Clinopyroxenes from the Square Top intrusion, Nundle, New South Wales

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Summary. Despite a wide range in parent rock compositions, from analcime–olivine theralite to analcime-tinguaite, clinopyroxene phenocrysts in the Square Top intrusion show limited compositional variation. The crystallization trend of the pyroxenes (principally sahlites) lies approximately parallel to the diopside–hedenbergite join of the pyroxene quadrilateral, and in addition reveals slight enrichment in acmite. The limited iron enrichment in the pyroxenes (and in olivine phenocrysts in the theralites and tinguaites) stemmed from progressively more hydrous liquid fractions whose ferric/ferrous iron ratios increased during differentiation.

The Square Top intrusion, a small plug-like mass with an exposed thickness of 250–300 ft, located 2 miles west of Nundle, New South Wales, reveals the transition from base to top of analcime–olivine theralite, through leucocratic theralite and melanocratic tinguaite, to analcime-tinguaite. Clinopyroxene and olivine, the most important ferromagnesian minerals of the various facies, both decrease in abundance in successive differentiates. The principal geochemical trend with differentiation was alkali enrichment (Wilkinson, 1965*a*, fig. 3). The most salic tinguaites (differentiation indices = 77·7 and 79·4) plot in the lowest temperature region in the undersaturated portion of the $NaAlSi0_4$–$KAlSi0_4$–$Si0_2$ system and their production from theralite is considered to have resulted from fairly rapid but nevertheless highly effective fractional crystallization processes.

Petrographic and optical data

In the theralites and tinguaites, clinopyroxene occurs as euhedral phenocrysts, in places glomeroporphyritic, and commonly peppered with opaque oxide inclusions. Groundmass clinopyroxenes in the tinguaites contrast texturally with the phenocrysts in exhibiting subophitic relationships with laths of alkali feldspar.

TABLE I. Chemical analyses and optical properties of clinopyroxenes and olivines from the Square Top intrusion

Analysis no.	1	2	3	4	5	6	7
Specimen no.	ST. 18	ST. 16	ST. 12	ST. 12	ST. 11	ST. 28	ST. 20
SiO_2	46·95	47·78	51·25	50·68	51·54	37·00	36·67
TiO_2	2·12	2·18	0·71	0·59	0·71	0·09	0·08
Al_2O_3	7·33	5·89	3·35	2·71	2·09	0·09	0·22
Fe_2O_3	2·96	3·35	4·83	7·28	5·86	0·92	1·08
FeO	4·60	4·85	5·30	3·24	4·82	25·10	26·02
MnO	0·10	0·12	0·26	0·31	0·32	0·45	0·49
MgO	12·95	13·08	11·98	12·14	12·30	35·55	34·56
CaO	21·42	21·26	19·57	21·11	21·05	0·56	0·50
Na_2O	0·69	0·80	1·90	1·81	1·85	0·05	0·08
K_2O	tr.	tr.	0·13	0·08	0·02	tr.	tr.
H_2O^+	0·47	0·40	0·46	0·05	nil	0·26	0·20
H_2O^-	0·16	0·29	0·26	nil	nil	0·10	0·20
Total	99·75	100·00	100·00	100·00	100·56	100·17	100·10
α	1·695	1·695	1·695	1·695	1·695	—	—
β	1·699	1·700	1·700	1·702	1·702	1·713–1·718	1·719
γ	1·720	1·720	1·720	1·722	1·722	—	—
$2V_\gamma$	46–54°	51–61°	56°	60–65°	59–63°	—	—
atom %							
Ca	47·4	46·6	44·5	46·0	45·5	—	—
Mg	39·9	39·8	37·9	36·8	36·9	71·3	69·9
Fe	12·7	13·6	17·6	17·2	17·6	28·7	30·1

