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Zn-Chromspinels of Middle Timan and the Near-Polar Urals

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Presented by Academician N.P. Yushkin March 17, 2005

Received April 5, 2005

The analysis of indicator-minerals from differentaged terrigenous rocks with a potential for native diamond prospects and intermediate collectors has revealed an interesting feature of the composition of accessory chromspinels: an anomalous Zn content that is tens or even hundreds of times higher than that in chromspinels from Alpine-type ultrabasic rocks [2, 3]. In addition to the typical Zn-poor varieties of chromspinels, xenomorphous grains and octahedral crystals (ZnO 1–27%) and gahnite ZnAl₂O₄ (Zn-spinel) were detected in some places. The Zn-bearing chromspinels have already been detected in the following four areas of Middle Timan: (1) Middle Devonian conglobreccia horizon in the Vol'sk-Vymsk Range (Ichet"yu diamond prospect) [4–7]; (2) Paleogene weathering crust in manganese prospects and Quaternary alluvial sediments along the entire eastern slope of the Chetlas Kamen Plateau; (3) Middle Jurassic sandstones of the Sysol Formation in the northern Ukhta area [8]; and (4) lamprophyre dikes in the Chetlas Kamen Plateau. In addition, we found Zn-rich chromspinels in Upper Cambrian-Lower Ordovician sandstones (Al'kesvozh Formation) at upper reaches of the Balban'yu River. Two small (0.1–0.3 mm) octahedral diamond crystals were also detected in prospecting drifts in this area. The native source and genesis of Znchromspinels found in different areas and settings [6-9] have long remained a puzzle. An elucidation of these aspects would have been helpful in solving the problem of the native sources of diamond.

The composition and morphology of chromspinels and other indicator-minerals were studied by the routine procedure using a JSM-6400 SEM microanalyzer equipped with the energy-dispersive Link ISIS-300. The representative chemical analyses of Znchromspinels from four areas are presented in Table 1, and their recalculations into crystallochemical coefficients are presented in Table 2.

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We investigated a panned sample taken from the productive conglobreccia horizon in Middle Devonian sandstones of the Ichet"yu diamond prospect. The sample has a variable mineral composition. Ilmenite, rutile, anatase, and leucoxene are the major minerals. Rare metal and rare earth minerals are represented by zircon, ilmenorutile, columbite, monazite, kularite, and xenotime. Chromspinels, pyrite, gold, and curvifaced diamond crystals are rare [4, 5]. The major and accessory minerals of local metamorphic rocks are represented by garnets (almandine, pyrope-almandine, grossular, and others), staurolite, tourmaline, disthene, amphibole, magnetite, and hematite. Chromspinels are present in the heavy fraction as black and brown irregular, less common octahedral and cuboctahedral crystals with different grades of roundedness (Fig. 1). The surface is smooth (bright in black octahedral crystals and corroded in rounded brown grains). The individual grain size varies from 0.2 to 0.6 mm (average 0.45 mm). The average content of chromspinels in the heavy concentrate is 1-2% (maximum 30 g/cm³). The content of chromspinels in the diamondiferous horizon is correlated with the contents of monazite, kularite, columbite, and rutile. The content of chromspinels also shows a qualitative positive correlation with the concentration of diamond. The chromspinels are mainly represented by aluminous varieties, such as chrompicotite, alumochromite, and subferrialumochromite (Tables 1, 2; Fig. 2). Based on an examination in the SEM Compo regime, we discovered pale rims of Zn-rich chromspinels on the surface of many chromspinel grains (Figs. 1a, 1b).

We investigated panned samples of Paleogene weathering crust and recent alluvium taken from the eastern slope of the Chetlas Kamen Plateau (some of these samples were kindly placed at our disposal by the geologists from Ukhta V.A. Lebedev and N.V. Povonskaya). Results of the comprehensive study of nearly 20 heavy fractions (Tables 1, 2; Fig. 2) show that chromspinels in these samples are similar to those described above in terms of chemical composition, mineral assemblage (ilmenite, rutile, ilmenorutile, columbite, monazite, and xenotime), and major silicates. The Zn-rich rim is developed on the surface of nearly 50% of chromspinel grains.

