This discussion paper is/has been under review for the journal Solid Earth (SE). Please refer to the corresponding final paper in SE if available.

Picroilmenites in Yakutian kimberlites: variations and genetic models

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Received: 8 July 2013 – Accepted: 20 July 2013 – Published: 20 August 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

Major and trace element variations in picroilmenites from Late Devonian kimberlite pipes in Siberia reveal similarities within the region in general, but show individual features for ilmenites from different fields and pipes. Empirical ilmenite thermobarometry (Ashchepkov et al., 2010), as well as common methods of mantle thermobarometry and trace element geochemical modelling shows that long compositional trends for the ilmenites are a result of complex processes of polybaric fractionation of protokimberlite melts, accompanied by the interaction with mantle wall rocks and dissolution of previous wall rock and metasomatic associations. Evolution of picroilmenite’s parental magmas was estimated for the three distinct phases of kimberlite activity from Yubileynaya and closely located Aprelskaya pipes showing heating and increase of Fe of mantle peridotites minerals from stage to stage and splitting of the magmatic system in the final stages. High pressure (5.5–7.0 GPa) Cr-bearing Mg-rich ilmenites (Group 1) reflect the conditions of high temperature metasomatic rocks at the base of the mantle lithosphere. Trace element patterns are enriched to 0.1–10/C1 and have flattened, spoon-like or S- or W-shaped REE patterns with Pb > 1. These result from melting and crystallization in melt – feeding channels in the base of the lithosphere, where high temperature dunite – harzburgites and pyroxenites were formed. Cr-poor ilmenite megacrysts (group2) trace the high temperature path of protokimberlites developed as result of fractional crystallization and wall rock assimilation during the creation of the feeder systems prior to the main kimberlite eruption. Inflections in ilmenite compositional trends probably reflect the mantle layering and pulsing melt intrusion during the melt migration within the channels. Group 2 ilmenites reveal inclined REE enriched patterns (10–100)/C1 with La/Ybn 10–25 similar to those derived from kimberlites, and HFSE peaks (typical megacrysts). A series of similar patterns results from polybaric AFC crystallization of protokimberlite melts which also precipitated sulfides (Pb < 1) and mixed with partial melts from garnet peridotites. Relatively low-Ti ilmenites with high Cr content (Group 3) probably crystallized in the metasomatic front under the
rising protokimberlite source and represent the product of crystallization of segregated partial melts from metasomatic rocks. Cr-rich ilmenites are typical for veins and veinlets in peridotites crystallized from highly contaminated magma intruded into wall rocks in different levels within the mantle columns. The highest in TRE ilmenites 1000/C1 have REE patterns similar to those of perovskites. Low Cr contents suggest relatively closed system fractionation which occurred from the base of the lithosphere up to the garnet–spinel transition, according to monomineral thermobarometry for Mir and Dachnaya pipes. Restricted trends were detected for ilmenites from Udachnaya and most other pipes from the Daldyn-Alakit fields and other regions (Nakyn, Upper Muna and Prinanabarie), where ilmenite trends extend from the base of the lithosphere mainly up to 4.0 GPa. Interaction of the megacryst-forming melts with the mantle lithosphere caused heating and HFSE metasomatism prior to kimberlite eruption.

1 Introduction

Magnesian ilmenites or picroilmenites occur in most kimberlites (Boyd and Nixon, 1973; Sobolev, 1974; Dawson and Smith, 1977; Mitchell, 1977; Gurney et al., 1979; Garanin et al., 1979; Agee et al., 1982; Amshinsky and Pokhilenko, 1983; Jones and Wyllie, 1985; Nixon, 1987; Rodionov et al., 1991; Moore et al., 1992; Schulze et al., 1995; Griffin et al., 1997; Kostrovitsky et al., 2004; Wyatt et al., 2004; Alymova et al., 2008; Robles-Cruz et al., 2009) as discrete nodules or in intergrowths with phlogopites, olivines, Cr-poor pyropes (Gurney et al., 1979; Smith et al., 1975; Harte and Gurney, 1975; Rodionov et al., 1991; Schulze et al., 2001) or clino- and orthopyroxenes (Dawson and Reid, 1970; Boyd and Nixon, 1973; Rodionov et al., 1993) or as inclusions in these minerals. Ilmenites were found in different pyroxene xenoliths (McCallister et al., 1975; Pokhilenko et al., 1999; Kopylova and Caro, 2004; Kopylova et al., 2009; Aulbach et al., 2007), in mica-amphibole-rutile-ilmenite-clinopyroxenes (MARIDs) (Dawson and Smith, 1977; Wagner et al., 1996; Kramers et al., 1983; Gregoire et al., 2002) and other metasomatic associations (Haggerty, 1983; Dowson, 1987;
Gregoire et al., 2002; Simon et al., 2003), including diamond-bearing varieties (Ponomarenko et al., 1971; Pokhilenko et al., 1976). More rarely they were described in eclogites (Smith and Dawson, 1975; Pyle and Haggerty, 1998). Groundmass ilmenites in kimberlites are lower in MgO, NiO and Cr$_2$O$_3$ (Pasteris, 1980; Mitchell, 1986).

Picroilmenites (Ilm) are used as indicator minerals for kimberlite prospecting due to their high density and relative resistance to alteration (Sobolev, 1980; Afanas’ev et al., 2008). Within the same field they show similarities of major and trace elements (Mn, Al, Nb, V, Ni) (Amshinsky and Pokhilenko, 1982; Kostrovitsky et al., 2003; Wyatt et al., 2004; Alymova et al., 2004, 2008; Alymova, 2006).

Ilmenite megacrysts are sometimes zoned and fibrous (Nikolenko and Afanasiev, 2008; Robles-Cruz et al., 2009) and contain blebs from fluid inclusions which suggest rapid crystallization and dissolution events reflecting an origin in dynamic fluid-rich systems (Kopylova et al., 2009).

Cr-bearing picroilmenites occur as intergranular grains in peridotites, in metasomatic veins (Grégory et al., 2002, 2003) and veinlets, at the contacts of megacrystalline assemblages with deformed peridotites Moore and Lock, 2001) and in the rims of large low-Cr grains in polycrystalline ilmenite nodules (Schulze et al., 1995).

Comparing megacryst and xenoliths compositions from > 90 kimberlite pipes from Yakutia (Fig. 1) using original (Ashchepkov et al., 2010, 2013a) and published data (Sobolev, 1974; Amshinsky and Pokhilenko, 1983; Kostrovitsky et al., 2003; Alymova, 2006; Alymova et al., 2008), we checked the hypothesis of ilmenite megacryst formation during polybaric fractionation of protokimberlite melts (Ashchepkov et al., 2010, 2012, 2013a) in channels and accompanying mantle veins and metasomatic systems. This model develops earlier ideas about crystallization in large pegmatite-like bodies in the base of the subcratonic lithospheric mantle (SCLM) (Gurney et al., 1979; Griffin et al., 1997; Moore and Lock, 2001; Moore and Belousova, 2005).
2 Analytic methods and data set

Ilmenite grains were analyzed in the Institute of Geology and Mineralogy (Novosibirsk) using a CamebaxMicro electron microprobe. All analyses were made in wavelength-dispersive (WDS) mode using a set of natural reference minerals and synthetic glasses for calibration. For the ilmenites it was used standard GF-55 (Lavrentyev et al., 1987). The accelerating voltage 15 kV and a focused beam current 20 nA were used. Reduction procedure using “Karat program” (Lavrent’ev and Usova, 1994) was applied to the analyses. The relative standard deviation did not exceed 1.5 %, the precision was close to 0.02–0.015 % for minor elements. Xenolith analyses include data for 140 veined peridotite and websterite xenoliths from the Sytykanskaya pipe (Fig. 2), and ilmenites from heavy mineral separates from kimberlite pipes in several regions: Daldyn, Alakit, Malo-Botuobinsky, Upper-Muna, Nakyn and Anabar kimberlite fields (see Kostrovitsky et al., 2007, Fig. 1). Ilmenite associations from Mir, Udachnaya and other Yakutian pipes (Alymova, 2006; Alymova et al., 2008) and additional data for pyroxenites (Kuligin, 1997) and peridotites (Malygina, 2000) from Udachnaya (Malygina, 2000; Logvinova et al., 2005; Pokhilenko, 2006; Solovieva et al., 1997, 2008) were included in the database containing ~ 4000 ilmenites from Yakutian kimberlites (~ 30 000 minerals altogether).

Trace element analyses for > 90 ilmenites from Yakutian kimberlite concentrates and xenoliths and ~ 800 for other minerals (garnet, clinopyroxenes, phlogopites etc.) were obtained in the Analytic Centre of UIGGM on a Finnigan Element ICPMS with a UV LaserProbe using international reference standards NIST 612–614.

The major and trace element compositions and the program for the calculations of PT conditions are available in the supplementary files 1–3.

3 Variations of picroilmenite compositions in Yakutian kimberlites

All types of mantle ilmenite-bearing associations described in the literature were found among the Kimberlite xenoliths from Siberia (Ponomarenko, 1971; Pokhilenko et al.,
1976, 1999; Sobolev et al., 1984; Kostrovitsky et al., 2003; Alymova et al., 2006; Nikolenko and Afanasiev, 2008; Solovieva et al., 2008 etc.).

3.1 Megacrysts and their textural variations

Ilmenite megacrysts occur as discrete nodules of different sizes (up to 9–10 cm) and are mostly monocrystals. In several localities, such as the large nodules like in Sytykan pipe often reveal polycrystalline structures (Fig. 2a, b) and contact relationships. Polycrystalline aggregates from Nebaibyt and other pipes from the Anabar region contain intergranular rutile, perovskite or apatite, similar to those in the Kelsey Lake pipe (USA) (Schulze et al., 1995; Ashchepkov et al., 2001, 2013c). Ulvospinel crystals surrounding ilmenite grains were found in Upper Muna pipes (Kostrovitsky and Bruin, 2004; Kostrovitsky et al., 2007; Yakovlev et al., 2008).

