

LETTER

**Structural parameters of chromite included in diamond and kimberlites from Siberia:
A new tool for discriminating ultramafic source**

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ABSTRACT

Siberian chromite included in diamond, kimberlite, and spinel peridotite as well as Cr-spinel from garnet-spinel peridotite have been studied by single-crystal X-ray diffraction and electron microprobe analysis. Cell edges and oxygen positional parameters, u , of chromite in diamond and in kimberlite are comparable (cell edge, 8.3249–8.3390 Å; u , 0.26175–0.26213). The structural parameters of chromite in the spinel peridotite are similar to those of chromite grains from ophiolitic complexes, and those of Cr-spinel from garnet-spinel peridotite are comparable to those of Cr-spinel in lherzolitic mantle xenoliths. With the exception of the chromite in garnet-spinel peridotite, all analyzed spinels have a high Cr content. Recasting the chemical analyses according to spinel stoichiometry reveals negligible or no Fe³⁺. Chrome spinel may be present in heavy concentrates derived from serpentinized mafic and ultramafic rocks as the sole surviving primary mineral and, as such, their particular structural and chemical parameters may represent a new prospecting tool for discriminating the ultramafic source.

Keywords: Siberia, diamond, chromite, crystal chemistry

INTRODUCTION

Cr-spinels are typical accessory minerals in a wide variety of ultramafic rocks including dunite, harzburgite, and lherzolite from a variety of different geological settings. Cr-spinel also is a common accessory mineral in graphite- and diamond-bearing garnet-peridotite xenoliths in kimberlite (Sobolev et al. 1984; Pearson et al. 1994). These disaggregated xenoliths are the source of the chromite macrocrysts in kimberlite concentrates. Chromite is also a typical inclusion in diamond (Sobolev 1977; Meyer 1987) associated with inclusions of olivine, subcalcic Cr-pyrope, and enstatite.

Kimberlite xenoliths contain some extremely Cr-rich chromite grains, and some of the most Cr-rich chromite grains found in nature are present as inclusions in diamond (Barnes and Roeder 2001). These chromites show high Cr/(Cr + Al), low ferric iron, and low TiO₂ (Barnes and Roeder 2001) and represent the so-called “kimberlite trend,” a trend of increasing Fe³⁺ and TiO₂ at nearly constant Cr/(Cr + Al). They also maintain nearly constant Fe²⁺/(Fe²⁺ + Mg) over a wide range in Fe³⁺ (Barnes and Roeder 2001). The increase in Ti is a consequence of the increased tendency of Ti to partition into spinels with higher magnetite contents. Accessory chromite has been studied from several xenoliths of megacrystalline diamondiferous harzburgite, dunite, and kimberlite from Yakutia (Republic of Russia), the data for which are summarized by Sobolev et al. (1984), Sobolev and Yefimova (1998), and Sobolev and Logvinova (2005). Their compositional variation is narrow with Cr/(Cr + Al) within the range 80–95 and Mg/(Fe²⁺ + Mg) within 50–75 (Sobolev et al. 2004; Sobolev and Logvinova 2004, 2005).

Several geological occurrences of Cr-bearing spinel have

been studied by others to determine their structural parameters (Della Giusta et al. 1986; Princivalle et al. 1989; Carbonin et al. 1996; Carraro 2003; Bosi et al. 2004; Uchida et al. 2005; Lenaz et al. 2004a, 2007), but this is the first such study concerning chromite grains included in diamond.

GEOLOGICAL SETTING

The diamond deposits of Siberia (Russia) compose the Yakutian kimberlite province, located in the northwestern region of the Siberian craton (Fig. 1¹). About 1000 kimberlite bodies of a wide range of emplacement ages from Early Paleozoic to Late Mesozoic are known within several kimberlite fields. However, all commercial diamond deposits including the Udachnaya mine (Daldyn kimberlitic field, close to Arctic Circle), the Mir and Internatsionalnaya mines (Malo-Botuobiya kimberlite field, about 500 km to the south) are all of Upper Devonian-Early Carboniferous age (e.g., Sobolev et al. 2004). The Obnazhennaya barren pipe of Upper Jurassic age is located farther north within the Kuoika kimberlite field (e.g., Sobolev 1977). All samples studied herein are from the Udachnaya, Mir, Internatsionalnaya high-grade diamond mines, and the barren pipe of Obnazhennaya.

