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MINERALS
AND MINERAL ASSEMBLAGES

Ilmenite Group Minerals in the Russia's Oldest Diamondiferous Kimberlites of Kimozero, Karelia

E. V. Putintseva[a], * and E. M. Spiridonov[b], **

[a]Institute of the Earth Sciences, St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, 199034 Russia
[b]Geological Faculty, Moscow State University, Moscow, 119991 Russia
**e-mail: e.putintseva@spbu.ru*
***e-mail: ernstspiridon@gmail.com*
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Abstract—The paper discusses the morphology and compositional variations of ilmenite group minerals from kimberlites of two phases at the Kimozero locality, the oldest in Russia. Phenocrysts of Mn-rich picroilmenite and Fe-rich geikielite in kimberlites of both phases are similar in morphology and composition. Ilmenite from cement in the second-phase kimberlites enriched in Mg and rimming small regularly shaped chrome spinel phenocrysts is not present in the first-phase kimberlites. Ilmenite, manganilmenite, and Fe-bearing pyrophanite (22–24 wt % MnO) abundant in the cement of the second-phase kimberlites are twice as rich in Nb and substantially richer in Mn than ilmenite up to manganilmenite from the cement of the first-phase kimberlites. Ilmenite and manganilmenite of the first-phase kimberlites is enriched in Zn (up to 1.5 wt % ZnO). Ilmenite from the second-phase kimberlites contains up to 3 wt % Cr_2O_3. In Nb concentration, kimberlitic rocks of the Kimozero are similar to those found in other parts of the world (up to 3.5 wt % Nb_2O_5). Significant Mn-enrichment of the ilmenite group minerals is a common feature of Kimozero kimberlitic rocks. It is suggested that kimberlites in which all ilmenite group minerals—from megacrysts and phenocrysts to small segregations in the cement—are enriched in Me, formed with the participation of carbonatite melts with increased alkalinity.

Keywords: kimberlite, ilmenite group minerals, picroilmenite, manganilmenite, manganese-bearing, Kimozero, Karelia

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INTRODUCTION

Kimberlites are the most important source of diamonds and one of the most interesting petrological objects. Kimberlites are produced from alkali ultramafic carbonate–silicate melts with variable proportions of silicate and carbonate constituents. The carbonate constituent is consistent with calcite carbonatite; much less frequently, with dolomite or calcite carbonatites enriched in Mn; and very rarely, with alkali-rich natrocarbonatite (Dowson, 1983; Nikishov, 1984; Gaspar and Wylley, 1984; Jones and Wylley, 1985; Mitchell, 1986; Jaques et al., 1986; Milashev, 2015).

Titanium easily dissolves in alkali melts. Therefore, ilmenite group minerals (ilmenite $FeTiO_3$, hematite $FeFeO_3$, geikielite $MgTiO_3$, pyrophanite $MnTiO_3$, escolaite $CrCrO_3$, karelianite VVO_3, ecandrewsite $ZnTiO_3$, and corundum $AlAlO_3$) are characteristic constituents of kimberlites. At a high temperature, they form ilmenite–hematite, ilmenite–geikielite, and ilmenite–pyrophanite solid solution series. Ilmenite enriched in Mg or Mn is picroilmenite or manganilmenite, respectively. Ilmenite enriched in Fe^{3+} is ferri-ilmenite, hemo-ilmenite, or ilmenohematite if the hematite endmember predominates.

Several types of the ilmenite group minerals are present in kimberlites: (1) picroilmenite lamellae in xenoliths of deep-seated ultramafic rocks and their disintegration products; (2) subgraphic structures with clinopyroxene or orthopyroxene in deep-seated inclusions; (3) intergrowths with phlogopite, alkali amphibole, rutile, and diopside; (4) large oval crystals (megacrysts, autoliths, and phenocrysts of ilmenite, ferri-geikielite, and rare manganilmenite) commonly enriched in Cr and frequently with chrome spinel exsolution lamellae; and (5) small crystals of ilmenite, manganilmenite, and rare pyrophanite in kimberlite cement (Frantsesson, 1968; Danchin and O'Rey, 1972; Ilupin et al., 1974; Blagulkina et al., 1975; Sobolev et al., 1976; Garanin et al., 1978; Wyatt, 1979; Boctor and Boyd, 1981; Agel et al., 1982; Timofeev et al., 1984; Kostrovitsky, 1986; Genshaft, Ilupin, 1987; Bagdasarov and Ilupin, 1988; Voitkovsky et al., 1991; Edwards et al., 1992; Hood and McCandell, 2004; Kostrovitsky et al., 2004a, 2004b; Wyatt et al., 2004; Malkov and Filippov, 2005). Ilmenite crystals of all types are frequently rimmed by reaction perovskite.

Perovskite pseudomorphs after macro- and microcrystals of ilmenite are frequent. The most recent manganilmenite and pyrophanite occasionally rim perovskite crystals (Pasteris, 1980; Tompkins and Haggerty, 1985; Chakhmouradian and Mitchell, 1999) or occur as pseudomorphs after perovskite (Malkov and Filippov, 2005). The ilmenite group minerals in kimberlites contain appreciable Nb, usually less than 5 wt % Nb_2O_5, but occasionally up to 12 wt % (Chakhmouradian and Mitchell, 1999).

The Kimozero diamondiferous kimberlites were discovered in 1992 (Ushkov, 2001). Their composition was studied to varying degrees. Ushkov (2001) and Ustinov et al. (2009) reported the first data on the compositions of chrome spinels and ilmenite group minerals. Taking into account the enormous lateral size of the Kimozero deposit (more than 2 km) and the wide variety of kimberlites within it, data supplementing the chemical composition and the evolution of its kimberlite typomorphic minerals, including the ilmenite group minerals, remain relevant.

MATERIALS AND METHODS

A collection of Kimozero kimberlitic rocks from outcrops and drill cores has been studied. Most backscattered electron images and determinations of the chemical compositions of minerals were obtained with a Jeol JSM-6480 LV scanning electron microscope equipped with an EDS under standard conditions at the Laboratory of High Spatial Resolution Analytical Techniques, Department of Petrology, Moscow State University (analyst N.N. Korotaeva).

BRIEF GEOLOGICAL DESCRIPTION

The Kimozero occurrence of diamondiferous kimberlites is located in the southeastern part of the Baltic Shield of the Russian Platform within the Onega structural formation of the Karelia Craton, the basement of which is the Vedlozero block of the Neoarchean stabilization (Ushkov, 2001; Putintseva et al., 2009). Kimozero is one of the oldest kimberlite occurrences; its isotopic age ranges from 1.99 to 1.74 Ga (Makhotkin, 2003; Samsonov et al., 2009). Kimberlitic rocks of at least two intrusion phases make up a large extensive (near 2 km) flattened deposit and some steeply dipping pipelike bodies predominantly composed of kimberlite breccias and tufflike and massive kimberlites.

Kimberlitic rocks of the first phase with numerous olivine and phlogopite phenocrysts are appreciably more magnetic than those of the second phase. Phlogopite (occasionally rimmed by tetraferriphlogopite) is Ti-bearing and enriched in Cr as indicated by abundant titanite and Cr-bearing clinochlore as its alteration products. Magnesiochromite, alumochromite, ilmenite, and picroilmenite are phenocrysts in the first-phase kimberlites. The second-phase kimberlitic rocks are enriched in bladelike magmatic calcite. Olivine, magnesiochromite, alumomagnesiochromite, ilmenite, and picroilmenite phenocrysts are present in the second-phase kimberlites. Morphology of tremolite–actinolite pseudomorphs riming large grains of serpentinized olivine suggests that olivine from the second-phase kimberlites was initially rimmed by monticellite. Olivine and phlogopite are abundant in the cement of the Kimozero kimberlites; ilmenite, titanomagnetite, chromite, and perovskite (as indicated by the morphology of the replacement products) are frequent; apatite, baddeleyite, and zircon are rare.