3.2 Ilmenites in pyroxenites and other Cr-low rocks

In Dalnyaya pipe, ilmenites occur as giant-grained crystals with inclusions of low-Cr clinopyroxenes (Rodionov et al., 1988), low-Cr pyropes and often olivines. In Udachnaya and in Mir Cr-poor pyroxenites (< 0.5 % Cr$_2$O$_3$) are more typical (Alymova et al., 2008). Megacrystalline garnets zoned in CaO (Sobolev et al., 1975) contain picroilmenite inclusions (4–5 % MgO, 3.5 % Cr$_2$O$_3$). Carbonate intergranular veinlets in megacrystalline associations also contain picroilmenites. Giant-grained ilmenite and phlogopite intergrowths and glimmerites with ilmenites occur kimberlites from Anabar. Ilmenite with rutile grains are commonly found in phlogopite megacrysts in the Alakit kimberlites (Babushkina and Marshintsev, 1997; Ashchepkov et al., 2004). Ilmenites in high temperature (HT) Ti-rich garnet pyroxenites form symplectites with pyroxenes in Mir pipe (10–12 % MgO).

Mg-rich ilmenites (8–12 % MgO) occur in pyroxenite xenoliths (Pokhilenko et al., 1999; Taylor et al., 2003; Roden et al., 2006; Alymova, 2008) from the Udachnaya and Mir pipes. They are analogous to ilmenite-pyroxene symplectite intergrowths found
Picroilmenites in Yakutian kimberlites: variations and genetic models

I. V. Ashchepkov et al.

3.3 Ilmenites in peridotites

Rare ilmenite associations with Cr-rich (9–13.5 % Cr$_2$O$_3$), Ti-bearing pyropes (up to 1.5 % TiO$_2$) in harzburgites from Udachnaya (Alymova, 2008) are similar to those from Kelsey Lake pipes (USA) (Schulze et al., 1995; Ashchepkov et al., 2001, 2013c). Fragments of the contacts of megacrystalline ilmenite with sheared peridotites containing Cr-diopsides similar to those described in South African kimberlites (Moore and Lock, 2001) (Fig. 2a) (9–10 % MgO; 2.5 % Cr$_2$O$_3$) are found among the xenoliths from Sytykanskaya pipe. Sheared peridotites with abundant intergranular ilmenite grains were also found in Komsomolskaya pipe (Fig. 2b). Fine-grained polycrystalline monomineral ilmenite aggregates sometime intrude peridotites and cut large mineral grains such as garnet porphyroclasts. This fact, and the rounded shape of ilmenite grains in interstitial space filled by carbonates, suggest their possible origin from an immiscible oxide liquid (Clarke and Mackay, 1990).

Zircon-bearing peridotites and Cr-diopside pyroxenites with ilmenites (Dawson et al., 2001) were found in the Alakit region; zircon megacrysts (Spetsius et al., 2002) may be associated with ilmenites. Highly Cr-rich picroilmenites (2–8 % Cr$_2$O$_3$) are widespread in metasomatic and veined peridotites (Harte, 1987; Konzett et al., 2000; Dawson et al., 2001; Gregoire et al., 2002) in the Alakit region, especially in Sytykanskaya and Komsomolskaya pipes. Such ilmenites were discovered in rare diamondiferous peridotite xenoliths from Mir (Ponamarenko, 1971) and Udachnaya (Pokhilenko et al., 1976; Solovieva et al., 1997; Alymova, 2006). Ilmenites are common in high temperature
(HT) dunites and megacrystalline harzburgites which possibly represent contact zones of magmatic conduits and veins (10–12 % MgO, 0.8–1.5 % Cr₂O₃). They are also common in hybrid Cr-bearing garnet pyroxenites from Obnazhennaya (Ovchinnikov, 1990; Taylor et al., 2003) (5–6 % MgO in ilmenites) and some other pipes.

Some phlogopite–Cpx veins with rutile and apatite in contact with garnet peridotites from Udachnaya pipe may represent the analog of so-called MARIDS (Dawson and Smith, 1977; Gregoire et al., 2002).

In Udachnaya pipe there are xenoliths of peridotite breccias where the material cementing microxenolith and olivine xenocrysts is phlogopite-diopside-amphibole with -Ti-chromite and picroilmenites (7 % MgO); large ilmenites are also found as xenocrysts in breccia (9–10 % MgO).

### 3.4 Ilmenites in diamond – bearing associations

Diamond inclusions rarely contain ilmenites as described in Sputnik pipe (Sobolev et al., 1997). Ilmenites found as diamond inclusions have the highest Cr₂O₃ (8–12 %) and Mg contents (Meyer and Svisero, 1975; Sobolev et al., 1997), similar to those from ilmenite-bearing peridotites (Pokhilenko et al., 1976) (~ 8 % Cr₂O₃). Ilmenite diamond inclusions (Taylor and Anand, 2004; Stachel et al., 2004; Sobolev et al., 1997, 2003) often are Cr-poor (Cr₂O₃ % < 0.2 %) and similar to compositions typical for diamond-bearing eclogites (De Stefano et al., 2009) of B and C type and sometime contain essential amounts of MnO. Cr-poor ilmenites (0.04 to 0.23 % Cr₂O₃; 9.7 to 11.3 % MgO) occur as intergrowths with type II diamonds (Moore, 2009) at the Mir pipe (Sobolev, 1974) and belong to the megacrystic suite. Cr-Mg-poor and Mn-bearing (Kaminsky et al., 2001; Kaminsky and Belousova, 2009) ilmenites occur in diamonds with ultra-deep mantle inclusions. But most of Mg-eclogites are not rich in Mn (Beard et al., 1996; Snyder et al., 1997) as is typical for South Africa eclogites (Appleyard et al., 2007). Cloudy diamonds also include nano-crystalline ilmenites together with phlogopites, carbonatites, apatites in the dark fluid matter (Logvinova et al., 2008; Sobolev
et al., 2009). The ultra-deep diamonds from Juina also contain ilmenites (Wirth et al., 2009).

4 Ilmenite compositional trends in Siberian kimberlites

We choose in variation diagrams TiO$_2$ as the main axe in variation diagrams as pressure dependent-component, though variations are commonly described relative to MgO (Mitchell, 1977; Moore et al., 1992; Wyatt et al., 2004). Metasomatic peridotite xenoliths (Fig. 3) are characterized by ilmenites with $> 0.5\%$ Cr$_2$O$_3$ (black dots, shaded area in TiO$_2$-Cr$_2$O$_3$ diagram). Very high Cr$_2$O$_3$ values ($\sim 8\%$) occur in diamond-bearing ilmenite peridotites (Ponomarenko et al., 1971; Pokhilenko et al., 1976) and as diamond inclusions (Sobolev et al., 1997).

Ilmenites from garnet pyroxenites are lower in Cr$_2$O$_3$ and higher in MgO (shaded area in TiO$_2$ vs Al$_2$O$_3$ diagram). MgO-, TiO$_2$-rich ilmenites from MARIDs all show relatively low Al and Cr contents. Altogether, ilmenites from metasomatic peridotites, pyroxenites, eclogites and MARIDs form a long and rather regular linear and TiO$_2$-MgO and TiO$_2$-FeO trends (Fig. 3) similar to those for ilmenites from individual pipes (Wyatt et al., 2004). These correlations are suggested to be the signs of crystal differentiation of protokimberlite magmas (Griffin et al., 1997; Wyatt et al., 2004). Different types of compositional zonation (Schulze et al., 1995; Afanasiev et al., 2008; Robles-Cruz et al., 2009) with more Mg-rich cores (or the opposite with Cr- and Mg-enriched rims) are found among the ilmenites from Mir, Sytykanskaya and other pipes, especially in the polycrystalline aggregates which occur in contact with sheared peridotites (Moore and Lock, 2001). They also occur in polymict breccias (Morfi et al., 1999; Zhang et al., 2001; Pokhilenko, 2009; Giuliani et al., 2013) showing varying Cr-content within the same samples. Nevertheless, commonly discrete megacrysts have rather constant compositions and probably reflect conditions of the same evolving magma portions.

Comparisons of the compositions of ilmenites from concentrates and xenoliths for Udachnaya, Dalnyaya, Sytykanskaya and Mir pipes (Fig. 4a–c) show their overlap but...
commonly ilmenites from xenoliths are more Mg and Ti-rich. Those from pyroxenite Cr-low xenoliths have peridotite xenoliths.

4.1 Daldyn field

In variation diagrams, continuous trends in the interval from 55 to 45 % TiO$_2$ are typical for ilmenites from the Daldyn pipes (Amshinsky and Pokhilenko, 1983; Rodionov et al., 1988; Pokhilenko et al., 1999; Ashchepkov et al., 2003; Kostrovitksy et al., 2003; Alymova et al., 2004). TiO$_2$ show continuous negative correlations with FeO and positive with MgO according to crystal chemistry. Diagrams TiO$_2$-Al$_2$O$_3$, NiO, Cr$_2$O$_3$ and V$_2$O$_5$, consists from several separate arrays with varying inclinations (Fig. 5a). Increase in Fe and incompatible elements accompanies decrease of MgO, TiO$_2$ and NiO controlled by olivine fractionation. Nearly constant and low Al$_2$O$_3$ content evidence for a very low fraction of precipitating garnet. But in Dalnaya megacrysts this component in megacryst are higher.

The stepwise increase of Cr$_2$O$_3$ content in three intervals from 0.5 to 2 % Cr$_2$O$_3$ in ilmenites from Zarnitsa (Amshinsky and Pokhilenko, 1983) is typical for nearby pipes in the Daldyn region (Alymova et al., 2004) (Fig. 5a). For most Daldyn ilmenites, an increase in Cr is found at the beginning and the end of the crystallization trend.