EXPERIMENTAL METHODS

X-ray diffraction data were recorded on an automated KUMA-KM4 (K-geometry) diffractometer, using MoK α radiation, monochromatized by a flat graphite

¹ Deposit item AM-09-034, Figure 1, map. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

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crystal, at the University of Trieste (Italy). Data collection was made, according to Della Giusta et al. (1996), up to 55° of 2θ in the ω-2θ scan mode, scan width 1.8° 2θ, counting time from 20 to 50 s depending on the peak standard deviation. Twenty-four equivalent reflections of (12 8 4) peak, at about 80° of 2θ, were accurately centered at both sides of 2θ, and the α₁ peak baricenter was used for cell parameter determination. Corrections for absorption were performed according to North et al. (1968). Structural refinement using the SHELX-97 program (Sheldrick 1997) was carried out against F_o in the Fd3m space group (with origin at 3m), since no evidence of different symmetry appeared. Refined parameters were the scale factor, oxygen positional parameter (u), tetrahedral and octahedral site occupancies, and isotropic atomic displacement parameters (U). Scattering factors were taken from the *International Tables for Crystallography* (Ibers and Hamilton 1974) and Tokonami (1965). The neutral scattering curves, Mg vs. Fe in the tetrahedral (T) site and Cr vs. Al in octahedral (M) site, were assigned to sites involved in isomorphous replacements, with the constraints of full site occupancy, whereas

oxygen was considered to be in a partly ionized state (70%). No constraints were imposed by chemical analyses. Crystallographic data are listed in Table 1.

Ten to 15 spot analyses were performed on the same crystals used for X-ray data collection, using a CAMECA-CAMEBAX electron microprobe operating at 15 kV and 15 nA. A 20 s counting time was used for both peak and total background. Synthetic oxide standards (MgO, FeO, MnO, ZnO, NiO, Al₂O₃, Cr₂O₃, TiO₂, and SiO₂) were used. Raw data were reduced by PAP-type correction software provided by CAMECA. The chemical analyses are presented in Table 2.

The cation distribution (Table 2) between the T and M sites was obtained with the method described by Carbonin et al. (1996) and Lavina et al. (2002), in which crystal-chemical parameters are calculated as a function of the atomic fractions at the two sites and fitted to the observed parameters. Site atomic fractions were calculated by minimizing the function F(x) (Table 2), which takes into account the mean of the square differences between calculated and observed parameters, divided by their squared standard deviations.

TABLE 1. Refined structural parameters for chromite and Cr-spinel

Type	DI	DI	DI	DI	K	K	SP	GSP	GSP
Sample	UDK1	UDK3	UDK4	UDK 5	Inter-1	Mr-1a	UV-170	O-119	O-601
a (Å)	8.33273(8)	8.3264(3)	8.3266(3)	8.3249(2)	8.3293(3)	8.3390(2)	8.3055(1)	8.1821(3)	8.17149(7)
u	0.2621(1)	0.26175(8)	0.26198(8)	0.26203(8)	0.26213(8)	0.26197(9)	0.26237(9)	0.26299(9)	0.26302(4)
T occ.	0.42(2)	0.370(8)	0.41(1)	0.39(1)	0.47(2)	0.44(1)	0.39(2)	0.234(8)	0.245(6)
M occ.	0.91(3)	0.89(1)	0.90(2)	0.91(2)	0.89(2)	0.89(2)	0.79(3)	0.321(6)	0.274(6)
m.a.n. X-ray	64.0(1.7)	62.8(7)	63.4(1.1)	63.6(1.8)	64.2(1.2)	64.1(1.1)	60.8(1.5)	48.4(2)	47.5(3)
m.a.n. EPMA	64.0	63.2	63.4	62.9	63.9	63.8	61.6	48.5	47.6
U(M) (Å ²)	0.0037(1)	0.00323(8)	0.00460(8)	0.0041(1)	0.00407(9)	0.0054(2)	0.0031(1)	0.00489(7)	0.00429(7)
U(T) (Å ²)	0.0058(3)	0.0051(2)	0.0069(2)	0.0064(2)	0.0065(2)	0.0079(2)	0.0052(2)	0.0068(1)	0.0062(1)
U(O) (Å ²)	0.0052(3)	0.0048(2)	0.0063(2)	0.0058(3)	0.0056(2)	0.0070(2)	0.0052(2)	0.00764(9)	0.0071(1)
No. refl.	170	170	162	163	180	176	179	172	168
R _{int} (%)	5.61	9.19	7.04	11.28	5.88	12.58	5.92	5.04	4.96
R1 (%)	2.49	2.09	1.98	1.87	2.13	2.23	2.50	1.39	1.70
wR2 (%)	5.85	3.65	3.81	3.77	4.11	4.44	5.66	2.58	2.66
GooF	1.163	1.210	1.167	1.019	1.274	1.046	1.252	1.283	1.283
EXTI	0.072(5)	0.013(1)	0.0025(6)	0.022(2)	0.008(1)	0.087(5)	0.060(5)	0.091(4)	0.082(5)

