in the diopside field

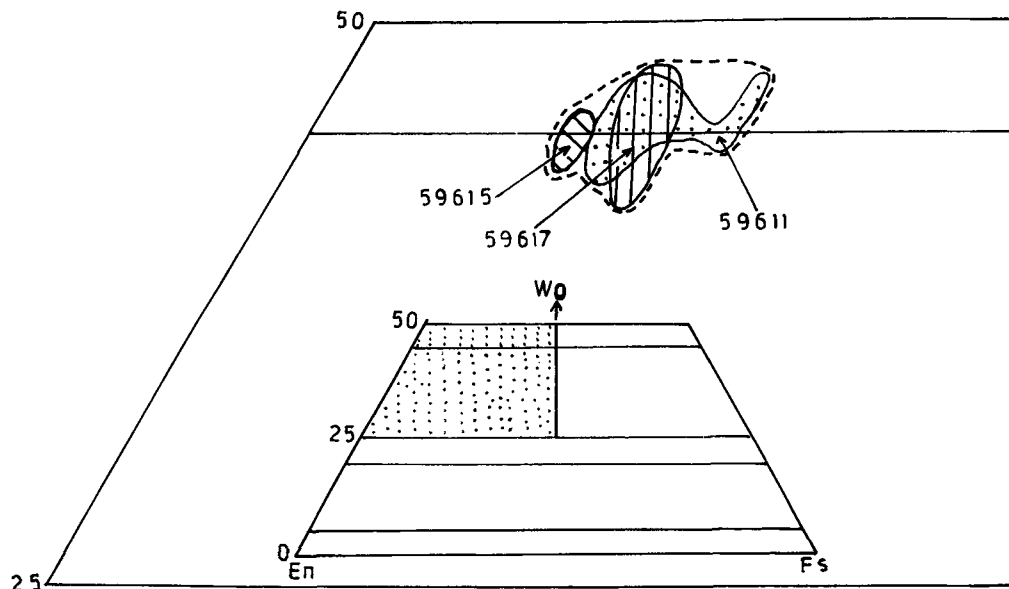


FIG. 1. Fields of relict clinopyroxene analyses from the individual samples of the Petroi Metabasalt plotted in terms of the atomic ratio Ca : Mg : (Fe + Mn). Dotted line encloses clinopyroxene fields of three metadolerites.

with a few in the augite field (new pyroxene classification and nomenclature scheme; Morimoto *et al.*, 1988). Also, all of the Petroi clinopyroxenes plot in the chemical group of the Ca-Mg-Fe 'quadrilateral' pyroxenes (Fig. 2) on the Q-J diagram of Morimoto *et al.* (1988).

Clinopyroxenes of pumpellyite-actinolite or even greenschist facies metabasics are generally regarded as relict magmatic phase (Vallance,

1969, 1974*a,b*; Coleman, 1977; Nisbet and Pearce, 1977; Letierrier *et al.*, 1982; Asthana, 1990; etc.). However, recently clinopyroxenes indicating subsequent structural and chemical modifications have also been reported from low-grade metabasics as well as from unmetamorphosed slowly cooled igneous bodies. Such modifications may include reequilibration at different temperature, pressure and f_{O_2} (e.g. Himmelberg *et al.*, 1987; Asthana, 1990) that may or may not result in exsolution features (Fodor *et al.*, 1980; Lindsley, 1983; Lindsley and Andersen, 1983; Perfit and Fornari, 1983; Sen, 1986; Mellini *et al.*, 1988) or subsolidus reequilibration due to hydrothermal alteration and metamorphism (Maruyama and Liou, 1985; Manning and Bird, 1986; Laverne, 1987; Nabelek *et al.*, 1987; and references therein). Therefore, a secondary origin for the Petroi clinopyroxenes is a distinct possibility, especially in view of the large scatter exhibited by clinopyroxene analyses on the pyroxene quadrilateral (Fig. 1). However, this is considered highly unlikely, since: (a) only unaltered and clear portions of clinopyroxene grains were used in the present study. This was confirmed by routine checks with back-scattered electron images; (b) secondary clinopyroxenes are texturally as well as chemically quite distinct from magmatic clinopyroxenes; (c) the major and minor element variations of the Petroi clinopyroxenes are consistent

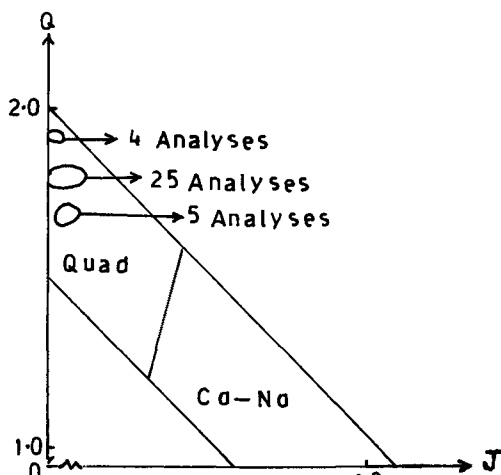


FIG. 2. Q-J diagram of the Petroi clinopyroxenes.