Ilmenites from Osennyaya pipe repeat the variations found for ilmenites from Zarnitsa but shift the interval to 44–50 % TiO$_2$ and are higher in MgO (Fig. 5b). The extended TiO$_2$ range is found in ilmenites from Aeromagnitnaya pipe, located 6 km to the west, and all the pipes in Zarnitsa cluster having similar ilmenite compositional variations (Alymova et al., 2004). In the MgO-TiO$_2$ diagram (Wyatt et al., 2004), ilmenites from Daldyn plot in the less oxidized part of diagram than those from the Alakit field. The compositional trends for ilmenites from the smaller pipes are shorter than those for Zarnitsa and other large pipes. In the heavy mineral concentrate of the micaceous type II kimberlite from Bukovinskaya pipe (Kostrovitksky and Bruin, 2004) Ti-chromites are more common than ilmenites.
4.2 Alakit field

Ilmenite trends from kimberlite pipes in the Alakit field are more variable in Cr$_2$O$_3$ content (Figs. 4c, 5b, 6b) than those from the Daldyn field. The Cr-poor (< 0.5% Cr$_2$O$_3$) sub-trends are short (55–49% TiO$_2$) for ilmenites from Sytykanskaya pipe and more extended for those from Yubileynaya and other pipes. In general, Cr content increases towards the low-Ti part of the diagram. Comparison with ilmenites in xenoliths shows that sometimes Cr variations with close Ti content corresponds to Cr variations found in different part within the same veins in peridotite xenoliths. Dashed subvertical lines in the TiO$_2$-Cr$_2$O$_3$ diagrams correspond to nearly equal pressures as determined by the PT calculations (see thermobarometry). A subsequent increase in Cr$_2$O$_3$ accompanying decrease of TiO$_2$ is characteristic for Yubileynaya ilmenites (Fig. 5b). The decrease in both Al and Ti is typical for ilmenites from this field. Ilmenites from the heavy mineral fraction of the Ozernaya pipe, which cuts the Yubileinaya pipe in quarry, are more enriched in Cr$_2$O$_3$ and show a wider compositional range, while those from the Ottorzhzenets body are restricted in TiO$_2$ content, lower in Cr$_2$O$_3$ but higher in Al$_2$O$_3$. In the right Mg-Ti-rich part of diagram Cr-bearing varieties also present. Variation in Cr content of ilmenite from the Yubileynaya pipe (Fig. 5b) and the kimberlite phases found in the same quarry (Ozernaya and Ottorzhzenets) demonstrate evolution of protokimberlite magmas and in the associated veins in peridotites. Ilmenites from the nearby Aprelskaya pipe located not far repeat some compositional features of ilmenites from the kimberlite bodies from Yubileynaya quarry.

In Sytykanskaya (Fig. 4b), Komsomolskaya and other pipes where metasomatic minerals are common, Cr-rich associations prevail and Cr-poor ilmenite compositions are confined to the TiO$_2$-rich Cpx bearing associations. The subtrends with 2–6% Cr$_2$O$_3$ ranges for Ilm are found within the some veined metasomatic Phl in peridotite xenoliths from Sytykanskaya. This is common for most pipes from the Alakit field and in some from the Upper Muna field. For the Aykhal pipe, the ilmenite trend is restricted (46–53% TiO$_2$). It may be subdivided into 7–8 groups or more, as with ilmenites from
Yubileynaya. At the end of the trend, MgO, NiO and Al$_2$O$_3$ contents decrease rapidly with TiO$_2$.

### 4.3 Malo-Botuobinsky field

Ilmenite megacryst trends from Malo-Botuobinsky pipes (Logvinova and Ashchepkov, 2008; Ashchepkov et al., 2010) (Figs. 4c, 6c) are very long (31–50 % TiO$_2$), with those from Mir and Dachnaya showing logarithmic shapes probably formed by continuous fractionation, as suggested for ilmenites from Monastery kimberlites and other pipes from South Africa (Moore et al., 1992; Griffin et al., 1997) and North America (Wyatt et al., 2004). The Ti-rich, Cr-poor ilmenites from pyroxenite xenoliths (Alymova, 2006) form a dense cluster at the beginning of the trend and occur in the lower part of the SCLM according to thermobarometry. The Cr-rich varieties from metasomatites do not cover the entire trend of megacrysts (Fig. 6). Low Ni and Cr contents are typical for large megacrysts (commonly 50–47 % TiO$_2$). Cr contents increase at the beginning and end of the crystallization trend and in the middle part of the ilmenite trends from Mir and Dachnaya pipes. The small continuous rise of Al$_2$O$_3$ for the Ti-poor varieties suggests a lack of garnet among the main precipitating phases during fractional crystallization, while for most of the other pipes the Al$_2$O$_3$ content rapidly decreases. Comparison of ilmenites from the whole pipe and from the one separate kimberlite specimen from Mir (black dot in Fig. 4c) shows more restricted variations relative to the whole ilmenite population. Ilmenites from Amakinskaya and International'naya pipes reveal shorter TiO$_2$ trends divided into four separate intervals.

### 4.4 Upper-Muna field

The crystallization trend for picroilmenites from the Deimos pipe is similar to those from Alakit pipes (Fig. 5c), showing an increase in Cr in the middle part of the trend, possibly due to contamination from peridotite. An increase in Cr$_2$O$_3$ accompanying decrease of TiO$_2$ is typical for metasomatic veins in peridotites. This continuous trend may be
separated into 7–8 groups (repeated in PT diagram). Similar trends that are longer and more discrete were determined for ilmenites from Zapoljarnaya pipe (Fig. 7b). In the other Upper-Muna kimberlite pipes, ilmenites are rare in heavy mineral concentrates. Ilmenites from the Poiskovaya pipe are unusual in their compositional range, being lower in TiO$_2$ and higher in Al$_2$O$_3$.

4.5 Nakyn field

In the Nakyn field (Lapin et al., 2007) (Fig. 7a), picroilmenites are abundant only in the tuffs from the Nyurbinskaya pipe. They reveal a restricted range of TiO$_2$ from 55 to 48 % and can be divided to three groups. Rapid decrease of NiO and MgO and increase of FeO and V$_2$O$_5$ may be explained by olivine fractionation. Ilmenites from the placer near Nyurbinskaya pipe reveal a much longer trend which also splits into three groups but is much longer (Fig. 7a). Metasomatic increase in Cr is accompanied by a decrease in Al, possibly due to garnet co-crystallization.

4.6 Prianabarie

In kimberlites from Prianabarie, including mainly pipes from Kuranakh an Ary-Mastakh fields, ilmenites are more common in heavy mineral separates than chromites. Their trends are commonly restricted to 55–40 % TiO$_2$ interval but in several pipes rare Fe-rich ilmenite compositions occur. Most ilmenites (42–50 % TiO$_2$) show low Cr-content, increasing only for varieties with > 50 % TiO$_2$. Only in Trudovaya pipe (Kuranakh) a stepwise decrease from 4 to 1 % Cr$_2$O$_3$ accompanies a decrease in TiO$_2$. Polycrystalline ilmenites from the Nebaibyt pipe have Cr-rich cores, unlike ilmenites in North American kimberlites where Cr- and Mg-rich rims are more common (Hunter and Taylor, 1984; Schulze et al., 1995) (Fig. 7c).
5  Monomineral ilmenite thermobarometry

The empirical dependence of the geikilite component in ilmenites on pressure can be used for approximate estimates of the diamond grade of kimberlites (Sobolev, 1977, 1980; Sobolev and Yefimova, 2000). The influence of Cr₂O₃ should be accounted also (Semytkivska and Ulmer, 2008).

Ilmenites in peridotites are practically the main concentrator of TiO₂ in peridotite assemblages because rutile is found only in grain boundaries. Even Cpx can not seriously influence on the TiO₂ balance in ilmenite. So monomineral thermobarometry which is mainly based on the cell sizes like for pyroxenes (McGregor, 1974; Nimis and Taylor, 2000).

Ilmenite has two types of positions in structure. The distance between the Fe (or Mg)-O is highly dependent from the temperature an order of 1 magnitude more than between Ti–O distance (Wechsrel et al., 1984). So the exchange FaTiO₃-MgTiO₃ is suitable for the temperature estimates.

We used the large database of ilmenite bearing associations (Alymova, 2008 and new data) for the more precise calibration of the equations of the monomineral thermobarometer for ilmenites. Dependence of the geikilite mole fraction in hematite-geikilite solid solutions (Lindsley, 1965; Bishop, 1980; O’Neill et al., 1988; Brown and Navrotsky, 1993; Wechsler and Prewitt, 1984; Mitchell, 2003) on the cell size allows us to use the internal substitutions in ilmenites FeFeO₃-MgTiO₃ for monomineral barometry (Ashchepkov, 2006b).

The FeTiO₃-MgTiO₃ internal exchange accounting for the influence of the other components was used for Ol-Ilm thermometry (Taylor et al., 1998); which is cited here:

\[ T^0K = \left( -13715 + P1000DVT + 3785(2Fe#Ol-1) + 2830(Gk-Ilm) - 19560Hem-7840 Esk + 45122Hem Esk \right) / (2.231 – 8.3143\ln(Kd)) \]
where $\text{Mg#Ol} = 1 - \text{Fe#Ol}$; $\text{Esk(esklaite)} = \text{Cr}/2$; $\text{Hem(hematite)} = 1 - \text{Esk-Ti + Mn}$, all components are given in formula units (f.u.);

$$\text{Gk(geikilite)} = \text{Mg}; \text{Ilm} = 1 - \text{Esk-Hem-Gk};$$

$$\text{DVT} = 0.011(\text{Gk-Ilm}) - 0.047 + 0.015(2\text{Fe#Ol}-1)$$

$$\text{KD} = (1 - \text{Fe#Ol})/\text{Ilm}/(\text{Fe#Ol Gk})$$

To obtain the agreement with the (Nimis and Taylor, 1998) Cpx thermometry the following corrections were introduced $T^0 K = (T^0 K - 10(25 - P) - 250 + 400\text{Hem})0.95$

In the monomineralic formulation takes into account the forsterite content ($\text{Fo} = 1 - \text{Fe#Ol}$) according to:

$$\text{Fe#Ol (Ilm)} = (\text{Fe#Ilm} - 0.35)/2.25 - 0.000035(T^0 K - 750) \text{(f.u.)},$$

where $\text{Fe#Ilm} = \text{Fe}/(\text{Fe} + \text{Mg})$

A further correction $\text{Fe#Ol} = 0.1027 \ln(\text{Fe#Ol(Ilm)}) + 0.365$ (see Fig. 8c) gives good agreement with the observed values in xenoliths. Substitution of these values in the Ol-Ilm thermometer (Taylor et al., 1998) shows not a bad correlation with estimates based on clinopyroxene (Nimis and Taylor, 2000; Ashchepkov et al., 2010) thermometers (Fig. 8a). Comparison of calculated Fe#Ol for olivine coexisting with the ilmenites and silicate minerals yields realistic values for most of the PTX diagrams (Figs. 9–13) (Ashchepkov et al., 2010).

