

## Olivine, pyroxene, feldspar, and spinel in ultramafic nodules from Auckland, New Zealand

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**SUMMARY.** Chemical, optical, and X-ray data are presented for forsteritic olivine, bronzite–enstatite, diopsidic augite, anorthite, and spinel from ultramafic nodules at seven localities in Auckland province. Olivine has a composition range from  $\text{Fo}_{79-93}$  for large primary crystals to  $\text{Fo}_{80-100}$  for smaller interstitial grains. Orthopyroxenes ( $\text{En}_{83-96}$ ) carry exsolution lamellae of clinopyroxene parallel to (100); clinopyroxenes are mainly diopsidic augites with exsolved bronzite. The plagioclase ( $\text{An}_{97}$ ) has high-temperature characteristics and a lattice structure probably transitional between primitive and body-centred anorthite. Spinels include chromite, picotite, ceylonite, hercynite, and magnetite. Element distribution indicates that the ultramafic assemblages attained equilibrium at temperatures near 1250 °C and at moderate pressures, corresponding to the melting interval of anhydrous basaltic magmas within the uppermost mantle.

At seven localities in the Auckland province, listed in table I, ultramafic nodules are abundant inclusions in lava flows and dykes. In six of the occurrences the host rocks are Quaternary alkali olivine-basalts while the seventh is a Miocene olivine nephelinite at Arapohue. Descriptions of the fabrics and textures of these nodules have been given by Brothers and Rodgers (in press) and of the petrography and petrochemistry by Rodgers, Brothers, and Searle (in preparation). The present paper is intended as a compilation of significant mineral data from the same rocks.

In approximately 450 nodules studied the mineral assemblages represent dunite, harzburgite, wehrlite, lherzolite, feldspathic peridotite, clinopyroxenite, and, rarely, gabbro. At all localities olivine is the dominant component in the majority of nodules as both large primary and smaller secondary crystals; it is rare or absent only in some nodules with dominant clinopyroxene or feldspar. Orthorhombic and monoclinic pyroxenes are consistent members of the assemblages, except in dunites, with clinopyroxene showing the greatest variation in mode of occurrence as a primary constituent in large crystals, as a fine-grained intergranular component, and as a product of reaction at interfaces between nodule and host rock. Plagioclase is the only notable non-mafic mineral in the nodules in quantities that range from rare in peridotites to abundant in gabbros and in anorthitites, which contain up to 85 % modal feldspar. Accessory phases include spinel, biotite, zeolite, and glass. Texture is usually hypidiomorphic to allotriomorphic granular with poorly defined fissility or mineralogical foliation in a few cases. Particularly in the peridotites there is a wide range of grain size, from less than 0.1 mm in some intergranular mosaics to 25 mm for the larger ferromagnesian crystals.

The modal compositions of nodules from which full analyses of mineral separates

were made are given below; sample numbers refer to the petrology collection at the University of Auckland and full details of all localities are given by Rodgers (1966).

	9232	9214	4387	9150	9183	7887	5283	9182	9207	9193
olivine	97	96	93	91	63	72	3	12	59	1
orthopyroxene					35	12		4		1
clinopyroxene		1			1	10	96	61	24	10
spinel	3	3	6	7	1	1	1		2	3
plagioclase								2		74
accessories			1	2		5		21	15	11

Chemical determinations of mineral compositions have been made in parallel with optical, density, and X-ray techniques. Some problems were encountered in obtaining pure separates for analysis. Exsolution lamellae in pyroxene proved very difficult to separate from the host crystals and whereas pure clinopyroxene was readily separated

TABLE I. *Ultramafic nodule localities of the Auckland Province, New Zealand, listed in order of probable increasing age*

Locality	N.Z.M.S. 1* Grid reference	Age	Parent formation
Shoal Bay volcanic complex, Auckland City	N42/277687P	> 23 000 B.P.	Auckland Basalts
Stevenson's Quarry, Ramarama	N47/508223P	Penultimate Glaciation	Franklin Basalts
Bridal Veil Falls, Raglan	N65/421325P	?	Te Mata Basalts
Kirikiripu Volcano, Raglan	N64/410444P	?	Not named
Roose's Quarry, Bombay	N47/501435P	Lower Pleistocene	Bombay Basalts
Ngatutura Point, Ohuka, Port Waikato	N55/271798P		
Todd's Quarry, Arapohue	N23/508608P	Miocene	Ngatutura Basalt Manukau Breccias

\* New Zealand Mapping Series 1, 1:63 360 (1942), Provisional Series.

from nodules rich in this mineral, only a few milligrams of pure orthopyroxene could be obtained from lherzolitic and harzburgitic assemblages. With the wet chemical techniques used for analyses only the partial data for orthopyroxenes given in table VI could be determined with a satisfactory degree of confidence. No trace element studies have been made.

### *Olivine*

The habit of the olivine crystals changes with rock type and with textural setting. In dunites the grains appear in thin-section as equant, subhedral to anhedral polyhedra. With increase in pyroxene content, well-defined interstitial mosaics of fine-grained minerals are present and in this setting the larger olivine crystals are distinctly tabular and euhedral to subhedral. Stereographic plots of face poles indicate strong

development of {010} and {021}, while {110}, {120}, {101}, and {100} by comparison are suppressed and less frequently present.

