



Unique Amphibole-Bearing Mantle Column Beneath the Leningrad Kimberlite Pipe, West Ukukit Field, NE Yakutia

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Abstract

In the subcratonic lithospheric mantle (SCLM) beneath Leningrad pipe (West Ukukit field), Yakutia garnet thermobarometry allows us to identify seven horizons (paleo subduction slab). Microprobe data for Cr-bearing amphiboles >500 grains from mantle xenoliths and concentrates reveal a broad range of compositions changing from Cr-pargasitic hornblendes to pargasites, edinites, kataforites, K-richterites with increasing pressure determined with new amphibole thermobarometer constructed by the first author. The low pressure (LP) Cr-hornblendes and pargasites compile the high-temperature branch (90-60 mw/m²) from 3.5 GPa to Moho traced by basaltic cumulates. In the middle part of SCLM edinites mark 35 to 40 mw/m² geotherms. At high pressures kataforites also vary in thermal conditions. Richterites near the lithosphere base trace both low- and high temperature convective branches. The amphiboles reveal divisions into 9 chemical groups. The melts coexistence with amphiboles has concave patterns typical for subduction related melts. LP varieties reveal Eu inflection U, Rb, Ba, Sr peaks and deep troughs in HFSE (except Zr), Pb. The pargasites show high U peaks and relatively less HFSE depressions. Increasing in pressure for edinites, kataforites and richterites are accompanied by rise in U and Zr peak gentling of depressions in Th, Sr, Nb and Hf and less in Nb, Ta, Hf and peak in Zr and also decrease in LREE and REE. Clinopyroxenes and garnets show variable trace element patterns and divisions in groups with the plume and subduction signatures. The contrasting behaviour of Ta and Nb is regulated by the rutile partition coefficients likely for primary eclogites. A subduction and Na and K (siliceous) type of fluids percolated through the mantle with abundant eclogites possibly was accompanied by amphibolization at the different levels through all the mantle column. The plume melts produced hybridism with the mantle metasomatic assemblages which created smoother trace element patterns in reacted minerals, clinopyroxene. The new version of monomineral amphibole thermobarometry is suggested.

Keywords: Kimberlite; Garnet; Amphibole; Clinopyroxene; Chromite Mantle lithosphere; Thermobarometry

Introduction

The northern kimberlite fields in Yakutian kimberlite province (YKP) in Siberia belong mainly to the Early Mesozoic plume activity and mostly are barren in diamonds [1-5]. Several kimberlite pipes like Molokuonamskaya, Leningrad, Ruslovaya, Lorik, Svetlana, Djanga, Aerogeologicheskaya, and Universitetskaya contain diamonds in small amounts [6,7]. However, there are plenty of very rich diamond placers in several areas of the northern part of YKP including Kuoyka, Molodo fields, in Ebelyakh and Prilenie [8]. The sources of these rich placers should be Paleozoic or Precambrian, while the most of pipes in the North of YKP are low Triassic to Cretaceous [4,5] (Figure 1).

The pipe Leningrad is one of the largest of the known pipes in the Northern part of YKP. Leningrad is the first kimberlite body identified in Russia and Yakutia by Ziburin KS (NIIGA) in 1952 in the riverbed of the Omonos river [9].