Kimberlitic rocks of Kimozero together with Lyudikovian country gabbrodolerite and terrigenous and volcanic rocks, are markedly tectonized and metamorphosed.

ILMENITE GROUP MIERALS OF THE FIRST-PHASE KIMBERLITIC ROCKS

Oval, markedly corroded phenocrysts up to 1.5 mm in size similar in morphology (Fig. 1) and composition to picroilmenite of classic kimberlite megacrysts are rare in the studied rocks. The composition of the Kimozero minerals (analyses 1, 2) is, wt %: 11.95 and 11.19 MgO, 0.25 and 0.29 NiO, 23.27 and 17.53 FeO, 0.75 and 4.31 MnO, 0.12 and 0.30 ZnO, 9.14 and 0.12 CaO, 50.94 and 47.25 TiO_2, 9.83 and 17.26 Fe_2O_3, 0.30 and 0.15 V_2O_3, 2.88 and 0.22 Cr_2O_3, 0.14 and 1.76 Nb_2O_5, total 100.57 and 100.30%; the FeO and Fe_2O_3 contents are calculated from stoichiometry. The end-member contents are, mol %: 41.1 and 39.1 $MgTiO_3$, 44.9 and 34.4 $FeTiO_3$, 1.5 and 8.6 $MnTiO_3$, 0.2 and 0.5 $ZnTiO_3$, 0.3 $CaTiO_3$, 0.5 $NiTiO_3$, 8.6 and 15.3 Fe_2O_3, 2.7 and 0.2 Cr_2O_3, 0.3 and 0.1 V_2O_3, 0.1 and 1.0 Nb_2O_5. Composition 1 is consistent with Cr-bearing picroilmenite; composition 2 corresponds to Mn–Fe-bearing geikielite enriched in Fe^{3+} and Nb.

Isolated unzoned ilmenite crystals up to 150 μm across are common in the cement of the first-phase kimberlites. They are divided into three groups by composition. Group 1 ilmenite crystals depleted in Mg and Mn (Table 1, analyses 3, 4) are the most abundant. This ilmenite contains up to 1 wt % MnO, approximately 6 wt % Fe_2O_3, up to 1 wt % Cr_2O_3, minor Nb, and trace Ca and Zn. Grains of group 2 ilmenite depleted in Mg and enriched in Fe^{3+} and Mn are common. This ilmenite contains, wt %: 2–6 MnO, up to 13.5 Fe_2O_3, up to 1 Cr_2O_3, up to 0.8 ZnO, up to 0.4 V_2O_3, and up to 0.3 Nb_2O_5 (Table 1, analyses 5–9). Group 3 ilmenite is rare. This is manganilmenite depleted in Mg and enriched in Zn. It contains, wt %: 11 MnO, 2 Fe_2O_3, 1.5 ZnO, 0.3 V_2O_3, 0.2 Cr_2O_3 (Table 1, analyses 10). Thus, ilmenite from the first-phase kimberlitic rocks is variable in composition, from Cr-bearing picroilmenite and Mn–Fe-bearing geikielite to common ilmenite and manganilmenite. Most of the ilmenite group minerals, from earliest to latest, have

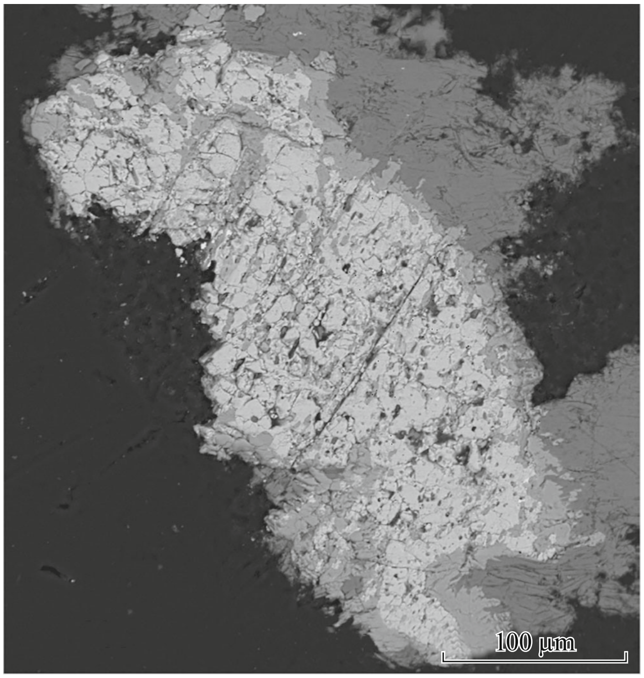

Fig. 1. Backscattered electron image of fragments of Cr-bearing picroilmenite (analysis 1) from first-phase kimberlites of Kimozero. Crystal is markedly corroded and rimmed by replacing titanite (gray).

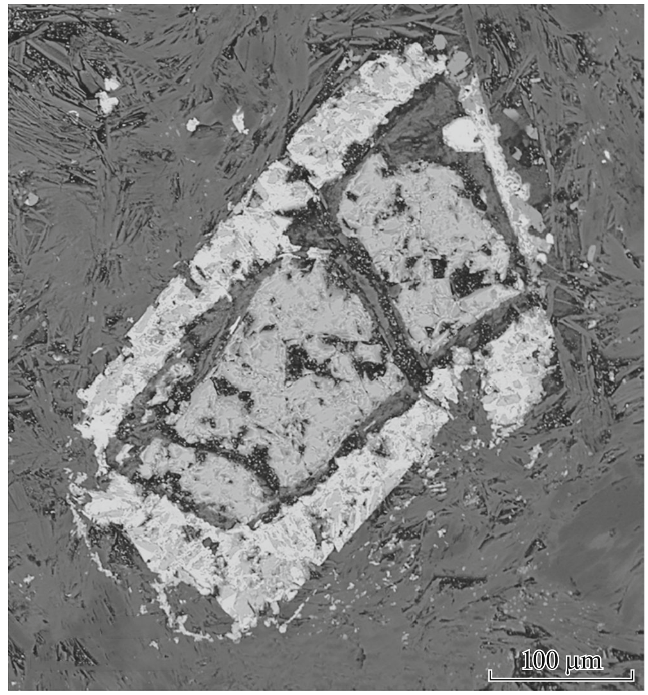

Fig. 2. Backscattered electron image of Mg-bearing bearing ilmenite (analysis 15) rimming small chrome spinel phenocryst (gray) in matrix of second-phase kimberlite at Kimozero. Zircon crystal (white) is on inner side of rim. Ilmenite is markedly corroded.

an elevated Mn concentration. The Fe^{3+} content is highest in the earliest high-temperature Fe-bearing geikielite. The Cr and Nb concentrations are not correlated and are relatively highly variable. Elevated Zn is characteristic of manganilmenite. Taking into account the compositions not given in Table 1, ilmenite from the first-phase kimberlites contains on average, wt %: 2.4 MnO, 0.29 Nb_2O_5, 0.45 Cr_2O_3, 0.25 V_2O_3 (n = 17).

