

Chrome-spinels from the Massif du Sud, southern New Caledonia

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SUMMARY. Approximately forty, variously shaped, chromitite bodies occur in dunites and harzburgites of the alpine-type peridotite complex of southern New Caledonia. The chromitites consist of picrochromite (59 to 42 % Cr_2O_3) and serpentized olivine (Fo_{96-92}) and display a variety of textures (massive, disseminated, and orbicular) consistent with a magmatic cumulate origin. Dunites contain olivine (Fo_{93-87}) and 1 to 3 % picrochromite (50 to 39 % Cr_2O_3). Harzburgites have less than 1 % spinel, ranging from picrochromite to ceylonite (45 to 28 % Cr_2O_3) and often forming symplectic intergrowths with bronzite. Temperatures of crystallization of the cumulate picrochromites are believed to have been about 1200 °C while the more aluminous symplectic spinels equilibrated under different conditions and may reflect a late stage recrystallization episode.

THE New Caledonian ultramafic belt is an alpine-type, peridotite-gabbro-granodiorite complex, which outcrops over the entire 500 km length of the archipelago as a series of spectacular, upstanding massifs and covers some 41 % of the islands' surface of 17 130 km². The southern portion of the largest, the Massif du Sud, consists predominantly of partially serpentized harzburgite containing a cumulate dunite and eucrite core and intruded by felsic plutons. Chrome-rich spinels occur both as accessory minerals throughout the peridotites and also as podiform aggregations often of economic importance. Over forty such chromitite deposits have been exploited in southern New Caledonia from the Pirogues Valley and its environs where they are largely confined to the dunites of the core and the harzburgites of the south-western edge of the massif (fig. 1). Other swarms of chromitite pods have been noted further north at Tontouta, Montagne des Sources, Pourina-Ouina (Maurejol and Cochet, 1958) and from the Tiegbahi dome, described in detail by Routhier (1963).

Geological relationships

Most of the southern chromitite occurrences were totally worked out prior to 1939 and geological relationships are now poorly preserved. Several accounts of a few mines exist (Maxwell, 1949; Stanton, 1958; Maurejol and Cochet, 1958; Toni, 1965) that enable the basic internal and external relationships of the chromitite bodies to be established.

Nearly all chromitite bodies are associated with dunite gangue, which in the immediate vicinity of the ore is markedly more serpentized than the typical peridotite of the region. The transition from pale yellowish green, sometimes sheared gangue to dark-green country peridotite is often sharply defined, e.g. La Coulée, and on other

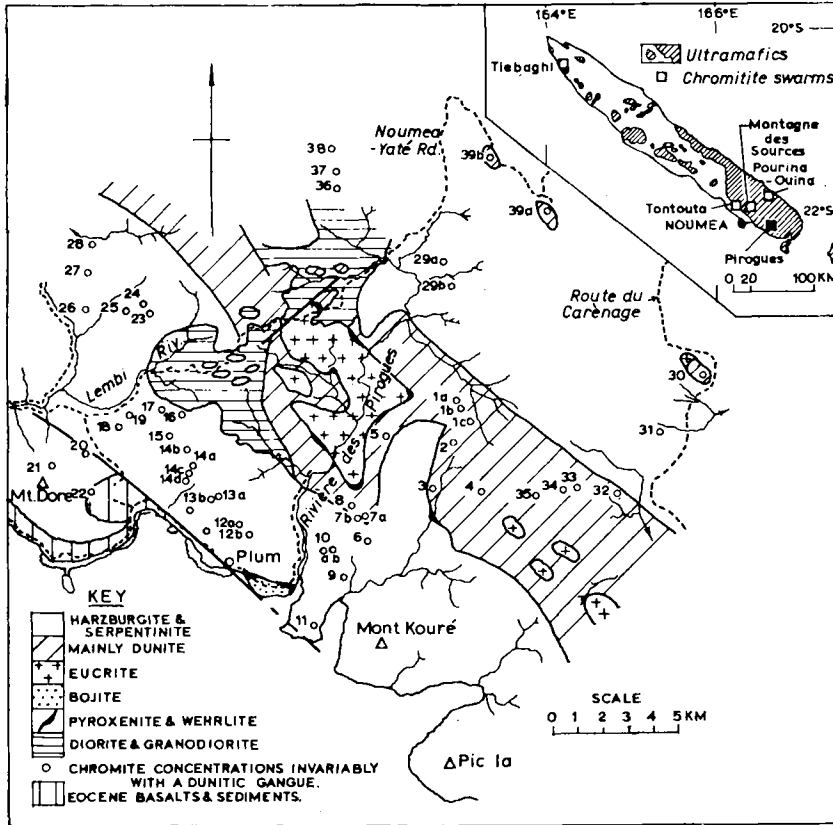


FIG. 1. Petrological sketch map of Pirogues Valley and environs showing location of chromitite deposits. *Inset*: Map of New Caledonia showing ultramafic belt and location of some of the major chromitite swarms.

Permit and concession names corresponding to numbers on the map.

1 a, b, c	Alice-Louise	14 a, b, c, d	Lucky hitt	27	Ste-Thérèse 6
2	Georges Pile	15	Nelly Redon	28	Ste-Thérèse 6 ext.
3	14 Juillet	16	Chrome rouge	29	a, b Elisabeth
4	Mary ext. 2	17	Trafalgar	30	Anna-Madeleine
5	Bien sûr	18	Bel espoir	31	Retouchée Rédon
6	Aiglon	19	Valérie	32	H.F.V. 1
7 a, b	Consolation	20	Coulée ext.	33	La Tchaux
8	Vivian	21	Napoléon	34	Bonne Veine
9	Emouchet	22	St-Brisson	35	Baba 20
10 a, b	Peut-être	23	G.R. 2H	36, 37, 38	Bon secours ext. 1-2
11	Bataille de Verdun ext. 13	24	Coco 9	39 a, b	Marais Kiki
12 a, b	Bataille de Verdun ext. 1	25	G2. HR	40	Moisde Mai
13 b	Quintonine ext.	26	Olympia	41	Ernoule

occasions gradational, e.g. La Constellation, Ste-Thérèse 6. There is no evidence of a discontinuity, such as an intrusive contact or vein wall at the margins of the chromitite bodies. Serpentine fibre veins lace all the masses, cutting across contacts, earlier chrysotile fibre-networks and pyroxenite veins.