The larger olivines, here referred to as primary, have an average size of 1 or 2 mm, but tabular crystals reach as much as 20 mm in length. In general, grain size diminishes with decrease in olivine content, yet the largest crystals are often found in nodules

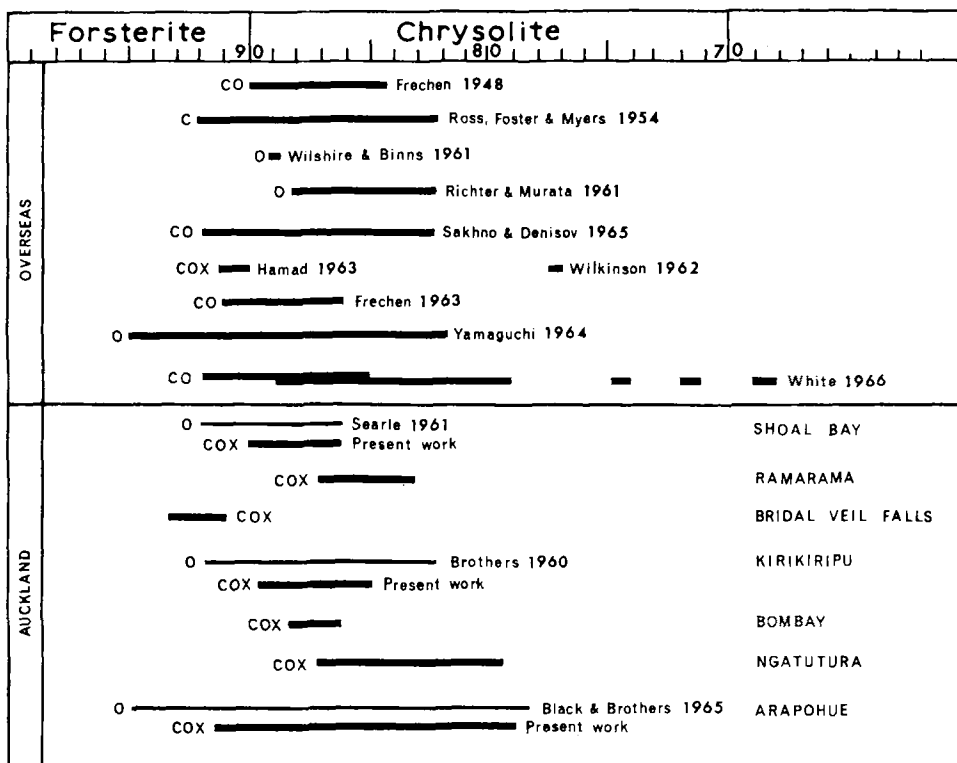


FIG. 1. Compositional ranges of primary olivines from the seven Auckland nodule localities and other examples in the literature. C = chemical determination; O = optical; X = X-ray.

containing abundant pyroxene. Kink bands parallel to {100} are present in many of the larger grains and in a few smaller ones where the texture is close-packed. No evidence of zony structure could be found in thin-section examination. Liquid carbon dioxide inclusions from olivines of some of these Auckland nodules have been described by Roedder (1965). Extrapolation of the data of Kennedy (1954) for the CO<sub>2</sub> system indicates possible filling pressures in excess of 6000 bars, assuming a temperature of formation of 1200–1300 °C.

Fig. 1 summarizes the complete range of olivine composition in all the nodules examined and compares this information with other examples in the literature. The Auckland olivines are all highly magnesian, Fo<sub>78-93</sub>, and it is notable that where

TABLE II. *Analyses, structural formulae, atomic ratios, and physical properties of six olivines from the Auckland nodules. Analyst: K. A. Rodgers*

	9232	9214	4387	9150	9183	7887
SiO <sub>2</sub>	40.26	40.21	40.81	40.63	39.12	39.99
TiO <sub>2</sub>	0.03	0.02	0.03	0.08	0.03	0.10
Al <sub>2</sub> O <sub>3</sub>	0.25	0.48	0.11	0.52	0.74	0.36
Cr <sub>2</sub> O <sub>3</sub>	0.03	0.11	0.06	0.04	0.02	tr.
Fe <sub>2</sub> O <sub>3</sub>	0.74	1.03	0.30	0.03	0.97	0.62
FeO	9.20	11.24	8.96	9.75	13.20	13.44
MnO	0.01	0.06	0.00	0.11	0.13	0.08
MgO	48.99	46.12	49.08	48.40	44.37	45.12
CaO	0.10	0.18	0.20	0.29	0.25	0.14
NiO	0.23	0.28	0.31	n.d.	0.44	n.d.
Na <sub>2</sub> O	0.02	0.03	0.01	0.02	0.01	0.00
K <sub>2</sub> O	0.00	0.02	0.00	0.01	0.00	tr.
P <sub>2</sub> O <sub>5</sub>	0.01	tr.	0.00	0.00	tr.	tr.
H <sub>2</sub> O <sup>+</sup>	0.11	0.21	0.09	0.09	0.20	n.d.
H <sub>2</sub> O <sup>-</sup>	0.07	0.05	0.02	0.26	0.16	n.d.
Total	100.05	100.04	99.98	100.23	99.64	99.85
<i>Number of ions on the basis of 4 oxygen</i>						
Si	0.987	0.996	0.999	1.001	0.992	1.003
Al	0.007	0.014	0.005	0.018	0.021	0.010
Ti	0.000	0.000	0.000	0.000	0.000	0.004
Fe <sup>3+</sup>	0.013	0.019	0.005	0.000	0.026	0.012
Mg	1.790	1.704	1.793	1.777	1.678	1.686
Fe <sup>2+</sup>	0.188	0.233	0.184	0.201	0.280	0.282
Mn	0.000	0.001	0.000	0.002	0.002	0.001
Ca	0.002	0.005	0.005	0.007	0.007	0.004
Ni	0.006	0.005	0.006	—	0.009	—
Cr	0.001	0.002	0.001	0.001	0.006	—
Total X <sup>2+</sup> Y <sup>3+</sup>	2.007	1.983	1.999	2.006	2.029	1.999
<i>Atomic ratios</i>						
Mg <sup>2+</sup>	90.5	88.0	90.7	89.8	85.7	85.7
Fe <sup>2+</sup>	9.5	12.0	9.3	10.2	14.3	14.3
α	1.654	1.661	1.650	1.653	1.664	1.663
β	1.672	1.679	1.668	1.670	1.684	1.682
γ	1.691	1.697	1.685	1.687	1.700	1.696
2V <sub>γ</sub>	88°	90	90	87	90	90
D	3.38	3.45	3.50	3.40	3.49	3.45
d <sub>130</sub>	2.7727 Å	2.7752	2.7722	2.7719	2.7756	2.7752

9232 = dunite olivine (Kirikiripu).