ILMENITE GROPUP MINERALS FROM THE SECOND-PHASE KIMBERLITIC ROCKS

Oval phenocrysts up to 2 mm in size, also close in composition to picroilmenite from classic kimberlite megacrysts, are present in these rocks. The composition of the Kimozero mineral (analysis 11) is, wt %: 11.75 MgO, 0.11 NiO, 12.83 FeO, 2.37 MnO, 0.51 ZnO, 0.13 CaO, 41.45 TiO_2, 29.69 Fe_2O_3, 0.16 V_2O_3, 1.14 Cr_2O_3, 0.28 Nb_2O_5, total 100.62; the FeO and Fe_2O_3 contents are calculated from stoichiometry. The endmember contents are, mol %: 41.5 $MgTiO_3$, 25.0 $FeTiO_3$, 4.7 $MnTiO_3$, 0.9 $ZnTiO_3$, 0.3 $CaTiO_3$, 0.2 $NiTiO_3$, 26.1 Fe_2O_3, 1.1 Cr_2O_3, 0.1 V_2O_3, 0.1 Nb_2O_5. This composition is consistent with Mn–Fe-bearing geikielite in the proportions of the major elements.

Ilmenite enriched in Mg and rimming small regularly shaped chrome spinel phenocrysts (Figs. 2, 3, 4) is common. The thickness of the ilmenite rims ranges from 20 to 50 µm. Zircon occasionally overgrows their inner side (Fig. 2). This ilmenite contains up to, wt %: 6.5 MgO, 14 Fe_2O_3, 4 MnO, 3.5 Nb_2O_5, 1 Cr_2O_3, and 0.7 V_2O_3; Zn was not detected (Table 2). Ilmenite enriched in Fe^{3+} was exsolved and conversed to the ilmenite matrix with numerous hematite lamellae (Fig. 2).

Isolated grains of the ilmenite group minerals up to 250 µm across are common in the cement of the second-phase kimberlites (Figs. 5, 6). They are divided into four chemical groups. Unzoned ilmenite crystals of group 1 depleted in Mg and relatively enriched Mn (Fig. 5; Table 3) are the most abundant. This ilmenite contains, wt %: 2–9 MnO, up to 5 Fe_2O_3, up to 2.5 Cr_2O_3, up to 1.5 Nb_2O_5, up to 1 CaO, up to 0.7 ZnO, and up to 0.4 V_2O_3. Zoned crystals of group 2 ilmenite depleted in Mg and relatively enriched in Mn are observed less frequently. The composition of two such crystals is given in Table 4. Substitution of Fe^{2+} for Mn^{2+} is clearly demonstrated in this ilmenite type: the cores and rims of crystals are enriched in Fe and Mn, respectively. Group 2 ilmenite contains, wt %: 6–15 MnO, up to 5 Fe_2O_3, up to 2 Nb_2O_5, up to 1 CaO and ZnO, and up to 0.4 V_2O_3; Cr was not detected (Table 4). Unzoned crystals of group 3 ilmenite depleted in Mg and Cr and significantly enriched in Mn are quite common. This manganilmenite contains, wt %: 11.5–

Table 1. Chemical composition (wt %) of isolated ilmenite crystals from cement of first-phase kimberlites

Component	Analysis							
	3	4	5	6	7	8	9	10
MgO	0.19	0.26	1.36	0.23	0.24	0.22	3.05	0.59
NiO	—	—	—	—	—	—	—	—
FeO	42.97	42.30	35.63	40.34	37.55	36.49	29.33	31.92
MnO	0.44	0.82	1.91	2.53	3.36	3.65	5.93	10.79
ZnO	—	—	0.23	0.22	0.71	0.78	—	1.45
CaO	0.05	—	0.10	—	—	—	0.13	—
TiO_2	48.74	48.49	44.84	48.33	46.68	47.76	45.45	51.08
Fe_2O_3	6.22	5.78	13.26	7.00	10.10	8.05	13.45	1.80
V_2O_3	—	0.33	0.23	0.39	0.33	0.40	0.16	0.34
Cr_2O_3	—	1.07	0.11	0.38	0.38	0.24	—	0.24
Nb_2O_5	0.34	0.24	0.14	0.20	0.17	0.17	0.28	—
Total	98.95	99.29	97.81	100.62	99.52	97.76	98.78	98.21
Atoms per formula unit calculated on basis of two metal atoms								
Mg	0.007	0.010	0.051	0.009	0.009	0.008	0.115	0.022
Fe^{2+}	0.920	0.901	0.766	0.841	0.899	0.810	0.622	0.702
Mn	0.010	0.018	0.042	0.054	0.073	0.079	0.127	0.234
Zn	—	—	0.004	0.004	0.013	0.015	—	0.027
Ca	0.001	—	0.003	—	—	—	0.004	—
Ti	0.938	0.929	0.867	0.918	0.895	0.912	0.868	0.985
Fe^{3+}	0.120	0.113	0.257	0.152	0.104	0.162	0.257	0.018
V	—	0.007	0.005	0.002	0.007	0.008	0.003	0.007
Cr	—	0.022	0.002	0.008	0.008	0.006	—	0.005
Nb	0.004	0.003	0.002	0.002	0.002	0.002	0.003	—

Here and in Tables 2–6, FeO and Fe_2O_3 contents are calculated from stoichiometry; dash denotes element content below detection limit.

21.5 MnO, up to 4 (usually below 1) Fe_2O_3, up to 3 Nb_2O_5, up to 1 CaO and ZnO, and up to 0.5 V_2O_3 (Table 5). Rare Fe-bearing pyrophanite microscopically indistinguishable from above described species (Fig. 6) presents group 4. Pyrophanite contains, wt %: 22–24 MnO, up to 3 Fe_2O_3, up to 0.7 ZnO, and up to 0.5 Nb_2O_5 and V_2O_3 (Table 6).

Thus, ilmenite from the second-phase kimberlitic rocks at Kimozero is variable in morphology and composition, from Mn–Fe-bearing geikielite through ilmenite enriched in Mg and Mn to ilmenite, manganilmenite, and pyrophanite depleted in Mg and enriched Mn. The high Mn concentration is characteristic of the ilmenite group minerals from the earliest to the latest generation. The Fe^{3+} content is the highest in the early highest-temperature Fe-bearing geikielite. The Cr and Nb concentrations in ilmenite are not correlated and are relatively highly variable. Ilmenite with elevated Mg concentration is more frequently enriched in Cr, whereas ilmenite with elevated Mn is enriched in Nb. Taking into account the compositions not given in Tables 2–6, ilmenite from the second-phase kimberlites contains on average, wt %: 10.2 MnO, 0.54 Nb_2O_5, 0.24 Cr_2O_3, 0.33 V_2O_3 (n = 39). Minor Ni and Zn are characteristic of Mg- and Mn-bearing ilmenite, respectively. Constant minor Ca in ilmenites is noteworthy.

COMPARISON OF ILMENITE GROUP MINERALS FROM THE FIRST- AND SECOND-PHASE KIMBERLITIC ROCKS

Early generation picroilmenite and Fe-bearing geikielite in kimberlites of the both phases at Kimozero are similar in morphology and composition (Figs. 7, 8). Later ilmenite enriched in Mg and rimming regularly shaped chrome spinel crystals from the second-phase kimberlites was not found in the first-phase kimberlites. Later ilmenite, the most abundant in the cement of the second-phase kimberlites, is two times richer in Nb and substantially richer in Mn (Fig. 8b) than that

Fig. 3. Backscattered electron image of Mg-bearing bearing ilmenite (analysis 12) containing tiny chrome spinel octahedron and rimming small chrome spinel phenocryst (gray) in matrix of second-phase kimberlites. Zircon occurs as fine white crystals in matrix. Ilmenite is strongly corroded.