Notes: m.a.n. = mean atomic number; U(M), U(T), U(O) = isotropic displacement parameters for M site, T site, and O (Å²); No. refl. = number of reflections; R_{int} (%), R1 (%), wR2 (%), GooF, and EXTI as defined in Sheldrick (1997). The estimated standard deviations are in parentheses. Symbols for samples: DI = chromite inclusions in diamonds; K = chromite in kimberlites; SP = chromite in spinel-peridotite; GSP = Cr-spinel in garnet-spinel peridotite; UDK and UV = Udachnaya mine; Inter = Internatsionalnaya mine; Mr = Mir mine; O = Obnazhennaya pipe.

TABLE 2. Mean chemical analyses and cation distribution in T and M sites of the analyzed chromite and Cr-spinel

Type	DI	DI	DI	DI	K	K	SP	GSP	GSP
Sample	UDK1	UDK3	UDK4	UDK 5	Inter-1	Mr-1a	UV-170*	O-119*	O-601*
MgO	11.4(2)	12.2(2)	11.9(2)	12.3(2)	11.0(1)	11.5(2)	11.9(2)	18.17(5)	18.0(2)
Al ₂ O ₃	4.79(7)	5.7(1)	5.54(5)	6.26(9)	5.78(8)	5.50(8)	10.3(1)	41.6(3)	44.6(2)
TiO ₂	0.15(3)	0.08(2)	0.50(4)	0.01(1)	0.14(2)	1.42(2)	0.05(2)	0.23(2)	0.21(3)
Cr ₂ O ₃	65.9(7)	65.8(5)	65.1(7)	64.4(4)	64.0(6)	58.5(2)	62.1(7)	28.9(4)	25.1(4)
MnO	0.34(5)	0.27(6)	0.30(7)	0.27(6)	0.33(5)	0.33(5)	0.30(6)	0.08(6)	0.13(3)
FeO _{tot}	17.2(2)	16.2(2)	16.4(3)	15.5(2)	18.4(3)	21.3(3)	15.3(3)	10.4(2)	10.7(3)
NiO	0.08(6)	0.09(6)	0.06(4)	0.11(5)	0.09(4)	0.11(5)	0.07(5)	0.32(7)	0.24(8)
Sum	99.86	100.16	99.8	98.85	99.74	98.66	100.02	99.7	98.98
FeO	15.1(2)	14.2(2)	14.9(2)	13.6(2)	15.8(3)	15.9(3)			
Fe ₂ O ₃	2.25(8)	2.29(9)	1.64(8)	2.17(9)	2.8(1)	6.00(1)			
Sum	100.01	100.30	99.94	99.12	99.94	99.26			
T site									
Mg	0.567(8)	0.587(7)	0.563(7)	0.591(8)	0.519(6)	0.522(6)	0.567(9)	0.675(8)	0.648(5)
Al		0.039(2)	0.026(1)	0.016(1)		0.023(1)	0.022(1)	0.096(2)	0.110(2)
Mn	0.009(1)	0.007(2)	0.008(2)	0.008(2)	0.009(2)	0.009(1)	0.008(2)	0.009(1)	0.003(1)
Fe ²⁺	0.401(6)	0.366(6)	0.402(7)	0.373(6)	0.434(8)	0.430(8)	0.404(6)	0.229(4)	0.239(5)
Fe ³⁺	0.022(5)			0.012(4)	0.037(6)	0.015(2)			
M site									
Mg		0.014(1)	0.025(1)	0.018(1)	0.029(2)	0.052(2)	0.010(1)	0.083(3)	0.097(2)
Al	0.190(3)	0.183(4)	0.193(2)	0.230(3)	0.228(3)	0.196(3)	0.375(4)	1.263(9)	1.337(7)
Ti	0.004(1)	0.002(1)	0.013(1)		0.004(1)	0.036(1)	0.001(1)	0.005(1)	0.004(1)
Cr	1.75(1)	1.721(8)	1.72(1)	1.701(8)	1.70(1)	1.560(7)	1.60(1)	0.631(8)	0.544(7)
Fe ²⁺	0.022(1)	0.022(1)	0.008(1)	0.005(1)	0.007(1)	0.015(5)	0.011(1)	0.012(1)	0.013(1)
Fe ³⁺	0.034(6)	0.056(7)	0.041(8)	0.042(7)	0.032(5)	0.137(7)			
Ni†				0.003(1)	0.002(1)	0.003(1)		0.007(2)	0.006(2)
F(x)	0.219	0.356	0.382	0.084	0.127	0.249	0.175	0.113	0.283