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Ord. no.	Oxides, wt %										Coefficients	
	FeO	MgO	MnO	NiO	ZnO	Cr ₂ O ₃	Al ₂ O ₃	TiO ₂	V ₂ O ₅	Fe ₂ O ₃	ΣFe	MCr
1	20.51	0	0.88	0	12.64	48.25	4.40	1.49	0.00	11.82	31.15	1.55
2	26.85	0	0	0	7.43	48.01	8.66	1.13	0.98	6.94	33.10	1.45
3	25.25	3.75	0	0	4.19	48.01	16.78	0.46	0	1.56	26.66	1.80
4	27.79	0	0	0	7.17	45.35	13.98	0.57	0.36	4.77	32.08	1.41
5	21.88	0	1.43	0	12.09	44.00	8.84	3.69	0.56	7.51	28.64	1.54
6	29.55	0	0.87	0	4.95	44.13	17.21	0.73	0	2.56	31.85	1.39
7	27.01	4.51	0	0	1.72	44.98	20.15	0.80	0	0.83	27.76	1.62
8	24.83	1.15	0	0	9.84	40.63	22.04	0.36	0	1.15	25.87	1.57
9	25.63	2.26	2.60	0	3.81	38.95	19.57	0.49	0	6.70	31.66	1.23
10	24.77	0	0.81	0	11.09	35.79	22.02	1.05	0	4.46	28.79	1.24
11	25.64	2.81	0.58	0	6.47	32.90	27.20	0.53	0	3.88	29.13	1.13
12	26.96	0.14	0.26	0	6.30	56.29	5.71	0.95	0.75	2.65	29.34	1.92
13	27.81	0.04	0.27	0.03	5.88	56.27	7.43	1.10	0.73	0.43	28.20	2.00
14	27.33	0	0.44	0.14	6.26	52.25	7.99	1.29	0.96	3.32	30.32	1.72
15	27.41	0	0.20	0.11	6.48	51.63	8.04	1.30	0.76	4.07	31.08	1.66
16	27.27	0.01	0.66	0.02	5.71	49.00	6.31	0.94	0.75	9.34	35.67	1.37
17	27.30	0.12	0.37	0	6.06	45.85	7.61	1.01	1.01	10.67	36.91	1.24
18	24.15	2.30	0.30	0.30	8.75	34.49	26.20	0.46	0.10	2.95	26.81	1.29
19	22.14	6.26	0.34	0	5.51	32.67	31.08	0.59	0	1.40	23.41	1.40
20	11.72	16.30	0.28	0.32	0.12	28.99	33.51	0.54	0.31	7.90	18.83	1.54
21	22.86	0.21	2.82	0.27	6.31	23.39	3.42	0.31	0	40.41	59.23	0.39
22	28.20	0.83	0.74	0.07	1.04	65.77	3.04	0.14	0.17	0	28.20	2.33
23	21.14	6.90	0.38	0.10	1.22	58.17	11.70	0.17	0.22	0	21.14	2.75
24	22.05	6.44	0.46	0.30	1.00	49.27	9.28	0.65	0.04	10.51	31.51	1.56
25	27.28	3.36	1.40	0.03	1.09	47.59	17.13	0.35	0	1.77	28.87	1.65
26	27.63	1.70	0.88	0.52	1.32	46.62	5.54	0.35	0.09	15.35	41.45	1.12
27	24.11	4.69	0.73	0.18	1.18	44.03	7.30	1.04	0	16.73	39.17	1.12
28	29.12	2.01	1.21	0	1.48	48.57	16.51	0.31	0.44	0.35	29.44	1.65
29	25.70	3.55	0.84	0.25	1.00	39.85	6.57	1.14	0.15	20.95	44.55	0.89
30	21.47	6.82	1.09	0	2.31	36.60	18.22	1.21	0.34	11.94	32.22	1.14
31	4.69	2.52	0.12	0	34.95	0	55.67	0	0	2.06	6.54	0
32	7.38	1.78	0.61	0	32.99	0	57.15	0	0	0.08	7.45	0
33	3.10	0.25	8.59	0	21.75	62.67	0.48	0.13	0.16	2.87	5.68	11.03
34	15.95	2.03	7.67	0	5.68	61.42	6.76	0.09	0.41	0	15.95	3.85
35	17.15	2.24	8.09	0	4.99	59.24	7.90	0	0.23	0.16	17.30	3.42
36	12.98	2.01	6.26	0	11.87	58.86	7.59	0	0.19	0.24	13.19	4.46
37	10.02	3.49	6.30	0.05	11.61	56.74	11.66	0.12	0.01	0	10.02	5.66
38	8.64	3.15	6.15	0	13.94	56.34	11.37	0	0.40	0	8.64	6.52
39	10.75	3.18	6.80	0	12.43	55.18	11.39	0.11	0.06	0.09	10.83	5.10
40	11.76	3.35	7.92	0	9.15	54.86	12.63	0	0.33	0	11.76	4.66
41	10.88	2.54	11.40	0.08	8.31	52.85	12.08	0.06	0.08	1.72	12.42	4.26
42	1.39	0.09	5.97	0	27.36	50.05	7.81	0.06	0.10	6.67	7.39	6.77
43	8.10	0	4.30	0.19	23.81	45.45	15.68	0	0	2.49	10.34	4.40
44	0.09	0	0.19	0	38.70	0.02	61.00	0	0	0	0.09	0.22