The serpentized nature of the gangue appears directly attributable to shearing, faults and fracture zones being commonly associated with the ore bodies. Most of the faults strike NW.-SE. and are vertical or sub-vertical reverse faults. Often the body or bodies of ore parallel the direction of shearing or the fault plane, e.g. La Coulée, Georges Pile. On other occasions direction of orientation of the ore body cuts sharply across exposed faults, e.g. Anna Madeleine, where faults strike 306° and ore bodies strike 40° .

The shape and nature of ore bodies is quite variable even within one mine. Generally, tabular lenses, irregular pencils or combinations of these two represent the basic form. At La Coulée chromitites occur as discrete thin lenses, small (1 to 3 m) chunky blocks and larger sack-form masses set in a matrix of disseminated olivine-chromitite ore.

La Constellation appears to provide an example of what Thayer (1960) describes as a lineate schlieren chromite body. The boundaries of podiform bodies may be well defined (Mois de Mai) or diffuse (La Coulée). The borders are generally marked by small irregularities fraying out from high to low grade ore (Anna Madeleine).

Dykes are intimately associated with many of the ore masses. Pyroxenites are the most common, intruding both ore body and country rock, e.g. Anna Madeleine, La Coulée, Bien Sûr. In contact with the serpentized dunite they are altered to bastite, suggesting emplacement prior to serpentization, while Maxwell (1949) has described reaction effects between the pyroxene of the dykes and the chrome spinel of the ore body. Eucrites and other pyroxene gabbros are less common but again post-date formation of the ore, e.g. Mois de Mai, Bataille de Verdun. Hornblende gabbros and hornblendites are rare, e.g. Mois de Mai, Bien Sûr. Coarse mica-bearing granodioritic rocks (the granites of Maurejol and Cochet, 1958) are widespread throughout the mines of the Pirogues Valley, e.g. Bien Sûr, Georges Pile, but are absent from chromite deposits outside this region. They post-date all other rocks and are usually along former faults and fracture zones. Invariably they occur at the base of the ore bodies.

PETROGRAPHY

The majority of the individual rock types of the Massif du Sud are characterized by uniformity of texture, grain size, modal and chemical composition. All ultramafic and mafic members show some degree of deformation and recrystallization.

Peridotites

The dominant harzburgites consist of olivine, Fo_{87-92} (c. 85 %), orthopyroxene, En_{89-92} (c. 15 %) and chrome-spinel (< 1 %). The original, possibly hypautomorphic-granular texture is now largely obscured by alteration to chrysotile plus lizardite, which affects at least 20 % of an individual specimen. Deformation and recrystallization appear more pronounced in these rocks than in the dunites, which also lack orthopyroxene and contain a greater proportion of the chrome-spinel (1 to 3 %).

In dunite the spinel is a picrochromite. Crystals range over 0.01-2 mm dia. and may be euhedral, polygonal, or show irregular, skeletal shapes. Symplectic intergrowths of bronzite and spinel occur in rare sections. Often, in this association, partially serpen-

tinized bronzite poikolitically encloses an embayed and corroded spinel core and is itself partially or completely surrounded by a thin rind of spinel. In harzburgites the majority of grains are irregular, either conforming to the shape of intergranular spaces or frequently forming symplectic intergrowths with bronzite (fig. 2*a*). The compositional range extends from picrochromite to ceylonite.

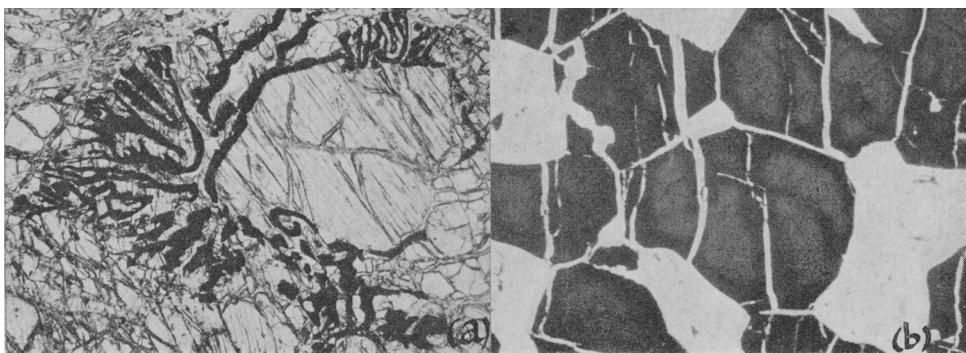


FIG. 2*a*, left: Symplectic intergrowth of bronzite and ceylonite about bronzite core in serpentinized harzburgite; $\times 32$, transmitted light. *b*, right: Subhedral picrochromite grains in disseminated chromitite, Mine Marais Kiki, showing dark opaque borders and cross cutting lines; $\times 50$, transmitted light. Photograph has been deliberately over exposed and underdeveloped to bring out borders.

Chromitites

The chromitite bodies contain more than 25 % picrochromite with olivine and serpentine as their only other major constituents. In thin section, serpentine fibre veins, rather than olivine, are in direct contact with the chrome-spinel grains and a serpentine mesh structure pervades the majority of samples examined. Accessory minerals include faint dustings of hematite and limonitic iron oxides, rare magnetite, periclase, and brucite. The last two occasionally occur as minute inclusions (< 0.01 mm) within the chromite. Secondary clay minerals are common and are generally magnesium-rich montmorillonites.