Evaluation of the single grain thermobarometry for olivine (De Hoog et al., 2010) shows that, if concentration of element in one of the minerals is negligible compared to the variation in the other mineral, the equation is simplifies to: $P = T(a - \ln C^I) - b$ where $C^I$ is concentration of trace elements. The $- \ln C^I$ is positive for minor components. But for major components forming the crystal structure as Ti the logarithmic equation may be simplified.

Close to lineal correlations is found between the cell sizes and experimental pressures (Fig. 8b) (Reynard et al., 1996; Karki et al., 2000) (Fig. 8). Rutile have essentially
lower in sizes cell unit (Liu, 1975) then ilmenite. Many ilmenites has an exsolutions of rutile in natural assemblages (Ashchepkov et al., 2001) and experimental products (Bataleva et al., 2012). Admixture of rutile suggest that essential reduction lineal correlation with the pressure in this exchange. The simplified equation \( P = A \text{Ti} + B T_0 + C \) where \( B \) includes corrections to Mg and Cr. These corrections were found using compositions minerals in the xenoliths with ilmenites varying in Cr and xenocrysts with zonal cores in rims.

Pressure estimates produced with clinopyroxene thermobarometry (Ashchepkov, 2003; Ashchepkov et al., 2010; Nimis and Taylor, 2000) for 110 ilmenite-bearing associations (Alymova, 2006; Ashchepkov, 2006b; Ashchepkov et al., 2010). Ilmenites often are not in complete equilibrium with all minerals in associations. We selected mainly analyses from closely located Ilm and Cpx. Best agreement between pressure estimates based on Cpx and Ilm was obtained for the peridotite xenoliths from Sytyanskaya pipe. The approximation allowed us to calibrate the barometer as following:

\[
P_0 = (\text{TiO}_2 - 23.1)2.152 - (T^0K - 700)/20.1\text{MgOCR}_2\text{O}_3
\]

and yielded a further correction \( P = P + 8.1(6.0 - P_0)/\text{Fe#Ol} \) (all components are in wt % and \( P \) in GPa).

This yields a better agreement then previous version (Ashchepkov et al., 2010). Nearly linear correlation of pressure between clinopyroxene and ilmenite estimates (using the same temperatures) was found within 7.0–3.5 GPa interval (Fig. 8b).

This equation is calibrated for the associations crystallized in Mg-rich protokimberlite melts and peridotite rocks and does not work well for the basaltic system as it overestimates the pressures. It is necessary to introduce an additional correction to Fe.

Checking this thermobarometric method for the large amount of kimberlitic concentrates and xenoliths from Yakutia and worldwide kimberlites (Ashchepkov et al., 2010, 2012, 2013a–c; Afanasiev et al., 2013) shows good agreement of the ilmenite PT parameter with those produced by the orthopyroxene (McGregor, 1974), clinopyroxene
(Nimis and Taylor, 2000) and Opx-Gar thermobarometric methods for mantle peridotites (Brey and Kohler, 1990; Nickel and Green, 1985).

The equation derived from the correlation with pressure values based on clinopyroxenes using the database for xenoliths from Mir and Udachnaya pipes (Alymova, 2006), data for xenoliths from Sytykanskaya pipe (Ashchepkov et al., 2004) and Dalnyaya from the published analyses (see list of references), yielded good agreement for the pressure using the same temperatures (Figs. 11 and 12). The correlations between the methods of mineral thermobarometry and PT diagrams based on pyroxenes and ilmenites show good agreement (Fig. 9b). The barometer works better at higher pressures than for shallow mantle conditions.

According to FeO/Fe$_2$O$_3$ ratios (Green and Sobolev, 1975; Wyatt et al., 2004) and calculations using the Ilm-Ol oxybarometer (Taylor et al., 1998), the degree of oxidation varies from −3 to +1 $\Delta$log QMF (Quartz-Magnetite-Fayalite) buffer and became positive for the Fe-rich ilmenites (Nikolenko and Afanasiev, 2010). The values for megacrystalline ilmenite are higher in general than diamond stability filed (McCammon et al., 1998; McCammon and Kopylova, 2004) and are close to the EMOG/D buffer (Stagno and Frost, 2010). Similar values above QMF are given by ilmenite-rutile oxygen barometry (Zhao et al., 1999). Direct measurements of intrinsic oxygen fugacity (Arculus et al., 1984; Haggerty and Tompkins, 1983, 1984; Kadik et al., 1989) for xenoliths and xenocrysts also give similar values. We calculated the oxygen fugacity values using the monomineral versions of the ilmenite-olivine and spinel olivine (Taylor et al., 1998) and garnet (Gudmusson and Wood, 1995) oxybarometers and corrected equations for clinopyroxene (Ashchepkov et al., 2012).

6 Regularities of the distribution of ilmenite associations in the mantle sections worldwide

The conditions obtained from pyroxene thermobarometry for ilmenite-bearing associations shown on the PT diagram (Fig. 10) reveal a similarity with those produced by
Ilmenite PT equations. The highest pressure part of the diagram (7.0–6.0 GPa) reflects PT estimates for the hottest pyroxenites and eclogites (Boyd, Nixon, 1973) and ilmenite-bearing pyroxenites which trace the convective branch of the geotherm corresponding to deformed garnet peridotites (Boyd et al., 1997). PT conditions for hybrid pyroxenites and HT metasomatic xenoliths plot within the transition between the SCLM base and lithospheric mantle (5.5 to 6.5 GPa) MARIDs (Dawson and Smith, 1977; Hamilton et al., 1998; Gregoire et al., 2002). Commonly PT clusters for Ilm-bearing metasomatic veins and megacrysts in the lower part of lithospheric mantle columns coincide in pressures but differ in temperatures and Fe# of coexisting Ol (Figs. 11–14).

7 Thermobarometry of ilmenite associations for mantle columns beneath Siberian kimberlite pipes

Enhanced calibrations of the thermobarometric equations for clinopyroxenes and garnets well as for ilmenites highlight the sharp layering of mantle sequences and divisions with the realistic arrays for the peridotite, pyroxenite and subcalcic garnets.

Ilmenite thermobarometry and other monomineral methods were used to show the positions of the megacrystalline series, pyroxenites and metasomatites in PT diagrams (Ashchepkov et al., 2010, 2012, 2013a, b).

All data are compiled together including the PT values for minerals from heavy mineral separates (Ashchepkov et al., 2010) and xenoliths from Udachnaya (Boyd et al., 1997; Kuligin, 1997; Pokhilenko et al., 1999; Alymova, 2006; Pokhilenko, 2006; Ionov et al., 2010), Mir (Beard et al., 1996; Roden et al., 2006; Logvinova et al., 2008) and Sytykanskaya pipes (Reimers et al., 1998; Alymova, 2006; Ashchepkov, 2010).

Wide variations of PT conditions for small xenoliths from Udachnaya pipe (Ashchepkov et al., 2013b) overlap those obtained previously for large and equilibrated xenoliths (Boyd et al., 1997). Regular linear geotherms with an inflection at the base determined for SCLM in South Africa (Boyd, 1973; Bell et al., 2003; Griffin et al., 2003) and the Slave craton (Russell and Kopylova, 1999; Kopylova and Caro, 2004) contrast with
the wide ranges of PT values from Siberia (Griffin et al., 2004; Aulbach et al., 2007; Ashchepkov et al., 2010). Adding the larger amount of PT points for Udachnaya xenoliths (> 200 new original and > 400 from the literature (Kuligin, 1997; Malygina, 2000; Pokhilenko, 2006; Alymova, 2006; Logvinova et al., 2005; Solovieva et al., 2008; Ionov et al., 2010; Yaxley et al., 2012; Agashev et al., 2013; Douchet et al., 2013) yielded a high dispersion of PT estimates obtained by garnet-orthopyroxene thermobarometry (Brey and Kohler, 1990).

PT conditions for megacrystalline ilmenites from Udachnaya trace advective PT path rising along the 40 mw m^{-2} geotherm from the SCLM base at 7.5 GPa to the boundary between the lower and upper parts of the SCLM at 4.0–3.5 GPa (Ashchepkov et al., 2010) (Fig. 11a). This PT path generally coincides with the HT PT estimates for some sheared and porphyroclastic peridotites obtained from polymineral (Brey and Kohler, 1990) and monomineral clinopyroxene thermobarometry. It is close to the PT conditions for the HT eclogites and chromite inclusions in diamonds (Logvinova et al., 2005).

PT estimates for ilmenite-bearing pyroxenites and peridotites together create lines of nearly equal pressures covering the range of heating from 35 to 45 mw m^{-2} in PT and P-Fe#Ol diagrams (Fig. 11a) at 5.0 and 5.5 GPa. The HT pyroxenites with ilmenites occur more frequently at pressures near 6.0–7.0 GPa, corresponding to the inflection in the pyroxene geotherm found for deformed peridotites (Boyd et al., 1997; Agashev et al., 2013) and for the positions of the eclogites. Hydrous minerals in veined and metamorphic peridotites occur in the 7.0–2.5 GPa pressure interval beneath Udachnaya (Ashchepkov et al., 2010, 2013b). On the P vs. Fe#Ol diagram (Fig. 11a), calculated variations for Fe# for the megacrysts increase from 0.1 to 0.15 in the 7.0–4.0 GPa pressure interval, partly coinciding with the Fo content for IIm-Cpx, Ol intergrowths with the ilmenites. But the Fe-lherzolite xenoliths and pyroxenites with IIm correspond to the lower values of Fe#Ol (0.1–0.12) values for (Alymova, 2006; Alymova et al., 2008; Solovieva et al., 2008). Lowest Fe# values of 0.05–0.06 are found in the harzburgites and most depleted diamond-bearing associations (Pokhilenko et al., 1976).
New data for Dalnyaya pipe base most on mantle xenoliths (> 110) (Ashchepkov et al., 2013) and for concentrate as well as previous data for pyroxenites (Rodionov et al., 1988, 1991; Alymova, 2006) give the most deep and HT plot of the mantle section in Yakutia. The Porhyroclastic and sheared peridotites are mainly correspondent to the 7–5 GPa interval which is overlapped also by the PT estimates for ilmenites which prevail in concentrate over chromites. Many of them are from the Ilm megapyroxenites sometimes with garnet (Rodionov et al., 2008). They are not the most HT xenoliths. But some peridotite xenoliths with sporadic ilmenites are corresponding to the 45 mwm\(^{-2}\) geotherm which locate in three level in the SCLM beneath this pipe. Xenolith are mainly lower in Fe\# then common megacrystalline ilmenite nodules some of them are coinciding with garnets (from peridotites) the other to Cr poor pyroxenes which are in association. The contamination of Ilm in Cr is notable but not high comparing to ilmenites from most other Daldyn and Alakit pipes (Fig. 11b).