Table 1. Chemical composition of Zn-chromspinels in Middle Timan and the Near-Polar Urals

Note: Chromspinels: (1–11) Middle Devonian conglobreccia horizon, Vol'sk–Vymsk Range, Ichet"yu prospect; (12–19) Paleogene Mnbearing weathering crust, eastern slope of the Chetlas Kamen Plateau; (20, 21) zonal grain of accessory chromspinel from lamprophyre vein, Chetlas Kamen Plateau; (22–32) Middle Jurassic sandstones, Ukhta area [8]; (33–44) sandstones, Al'kesvozh Formation (Upper Cambrian–Lower Ordovician), Near-Polar Urals [6]. $\Sigma Fe = FeO + 0.9Fe_2O_3$ (Fe modulus); *M*Cr = Cr₂O₃/ ΣFe (Cr modulus).

Ord. no.	Name	Formula coefficients										
		Fe ²⁺	Mg ²⁺	Mn ²⁺	Ni ²⁺	Zn ²⁺	Cr ³⁺	Al ³⁺	Ti ⁴⁺	V ⁵⁺	Fe ³⁺	<i>к</i> ₀ ге
1	Fe-SAFC	5.039	0	0.220	0	2.742	11.206	1.523	0.659	0.000	2.612	1.929
2	FeSFAC	6.430	0	0	0	1.570	10.869	2.923	0.488	0.226	1.495	4.301
3	Fe-AC	5.669	1.501	0	0	0.830	10.190	5.310	0.185	0.000	0.315	17.99
4	FeSFAC	6.515	0	0	0	1.485	10.052	4.619	0.242	0.082	1.005	6.483
5	Fe-SFSA	5.148	0	0.340	0	2.512	9.789	2.933	1.561	0.126	1.591	3.236
6	FeAC	6.793	0	0.202	0	1.005	9.590	5.576	0.304	0.000	0.530	12.82
7	Fe-AC	5.911	1.757	0	0	0.332	9.307	6.215	0.316	0.000	0.163	36.26
8	Fe-AC	5.584	0.461	0	0	1.955	8.637	6.985	0.145	0.000	0.233	23.96
9	FeSFAC	5.751	0.902	0.592	0	0.755	8.262	6.188	0.197	0.000	1.353	4.251
10	Fe-SFAC	5.600	0	0.185	0	2.214	7.649	7.016	0.428	0.000	0.907	6.174
11	Fe-CP	5.553	1.084	0.126	0	1.236	6.736	8.301	0.208	0.000	0.755	7.355
12	FeSFC	6.528	0.062	0.063	0	1.346	12.887	1.949	0.412	0.174	0.577	11.31
13	FeChr	6.667	0.018	0.065	0.007	1.244	12.752	2.511	0.476	0.168	0.093	71.79
14	FeSFC	6.538	0	0.107	0.033	1.322	11.815	2.692	0.556	0.221	0.715	9.145
15	FeSFC	6.559	0	0.047	0.026	1.368	11.677	2.712	0.559	0.175	0.877	7.480
16	FeSFC	6.607	0.004	0.162	0.005	1.221	11.226	2.154	0.409	0.175	2.037	3.244
17	FeSAFC	6.572	0.051	0.089	0.000	1.288	10.435	2.582	0.438	0.233	2.312	2.842
