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FE-RICH ILMENITE AND KIMBERLITE MELT INTERACTION, EXPERIMENTAL RESEARCHES

Nikolenko EI, Afanasiev VP, Chepurov AI

V.S. Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russian Federation

Magnesian ilmenite (picroilmenite), a common kimberlite mineral, has been largely studied but many issues of its genesis remain poorly understood. Investigation of this kind is difficult for the scarcity of its natural mantle-derived parageneses which would provide clues to the formation conditions.

Most often ilmenite in kimberlites is high in magnesium (> 6 wt % MgO) and titanium (> 43 wt % TiO₂) and is paramagnetic at room temperature (Garanin et al., 1984), but paramagnetic ilmenite may coexist in some fields with a ferrimagnetic variety that contains more iron but less titanium. Specifically, ferrimagnetic ilmenite reaches 20-40 % in kimberlites from the Malaya Botuobia area (Yakutian diamond province), and may be even 90 % as in the case of the recently discovered Massadou kimberlite field in Guinea (Afanasiev et al., 2008).

As our studies have shown, magnetic ilmenite from the Massadou kimberlite has a zoned structure, with a hematite-rich ferrimagnetic core and a rim of typical paramagnetic picroilmenite (Fig. 1). The latter bears high contents of TiO₂, Cr₂O₃, MnO, MgO and low Al₂O₃ and FeO. The difference in TiO₂ and MgO percentages within a single grain may amount to 15 and 7-8 wt.%, respectively (Table 1).

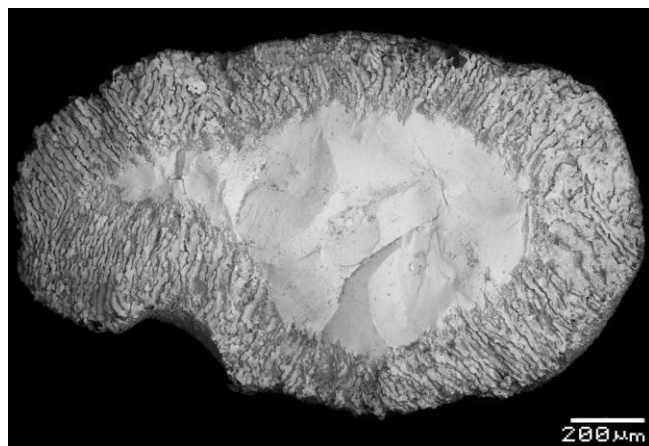


Fig. 1. SEM image of the natural zoned picroilmenite from Guinea.

Table 1. Major-oxide compositions of zoned ilmenites: c - core, r - rim, 1, 2 - dike №5 (Africa), 3, 4 - p. Dachnaya (Yakutia).

№	1c	1r	2c	2r	3c	3r	4c	4r
MgO	2.9	9.4	2.7	8.6	3.9	12.9	4.0	12.7
Cr ₂ O ₃	1.61	2.42	1.48	2.40	2.60	4.04	3.69	5.04
MnO	0.18	0.41	0.19	0.36	0.15	0.47	0.14	0.30
Al ₂ O ₃	0.34	0.08	0.34	0.01	0.80	0.33	0.77	0.27
FeO	61.3	39.4	61.7	39.1	57.3	32.8	56.5	32.0
TiO ₂	30.1	45.5	30.1	47.6	32.7	48.5	32.5	48.7
NiO	0.03	0.14	0.03	0.13	0.12	0.09	0.11	0.14
Nb ₂ O ₅	0.49	0.57	0.59	0.68	0.26	0.03	0.29	0.15
V ₂ O ₃	0.51	0.42	0.52	0.17	0.27	0.38	0.11	0.21
ZrO ₂	0.14	0.07	0.11	0.12	0.21	0.10	0.16	0.03
Total	97.6	98.4	97.7	99.2	98.3	99.6	98.3	99.6

Similar zoned ferrimagnetic ilmenites were found later in the Dachnaya, Yagodka, Mir (Yakutia), and Katoka (Angola) pipes (Nikolenko et al., 2010, Robles-Cruz et al., 2009). Ilmenites from the African and North American kimberlites typically have reaction rims rich in Mg and quite often in Cr (Haggerty et al., 1979).