In the PT diagram for the SCLM beneath the Mir pipe (Fig. 12a), the PT values for ilmenite megacrysts also trace a HT branch heated to 50–100°C above the conductive geotherm ~ 38 mw m\(^{-2}\) typical for Siberian mantle (Boyd at al., 1997) from 7.0 to 2.0 GPa. The inflection of geotherm called the convective branch (Boyd, 1973; Boyd et al., 1997) at 7.0 to 6.0 GPa is traced by ilmenites overprint the PT conditions for the Fe-enriched minerals. Further near 4.0 GPa geotherm is splitting and ilmenites trace the HT PT advective arrays close to PT conditions of clinopyroxenes from pyroxenites. The long stepped HT PT path refer to megacrysts geotherm (Egglor and McCalum, 1976) but several estimates in the lower part for the pyroxenites are close to the 37 mw m\(^{-2}\) low temperature (LT) geotherm. Symplectites with pyroxenes are found in the lower part of the convective branch.

In the P-Fe\#Ol diagram (Fig. 11b) the values for garnets, chromites and ilmenites form fluctuating lines, possibly reflecting primary layering of the SCLM formed by paleosubduction slabs (Pearson et al., 2003). The clots of ilmenite PT estimates may trace the boundaries of the primary layering. There are at least three P-Fe\#Ol arrays. The lower Fe\# values refer to the contact zones of megacrystalline associations while the
middle one corresponds to the common megacrysts. The most Fe-rich array is for ilmenite megapyroxenites. The Contamination in Cr is not typical for the Ilm from Mir pipe. Cr bearing metasomatic associations are found near 3 GPa and one at 5 GPa.

PT estimates for minerals from concentrates and xenoliths from Sytykanskaya pipe (Fig. 12b) can be used to reconstruct the SCLM section in the northern part of the Alakit region. The PT paths for ilmenite megacrysts create a stepped trend divided into three parts: two broad clusters at the base of the SCLM (7.0–6.5 GPa) and in the 5.0–3.0 GPa pressure interval, and a narrower chain connecting them. A broad scatter of the calculated Fe#Ol values is typical for the upper part near 4.0 GPa where the dense cluster suggests a large proportion of metasomatic veins (Reimers et al., 1998; Ashchepkov et al., 2010). The increase in Fe# and Cr for the ilmenites from the bottom to the upper part of the mantle section is typical for most of mantle sections beneath this kimberlite and most pipes in Yakutia especially in Alakit field (Ashchepkov et al., 2010). The abrupt increase of Cr and decrease of Fe# near 3.5 GPa and above in the mantle section corresponds to ilmenite crystallization mainly within metasomatic veins forming dense stockworks as at seen in xenoliths. The ilmenite-bearing xenoliths with the veinlets of Ilm and Cpx are widespread, mainly in the middle part of the mantle column.

PT values for ilmenites from the three kimberlite phases found in the Yubileinaya pipe quarry, i.e. autholithic kimberlite (Kurszlauskis et al., 2008; Zinchuck and Koptil, 2008), the Ozernaya pipe and Ottorzhenets body represent three stages of kimberlite activity (Figs. 13a, b, 14a). Ilmenites in heavy mineral fractions from the autholithic kimberlite show the deepest (≈ 7.5 GPa) and relatively HT conditions. The highest temperature values at the base of the SCLM correspond to a geothermal gradient of 43 mw m⁻² with deviations to the 35 mw m⁻² conductive geotherm. The continuation of the ilmenite PT path traces the 40 mw m⁻² geothermal gradients upward. The wide PT plots in the lower and middle part of the DCLM are nearly overlapping the continuous rise of Cr with decreasing pressure suggests connections of the stockworks of veins in the lower and upper parts of mantle sections and continuous contamination of rising melts. But
PT estimates for the Ozernaya mantle column (Fig. 13b) also reveal that the base of the SCLM is situated at 7.5 GPa. A wide scatter of temperature estimates between the 35 and 45 mW m\(^{-2}\) geotherms which is close to those of the Fe–enriched Cpx corresponds to the veined metasomatities. The Ilmenite PT clusters are located at 7.5–5.5 GPa and around 4.5 GPa.

PT values for ilmenites from the Ottorzhensets body (Fig. 14a) phase trace the 40 mW m\(^{-2}\) geotherm with deviations at the base of the SCLM. The garnets show a sharp difference in Fe#. Their PT values show lines of P-Fe#Ol which are close to those found for Yubileinaya. Hence the PT estimates determined for the three stages of magmatic evolution of the single kimberlite pipe show sharp differences in degree of heating and Fe, and an increase of scatter which is also shown by clinopyroxene PT values. The nearby large kimberlite pipe Aprelskaya (Fig. 14b) which is not highly diamondiferous shows PT diagram based on minerals from concentrate consisting from the separate arrays which are more evident in P-Fe# and -FO\(_2\) diagrams. Ilmenites in general mark the same level of the deep magmatic chamber split into two levels. But the lower one coincides with PT estimated of Ti-rich chromites which probably represent the more oxidized peridotite mater. In some mantle columns Ol-Ti-chromites veins probably dissolved and overprinted the earlier veins with ilmenites.

8 Trace element geochemistry of ilmenite megacrysts

The LAM ICP-MS study of ilmenite compositions (Ashchepkov et al., 2008b) reveals three main groups (Figs. 15–18). The first one (group 1) has low rare earth element (REE) concentrations and flatter, spoon-like or complex curved REE patterns. They have high peaks for Ta and Nb and slightly lower in Zr and Hf, similar to those for ilmenites from South Africa (Dawson et al., 2001; Gregoire et al., 2003). The Pb peaks are a characteristic feature. For the second group (gr2), inclined linear REE
8.1 Trace elements of ilmenites from Daldyn kimberlite field

In Udachnaya group 1 ilmenites prevail (Fig. 15a), with compositions of REE (0.1/C1) forming a series of patterns from spoon-like to flatter slightly REE-enriched patterns. Very high Ta-Nb peaks are in contrast to low REE concentrations. Ilmenites from Ukrainskaya and Zarnitsa (Ashchepkov et al., 2003) (Fig. 15c, d) show inclined or W-shaped REE patterns with varying La/Ybₙ > 10, which may be produced by melting of a source containing ~ 3–2 % garnet which is common for mantle lherzolites. The Pb dips shows separation of sulfides typical for the 2nd ilmenite group. Ilmenites from Festival’naya pipe (Fig. 15e) also show inclined La/Ybₙ patterns possibly produced by partial melting. The high Hf peak relative to Zr, as well as enrichment of Ba and Th found in some of these compositions, are unusual for ilmenites from the other pipes. Ilmenites from Dal’nyaya pipe have the lowest REE content and close to W-shaped REE patterns (Fig. 15b). Small negative Y anomalies were found only in ilmenites from Dal’nyaya and Ukrainskaya pipes.

8.2 Trace elements of ilmenites from Alakit kimberlite field

Ilmenites from different pipes in the Alakit region vary in trace element patterns. Those from the Aykhal pipe (group 1) show slightly inclined REE patterns for the most Ti-rich (deepest) samples (Fig. 16a). Ilmenites from Komsomolskaya pipe have W-shaped inclined REE patterns with an inflection at Gd and a peak at Pb (Fig. 16b). The mildly-enriched group ~ 100 relative to C1 chondrite (100/C1) of picroilmenites (gr2) also
shows trace element patterns typical for group 2 (Fig. 15b–d). Ilmenites from Yubileynaya have REE patterns (Fig. 15c) that are almost S-shaped, similar to those determined for chromites. The patterns of ilmenite from Ozernaya pipe (Fig. 15b) which lack REE enrichment $\sim 1/C1$ are flat. The high inclination of patterns (La/Yb$_n$) for LREE-enriched ilmenite grains with Pb $> 1$ differs from the moderate inclination of (gr2) ilmenite.

A low and flat REE pattern was found for Mg-rich ilmenites from Sytykanskaya which are Cr-rich, typical for garnet-free melting assemblages. However, ilmenites from the veins in xenoliths and large megacrysts in contact with peridotites show inclined patterns, which are slightly U-shaped in HMREE (Fig. 15f). Enrichment in Ta and Nb is also higher for the Cr-bearing megacrystalline ilmenite (Figs. 16e, 20b) (sample Stk1) (Fig. 2) than for ilmenite from phlogopite-clinopyroxene veins in lherzolites.

### 8.3 Trace elements of ilmenites from Malo–Botuobinsky kimberlite field

Trace element patterns for ilmenites from Mir (gr1) $\sim 0.1C1$ are flat in MHREE but vary in LREE patterns rising together with most of the trace elements. Typical group 2 patterns are found for two ilmenites from the middle part of the mantle column. The rim of one ilmenite from Mir reveals an abrupt enrichment in trace elements resembling that of group 3 samples, while the inner core is closer to group 2 in composition (Fig. 17a).

Ilmenites from the International'naya pipe show a REE pattern similar to garnets of pyroxenitic type with a hump in MHREE. Trace element diagrams reveal Y minima typical for low-Ca garnets (Stachel et al., 2008) and Siberian diamonds (Afanasiev et al., 2005) that show signs of depletion of the melt source. One ilmenite has a small minimum at Eu (Fig. 17b).

### 8.4 Trace elements of ilmenites from Nakyn and Upper Muna kimberlite fields

In the Nakynsky region (Fig. 17c) most of the high-pressure ilmenite (gr1) show flat REE patterns with gentle minima in MHREE and fluctuations in LREE especially in Ce.
The enriched (gr2) varieties demonstrate inclined linear trace element patterns similar to those of alkali basalts. The most enriched sample show the trace element (TRE) abundance close to the host kimberlite.

A flat REE pattern and very high enrichment in HFSE with Pb peak is found for ilmenite from Novinka pipe, Upper Muna (Fig. 17d).