9214 = dunite (Bombay).

4387 = dunite (Ramarama).

9150 = dunite (Bridal Veil Falls).

9183 = harzburgite (Ngatutura).

7887 = lherzolite (Arapohue).

composition has been determined by optical methods only, there is greater compositional spread.

The six analysed olivines in table II come from four dunites, a lherzolite, and a harzburgite. In the analyses, the structural formulae contain small amounts of various cations. Some of these, such as Al, Na, and K, may be due to inclusions contained by the analysed mineral; others are more likely to be ions substituting for Mg<sup>2+</sup> and Fe<sup>2+</sup>.

Ferric iron has been reported in many olivine analyses and may be an original constituent (Bowen and Schairer, 1932), but in the case of specimen 9150 it possibly represents small exsolved plates of magnetite or ferrochromite, which are strongly aligned parallel to *c* of the olivine. On the other hand, the relatively high values of Fe<sup>3+</sup> in some of the present analyses, especially 9214, could be due to oxidation of the olivine either naturally or during grinding. Chromium and nickel are not unusual in trace quantities in magnesian-rich olivines and samples 9232, 9214, and 4387 have nickel contents comparable to those with a similar fayalite composition described by

TABLE III. Average forsteritic composition of Auckland nodules compared with decreasing olivine content; data derived from optical and diffractometry measurements

Modal % of olivine	100-90	90-80	80-60	60-40	40-20	20
Locality	Average forsteritic content of olivines					
Shoal Bay	88	86	88	—	—	—
Ramarama	86	85	87	83	—	—
Bridal Veil Falls	91	93	92	—	—	—
Kirikiripu	85	85	86	86	86	83
Bombay	86	87	—	—	—	—
Ngatutura	85	83	83	81	86	81
Arapohue	90	97	88	—	83	80

Ross, Foster, and Myers (1954), by Talbot, Hobbs, Wilshire, and Sweatman (1963), and by Forbes and Banno (1966), but sample 9183 contains nearly twice as much nickel. Preliminary determinations of chemical composition for olivines of the host rocks appear to agree with Forbes and Banno's recognition of a compositional gap in nickel content.

With ratios of Mg<sup>2+</sup>:Fe<sup>2+</sup> between 90.7:9.3 and 88.0:12.0 the analysed dunite olivines are similar to those listed by Ross *et al.* (1954) and are distinctly more magnesian than olivine from the harzburgite and lherzolite in table II. Nevertheless, a tendency for decrease in the forsterite component with decrease in the modal proportion of olivine cannot be demonstrated generally for the Auckland nodule assemblages. In table III the average forsterite content of primary olivine is compared with decreasing modal percentage of the mineral in a selection of nodules from the seven Auckland localities. Similar studies of the differing rock types and textural settings failed to show any simple variation in the composition of the olivine.

In many thin-sections with loose-packed texture, interstitial pools of finely crystallized minerals contain smaller olivines, referred to here as secondary. On the evidence of optic axial angles, these grains have compositions apparently different from those of the larger primary group. Andreatta (1938), Chudoba and Frechen (1941), and Black and Brothers (1965) recorded lower magnesium in similar secondary crystals and lower tenors again in phenocrysts from the host basalts, but this trend in compositional variation has not been supported by the work of Ross *et al.* (1954), Derui (1959), Wilshire and Binns (1961), and Talbot *et al.* (1963). Using the methods of

Jackson (1960), detailed X-ray examination of olivine separates from nodules containing both primary and secondary crystals indicated the presence of two compositionally distinct phases; careful correlation with  $2V$  values from the same samples allowed the separate identification of the compositions given in table IV. Although the forsterite content of olivines from the host rocks tends to be lower than that in the nodules, larger crystals in the latter may be either richer or poorer in forsterite than the secondary grains. In the Palisades Sill, Walker (1940) found a range of  $Fo_{80-70}$  for the primary crystals and  $Fo_{70-65}$  for the secondary; the same trend is apparently true for the Arapohue (7886), Shoal Bay (9164), and Ramarama (9197) nodules. In comparison, the Bombay (9212) and Kirikiripu (5559) samples show forsterite enrichment in the smaller crystals.

TABLE IV. *Compositions of primary and secondary olivines from the same nodule, and olivine composition range in the host rocks*

	Primary olivines			Secondary olivines			4
	1	2	3	1	2	3	
5559	2.922	90	86	2.68	83	100	83-75
9164	2.887	89	88	2.957	93	84	90-80
9212	2.903	89	87	2.730	85	95	87-75
7886	2.941	91	85	3.042	93	80	93-70
9197	2.900	89	87	2.958	91	84	86-74
Kirikiripu*	—	—	95-82	—	81-3	100	—
Arapohue†	—	—	95-82	—	90-8	85-70	93-70

1.  $2\theta$  (062) olivine— $2\theta$  (220) LiF

2.  $2V$ , average or range

\* Data from Brothers (1960)

3. Average forsterite composition of olivine

4. Range in forsterite composition of host rock olivines

† Data from Black and Brothers (1965)

### *Orthopyroxene*

Anhedral to subhedral orthopyroxenes, with maximum size 5-6 mm, are common in all nodules except those rich in clinopyroxene, but only rarely does the mineral exceed 30 % of the primary modal constituents. The crystals are colourless to pale yellow, non-pleochroic, and have a well-developed perfect {210} cleavage. Orthopyroxene and olivine have a primary textural relationship, often in intimate irregular intergrowths. In some nodules orthopyroxene dwarfs the associated primary olivine; in finer-grained specimens it often forms a close-packed interlocking mosaic with spinel.

Ragged and embayed orthopyroxenes are evidence of extensive reaction within the fabric of many nodules and also near nodule margins or where veins of magmatic fluids from the host rock have penetrated along fractures. Widely separated orthopyroxene remnants in optical continuity are often set in pools of intergranular clinopyroxene and spinel.

