Chemical characteristics of chrome spinel in the magnesite-rich rocks from Swat, northwestern Pakistan

MOHAMMAD ARIF

Department of Geology, University of Peshawar, Pakistan

ABSTRACT: *The magnesite-rich rocks (magnesite ± talc ± quartz ± fuchsite ± tourmaline ± chlorite), which locally host emerald mineralization, contain trace to accessory amounts of disseminated grains as well as small nodular segregations of chrome spinel. The spinel displays unusually high Cr/(Cr+Al) and low Mg/(Mg+Fe^{2+}) ratios. A detailed investigation reveals that the present chemical characteristics of the chrome spinel are probably the result of modification related to the formation of the host rocks by a low-grade metamorphism in the presence of a CO$_2$-bearing fluid.*

INTRODUCTION

The Main Mantle Thrust Melange Group (MMTMG) in the Swat area consists of a range of lithologies including magnesite-rich rocks (Arif, 1994). These rocks occur as small lenticular bodies in a number of places, namely: the Alpurai-Lilaunai area, the Barkotkai and Gujar Kili villages, the Spin Obo-Kuh area, and the area north of the Mingora town (Fig. 1). In most of these occurrences, they are spatially associated with variably serpentinized ultramafic rocks, either occurring as small patches within them or distributed along the contact zones between them and the metasediments.

Beside other phases, the magnesite-rich rocks contain trace to accessory amounts as well as small nodular segregations of chrome spinel. A detailed investigation of the compositional characteristics of the chrome spinel and a discussion of their origin are the objectives of this paper.

SAMPLES AND METHODS

A total of 60 samples including a chromitite (M30), representing all the different occurrences of the carbonate-rich lithologies in the study area (Fig. 1) were studied petrographically and polished thin sections of some of them were used for mineral chemical analyses by electron microprobe. The analyses were carried out by Jeol Superprobe model JXA-8600 equiped with an on-line computer for ZAF corrections. Quantitative analyses were conducted using wavelength dispersive system and natural and synthetic standards under the following operating conditions: 15 Kv accelerating voltage; 30 x 10^{-9} A probe current; 20 (2 x 10) seconds peak, 10 (2 x 5) seconds negative background and 10 (2 x 5) seconds positive background counting times. The accuracy of the ZAF correction is generally better than 2 %.