	Numbers of ions on the basis of 6 oxygens					*Numbers of ions on the basis of 4 oxygens*			
Si	1·758	1·789	1·918	1·892	1·915	0·984		0·982	
Al	0·242	0·211	0·082	0·108	0·085	—		—	
Al	0·082	0·049	0·066	0·011	0·007	0·003	2·021	0·007	2·022
Ti	0·060	0·061	0·020	0·017	0·020	0·002		0·002	
Fe^{3+}	0·083	0·094	0·136	0·205	0·164	0·019		0·022	
Fe^{2+}	0·144	0·152	0·166	0·101	0·150	0·558		0·583	
Mn	0·003	0·004	0·008	0·010	0·010	0·010		0·011	
Mg	0·723	0·730	0·668	0·675	0·681	1·410		1·379	
Ca	0·859	0·853	0·785	0·844	0·838	0·016		0·014	
Na	0·050	0·058	0·138	0·131	0·133	0·003		0·004	
K	tr.	tr.	0·006	0·004	0·001	—		—	
Z	2·000	2·000	2·000	2·000	2·000	—		—	
WXY	2·004	2·001	1·993	1·998	2·004	—		—	

Analyses 1 to 5, clinopyroxenes.

1 From analcime–olivine theralite ST. 28, close to lower western contact.

2 From melanocratic natrolite–analcime *tinguaite* ST. 16, *southern face*, approximately 90 ft above theralite ST. 20.

3 Pink cores of phenocrysts from analcime-tinguaite ST. 12, from exposed top of intrusion.

4 Pale green clinopyroxene from analcime-tinguaite ST. 12.

5 Pale green clinopyroxene from analcime-tinguaite ST. 11, from exposed top of intrusion.

Analyses 2 and 3 have been recalculated to 100 % to correct for apatite impurities (P_2O_5 = 0·30 and 0·66 respectively).

Analyses 6 and 7, olivines.

6 From analcime–olivine theralite ST. 28.

7 From leucocratic analcime–olivine theralite ST. 20, on southern face approximately 70 ft above theralite ST. 28.

Analyses 1, 2, 3, 5, 6, 7 by M. Chiba.

Analysis 4 by J. H. Pyle.

The clinopyroxene phenocrysts in the theralites form pinkish brown, slightly pleochroic prisms up to 3 mm long, which display well-developed colour zoning, hour-glass structure, and strong inclined dispersion. Most groundmass clinopyroxenes are also pinkish but some crystals have pale green margins. The latter type of zoning is more clearly developed in the groundmass pyroxenes of leucocratic theralites. Because their titania contents decreased with differentiation, only a small percentage of the pyroxene phenocrysts in the tinguaites retain a pink colour, generally confined to their cores. Most tinguaite phenocrysts (up to 3×2 mm) are pale green and slightly pleochroic (α very pale green, γ pale green) (*cf.* table I, analyses 4 and 5). The development of pale green margins on the phenocrysts is first observed in the melanocratic tinguaites. The pale green phenocrysts may deepen slightly in colour in their outer portions, whose increased optic axial angles, compared with the optic axial angles of the cores, indicate enrichment in $NaFe^{3+}Si_2O_6$. The optic axial angles of the pale green pyroxene phenocrysts in the tinguaites also tend to be greater than the 2V's of the phenocrysts in the theralites (table I).

Some pale green phenocrysts in the coarsest grained tinguaites develop a thin discontinuous rim or irregular projections of a deeper green pyroxene (α bright green, γ yellowish green) whose negative elongation, low extinction angles, higher birefringence, and higher refractive indices (β 1·74 to 1·77) indicate a highly acmitic variety, contrasting with the more common pale green diopsidic cores or phenocrysts. The change from a pale green to a dark green clinopyroxene in individual crystals is accompanied by a rather abrupt change in optical properties. Groundmass pyroxenes, particularly in the coarser-grained tinguaites, possess optical properties similar to the deeper coloured outer zones of the phenocrysts.