The compositions of representative orthopyroxenes, as determined by optical methods, are presented in fig. 2. All are magnesium-rich in the bronzite-enstatite range and in some cases there is noteworthy variation between separate nodules of the

same rock type at one locality.  $2V_{\alpha}$  is always greater than  $80^{\circ}$  and  $\gamma$  always less than  $1.687$ , and no close approach to hypersthene compositions is evident. Partial chemical analyses for MgO and FeO in some orthopyroxene separates are given in table VI and the range of Mg:Fe<sup>2+</sup> from 83.1:16.9 to 90.3:9.7 supports optical determinations of composition. In a comparison with orthopyroxenes described from nodules in other countries (fig. 2) the Auckland samples show wider compositional variation.

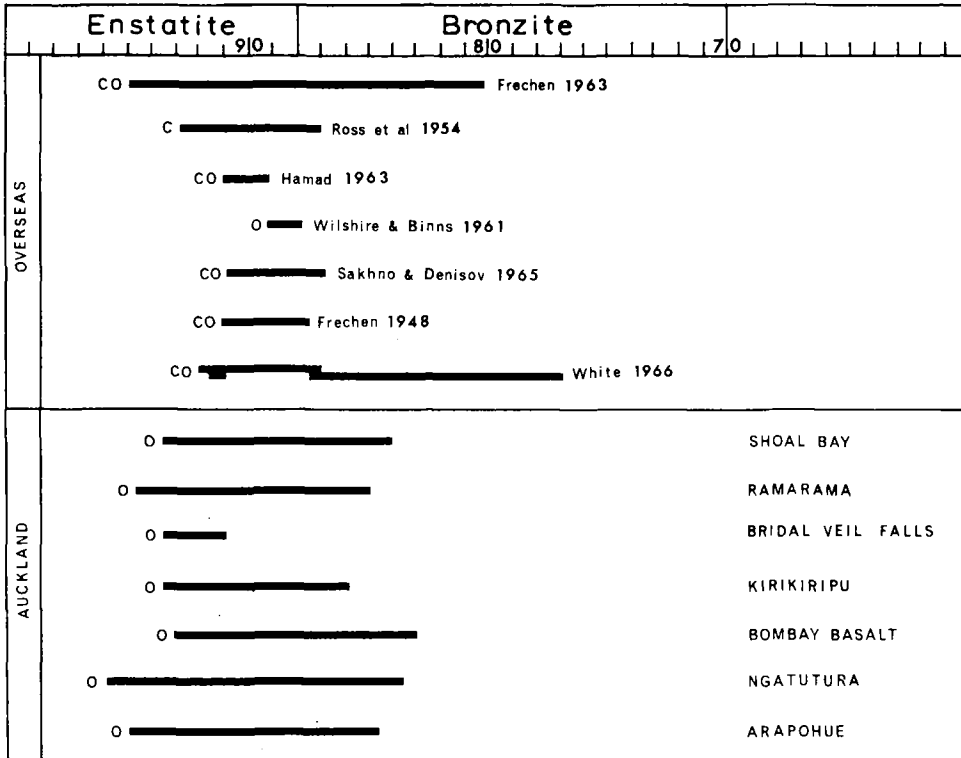


FIG. 2. Compositional ranges of enstatites from the seven Auckland nodule localities and other examples from the literature. C = chemical determination; O = optical.

Offsets or kink bands are not uncommon in the larger orthopyroxenes and are emphasized as planes of disruption with rotations of up to  $15^{\circ}$  across ruptured lamellae of exsolved clinopyroxene. Some enstatite crystals contain as many as eight subgrains developed in this manner, with small but measurable differences in optical orientation. The boundaries between subgrains are subparallel to  $\{001\}$  of the orthopyroxene and often are irregular or imperfect. The glide mechanism appears to conform to the system determined by Turner, Heard, and Griggs (1960) and Raleigh (1965) where  $T = (100)$ ,  $t = [001]$ . In some examples the included exsolution lamellae have been deformed into curved and recurved arcs. Wide spacing of the ruptures and the small angles of offset are possibly due to the roughly orthogonal relationship between the

subgrain interfaces parallel to  $\{001\}$  and the strongly bonded silicon–oxygen chains parallel to  $c$  in the host crystal.

In nodules from all localities some enstatite crystals carry thin bands of exsolved clinopyroxene generally less than 0.005 mm wide. In thin-section the lamellae appear either fine, straight, and continuous or as rows of flattened blebs. They are often most prominently developed in the centres of the host crystals and invariably pinch out

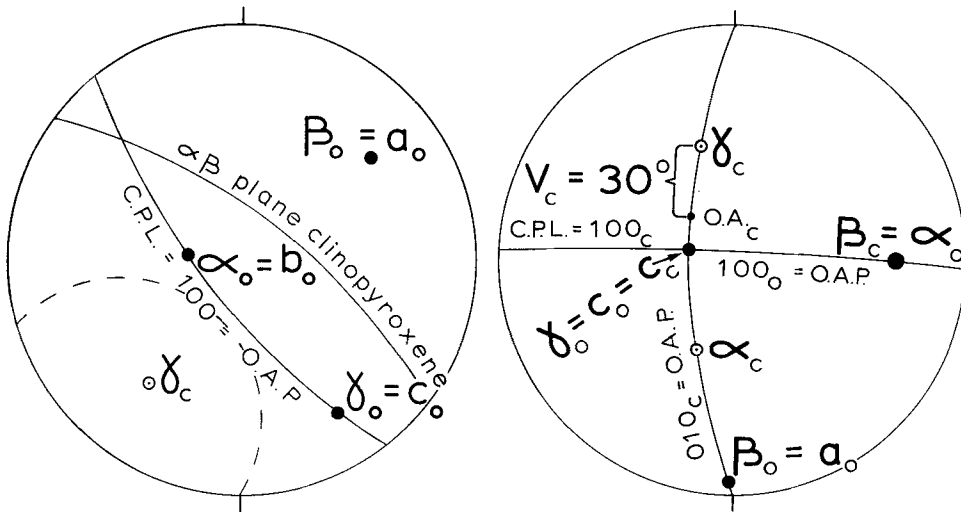


FIG. 3. Lower hemisphere stereographic projections of optical directions in pyroxenes and their included lamellae with, C.P.L. = composition plane of lamella; O.A.P. = optic axial plane; subscript o = orthopyroxene; subscript c = clinopyroxene. FIG. 3a (left). Enstatite containing diopside lamella; small circle arc lying at  $40^\circ$  radius about  $\gamma_c$  represents possible positions of  $c$  for diopside. FIG. 3b (right). Diopside containing orthopyroxene.