HOST ROCK PETROGRAPHY AND OCCURRENCE OF CHROME SPINEL

The fine grained, relatively soft, magnesite-containing rocks of the Swat area have a greyish white to yellowish white colour locally displaying a reddish brown tint due to limonitization. They invariably consist of abundant magnesite and
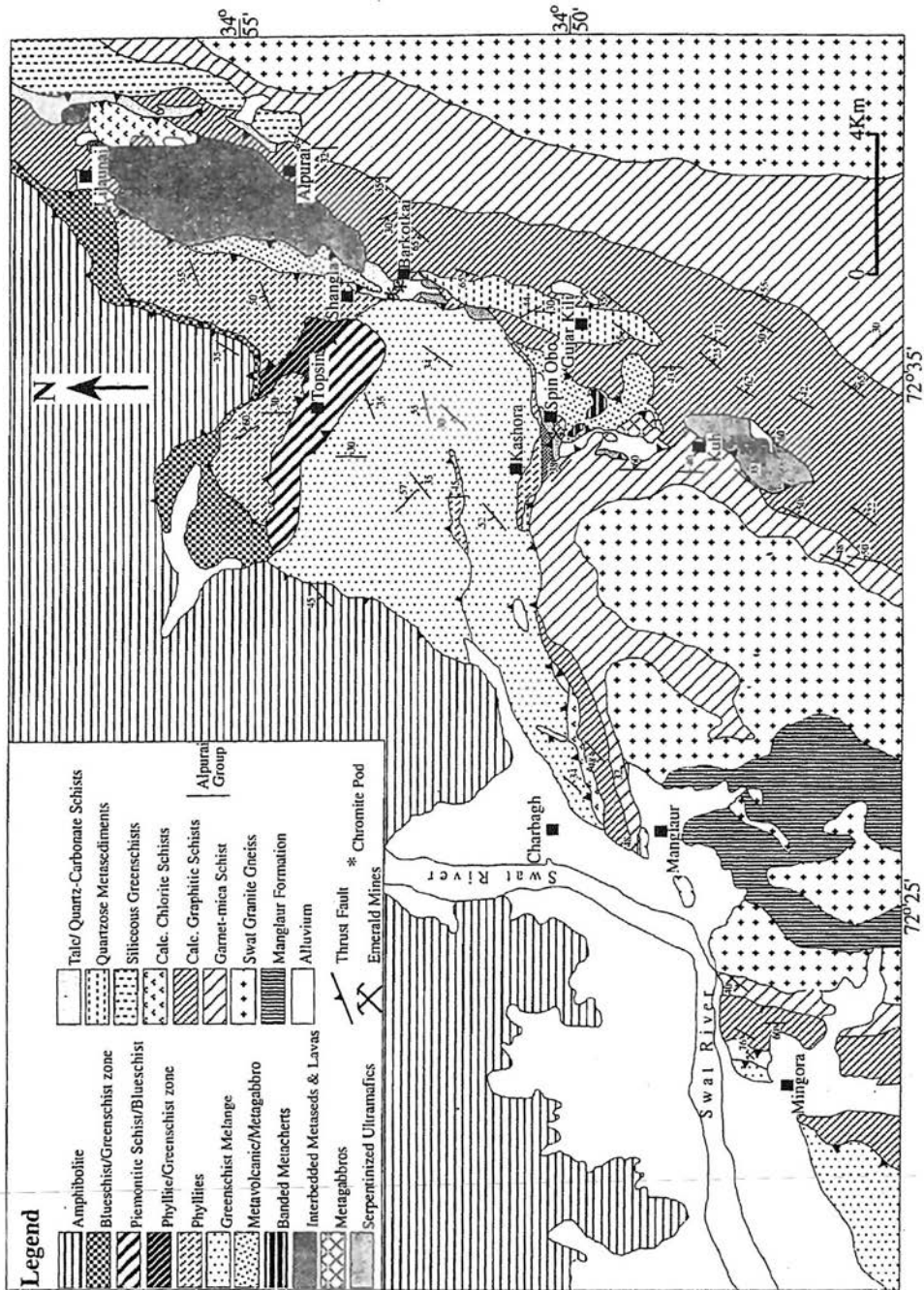
Fig. 1. Geological map of the Mingora-Lilaunai area, Swat (modified after Kazmi et al., 1984).

Legend

Amphibolite	
Blueschist/Greenschist zone	
Piemontite Schist/Blueschist	
Phyllite/Greenschist zone	
Phyllites	
Greenschist Melange	
Metavolcanic/Metagabbro	
Banded Metacherts	
Interbedded Metaseds & Lavas	
Metagabbros	
Serpentinized Ultramafics	

Talc/ Quartz-Carbonate Schists	
Quartzose Metasediments	
Siliceous Greenschists	
Calc. Chlorite Schists	
Calc. Graphitic Schists	Alpurai Group
Garnet-mica Schist	
Swat Granite Gneiss	
Manglaur Formation	
Alluvium	
Thrust Fault * Chromite Pod	
Emerald Mines	

accessory to trace amounts of chrome spinel accompanied by one or more of such phases as talc, quartz and dolomite. The abundance of talc has given rise to a strongly developed fissile character in most of the rocks.

Beside the above mentioned phases, some of the magnesite-rich rocks also contain fuchsite and tourmaline. In most such assemblages, these two minerals coexist, forming veins and clusters. Tourmaline and fuchsite also occur as fine-grained disseminations in some of the rocks and are associated with vein quartz in some of the other samples. In one of the rocks, fuchsite occurs as aggregates, clusters or clots of very fine grained flaky crystals within the magnesite matrix. Their squarish outlines (reflecting a cubic morphology of the precursor) suggest that these could be the product of a pseudomorphic transformation from the disseminated chrome spinel grains that were present in the parent rock. Rarely, the fuchsite itself shows alteration to chlorite.

Trace amounts of chrome spinel occur as finely disseminated grains in the magnesite-dominated matrix of most of the samples. These grains are optically as well as chemically homogeneous. However, chrome spinel grains in some of the samples are bordered by fuchsite. Chrome spinel also occurs in the form of small segregations (1 to 5 cm across) consisting of abundant chromite (more than 50 volume %) which is distributed as nodular grains in the magnesite-rich rocks of the Mingora emerald mines area. The gangue minerals of chromite in these samples include magnesite, fuchsite and/or talc, with fuchsite mostly occurring around as well as along fractures within the chromite nodules.