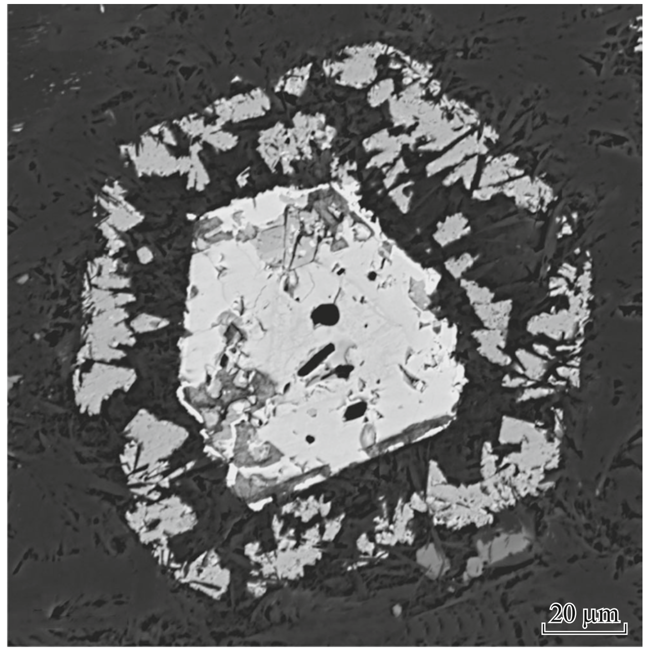

Fig. 4. Backscattered electron image of Mg-bearing bearing ilmenite enriched in Nb (analysis 13) rimming chrome spinel phenocryst (white) in matrix of second-phase kimberlites at Kimozero. Ilmenite is markedly corroded.

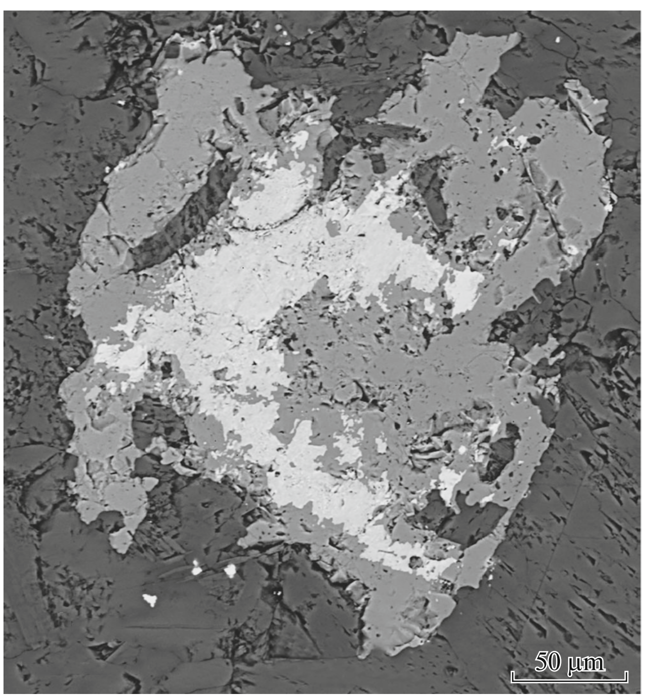

Fig. 5. Backscattered electron image of isolated Mn-bearing ilmenite crystal (analysis 23) in matrix of second-phase kimberlites at Kimozero. Ilmenite is strongly replaced by titanite (gray).

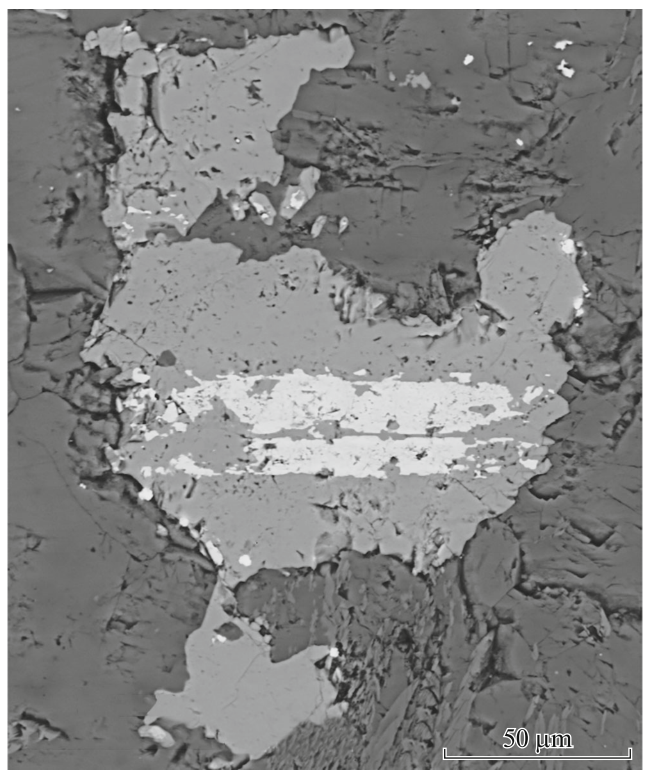

Fig. 6. Backscattered electron image of isolated Fe-bearing pyrophanite crystal (analysis 42) in matrix of second-phase kimberlite at Kimozero. Pyrophanite is massively replaced by titanite (gray).

Table 2. Chemical composition (wt %) of ilmenite enriched in Mg rimming chrome spinel crystals from second-phase kimberlites

Component	Analysis			
	12	13	14	15
MgO	6.30	4.16	4.15	3.67
NiO	0.13	—	—	0.12
FeO	30.36	30.17	34.34	36.38
MnO	3.46	2.61	4.11	0.08
ZnO	—	—	—	—
CaO	0.19	0.32	0.05	0.37
TiO_2	50.57	50.63	51.07	45.15
Fe_2O_3	7.90	2.55	6.15	13.75
V_2O_3	0.45	0.69	0.31	0.49
Cr_2O_3	0.42	—	0.03	1.13
Nb_2O_5	—	3.25	—	1.03
Total	99.78	99.31	100.21	99.17
Atoms per formula unit calculated on basis of two metal atoms				
Mg	0.227	0.155	0.151	0.137
Ni	0.003	—	—	0.002
Fe^{2+}	0.614	0.734	0.703	0.698
Mn	0.071	0.055	0.085	0.002
Ca	0.005	0.007	0.001	0.010
Ti	0.920	0.951	0.940	0.849
Fe^{3+}	0.144	0.048	0.113	0.259
V	0.009	0.014	0.006	0.010
Cr	0.008	—	0.001	0.022
Nb	—	0.037	—	0.012

Table 3. Chemical composition (wt %) of isolated ilmenite crystals in cement of second-phase kimberlites