A variety of textural types are displayed within and between the various chromitite bodies. The terminology used here is that of Cheng (1965):

Massive homogeneous ore, commonly forming irregular, sack-form masses, is transitional from either disseminated ore (e.g. Ernoule, Marais Kiki) or orbicular ore (e.g. Anna Madeleine). Veins of serpentinized olivine or pyroxene lace the mass; grain size varies but often exceeds 10 mm.

Homogeneous disseminated textures, ranging from dense dissemination through to mineralized dunite, are as common as the massive variety (e.g. La Coulée, Marais Kiki). Chrome-spinel grains, usually less than 1 mm across, may be separate or in aggregates of two to five crystals (fig. 3*a*).

Orbicular and anti-orbicular textures are less common and consist of rounded ellipsoidal masses of chrome-spinel (or olivine) of varying size set in a ring-like mesh of serpentinized olivine (or chrome-spinel) (fig. 3*b*). This texture appears transitional

between massive and disseminated ore at Anna Madeleine but predominates at Georges Pile. Grain size is generally less than 5 mm. Rare examples of *stain-spotted texture* (Bataille de Verdun, Georges Pile), *micro-reticulated and reticulated ring structures* (Anna Madeleine), and *banded texture* (La Constellation) were observed.

These textures are generally regarded as being of magmatic cumulate origin (Sokolov, 1958; Cheng, 1965; Pavlov and Chuprykina, 1967), although orbicular and anti-orbicular textures have been explained by solidification of gels, remelting of massive ore, immiscibility, and assimilation. In New Caledonia orbicular texture appears to

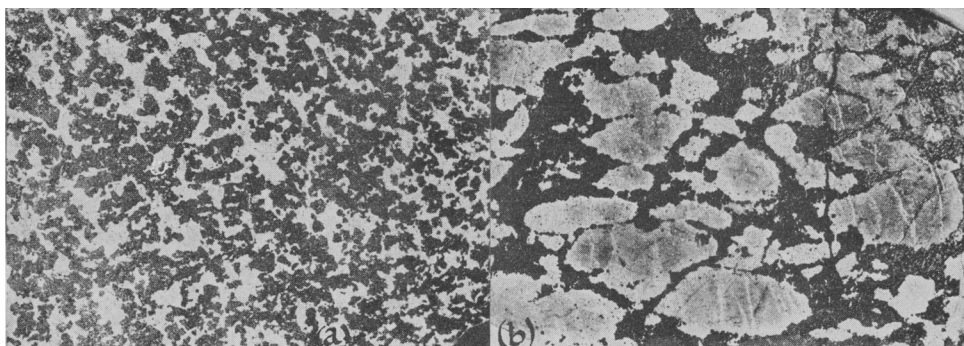


Fig. 3a, left: Disseminated chromitite, Mine Marais Kiki, showing multicrystal aggregate nature of spinel clots. Polished slab, $\times \frac{2}{3}$. b, right: Anti-orbicular chromitite, Anna Madeleine. The outlines of the large olivine crystals (up to 1 cm dia.) that comprise the nodular forms are totally obscured by γ -chrysotile fibres. Note possible surface tension effects. Polished slab, $\times \frac{2}{3}$.

be an extension of the ring structures with which it is always associated, as at Anna Madeleine, and is regarded here as resulting from a phase of increased precipitation from the melt whereby a number of olivine crystals became trapped among an expanding chrome-spinel mesh.

Occasionally, massive and orbicular ores show pull-apart texture (Thayer, 1946). Chrome-spinel in a few of the more massive ores shows almost perfect parting on $\{111\}$, while remnant olivines in some serpentized gangues show signs of recrystallization.

Automorphism is most common among the disseminated ores with the number of crystals showing anhedral habits increasing as the modal percent of chromite increases. In the massive, anti-orbicular, transitional, and reticulated ring ores few straight crystal boundaries can be seen. The manner of development of the numerous curved surfaces that bound spinel aggregates has been described by Sokolov (1958) and implies contemporaneous crystallization of spinel and gangue.

In New Caledonia tiny inclusions of 'fresh' olivine (< 0.01 mm) are not uncommon in the chromites whereas chrome-spinel other than in the finest, opaque, dust-like particles was never observed in olivine. Occasionally, the olivine inclusions show pronounced euhedral habit with dome and pinacoid forms, implying that some fraction of the olivine had commenced to crystallize before the spinel.

MINERALOGY

Olivine. Optical ($2V_\gamma$ and β), X-ray (d_{130}), and chemical determinations of olivines show a compositional range from Fe_{92-96} in chromitites, through Fe_{87-93} in dunite and harzburgite, to Fe_{78-89} in eucrite where olivine is subordinate and chrome-spinel is rare. Representative analyses of olivine from each of the major spinel-bearing rock types are given in Table I.

TABLE I. *Representative analyses and structural formulae of olivines coexisting with chrome spinels in the peridotites of southern New Caledonia. Analyst: K. A. Rodgers*

	1	2	3		1	2	3
				<i>No. of ions on basis of 4 oxygens</i>			
SiO ₂	40.20	40.60	41.08	Si	0.987	0.985	1.001
TiO ₂	0.01	0.02	0.01	Al	0.003	0.010	0.010
Al ₂ O ₃	0.11	0.37	0.35	Fe ³⁺	0.011	0.010	0.013
Cr ₂ O ₃	0.02	0.02	0.03	Fe ²⁺	0.152	0.110	0.161
Fe ₂ O ₃	0.61	0.55	0.72	Ni	0.007	0.008	0.009
FeO	7.40	5.40	7.90	Mn	0.002	0.002	0.002
NiO	0.35	0.41	0.46	Mg	1.846	1.879	1.789
MnO	0.08	0.09	0.11	<i>Atomic ratios</i>			
MgO	50.51	51.96	49.26	Mg ²⁺	92.4	94.5	91.7
CaO	0.01	n.f.	n.f.	Fe ²⁺	7.6	5.5	8.3
Na ₂ O	n.f.	n.f.	n.f.	<i>Physical properties</i>			
H ₂ O ⁺	0.42	0.21	0.31	α	1.649	1.645	1.649
H ₂ O ⁻	0.48	0.42	0.23	β	1.663	1.661	1.666
Total	100.20	100.05	99.97	γ	1.688	1.683	1.684
				$2V_\gamma$ (av.)	89°	86°	90°
				<i>D</i>	3.26	3.25	3.25

1. Dunite, 20001, Pirogues Valley.

2. Anti-orbicular chromitite, 20014, Mine Anna Madeleine.

3. Harzburgite, 20000, with symplectic spinel, Fausse Yate.

n.f. = not found.

