

SHORT COMMUNICATIONS

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Electron-probe investigation of some chrome-spinels from southern New Caledonia

CHROME-SPINELS have been described from the alpine-type peridotite complex of New Caledonia by Guillon (1970) and Rodgers (1973). Rodgers's work, like that of most preceding authors that he reviewed, was based on wet-chemical analyses of spinel concentrates. Physical measurements suggested some degree of inhomogeneity within individual concentrates but he was unable to confirm this chemically or to establish whether the individual grains were homogeneous. Guillon reported probe data and his results differed from those of wet chemistry in having lower Mg/Fe²⁺ ratios but his analyses had low totals and suggested a pronounced degree of non-stoichiometry not found by other workers.

During 1974-5 several of the samples discussed by Rodgers (1973, 1976) were examined at the British Museum (Natural History) to investigate whether the individual grains were homogeneous, to gauge the amount of variation within an individual sample, and to attempt to correlate wet-chemical with microprobe results.

Results. Corrected probe analyses¹ for representative spinels are given in Table I along with their structural formulae, approximate levels of trace NiO, CoO, and V₂O₅, and MgO and FeO* values for some of the coexisting silicates. Some totals are slightly low despite several attempts to improve on the analysis. In most grains it is the rim, or in the case of symplectites, the fine veins, that give poor totals, probably as a result of excitation of adjacent silicates.

All grains examined proved to be inhomogeneous, although Rodgers (1973a, p. 332) implies this not to be so. Both the type and degree of inhomogeneity (e.g. in Mg/Fe²⁺ or Cr/Al) varied within individual grains, between different grains of the one sample, and between rock types (Table I and fig. 1). Such is the nature and extent of the variation that few rigorous rules can be laid down concerning it with the data available but certain general tendencies were found. The nomenclature is that of Simpson (1921).

The majority of New Caledonian spinels analysed to date, whether by wet-chemical means or microprobe, are picrochromites (*var.* chrome-picotites). In these spinels magnesium exceeds ferrous iron and chromium exceeds aluminium, but not to such an extent that a picrochromite (*s.s.*) has been found, and usually such that as Mg/Fe²⁺ increases there is a corresponding increase in Cr/Al. Only in the cores of some chromitite spinels (Mg ≫ Fe²⁺), in symplectites (Mg ≳ Fe²⁺, Cr ≳ Al), and in spinel lamellae in diopsides (Mg < Fe; Rodgers, 1977) have these conditions not been found. In contrast, all but one of the analyses reported by Guillon (1970) plot as chromites (*var.* beresofite).

The chromitite spinel grains show the greatest inhomogeneity and many are strongly zoned. As in the example shown here (Table I, analyses 1a, b, c), a small, magnesium-rich core often gives way rapidly to a more iron-rich grain body, which, in turn, grades slightly towards the rim. There is little change in Cr/Al but such is the level of Mg in the core that in order to obtain stoichiometry most of the iron must be assigned to R³⁺ when calculating the formula.

¹ Made on a Cambridge Instruments Geoscan with independently analysed mineral and pure metal standards and the BM-IC-NPL Z.A.F. correction program (Mason *et al.*, 1969).

TABLE I. *Representative analyses and structural formulae of chrome spinels from southern New Caledonia*