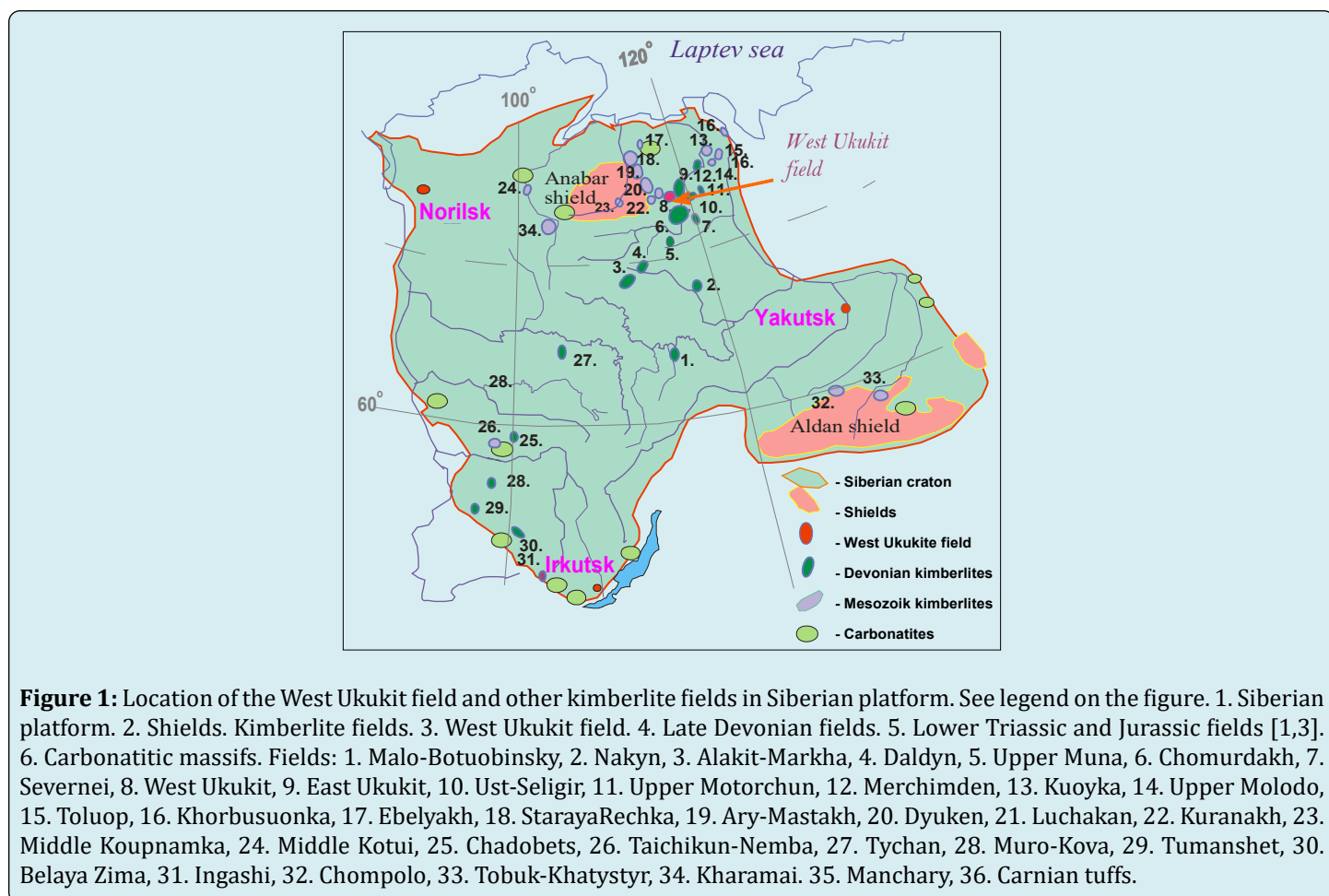
The amphiboles are not common in mantle xenoliths in the kimberlites Worldwide. But in Siberian SCLM, where they were found in the mantle xenoliths of Sytykanskaya

Yubileynaya, Komsomolskaya pipes [10-13], in Alakit field [11]. The Ca amphiboles are rather frequent in the relatively low pressure (to 4.0 GPa) xenoliths from Obnazhennaya pipe [14,15] and in Priyanabarie [16].

The Leningrad pipe mantle xenoliths amphiboles are more frequent than clinopyroxenes. They cover all the compositional variations of the mantle amphiboles [10-29].

In his paper we introduce new amphibole thermobarometry calibrated to 9 GPa using experimental data [18-24] while published before amphibole barometers are calibrated to 4 GPa [18-20]. We try to solve the questions how the compositional variations and geochemical features are corresponding to the positions in the mantle column and represent the ages determined for the mica and amphiboles from xenoliths.

The trace element (TRE) geochemistry of the mantle amphiboles is studied only for the shallowest spinel lherzolites in orogenic massifs [25,26], in alkali basalts [27,28] and high-pressure kimberlite xenolith [29].



In the Leningrad kimberlites pipe (West Ukukite filed) amphiboles are frequent both in mantle xenoliths [30,31] and concentrates revealing the very wide range. We determined the positions of the different groups of amphiboles in the mantle columns and suggest the model of their creation. Their formation corresponds to the plume related metasomatism and hybridism with the earlier subduction-related metasomatism.