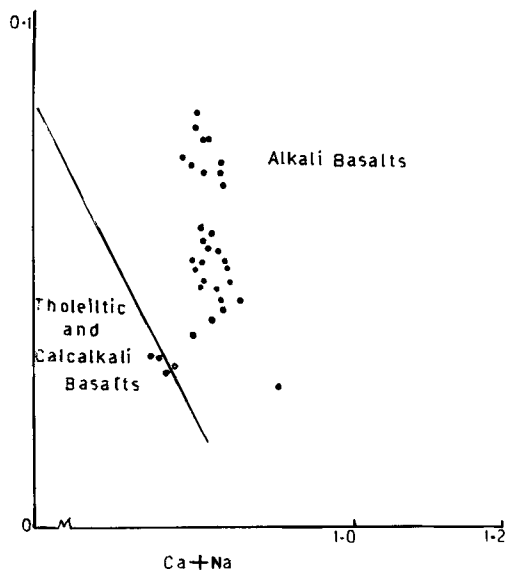


Fig. 3. Ti versus Ca + Na (atomic) plot of Petroi clinopyroxenes. Fields of alkalic basalts and tholeiitic and calcalkali basalts are those of Leterrier *et al.* (1982).

with well-accepted trends that result from crystallisation differentiation of clinopyroxenes from alkaline magmas (e.g. Gibb, 1973; Schweitzer *et al.*, 1979); (d) the overall smooth Petroi clinopyroxene trend (Fig. 4) is quite similar to clinopyroxene trends from other well established mildly alkaline basic magmas—a conclusion also supported by the various clinopyroxene discriminant diagrams and the 'immobile trace-element' chemistry of the host rocks; and (e) the scatter shown by Petroi clinopyroxenes is comparable to that shown by pristine clinopyroxenes from other alkalic bodies, (cf. Gibb, 1973; Fig. 3; Shimizu and leRoex, 1986, Fig. 4; Faraone *et al.*, 1988, Fig. 3). Also, granular exsolution is confined to plutonic rocks only (Lindsley, 1983; Nabelek *et al.*, 1987), whereas other exsolutions would not affect the result of the present study, since 'the original composition may be derived by averaging several sets of microprobe data' (Mellini *et al.*, 1988; also Lindsley, 1983; Nabelek *et al.*, 1987). Furthermore, clinopyroxenes with Ca > 0.6 a.f.u. exist as a single phase at subsolidus temperatures (Mellini *et al.*, 1988).

Therefore, the scatter of the Petroi clinopyroxenes on the pyroxene quadrilateral are *mainly* attributed to one (or a combination) of the following factors or mechanisms:

1. Sector zoning (e.g. Nakamura and Coombs,

1973; Thompson and Humphris, 1980; Matthey and Muir, 1980; etc.), and/or

2. Real variations in Petroi clinopyroxene compositions, reflecting intensive parameters and cation exchanges during their formation (i.e. each clinopyroxene analysis represents a distinct liquid composition, cf. Gibb, 1973; Shimizu and leRoex, 1986; Sen, 1986), and
3. Analytical errors inherent in microprobe analyses (e.g. Presnall and Hoover, 1984) and especially, the uncertainties involved in the estimation of Fe³⁺ contents (e.g. Otten and Busek, 1987).

C.I.P.W. norms of the 34 Petroi clinopyroxene analyses showed 30 with normative nepheline, implying an alkalic parentage for the Petroi magma (Coombs, 1963). This is also apparent in the Si versus Al and Ti versus Al plots of Kushiro (1960). Almost all the Petroi clinopyroxenes plotted on the Ca + Na versus Ti discriminant diagram of Leterrier *et al.* (1982) fall in the alkalic field with a sharp vertically elongated distribution (Fig. 3). Most Petroi clinopyroxenes (21 out of 34) plot in a within-plate alkali basalt field, whereas the rest plot in the field common to all tectonic settings in the Na₂O:MnO:TiO₂ triangular discriminant diagram of Nisbet and Pearce (1977).

Fractionation trend

Variations in the atomic proportions of Wo, En and Fs in the Petroi clinopyroxenes mostly involve the interchange of En and Fs, typical of crystallisation with En being replaced by Fs during fractionation (e.g. Gibb, 1973).

Individual analyses plotted on the pyroxene quadrilateral have scattered Wo contents between 42% to 48% (Fig. 1). The least and most fractionated clinopyroxenes have Fs contents of about 10% and 16% respectively. Average clinopyroxene compositions from the three samples (59611—Wo₄₆,En₄₁,Fs₁₃; 59615—Wo₄₅,En₄₅,Fs₁₀ and 59617—Wo₄₆,En₄₁,Fs₁₃) are plotted in Fig. 4, after Carmichael (1967) and Fodor *et al.* (1975), together with clinopyroxene crystallisation trends of strongly alkaline (Wilkinson, 1956), mildly alkaline (Aoki, 1964) and tholeiitic (Brown, 1957) rocks. The Petroi averages plot closest to the Japanese mildly alkaline trend.