Some tinguaites contain minor amounts of a dark purplish-brown amphibole as small crystals in the groundmass or as outgrowths on sodic clinopyroxene. The colour, relatively low birefringence, and somewhat anomalous interference colours of this amphibole suggest a katophoritic variety.

Chemistry

Table I lists analyses of clinopyroxenes from the most basic theralite and from 3 tinguaites, with atomic ratios calculated on a basis of 6 oxygens. Analyses 3 and 4 are analyses of the fractions obtained by splitting the bulk clinopyroxene concentrate ($D < 3{\cdot}45$) on a Frantz isodynamic separator into pink (less magnetic) and pale green (more magnetic) pyroxene fractions. The concentrates of the pale green pyroxenes (analyses 4 and 5) were optically checked for darker green pyroxene to ensure that, as far as possible, pyroxenes of differing generations were not analysed. In fig. 1, the clinopyroxenes are plotted on the standard pyroxene diagram on a basis of $\mathrm{Ca}+\mathrm{Mg}+\Sigma\mathrm{Fe} = 100$ atom % ($\Sigma\mathrm{Fe} = \mathrm{Fe}^{2+}+\mathrm{Fe}^{3+}+\mathrm{Mn}$). Because several clinopyroxenes contain significant amounts of Na and Fe^{3+}, this method of plotting does not provide the optimum representation of their compositions, and an additional plot (fig. 2) on a basis of Mg, (Na+K), and ($\mathrm{Fe}^{2+}+\mathrm{Mn}+\mathrm{Fe}^{3+}$) has been adopted, Fe^{3+} representing the excess, if any, of trivalent iron over (Na+K) (*cf.* Carmichael, 1962).

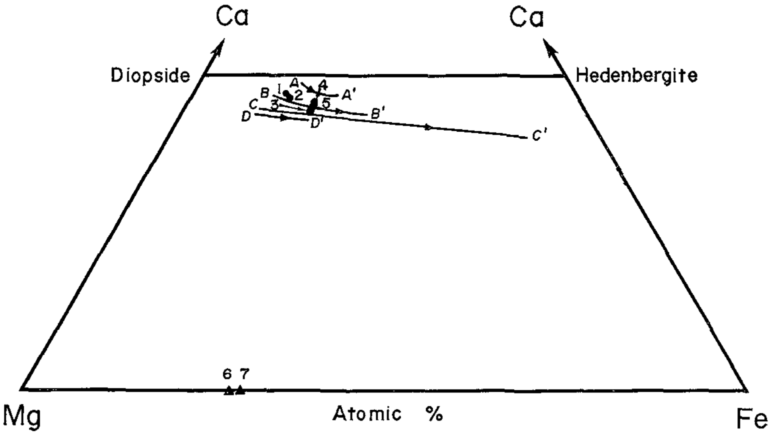

FIG. 1. The compositions of clinopyroxenes from some alkali differentiation series plotted in terms of variation in Ca, Mg, and Fe. ●, Square Top clinopyroxenes; ▲, Square Top olivines. Compositions 1–7 refer to analysis numbers in table I. The Square Top clinopyroxene trend is in the direction 1 → 5. AA′ Black Jack clinopyroxene crystallization trend (Wilkinson, 1957*a*), BB′ Garbh Eilean clinopyroxenes (Murray, 1954), CC′ Japanese alkali-basalt–trachyte clinopyroxenes (Aoki, 1964), DD′ clinopyroxenes from the Gough Island volcanic series (Le Maitre, 1962). Clinopyroxenes from the Mount Dromedary intrusion (Boesen, 1964) and the Okonjeje alkali series (Simpson, 1954) plot close to the Garbh Eilean trend.

The clinopyroxene from the analcime–olivine theralite and that from the melanocratic natrolite–analcime tinguaite are titaniferous sahlites, similar in composition to many lime-rich clinopyroxenes from alkaline rocks. The remaining pyroxenes (table I, analyses 3 to 5), containing significant Na and Fe^{3+}, may be regarded as sodian augite (the pinkish cores of the phenocrysts of analcime-tinguaite ST. 12) and sodian sahlites (pale green phenocrysts from tinguaites ST. 12 and ST. 11) (*see* Yagi, 1953, p. 781; Deer, Howie, and Zussman, 1963, p. 119).