18	Fe-CP	5.286	0.896	0.066	0.063	1.690	7.135	8.080	0.182	0.022	0.582	9.088
19	Fe-CP	4.600	2.319	0.071	0	1.010	6.416	9.100	0.222	0.000	0.262	17.54
20	MgSFCP	2.260	5.604	0.055	0.060	0.021	5.286	9.103	0.189	0.048	1.371	3.856
21	Fe-SACM	5.729	0.095	0.715	0.065	1.396	5.540	1.209	0.139	0	9.111	0.608
22	FeChr	7.180	0.377	0.191	0.017	0.234	14.877	1.024	0.060	0.039	0	0
23	Fe-Chr	4.832	2.812	0.088	0.023	0.246	12.222	3.663	0.070	0.046	0	0
24	Fe-SFAC	5.017	2.611	0.106	0.065	0.201	10.598	2.974	0.267	0.009	2.152	2.33
25	FeChr	6.117	1.342	0.318	0.007	0.216	10.089	5.413	0.141	0	0.357	17.16
26	FeSAFC	6.656	0.728	0.214	0.120	0.281	10.617	1.881	0.152	0.021	3.328	2.00
27	FeSAFC	5.604	1.942	0.171	0.041	0.242	9.674	2.391	0.436	0	3.499	1.60
28	FeAChr	6.612	0.814	0.278	0	0.296	10.424	5.282	0.126	0.096	0.072	91.55
29	FeSAFC	6.047	1.489	0.201	0.056	0.207	8.865	2.180	0.483	0.035	4.436	1.36
30	Fe-SFSA	4.672	2.645	0.240	0	0.443	7.530	5.589	0.473	0.07	2.339	2.00
31	ZnSpl	0.935	0.894	0.024	0	6.147	0	15.632	0	0	0.368	2.54
32	ZnSpl	1.465	0.631	0.123	0	5.781	0	15.986	0	0	0.014	106.7
33	MnZnChr	0.788	0.114	2.213	0	4.885	15.072	0.173	0.060	0.039	0.657	1.199
34	MnZnChr	3.945	0.894	1.922	0	1.239	13.634	2.236	0.039	0.092	0	0
35	MnZnChr	3.111	0.858	1.519	0	2.513	13.338	2.565	0	0.044	0.052	59.83
36	Fe-Chr	4.066	0.947	1.942	0	1.045	13.275	2.638	0	0.053	0.034	119.6
37	MnZnChr	2.108	1.370	1.520	0	3.002	12.230	3.681	0	0.089	0	0
38	MnZnChr	2.434	1.513	1.550	0.012	2.490	12.209	3.739	0.060	0.002	0	0
39	MnZnChr	2.510	1.321	1.607	0	2.562	12.174	3.747	0.047	0.014	0.019	132.1
40	MnZnAC	2.780	1.414	1.895	0	1.910	11.858	4.069	0	0.073	0	0
41	MnZnSFC	0.469	0.040	1.500	0	5.991	11.734	2.723	0.027	0.024	1.488	0.315
42	MnZnAC	2.533	1.054	2.687	0.018	1.708	11.632	3.965	0.025	0.018	0.360	7.036
43	MnZnAC	1.925	0	1.035	0.043	4.998	10.216	5.253	0	0	0.532	3.618
44	ZnSpl	0.020	0	0.045	0	7.935	0.004	15.996	0	0	0	0