Sample numbers referred to in this and other tables are those of Geology Department, University of Auckland, petrology collection.

Serpentine minerals. Within the chromitites and dunites γ -serpentine forms a network of longitudinally divided cross fibre veins lacing the olivine. Olivine fragments within the network are replaced by isotropic fibrous mats of α - and γ -serpentine. Solution studies and X-ray examination indicate that α - and γ -serpentine fibre veins and fibrous mats consist of chrysotile with possibly a little intergrown lizardite; the serpentine platelets are almost entirely lizardite.

Chrome-spinel. Picrochromite occurs as both opaque and translucent grains in thin section. Disseminated ores are generally black or deep red-brown but the other textural variants display a range of colours from deep red-brown through cherry red, medium red, light brownish red to pale orange and even lemon yellow, suggesting a variation in chromium content (Stanton, 1958).

The majority of chrome-spinel grains in 0.04–0.03 mm sections show dark opaque borders, 0.05–0.08 mm wide, and similar cross cutting lines, 0.02–0.1 mm wide (fig. 2*b*), but these features are not always present, e.g. in the massive ore of Mine Bien Sûr (cf. Stanton, 1958). The contacts between translucent and opaque portions of a grain are always transitional, while the borders are rarely discontinuous as in some sections from Anna Madeleine. In very thin sections, grains show translucent borders, which stand out as haloes of slightly deeper colour than that of the rest of the crystal, e.g. a red border around an amber core. For sections of constant thickness there is some variation in translucency, border width, and chrome-spinel colour from one ore body to another but a fair consistency within each. In sections thicker than about 0.5 mm, all grains appear opaque, but measurements failed to show the variation in reflectivity corresponding to opacity that usually occurs where the border is due to an iron-rich zonal overgrowth (cf. Panagos and Ottemann, 1966).

Electron microprobe scans and spot counts were made of twelve samples from a variety of textural settings, ore bodies, and colour variants. No chemical distribution of Cr, Mg, Fe, Al, Si, Ti, or Mn was observed that might account for the differential opacity of the grain borders.

Chrome-spinel composition. Measurement of unit-cell edge, by extrapolation, and refractive index, by immersion, of a number of chrome-spinel concentrates from the chromitites indicate an approximate range of Cr_2O_3 content from 59 to 42 % (a 8.324–8.242; n 2.01–1.94); concentrates from the dunites showed a range of 50 to 39 % Cr_2O_3 (a 8.280–8.227; n 2.03–1.94) and the harzburgites from 45 to 28 % (a 8.228 to 8.195; n 1.96–1.91).

Results of eight new analyses of southern New Caledonian chrome-spinels are given in Table II together with their physical properties and a compilation of existing data. A small degree of inhomogeneity within some of the concentrates is suggested by the splitting of various diffractometer reflections and differences in magnetic susceptibility of fractions of individual concentrates, e.g. the anti-orbicular ore (20014) from Anna Madeleine showed a series of strong reflections that could be related to a 8.268 cell edge and a series of weak, but distinct, reflections corresponding to a 8.246 cell edge.

The problems in obtaining precise analytical results for this mineral group have been discussed by Irvine (1965) and Rodgers (1972) and are well illustrated by the current group of analyses. With the exception of Glasser's (1904) analysis (no. 15) all earlier data are incomplete and total iron given as FeO. The structural formulae, based on 32(O), for these incomplete analyses were calculated to bring RO/R_2O_3 to unity, if possible, by distributing total iron among FeO and Fe_2O_3 , after removing SiO_2 and TiO_2 as $2\text{MgO} \cdot \text{SiO}_2$ and $\text{FeO} \cdot \text{TiO}_2$. Analysis 9 is still unsatisfactory after oxidizing all the iron. Analyses 10 and 11 show a deficiency of magnesia as a result of satisfying SiO_2 . Analysis 12 is the most satisfactory of a series of 26 analyses presented by Koch (1958) and Maurejol and Cochet (1958). Many of these show higher silicas or lower totals. Analyses 13 and 14 are the only two published analyses from the Tiebaghi dome, the largest spinel ore body in New Caledonia. Analysis 15 is the only existing complete

spinel analysis but is from an unspecified locality and displays a somewhat unusual composition, being richer in Cr_2O_3 and poorer in Al_2O_3 than any other. Analyses 15, 18 to 21, and 23, and 24 are from a series of microprobe analyses cited by Guillon (1970) and recalculated here as weight percent oxides. Most are non-stoichiometric, have low totals, and differ from the other analyses in having lower Mg/Fe^{2+} ratios (fig. 4).

Non-stoichiometric ratios of $R_2\text{O}_3$ and RO are not always the result of poor analysis. A slight excess of $R_2\text{O}_3$ over RO can result from secondary alteration of the spinels by oxidation. An excess of RO over $R_2\text{O}_3$ can be brought about by the presence of inclusions such as periclase and brucite within the ore. However, departure from the model formula is usually due to an excess of either Fe^{2+} or Fe^{3+} . The iron ratio is probably the major source of error in analysis and the factor most affected by secondary alteration. Addition of TiO_2 to the $R_2\text{O}_3$ group does not improve the stoichiometry to any extent. Irvine (1965, p. 649) found that Ti ions often enhanced an imbalance in R^{3+} . Departures of spinel itself from the ideal formulae are negligible and the presence of cation-deficient structures are not detectable by current analytical methods.

