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On genetic classification of chromian spinels in deep-seated rocks from continental structures

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Abstract. A large data base of 1821 chromian spinel compositions ($Cr_2O_3 > 2$ wt %) in ultramafic nodules from basalts, kimberlites, lamproites, ultramafic massifs, and from the diamond assemblage has been analyzed using mathematical statistics methods. For each spinel component under study (TiO_2, Al_2O_3, Cr_2O_3, FeO^*, MnO, MgO), a considerable overlap is observed, spinels with the highest Cr-number (#Cr) being found in the diamond assemblage and those with the highest Mg-number (#Mg), in nodules from basalts. The lowest oxidation degree is detected in spinels from nodules in basalts and from the diamond assemblage. Spinels from ultramafic massifs have the highest oxidation degrees and Fe-numbers. In ultramafic massifs from kimberlite to lamproite through to the diamond type, spinel compositions follow the same variation trends. Spinels from the basaltic group fall away from these trends. Compositional variability of spinels is due chiefly to isomorphic replacement of Fe^{+2} for Mg and of Al and Mg for Cr. Kimberlite-type spinels have high and broadly variable Ti contents. Igneous and metamorphic/metasomatic origins for spinels of the five groups under study are discussed. Spinel compositions from ultramafic rocks found in continental structures are shown to indicate that at depth beneath these structures, there exist physicochemical conditions for crystallization inherent to all the principal tectonic features of the earth-continents, oceans, and transition zones (island arcs).

Introduction

Spinel is a typomorphic mineral in mafic and ultramafic rocks of various depth facies. As a rule, spinel, a mineral that forms a variety of solid solution series with end members such as noble spinel, hercynite, magnetite, ulvospinel, picrochromite, and chromite, has a range of proportions of the following cations: Al^{+3}, Cr^{+3}, Mg^{+2}, Fe^{+2}, Fe^{+3}, and Ti^{+4}. The principal microcomponents are Mn and Zn. In deep-seated rocks of ultramafic composition, the most common varieties are chromian spinels. Rocks with spinels of such composition are represented by alpine-type ultramafites, nodules in alkaline basalts, kimberlites, and lamproites, as well as inclusions in deep-seated minerals, of which diamonds are of the greatest interest. Accordingly, one can discuss 5 groups of chromian spinel compositions corresponding to the rock types just listed.

We studied chemical compositions of chromian spinels from the above 5 groups by means of mathematical statistics methods—primarily, hierarchic cluster analysis using nearest neighbor search in Euclidean space and principal-component factor analysis. Minerals having more than 2% Cr_2O_3 were classed with chromian spinels. Besides, a chemical screen of $TiO_2 < 8\%$ was introduced. High-Ti chromites are rare in terrestrial rocks and common in Lunar rock samples; they are crystallized under highly reducing conditions [*Agrell et*

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Table 1. Partial analyses of spinels (wt %) from kimberlitic pipes of the Yakutian province according to different authors

Pipe	Author	Number of grains	Cr_2O_3	Al_2O_3	TiO_2
Mir	[*Bobrievich et al.,* 1964]		45.51	22.07	0.14
	[*Sobolev et al.,* 1975]	163	50.80	13.20	0.90
	I. P. Ilupin	10	48.31	17.86	0.57
Aikhal	[*Bobrievich et al.,* 1964]		42.07	26.54	0.17
	[*Sobolev et al.,* 1975]	162	53.00	12.90	0.50
	I. P. Ilupin	19	51.26	15.52	0.31
Udachnaya	[*Bobrievich et al.,* 1964]		52.81	16.42	0.12
	[*Sobolev et al.,* 1975]	76	55.50	6.80	1.20
	[*Garanin et al.,* 1980]	15	49.14	16.99	0.86
	[*Matsyuk et al.,* 1989]	60	45.39	22,98	0.35
	I. P. Ilupin	10	56.54	10.73	0.21

al., 1970]. This type of chromian spinels is beyond the scope of our study. Our data set, totaling 1821 analyses, was represented by spinels from rocks of ultramafic massifs (alpine-type ultramafites, n = 318), nodules from basalts (n = 340), lamproites (n = 106), kimberlites (n = 928), and from diamond assemblages (n = 129). Overall, the spinels have broad ranges of all the components selected for analysis – Ti, Al, Cr, Fe, Mg, and Mn oxides. Inasmuch as the overwhelming majority of analyses are X-ray spectral microanalysis (PCM) data, the processing involved total iron as ferric iron, FeO^*. When considering spinel compositions averaged within the established clusters, the proportion of ferric iron, calculated stoichiometrically using the well-known MINFILE program, was taken into account. Mathematical processing of the sets of analyses was carried out using the Statistica 5.0 program [*Borovikov and Borovikov,* 1997].

On the Possible Grain Size Dependence of Spinel Compositions

When compiling the data base for spinel chemical compositions, it caught our attention that different authors cite appreciably dissimilar chromite compositions for the same kimberlite pipes. Thus, [*Bobrievich et al.,* 1964; *Garanin et al.,* 1980; *Sobolev et al.,* 1975] listed partial and complete compositions of spinels for the Mir, Aikhal, and Udachnaya pipes of the Yakutian kimberlite province, which we compared to I. P. Ilupin's unpublished data (Table 1). Grains to be analyzed were taken from concentrates or from hand samples; *Bobrievich et al.* [1964] give results obtained by wet chemistry from a large number of grains, while the rest of the data come from PCM measurements. It is readily apparent that Al and Ti have appreciable ranges of variation. *Sobolev et al.* [1975] surmised that deviations from the data of [*Bobrievich et al.,* 1964] are due to differences in beneficiation and spinel separation techniques. However, the same sampling procedures, when used by other workers, yielded strongly dissimilar results. The cause of these discrepancies, to our mind, remains unclear.