Component	Analysis							
	16	17	18	19	20	21	22	23
MgO	0.17	0.23	0.13	1.51	0.37	0.09	0.07	0.17
NiO	—	—	—	—	0.05	—	—	—
FeO	41.98	42.46	40.45	37.53	38.27	38.50	36.43	35.27
MnO	2.29	2.64	3.44	3.45	4.26	6.07	8.53	9.04
ZnO	—	—	—	0.36	0.67	—	0.18	—
CaO	0.91	0.04	0.93	0.15	0.10	0.31	0.44	1.01
TiO_2	50.96	51.27	50.36	49.22	48.97	50.18	51.02	51.15
Fe_2O_3	0.67	0.93	1.98	5.09	3.17	4.25	2.94	0.31
V_2O_3	0.34	0.19	0.31	0.20	0.40	0.33	0.23	0.31
Cr_2O_3	0.44	—	0.92	1.29	2.64	—	—	—
Nb_2O_5	0.41	0.17	0.26	0.12	0.16	0.14	—	1.47
Total	98.07	98.73	98.78	98.92	98.96	99.87	99.84	98.63
Atoms per formula unit calculated on basis of two metal atoms								
Mg	0.006	0.009	0.005	0.057	0.014	0.003	0.003	0.006
Ni	—	—	—	—	0.001	—	—	—
Fe^{2+}	0.902	0.921	0.863	0.794	0.815	0.814	0.769	0.756
Mn	0.050	0.057	0.074	0.074	0.092	0.130	0.182	0.196
Zn	—	—	—	0.007	0.013	—	0.003	—
Ca	0.025	0.001	0.025	0.004	0.003	0.008	0.012	0.028
Ti	0.983	0.988	0.967	0.936	0.938	0.955	0.969	0.986
Fe^{3+}	0.013	0.018	0.038	0.097	0.061	0.081	0.056	0.006
V	0.007	0.004	0.006	0.004	0.008	0.007	0.005	0.004
Cr	0.009	—	0.019	0.025	0.053	—	—	—
Nb	0.005	0.002	0.003	0.002	0.002	0.002	—	0.017

Table 4. Chemical composition (wt %) of isolated zoned ilmenite crystals from cement of second-phase kimberlites

Component	Analysis							
	24 core	25 intermediate	26 intermediate	27 rim	28 core	29 intermediate	30 intermediate	31 rim
MgO	0.09	0.07	0.13	0.29	0.12	0.17	0.08	0.17
NiO	—	—	—	—	—	—	—	—
FeO	38.15	36.82	31.33	26.20	36.75	384.02	28.41	29.10
MnO	6.07	8.53	8.89	15.33	6.62	9.04	15.01	15.28
ZnO	0.31	0.18	0.48	0.98	0.47	0.39	0.62	0.79
CaO	0.31	0.44	0.89	0.90	0.93	1.01	0.65	0.73
TiO_2	50.18	51.02	49.80	49.20	50.40	50.15	50.18	51.69
Fe_2O_3	2.42	1.40	1.98	5.93	2.54	2.81	4.02	0.27
V_2O_3	0.33	0.23	0.36	0.31	0.29	0.21	—	0.27
Cr_2O_3	—	—	—	—	—	—	—	—
Nb_2O_5	0.14	0.11	0.12	2.18	0.21	1.47	0.19	1.05
Total	98.08	98.80	98.70	100.43	99.92	99.27	99.16	99.32
Atoms per formula unit calculated on basis of two metal atoms								
Mg	0.003	0.003	0.005	0.011	0.005	0.006	0.003	0.006
Fe^{2+}	0.822	0.786	0.728	0.554	0.787	0.726	0.604	0.619
Mn	0.132	0.184	0.192	0.329	0.143	0.195	0.323	0.329
Zn	0.006	0.003	0.009	0.018	0.009	0.007	0.012	0.015
Ca	0.009	0.003	0.024	0.024	0.026	0.028	0.018	0.020
Ti	0.972	0.979	0.958	0.936	0.970	0.962	0.960	0.989
Fe^{3+}	0.047	0.027	0.075	0.096	0.049	0.054	0.077	0.005
V	0.007	0.005	0.007	0.006	0.006	0.004	—	0.005
Nb	0.002	0.001	0.001	0.025	0.002	0.017	0.002	0.012

Table 5. Chemical composition (wt %) of isolated ilmenite crystals enriched in Mn from cement of second-phase kimberlites

Component	Analysis							
	32	33	34	35	36	37	38	39
MgO	0.18	0.09	0.16	0.17	0.29	—	0.60	0.22
NiO	—	—	—	—	—	—	—	—
FeO	34.38	32.01	30.83	29.77	27.23	29.59	24.37	22.66
MnO	11.41	13.63	14.52	15.28	15.33	16.10	18.62	21.48
ZnO	—	—	—	—	—	0.29	0.32	0.51
CaO	0.19	0.36	0.25	0.73	0.89	0.28	0.56	0.07
TiO_2	51.70	51.61	51.26	51.69	49.20	51.70	50.51	50.40
Fe_2O_3	0.58	0.73	1.20	1.74	3.90	0.94	0.21	3.03
V_2O_3	0.30	0.49	0.54	0.24	0.31	0.28	0.34	0.55
Cr_2O_3	—	—	—	—	—	0.35	0.13	—
Nb_2O_5	—	—	—	1.74	2.18	0.30	2.88	0.47
Total	98.84	98.92	98.76	100.67	99.33	99.83	98.54	99.09
Atoms per formula unit calculated on basis of two metal atoms								
Mg	0.007	0.003	0.006	0.006	0.011	—	0.026	0.008
Fe^{2+}	0.733	0.681	0.657	0.624	0.581	0.625	0.524	0.481
Mn	0.246	0.294	0.313	0.325	0.332	0.345	0.405	0.462
Zn	—	—	—	—	—	0.005	0.006	0.010
Ca	0.005	0.010	0.007	0.020	0.024	0.008	0.015	0.002
Ti	0.991	0.988	0.983	0.975	0.945	0.983	0.976	0.963
Fe^{3+}	0.011	0.014	0.023	0.033	0.075	0.018	0.004	0.058
V	0.006	0.010	0.011	0.005	0.006	0.006	0.007	0.011
Cr	—	—	—	—	—	0.007	0.003	—
Nb	—	—	—	0.012	0.025	0.003	0.033	0.005

Table 6. Chemical composition (wt %) of isolated Fe-bearing pyrophanite from cement of second-phase kimberlites

Component, wt %				Atoms per formula unit			
Analysis	40	41	42	Analysis	40	41	42
MgO	0.14	0.26	0.18	Mg	0.005	0.010	0.007
NiO	—	—	—	Ni	—	—	—
FeO	22.26	21.00	21.42	Fe^{2+}	0.480	0.447	0.452
MnO	21.99	22.57	23.93	Mn	0.461	0.487	0.511
ZnO	0.55	0.71	0.71	Zn	0.011	0.013	0.013
CaO	0.50	0.18	0.12	Ca	0.014	0.005	0.003
TiO_2	51.04	50.25	51.97	Ti	0.991	0.962	0.986
Fe_2O_3	0.31	3.07	1.05	Fe^{3+}	0.006	0.059	0.020
V_2O_3	0.49	0.61	0.737	V	0.010	0.012	0.007
Cr_2O_3	—	—	—	Cr	—	—	—
Nb_2O_5	0.22	0.38	0.14	Nb	0.003	0.004	0.002
Total	97.50	99.03	99.85			2	

from the cement of the first-phase kimberlites (Fig. 7b). Ilmenite from the first-phase kimberlites is markedly richer in Zn. The positive correlation between Mg and Fe^{3+} concentrations and between contents of geikielite and hematite endmembers is characteristic of ilmenite group minerals from kimberlites of the both phases. This correlation is more pronounced in the second-phase kimberlites (Figs. 7a, 8a). Significant enrichment in Mn is a common feature of ilmenite group minerals from the Kimozero kimberlites (Figs. 7b, 8b).