before reaching the margins in the manner described by Brown (1957). Brothers (1960) recorded similar lamellae parallel to  $(010)$  of orthopyroxene from Kirikiripu. Using the orientation  $a = \beta$ ,  $b = \alpha$ ,  $c = \gamma$  for the orthopyroxene, measurements on clinopyroxene lamellae from the other six localities showed them to be aligned parallel to  $\{100\}$  of the host enstatite (note that Brothers (1960) used the orientation  $a = \alpha$ ,  $b = \beta$ ,  $c = \gamma$  for orthopyroxene, following Dana, 1949). Although the lamellae generally were too thin for accurate determinations of  $\beta$  and  $\gamma$  orientations, there was clearly lack of correspondence between the indicatrices of the two pyroxenes and  $c$  of orthopyroxene did not coincide with  $c$  of clinopyroxene;  $\gamma$  clinopyroxene plotted  $64^\circ$  away from  $\gamma$  orthopyroxene and  $55^\circ$  from  $\alpha$  orthopyroxene (fig. 3). This orientation differs from that of the Bushveld type of Hess and Phillips (1938) and Hess (1960) where the host and exsolved clinopyroxenes have mutual  $b$  and  $c$  axes in the composition range  $\text{Fs}_{12}$  to  $\text{Fs}_{30}$ ; further, the Bushveld lamellae lie parallel to a common  $(100)$  plane on which both pyroxenes have the same structure and thus share a minimal energy interface suitable for unmixing. In the Auckland examples, exsolved ions appear



to have migrated across a higher energy surface, possibly accounting for the small size of the lamellae.

### *Clinopyroxene*

Clinopyroxenes show gradations in size from anhedral and subhedral crystals, more than 5 mm across, to very small irregular grains in intergranular mosaics. A good cleavage has developed parallel to  $\{110\}$  and more rarely a parting parallel  $\{001\}$ ;

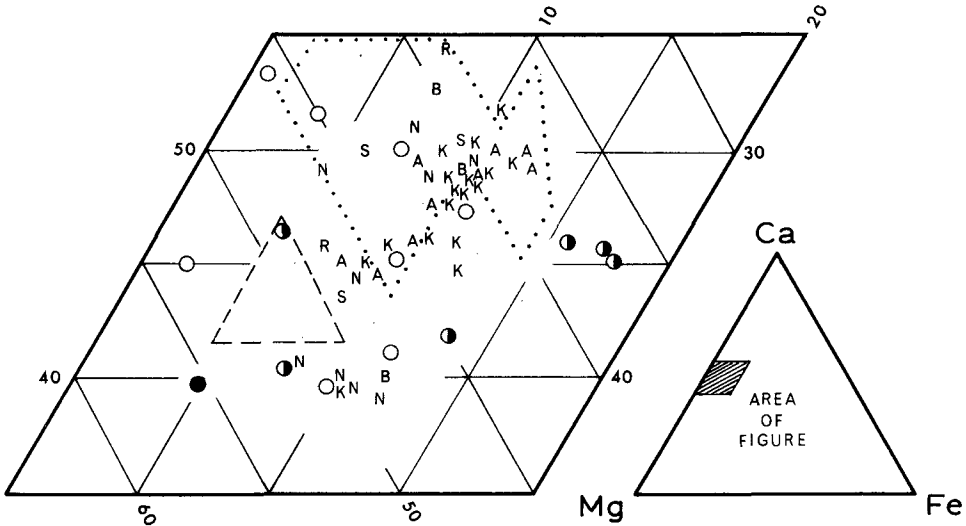


FIG. 4. Compositions of some clinopyroxenes from the seven Auckland nodule localities and other examples from the literature. S = Shoal Bay; R = Ramarama; K = Kirikiripu; B = Bombay; N = Ngatutura; A = Arapohue; O = Yamaguichi (1964); ● = Hamad (1963); ◐ = Wilshire and Binns (1961); ---- = range of compositions given by Ross *et al.* (1954); ····· = range of compositions from White (1966).

polysynthetic and simple twinning on (100) and (001) were recorded at all sample localities. The colour range is from colourless to pale green and pink with faint pleochroism. At contacts between nodule and surrounding flow rock the clinopyroxene is often sharply zoned, the commencement of the outer zone being distinguished by a discontinuous dusting of fine-grained ores. In reaction pools surrounding embayed orthopyroxene, the newly generated clinopyroxene shows optical alignment with exsolution lamellae contained by the bronzite–enstatite.

In thin-section, bronzite exsolution lamellae are common as hair-line or short tabular crystals oriented parallel to (100) of the host clinopyroxene as described by Poldervaart and Hess (1951) and Brown (1957). Details of lamellae orientation for ortho- in clinopyroxene at Kirikiripu have been given by Brothers (1960) and measurements at all other localities were found to be similar (fig. 3):  $\alpha$  orthopyroxene =  $\beta$  clinopyroxene;  $\gamma_{\text{opx}} = c_{\text{opx}} = c_{\text{epx}}$ ;  $\beta_{\text{opx}} = \perp$  lamella =  $\perp$  (100)<sub>opx</sub>;  $\beta_{\text{opx}} : \gamma_{\text{opx}} = 50^\circ$ . In many nodules diopsidic augite contains exsolution lamellae of bronzite while coexisting orthopyroxene carries exsolved clinopyroxene.