Table 2. Results of the recalculation of microprobe analysis of Zn-chromspinels into crystallochemical coefficients

Note: (Fe) Ferro; (Fe-) Fe-bearing; (Mg) magnesium; (Chr) chromite; (AC) alumochromite; (CP) chrompicotite; (SFC) subferrichromite; (SFAC) subferrialumochromite; (SAFC) subalumoferrichromite; (SFSA) subferrisubalumochromite; (SFCP) subferrichrompicotite; (SACM) subalumochrommagnetite; (ZnSpl) gahnite (Zn-spinel); (MnZnChr) manganozincochromite; (MnZnAC) manganozincoalumochromite; k_0 Fe = Fe²⁺/Fe³⁺.



Fig. 1. SEM images of chromspinels from the Ichet"yu ore prospect (Vol'sk–Vymsk Range, Middle Timan). Polished sections, Compo regime. One can see partially eroded pale Zn-rich rim.

The heavy fraction of Middle Jurassic rocks of the Sysol Formation is composed of the zircon–garnet or staurolite–zircon–garnet assemblage [8]. The yield of heavy fraction in the samples increases from 23 g/m³ in fine-grained varieties to 885 g/m³ in coarse-grained varieties (gritstones and conglomerates with the clayey matrix from the variegated kaolinite clays). Pyrite is often abundant. It is remarkable that the content of chromspinels in the heavy concentrate (8–28%)



Fig. 2. Data points of Zn-chromspinels in the N.V. Pavlov ternary diagram. Chromspinels of Middle Timan: (1) Conglobreccia horizon, Ichet"yu diamond prospect; (2) weathering crust and alluvium on the eastern slope of the Chetlas Kamen Plateau; accessory zonal chromspinel; (3) lamprophyres in the Chetlas Kamen Plateau (arrow connects data points of compositions in the core and rim); (4) Middle Jurassic terrigenous rocks in the Syuz'yu River; (5) Mn–Zn-chromites in terrigenous rocks of the Upper Cambrian-Lower Ordovician Al'kesvozh Formation (the Near-Polar Urals).

decreases to 1-7% in samples from the upper parts of sections. The yield of chromspinels is as much as 109.7–185.8 g/m³. The content of chromspinels increases in all sections north of Ukhta, where basalts of the Sysol Formation are exposed. Uvarovite, pyropes (including the knorringite end member), monazite, florencite, xenotime, and moissanite are observed as rare minerals associated with chromspinels. A halo with a high content of chromspinels extends over 6 km along the Syuz'yu River. It is worth noting that small octahedral chromspinel crystals are very well preserved and are diverse in composition. Their smooth faces lack any signs of roundedness or wear [8]. The chromspinels are divided into the high-Cr (probably related to the diamondiferous dunite association), high-alumina (harzburgite-lherzolite association), and high-Fe (metamorphic association) varieties.

Accessory chromspinels from terrigenous rocks of the Upper Cambrian–Lower Ordovician Al'kesvozh Formation (Maldynyrd Plateau, Near-Polar Urals) in the Al'bov Ridge area, which is located on the left bank of the upper reaches of the Balban'yu River and its tributary (Al'kesvozh Creek), have very unusual compositions (Tables 1, 2; Fig. 2). The terrigenous rocks are composed of inequigranular sandstones with gritstone and conglomerate interlayers containing a constant but minor amount of chromspinels. The terrigenous rocks are underlain by diaspore–pyrophyllite shales that represent the Upper Cambrian weathering crust formed after the underlying (Vendian–Proterozoic) rhyolites and gabbroids [6]. The sample of diaspore–pyrophyllite shales yielded small (80–100 μ m) octahedral crystals



Fig. 3. Manganozincochromite with Cr-mica (fuchsite) inclusions. (a) Slightly polished fractured grain $(150 \times 170 \,\mu\text{m})$; (b) closeup of (a) showing the induction surface of the joint growth of mica (dark) and manganozinco-chromite (pale).

of red spinel that turned out to be Zn-spinel (gahnite). Chromspinel grains (150–300 μ m) from the Upper Cambrian–Lower Ordovician terrigenous sequence have a rounded, slightly polished corroded form without any signs of faceting. Figure 3 shows that some chromspinel grains are fractured and the fractures are filled with Cr-mica (fuchsite). The character of the overgrowth of chromspinels with fuchsite and the presence of induction surfaces of the joint growth testify to their simultaneous formation from a single assemblage.