Individual analyses plotted into groups with equal Fs contents (at 0.5 Fs intervals) with their average compositions (Table 1) on the pyroxene quadrilateral (Fig. 4), give a smoother trend, almost parallel to the diopside-hedenbergite join

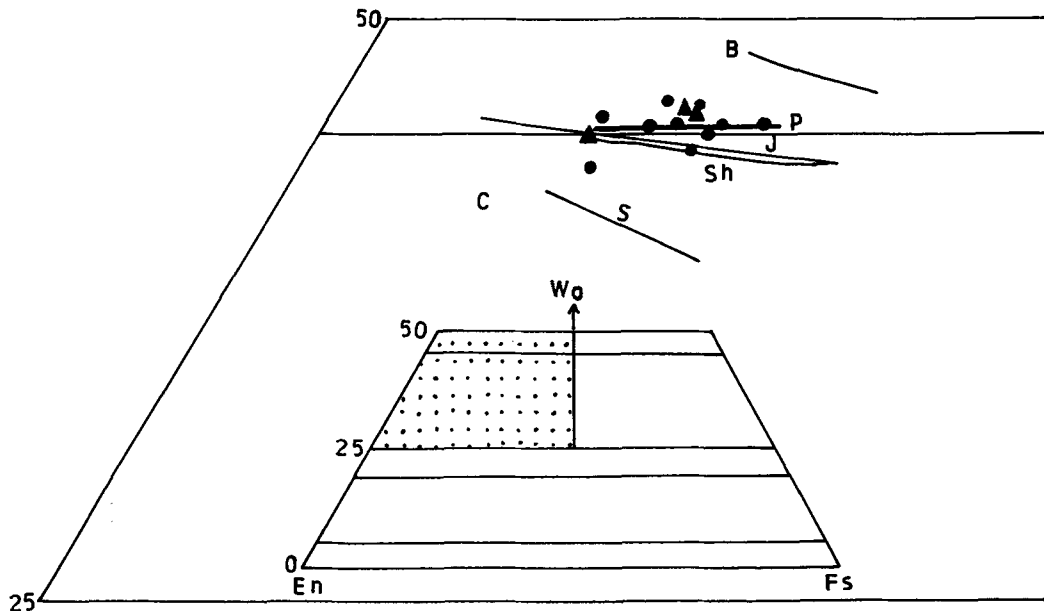


Fig. 4. Average composition of pyroxenes from the three Petroi metadolerites plotted in terms of the atomic ratio $\text{Ca} : \text{Mg} : (\text{Fe} + \text{Mn})$ (triangles). Averaged composition of Petroi clinopyroxene groups (equal Fs intervals) plotted in terms of the atomic ratio $\text{Ca} : \text{Mg} : (\text{Fe} + \text{Mn})$ (dots) and the inferred clinopyroxene trend of the Petroi Metadolerite (P). Also shown are clinopyroxene trends from Japanese alkalic rocks, J (Aoki, 1964), Shiant Isles, Sh (Gibb, 1973), Blact Jack sill, B (Wilkinson, 1956), and the Skaergaard intrusion, S (Brown, 1957).

between Fs_{10} and Fs_{16} . This trend contrasts to that of tholeiitic rocks (e.g. Brown, 1957; Huebner, 1980) and strongly alkaline rocks (e.g. Wilkinson, 1956, 1957; Myers *et al.*, 1975; Larsen, 1976). It resembles the clinopyroxene trends of mildly alkaline basic rocks, e.g. the Japanese alkaline basalt (Aoki, 1964) and the Mg-rich portion of the Shiant Isles (Gibb, 1973). This similarity, the lack of subcalcic pyroxenes, an absence of pronounced dip in Wo with fractionation and the range of Wo_{42} to Wo_{48} , all imply a mildly alkaline parentage of the Petroi rocks, as does the trace-element chemistry (Asthana, 1984; Asthana and Leitch, 1985). Therefore, the scatter in clinopyroxene analyses on the pyroxene quadrilateral, is due to second-order variations, but their overall composition was largely controlled by the mildly alkalic composition of the Petroi magma.

Major and minor element variations

The Petroi clinopyroxenes show considerable intra- and inter-sample variation in Si, Ti and Al. In Fig. 5, Si, Al and Ti are plotted against X_{Fe} [$X_{\text{Fe}} = \text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$; Schweitzer *et al.*, 1979; Papike, 1980]. An overall decrease in Al (mostly present as Al_z) and increase in Si with

fractionation (Figs. 5a,b), shows the antipathetic relationship between Si and Al (Kushiro, 1960; LeBas, 1962). There is no obvious link between Ti and fractionation (Fig. 5c).