The compositions of 43 clinopyroxenes from the Auckland nodules were determined by optical methods and the extent of Ca:Mg:Fe variation is shown in fig. 4. In table V the chemical analyses of three clinopyroxenes are presented together with their structural formulae constructed on a basis of 6 oxygens to the unit cell. The optical data indicate compositions from iron-rich diopsides to magnesian sahlites and calcic augites, which are more restricted than the ranges given by Wilshire and Binns (1961),

TABLE V. *Analyses and structural formulae for three clinopyroxenes from Auckland nodules. Analyst: K. A. Rodgers*

	5283	9182	9207		5283	9182	9207
				<i>Number of ions in the basis of 6 oxygens</i>			
SiO <sub>2</sub>	51.05	51.98	49.78	Si	1.889	1.871	1.841
TiO <sub>2</sub>	0.45	0.40	0.36	Al <sub>z</sub>	0.111	0.129	0.159
Al <sub>2</sub> O <sub>3</sub>	3.91	3.62	4.21	Al <sub>y</sub>	0.059	0.025	0.024
Fe <sub>2</sub> O <sub>3</sub>	1.91	2.31	2.03	Ti	0.012	0.011	0.010
Cr <sub>2</sub> O <sub>3</sub>	0.77	0.63	1.06	Fe <sup>3+</sup>	0.053	0.062	0.056
FeO	3.27	3.07	3.98	Cr	0.003	0.002	0.031
MnO	0.02	0.01	0.10	Mg	0.911	0.892	0.841
NiO	0.03	0.03	0.04	Ni	0.000	0.000	0.000
MgO	16.51	16.62	15.36	Fe <sup>2+</sup>	0.101	0.092	0.123
CaO	20.35	20.91	21.34	Mn	0.000	0.000	0.003
Na <sub>2</sub> O	0.71	0.52	1.02	Ca	0.807	0.807	0.845
K <sub>2</sub> O	0.05	0.05	0.07	Na	0.051	0.037	0.073
H <sub>2</sub> O <sup>+</sup>	0.51	0.04	0.50	Z	2.00	2.00	2.00
H <sub>2</sub> O <sup>-</sup>	0.42	0.11	0.13	W	0.86	0.84	0.92
Total	99.96	100.30	99.98	X+Y	1.25	1.21	1.09
				W+X+Y	2.11	2.05	2.01
$\beta$	1.678	1.680	1.682	<i>Atomic ratios</i>			
2V <sub>z</sub> (av.)	52°	52°	51°	Mg	50.1	49.8	46.7
$\gamma$ : [001] (av.)	39°	40°	41°	Fe	7.2	5.1	6.7
				Ca	42.7	45.1	46.6

5283 = clinopyroxenite (Kirikiripu).  
9207 = werhlite (Ramarama).

9182 = clinopyroxenite (Ngatutura).

Hamad (1963), and Yamaguchi (1964), and more varied than the chemically defined compositions of Ross *et al.* (1954). But optical properties may be affected by Al<sup>3+</sup>, Fe<sup>3+</sup>, and Ti<sup>4+</sup> (Deer *et al.*, 1963a); the three chemical analyses show that these elements are present in slightly higher concentrations than are usually encountered in igneous diopsides; Al<sup>3+</sup> in tetrahedral coordination could lower the optic axial angle, while Al<sup>3+</sup>, Ti<sup>4+</sup>, or Fe<sup>3+</sup> in octahedral coordination may increase refractive index and optic axial angle. Optical determinations are in agreement with the analysed composition for 5283, but 9182 and 9207 appear richer in iron and poorer in calcium than indicated by analysis.

#### *Conditions of pyroxene crystallization*

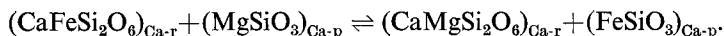
In the analyses of table V the aluminium content is sufficient to make the Z group 2.00 without adding titanium, the excess aluminium being added to the XY group.

The extent of substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in  $Z$  is comparable with clinopyroxenes analysed by Rose *et al.* (1954) and by Wilshire and Binns (1961), but is less than that described by Hamad (1963) in nodules from Derbyshire. According to Le Bas (1962) high load pressures during crystallization produce relatively small  $\text{Al}_z$  values and large  $\text{Al}_y$  values; low pressures should give the reverse. In this respect the evidence provided by the distribution of aluminium among tetrahedral and octahedral sites in the present analyses is somewhat inconclusive and is probably affected by the presence of significant quantities of  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  in the structural formula; in general the data do not support crystallization or recrystallization at unduly high pressures.

TABLE VI.  $K_p$  values for eight coexisting pyroxene pairs from the Auckland nodules  
Compositions determined chemically

	Clinopyroxene				Orthopyroxene			$K_p$
	Ca	Mg	$\text{Fe}^{2+}$	$\text{Fe}^{2+}/\text{Mg}$	Mg	$\text{Fe}^{2+}$	$\text{Fe}^{2+}/\text{Mg}$	
9156	45.4	49.1	5.5	0.112	89.2	10.8	0.121	1.1
9212	42.0	51.3	6.7	0.130	84.8	15.2	0.180	1.4
9200	42.8	52.5	4.7	0.090	90.3	9.7	0.107	1.2
9167	42.8	51.3	5.9	0.115	88.6	11.4	0.129	1.1
9279	41.2	50.3	8.5	0.169	84.5	15.5	0.184	1.1
5283	46.0	45.2	8.8	0.195	83.1	16.9	0.204	1.0
5289	42.1	50.8	7.1	0.140	85.2	14.8	0.174	1.2
9201	46.3	47.2	6.5	0.138	85.6	14.4	0.168	1.2

Studies of the magnesium/iron distribution between coexisting minerals of ultramafic nodules has been used as a measure of the temperature of crystallization for the ferromagnesian phases. Kretz (1961) and Bartholomé (1962) have examined this method on a thermodynamic basis with chemical equilibrium between calcium-rich (Ca-r) and calcium-poor (Ca-p) pyroxenes expressed as



Average values for an equilibrium constant,  $K_p(T)$ , of this reaction for igneous and metamorphic pyroxenes are respectively 1.4 and 1.8, and a  $K_p$  value of 1.6 occurs only rarely. The analyses of coexisting pyroxenes from nodules, as listed by Ross *et al.* (1954), give an average value of 1.2.