COMPARISON OF ILMENITE GROUP MINERALS FROM KIMBERLITIC ROCKS AT KIMOZERO AND OTHER DIAMONDIFEROUS KIMBERLITES

Diamondiferous kimberlites contain picroilmenite and ferri-geikielite, which are enriched in Cr to varying degrees (Holmes, 1936; Nixon et al., 1963; Boctor and Boyd, 1980; Frantsesson et al., 1982; Haggerty and Tompkins, 1985; Mitchell, 1986; Genshaft and Ilupin, 1987; Bagdasarov and Ilupin, 1988; Edwards et al., 1992; Hood and McCandell, 2004; Kjarsgaard et al., 2004; Kostrovitsky et al., 2004; Masum et al., 2004; Wyatt et al., 2004; Kostrovitsky et al., 2006; Milashev, 2015). The positive correlation between Mg and Fe^{3+} concentrations and between contents of geikielite and hematite endmembers is characteristic of ilmenite group minerals from many diamondiferous kimberlites. Megacrysts of ilmenite group minerals frequently have appreciable Nb. The content of these ilmenite group minerals is low in kimberlites of both phases at Kimozero, which is consistent with the low diamond grade in these kimberlites (Ushkov, 2001; Lukyanova et al., 2006; Ustinov et al., 2009).

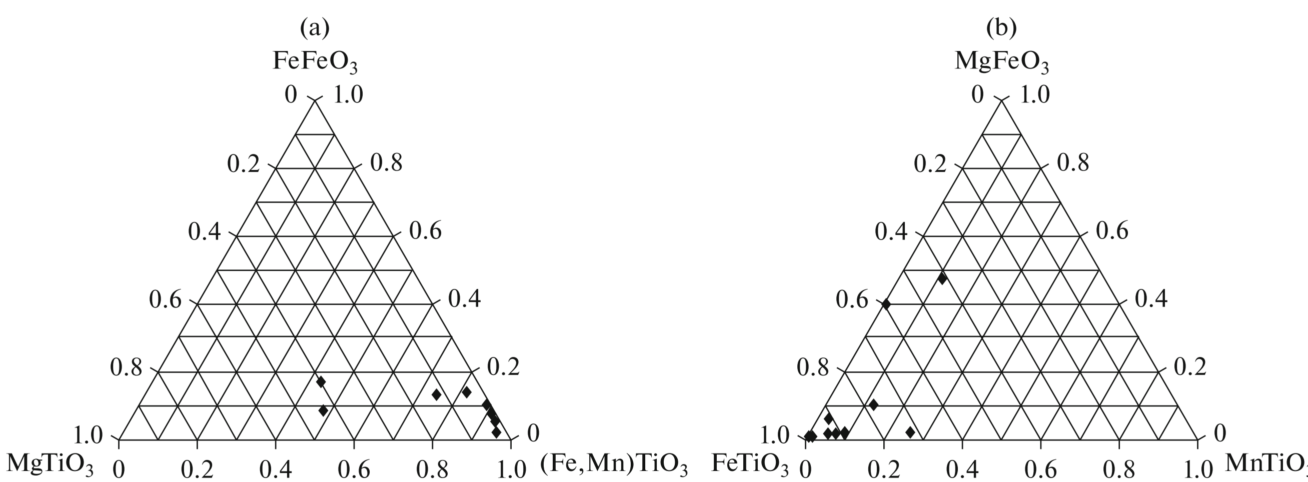

Fig. 7. Triangular plots in terms of (a) $FeFeO_3$–$MgTiO_3$–$(Fe,Mn)TiO_3$ and (b) $MgTiO_3$–$FeTiO_3$–$MnTiO_3$ illustrating composition of ilmenite group minerals from first-phase kimberlites at Kimozero.

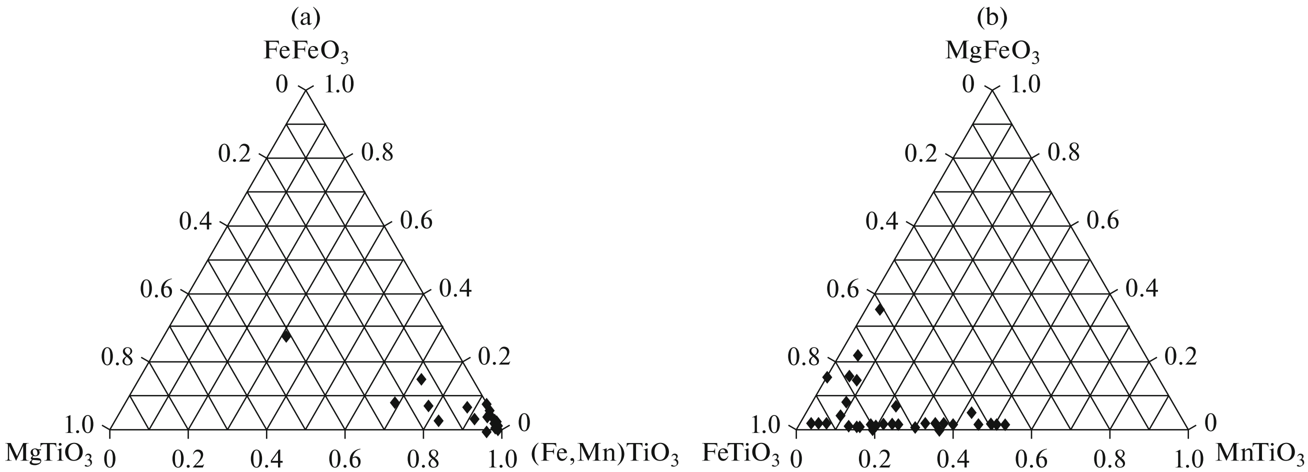

Fig. 8. Triangular plots in terms of (a) $FeFeO_3$–$MgTiO_3$–(Fe,Mn)TiO_3 and (b) $MgTiO_3$–$FeTiO_3$–$MnTiO_3$ illustrating composition of ilmenite group minerals from second-phase kimberlites.

The vast majority of picroilmenite and ferri-geikielite megacrysts from diamondiferous kimberlites is Mn-poor, 0.3–0.5 wt % MnO. The Kimozero picroilmenite and Fe-bearing geikielite are enriched in this element, 0.8–4.3 wt % MnO. Rare types of diamondiferous kimberlites containing megacrysts of ilmenite enriched in Mn and manganilmenite are known in Brazil (Kaminsky and Belousova, 2009). In this respect, the Kimozero kimberlites are no exception.

Microcrystalline ilmenite from the cement of the vast majority of kimberlites is Mn-poor: only rims of crystals are enriched in this element (Blagulkina et al., 1975; Garanin et al., 1978; Boctor and Boyd, 1981; Agel et al., 1982; Dowson, 1983; Nikoshov, 1984; Timofeev et al., 1984; Tompkins and Haggerty, 1985; Mitchell, 1986; Genshaft and Ilupin, 1988; Voitkovsky et al., 1991; Ilupin, 1997; Edwards et al., 1992; Hood and McCandell, 2004; Wyatt et al., 2004; Malkov and Filippov, 2005; Kostrovitsky et al., 2006; Kaminsky and Belousova, 2009). Rare types of kimberlites contain Mn-rich ilmenite, manganilmenite, and pyrophanite in the cement (Wyatt, 1979; Pasteris, 1980; Tompkins, Haggerty, 1985; Chakhmouradian and Mitchell, 1999; Malkov and Filippov, 2005; Kaminsky and Belousova, 2009). Such are the Kimozero kimberlites. These kimberlites contain a significant proportion of carbonatites. The same Mn-rich ilmenite group minerals are present in high-alkali carbonatites (Jakupiranga, Brazil; Western Australia) (Mitchell, 1978; Gaspar and Wylley, 1983; Jaques et al., 1986).

It can be suggested that kimberlites in which all types of ilmenite group minerals from megacrysts and phenocrysts to fine grains in the cement are enriched in Mn originated with the participation of high-alkali carbonatite melts, whereas standard kimberlites with ilmenite group minerals depleted in Mn were formed with the involvement of low-alkali carbonatite melts. High-alkali carbonatites enriched in Mn are known in the eastern part of the Baltic Shield (Dudkin et al., 1984).