Al_z along with Ti_y and Fe_y^{3+} account for more than 80% of the 'non-quadrilateral components' (or the 'other components'; Schweitzer *et al.*, 1979) in the Petroi clinopyroxenes. There are linear relationships between Si and Al (Fig. 6a) and a crude relationship between Ti and Al (Fig. 6b) and Fe_y^{3+} and Al_z (Fig. 6c). These suggest that $\text{M}_y^{2+} + 2\text{Si}_z \rightleftharpoons \text{Ti}_y + 2\text{Al}_z$ and $\text{M}_y^{2+} + \text{Si}_z \rightleftharpoons \text{Fe}_y^{3+} + \text{Al}_z$ ($\text{Fe}^{3+} \gg \text{Na}$) are the two major substitutional couples in the Petroi clinopyroxenes. They lead to the idealised titanium pyroxene and esseneite end-members, $\text{CaTiAl}_2\text{O}_6$ and $\text{CaFe}^{3+}\text{AlSiO}_6$ respectively (e.g. Tracey and Robinson, 1977; Schweitzer *et al.*, 1979; Papike, 1980; hereafter called Tp and FATS respectively; Onuma, 1983). Minor additional idealised end-members are $\text{CaFe}_2^{3+}\text{SiO}_6$ (0 to 1.3% tetrahedral sites being occupied by Fe^{3+} ; Huckenholz *et al.*, 1974; Ghose *et al.*, 1986; Foit *et al.*, 1987) and $\text{CaAl}_2\text{SiO}_6$ (Gibb, 1973; Scott, 1976). They relate to clinopyroxene analyses that plot below and above the saturation line $\text{Si} + \text{Al} = 2.00$ respectively, in Fig. 6a.

The proportion of Al_z balanced by Ti increases

Table 1. Average compositions of Petroi Clinoproxene groups of equal Fs content (at 0.5 Fs content intervals).

No. of analyses	1.	1.	1.	3.	5.	5.	6.	5.	4.	1.	2.
SiO ₂	48.43	51.15	47.72	48.17	47.36	47.75	47.32	47.87	47.50	46.23	48.86
Al ₂ O ₃	5.40	3.56	5.44	5.05	5.82	5.32	5.79	4.91	5.41	5.68	3.44
TiO ₂	1.85	1.10	1.94	1.88	1.87	2.06	2.19	1.83	1.84	2.47	1.53
***Cr ₂ O ₃	0.18	0.00	0.18	0.25	0.15	0.14	0.18	0.08	0.08	0.10	0.00
MgO	15.42	16.29	14.28	14.63	14.03	14.23	13.78	14.29	13.80	13.55	12.97
*FeO ^t	6.10	6.56	6.87	7.17	7.33	7.60	7.85	8.28	8.49	8.72	9.68
MnO	0.17	0.22	0.13	0.18	0.16	0.17	0.19	0.19	0.21	0.16	0.27
CaO	22.27	21.80	22.17	22.33	22.22	21.86	21.97	21.62	21.67	21.66	21.85
Na ₂ O	0.12	0.15	0.37	0.31	0.38	0.32	0.39	0.35	0.39	0.37	0.78
Total	99.94	100.83	99.10	99.97	99.32	99.45	99.66	99.42	99.39	98.94	99.38
Formulae per 4 cations											
Si	1.783	1.865	1.779	1.780	1.763	1.778	1.761	1.784	1.773	1.738	1.833
Al	0.217	0.135	0.221	0.220	0.237	0.222	0.239	0.216	0.227	0.252	0.152
**Fe ³⁺	-	-	-	-	-	-	-	-	-	0.010	0.015
	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Al	0.017	0.018	0.018	-	0.018	0.012	0.015	-	0.011	-	-
**Fe ³⁺	0.101	0.068	0.117	0.131	0.138	0.113	0.125	0.137	0.138	0.126	0.108
Ti	0.051	0.030	0.054	0.052	0.052	0.058	0.061	0.051	0.052	0.070	0.043
Cr	0.005	0.000	0.005	0.007	0.004	0.004	0.005	0.002	0.002	0.003	0.000
Mg	0.825	0.884	0.793	0.806	0.778	0.790	0.764	0.794	0.768	0.759	0.725
Fe ²⁺	-	-	0.013	0.004	0.010	0.023	0.030	0.016	0.029	0.042	0.124
	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Mg	0.021	-	-	-	-	-	-	-	-	-	-
Fe ²⁺	0.087	0.132	0.084	0.091	0.080	0.101	0.089	0.105	0.098	0.096	0.057
Mn	0.005	0.007	0.004	0.006	0.005	0.005	0.006	0.006	0.007	0.005	0.009
Ca	0.878	0.851	0.885	0.881	0.888	0.871	0.877	0.864	0.867	0.872	0.877
Na	0.009	0.010	0.27	0.022	0.027	0.023	0.028	0.025	0.028	0.027	0.057
	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Quad Components											
Wo	45.81	43.81	46.68	46.01	46.76	45.77	46.38	44.95	45.46	45.66	45.80
En	44.12	45.53	41.81	42.08	40.97	41.51	40.40	41.31	40.28	39.74	37.86
Fs	10.07	10.65	11.51	11.91	12.27	12.72	13.22	13.74	14.26	14.60	16.34
Note :	* FeO ^t = Total FeO, electron microprobe value.										
	** Fe ³⁺ calculated by the method of Papike <i>et al</i> 1974.										
	*** Values calculated from analyses in which they were analysed.										