Notes: F(x) = minimization factor that takes into account the mean of the square differences between calculated and observed parameters, divided by their squared standard deviations. The estimated standard deviations are in parentheses. Type symbols for sample are identical to those in Table 1.

* Fe₂O₃ is not present.

† Nickel cation distribution is not reported when the standard deviation on chemistry is higher than the half of the mean value.

RESULTS

The structural parameters of chromite present as diamond inclusions and chromite grains in kimberlite are similar to each other. The analyzed chromite grains enclosed in diamond show cell edges and oxygen coordinate parameters that range from 8.3249(2) to 8.33273(8) Å and 0.26175(8) to 0.26213(11), respectively (Table 1), whereas those from kimberlite range from 8.3293(3) to 8.3390(2) Å and 0.26197(9) to 0.26213(8) (Table 1).

Two Cr-spinels from a garnet-spinel peridotite have also been analyzed. They have cell edges of 8.17149(7) and 8.1821(3) Å and oxygen positional parameters equal to 0.26302(4) and 0.26299(9), respectively (Table 1). Structural parameters of these spinels are similar to those for Cr-spinels found in lherzolite mantle xenoliths (Della Giusta et al. 1986; Princivalle et al. 1989; Carraro 2003; Uchida et al. 2005). The Cr-spinel studied from a spinel peridotite has a cell edge equal to 8.3055(1) Å and oxygen parameter equal to 0.26237(9) (Table 1).

The chromite grains included in diamond are characterized by high Cr content (1.701–1.749 apfu), Mg in the range 0.568–0.610 apfu, Fe²⁺ between 0.378 and 0.422 apfu, Ti between 0.001 and 0.036 apfu, and Al between 0.191 and 0.246 apfu (Table 2). Ferric iron, calculated on the basis of spinel stoichiometry and structural refinement, ranges from 0.042 and 0.057 apfu. The cation distribution is ordered with Mg and Fe²⁺ in the T site and Al in the M site (inversion degree close to 0), respectively.