In the terminology of Simpson (1921) the dunite and most chromitite spinel analyses are those of picrochromites, subspecies chrome-picotites. The analysed harzburgite spinel is spinel (*s.s.*) subspecies ceylonite.

The compositional data are plotted in fig. 4, which represents two sides of the spinel compositional prism most pertinent to the current study. Both the $\text{Cr}/(\text{Cr}+\text{Al})$ and $\text{Fe}^{3+}/(\text{Cr}+\text{Al}+\text{Fe}^{3+})$ ratios of the New Caledonian picrochromites are comparable to those recorded from the majority of stratiform, zoned, and alpine-type bodies but, except for the data of Guillon (1970), the high Mg/Fe^{2+} values are more typical of spinels from alpine-type associations. The $\text{Cr} \rightleftharpoons \text{Al}$ exchange exceeds the $\text{Fe}^{2+} \rightleftharpoons \text{Mg}$ substitution by about 3:1, as is invariably found in alpine-type complexes (Thayer, 1946, 1960; Irvine, 1967). Of the stratiform bodies only the magnesium-rich portions of the Great Dyke, Stillwater, and Bushveld Complexes have spinels that show comparable atomic ratios to those in fig. 4 (cf. Irvine, 1967).

Conditions of spinel crystallization

Irvine (1965) calculated a series of 'equipotential surfaces' within the spinel prism, which represent possible equilibrium spinel-olivine assemblages for given pressures and temperatures, and which can be contoured according to small differences in olivine composition. Plots of New Caledonian/chrome-spinels (fig. 5) show reasonable conformity with the traces of Irvine's theoretical surfaces for the more reliable analyses of Table II. Loney *et al.* (1971) found that chrome-spinels from Burro Mountain could be contoured similarly and used this behaviour to support their conclusion that the majority of their olivine-spinel pairs had equilibrated under a similar range of conditions.

Comparison of fig. 4a and fig. 5 shows that the field of alpine-type chrome spinels occupies a narrow area within Irvine's (1965) diagram where little iron enrichment of coexisting minerals occurs (cf. Irvine, 1965, Fig. 9; Loney *et al.* 1971, Fig. 40). At the same time, the field trends roughly parallel to the equipotential surfaces. It could

TABLE II. *Analyses and structural formulae of chrome*

	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	0·76	0·50	0·42	0·32	0·72	0·82	—	—	—	6·68	5·52	1·20
TiO ₂	0·10	0·06	0·09	0·11	0·10	0·05	—	0·26	—	—	—	—
Cr ₂ O ₃	50·79	51·01	49·74	55·56	48·35	53·81	66·54	51·98	45·30	45·52	48·03	54·60
Al ₂ O ₃	16·64	17·40	18·78	14·78	18·78	15·34	4·51	19·14	10·30	13·72	13·54	13·80
Fe ₂ O ₃	3·00	2·89	3·22	1·95	2·99	2·10	—	—	—	—	—	—
MgO	13·43	13·26	11·86	12·13	15·95	13·67	10·85*	14·36*	12·67*	11·68*	12·24*	13·25*
MnO	14·30	14·51	15·05	14·70	12·95	14·27	15·03	13·45	20·27	19·42	18·11	15·21
CaO	0·15	0·11	0·09	0·09	0·14	0·12	—	0·45	—	—	—	—
H ₂ O	0·47	0·29	0·61	0·46	0·18	0·28	3·54	0·79	—	—	—	—
Total	99·64	100·03	99·86	100·10	100·16	100·46	100·47	100·42	88·54	97·02	97·44	98·06
<i>Structural formula on basis of 32 oxygen:</i>												
Cr	10·351	10·215	9·880	11·187	9·772	10·940	14·123	10·283	9·712	11·157	11·346	11·412
Al	5·056	5·198	5·562	4·438	5·660	4·651	1·426	5·648	3·292	4·997	4·770	4·302
Fe ³⁺	0·582	0·551	0·610	0·373	0·574	0·405	0·452	0·069	2·868	—	—	0·287
Fe ²⁺	2·877	2·800	2·476	2·562	3·393	2·931	1·984	2·889	—	3·018	3·060	2·642
Mg	5·104	5·227	5·425	5·418	4·566	5·048	6·014	5·016	8·192	4·812	4·766	5·357
Mn	0·032	0·023	0·020	0·020	0·031	0·026	—	0·095	—	—	—	—
R ³⁺	15·99	15·96	16·05	16·00	16·01	16·00	16·00	15·87	16·15	16·12	16·12	16·00
R ²⁺	8·01	8·05	7·92	8·00	7·99	8·00	8·00	8·00	8·19	7·83	7·83	8·00
2R ²⁺ /R ³⁺	1·00	1·01	0·99	1·00	1·00	1·00	1·00	1·00	1·03	0·97	0·97	1·00
% Cr	34·75	34·90	34·03	38·02	33·08	36·82	45·53	35·57	31·00	31·15	32·86	37·36
% Fe	12·54	12·35	11·40	10·80	14·49	12·09	8·43	11·16	9·85	9·08	9·51	10·30
<i>Physical properties</i>												
n (av)	1·94	1·96	1·95	1·99	1·96	1·96	—	—	—	—	—	—
n _D , Å	8·246	8·264	8·268	8·289	8·257	8·281	—	—	—	—	—	—
D ₄	4·39	4·49	4·45	4·62	4·45	4·50	—	—	—	—	—	—
X _{Mg} ^{ol} , §	0·938	0·948	0·945	0·956	0·921	0·943	—	—	—	—	—	—