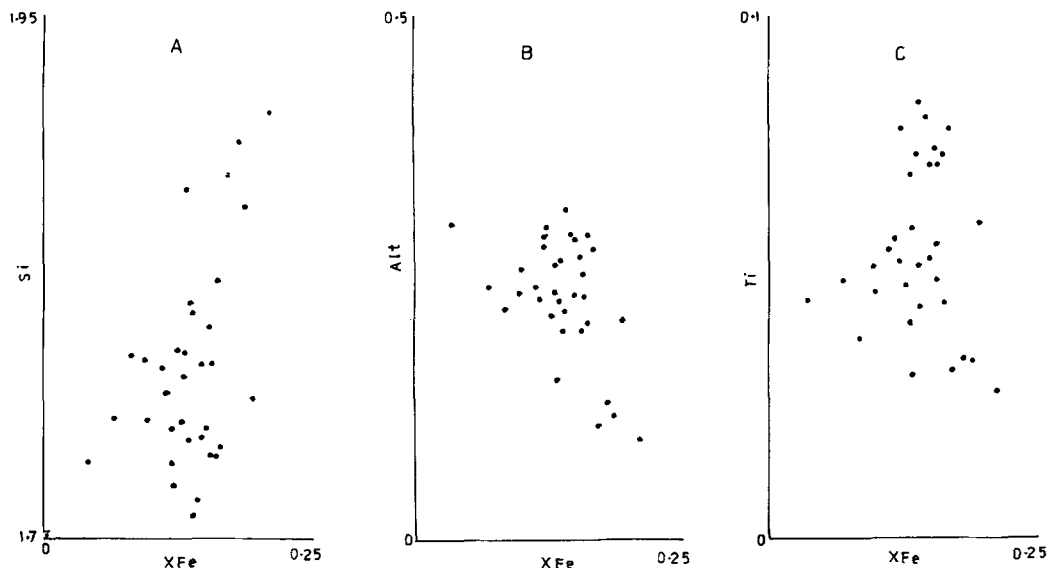


Fig. 5. (a) Si versus X_{Fe} (atomic); (b) Al (total) versus X_{Fe} ; and (c) Ti versus X_{Fe} plots of the Petroi clinopyroxenes.

with fractionation from around 1/8 to 1/4 (Fig. 7). This implies an increase in Tp (25–50%) and decrease in FATS (75–50%). The FATS component strongly reflects oxygen fugacity (e.g. Schweitzer *et al.*, 1979; Vieten, 1979; Akasaka and Onuma, 1980; Papike, 1980; Onuma, 1983), so that entry of Al_z and Ti_y in the Petroi clinopyroxenes was probably controlled by the f_{O_2} of the Petroi magma (cf. Cundari and Salviulo, 1989). In alkaline magmas differentiation normally decreases Si and increases Ti_y and Al_z in clinopyroxenes (e.g. LeBas, 1962), although the reverse is also reported (e.g. Aoki, 1964; Wilkinson, 1966; Myers *et al.*, 1975). Several researchers (e.g. Verhoogen, 1962; Gupta *et al.*, 1973; Gibb, 1973) related Al and Ti contents of clinopyroxenes to the silica, Al and Ti activity of the melt and the physico-chemical conditions (e.g. f_{O_2} in Petroi magma) of crystallisation (e.g. Barberi *et al.*, 1971; Cundari and Salviulo, 1989). However, clinopyroxenes with tetrahedral sites nearly fully occupied by Si have also been reported from strongly alkaline rocks (e.g. Faraone *et al.*, 1988).

Na contents of the Petroi clinopyroxenes change incoherently with fractionation (Fig. 8a). Apart from one analysis (59611-22), Na contents generally accord with Fe^{3+} (Fig. 9b), suggesting $Na_x + Fe_y^{3+} \rightleftharpoons Ca_x + M_y^{2+}$ as a minor substitutional couple, leading to the end-member $NaFe^{3+}Si_2O_6$, i.e. aegirine (e.g. Gibb, 1973). This implies that Na in the Petroi clinopyroxenes was largely controlled by Fe^{3+} , i.e. the f_{O_2} of the

Petroi magma (cf. Gibb, 1973). However, the Petroi clinopyroxenes are not as evolved as clinopyroxenes from other alkaline suites (e.g. Nash and Wilkinson, 1970; Gibb, 1973; Larsen, 1976) and their Na contents are small.

Cr contents of the Petroi clinopyroxenes seem insensitive to fractionation (Fig. 8c), implying a magma already effectively depleted in Cr by early crystallisation (Asthana, 1984) or co-precipitation of a spinel phase. Mn contents are low, but suggest enrichment with fractionation (Fig. 8b), via the strong geochemical affinity of Mn with Fe.