A study on chromian spinel compositions in ultramafites of the Kempirsai massif was used to demonstrate that in the grain size range between <40 μm to 400 μm, Cr and Ti contents decrease with grain size [*Pustotsvetov et al.,* 1992]. This effect is especially conspicuous in grains of <200 μm. In peridotites of the Miamori massif and in nodules from basalts of Ichinomegata crater, the Mg-number of spinels was shown to depend on grain size, with spinel Cr-number remaining virtually constant [*Ozawa,* 1983]. In order to further verify the grain-size dependence of spinel compositions, we correlated data obtained for grains ranging 0.2–0.4 mm (n = 26) and 0.6–0.9 mm (n = 20) from the Yakutskaya (eastern part), Aerosyemochnaya, Ukrainskaya (Daldynskoe field) and Zapolyarnaya (Munskoe field) pipes. Average values and standard deviations for each oxide proved to be closely similar in both data sets (Table 2). Hence, for grains in the range 0.2–0.9 mm, no grain-size dependence for spinel composition has been established.

Compositional grouping of chromian spinels

A review of published data shows that the main parameters used in compositional classifications for chromian spinels are their #Cr = Cr/(Cr+Al), #Mg = $Mg/(Mg+Fe^{+2})$, and proportion of ferric iron $\#Fe^{+3} = Fe^{+3}/(Fe^{+3}+Cr+Al)$ [*Basu and Mac Gregor,* 1975; *Bazylev,* 1995; *Dick and Bullen,* 1984; *Irvine,* 1967; *Rasskazov and Genshaft,* 1987; *Roeder,* 1994; *Sack and Ghiorso,* 1991]. Diagrams plotted on these parameters as a reference frame discriminate spinel fields for deep-seated nodules, alpine-type and stratiform peridotites [*Irvine,* 1967], and alpine-type and abyssal ultramafites [*Dick and Bullen,* 1984], also demarcating compositional fields of spinels from kimberlites and alkaline basalts [*Basu and Mac Gregor,* 1975]. A variety of studies have shown spinel compositions, primarily #Cr and #Mg, to be defined largely by the type of their host ultramafites. According to *Dick and Bullen* [1984], spinel composition depends first of all on melt composition and crystallization pressure—i.e., it is a function of the degree of mantle melting. These workers identified three rock groups as to spinel composition, with #Cr<0.6 (Group I), #Cr>0.6 (Group III), and Group II, with #Cr transitional between the values characteristic of Groups I and III. An essential distinction between Group I and Group III peridotites is whether or not the restite contains clinopyroxene. Based on this criterion, abyssal peridotites belong to Group I. Group III comprises alpine-type peridotites only, albeit some of them can be classed with Group I. It is shown that 70% of abyssal peridotites dredged from mid-ocean ridges are plagioclase-free spinel harzburgites and lherzolites. Mineralogically and texturally, these resemble the pertinent alpine-type peridotites and are interpreted as crystalline residues after partial melting of ultramafic mantle material. Judging by CIPW norms for clinopyroxene, which point to the melting degree, alpine-type peridotites are more refractory than abyssal peridotites.

Different genetic types of peridotites, including those from ophiolite assemblages metamorphosed in the amphibolite facies, have been discussed in [*Bazylev,* 1995; *Bazylev and Kamenetsky,* 1998]. Spinel composition is indicative of formative conditions for these rocks. Thus, a case study on Macquarie Island ophiolite, SW Pacific, exemplifies variations in #Cr, #Fe^{+3}, and TiO_2 in spinels from spinel- and plagioclase harzburgites, plagioclase cumulate peridotites, and olivine orthopyroxenites. In terms of spinel #Cr, the rocks encompass all three groups delineated in [*Dick and Bullen,* 1984]. *Bazylev and Kamenetsky* [1998] analyzed the effect of redox conditions on spinel composition at different stages of metamorphic recrystallization of ultramafic rocks.

Spinel compositions specific to kimberlitic sources are delimited in [*Bushueva et al.,* 1991], and for a broader range of rocks, including non-kimberlitic sources (ultramafic nodules in basalts), in [*Matsyuk et al.,* 1989]. It is shown that, overall, with an appreciable overlap of spinel compositions in rocks of the series dunite–harzburgite–lherzolite, increase in the proportion of pyroxenes (especially, clinopyroxene) leads to a decrease in #Cr and an increase in #Mg of the mineral in point [*Matsyuk et al.,* 1989; *Roeder,* 1994]. This is particularly notable when correlating different types of ultramafites from the same kimberlite deposit (e.g., Udachnaya pipe). *Dawson* [1983] reports inverse relations between ultramafite types and spinel compositions, with spinel #Cr being highest in lherzolites and lowest in harzburgites.

Spinels associated with diamonds make the highest-Cr group [*Fipke,* 1994; *Sobolev,* 1974]. A recent study [*Vaganov et al.,* 1999) was dedicated to chromian spinels as indicators for the appraisal of diamond potential of rocks based on analysis of a data bank for spinel compositions from kimberlites, lamproites, komatiites, meymechites, certain types of basalts, and alpine-type peridotites. The scope of that study was limited to the discussion of data presented in terms of #Fe^{+3}–#Fe^{+2}, #Cr–#Fe^{+2}, Cr_2O_3–MgO, and some other diagrams; it focused solely on the character of variation trends for chromites from different rock assemblages without identifying the genetic nature of these trends. It is shown that the use of a number of diagrams affords the delineation of the fields for spinels from kimberlites and lamproites, including the discrimination between diamondiferous and diamond-free types of rocks.