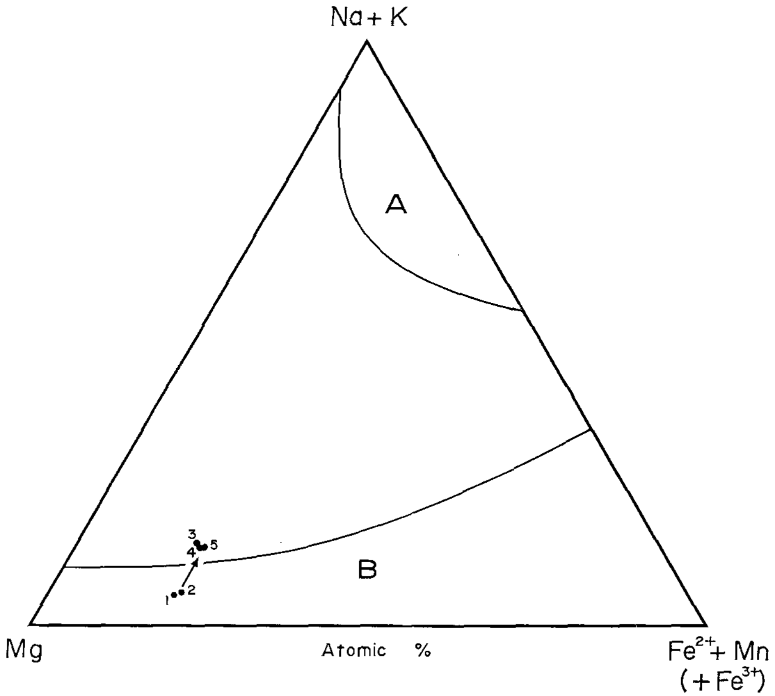

FIG. 2. Crystallization trend of the Square Top clinopyroxenes with respect to variation in Mg, Na + K, and Fe^{2+} + Mn(+ Fe^{3+}). Points 1 to 5 refer to analyses in table I. Areas A and B delineate the fields of Na-rich and Ca-rich clinopyroxenes from alkali rocks (after Aoki, 1964).

Silicon and aluminium vary antipathetically (*cf.* Kushiro, 1960; Le Bas, 1962). Most of the Al is in the tetrahedral position, and the amount of Al in the Z group decreases with differentiation (fig. 3*a*). Both Al and Ti decrease with differentiation (fig. 3*b*). Clinopyroxenes from theralite ST. 28 and tinguaite ST. 16 are not notably enriched in Ti and their relatively high Al contents render it unnecessary to allot any Ti to make $Z = 2$. The entry of appreciable Al in the Z group resulted from higher temperatures in the lower levels of the intrusion (Wilkinson, 1965*a*) and from the comparatively undersaturated parent liquid (Kushiro, 1960). As differentiation proceeded, crystallization temperatures decreased and less Al replaced Si in the *Z* group (*cf.* table I, analyses 1 and 5). Clinopyroxene ST. 28 is markedly silica-deficient in that its norm reveals nepheline and calcium disilicate whereas the norm of pyroxene ST. 16 contains nepheline and albite (*cf.* Coombs, 1963).