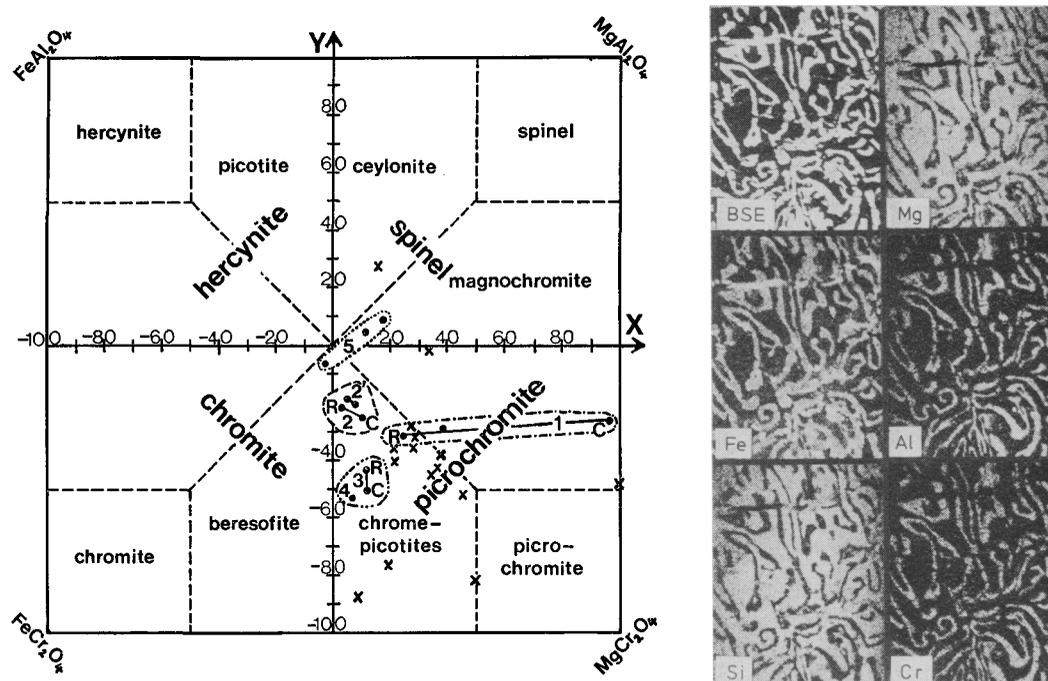
	1a	1b	1c	2a	2b	2c	2'a	2'b	2'c	3a	3b	4	5	5'	5''
<i>Corrected analysis – weight percent</i>															
V ₂ O ₅	0.09	0.09	0.08	0.28	0.30	0.26	0.34	0.22	0.32	0.18	0.24	—	0.22	0.30	0.28
TiO ₂	—	—	—	0.11	0.11	0.11	0.11	0.09	0.09	—	—	—	0.13	0.11	0.13
Al ₂ O ₃	16.90	17.87	17.37	20.03	19.95	19.12	20.32	20.49	18.93	11.45	13.57	12.26	22.75	27.80	26.31
Cr ₂ O ₃	46.83	50.20	50.93	47.68	48.00	46.84	47.42	47.02	45.45	55.99	52.47	53.07	41.12	33.97	36.43
FeO*	13.16	14.74	14.93	20.12	20.08	21.46	20.24	20.39	22.81	20.68	20.87	22.17	22.98	22.60	22.94
MnO	—	—	—	0.32	0.31	0.40	0.37	0.38	0.40	—	—	—	0.31	0.31	0.31
MgO	22.48	14.91	14.45	11.35	11.07	10.80	11.18	11.19	10.70	11.49	11.46	10.64	10.28	12.89	12.19
CoO	0.03	0.03	0.03	—	—	—	—	—	—	0.10	0.10	—	—	—	—
NiO	0.07	0.05	0.06	0.07	0.02	0.06	0.03	0.04	0.10	0.07	0.10	—	0.03	0.07	0.03
Total	99.56	97.89	97.85	99.96	99.05	99.05	100.01	99.82	98.80	99.96	99.81	98.14	97.82	98.05	98.62
<i>Structural formulae on a basis of 32(O)</i>															
V	0.015	0.015	0.002	0.047	0.050	0.044	0.056	0.022	0.033	0.031	0.042	—	0.037	0.049	0.046
Ti	—	—	—	0.021	0.021	0.022	0.021	0.017	0.018	—	—	—	0.025	0.020	0.024
Al	4.899	5.355	5.233	5.964	5.526	5.799	6.045	6.114	5.793	3.554	4.220	3.305	6.909	8.160	7.756
Cr	9.102	10.088	10.288	9.519	9.604	9.527	9.459	9.408	9.327	11.652	10.942	11.281	8.374	6.687	7.199
Fe ^{3†}	2.636	0.711	0.634	0.552	0.577	0.772	0.513	0.564	1.076	0.986	1.033	1.303	0.871	1.405	1.262
Fe ^{2†}	0.071	2.422	2.557	3.697	3.674	3.846	3.758	3.752	3.877	3.568	3.572	3.683	4.079	3.300	3.532
Mn	—	—	—	0.068	0.067	0.087	0.079	0.082	0.087	—	—	—	0.068	0.066	0.066
Mg	8.236	5.648	5.503	4.272	4.176	4.937	4.204	4.220	4.140	4.508	4.505	4.262	3.947	4.782	4.540
Co	0.006	0.006	0.006	—	—	—	—	—	—	0.021	0.021	—	—	—	—
Ni	0.013	0.009	0.012	0.014	0.005	0.012	0.006	0.008	0.020	0.014	0.021	—	0.006	0.013	0.006
<i>Ratios</i>															
Cr/Al	1.85	1.88	1.96	1.59	1.73	1.64	1.56	1.54	1.61	3.28	2.59	3.41	1.21	0.82	0.93
Mg/Fe ^{2†}	116.00	2.33	2.14	1.16	1.13	1.28	1.12	1.12	1.07	1.26	1.26	1.16	0.97	1.45	1.28
Fe ^{2†} /Fe ^{3†}	0.03	3.41	4.03	6.70	6.36	4.98	7.32	6.65	3.60	3.62	3.46	2.83	4.68	2.35	2.80