Table 2. Chemical compositions of spinels of different grain sizes from kimberlitic pipes of the Yakutian province (wt %)

Oxide	Grain size, mm	
	0.2–0.4	0.6–0.9
TiO_2	3.01 1.57	2.29 1.84
Al_2O_3	12.55 6.56	12.75 6.77
Cr_2O_3	43.64 6.93	46.03 6.69
FeO*	24.20 2.29	22.51 3.16
MnO	0.30 0.08	0.31 0.08
MgO	14.84 1.59	14.60 1.24
n	26	20

A number of studies [*Bagdasarov,* 1983; *Bagdasarov and Poroshin,* 1980; *Bagdasarov et al.,* 1979] address compositional features of chromian spinels from various mafite-ultramafite rocks, including ultramafites of Kamchatka and the Maimecha–Kotui region, Kilauea basalts, Archean komatiites, Guli dunite-peridotite intrusion, Uralian and Sikhote Alin picrites, layered intrusions, alpine-type massifs, and kimberlites. On #Cr–#Mg and #Fe^{+3}–#Mg plots, various rock assemblages are shown to have both overlapping fields of spinel compositions and distinctions in terms of their fields and variation trends. Relatively limited analytical data are used to draw important conclusions on how spinel compositions depend on bulk rock composition, crystallization depth and temperature, and oxidation conditions. The tenet of the "early igneous" variation trend for spinel compositions, as inferred from experimental data [*Hill and Roeder,* 1974] on positive correlation between #Cr and #Mg, is further supported. Negative correlation, according to [*Bagdasarov et al.,* 1979], is inherent in spinels from alpine-type ultramafites, peridotite xenoliths in kimberlites, and constituent minerals of kimberlites proper.

Noteworthy is the review of *Roeder* [1994], who analyzed a voluminous data bank comprising some 17,000 spinel analyses from all types of terrestrial rocks and meteorites. This study addresses the nature of variability of spinel compositions and certain traits of spinel compositions from igneous and metamorphic rocks.

Compositions of chromian spinels were used to classify mantle peridotites [*Palandzhyan and Dmitrenko,* 1989; *Poroshin,* 1988] and a large group of volcanic rocks and peridotites from a range of tectonic structures [*Young Il Lee,* 1999] with respect to tectonic setting.

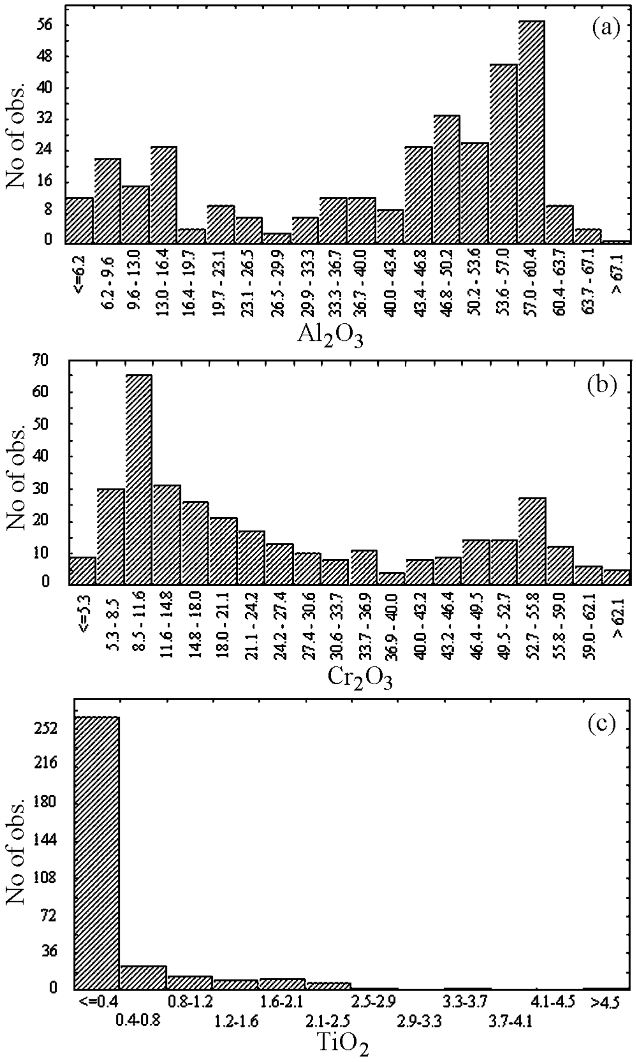

Figure 1. Histograms of Al_2O_3 (a), Cr_2O_3 (b), and TiO_2 (c) contents in spinels from ultramafic nodules in basalts.

Results

As is seen from histograms and binary plots for spinel components, in each group there exist individual populations of spinels with distinctive compositional regularities. This is manifest in the non-monomodal distribution of particular oxides and in the multiplicity of covariation trends for different components. Thus, spinels from nodules in basalts have bimodal distributions of Al_2O_3 (maxima at 5–17% and 55–60%), Cr_2O_3 (maxima at 5–10% and 50–55%), and, possibly, TiO_2 (maxima at <0.05% and 1.5–2%) (Figure 1). The clearly bimodal distribution of Al_2O_3 is apparent for spinels from ultramafic massifs as well (maxima at 7–9% and 50–55%) (Figure 2), each maximum (or mode) having distinctive, normal or log-normal (or asymmetric) distributions. In binary diagrams Al_2O_3–MgO and Cr_2O_3–MgO for spinels from ultramafic massifs (Figure 3), two trends are also evident: high Mg contents are positively correlated to Al and negatively, to Cr, whereas high-Cr grains are distinguished by positive correlation of Mg with Cr, while Mg contents are relatively low. Two trends are seen clearly in the diagram FeO*–Cr_2O_3 (Figure 4a) as well. Likewise, two trends are seen in a similar diagram for spinels from nodules in basalts (Figure 4b). Evidently, in each group spinels from rocks that have experienced different histories—igneous, metamorphic, etc.—are present. Spinels from the diamond assemblage are more uniform as compared to the other groups. Yet even

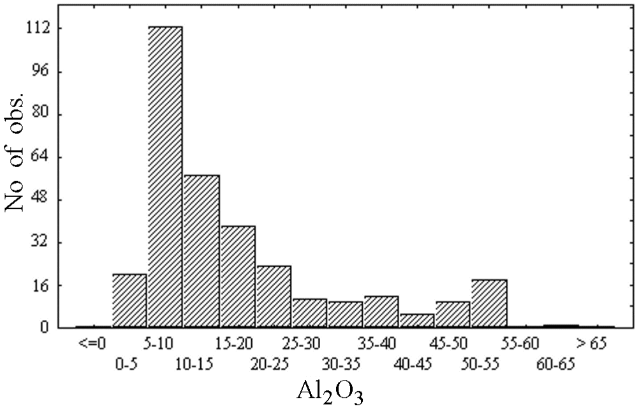

Figure 2. Histogram of Al_2O_3 contents in spinels from ultramafic massifs.