The Kimozero kimberlitic rocks are similar in Nb concentration to standard kimberlites.

ALTERATION

The Kimozero kimberlites, country Lyudikovian gabbrodolerite, and sedimentary and volcanic rocks are tectonized and predominantly metamorphosed under prehnite–pumpellyite facies conditions. The Kimozero metakimberlites are composed of antigorite and less frequent lizardite, actinolite–tremolite, carbonates, chlorites, and titanite; their proportions are highly variable (Lukyanova et al., 1986; Ustinov et al., 2009; Putintseva, 2015). Many of the ilmenite group minerals in metakimberlites are corroded (Figs. 1, 2, 3), partly replaced by titanite (Figs. 4, 5, 7), and less frequent ferro-pseudobrookite $FeTi_2O_5$ and fine-grained aggregates of rutile and hematite. Complete pseudomorphs of titanite after ilmenite are rather common.

CONCLUSIONS

Oval Mn-bearing picroilmenite and Fe-bearing geikielite phenocrysts in the Kimozero kimberlites of both phases are close in morphology and composition to megacrysts from standard diamondiferous kimberlites. The low content of these ilmenite group minerals in the Kimozero kimberlites is consistent with the low diamond grade in these rocks. Ilmenite enriched in Mg and rimming small regularly shaped chrome spinel phenocrysts in the cement of the second-phase kimberlites was not found in the first-phase kimberlites. Ilmenite, manganilmenite, and Fe-bearing pyrophanite (22–24 wt % MnO) common in the cement of the second-phase kimberlites are two times richer in Nb and substantially richer in Mn than ilmenite and manganilmenite from the cement of the first-phase kimberlites. Ilmenite and manganilmenite from the first-phase kimberlites are richer in Zn (up to 1.5 wt % ZnO). Ilmenite from the second-phase kimberlites contains up to 3 wt % Cr_2O_3. The Nb content (up to 3.5 wt % Nb_2O_5) in the Kimozero kimberlitic rocks is similar in to that in standard kimberlites. Significant enrichment in Mn is a common feature of ilmenite group minerals of the Kimozero kimberlitic rocks. It can be suggested that kimberlites in which all types of ilmenite group minerals—from megacrysts and phenocrysts to fine grains in the cement—are enriched in Mn formed with the participation high-alkali carbonatite melts.

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REFERENCES

Agel, J.J., Garrison, J.A., and Taylor, L.A., Petrogenesis of oxide minerals in kimberlite Elliot County, Kentucky. *Amer. Miner*, 1982, vol. 67, pp. 28–42.

Bagdasarov, E.A. and Ilupin, I.P., Evolution of compositions of micro- and macro-crystalline kimberlitic ilmenites, *Dokl. Akad. Nauk SSSR*, 1988, vol. 302, pp. 1201–1203.

Blagulkina, V.A., Gubanov, V.A., Umanets, V.N., and Futergendler, S.I., Microcrystals of ilmenite from kimberlites of the Luchakan region, in *Minerals and Mineral Parageneses of Endogenous Deposits,* Leningrad: Nauka, 1975, pp. 11–18.

Boctor, N.Z. and Boyd, F.R., Oxide minerals in the Lighobong kimberlite, Lesotho, *Am. Mineral.,* 1980, vol. 65, pp. 631–638.

Boctor, N.Z. and Boyd, F.R., Oxide minerals in layered kimberlite–carbonatite sill from Benfontain, South Africa, *Contrib. Mineral. Petrol.*, 1981, vol. 76, pp. 253–256.

Chakhmouradian, A.R. and Mitchell, R.H., Niobian ilmenite, hydroxylapatite and sulfatian monazite: alternative hosts for incompatible element in calcite kimberlite from International'naya, Yakutia, *Can. Mineral,* 1999, vol. 37, pp. 1177–1189.

Danchin, R.V. and F. O'Rey, Chromian spinel exsolution in ilmenite from the Premier mine, Transvaal, South Africa. *Contrib. Miner. Petrol.,* 1972, vol. 35, pp. 43–49.

Dawson, J.B., *Kimberlites and their xenolites*, Berlin, New York: Shpringer-Verlag, 1980.

Dudkin, O.B., Minakov, F.V., Kravchenko, M.P., et al., *Karbonatity Khibin* (Carbonatites of the Khibiny Mountains), Apatity: Kol'sk. Nauchn. Ts. Akad. Nauk SSSR, 1984.

Edwards, D., Rock, N.M.S., Taylor, W.R., Griffin, B.J., and Ramsay, R.R., *Mineralogy and Petrology of the Aries diamondiferous kimberlite pipe, Central Kimberley block, Western Australia, J. Petrol.*, 1992, vol. 33, pp. 1157–1191.

Frantsesson, E.V., *Petrologiya kimberlitov* (Petrology of Kimberlite), Moscow: Nedra, 1968.

Frantsesson, E.V., Gareeva, R.K.H., Panteleev, V.V., and Dudar, L.P., Indicator minerals of diamond in alkaline-ultrabasic breccias of Middle Timan, *Proc. TSNIGRI,* 1982, vol. 175, pp. 69–77.

Garanin, V.K., Kudryavtseva.G.P., and Lapin, A.V., Typomorphic features of ilmenites from kimberlites, alkaline ultrabasic intrusions, and carbonatites, *Geol. Ore Deposits,* 1978, no. 4, pp. 3–32

Gaspar, J.C. and Wylley, P.J., Ilmenite (high Mg, Mn, Nb) in the carbonatites from the Jacupiranga Complex, Brazil, *Am. Mineral.,* 1983, vol. 68, pp. 960–971.

Gaspar, J.C. and Wylley, P.J., The alleged kimberlite–carbonatite relationship: evidence from ilmenite and spinel from Premier and Wesselton mines and the Benfontein sill, South Africa, *Contrib. Miner. Petrol.,* 1984, vol. 85, pp. 133–140.

Genshaft, Yu.S. and Ilupin, I.P., Deep parageneses of ilmenite in kimberlites of Yakutiya, in *Issledovaniya vysokobaricheskikh mineralov* (Study of High-Pressure Minerals), Moscow: Inst. Fiz. Zemli Akad. Nauk SSSR, 1987, pp. 25–68.

Haggerty, S.E. and Tompkins, L.A., *Subsolidus reactions in kimberlitic ilmenites: exsolution, reduction and the redox state of the mantle, in Kimberlites I. Proc. 3rd Int. Kimberlite Conf.*, 1984, vol. 1, pp. 335–357.

Holmes, A., Contribution to the petrology of the kimberlite and its inclusions, *Trans. Geol. Soc. S. Africa,* 1936, vol. 39, pp. 379–428.

Hood, C.T.S. and McCandless, T.E., Systematic variations in xenocrysts mineral composition at the province scale, Buffalo Hills kimberlites, Alberta, Canada, *Lithos*, 2004, vol. 77, pp. 733–747.

Ilupin, I.P., Milashev, V.A., Tomanovskaya, Yu.I., and Evdokimov, A.N., Ilmenite from kimberlites of Yakutiya, in *Mineralogiya, geokhimiya, I prognozirovanie almaznykh mestorohdenii* (Mineralogy, Geochemistry and Forecasting of Diamond Deposits), Leningrad: NIIGA, 1974, pp. 5–29.

Ilupin, I.P., *Manganese as the indicator of mantle heterogeneity beneath the Siberian kimberlite province,Geochem. Int,* 1997, no. 3, pp. 227–234.

Jaques, A.L., Lewis, J.D., and Smith, C.B., The kimberlites and lamproites of Western Australia. *Geol. Surv. Western Australia, Bull.*, 1986, vol. 132.