- 1 : Anti-orbicular chromitite, 20014, Mine Anna Madeleine, Plaine des Lacs. (cf. Rodgers, 1973, Table II, anal. 3)
- 2, 2' : Two grains. Dunite, 26101, RT2, headwaters of Riv. des Pirogues. Coexisting olivine has MgO = 49.95%, FeO* = 9.58%
- 3 : Harzburgite, 20026, Pirogues Valley. Coexisting enstatite has MgO = 37.77%, FeO* = 5.11%.
- 4 : Harzburgite, 20022, la Madeleine, Plaine des Lacs.
- 5, 5', 5'' : Three different areas of single spinel symplectite. Dunite, 20003, Vallee de la Rivière Bleue. Intergrown diopside has MgO = 16.57%, FeO* = 1.24%.
- a : Core of grain.
- b : Intermediate position between grain core and rim.
- c : Rim of grain.
- * : Total iron as FeO.
- † : Fe² and Fe³ calculated to give $2R^{2+}/R^{3+} = 1.00 \pm 0.01$.
- Analyst: J. C. Bevan

The resulting calculated Fe²⁺/Fe³⁺ ratio is entirely different from that found in any other primary mineral of the New Caledonian ultramafic belt. Without precise knowledge of the oxidation state of iron and its crystal chemical role in such spinel cores no firm deductions can, or should, be drawn at this stage.

Most chromitite spinels have higher Mg/Fe²⁺ ratios than those of dunites or harzburgites. Harzburgite spinels often show higher Cr/Al ratios. Dunites tend to possess spinels with both ratios lower than in the other two rock types. Although the dunite and harzburgite spinels are not as variable in composition as their chromitite counterparts, they do tend to fall into two distinctive groups within the picrochromite field while the calculated Fe²⁺/Fe³⁺ ratio of dunite spinels is often higher than that found in harzburgites.

As suggested by analysis 22 (Table II) given by Rodgers (1973) the symplectic spinels are quite distinctive in composition. They also prove to be often highly variable within a single symplectite (fig. 2). The example given here spans the beresofite, picrochromite, and magnochromite fields. Usually, both Mg/Fe^{2+} and Cr/Al are close to 1, but few conclusions can be drawn, particularly in respect of Fe^{2+}/Fe^{3+} , as these mineral intergrowths proved extremely difficult to analyse and all totals are less than 100 %.



FIGS. 1 and 2: FIG. 1 (left). Classification of the chrome spinels after Simpson (1921). \times = analyses of Rodgers (1973); \bullet = analyses of this paper, numbers as for Table I; R = rim; C = core; - - - - - = chromitite; - - - - - = dunite; = harzburgite; = symplectite. FIG. 2 (right). X-ray and back scattered electron scanning photographs of analysed symplectite. Length of scan 500 μ m.

Discussion. Despite the inhomogeneity of the New Caledonian spinels, wet-chemical analyses have proved successful in determining spinel type and major trends, but only because variation within one rock and within one grain was generally small. Where variation is greater, as in some chromitites, a bulk analysis is at best a weighted average and gives little clue as to the true nature and history of the mineral. The cautions of Rodgers (1970, pp. 882-3) could be noted here and may well be reflected in his analysis (1973, Table II, col. 17) for a dunite spinel, no comparable example being found in the present study. Nevertheless, if there is no evidence to the contrary, homogeneity must often be assumed and bulk analyses be made.

To show the full extent and nature of the variations with the New Caledonian chrome-spinels requires many more analyses than are warranted at this time. It is believed that the limited study here points out the major variations and, at the same time, conforms with the main ideas on the New Caledonian ultramafics outlined by Rodgers (1973, 1976) without in any way confirming them. The high Cr/Al of the harzburgite spinels is in keeping with their being regarded as part of a refractory residue. The Cr/Al and Mg/Fe^{2+} ratios of the chromitite

and dunite spinels and the variation within the grains can be related to their being regarded as the products of early fractional crystallization. The symplectites, with their contrasting and highly variable composition, may still be regarded as the products of a later recrystallization episode.

No consistent chemical compositional variation was found that might account for the black rims around some spinel grain boundaries and cross-cutting lines described by Rodgers (1973).

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Rosenhahnite $\text{Ca}_3\text{Si}_3\text{O}_8(\text{OH})_2$ —a further occurrence

ROSENHAHNITE was first discovered experimentally by Pistorius (1963), who reported it as a possible high-pressure polymorph of xonotlite occurring below 450 °C and in excess of 20 kb. The first natural occurrence was recorded by Pabst *et al.* (1967) from a stream boulder in Franciscan greywacke, California. They described rosenhahnite in veins and cavities cutting brecciated metasediments composed of hard, fine-grained diopside, hydrogrossular, tremolite, and titanite. Associated with the rosenhahnite were veins of pectolite and xonotlite. Recently, Dunn (1975) has reported the first, natural, *in situ* occurrence from Wake County, North Carolina. Here the mineral was found as irregular segregations intergrown with prehnite, gyrolite, apophyllite, and okenite. The association of the high-pressure calcium silicate phase with a low-pressure zeolite assemblage made this occurrence of special interest.

In a recent re-examination of the metasomatized gabbro and rodingites of the Wairere Serpentinite described by O'Brien and Rodgers (1973a, b), rosenhahnite was found in association with pectolite, as angular to rounded fragments located in a brecciated zone at the base of a highly weathered pectolite–prehnite crust occurring at a rodingite–serpentinite contact.