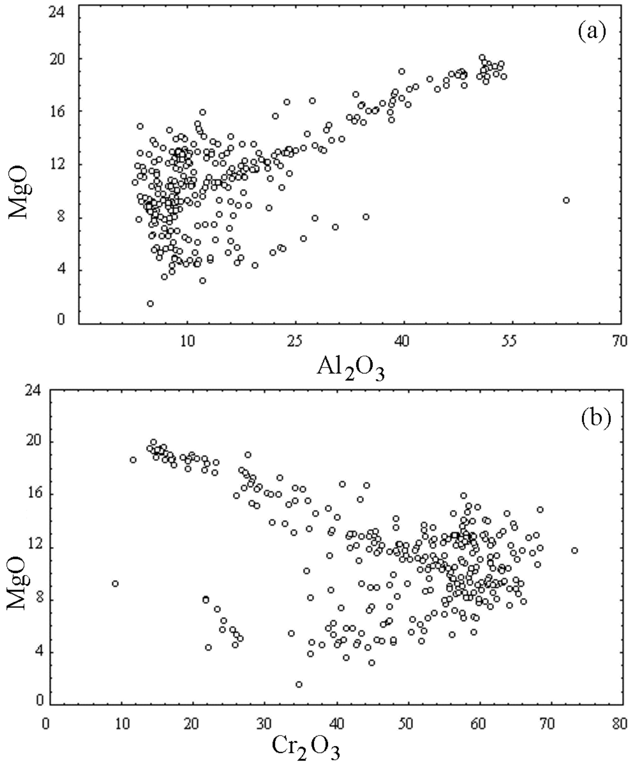

Figure 3. Covariations of Al_2O_3 vs. MgO (a) and Cr_2O_3 vs. MgO (b) contents in spinels from ultramafic massifs.

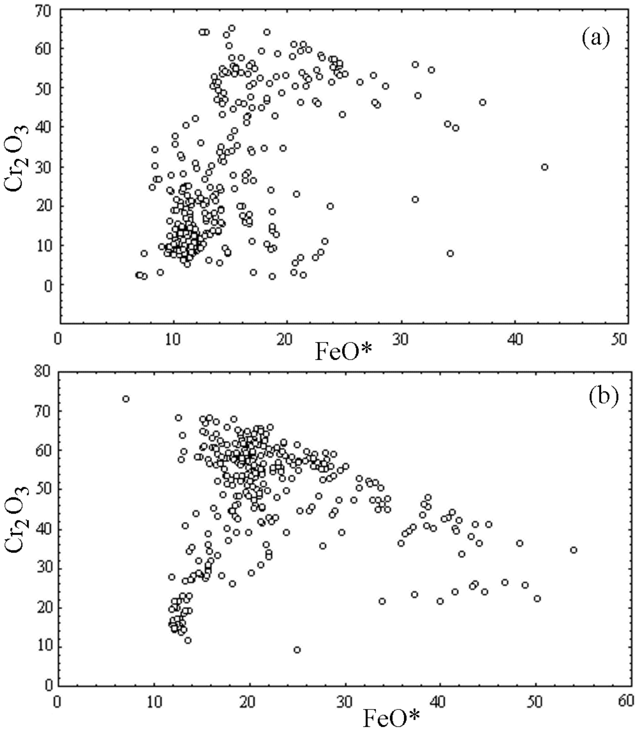

Figure 4. Covariations of FeO* vs. Cr_2O_3 contents in spinels from ultramafic nodules in basalts (a) and in ultramafic massifs (b).

in this case, one can note the non-uniformity of relationships between components such as Cr_2O_3–FeO*, Cr_2O_3–MgO, TiO_2 vs. the other oxides, Al_2O_3–MgO, etc.

Clusterization of compositions in each of the five groups shows that, alongside large clusters, i.e., those incorporating large numbers of analyses, there are small clusters, which comprise 1 to 10 compositions. For this reason, clusterization was carried out so as to obtain at least three large clusters. In each group, thus, a specific clusterization step was selected. Small clusters were rejected from further consideration. Overall, in each of the five groups, proportions of those analyses that entered small clusters are 6% for spinels from massifs, 17.6% for spinels from "basalts," 5% for spinels from "kimberlites," 23.6% for spinels from "lamproites," and 29.4% for "diamond" spinels. The proportion of large to small clusters is as follows: spinels from massifs, 7 to 10; spinels from "basalts," 10 to 22; spinels from "kimberlites," 9 to 12; spinels from "lamproites," 4 to 5; and "diamond" spinels, 3 to 11.

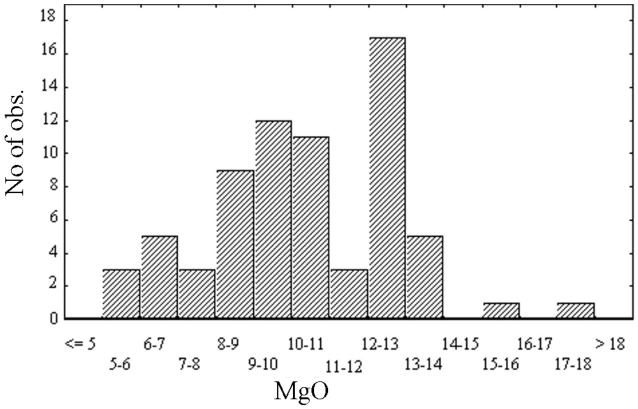

Figure 5. Histogram of MgO contents in spinels from one of the clusters of the group of chromites from ultramafic massifs (n = 70).