Jones, A.P. and Wylley, P.J., Paragenetic trends of oxide minerals in carbonate-rich kimberlites, with new analyses from the Benfontein sill, South Africa, *J. Petrol*, 1985, vol. 26, pp. 210–222.

Kaminskiy, F.V. and Belousova, E.A., Manganoan ilmenite as a kimberlite diamond indicator mineral, *Russ. Geol. Geophys.,* 2009, no. 12, pp. 1212–1220.

Kjarsgaard, I.M., McClenaghan, M.B., Kjarsgaard, B.A., and Henman, L.M., *Indicator mineralogy of kimberlite boulders from eskers in the Kirkland Lake and Lake Timiskanning areas, Ontario, Canada, Lithos*, 2004, vol. 77, pp. 705–751.

Kostrovitsky, S.I., *Geokhimicheskie osobennosti mineralov kimberlitov* (Geochemical Features of Kimberlite Minerals), Novosibirsk: Nauka, 1986.

Kostrovitsky, S.I., Alymova, N.V., Yakovlev, D.A., Serov, I.V., Ivanov, A.C., and Serov, V.P., Specific features of picroilmenite composition in various diamondiferous fields of the

Yakutian province, *Dokl. Earth Sci.,* 2006, vol. 406, no. 1, pp. 19–24.

Kostrovitsky, S.L., Malkovets, V.G., Verichev, E.M., and Garanin, V.K., Megacrysts from the Grib kimberlite pipe (Arkhangelsk Province, Russia), *Lithos*, 2004, vol. 77, pp. 511–523.

Lukyanova, L.I., Lobkova, L.P., and Alekhina, B.B., Special features of the composition of the Kimozero kimberlite in Karelia, in *Almazy i blagorodnye metally Timano-Ural. regiona* (Diamonds and Noble Metals of the Timan-Urals Region), Syktyvkar: Inst. Geol. Komi Nauchn. Ts. Ural. Otd. Ross. Akad. Nauk, 2006, pp. 86–88.

Makhotkin, I.L., The age and petrology of kimberlites and related rocks from the Kimozero area, northern shore of Lake Onega, Karelia, in *Geokhimiya magmaticheskikh porod. Mater. 21st Vseroos. Nauchn. Shkoly po geokhimii magmaticheskikh porod,* (Geochemistry of Igneous Rocks. Proc. 21st All-Rus. Workshop Geochem. Igneous Rocks), Apatity, 2003, pp. 107—109.

Malkov, B.A. and Philipov, V.N., *Bariophlogopite and accessory pyrophanite in the diamond-bearing kimberlite from the Yermak-7 pipe on the Kola peninsula, Vestn. Inst. Geol. Komu Nauchn Ts.*, 2005, vol. 128, no. 6, pp. 5—10.

Masum, K.M., Doyle, B.J., Ball, S., and Walker, S., The geology and mineralogy of the Anuri kimberlite, Nunavut, Canada, *Lithos,* 2004, vol. 76, pp. 75–96.

Milashev, V.A., *Evolyutsiya kimberlitovogo magmatizma* (Evolution of the Kimberlite Magmatism), St. Petersburg: VNIIOkeangeologiya, 2015.

Mitchell, R.H., Manganoan magnesian ilmenite and titanian clinohumite from the Jacupiranga carbonatite, Sao Paulo, Brazil, *Am. Mineral.*, 1978, vol. 63, pp. 544–547.

Mitchell, R.H., *Kimberlites: their Mineralogy, Geochemistry and Petrology*, New York: Plenum Press, 1986.

Nikishov, K.N., *Petrologogeokhimicheskaya model kimberlitovogo protsessa* (The Petrology and Mineralogy Model of the Kimberlitic Process), Moscow: Nauka, 1984.

Nixon, P.H., von Knorring, O., and Rooke, J., Kimberlites and associated inclusions of Basutoland: a mineralogical and geochemical study. *Am. Mineral.*, 1963, vol. 48, pp. 1090–1132.

Pasteris, J.D., The significance of groundmass ilmenite and megacryst ilmenite in kimberlites. *Contrib. Miner. Petrol.,* 1980, vol. 75, pp. 315–325.

Putintseva, E.V., Kimberlites and metakimberlites of Kimozero (Karelia), in *Petrografiya magmaticheskikh i metamorficheskikh porod* (Petrography of Magmatic and Metamorphic Rocks), Petrozavodsk: Karel'sk. Nauchn. Ts., 2016, pp. 481–483.

Putintseva, E.V., Zhitnikov. I.A., Salnikova, E.B., Nosova, A.A., Ipat'eva, I.S., Pimenova, Yu.G., Yakovleva, S.Z., and Plotkina, Yu.V., Isotope geochemistry and geochronology of the Paleoproterozoic kimberlites of the Kimozero occurrence (Karelia), *Mat. 4th Ross. Konf. Isotop. Geokhronol.*, (Proc. 4th Russ. Conf. Isotope Geochronol), St. Petersburg, 2009, pp. 158–161.

Samsonov, A.V., Larionova, Yu.O., Salnikova, E.B., Nosova, A.A., Ipatiyeva, I.S., Pimenova, Yu.G., Yakovleva, S.Z., and Plotkina, Yu.V., Isotopic geochemistry and geochronology of Paleoproterozoic kimberlite Kimozero occurence (Karelia), in *Mat. 4th Ross. Konf. Isotop. Geokhronol.*,Proc. 4th Russian Conf. Isotope. Geochronol.), St. Petersburg, 2009, pp. 158–161.

Sobolyev, N.V., Botkunov, A.I., Lavrentyev, Yu.G., and Usov, L.V., New data about the composition of the minerals associated with the diamonds of the kimberlitic pipe Mir, *Russ. Geol. Geophys.,* 1976, no. 12, pp. 3–15.

Timofeev, A.A., Ilulpin, I.P., and Genshaft, Yu.S., The spatial distribution of ilmenites with different content of magnesium in kimberlites of Yakutiya, *Dokl. Akad. Nauk SSSR,* 1984, vol. 278, pp. 461–464.

Tompkins, L.A. and Haggerty, S.E., Groundmass oxide minerals in the Koidu kimberlites dikes, Sierra Leone, West Africa, *Contrib. Mineral. Petrol.*, 1985, vol. 91, pp. 245–263.

Ushkov, V.V., Kimozero occurence of diamond-bearing kimberlites in the Onega structure. *Geol. Polezn. Iskop. Karelia,* 2001, no. 3, pp. 94–98.

Ustinov, V.N., Zagainyyi, A.K., Smith, C.B., Ushkov, V.V., Lazko, E.E., Lukyanova, L.I., and Lobkova, L.P., Early Proterozoic diamond-bearing kimberlites of Karelia and their formation peculiarities, *Russ. Geol. Geophys.*, 2009, no. 9, pp. 739–750.

Voytkovskiy, Yu.B., Podgaetskiy, A.B., Zinchuk, N.N., Kotelnikov, D.D., and Generalov, O.N., Ilmenite in the xenolites and the graundmass of kimberlite of Mir and Sytykapskaya pipes, *Dokl. Akad. Nauk SSSR,* 1991, vol. 317, pp. 1215–1219.

Wyatt, B.A., Manganoan ilmenite from the Premier kimberlite, *Extended Abstracts of Kimberlite Symp., Cambridge, 1979* (Cambridge, 1979), pp. 274—284.

Wyatt, B.A., Baumgartner, M., Anckar, E., and Grutter, H., Compositional classification of "kimberlitic" and "nonkimberlitic" ilmenites, *Lithos,* 2004, vol. 77, pp. 819–840.

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