Ratios of  $\text{Fe}^{2+}:\text{Mg}$  in eight coexisting pyroxene pairs from Auckland nodules are given in table VI where the range in  $K_p$  from 1.0 to 1.4 has an average at 1.2. Since the equilibrium constant decreases with increasing temperature, the notably low figures for these nodule pyroxenes point to a higher temperature than that required by the  $K_p$  values for other pyroxenes of similar bulk composition and of known magmatic or metamorphic origin. From Bartholomé's (1962) approximation of a  $K_p$  versus temperature curve, the thermal environment would have been in the order of 1100–1400 °C.

O'Hara and Mercy (1963) and O'Hara (1964, 1967) have investigated the above method, concluding that the underlying assumption of ideal thermodynamic behaviour

of the pyroxene assemblages is invalid and that distribution of Mg and Fe<sup>2+</sup> are considerably affected by the presence of Ca and Al. O'Hara (1967) utilises the CaSiO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> contents of pyroxenes as a guide to the conditions of mineral formation. The two parameters suggested by him to provide the necessary pressure/temperature data for clinopyroxene are  $\alpha_c = 100 \times \text{CaSiO}_3 / (\text{CaSiO}_3 + \text{MgSiO}_3)$  and  $\beta_c = 100 \times \text{Al}_2\text{O}_3 / (\text{CaSiO}_3 + \text{MgSiO}_3 + \text{Al}_2\text{O}_3)$ , where CaSiO<sub>3</sub> = wt. % CaSiO<sub>3</sub> equivalent to all CaO; MgSiO<sub>3</sub> = wt. % MgSiO<sub>3</sub> equivalent to all MgO, MnO, NiO, and FeO; and Al<sub>2</sub>O<sub>3</sub> = wt. % Al<sub>2</sub>O<sub>3</sub> equivalent to all Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> less any amount equivalent to any Na<sub>2</sub>O or K<sub>2</sub>O present.

The analysed pyroxenes of table V give the following values:

$$5283: \alpha_c = 47.3, \beta_c = 5.5; 9182: \alpha_c = 48.1, \beta_c = 5.7;$$

$$9207: \alpha_c = 47.9, \beta_c = 6.4.$$

All these values are very similar and probably within the limits of error of the method. From O'Hara's provisional pressure/temperature projection for ultramafic mineral facies the Auckland pyroxenes would plot in the field of his spinel-lherzolite facies and close to or within the melting interval of his diagram corresponding to 10–13 kb pressure at 1200–50 °C. These values are comparable to those obtained by O'Hara (1967) from some nodule pyroxene analyses listed by Ross *et al.* (1954), Wilshire and Binns (1961), and Frechen (1963).

#### *Plagioclase feldspar*

Nodules in alkali olivine-basalt at Ngatutura Point contain anorthite feldspar, which is rare in the peridotite assemblages but abundant in gabbros and anorthitites. Chemical, X-ray, and optical determinations of composition have shown the feldspar to be notably richer in calcium than other plagioclases from similar gabbroic nodules recorded in the literature (Le Maitre, 1965). The plagioclase has two contrasted modes of occurrence. Large anhedral crystals typically form tight-packed interlocking textures and are usually clouded by inclusions, some of which appear to be fluid while others are minute rods and flecks of solid material often confined to limited areas of the host crystal. Smaller equidimensional unclouded polyhedra of the plagioclase are either interstitial to the larger grains or form distinct veins and pools within the fabric of the nodules. These smaller grains are very similar in appearance to recrystallized plagioclases described from Kerguelen by Talbot *et al.* (1963). Zoned crystals are absent, twins are common, and cleavage is well developed in most individuals. Twin types encountered in the anorthite-rich nodules include Carlsbad (rare), albite-Carlsbad (frequent), ?albite-ala B (very rare), albite (abundant), pericline (frequent), and ?acine (rare). The three latter twin laws are most common in igneous rocks while Carlsbad and albite-Carlsbad are more characteristic of metamorphic rocks (Gorai, 1951; Turner, 1951) but in the Ngatutura examples there is a possibility of modification of twin type during recrystallization, as found by Subramaniam (1956) at Sittampundi.

Optical methods (Slemmons, 1962) gave preliminary estimates of composition in a number of nodules over a range from An<sub>71</sub> to An<sub>100</sub>, with common values at An<sub>97–8</sub>.

In individual nodules the tenor of anorthite content generally varied only slightly and there was no significant difference in composition between the larger cloudy grains and the smaller clear polyhedra. A pure sample of the feldspar was separated from an anorthitite nodule (9193); the analysis and optical properties are given in table VII.

The analysis with molecular percentages  $Ab_{2.8}An_{96.7}Or_{0.5}$  shows a slight deficiency of alumina and requires  $Fe^{3+}$  and  $Ti^{4+}$  to be added to the Z group summation to give

TABLE VII. *Analysis and structural formula and physical properties of anorthite 9193, Ngatutura Point. Analyst: K. A. Rodgers*