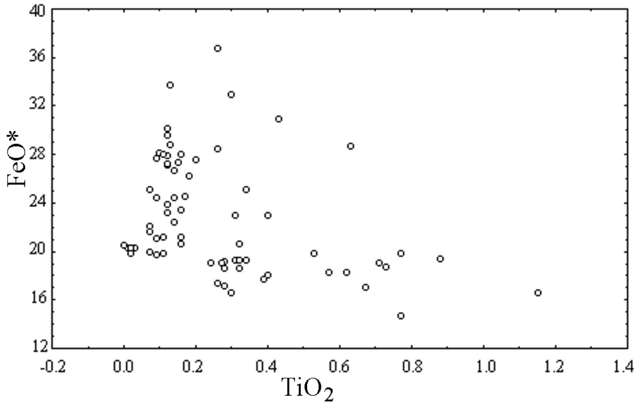

Figure 6. Covariations of TiO_2 vs. FeO* contents in spinels from one of the clusters of the group of chromites from ultramafic massifs (n = 70).

Large clusters obtained through the above procedure are not quite uniform. Thus, one cluster for spinels from massifs (n = 70) has a bimodal distribution of MgO (Figure 5) and, possibly, two trends in the TiO_2–FeO* diagram (Figure 6). Within a group, different clusters have different correlationships between oxides. However, one should note that these correlations are persistent enough. Thus, in the group of spinels from massifs, all the clusters exhibit a marked negative correlation in the pairs FeO*–MgO, Cr_2O_3–Al_2O_3, and, in most clusters, Cr_2O_3–FeO*. In a number of instances, Cr_2O_3 and MgO are positively correlated. Such relationships exist in the clusters for "basaltic" spinels. For certain clusters, no significant correlations are to be observed, so that one can discuss mere tendencies towards correlations between one or another oxide (e.g., in the groups of spinels from "lamproites" and "diamonds").

Cluster and factor analyses enabled us to identify the most significant compositional components responsible for spinel variability in each particular group and in individual clusters. In this context, the groups of spinels of the kimberlitic, lamproitic, and diamond types can be contrasted with spinels of alpine-type massifs and the basalt type. In the former group, compositional variability is due mainly to changes in #Mg and abundances of iron (ferric, ferrous, and total), whereas the latter is characterized primarily by variations in Cr and Al contents. This feature is clearly seen from the factor load diagram in the first/second factor coordinates, where joint contribution of both factors to compositional variability of spinels is 85% (Figure 7). Table 3 lists factor analysis results from each of the 5 groups, including

Table 3. Factor analysis results for chromian spinels of 5 groups

Group	Number of clusters	Factor	Contrib. %	Significant components
Massifs	17	F1	38.6	Mn, Fe–Mg
		F2	31.8	Al–Cr
		F3	17.5	–Ti
Basalts	32	F1	62.6	Cr–Al, Mg
		F2	18.8	Ti, Mn, Fe–(Mg)
Kimberlites	21	F1	41.5	Mg–Fe, Ti
		F2	27.6	Al–Cr
Lamproites	9	F1	68.1	Ti, Mn, Fe–Mg
		F2	22.7	Cr–Al
Diamonds	14	F1	48.6	Al–Cr
		F2	27.9	Fe–Mg

large and small clusters alike. One can see that each group has its distinctive features of spinel composition variations, with compositional components having different contributions to these variations. Overall, it can be ascertained that all the spinels in point are characterized primarily by isomorphic replacements of Al for Cr and of Mg for Fe, which is in perfect agreement with the previously published data of various workers. Spinels from kimberlitic and lamproitic sources, often including high-Ti varieties, are distinguished by their compositional variability being largely due to contribution from Ti variations.

Clusterization of the entire set of compositions (n = 1821) yielded 40 clusters, of which 6 accommodate over 100 analyses each, and 10, between 10 and 100. Diamond-related spinels entered chiefly the 5 large clusters (89% of the entire sample). In none of the clusters, however, did they constitute a majority of analyses. The relationships are as follows: Cluster 1, a total of 166 analyses, including 64 diamond-related, 61 kimberlitic, 23 from massifs, 15 lamproitic, and 3 basaltic; Cluster 2, a total of 39 analyses, including, in the same order, 18, 11, 5, 3, and 2; Cluster 3, a total of 148 analyses, including 11, 86, 39, 15, and 7; Cluster 4, a total of 246 analyses, including 26, 118, 86, 8, and 8; and Cluster 5, a total of 41, including, respectively, 6, 9, 19, 0, and 7. A more appreciable contribution to certain large clusters comes from kimberlitic and basaltic types of spinel. Thus, the cluster with n = 367 has 321 kimberlitic spinels (29 lamproitic, 4 diamond-related, 11 basaltic, and 2 from massifs); in the cluster with n = 16, all the spinels are kimberlitic in type (the highest-Ti ones having 4.58% TiO_2); both clusters are distinguished by high TiO_2. In the cluster with n = 185, the basaltic type is represented by 160 analyses (in addition, 17 are from massifs, 7 are kimberlitic, and 1 is lamproitic type). One cluster (n = 32) consists almost wholly of spinels from massifs (n = 30; and 2 are kimberlitic-type).

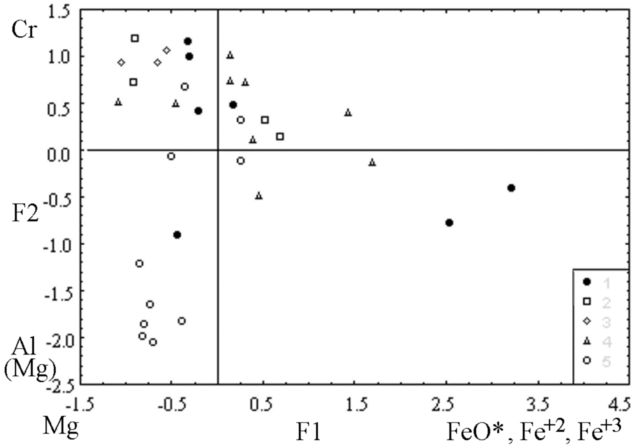

Figure 7. Component diagram for factor loads of spinels from large clusters of 5 groups, in F1–F2 coordinates. Plotted along the axes are compositional components contributing most heavily to compositional variability of spinels. Clusters for spinel groups from: 1 – ultramafic massifs, 2 – lamproites, 3 – diamonds, 4 – kimberlites, 5 – basalts.