In summary, the important substitutions in the Petroi clinopyroxenes are $M_y^{2+} + 2Si_z \rightleftharpoons Ti_y + 2Al_z$ and $M_y^{2+} + Si_z \rightleftharpoons Fe_y^{3+} + Al_z$. This implies the presence of two 'other components', Tp and FATS. With fractionation the relative proportions of Al_z forming FATS decrease at the expense of Tp, implying conditions of falling f_{O_2} in the Petroi magma. This also favoured entry of Al_z , Ti_y and Na_x in the Petroi clinopyroxenes. The linear increase in the Fe^{2+}/Fe^{3+} ratio with fractionation (Fig. 9a) also implies this (Vieten, 1979; Akasaka and Onuma, 1980), although it caused no absolute decrease in the Fe^{3+} contents of the Petroi clinopyroxenes.

Discussion

The initial composition of clinopyroxene crystallising from a basic magma is linked to silica activity (Smith and Lindsley, 1971; Gibb, 1973).

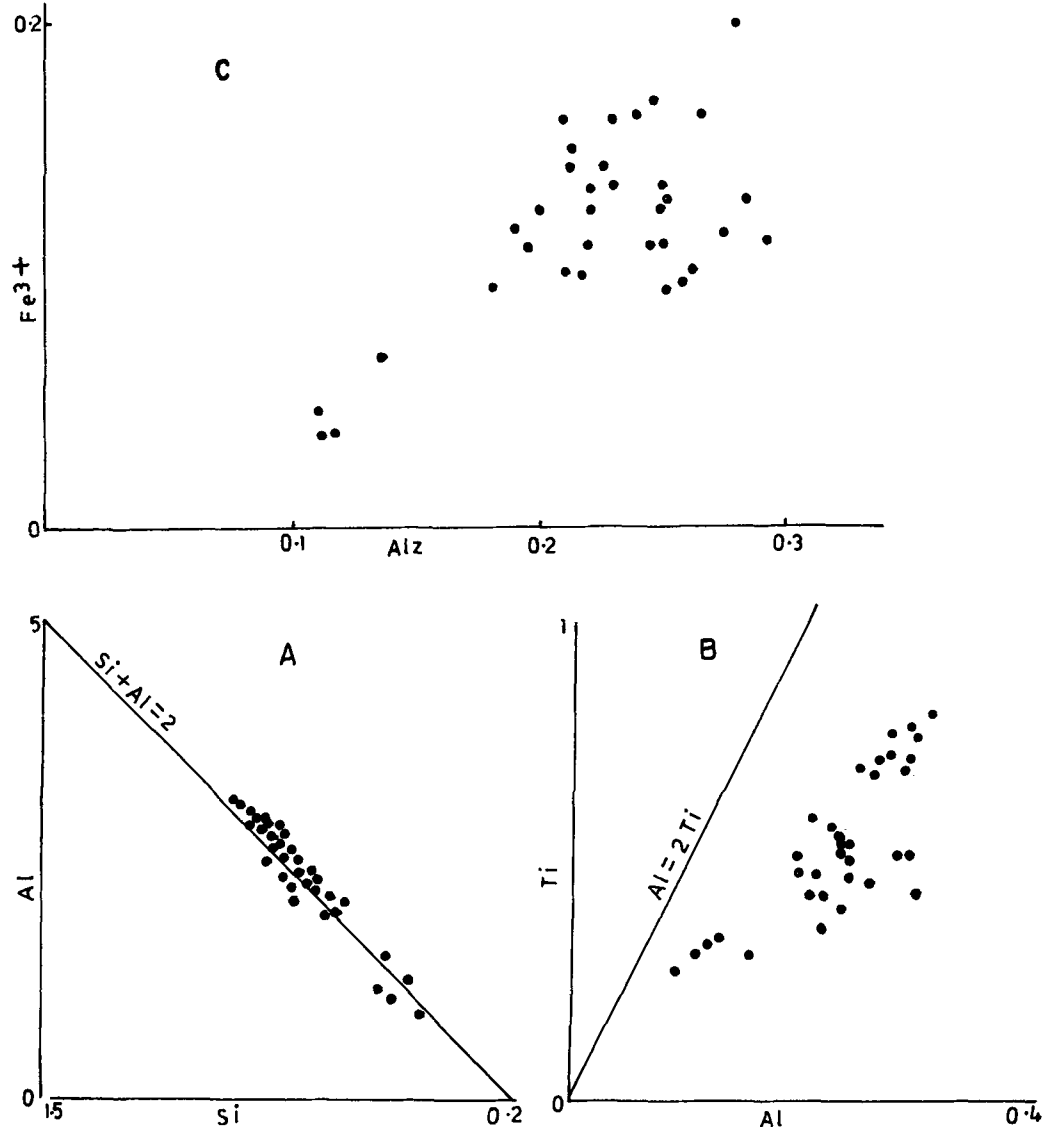


FIG. 6. (a) Si versus Al (atomic); (b) Ti versus Al, and (c) Fe^{3+} versus Al_2 plots of the Petroi clinopyroxenes.

Furthermore, with increasing undersaturation of the magma (i.e. alkalinity), the initial clinopyroxene composition approaches the diopside-hedenbergite join on the pyroxene quadrilateral (Gibb, 1973; Larsen, 1976). However, the subsequent trend is controlled by the physico-chemical conditions of crystallisation in the magma.