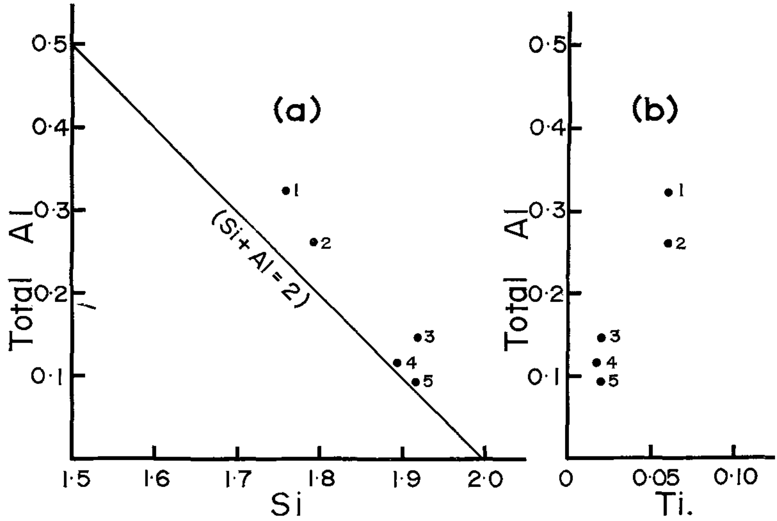

FIG. 3. (*a*) Relation between the atomic proportions of Si and Al in the Square Top clinopyroxenes. (*b*) Relations between the atomic proportions of Al and Ti. The atomic proportions are calculated on a basis of six oxygen atoms. The points 1 to 5 refer to analyses in table I.

Calcium and magnesium decrease slightly with differentiation, whilst Na and Fe^{3+} increase in the later stages. The increased amounts of Fe^{3+} were balanced by decreases in Ti, Ca, and Mg. Potassium tends to remain very low throughout, and Mn is enriched relative to Fe^{2+} and Fe^{3+}.

Discussion

In recent years several clinopyroxene crystallization trends have been defined in alkali differentiation sequences possessing varying ranges of parent rock compositions and displaying differing degrees of saturation (fig. 1). Clinopyroxenes from the mildly alkaline Garbh Eilean sill (Murray, 1954) and the slightly more undersaturated Black Jack sill (Wilkinson, 1957*a*) belong mainly to the diopside–hedenbergite series and reveal limited replacement of Mg by Fe^{2+}, despite wide variation in the olivine and total rock Fe^{2+}/Mg ratios. A comparable degree of iron enrichment is exhibited by the clinopyroxenes from the monzonitic Mount Dromedary complex, New South Wales (Boesen, 1964). The clinopyroxenes from the more felsic members of the alkalic rock sequence at Morotu, Sakhalin, trend away from the Ca–Mg–Fe plane towards acmite, $NaFe^{3+}$ replacing $Ca(Mg,Fe^{2+})$ (Yagi, 1953). However, in the more evolved members of some alkali volcanic series (*e.g.* in certain mugearites, trachytes, and pantellerites), the clinopyroxenes, while still lime-rich, reveal more extensive Fe^{2+}/Mg replacements, their compositions extending towards hedenbergite (Muir and Tilley, 1961; Carmichael, 1962; Aoki, 1964).

Although their parent rocks vary widely in composition,[1] the Square Top clinopyroxene phenocrysts possess a restricted range in composition, and plot mainly in the sahlite field, trending approximately parallel to the diopside–hedenbergite join (fig. 1). In their limited degree of iron enrichment and course of crystallization they closely resemble the Garbh Eilean, Black Jack, Okonjeje, and Mount Dromedary clinopyroxenes. The limited enrichment in acmite is illustrated by fig. 2 where the clinopyroxenes trend towards (Na+K), parallel with the Mg–(Na+K) join. This trend differs from clinopyroxene trends in some alkali rock sequences where the pyroxenes show concomitant enrichment in Na, Fe^{3+}, and Fe^{2+} (Carmichael, 1962, fig. 2; Aoki, 1964, fig. 3). At Square Top, the darker green pyroxene that rims the pale green variety or occurs as a groundmass mineral would probably plot much closer to the (Na+K) apex in fig. 2 but the available data are insufficient to establish any continuum in compositions between the diopsidic phenocrysts and the more acmitic rims and groundmass clinopyroxenes. The petrographic data on the Square Top clinopyroxenes, indicating a rather abrupt change in the compositions of the two pyroxene phases, are not inconsistent with Aoki's (1964) proposal that Ca-rich and Na-rich clinopyroxenes are separated by a wide immiscibility gap under magmatic conditions (fig. 2), acmite forming by reaction between hematite (magnetite in nature) and liquid.