CHEMISTRY OF CHROME SPINEL

Grains of Cr-spinel were analysed in ten samples representing four of the five occurrences of magnesite-rich rocks. The overall range in their composition can be summarised as follows (in wt. %): TiO_2 = 0.01-0.32; Al_2O_3 = 5.33-18.51; Cr_2O_3 = 40.35-57.67; V_2O_3 = 0.10-0.33; Fe_2O_3 = 0.00-11.90; FeO = 27.62-30.66; MnO = 0.18-0.80; MgO = 0.67-2.75; CaO = 0.01-0.44; NiO = 0.02-0.11; ZnO = 0.81-2.84. It should be noted that the amounts of V_2O_3 and ZnO were determined in most, but not all, of the analyses. Representative analyses are listed in Table 1 and the overall chemical variation and comparison with chrome spinel from other associations are illustrated in Figures 2 and 3. The diagnostic features of the composition of these chrome spinels are outlined below:

a. Borders and/or rims of ferritchromite and/or magnetite around grains of chrome spinel – an alteration (serpentinization)-related chemical (and optical) zoning commonly occurring in serpentinized ultramafic rocks – are extremely rare in the investigated samples.

b. Intergranular chemical variation within the domain of a thin section is limited.

c. Low to very low amounts of TiO_2 (< 0.3 wt. % in all but one analysis).

d. Low, but not unusual, and rather uniform MnO and NiO.

e. Low to very low MgO and high FeO [Mg # {=100 x Mg/(Mg + Fe^{2+})}= 4.1-15.1] (Figs. 2, 3).

f. Variable, but in most cases low to very low, Al_2O_3 and high to very high Cr_2O_3 [Cr # {=100 x Cr/(Cr + Al)}= 62.1-87.8)].

g. Rather low Fe^{3+} # [=100 x Fe^{3+}/(Cr + Al + Fe^{3+})] (0 to 5 in most samples, ranging up to ~ 10 in one sample, and from 13.2 to 16.2 in only four analyses from three different samples; Fig. 3).

Chemical analyses were also performed on the grains of chrome spinel in the chromite-rich

TABLE 1. REPRESENTATIVE ANALYSES OF CHROME SPINEL

Samp.[1]	G1	G2	G3	G5	G18	M16	M9	M28	M29	Sp43	M30	M30
SiO_2	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
TiO_2	0.12	<0.04	<0.04	<0.04	0.11	0.08	0.20	0.11	0.12	0.05	0.15	0.19
Al_2O_3	10.87	6.93	7.46	11.02	5.33	13.30	6.75	7.94	8.83	18.51	11.83	11.80
Cr_2O_3	51.12	57.35	56.79	54.65	57.28	40.35	57.52	48.78	45.57	45.14	54.69	54.85
V_2O_3	n. a.	n. a.	n. a.	n. a.	n. a.	0.10	0.21	0.17	0.33	0.22	n. a.	n. a.
Fe_2O_3	3.97	1.69	1.72	0.89	3.24	11.90	0.00	11.57	11.90	1.61	1.11	1.58
FeO	29.55	30.00	30.37	29.47	30.05	27.92	27.82	27.83	30.66	30.38	25.66	25.55
MnO	0.23	0.34	0.40	0.30	0.30	0.30	0.22	0.46	0.26	0.80	0.43	0.48
MgO	2.24	1.35	1.15	2.39	1.16	2.59	0.71	2.40	0.99	1.78	4.95	5.19
CaO	<0.02	0.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
NiO	0.04	<0.04	0.07	<0.04	0.06	0.06	0.09	0.11	0.09	<0.04	<0.04	<0.04
ZnO	n. a.	n. a.	n. a.	n. a.	n. a.	1.23	2.84	1.11	0.81	1.04	n. a.	n. a.
Total	98.15	97.74	97.97	98.77	97.54	97.84	96.38	99.49	99.56	99.55	98.85	99.65