The chemistry of chromite grains in kimberlite is variable. Sample Inter-1 (Cr 1.697; Fe²⁺ 0.441) resembles the spinel found as diamond inclusions, while Mr-1a is depleted in Cr (1.560) and enriched in Fe³⁺ (0.152). This variation in spinel chemistry seems to reflect the so-called “kimberlite trend” noted by Sobolev (1977) and Barnes and Roeder (2001), which consists of increasing Fe³⁺ and TiO₂ at nearly constant Cr/(Cr + Al) ratio and Mg/(Fe²⁺ + Mg) ratio over a wide range in Fe³⁺. Titanium increase is a consequence of the increased tendency of Ti to partition into spinels with higher magnetite content. The chromite from spinel peridotite has high Cr (1.603 apfu), and lower total iron and higher Al₂O₃. It is virtually Fe³⁺ free. The chemistry of Cr-spinels from garnet-spinel peridotites is quite different from the spinels discussed above. They are Al-rich spinels (up to 1.447 apfu) with MgO (~0.745) prevailing over FeO (~0.245). Also, in this case, Fe³⁺ is absent.

The cation distributions of chromite grains from kimberlite and spinel peridotite as well as the one Cr-spinel from garnet-spinel peridotite are highly ordered with Mg and Fe²⁺ in the T site and Al in the M site, respectively.

DISCUSSION

The structural parameters of the spinels studied here are plotted in Figure 2. For comparison, the figure also shows the structural parameters of spinel from lherzolite mantle xenoliths worldwide (Della Giusta et al. 1986; Princivalle et al. 1989; Carraro 2003; Uchida et al. 2005), websterite dikes and lherzolite in the Balmuccia peridotite complex (Basso et al. 1984) and lherzolite in the Ronda peridotite massif (Lenaz, unpubl. data), ophiolites (Bosi et al. 2004), layered complexes (Bushveld, Lenaz et al. 2007; Stillwater, Lenaz et al. unpubl. data), and Uralo-Alaskan complexes (Lenaz, unpubl. data). The structural parameters of synthetic spinel along the MgAl₂O₄-FeAl₂O₄ join (Andreozzi and Lucchesi 2002)

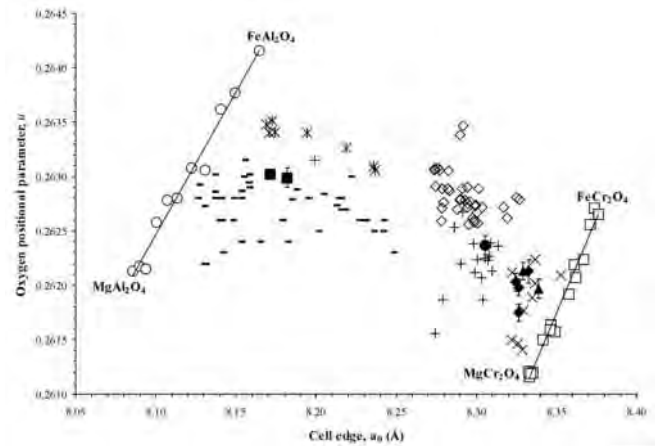


FIGURE 2. Oxygen positional parameter, u vs. cell edge, a_0 (Å). Solid diamonds = chromite included in diamond (this study); solid triangles = chromite in kimberlite (this study); solid circles = chromite in spinel peridotite (this study); solid squares = Cr-spinel in garnet-spinel peridotite (this study); asterisks = Cr-spinel from Balmuccia mantle peridotite and dikes (Basso et al. 1984) and Ronda peridotites (Lenaz, unpubl. data); dashes = Cr-spinel from mantle xenoliths worldwide (Della Giusta et al. 1986; Princivalle et al. 1989; Carraro 2003; Uchida et al. 2005); plus signs = Cr-spinel in ophiolites (Bosi et al. 2004); open diamonds = chromite from the Bushveld (Lenaz et al. 2007) and Stillwater layered complexes (Lenaz, unpubl. data); crosses = chromite in the Uralo-Alaskan complex (Lenaz, unpubl. data); open circles = synthetic spinel along the MgAl₂O₄-FeAl₂O₄ join (Andreozzi and Lucchesi 2002); open squares = synthetic spinel along the MgCr₂O₄-FeCr₂O₄ join (Lenaz et al. 2004b).