SiO <sub>2</sub>	43.97	Number of ions on basis of 32 oxygens		$\alpha$	1.575 ± 0.002
TiO <sub>2</sub>	0.02	Si	8.142	$\beta$	1.582 ± 0.002
Al <sub>2</sub> O <sub>3</sub>	35.90	Al	7.838	$\gamma$	1.587 ± 0.002
Fe <sub>2</sub> O <sub>3</sub>	0.15	Fe <sup>3+</sup>	0.021	Z =	16.00
FeO	0.04	Ti	0.002	Y =	3.99
MgO	0.02	Mg	0.006	2V <sub>y</sub> 101, 101, 101, 103, 102	
CaO	19.39	Fe <sup>2+</sup>	0.007	Dispersion $r < v$ weak	
Na <sub>2</sub> O	0.31	Na	0.111	Cleavage (001), (010) good,	
K <sub>2</sub> O	0.08	Ca	3.847	(110) poor	
H <sub>2</sub> O <sup>+</sup>	0.14	K	0.019	Twinning Albite, Pericline,	
H <sub>2</sub> O <sup>-</sup>	0.01			? Baveno, Carlsbad,	
Total	100.03			Carlsbad-Albite,	
				Acline, ?Albite-Ala	
				Density	2.754g/cm <sup>3</sup>

the theoretical 16 ions. Deer *et al.* (1963b) suggest that amounts of  $Fe^{2+}$  and  $Mg^{2+}$  in anorthite analyses could be substituting for  $Ca^{2+}$  in the lattice but these ions would have to be in an unstable eight-fold coordination to satisfy the demands of electrical stability. More likely, in the present case, they arise from dust-like impurities in the larger grains, possibly diopside or spinel; 0.02 % MgO would be equivalent to about 0.1 % of diopside. No discrete grains of impurities were observed in the analysed fraction nor could diopside and spinel reflections be detected in a diffractograph of the same sample. Compared with other analyses of calcic feldspars water is low, but Deer *et al.* (1963b) point out that appreciable  $H_2O^+$  in anorthite must be adsorbed along cleavages as there is insufficient room within the lattice itself. Also many of the existing analyses come from pegmatitic and massive feldspars, which probably contain liquid inclusions. The optical properties obtained for this analysed sample give an anorthite content of  $An_{96-8}$  in good agreement with the chemical determinations and are comparable with published data on similar calcium-rich feldspars. Optical methods indicate the presence of rare, less calcic crystals in some nodules ( $An_{96}$  in 9190;  $An_{71}$  in 9177) and in addition support a maximum compositional variation of  $An_5$  in the most calcic feldspar assemblages, possibly a result of chemical inhomogeneities developed during recrystallization.

X-ray diffraction examination of the analysed sample 9193 confirms the highly calcic nature of the plagioclase; the most diagnostic reflections agree well with data listed by Goodyear and Duffin (1954, 1955) and by Smith and Gay (1958). For example:

$$2\theta = 2\theta(220) - 2\theta(1\bar{3}2) = 0.815 = An_{95} \text{ (Goodyear and Duffin, 1955);}$$

$$2\theta' = 2\theta(132) + 2\theta(220) - 4\theta(1\bar{3}2) = 1.474 = An_{94} \text{ (Smith and Gay, 1958);}$$

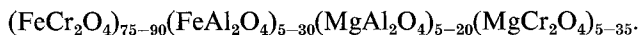
$$2\theta'' = 2\theta(1\bar{1}2) - 2\theta(\bar{2}02) = 0.730 = An_{97} \text{ (Smith and Gay, 1958).}$$

Some of the X-ray data also suggests that the anorthite possesses a lattice with high-temperature characteristics. This is supported by the value of the optic axial angles from a number of grains, which have an average value of  $2V_g = 100^\circ$ . Powder diffraction data does not allow unequivocal identification of the structural state in feldspars more calcic than  $An_{90}$  and the variety of twin laws made single crystal photographs difficult to interpret but several lines of evidence suggest that the Ngatutura plagioclase has a lattice of primitive anorthite type transitional towards a body-centred structure:  $2\theta'' = 0.730$  for a composition of  $An_{96.7}$  (Smith and Gay, 1958); type  $c$ -reflections ( $h+k$  even,  $l$  odd) are diffuse, although definitely present (Gay, 1953; Gay and Taylor, 1953; Laves and Goldsmith, 1954, *a, b, c*); and the  $1\bar{3}2$  reflection has a spacing of  $3.04 \text{ \AA}$  while two  $ms$  reflections at  $2.50$  and  $2.52 \text{ \AA}$  have a separation of  $0.023 \text{ \AA}$  (Goodyear and Duffin, 1954).

### *Spinel*

Within the Auckland nodules, members of the spinel group are ubiquitous accessories but never form more than 5% of the rock modes. Despite a wide range of spinels, some general patterns of occurrence seem clear: chromite is confined to dunites, picotite appears in a variety of rock types but is notably rare in pyroxenites, and hercynite was found only in a feldspar-rich gabbroic nodule. Identifications were made from refractive index and density and were confirmed by semi-quantitative microchemical tests for chromium, iron, aluminium, and magnesium.

In dunite nodules (4387, 8770, 9150, 9196, 9206, 9214) the characteristic spinel is opaque to reddish-brown chromite with  $n = 2.07\text{--}2.11$  and  $D = 4.82\text{--}4.95$ . The composition appeared to vary in the range



Picotite occurs in lherzolite (5290, 9163, 9242), harzburgite (7890, 9153, 9171), and dunite (9158) with  $n = 1.85\text{--}1.98$  and  $D = 4.20\text{--}4.61$ . Iron-rich ceylonite in feldspathic gabbro (9193), wehrlite (5303), and harzburgite (9171) has  $n = 1.80\text{--}1.83$  and  $D = 3.93\text{--}4.03$ . Hercynite in green octahedra was separately identified in gabbro (9193) and confirmed by X-ray diffractometry. Black and Brothers (1965) recorded granular magnetite with picotite in a nodule (7880) from the Arapohue locality.

### *Conclusions*

In the literature, data accumulating on ultramafic nodules suggests that their mineral assemblages crystallized or recrystallized at elevated temperatures and moderate to high pressures. In the Auckland examples high temperatures are indicated by the composition of individual and coexisting pyroxenes, and by the lattice characteristics of anorthite. Moderate, but definitely not high, pressures are favoured by O'Hara's pyroxene parameters, the percentage of aluminium in tetrahedral positions, and the filling density of carbon dioxide inclusions in olivine. A temperature/pressure environment of  $1250^\circ\text{C}$  at 11 kb appears most likely for element partitioning in the Auckland nodules. These conditions may be found within the melting interval of anhydrous basaltic magmas in the uppermost mantle, according to O'Hara (1967).

Petrofabric and textural evidence for either cognate or xenolithic origin of these nodules is discussed by Brothers and Rodgers (in press).

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