Cations per four oxygens

Si	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ti	0.003	0.001	0.000	0.001	0.003	0.002	0.006	0.003	0.003	0.001	0.004	0.005
Al	0.454	0.298	0.320	0.456	0.232	0.553	0.296	0.333	0.373	0.740	0.479	0.473
Cr	1.433	1.654	1.633	1.518	1.672	1.125	1.693	1.346	1.291	1.210	1.485	1.476
V	—	—	—	—	—	0.003	0.006	0.005	0.009	0.006	—	—
Fe^{3+}	0.106	0.046	0.047	0.024	0.090	0.316	0.000	0.310	0.321	0.041	0.029	0.040
Fe^{2+}	0876	0.915	0.924	0.866	0.928	0.823	0.866	0.829	0.918	0.862	0.737	0.727
Mn	0.007	0.011	0.012	0.009	0.009	0.009	0.007	0.014	0.008	0.023	0.013	0.014
Mg	0.118	0.073	0.062	0.125	0.064	0.136	0.039	0.127	0.053	0.090	0.253	0.263
Ca	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ni	0.001	0.001	0.002	0.000	0.002	0.002	0.003	0.003	0.003	0.000	0.001	0.000
Zn	—	—	—	—	—	0.032	0.078	0.029	0.021	0.026	—	—
Total	2.998	3.000	3.000	2.999	3.000	3.001	2.995	2.999	3.000	2.999	3.001	2.998
Cr#	76.0	84.7	83.6	76.9	87.8	67.0	85.1	80.2	77.6	62.1	75.6	75.7
Mg#	11.9	7.4	6.3	12.6	6.5	14.2	4.3	13.3	5.5	9.5	25.6	26.6
Fe^{3+}#	5.3	2.3	2.4	1.2	4.5	15.9	0.0	15.6	16.2	2.1	1.5	2.0

[1]Samples are designated after their locations: G = Gujar Kili emerald mine, M = Mingora emerald mines and Sp = Spin Obo-Kuh area (see Fig. 1); Except for M30 which is chromite-rich, the mineralogical composition of all the other samples is dominated by magnesite; n. a. = not analysed; Cr # = 100 x Cr/(Cr + Al); Mg # = 100 x Mg/(Mg + Fe^{2+}); Fe^{3+} # = 100 x Fe^{3+}/(Fe^{3+} + Al + Cr).
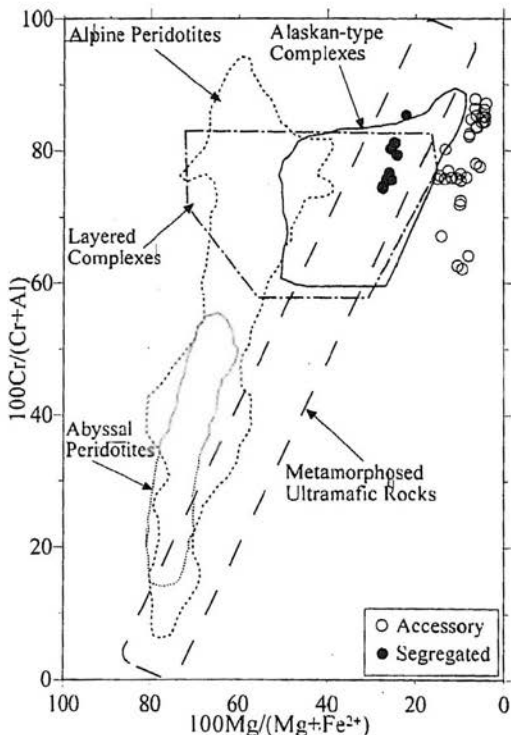
Fig. 2. Chrome spinel analyses plotted on the Ch-Hc-Sp-Pc face of the spinel compositional prism (after Irvine, 1965). Fields of the abyssal peridotites, alpine peridotites, stratiform and SE Alaskan-type complexes are after Jan and Windley (1990). The field of chrome spinel from metamorphosed ultramafic rocks is after Evans and Frost (1975) and that of Shangla chromite is based on the analyses of the least altered segregated and accessory chrome spinel in the serpentinized ultramafic rocks (Fig. 3b in Arif & Jan, 1993).

sample (M30). The chemical variation in these analyses is illustrated in Table 1 and Figures 2 and 3. Like the disseminated grains in carbonate-rich rocks, the chemical characteristics (especially the range of Mg #s) of this segregated chromite are markedly different from those of the chromitites enclosed in non-carbonated ultramafic rocks. The latter are at places (e.g. Barkotkai; Fig. 1) associated spatially with the rocks inves-

tigated. The high Cr and low to very low Mg and Fe^{3+} #s of the studied segregated chromite also make them different from those occurring in various tectonic settings elsewhere in the world (Figs. 2, 3).