* Total iron as FeO

† Determined by extrapolation; Å ± 0·006

‡ Density of concentrate; ± 0·03

§ Cation fraction of magnesium in coexisting olivine from wet chemistry or microprobe

1. Massive ore 20017.
2. Disseminated ore 20016, } Mine Anna Madeleine, Plaine des Lacs. Anal: K.A.R.
3. Anti-orbicular ore 20014 }
4. Massive ore 20020, Mine Marais Kiki, Lac de Yaté. Anal: K.A.R.
5. Disseminated ore 20021, Mine Bien Sür, Pirogues Valley. Anal: K.A.R.
6. Banded ore 20015, Mine La Constellation, Pirogues Valley. Anal: K.A.R.
7. Mine Anna Madeleine, Plaine des Lacs. Glasser (1904).
8. Mine Chromière, Pirogues Valley, Lacroix (1942), analysis 5. Anal: F. Raoult.
9. Mine Marais Kiki, Lac de Yaté. Koch (1958, p. 31).
10. Mine Lucky Hitt, Pirogues Valley, Maurejol and Cochet (1958).
11. Mine Henriette, Pirogues Valley, Maurejol and Cochet (1958).
12. Mine Canon, Tontouta, Koch (1958, p. 31).

be concluded that all alpine-type chrome spinels have equilibrated under similar conditions, but Gibb (1971) and others have shown that iron enrichment in both spinel and contemporaneously crystallizing silicates can be suppressed or even reversed over quite a wide temperature range by buffering the oxygen fugacity.

A further complication in the Mg-Fe²⁺ partitioning between spinel and coexisting magnesium silicates recognized by Irvine (1965) is the effect of trivalent cations, especially chromium and aluminium, which display a more or less complementary variation and greatly predominate over Fe³⁺ in the New Caledonian chrome-spinels.

Irvine (1965) found that the following relationship held: $\ln x_{Mg}^{ol} (1 - x_{Mg}^{sp}) / (1 - x_{Mg}^{ol})$
 $x_{Mg}^{sp} = y_{Cr}^{sp} \ln K_1 + C$, where x_{Mg}^{ol} and x_{Mg}^{sp} are the molar fractions of Mg in olivine

spinels from the ultramafic belt of southern New Caledonia

13	14	15	16	17	18	19	20	21	22	23	24	
—	0.80	—	—	1.56	—	—	—	—	0.31	—	—	SiO ₂
0.22	—	—	—	0.80	—	—	—	—	0.05	—	—	TiO ₂
62.48	55.50	68.00	48.17	38.99	52.64	49.15	46.03	42.93	29.89	56.42	57.56	Cr ₂ O ₃
10.38	11.00	3.00	16.99	25.47	16.42	20.94	23.21	27.53	34.89	15.69	11.83	Al ₂ O ₃
—	—	1.09	—	4.00	—	—	—	—	3.23	—	—	Fe ₂ O ₃
14.49*	16.20*	16.70	16.51*	12.80	18.76*	20.00*	20.69	20.58*	17.32	18.86*	19.49*	FeO
12.13	16.40	11.10	12.47	16.20	8.24	6.76	7.09	6.70	13.85	8.65	8.97	MgO
0.46	—	—	—	0.12	—	—	—	—	0.15	—	—	MnO
—	—	—	—	—	—	—	—	—	—	—	—	CaO
0.39	—	—	—	—	—	—	—	—	1.01	—	—	H ₂ O
100.65	99.90	99.89	94.14	99.94	96.06	96.85	97.02	97.74	100.70	99.62	97.45	Total
12.873	11.296	14.618	10.191	7.751	11.149	10.181	9.428	8.565	5.584	11.573	12.251	Cr
3.183	3.338	0.961	5.360	7.549	5.198	6.468	7.089	8.190	9.723	4.799	3.754	Al
—	1.364	0.222	0.595	0.755	—	—	—	—	0.574	—	—	Fe ³⁺
3.111	2.122	3.800	3.101	2.542	4.204	4.384	4.484	4.346	3.416	4.093	4.389	Fe ²⁺
4.703	5.899	4.500	4.974	5.286	3.291	2.639	2.737	2.521	4.731	3.345	3.600	Mg
0.102	—	—	—	0.086	—	—	—	—	0.030	—	—	Mn
16.06	16.00	15.80	16.15	16.05	16.35	16.65	16.52	16.75	15.88	16.37	16.00	R ³⁺
7.92	8.02	8.30	8.07	7.91	7.49	7.02	7.22	6.87	8.18	7.44	7.99	R ²⁺
0.99	1.00	1.05	1.00	0.96	0.92	0.84	0.87	0.82	1.03	0.91	1.00	2R ²⁺ /R ³⁺
42.75	37.98	46.53	32.96	26.67	36.02	33.62	31.50	29.38	20.45	38.61	39.39	% Cr
11.26	12.59	13.75	12.83	12.75	14.58	15.55	16.08	16.00	15.72	14.66	15.15	% Fe
—	—	—	—	1.94	—	—	—	—	1.93	—	—	<i>n</i> (av)
—	—	—	—	8.227	—	—	—	—	8.200	—	—	<i>a</i> t, Å
—	—	—	—	—	—	—	—	—	—	—	—	<i>D</i> †
—	—	—	—	0.924	0.908	0.889	0.904	0.877	0.917	0.917	0.930	X ^{ol} § Mg