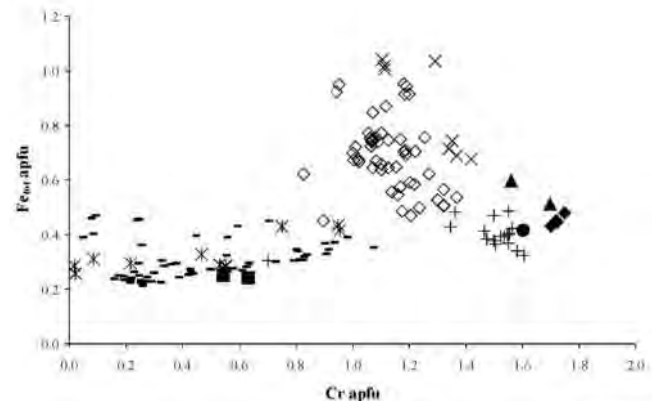


FIGURE 3. Fe_{tot} atoms per formula unit (apfu) vs. Cr apfu. Symbols are as presented in Figure 2.

and FeCr₂O₄-MgCr₂O₄ (Lenaz et al. 2004b) are also plotted.

It is evident that the structural parameters for chromite grains enclosed in diamond and within kimberlite are close to those found for synthetic spinels along the FeCr₂O₄-MgCr₂O₄ join. This suggests that changes in structural parameters (both cell edge and oxygen coordinate) must be considered as a consequence of limited Mg ↔ Fe²⁺ variations within the T site, since the M site is filled almost entirely by a high concentration of Cr (up to 1.749 apfu) at a nearly constant Al content.

The structural parameters of chromite from spinel peridotite fall in the field of ophiolitic spinel within harzburgite (Bosi et al. 2004). The structural parameters of Cr-spinel from garnet-spinel peridotite are similar to Cr-spinel from lherzolitic mantle xenoliths.

Ahmed et al. (2005) and Sobolev and Logvinova (2005)

pointed out that, in many cases, ultramafic rocks including kimberlite, lamproite, and peridotite of orogenic massifs are heavily serpentinized and that such alterations present difficulties in identifying the presence of olivine and pyroxene. On the contrary, chrome spinel may be present in heavy concentrates as the sole-surviving primary mineral. We have found that the compositional features of accessory chromite grains from xenoliths in granular peridotite and chrome spinel from kimberlite and lamproite heavy concentrates display a wide range in Mg/(Fe²⁺ + Mg) content (50–80) and Cr/(Cr + Al) content (20–90) similar to those of other chromite occurrences (Barnes and Roeder 2001; Kamenetsky et al. 2001; Nowicki et al. 2007). However, diamonds within kimberlite and lamproite are thought to be perfect containers that prevent primary mineral inclusions from retrograde changes. Accordingly, Sobolev and Logvinova (2005) suggested that useful information regarding the metamorphic history of serpentinite may be obtained from inclusions of sulfides and other minerals. A systematic study of accessory chrome spinel containing silicate and other mineral inclusions may be important for the identification of serpentinite paragenesis.

This study illustrates that the structural parameters of chromite grains could be a new tool for discriminating among different ultramafic source rocks (as already demonstrated for detrital Cr-spinels in sandstones; Lenaz and Princivalle 2005). Figure 2 shows that the studied chromite grains plot in a field quite different from other ultramafic sources such as those of Cr-spinel from ophiolites, layered intrusions, and mantle xenoliths. The only overlap is with chromite grains from Uralo-Alaskan complexes. When combined with EMPA, this approach may narrow down the source. Figure 3 is a plot of Cr vs. Fe_{tot} of chromite grains from diamond and kimberlite and those from Uralo-Alaskan complexes. The iron enrichment present in Uralo-Alaskan spinels (Barnes and Roeder 2001) is absent in our samples. Although the occurrence of native diamond in deep-seated garnetiferous xenoliths and kimberlites does not require reducing conditions, calculations indicate that high Fe³⁺ contents are stabilized in the garnet structure and that *f*₀₂ decreases with increasing depth (Wood et al. 1990). Consequently, Fe³⁺ content in chromite grains included in diamond and kimberlites is very low (and in spinel- and garnet-peridotite is absent), whereas it is high in chromite from the Uralo-Alaskan complex (Barnes and Roeder 2001).

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