DISCUSSION

The petrogenetic significance of the chemistry of chrome spinel has been discussed by several workers (e.g. Irvine, 1965, 1967; Dick & Bullen, 1984). That is why the trend of chemical variation of chrome spinel grains is used for investigating the predominant process responsible for the genesis of their host rocks. This is because the composition of chrome spinel is highly sensitive to reconstitution due to (a) a change in the magmatic process, i.e. partial melting (e.g. Mysen & Kushiro, 1977; Zhou & Kerrich, 1992) or fractional crystallization (e.g. Jaques, 1981), (b) post-cumulus modification due to variation in
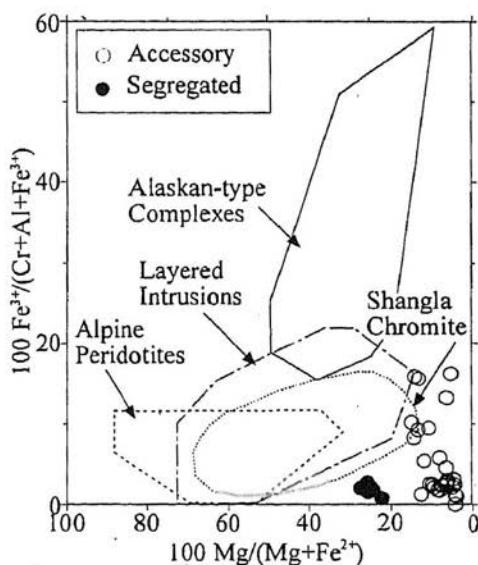

Fig. 3. Analyses of chrome spinel plotted on the Mf-Mt-Ch-Hc face of the spinel compositional prism (after Irvine, 1965). Fields are after Jan and Windley (1990).

13

the physicochemical conditions of the melt (e.g. Umino, 1986), (c) subsolidus exsolution (Jan et al., 1992) or re-equilibration with coexisting phases (e.g. Wilson, 1982), (d) low-temperature alteration such as serpentinization and chloritization (e.g. Jan & Windley, 1990), as well as (e) metamorphism (e.g. Evans & Frost, 1975).

The composition of disseminated chrome spinel in the carbonated ultramafic rocks of the MMTMG is different from that of their least altered counterparts in the magnesite-free serpentinized ultramafic rocks. The most notable sample to sample variation in the composition of the least altered disseminated chrome spinel grains in the serpentinized rocks consists of changes in Cr # whilst the Fe^{3+} # is almost uniformly low (Fig. 3; also see fig. 3 in Arif & Jan, 1993). Such changes are more likely to result from partial melting than any of the other processes mentioned above.

Compared to serpentinized rocks, chrome spinel in the investigated magnesite-rich rocks have distinctly low Mg and high Cr #s (Fig. 2). In fact, the level of their Mg #s is so low that they plot outside the fields for chromites from known igneous rock associations. Therefore, these peculiarities can either be due to (i) alteration, or (ii) metamorphism. The following features tend to preclude the first possibility and support the second:

a. There is no apparent zoning in individual grains and grain to grain variation is limited.

b. A comparison between the compositions of the altered margin and unaltered core of individual grains in the serpentinized rocks suggests that alteration mainly involves enrichment in Fe^{3+}, Mn, Ni and Ti (see Arif, 1994). None of these components in the disseminated chrome spinels from the studied magnesite-rich rocks is higher than the unaltered chrome spinel in the serpentinized ultramafic rocks.

c. The mineralogical composition of their host rock (talc + magnesite and quartz + magnesite assemblages) is clearly the result of metamorphism. Detailed field and mineralogical studies suggest that these rocks are probably formed by the carbonation of the spatially associated, previously serpentinized, ultramafic rocks. The process of carbonation may have taken place at 250-550 °C and was probably caused by the CO_2-bearing fluid released by the metamorphism of the associated metasedimentary rocks (Arif, 1994).

d. The drastic enrichment of chrome spinel in Fe^{2+} has been attributed to metamorphism by several workers (Evans & Frost, 1975; Hoffman & Walker, 1978; Lipin, 1984; Stoddard et al., 1988).