The initial composition(s) of the Petroi clinopyroxene(s) (Fig. 4 and Table 1) demonstrates low silica activity in the Petroi magma. The subsequent clinopyroxene trend (Fig. 4) can be understood by studying the factors which

controlled their Wo contents. High Wo contents are suggested to result from a substantial Ca-Tschermak's component (e.g. Brown, 1967; Barberi *et al.*, 1971; Huebner, 1980). However, only minor amounts of Al_y (i.e. Ca-Tschermak) in twenty four out of thirty four Petroi clinopyroxenes fail to explain high Wo contents in them. Rather, the low proportions of Al_y as compared to Al_z characterises low-pressure clinopyroxenes (e.g. Wass, 1979; Schweitzer *et al.*, 1979). In Petroi clinopyroxenes Wo was largely controlled by Al (Fig. 10). The Al is mostly Al_z , tied into

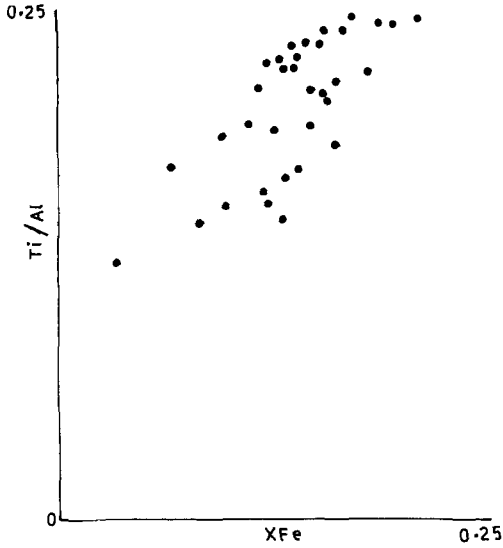


FIG. 7. Ti/Al versus X_{Fe} (atomic) plot of the Petroi clinopyroxenes.

coupling of Ti and Fe^{3+} with Ca, to give Tp and FATS 'other components' during fractionation, which indicates conditions of falling f_{O_2} in the Petroi magma.

Tracey and Robinson (1977) in their study on Tahiti titanagites concluded that low f_{O_2} conditions ($\log f_{O_2} = -11$ atm. at 1020 °C, slightly more reducing than the FMQ buffer) favour incorporation of the Tp component. Their results corroborate the findings from the Petroi clinopyroxenes, where the relative proportions of Tp with respect to FATS also increased with a fall of f_{O_2} and fractionation. Akasaka and Onuma (1980) have reported that if oxide minerals are present, low f_{O_2} conditions are necessary for the incorporation of the Tp component. Oxide minerals are represented in Petroi rocks by their degraded products.

Akasaka and Onuma (1980) and Onuma (1983) studied fassaitic pyroxenes in the system FATS–Tp–diopside (Di). They found that the FATS component is strongly influenced by f_{O_2} and temperature of the magma. Two alkali clinopyroxene trends were described in terms of the variations in their FATS, Tp and Di components. The Tahiti trend involves enrichment of Tp at constant FATS, implying uniformly low f_{O_2} conditions during their fractionation. The Hocheifel trend involves enrichment of both Tp and FATS, probably indicating increasing f_{O_2} with fractionation.

The Petroi clinopyroxene trend although simi-

lar to the Hocheifel clinopyroxene trend on the Di–FATS–Tp diagram, is distinct in that the proportion of FATS decreased at the expense of the proportion of Tp. This implies conditions of falling f_{O_2} with fractionation. Mueller and Saxena (1977, p. 320) have commented that 'as in the calc–alkaline sequence, a drop in oxygen fugacity along the differentiation sequence of alkaline magmas is indicated by the increase in $Fe^{2+}/(Mg + Fe^{2+})$ of the ferromagnesian minerals'. This has been documented in the Shonkin Sag Laccolith (Nash and Wilkinson, 1970), the Shiant Isles sill (Gibb, 1973) and the Petroi Metabasalt.

In summary, Petroi clinopyroxenes (Fig. 4) crystallised from a mildly alkaline basaltic magma, in which f_{O_2} was falling at a rate greater than that required to maintain a constant $Fe^{2+}:Fe^{3+}$ ratio. This caused the activity of Fe^{3+} in the magma to decrease. A drop in temperature