Examination of the chemical and mineral compositions of lamprophyre dikes in the Riphean Chetlas Kamen Plateau, which were previously defined as alkaline picrites, micaceous picrites, and so on [10], revealed that the dikes contain accessory chromspinels as small xenomorphous and rounded, less often octahedral (0.04–0.8 mm) zonal grains. Their yellowish brown core has a rather constant composition that matches alumochromite or chrompicotite from the typical Alpine-type lherzolites (Tables 1, 2; Fig. 4). Thin black rims (3–20 μ m) around the high-alumina chromspinels are late metamorphic or hydrothermalmetasomatic formations that drastically differ from the



Fig. 4. Zonal accessory chromspinels with high-alumina core and Fe–Zn-chrommagnetite (pale) rim in lamprophyre dikes in the Chetlas Kamen Plateau, Middle Timan. Compo regime, polish section.

primary cores in terms of composition. The rims are also zonal. The inner rim is composed of subalumochrommagnetite, while the outer (thicker) rim consists of magnetite or titanomagnetite. The accessory zonal Zn-chromspinel in lamprophyre dikes is associated with the Zn-vermiculite, while metasomatic albititemica selvages around the lamprophyre dikes contain sphalerite mineralization. On the whole, the lampro-

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phyre dikes and metasomatic selvages around them are appreciably enriched in Zn (from traces to 0.08%).

Thus, we have detected in Middle Timan a series of exposures with Zn-rich chromspinels. They extend from lamprophyre dikes on the Chetlas Kamen Plateau with metamorphosed accessory chromspinels and Znchromagnetite rims to the Paleogene weathering crusts and recent alluvial sediments on the eastern slope of the Chetlas Kamen Plateau and further to the Middle Devonian diamondiferous conglobreccias in the Ichet"yu prospect. Evidently, ancient pathways of the migration of terrigenous material extended precisely in this W-E direction over 60-70 km. The Zn-chromspinel is a prominent indicator of the runoff direction of useful components. In addition to chromspinels, other typical minerals of the heavy fraction of the Ichet"yu prospect (ilmenite, rutile, ilmenorutile, columbite, monazite, xenotime, and others) also make it possible to track such pathways. The Chetlas Kamen Plateau incorporates several prospects of niobium, yttrium, and rare earth minerals. The diamond crystals also bear evidence of similar origin or of association with a single native source. We have detected compositionally similar syngenetic (metallic) films of the natural Au-Pd alloy (Au₂Pd₃) on the surfaces of many diamond crystals from the Ichet"yu prospect (Vol'sk–Vymsk Range) and in one diamond crystal from Quaternary sediments in the Kos'yu River (Chetlas Kamen Plateau) [4, 10].

Thus, we have established that lamprophyre dikes of the Chetlas Kamen Plateau served as the source of Znchromspinels in Middle Timan. Like the well-known "pyrope track," the Zn-chromspinel can be used as an indicator-mineral in the prospecting for diamond. We believe that alkaline picrites or lamprophyres, which are similar to those with accessory Zn-chromspinels on the Chetlas Kamen Plateu (Middle Timan), may also be discovered in the Near-Polar Urals.

ACKNOWLEDGMENTS

The authors are sincerely grateful to V.N. Filippov for the microprobe analysis of indicator-minerals.

This work was supported by the Russian Foundation for Basic Research (project no. 04-05-64174) and the Foundation of the President of the Russian Federation for the Support of Leading Scientific Schools (project no. NSh-2250.2003.5).

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