The limited Fe^{2+}/Mg variation in the Square Top pyroxenes arose from the Fe^{2+} in successive liquid fractions becoming progressively more oxidized in the presence of increasing concentrations of water, which probably resulted in increased oxygen pressures. Modal analcime increased with differentiation, analcime comprising 20–30 % of the modes of the upper tinguaites where it may be accompanied by signi-

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[1] The Square Top differentiation sequence is chemically equivalent to the volcanic series, basanite → phonolite.

ficant natrolite. The Fe_2O_3 contents of the various differentiates increased with differentiation. At the same time MgO and FeO decreased but at comparable rates, the rock FeO/MgO ratios (0·98 to 1·11) remaining relatively constant in passing from theralite to tinguaite (Wilkinson, 1965*a*, table 1). However, it may be noted that the parent liquid was sufficiently reduced to precipitate a titanomagnetite with a normative ulvöspinel component of 66 % (titanomagnetite ST. 28). The chemistries of more differentiated titanomagnetites indicate successively more oxidized liquid fractions, the normative compositions of titanomagnetites from analcime–tinguaites ST. 12 and ST. 11 revealing excess Fe_2O_3 (Wilkinson, 1965*b*).

The limited range in the compositions of olivines from different members of the differentiation sequence parallels the restricted degree of Fe^{2+}/Mg variation in the clinopyroxenes. Olivines from theralites ST. 28 and ST. 20 have $Mg:Fe^{2+}$ atomic ratios of 71·3:28·7 and 69·9:30·1 respectively (table I, analyses 6 and 7). Olivines from melanocratic tinguaites ST. 18 and ST. 19 and from tinguaites ST. 32 and ST. 39 have $\beta \sim 1{\cdot}720$, indicating compositions close to Mg_{68} atom % (Deer, Howie, and Zussman, 1962, p. 22). The bulk compositions of olivine concentrates from specimens ST. 28, 20, and 19, determined by the X-ray method of Yoder and Sahama (1957), are respectively Fo_{71}, Fo_{69}, and Fo_{70} mol. %. However, the olivines are often normally zoned and the outer rims of many crystals are richer in Fe^{2+} than the average compositions cited above.

The compositional data on clinopyroxenes from alkalic differentiation sequences are not notably at variance with the proposal that members of the diopside–hedenbergite series in alkaline basic rocks are only rarely more iron-rich than $Ca_{45}Mg_{25}Fe_{30}$[1] (Wilkinson, 1956), particularly if hydrous mineral phases (analcime and other zeolites) are notable associates. The relatively high Fe_2O_3/FeO ratios of these hydrous melts resulted in limited clinopyroxene enrichment in Fe^{2+} (Wilkinson, 1957*b*; Le Maitre, 1962), compared with the more iron-rich clinopyroxenes from certain tholeiitic differentiation series. Fractionation of alkaline basic liquids precipitating nepheline as the sole under-saturated felsic mineral (and presumably deriving from comparatively more anhydrous liquids) may yield more Fe^{2+}-rich members of the Di–Hd series, Fe^{3+} and Na increasing also (*cf.* Tilley and Gittins, 1961). Those felsic alkali lavas with highly fayalitic olivine, hedenbergitic clinopyroxene, and

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[1] Most of the analysed clinopyroxenes belonging to the Di–Hd series are less iron-rich than $Ca_{45}Mg_{35}Fe_{20}$.

(sometimes) aenigmatite, which are often considered to derive by fractionation of more basic liquids, crystallized from highly reduced melts, compared with the felsic differentiates in most differentiated alkaline basic intrusions.

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