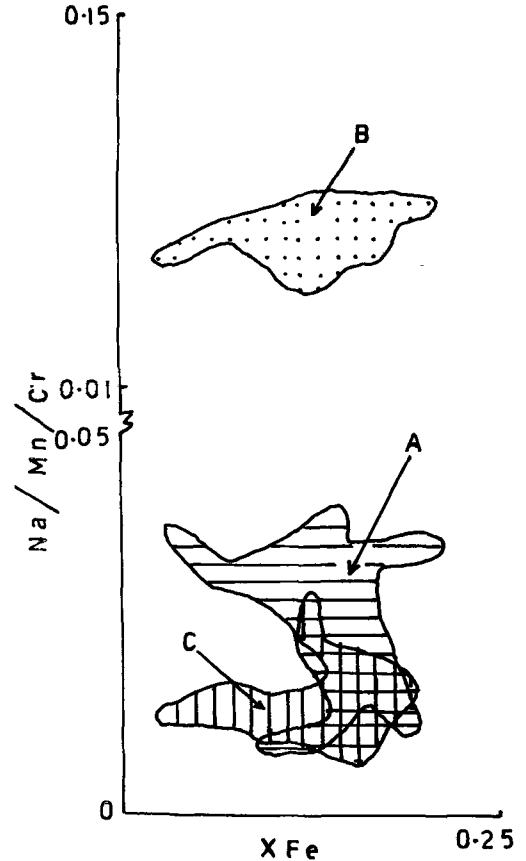


FIG. 8. (a) Field of Na versus X_{Fe} (atomic) plot of the Petroi clinopyroxenes (horizontal bars); (b) Field of Mn versus X_{Fe} (dots); (c) Field of Cr versus X_{Fe} (vertical bars).

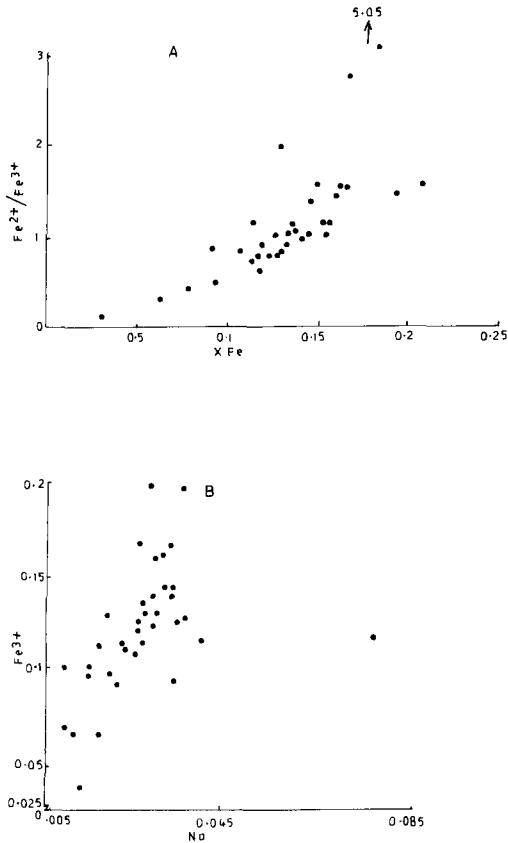


FIG. 9. (a) Fe^{2+}/Fe^{3+} versus X_{Fe} (atomic), and (b) Fe^{3+} versus Na plots of the Petroi clinopyroxenes.

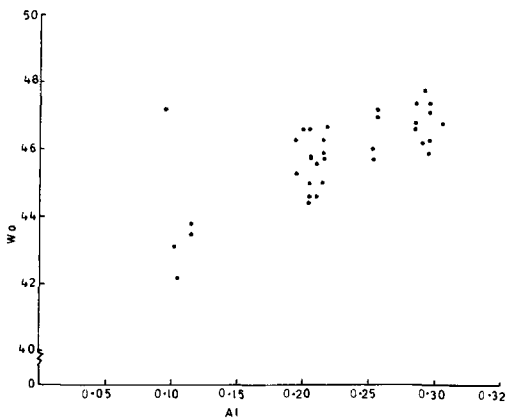


FIG. 10. Wo versus Al (atomic) plot of the Petroi clinopyroxenes.

with fractionation along with volatile loss, e.g. oxygen from the decomposition of water in the Petroi magma, could be a major factor in the fall of f_{O_2} (e.g. Scott, 1976; Mueller and Saxena, 1977). This model is similar to that proposed for the Shonkin Sag Laccolith (Nash and Wilkinson, 1970) and Shiant Isles sill (Gibb, 1973).

Conclusions

The detailed study of clinopyroxene grains from Petroi metadolerites suggests:

1. Clinopyroxene compositions and a crystallisation trend related to mildly alkaline magma, a conclusion also supported by the 'immobile trace-element' chemistry of the Petroi rocks.
2. FATS and Tp are the two major 'other components' of the Petroi clinopyroxenes. Their proportions vary linearly with fractionation and follow the behaviour of $Fe^{2+}:Fe^{3+}$ ratios. This implies that f_{O_2} of the Petroi magma decreased with progressive fractionation.
3. The decreasing f_{O_2} of the Petroi magma mainly controlled the evolution of the Petroi clinopyroxenes, including the entry of Al_z , Ti_y and Na_x .

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Notes

1. The Petroi Metabasalt outcrops in a triangular-shaped area in the core of a fault-truncated W-plunging syncline along the Branch Creek between grid references of 282047 and 292076 (Fig. 1 of Asthana and Leitch, 1985). The 6-digit grid-references are read from the 1:25,000 Five Day Creek sheet (1st edition 9336-I-S) published by the New South Wales Department of Lands. It is approximately 60 km E of SE from Armidale (N.S.W.).
2. Sample numbers correspond to the rock collection, Department of Geology and Geophysics, University of Sydney, Australia.