Similarly, the distinctly low Mg and relatively high Cr #s of the segregated chromite from the Mingora emerald mines area appear to be a result of metamorphism. This is indicated by (1) the metamorphic nature of the associated gangue minerals, i.e. magnesite and talc; and (2) alteration of the individual chromite grains to fuchsite. Furthermore, such Fe^{2+}-rich chromites have been described from the metamorphosed chromitites in the Blue Ridge and Piedmont areas of North Carolina (Lipin, 1984; Stoddard et al., 1988). The distinctive mineral assemblage of the Piedmont chromitites (consisting of chromite and other Cr-enriched phases such as fuchsite, kyanite, corundum and tourmaline) clearly indicates that the composition of their chromite has been drastically modified by a medium-grade (amphibolite facies) regional metamorphism. As mentioned above, the work by Evans and Frost (1975) also demonstrates that low grade metamorphism of ultramafic rocks causes a strong Fe^{2+}-enrichment of their chromian spinel.

14

REFERENCES

Arif, M., 1994. Studies of ultramafic rocks from Swat, northwestern Pakistan: Implications for the genesis of emerald and nickeliferous phases. Unpubl. Ph.D. Thesis, University of Leicester, UK.

Arif, M. & Jan, M. Q., 1993. Chemistry of chromite and associated phases from the Shangla ultramafic body in the Indus suture zone of Pakistan. In: Himalayan Tectonics (M. P. Searle & P. J. Treloar, eds.). Geol. Soc. London, Spec. Publ., 74, 101–112.

Dick, H. J. B. & Bullen, T., 1984. Chromian spinel as a petrogenetic indicator in abyssal and alpine-type peridotites and spatially associated lavas. Contr. Mineral. Petrol., 86, 54–76.

Evans, B. W. & Frost, B. R., 1975. Chromian spinel in progressive metamorphism: a preliminary analysis. Geochim. Cosmochim. Acta, 39, 959–972.

Hoffman, M. A. & Walker, D., 1978. Textural and chemical variations of olivine and chrome spinel in the East Dover ultramafic bodies, Vermont. Geol. Soc. Amer. Bull., 89, 699–710.

Irvine, T. N., 1965. Chrome spinel as a petrogenetic indicator. Part I, Theory. Canad. Jour. Earth Sci., 2, 648–671.

Irvine, T. N., 1967. Chrome spinel as a petrogenetic indicator. Part II, Petrologic applications. Canad. Jour. Earth Sci., 4, 71–103.

Jan, M. Q. & Windley, B. F., 1990. Cr-spinel-silicate chemistry in ultramafic rocks of the Jijal complex, NW Pakistan. Jour. Petrol., 31, 667–715.

Jan, M. Q., Khan, M. A. & Windley, B. F., 1992. Exsolution in Al-Cr-Fe^{3+}-rich spinels from the Chilas mafic-ultramafic complex, Pakistan. Amer. Mineral., 77, 1074–1079.

Jaques, A. L., 1981. Petrology and petrogenesis of cumulate peridotites and gabbros from the Marum ophiolite complex, Northern Papua New Guinea. Jour. Petrol., 22, 1–40.

Kazmi, A. H., Lawrence, R. D., Dawood, H., Snee, L. W. & Hussain, S. S., 1984. Geology of the Indus suture zone in the Mingora-Shangla area of Swat. Geol. Bull. Univ. Peshawar, 17, 127–144.

Lipin, B. R., 1984. Chromite from the Blue Ridge Province of North Carolina. Amer. Jour. Sci., 284, 507–529.

Mysen, B. O. & Kushiro, I., 1977. Compositional variation of coexisting phases with degree of melting of peridotite in the upper mantle. Amer. Mineral., 62, 843–865.

Stoddard, E. F., Wyllie, A. S., Jr., & Blake, D. E., 1988. Metamorphosed chromitite in the Falls Lake mélange, North Carolina Piedmont. Geol. Soc. Amer. Spec. Pap., 231, 33–44.

Umino, S., 1986. Magma mixing in boninite sequence of Chichijima, Bonin Islands. Jour. Volcanol. Geotherm. Res., 29, 125–157.

Wilson, A. H., 1982. The geology of the Great 'Dyke', Zimbabwe: the ultramafic rocks. Jour. Petrol., 23, 240–292.

Zhou, M. & Kerrich, R., 1992. Morphology and composition of chromite in komatiites from the Belingwe greenstone belt, Zimbabwe. Canad. Mineral., 30, 303–317.