8.5 Trace elements of ilmenites from Anabar kimberlite fields

In Prianabarie all three populations of analyzed ilmenites show different trace element patterns in the different pipes (Fig. 18). Ilmenites from Trudovaya pipe (Fig. 18a) demonstrate different types of trace element patterns like those from Aykhal pipe. Ilmenites having the REE level near 1/C1 display slightly inclined distributions with Pb peaks and a mild enrichment in Zr-Hf and Ta-Nb. Ilmenites with REE levels ~ 100/C1 (for La) demonstrate an inclination of the REE patterns close to primitive 1% melts produced in garnet – facies peridotites (McDonough and Sun, 1995). The most enriched ilmenites with the degree of enrichment up to 1000/C1 for La have La/Yb_n ~ 15. They show no Hf-Zr anomalies.

Ilmenites from the Nebaibyt pipe (Fig. 18b) have S-shaped patterns for REE and enrichment both in Nb-Ta and Zr-Hf and varying Y. Samples from the Khardakh pipe (Fig. 18c) display near flat (10/C1 for La) and U-shaped REE patterns or linear inclined basalt-like REE patterns and peaks in Pb. They are similar to those from Sytykanskaya pipe xenoliths.

9 Discussion

9.1 Model of origin based on PT estimates

General assumption about the origin of ilmenites at the base of the SCLM (Boyd and Nixon, 1973) from protokimberlites does not explain the observed wide compositional variation and contact relationships with different types of lherzolites which suggest...
a more complex magmatic source. The model of an origin by fractionation at the lithosphere base was suggested by Gurney et al. (1979) for ilmenites from the Monastery pipe (South Africa). It was based mainly on the PT estimates for Ilm–Opx symplectites (Harte and Gurney, 1981). However, direct calculations for clinopyroxenes coexisting with ilmenites (Dawson and Reid, 1970; Haggerty et al., 1979; Haggerty, 1995; Gurney et al., 1979, 1998) and orthopyroxenes from ilmenite intergrowths and from quenched nodules (Rowlinson and Dawson, 1979) show a pressure interval from 6.0 to 4.0 GPa suggested for the crystallization of megacrysts suite including type II diamond (Moore, 2009). A similar model of fractional crystallization in mantle pegmatitic bodies (Moore and Lock, 2001) considers the changes in ilmenite compositions to be the product of extensive fractionation in pegmatite-like bodies. The pegmatitic model is supported by evidence of fluid crystallization (Kopylova et al., 2009) for megacrystalline ilmenites.

Many localities show the gap in the crystallization trends between the Mg-rich and Fe-rich ilmenites, for example in Angola (Ashchepkov et al., 2009), and this may be solved by the crystallization of ilmenites in a system of polybaric magma chambers and channels. The estimation of a HT geotherm based on megacrysts (Eggler and Mccallum, 1976) was followed by the suggestion that megacrysts result from polybaric magma fractionation (Neal and Davidson, 1989) during crystallization of fluid-rich magma that produced megapyroxenites and ilmenites (Kopylova et al., 2009). Ilmenite-bearing pyroxenites (Alymova et al., 2008) including symplectites with pyroxenes, mainly relate to the convective branch from 5.5 to 6.5 GPa. The latter may be fragments of mantle pegmatites or some type of cotectic Ilm-Px crystallization in the melt conduits.

The complex contact relationships and deformation of megacrysts in alkali basalts led to conclusions about their pre-eruption origin (Ashchepkov and Andre, 2002). Ilmenites rarely occur in megacrystalline alkali basalts but are similar in appearance to those from kimberlites (Schulze, 1987; Litasov and Ashchepkov, 1996).

Combined estimates of PT conditions derived for Ti-rich ilmenite-bearing polymineral pyroxenites (Alymova, 2006; Alymova et al., 2008) and Fe-peridotites suggest a poly-

1284
baric nature for the ilmenite trend, as was earlier determined for kimberlite megacrysts (Eggler and McCallum, 1976). This is proved by pressure estimates using orthopyroxenes (McGregor, 1974; Brey and Kohler, 1990) and clinopyroxenes (Nimis, Taylor, 2000; Ashchepkov, 2003) associated with the ilmenites. The most HT metasomatites show the depths of origin near 8.0 GPa. This coincide will with the conditions determined for most of the thermobarometric methods. These PT conditions agree well with the SCLM thickness determined by seismic methods (O’Reilly et al., 2009) near 270 km. But the inflection of the geotherms and major field of the megacrysts associations start from 7–6.5 GPa refer to the minimum on the peridotite solidus in the lower part of mantle column (redox melting) (Tappe et al., 2007) and OI creep under the presence of volatiles (Peslier et al., 2012) and magma fracturing.

### 9.2 Model of fractionation and melting based and trace elements

Geochemistry of calculated parental melts (Fig. 19) determined with the Ilm (Zack and Brumm, 1998) shows that such trends are the products of differentiation of kimberlite-like melts that are strongly enriched in HFSE and other trace elements during the final stage of crystallization. Thus the original crystal fractionation model for the formation of ilmenites of protokimberlite melts (Moore et al., 1992; Griffin et al., 1997) has been transformed into a polybaric process taking place in melt feeders and intermediate magmatic chambers. Interaction with the melts is probably the reason for the high dispersion of the PT parameters in the whole mantle columns (Figs. 11–14), possibly reflecting polybaric interaction of mantle peridotites with percolating melts. Positions of the ilmenite-bearing pyroxenites often coincide with those determined for HT eclogites showing that they may be formed as a result of reaction between the protokimberlite melts that formed megacrysts and mantle eclogites. But mantle metasomatites which are close in pressures to the clots of the megacrysts PT points reflect refertilization events in peridotites.

Assuming that assimilation + fractional crystallization (AFC) processes occurred (Neal and Davidson, 1989), we can explain the behavior of Cr and increase of the com-
ponent together with the decreasing pressures during crystallization as due to continuous fractionation (probably in large channels) accompanied by assimilation (DePaolo, 1981). Contamination may have taken place in some intermediate level and in the feeders during their creation and melt upwelling. This explains why there is no principal difference in behavior of Cr-bearing and Cr-poor ilmenites (Moore and Belousova, 2005). According to the thermobarometry of coexisting clinopyroxenes (see Figs. 11–14) in ilmenite-bearing pyroxenites (Alymova, 2006; Alymova et al., 2008), the range from 50–55% to 45% TiO$_2$ corresponds to the interval of pressure from the base of the SCLM to the graphite–diamond transition (Kennedy and Kennedy, 1976). The fraction of dissolved and crystallized phases regulated the Cr content of the parental melt. Dissolution of chromite may result in the rapid increase in Cr of the parental liquid. An opposite reduction in Cr accompanied by an increase in Al may be formed by garnet dissolution. Compositions of ilmenites from the veined xenoliths are often similar to those of typical megacrysts. Megacrystalline ilmenite aggregates near the contacts (Fig. 2a) with the peridotites contain up to 2% Cr$_2$O$_3$. This suggests an intense exchange of melts as the partial melts penetrated into larger channels in the peridotites and crystallized megacrysts. Scattered ilmenite-bearing metasomatites should mark the vein stockwork in the mantle.

The V$_2$O$_5$ content of ilmenites generally correlates negatively with increasing MgO according to the differentiation model, reflecting variations of oxygen fugacity conditions (V$_2$O$_5$) of parental magma (Righter et al., 2006; Canil and Fedortchouk, 2000) and wall-rock reactions. Contamination during growth of veins and in their contacts causes variations in the minor components Cr$_2$O$_3$, NiO and MnO. Admixture of MnO is common in ilmenites associated with diamonds (Kaminsky et al., 2009) and in some eclogites (De Stefano et al., 2009).

Nearly constant Al, Cr and Ni contents are common for uncontaminated portions of the parental melts. The abrupt decrease of Al$_2$O$_3$ in some trends content probably corresponds to co-crystallization of garnet in the final stage. Common admixture of the Mn in some ilmenites may indicate presence of the subducted material in mantle which
may increase MnO in mantle melts that crystallized ilmenites (Wyatt, 1979; Patchen et al., 1997) due to dissolution of Mn-bearing eclogites.

The general regularities of REE and trace element diagrams for picroilmenites from Siberia are as follows. Ilmenites from the onset of crystallization (high TiO$_2$) as a rule show low concentrations of trace elements but their REE patterns differs. They have higher Ta-Nb and Ti concentrations (50–1500 relative to primitive mantle). Ilmenites formed in the middle part of mantle columns show linear inclined patterns for REE and high peaks of HFSE. The most enriched compositions corresponding to the final stage of crystallization and those that are lower in TiO$_2$ demonstrate very high concentrations of all elements up to 1000C1. Ta, Nb, Zr, Hf contents are not much higher than the adjacent elements on the spider diagrams.

These features are seen on the trace element patterns for the calculated parental melts of the ilmenites (Fig. 19) using KD for trace elements for ilmenites (Zack and Brumm, 1998; Klemme et al., 2006). The composition of the kimberlite melt for Yu-bileynaya pipe (Kostrovitsky et al., 2007) is also shown, as well as carbonatites from West Greenland (Tappe et al., 2009) and Oldoinyo Lengai (Bell and Simonetti, 1996). The parental ilmenite melt compositions are higher in LILE and Pb and lower in Sr than kimberlites.

We calculated the parental melts for the coexisting Cpx and Ilm from the low-Cr pyroxenite xenolith (UAS1300) from Udachnaya pipe and an Ilm-Cpx vein in a garnet peridotite xenolith (Stk135) (Fig. 20). The parental melts from the first sample are close to equilibrium in REE but the melt calculated from ilmenite is enriched in U-Ta-Nb; the Cpx’s parental melt shows a straight line trace element pattern close to that of the kimberlitic with small peaks in Zr and Sr. The patterns determined for the melts in equilibrium with the metasomatic vein show more equilibration but the magma in equilibrium with ilmenite was richer in all HFSE and Ba. This show that ilmenites which crystallized later were more enriched in HFSE (Zr, Hf, Nb and Ta). This would be possible if the remaining liquid was essentially carbonatitic.
It is evident that most group 1 ilmenites are lower in trace elements except for HFSE than their host kimberlites. The majority are close to the compositions of carbonatites. The parental melts for group 2 ilmenites were more evolved than the trace element pattern for carbonatites associated with ailikites (Tappe et al., 2007). The melts that crystallized group 3 ilmenites were more enriched than carbonatite from Oldoinyo Lengai (Bell and Simonetti, 1996). Some of them like those from the Anabar fields have similar Zr-Hf minima but mostly they have nearly constant Ta-Nb and Z-Hf contents.