- 13. Teibaghi dome, Lacroix (1942), analysis 4. Anal: F. Raoult.
- 14. Teibaghi massive ore, Koch (1958, p. 31).
- 15. Unspecified locality, Glasser (1904).
- 16. Mine Alice Louise, Plaine des Pirogues. Guillon (1970, analyses 5). ?Detrital chrome-spinel.
- 17. Dunite 20003, Yaté/Noumea Road. Anal: K.A.R.
- 18. Dunite, Riviere Odjioni, average of 3 analyses (Guillon, 1970, analysis 5).
- 19. Dunite with orthopyroxene, Montagne des Sources. Guillon (1970, analysis 6).
- 20. Dunite with plagioclase, clino- and ortho-pyroxene, Montagne des Sources (Guillon, 1970, analysis 7).
- 21. Olivine gabbro (?eucrite), Plaine des Pirogues (Guillon, 1970, analysis 8).
- 22. Harzburgite, 20000, Fausse Yaté. Symplectite chrome-spinel. Anal: K.A.R.
- 23. Harzburgite, Col du Dzumac (Guillon, 1970, analysis 1).
- 24. Dunite (from main harzburgite mass), Haute Couvelé (Guillon, 1970, analysis 2).

and spinel respectively, y_{Cr}^{SD} the molar fraction of Cr in spinel, K_1 the equilibrium constant for the reaction $MgCr_2O_4 + FeAl_2O_4 \rightleftharpoons FeCr_2O_4 + MgAl_2O_4$, and C a constant embodying reactions involving Fe^{3+} . A plot of the left-hand side of the above equation against y_{Cr}^{SD} should yield a straight line with a slope of $\ln K_1$. This is shown in fig. 6 where the majority of wet-analysed alpine-type spinels fit a line with a slope of 2.25 while spectrographic analyses of Mount Albert material (plotted by Irvine, 1965) fit a slope of 3.5. Regardless of the exact slope, K_1 has a magnitude of order 10 with a corresponding free energy of intercrystalline exchange, ΔG° , of about -10^4 cal mol⁻¹.

Jackson (1969) extended Irvine's (1965) arguments and derived the following

equation to allow temperatures of formation of coexisting olivine and spinel to be calculated: $T = (5580 y_{Cr}^{sp} + 1018 y_{Al}^{sp} - 1720 y_{Fe}^{sp}) / (0.90 y_{Cr}^{sp} + 2.56 y_{Al}^{sp} - 3.08 y_{Fe}^{sp} - 1.47 + 1.987 \ln K_2)$, where the temperature, T , is in $^{\circ}K$, y_{Cr}^{sp} , y_{Al}^{sp} , and y_{Fe}^{sp} are the molar fractions of Cr, Al, and Fe^{3+} respectively in the spinel, and K_2 is the ratio $x_{Mg}^{ol} (1 - x_{Mg}^{sp}) / (1 - x_{Mg}^{ol}) x_{Mg}^{sp}$. Temperatures calculated for analyses 1 to 6 of Table II

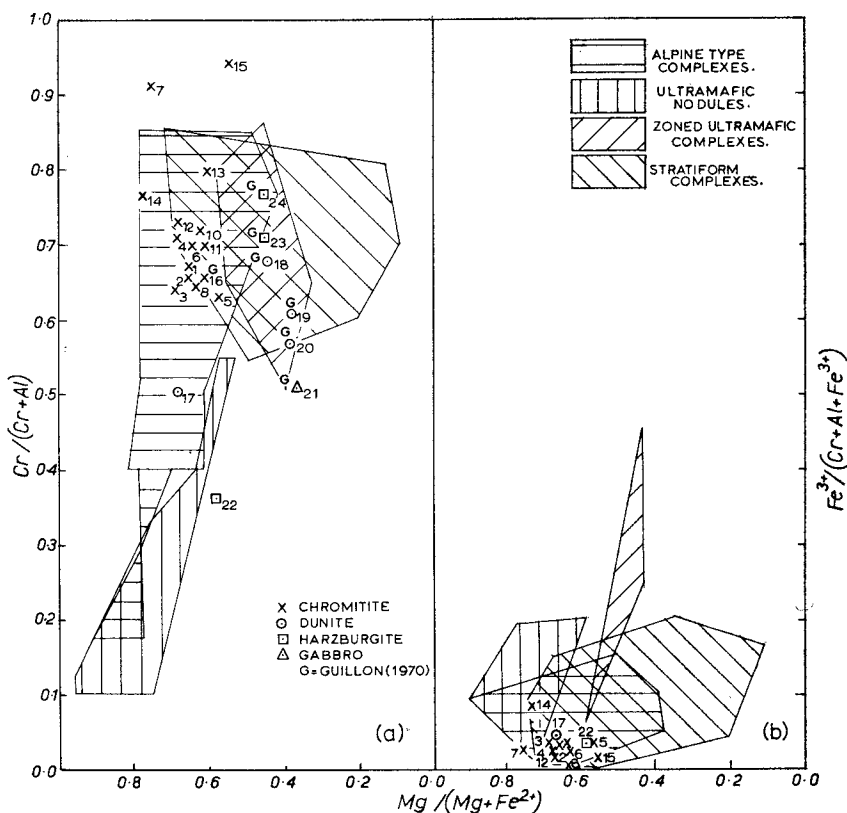
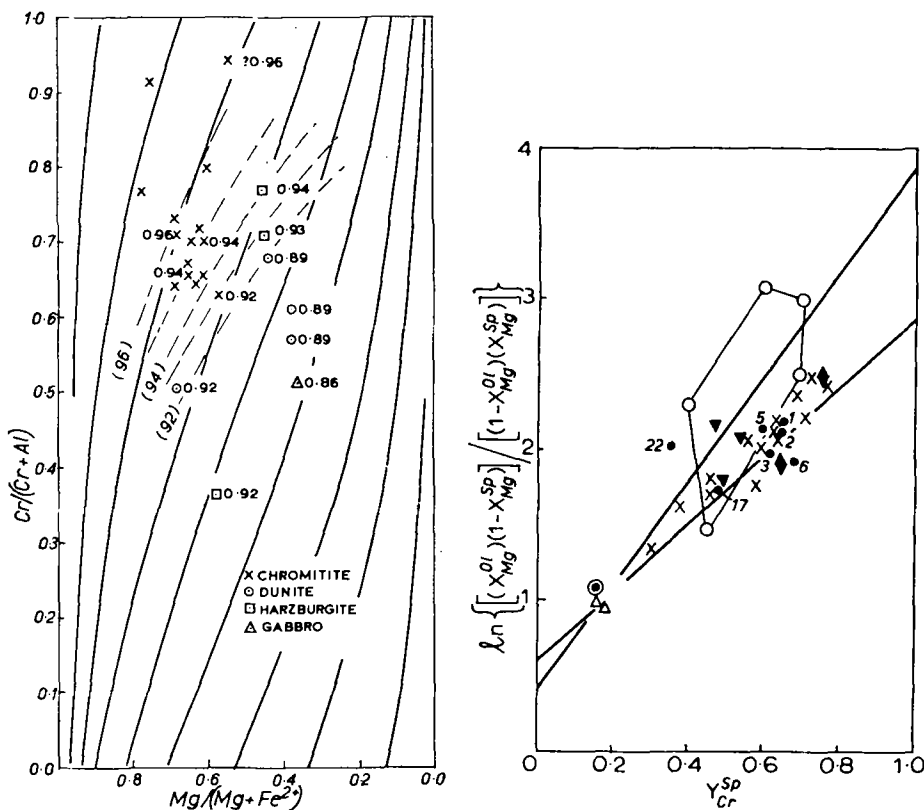