The observed zonation in mineral grains may be produced by interaction of high-Fe primary ilmenite (hemoilmenite) with kimberlite melt rich in Mg and Ti and may record an incomplete substitution process. As the rim progressively evolves, the primary grain becomes fully replaced; after that the fibrous rim may recrystallize in a monomineral phase corresponding to ordinary paramagnetic magnesian ilmenite and loose its reaction signature. This hypothesis is consistent with ideas of other authors (Haggerty et al., 1979; Shulze, 1995). The paths of ilmenite-fluid metasomatic reactions are controlled mainly by Mg/(Mg+Fe²⁺) ratios in the fluid and by oxygen fugacity. These parameters, however, are variable, and their changes in the course of late reactions control the transition from normal to reverse zonation in magnesian ilmenite (Boctor and Boyd, 1980).

The reported experimental study aimed at obtaining zoned picroilmenites which would be similar to natural kimberlite-hosted ones in structure and composition.

The preconditioning of samples included selection of ferrimagnetic ilmenites from a mineral concentrate of kimberlite dikes in the Massadou field (Guinea) and



isolation of their hematite-rich grain cores using an ultrasonic dispersant. For this we used kimberlite drill cores from the Poiskovaya pipe (Upper Muna field, Yakutia). The samples were powdered after having removed xenoliths of other rocks and their compositions were determined by the XRF analysis (Table 2).

Table 2. Major-oxide compositions (wt. %) of kimberlite from Poiskovaya pipe (Yakutiya).

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO
0.52	2.0	2.32	4.01	2.67	0.06	26.92
CaO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	H ₂ O	LOI
11.92	0.03	0.64	0.19	9.63	0.92	9.23

Zoned ilmenites similar to their natural counterparts were obtained in nine experimental runs, on a press-free high-pressure setup “split-sphere” (Chepurov et al., 1997). The samples consisting of hemoilmenite (10 mol. % Geik, 44 mol. % Ilm, 46 mol. % Hem), powdered kimberlite, and metal titanium (in some runs) placed in a Pt capsule were treated in a high-pressure cell for 30 to 5520 minutes at 2.0 ± 0.25 GPa and 1100 ± 20 °C (Table 3).

Table 3. Experimental conditions at 2.0 ± 0.25 GPa *

№ Exp	t, min	T, °C **	M (mg) Ti	M (mg) HIlm	M (mg) Kimb
1.	120	1350 ±20	-	17.25	180.25
2.	30	1100 ±20	-	12.1	193.0
3.	60	1100 ±20	-	34.4	212.80
4.	600	1100 ±20	-	47.7	182.0
5.	300	1100 ±20	85.9	34.2	165.5
6.	3000	1100 ±20	87.4	21.1	172.1
7.	5520	1100 ±20	86.4	10.5	168.0
8.	120	1100 ±20	96.2	12	164.8
9.	120	1100 ±20	-	14.8	162.2

*Pressures were calibrated at room temperature against Bi and PbSe phase transitions. **Temperatures were monitored with a PtRh 30/6 thermocouple placed in the heater center. After heating, samples were quench cooled.

There was a problem with the use of a Pt capsule: iron may react with the capsule walls at temperatures above 800 °C as Pt forms solid solutions with FeO (Hansen and Anderko, 1958). In order to estimate the amount of iron that can react with platinum, two tests were applied to the capsule wall, 120 min each, at 1100 °C and 2.0 GPa. Iron, of the maximum amount 2.24 wt. %, penetrated into the wall to a depth of 8 microns. As our calculations showed, no more than 3.5 wt. % FeO escaped from kimberlite, which hardly would bias significantly the experiment results.

According to the problem formulation, we were to reconstruct the experimental conditions at which a Fe-rich ilmenite grain would interact with kimberlite melt without melting itself. The capsule was examined after each run and several indicators of melt existence in its interior were

recognized: colorless liquid and gas released each time as the capsule was opened; a quench zone at the walls appearing after each run; presence of euhedral crystals of olivine, spinel, and perovskite; existence of a quench silicate melt which binds silicate and oxide phases (Fig. 2).