More clear distinctions between spinels from different groups were revealed through the clusterization of large clusters, isolated in each of the 5 groups (a total of 33; Table 4). In this case, a large group of basaltic clusters fell away distinctly, while diamond-related spinels merged together with kimberlitic, lamproitic, and those from alpine-type massifs (Figure 8). It was only one cluster of spinels with the highest

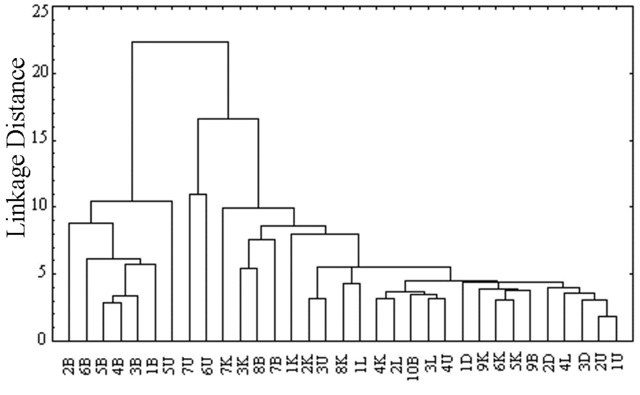

Figure 8. Hierarchical dendrogram for clusters of spinels of 5 groups. Symbols, as in Table 3.

Table 4. Mean chemical compositions (wt %) and major-element parameters of spinels from large clusters of 5 groups

Cluster	TiO_2	Al_2O_3	Cr_2O_3	Fe_2O_3	FeO	MnO	MgO	#Cr	#Mg	$\#Fe^{+3}$
1u	0.07	6.17	62.78	3.74	17.18	0.13	10.39	0.87	0.52	0.05
2u	0.03	5.35	63.65	3.59	16.34	0.47	10.49	0.89	0.53	0.05
3u	0.12	14.70	53.32	4.75	15.02	0.38	12.63	0.71	0.60	0.06
4u	0.32	11.47	53.77	5.95	17.21	0.30	10.79	0.76	0.53	0.07
5u	0.07	37.23	29.65	3.39	12.11	0.25	16.57	0.35	0.71	0.04
6u	1.01	16.74	35.62	15.57	22.15	0.49	8.31	0.59	0.40	0.20
7u	0.25	10.38	40.52	17.72	25.51	0.69	4.87	0.72	0.25	0.23
1b	0.33	53.09	12.97	2.83	11.53	0.08	18.96	0.14	0.75	0.03
2b	0.17	44.55	24.20	1.84	9.92	0.14	19.02	0.27	0.77	0.02
3b	0.12	59.39	8.54	1.37	8.98	0.20	21.06	0.09	0.81	0.01
4b	0.12	56.64	9.67	2.75	8.63	0.01	20.93	0.10	0.81	0.03
5b	0.13	56.81	11.47	1.08	9.95	0.05	20.29	0.12	0.78	0.01
6b	0.01	50.18	17.54	2.82	9.55	0.01	19.85	0.19	0.79	0.03
7b	0.22	21.96	45.78	4.23	12.61	0.24	14.90	0.58	0.68	0.05
8b	1.98	17.56	44.98	6.21	15.45	0.26	13.62	0.63	0.61	0.08
9b	1.12	8.78	58.03	4.75	14.33	0.24	13.01	0.82	0.62	0.06
10b	0.41	9.29	54.58	8.04	16.08	0.01	11.57	0.80	0.56	0.10
1l	0.55	11.50	58.33	2.30	12.84	0.17	13.85	0.77	0.66	0.03
2l	2.87	9.10	49.82	8.55	16.67	0.21	12.39	0.79	0.57	0.11
3l	0.80	10.75	51.52	7.52	17.17	0.34	10.79	0.76	0.53	0.10
4l	0.13	5.17	64.98	2.42	13.67	0.28	12.19	0.89	0.61	0.03
1d	0.11	5.95	63.66	3.95	10.76	0.13	14.,23	0.88	0.70	0.05
2d	0.17	5.40	60.26	4.51	12.35	0.33	12.31	0.88	0.64	0.06
3d	0.92	5.44	62.53	3.27	14.90	0.31	11.95	0.89	0.59	0.04
1k	4.28	7.62	45.56	12.02	18.57	0.47	11.76	0.80	0.53	0.17
2k	0.66	12.78	53.40	4.03	13.75	0.28	13.02	0.74	0.63	0.05
3k	1.65	19.78	41.16	8.71	14.49	0.14	14.39	0.58	0.64	0.10
4k	2.36	10.77	49.83	7.81	15.32	0.14	13.15	0.76	0.60	0.10
5k	2.73	6.36	55.94	5.65	16.35	0.63	12.00	0.86	0.57	0.08
6k	0.92	7.59	57.67	6.59	15.35	0.67	11.89	0.84	0.58	0.08
7k	1.70	2.92	53.43	11.81	19.31	0.38	8.97	0.92	0.45	0.16
8k	0.22	11.62	56.89	3.91	9.87	0.02	15.34	0.77	0.73	0.05
9k	2.14	5.18	59.38	4.92	15.52	1.03	11.90	0.88	0.58	0.07

u – ultramafic massifs, b – basalts, l – lamproites, d – diamonds, k – kimberlites; #Cr = Cr/(Cr+Al), #Mg = $Mg/(Mg+Fe^{+2})$, $\#Fe^{+3} = Fe^{+3}/(Fe^{+3}+Cr+Al)$.