FIG. 4. Projection of analyses of New Caledonian chrome-spinels on two sides of the spinel compositional prism. The compositional fields from other peridotites are in part taken from data given by Irvine (1967). Numbers correspond to those given in Table III; G = analyses of Guillon (1970).

range from 1180 to 1300 $^{\circ}C$ and compare favourably with those calculated for the Burro Mountain spinels (1098 to 1335 $^{\circ}C$) of Loney *et al.* (1971). Dunites show a similar range of about 1000 to 1300 $^{\circ}C$. Guillon's (1970) harzburgites (analyses 23 and 24) calculate in excess of 1300 $^{\circ}C$ while the symplectite spinel (analysis 22) gives a value of 790 $^{\circ}C$. The olivine gabbro of Guillon (analysis 21) falls at 990 $^{\circ}C$. These values must not be regarded as absolute because errors of ± 300 $^{\circ}C$ may be involved (Jackson, 1969).

The effect of moderate pressure on K_2 is negligible (Irvine, 1965) and little can be concluded about the magnitude of the pressures involved during crystallization of the bulk of the New Caledonian chrome-spinels. However, if the figure of $790\text{ }^\circ\text{C} (\pm 300\text{ }^\circ\text{C})$,



FIGS. 5 and 6: FIG. 5 (left). Comparison of New Caledonian chrome-spinels contoured according to Fo content (dashed lines) with traces of theoretical equipotential surfaces of Irvine (1965) (solid lines). Numbers beside plot points correspond to the cation fractions of Mg in coexisting olivine. FIG. 6 (right). Plots of Mg-Fe²⁺ distribution coefficients against the cation fraction y_{Cr}^{Sp} for olivine and chrome-spinel pairs from alpine-type ultramafics (in part after Irvine 1965). Numbers correspond to those given in Table II. Δ Lizard (Green, 1964); \blacktriangledown Dun Mt., Red Hills (Challis, 1965); \blacklozenge Dunites (Ross *et al.*, 1954); \times Burro Mt. (Loney *et al.*, 1971); \circ - \circ Mt. Albert (Macgregor *et al.*, 1963, 1965); \odot Analysed spinel of Gibb (1971) equilibrated at $1332\text{ }^\circ\text{C}$; \bullet New Caledonia (this study).

deduced for the symplectic ceylonite, represents a true equilibration temperature then the corresponding pressure could not have exceeded $5.8 \times 10^8\text{ N.m}^{-2}$ (5.8 kb) if the symplectitic assemblage is to remain in the stability field of pyroxene+spinel (Tazaki *et al.*, 1972).

Discussion

Data accumulating on chrome-spinels from alpine-type environments generally favour a cumulative origin, which is supported here by the textural and chemical evidence presented from the dunites and chromitites.

Field and petrographic studies of Guillon (1969) and Rodgers (1972) imply that if all the major rock types of the Massif du Sud crystallized from an igneous melt they did so in the sequence harzburgite, dunite+chromitite, wehrlite, eucrite. Relationships between harzburgite and dunite are ambiguous although a magmatic gradation from dunite to eucrite via wehrlite is recognized.

The nominal values of temperature of formation of most of the New Caledonian chrome-spinel-olivine pairs, deduced above, agree with such a magmatic sequence, but, if all the spinels are the products of continuous fractional crystallization only, the interstitial and symplectic relationships and more aluminous nature of the harzburgite chrome-spinels are difficult to explain. Interstitial relationships could result from continued growth of fractionated grains, which undergo continuous reaction with intercumulus liquid to become richer in alumina, but in this respect Irvine (1967) notes that aluminous spinel coprecipitates with forsterite in much greater amounts than does picrochromite, which is not the observed modal relationship in New Caledonia.

Aluminous interstitial liquid in an olivine accumulate could crystallize to spinel+pyroxene solid solutions, rather than olivine, at moderate pressure (Kushiro and Yoder, 1964). This in itself could produce symplectic relationships or an aluminous enstatite, which could recrystallize to spinel+pyroxene on decrease of load pressure (Green, 1964; Irvine, 1967).

The position occupied by the symplectic spinel in figs. 5 and 6 could indicate that it has formed under different conditions to the cumulate picrochromites of the dunites and chromites and the pressure cited above, as a maximum for the stability range of the symplectites, agrees with a pressure of 2 to 5×10^8 N.m⁻² deduced for a late stage, pre-emplacement, recrystallization episode for the New Caledonian harzburgites by Rodgers (1972).

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