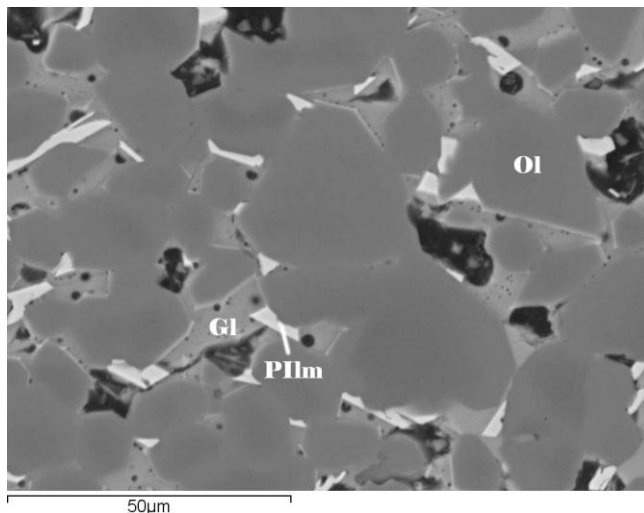


Fig. 2. SEM image of the sample after experiment №5: Pilm – picroilmenite, Ol – olivine, Gl – glass.

In the first run performed at 1200°C, Fe ilmenite was fully eliminated. Therefore, the following run was at a lower temperature and yielded a zonation in the ilmenites similar to that reported for natural grains from the Guinea and Yakutia kimberlites. The rim thicknesses almost did not change as the exposure time increased from 30 to 60 min. As the time was further increased to 600 min, the rim thickness grew from 100 up to 200-250 microns. Zonation appeared in Fe ilmenites in eight out of nine runs. The synthetic and natural zoned grains showed identical patterns in SEM images (Fig. 1 and 3).

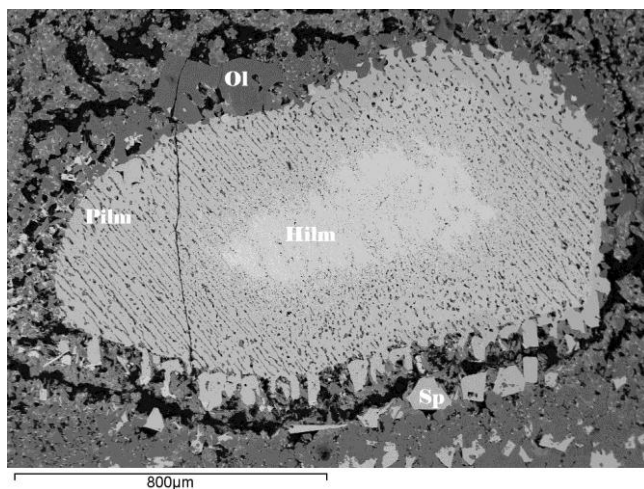


Fig.3. The synthetic sample of zoned picroilmenite from experiment №5: Pilm – picroilmenite, Hilm – hemoilmenite, Ol – olivine.



However, although being identical in the rim structure, the synthetic and natural ilmenites differed in compositions. The natural ilmenite grains have their rims enriched in Mg, Ti, and Cr but no TiO₂ has been observed in the experiments, possibly because of low titanium contents in primary kimberlite. In the following runs, metal Ti was added to the capsule which bound the oxidizing components and a reduced environment was thus maintained inside it.

X-ray analysis after the first stage of the experiment showed higher MgTiO₃ in the rim at constant Fe₂O₃, i.e., a major role in the reaction belongs to isovalent isomorphic substitutions ($\text{Mg}^{2+} = 2\text{Fe}^{2+}$).

At the second stage of the experiment, interaction of high-Fe ilmenite with Mg- and Ti-rich kimberlite melt led to complete replacement of the primary grains. The newly formed ilmenites had higher MgTiO₃/Fe₂O₃ ratios while FeTiO₃ remained the same, which is evidence of prevalent heterovalent isomorphism; the ilmenites had inhomogeneous fine-grained structures and compositionally belonged to high-Mg and high-Ti paramagnetic microilmenite.

The experiment results indicate that the rims in ferrimagnetic grains may form by reaction with kimberlite melt at 1100 ± 20 °C and 2.0 ± 0.25 GPa. The core-rim difference in Hem contents was as high as tens of percent, which prompts core formation in an oxidized environment and its later transformation into Mg-rich ilmenite in more reduced conditions. The substitution process was incomplete, as one may infer from a sharp boundary of the reaction front and a homogeneous composition of the cores. When it is complete, Fe-rich ilmenite fully transforms into Mg-rich ilmenite and reaction signatures disappear. The origin of primary Fe-rich ilmenite where from Mg-rich ilmenite is derived remains however unclear.

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