#Cr from basaltic nodules that fell in this group. Overall, this is in keeping with the position of diamond clusters in the factor load diagram in F1–F2 coordinates (Figure 7), where these clusters plot in a tight group at the intersection of variation trends for basaltic spinels and spinels from massifs on the one hand and for kimberlitic and lamproitic groups of clusters, on the other, in the region of highest-Cr varieties. Closely similar results were obtained in [*Afanasiev et al.,* 1998] by correlating spinel compositions from ultramafic intrusions, kimberlites, and lamproites, although the listed average Cr_2O_3 content in spinels of the diamond assemblage is highest. Generally, a large overlap area exists between chromite compositions from "crustal" (intrusions) and "mantle" (kimberlites, lamproites, diamonds) sources. Basaltic clusters are characterized chiefly by high-Mg and low-Cr types of spinel. Spinels with the highest #Fe prove to be found in ultramafic massifs.

Discussion

Average spinel compositions of the 5 groups, standard deviations, and minimum and maximum values of each component (Table 5), all indicate that the most uniform group of spinels is the one associated with diamonds. Their closest counterpart in terms of Cr_2O_3, FeO^*, and MgO contents is spinels from lamproites. Spinels from nodules in basalts differ most strongly from the rest of the groups in having the highest #Mg and Al and the lowest Cr abundances.

A number of workers proposed rather long ago that spinels have a variety of origins in different rocks [*Paneyakh,* 1989; *Prikhodko,* 1980; *Zhelyazkova-Panayotova,* 1971]. Discussion focuses mainly on the processes of high-temperature crystallization of spinel in equilibrium with melt and/or solid–solid phase transformations at a range of physicochem-

Table 5. Mean chemical compositions and standard deviations for spinels of 5 groups

Oxides	Massifs	Basalts	Kimberlites	Lamproites	Diamonds
TiO_2	0.19 0.32 0–3.02	0.46 0.80 0–4.96	1.92 1.87 0–8.84	1.39 1.60 0–4.91	0.32 0.59 0–3.98
Al_2O_3	17.52 13.92 2.74–62.39	40.32 18.80 2.81–70.52	12.40 10.10 0.82–64.36	13.40 10.99 1.82–51.83	6.23 3.39 1.26–26.91
Cr_2O_3	47.43 14.68 9.11–73.22	26.12 18.07 2.15–65.30	49.40 10.52 2.14–66.43	51.60 11.07 17.58–69.76	63.43 5.11 40.43–71.70
FeO^*	22.26 8.38 7.10–53.98	14.75 5.41 6.92–42.62	21.18 6.09 2.11–51.6	18.89 6.06 8.97–43.14	16.11 4.14 9.59–33.60
MnO	0.36 0.19 0–0.89	0.14 0.17 0–1.27	0.38 0.23 0–1.98	0.24 0.22 0–1.73	0.26 0.17 0–0.87
MgO	11.42 3.98 1.55–20.04	17.70 3.59 2.80–25.13	13.11 2.42 2.79–22.34	12.94 3.07 0.47–21.56	12.69 2.36 0.49–17.28
n	318	340	928	106	129

Each cell gives, from top to bottom, mean composition, standard deviation, and range of values. n, number of analyses.

ical conditions at depth. Accordingly, spinels of various compositions are shown to be genetically linked to different types and assemblages of rocks, from refractory dunites and harzburgites to igneous rocks such as picrite and alkaline ultramafites, including kimberlites and lamproites. As noted above, positive correlation of #Cr and #Mg in spinel suggests igneous origin for it. Negative correlation, intrinsic in spinels from most alpine-type massifs, points to a variety of processes of solid–solid phase transformation in rocks. Spinel recrystallization in ultramafic nodules from alkaline basalts under the influence of high-temperature fluids or melts increases the #Cr and reduces the #Mg of primary grains—i.e., it stays with this particular trend of subsolidus transformations [*Genshaft et al.,* 1989; *Rasskazov and Genshaft,* 1987]. Overall, the variation of spinel compositions from basaltic clusters clearly follows the metamorphic trend, which is consistent with subsolidus equilibrium temperatures for peridotite nodules from basalts and with the particularly low equilibrium temperatures for the pair olivine-spinel (T<1000°C). For the rest of the groups, one can conjecture the existence of two correlation trends, i.e., a polygenetic character of spinels, resultant from both igneous and metamorphic origins of the mineral. The ternary diagram MgO–Cr_2O_3–FeO^* clearly illustrates the above (Figure 9). In the Al–Cr diagram (Figure 10), the region of clusters of high-Cr spinels from kimberlites, lamproites, and ultramafic massifs also exhibits trends characteristic of igneous spinels.

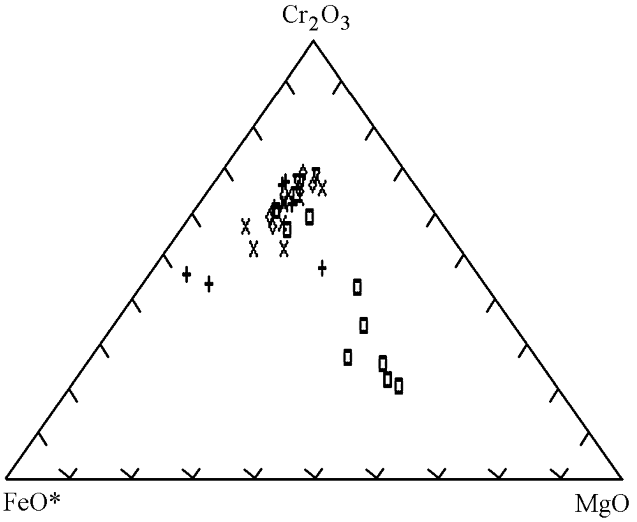

Figure 9. Position of spinel compositions for large clusters of 5 groups in the diagram MgO–Cr_2O_3–FeO. 1 – ultramafic massifs, 2 – basalts, 3 – kimberlites, 4 – lamproites, 5 – diamonds.