Ilmenite megacrysts are similar in isotopic features to their host kimberlites (Noyes, 2000; Nowell et al., 2004). Trace element compositions of the parental melts of picroilmenite differ from those of kimberlites in having higher concentrations of high-field-strength elements (HFSE) and other incompatible elements. This suggests a high degree of fractionation of parental (protokimberlite) melts responsible for megacryst formation (Griffin et al., 1997; Moore et al., 1992) or splitting of the protokimberlites into carbonatite and silicate melts (Safonov et al., 2007).

The trace elements determined for ilmenites in this work demonstrate that there are at least three different types of ilmenites with different trace element spidergrams and REE patterns (Figs. 17–20). Ilmenites with low concentrations of trace elements demonstrate different levels of Cr-enrichment due to admixture of partial melts from wall rock lherzolites, variation in the HREE may be due to varying proportions of garnet in the source. The S- and W- and spoon-like REE patterns for gr1 ilmenites were possibly formed by melt percolation as a result of chromatography. Melting of intergranular sulfides enriches the melts in Pb but during fractionation Pb precipitates with sulfides (Ashchepkov and Andre, 2002).

However, according to the thermobarometry Mg-rich (group 1) ilmenites which form the base of SCLM were formed with a minor influence of garnet and thus were produced from very primitive melts with flat REE or spoon-like patterns due to selective removal of Cpx. They may have crystallized within an essentially dunitic matrix which usually served as the conduit for melt movement.
Cr-poor ilmenites (gr2) demonstrate that parental melts were lower in trace elements (Figs. 20 and 21) and inclination of REE spectrum lower than those of Yubileinaya kimberlite (Kostrovitsky et al., 2007) and were derived from garnet-poor melting assemblages. Ilmenites from the middle part of the TiO$_2$–FeO trends, corresponding to the most common ilmenite compositions, demonstrate a subsequent enrichment due to fractionation and yield a pattern which is very close to those of kimberlites. But taking into account very low REE KD for ilmenites (Zack and Brumm, 1998; Klemme et al., 2006), the melts must have been enriched by a factor of 2 or more than the ilmenites. According to their geochemistry (Noyes, 2000; Nowell et al., 2004), the melts that crystallized such megacrysts were protokimberlites or carbonatites formed in the garnet stability field. In the final stages the calculated liquids show a deficit of HFSE typical for carbonatite liquids (Rudnick et al., 1993) (Fig. 18). This may have been formed by the prevailing precipitation of ilmenites or other oxides (rutile).

The minor garnet (3 %) and high Ol content caused a rather high enrichment factor of REE $\sim 2$ because Ol is not a concentrator of trace elements (Fig. 22a). Melting of the metasomatic association with 15 % garnet in the residual solid may have produced rather high inclination and difference in LREE by the factor of 3 or more (Fig. 21b). We used the partition coefficients from Bedard (2006) for silicates, and KDs for the ilmenites are from (Zack and Brumm, 1998; Klemme et al., 2006).

Calculations of fractionation using olivine (Ol) (90 %) and ilmenite (Ilm) (10 %) as the main crystallizing phases show that enrichment by 2 orders of magnitude means nearly complete crystallization of the protokimberlite or carbonatitic melts (Fig. 21). Each fractionation trend is restricted by the line with enrichment of 1.3 log units (Fig. 21). Hence the ilmenites with extreme enrichment to 1000/C1 must have been formed from melts that resulted from small degrees of partial melting of garnet-bearing associations very enriched in trace elements (apatites, perovskites or ilmenites). Perovskites (rims and intergranular space) may be responsible for the very high concentration not only HFSE and REE but also Th, U and LILE.
The most enriched samples may have been formed by low degree partial melts with high olivine mode in the remaining solid that effectively elevates the trace element patterns of the equilibrated liquid. Ilmenites from each pipe reveal their own trace element patterns like those from Nyurbinskaya pipe where the addition of U and Th possibly reflects the influence of carbonatite melts.

The trends of the major components (Figs. 3–7) reveal separate lines of enrichment in the TiO$_2$ vs. Cr$_2$O$_3$ diagram. Probably they reflect repeated pulses of melt within the magmatic feeders. This would have been accompanied by partial remelting of previously formed associations (Ashchepkov and Andre, 2002). This model, with melting of earlier cumulates and metasomatic rocks, explains the rapid enrichment in TiO$_2$ because a simple fractionation model and an origin from the kimberlites could never explain these phenomena. The most realistic mechanism for high enrichment of the incompatible elements including REE and especially HFSE is low degree partial melting of the contacts with metasomatized associations or the metasomatic front. Mixing of such partial melts with the new portion of protokimberlite melt will cause a strong increase in the trace elements content of the parental megacrystalline liquids.

9.3 Development of protokimberlites

Published isotopic data for ilmenites (Noyes, 2000; Kramers et al., 1983; Wagner, et al., 1996; Nowell et al., 2004; Schulze, 2001; Golubkova et al., 2013) and kimberlites (Tappe et al., 2007; Kostrovitsky et al., 2007) suggest in general there cognate relationships. The most ferehand uncontaminated kimberlites and their megacrysts are close to the HIMU asthenospheric component (Agashev et al., 2013; Paton et al., 2009). Contaminated in lithospheric mantle material megacryst varieties deviate in isotopic diagrams. This agree with the creation of the megacryst from the protokimberlite melts which formed the pre eruption melt feeder systems and evolved separately from the major magma portions.

For the development of magmatic system in the mantle before the kimberlite eruption, we suggest a three-stage model (Mitchell, 1986; Le Roex et al., 2003). In the ini-
tial stage, ultramafic plume-derived melts intruded the carbonated and hydrated base of the SCLM producing HT depletion of the peridotite and formation of chromites and ilmenites as precipitates in the feeder channels and surrounding wall rocks (rarely subcalcic garnets may also have grown within and adjacent to the feeders). Partial melting of the metasomatic pyroxenitic aureole enriched in incompatible elements resulted in a high concentration of carbonates, H$_2$O, silica and HFSE in the secondary hybrid melts which were formed during the next pulse of plume-derived melt.

Contamination and fractionation of secondary alkaline ultramafic magma caused separation into immiscible liquids: silicate, carbonatite, sulfide (Irvine, 1976) and probably oxide (Clarke and Mackay, 1990; Hurai et al., 1998) during cooling. Ilmenites may also have been formed by immiscible oxide melts in the final stages of crystallization (Hurai et al., 1998). Evidence for such melts is seen in xenoliths from the Sytykanskaya pipe where monomineral ilmenite aggregates cut large grains of garnets and other minerals in peridotites.

Rising protokimberlite melts formed due to melting of the enriched metasomatized mantle are similar to kimberlites in REE but have higher incompatible elements. Their intrusion during formation of the feeder system produced Ti-rich metasomatism in wall rocks near contacts and heating near the feeding channels. In the channels AFC created the megacrystalline ilmenites which show similar trace element patterns. The assimilated material was the partial melts from the wall rocks which contain melted chromites increasing Cr content. According to thermobarometry the fractionation trends finish close to the 4.0 GPa boundary which forms the top of the veins and veinlets that represent the metasomatic front. Further pulses of melt intrusion caused remelting of metasomatites and high enrichment of these melts in TiO$_2$. Step by step melt intrusion with contamination and partial dissolution of wall-rock resulted in continuous enrichment in Cr and TiO$_2$ and creation of ilmenite megacrysts which show a stepped Cr increase such as that found for ilmenites from Zarnitsa, Yubileynaya and other pipes. Three different Cr trends are found for ilmenites from the Mir pipe. At the top of the magmatic system ($P < 4.0$ GPa), ilmenites are in the stability field of amphi-
boles. Possibly contamination and enrichment in water resulted in the formation of the phlogopite-ilmenite veinlets in the peridotites. The enriched trace element patterns are the result of low degree melting ($\sim 0.01$), typical for hydrous metasomatic rocks. Fluctuations of Hf, Ba, HFSE, Y, Pb and Sr show that ilmenite crystallization, at least in the last low temperature stages, was accompanied by growth/dissolution of zircon, rutile, phlogopite, perovskite and apatite (Kalfoun et al., 2002).

The mechanism of protokimberlite magma formation and development include the three following models:

1. Intrusions of ultramafic kimberlite magma and formation of protokimberlites as the result of interaction and remelting of metasomatized rocks at the base of the SCLM (Mitchell, 1973, 1996; Hunter and Taylor, 1984; Le Roex et al., 2003 etc.) and creation of the HT magmatic source and fractionation of protokimberlite magma (Boyd et al., 1973; Gurney et al., 1979).

2. Development of rising magmatic channels by polybaric AFC fractionation (Neal and Davidson, 1989) of protokimberlite magma in magmatic conduits (Eggler and Mccullum, 1976) and intermediate magma chambers (Moore et al., 1992; Griffin et al., 1997), forming a semi-closed system interacting with wall rocks, formation the veins in surrounding peridotites and metasomatic rocks (Grégoire et al., 2003).

3. Mixing of rising melts enriched in volatiles with the products of partial melting of metasomatized rocks and cumulates of preceding stages.

During formation of individual pipes the process of protokimberlite differentiation in the magmatic conduits and chambers may have been a combination of these three simple models. The most possible mechanism of formation of the long ilmenite crystallization trends for the Mir and Dachnaya pipe is fractionation during development of the rising magma feeder. Nevertheless Cr-bearing ilmenite associations periodically appeared at different levels marking level of the interaction. For the Alakit pipes with shorter and more dispersed and branched trends, it is necessary to suggest several magmatic pulses with remelting of the earlier formed metasomatics and cumulates.
Complicated models of the development of protokimberlite magma may explain the different types of mineral and aggregate zonation. If we suggest a fast ascent of the magma that transported ilmenite aggregates as xenocrysts or crystal mush, it is possible to explain the difference in calculated PT conditions for ilmenite aggregates.

Variations in Fe at the same level of TiO$_2$ (Schulze et al., 1995; Nikolenko and Afanasiev, 2008; Robles-Cruz et al., 2009) possibly reflect a multi-stage origin of the ilmenite crystallization trends and reaction with the walls of magmatic conduits.

9.4 Significance of the ilmenite bearing association for the diamond formation

The PT conditions for the ilmenites and diamond inclusion especially chromites are often very close and are tracing heated geotherms and convective branches (Logvinova and Ashchepkov, 2008; Ashchepkov et al., 2010). Even diamond-bearing eclogites very often reveal irregular heated conditions associated with metasomatism. In addition the carbonate crystals which always occur in the diamonds in fluids (Logvinova et al., 2008) probably were derived from the protokimberlites which are according to TRE reconstructions reveal the carbonatite signatures at least at the graphite–diamond boundary (Dobosi and Kurat, 2002; Rege et al., 2008) (see Fig. 21). So the most realistic scheme of the growth of the diamonds is crystallization near the developing magmatic system during formation of the channels. In these conditions the reaction of the relatively oxidized CO$_2$ rich fluid and melts were reacted with the reduced peridotites and eclogites which was accompanied with the crystallization of newly formed diamonds which could coat the microdiamonds formed in the ancient times. The temperatures and fO$_2$ of the ilmenites are slightly higher and there associations and inclusions in diamonds are not frequent because they reflect different conditions. Ilmenites megacryst were formed in oxidizing conditions at the inner contacts of feeder vein or in outer contacts in solid–liquid mush forming polymict breccias (Morfi et al., 1999; Pokhilenko, 2009) and in surrounding metasomatites. Diamonds mainly should be crystallized at a distance from feeders in more reduced conditions from the fluid surrounding protokimberlite veins.
10 Conclusions

1. Crystallization trends of ilmenites in Siberian kimberlites reflect polybaric fractionation during formation of protokimberlite feeder systems.

2. The correlation of picroilmenite compositions with the mantle layering visible in the Fe# fluctuations in PTX diagrams is explained by interaction of the ilmenite-forming magmas with mantle wall rocks.

3. The regular structure of the mantle sections (i.e. a heated SCLM base and a division into two parts with a boundary near 4.0 GPa (Sobolev, 1974; Ashchepkov et al., 2008a) gives three levels and three possible stages of megacryst origin: (1) deep HT metasomatic pyroxenites and crystallization in the feeding systems; (2) fractionation of protokimberlite melts mixed with partial melt from the peridotite wall rocks; (3) low degree partial melting of hydrous metasomatic fronts and mixing with evolved protokimberlites.

4. Intrusion of protokimberlite melts rapidly changed the mantle beneath the kimberlite pipes due to large scale percolation of melts and fluids.

Supplementary material related to this article is available online at: http://www.solid-earth-discuss.net/5/1259/2013/sed-5-1259-2013-supplement.zip.

Acknowledgements. The work is supported by RBRF grants: 05-05-64718, 03-05-64146; 08-05-00524; 11-05-00060; 11-05-91060-PICS. The work contains the result of the projects 77-2, 65-03, 02-05 UIGGM SD RAS and ALROSA Stock Company. We are grateful to H. Downes who essentially improved the language, to N. V. Sobolev for the consultation about diamond bearing associations, to N. P. Pokhilenko for materials from Udachnaya and other kimberlite pipes, to S. I. Kostrovitsky for the analyses and kimberlite concentrates. to A. Moore for discussion about
fractionation and models of origin. To T. Ntaflos for the possibility to analyze in Vienna University thin sections materials from Udachnaya and Dalnyaya pipes.

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Picroilmenites in Yakutian kimberlites: variations and genetic models

I. V. Ashchepkov et al.


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Fig. 2. (a) Photograph of ilmenite megacryst in contact with peridotite (Sytykanskaya pipe, sample Stk1); (b) image of the thin section of the deformed peridotite with ilmenite, mica and clinopyroxenes in intergranular space (Sytykanskaya pipe, sample Stk35).
Fig. 3. Variation diagram for ilmenite associations in xenoliths using data from literature and new analyses. 1. Ilmenites from metasomatic xenoliths; 2. from pyroxenites; 3. from MARIDS.
Fig. 4. Comparison of the compositional variation of picroilmenites in xenoliths and in heavy mineral separates for large kimberlite pipes Udachnaya Dalnyaya, Sytykanskaya and Mir.
Fig. 5. Variations of ilmenite compositions in the different kimberlite phases for Yubileinaya pipe and cluster, for Zarnitsa and Deimos pipes. For (a) 1. Zarnitsa, 2. Aeromagnitnaya, 3. Osennyaya; (b) 1. Yubilnaya, 2.Ozernaya, 3.Ottorzhnents, 4. Aprelskaya; (c) 1. Deimos, 2. Zapolyarnaya, 3. Poiskovaya.
Fig. 6. Variations of ilmenite compositions from different regions Yakutian kimberlite province (Daldyn, Alakit and Malo-Botuobinsky fields).
Fig. 7. Variations of ilmenites from different regions within Yakutian kimberlite province (Nakyn, Upper Muna and Anabar fields). 1. Ilmenites from Nyurbinskaya pipe. 2. Ilmenites from placer.
Fig. 8. Correlations between the compression of unit cell volumes $V/V_0$ in ilmenite structure vs pressure (Karki et al., 2000; Reynard et al., 1996).
Fig. 9. Correlations of pressure (a) and temperature (b) for ilmenites (Ashchepkov et al., 2010) and clinopyroxenes (Ashchepkov, 2003) from the same associations.
Fig. 11. Caption on next page.
Fig. 11. (A) PTXFO$_2^*$ estimates for the minerals from xenocrysts and xenoliths from Udachnaya pipe, Daldyn field. Fe# is calculate Fe number of olivines, coexisting with Garnets, pyroxenes chromite and ilmenites. 1. Clinopyroxene thermobarometry $T^0C$ (Nimis and Taylor, 2000) – P(GPa) (Ashchepkov, 2003) for xenoliths (Boyd et al., 1997; Pokhilenko et al., 2000, 2007; Malygina et al., 2005). 2. The same for Cr-diopsides from heavy mineral separates. 3. The same for pyroxenites (Kuligin, 1997). 4. The same for common eclogites. 5. The same for diamond inclusions of eclogite affinity (Beard et al., 1996; Snyder et al., 1997; Taylor et al., 2003). 6. The same for diamond inclusions peridotite affinity (Sooblev et al., 1997, 2003, 2004; Logvinova et al., 2005). 7. The same for diamond eclogites (Jacob et al., 1999; etc.). 8. Orthopyroxene thermobarometry: $T^0C$ (Brey, Kohler, 1990) – P(GPa) (McGregor, 1974) for peridotites. 9. The same for diamond inclusions. 10. Garnet thermobarometry for peridotites (Ashchepkov, 2006). 11. The same for garnets from heavy mineral separates. 12. The same for diamond inclusions. 13. Cr-spinel thermobarometry: $T^0C$ (Taylor et al., 1998) – P(GPa) (Ashchepkov, Vishnyakova, 2006) for xenoliths. 14. The same for grains from heavy mineral separates; 15. the same for diamond inclusions. 16. Ilmenite thermobarometry: $T^0C$ (Taylor et al., 1998) – P(GPa) (Ashchepkov, Vishnyakova, 2006) for grains from heavy mineral separates. 17. The same for ilmenites from xenoliths (Alymova et al., 2006). (B) PTXFO$_2^*$ estimates for minerals from xenocrysts and xenoliths from Dalnyaya pipe. Symbols are the same as for (A).
Fig. 12. (A) PTXFO$_2$ estimates for minerals from xenocrysts and xenoliths from Mir pipe Symbols are the same as for Fig. 11a. (B) PT estimates for the minerals from xenocrysts and xenoliths from Sytykanskaya pipe and variations of the Fe# for coexisting olivines vs. pressure estimates obtained with monomineral thermobarometry. Symbols are the same as for Fig. 10.
Fig. 13. (A) PTXFO₂ estimates for minerals from Yubileynaya pipe. Symbols are the same as for Fig. 11a.
Fig. 14. (A) PTXFO$_2$ estimates for minerals from Ozernaya pipe. Symbols are the same as for Fig. 11a. (B) PTXFO$_2$ estimates for minerals from Aprelskaya pipe. Symbols are the same as for Fig. 11a.
Fig. 15. REE and trace element spider diagrams for ilmenites from heavy mineral separates from Daldyn field kimberlites.
Fig. 16. REE patterns and trace element spider diagrams for ilmenites from heavy mineral separates from Alakit field kimberlites. For Sytykanskaya: 1. ilmenite from Cpx intergrowth; 2 metasomatic vein.
Fig. 17. REE patterns and trace element spider diagrams for ilmenites from heavy mineral separates from kimberlites from the Malo-Botuobinsky, Nakynsky and Upper-Muna fields.
Fig. 18. REE patterns and trace element spidergrams for ilmenites from heavy mineral separates from Anabar kimberlites.
Fig. 19. Trace element patterns for parental melts for the ilmenites from the different regions in Yakutia. 1. Kimberlite from Yubileynaya pipe (Kostrovitsky et al., 2007); 2. Carbonatite associated with kimberlite 3. Carbonatite from Oldonio Lengai (Bell and Simonetti, 1996; Bizimis et al., 1993).
Fig. 20. Parental melts for the coexisting ilmenites from low Cr pyroxenite (UAS1300) (Udachnaya pipe) and metasomatic vein in peridotite xenoliths from Sytykanskaya pipe (Stk15). Trace element pattern for the Yubileinaya kimberlite (Kostrovitsky et al., 2007) is given for the comparison.
Fig. 21. Modeling trace element patterns for picroilmenites from Sytykanskaya pipe (see Fig. 14f). (a, b) Melting models with the given proportions of the solid phases and different melting degrees. (c, d) Fractionation models with the given proportions of the fractionated phases.
Fig. 22. Ta\textsubscript{n}-La\textsubscript{n} diagram for the ilmenites from Yakutian kimberlite province and modeling lines for the fractionation of parental melts with the different ilmenite/olivine proportions (from 0.9Ol–0.05Ilm to 0.05Ol–0.9Ol). 1. Daldyn kimberlite field. 2. Alakit field. 3. Upper Muna field. 4. Malo-Botuobinskoe field. 5. Anabar fields. The small crosses show the lines of the fractional crystallization with the different proportions of crystallization minerals ranging from: 0.9Ilm 0.05Ol to 0.05 Ilm0.9Ol. The small crosses reflect the fractional melting of the metasomatic associations consisting from following assemblages from 0.05Ilm 0.55Ol 0.20 Cpx0.20 Gar to 0.75 Ilm0.05 Ol0.20 Cpx020Gar.