Experimental data point to a strong dependence of spinel #Cr on oxygen fugacity [*Hill and Roeder,* 1974]: increase in pO_2 causes a decrease in Cr_2O_3, a slight decline in Al_2O_3, and a strong increase in the proportion of ferric iron and #Mg of spinel crystallizing from basaltic melt at T = 1200°C. With increasing crystallization pressure, Cr content decreases and Al increases in spinel crystallizing at a constant composition of the melt [*Bazylev,* 1995; *Dick and Bullen,* 1984]. It has been demonstrated using case studies on basaltic and kimberlitic melts [*Roeder,* 1994] that the composition of crystallizing medium and changes in oxygen fugacity during crystallization bear strongly on the resultant spinel composition.

Positive correlation of Cr and Fe^{+3}, noted earlier in the study of spinels from peridotite nodules in Transbaikalian basalts [*Rasskazov and Genshaft,* 1987], is clearly apparent for the entire set of basaltic clusters (Figure 11). The rest of the clusters, however, generally adhere to an inverse dependence, the lower-Cr, higher-Fe spinels having higher oxidation degrees. The content of ferric iron is proportionate to that of ferrous iron (and, consequently, to the total iron content). Such a relationship is easy to explain by spinel formation in the process of igneous differentiation in melt, accompanied by Cr depletion, Fe enrichment, and progressively increasing oxidation potential. The totality of evidence is thus suggestive of igneous origin for the ultramafites associated with the genesis of kimberlites and lamproites and with diamond crystallization. This notion is consistent with the correlations between compositions of spinels from concentrates and of their kimberlite hosts, reported recently by one of the present authors [*Ilupin,* 1997]. At the same time, one cannot but note that high-Ti, high-Fe spinels are clearly confined to within brecciated peridotites in kimberlites [*Matsyuk et al.,* 1989], which, in addition, are affected strongly enough by mantle metasomatism [*Genshaft,* 1993]. Therefore, the combination of igneous, metamorphic, and metasomatic processes overprinting the ultramafic material of cratonized lithosphere, is responsible for the spectrum of compositions and major-element correlationships exhibited by spinels from kimberlites, lamproites, and alpine-type massifs.

According to the spinel classification proposed in [*Palandzhyan and Dmitrenko,* 1989], a large group of clusters of basaltic spinels represents subcontinental mantle rocks (lherzolites and diopside harzburgites), least depleted in basaltic components. The suboceanic type (#Cr = 0.25–0.5), or Group I—the main body of abyssal peridotites [*Dick and Bullen,* 1984]—is represented virtually by a single cluster of spinels from alpine-type massifs. The rest of the clusters, or the bulk of alpine-type peridotites of Group III of the same authors, belong chiefly to the island-arc type (#Cr = 0.6–0.9), comprised of extremely depleted, olivine-rich harzburgites. The transitional type from oceanic to island-arc deep seated material (#Cr = 0.5–0.6) is portrayed by 2 basaltic clusters, 1 kimberlitic cluster, and 1 cluster for spinels from massifs. Therefore, spinel compositions from ultramafic rocks of continental structures imply that at depth beneath these structures, there exist physicochemical conditions of crystallization typical of all the principal tectonic features of the earth—continents, oceans, and transition zones (island arcs).

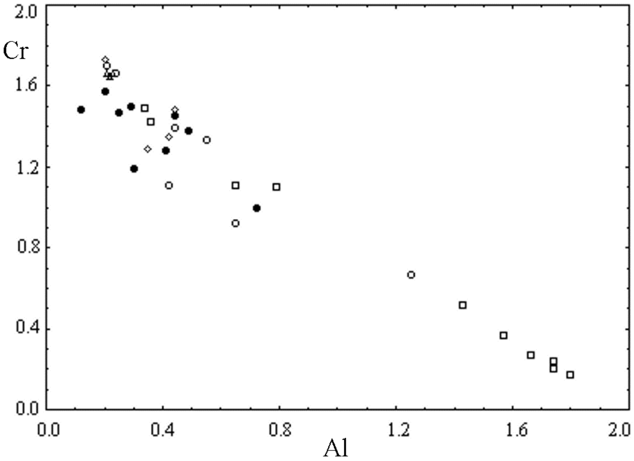

Figure 10. Covariations of Al vs. Cr contents in spinels from large clusters of 5 groups. Symbols, as in Figure 7.

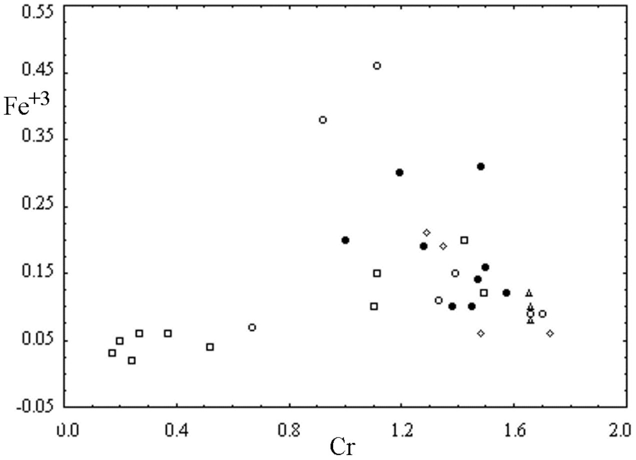

Figure 11. Covariations of Cr vs. Fe^{+3} contents in spinels from large clusters of 5 groups. Symbols, as in Figure 7.

In conclusion, we must emphasize once again (i) the detached character of most spinel-bearing rocks associated with basalts and (ii) the marginal position of spinel compositions from diamonds in the majority of diagrams. In terms of bulk chemical composition, the closest counterpart to diamond-related spinels is spinels from lamproites. The greatest contribution to compositional variability of spinels of different groups comes from isomorphic replacement of Al for Cr and of Fe for Mg.

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