Geology

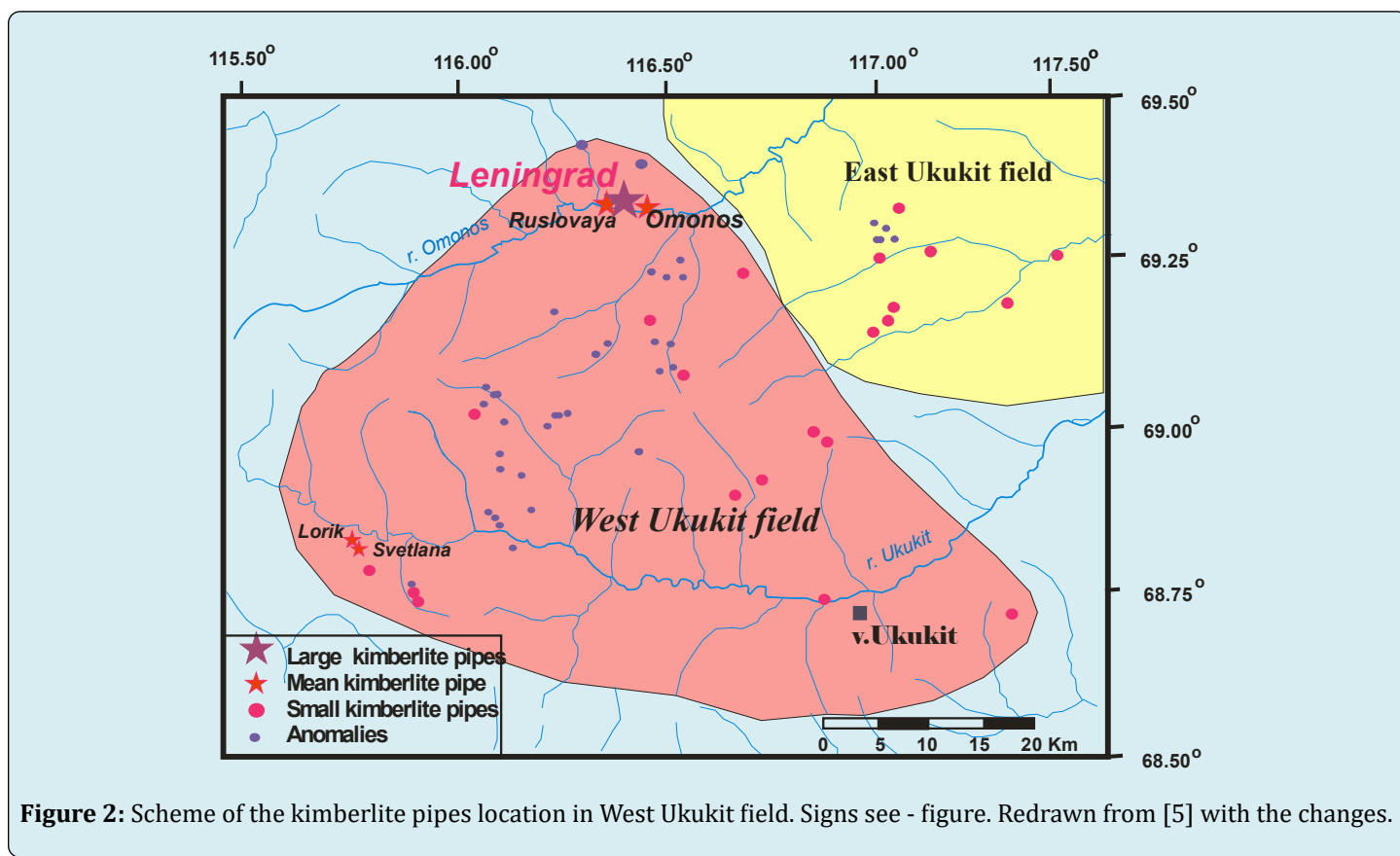
Leningrad pipe from West Ukukite field and is one of the largest pipes in the North of Siberia. This field (Figure 2) includes several large pipes Leningrad, Ruslovaya and Omonos in the northern part and Svetlana and Lorik pipes in the south-western part [5]. Most pipes are close to mica-bearing orangeates according to estimates of S.A. Babushkina though the main phase of Leningrad pipe contain abundant ilmenites and is tending to common Ca-Mg kimberlite type.

The Leningrad pipe consists of several types of breccia and at least two main intrusive phases [28]. The major phase is autholithic breccia, which contains a huge amount of

various xenoliths (Figure 3).

The brightly coloured transparent and well-shaped diamonds were found but in very small amounts <0.01 crt/t and 330 diamond crystals were described [7,29]. The pipe is dated by several methods showing wide variations of ages. The Rb/Sr isochrones on mica and bulk-rock give Devonian age from 380 to 350 Ma with the most probable values $\sim 368 \pm 1$ Ma [5]. The Ar-Ar for the Phl xenocryst gives 385 Ma [7]. The SHRIMP U/Pb age on zircon, refer to 378 Ma [30]. Thus the age of the Leningrad pipe was suggested as Devonian (368 Ma) and our data on phlogopites also are close (see $^{40}\text{Ar}/^{39}\text{Ar}$ dating). The earlier ages for the Phl xenocrysts refer most probable to the protokimberlites stage. The pipe Svetlana give similar age 365 Ma as well as several other anomalies. However, some small dykes reveal the younger ages to 350 Ma [5].

But new dating using zircon -U-Pb method give more younger age 144 Ma [32,33] referring to lates Jurassic kimberlite magmatism in Siberian craton. This may occur because the kimberlites of this stage are widely spread within the Siberian craton [1,3]. It may occur that the Leningrad is a complex body compiled by the polyphase intrusions.



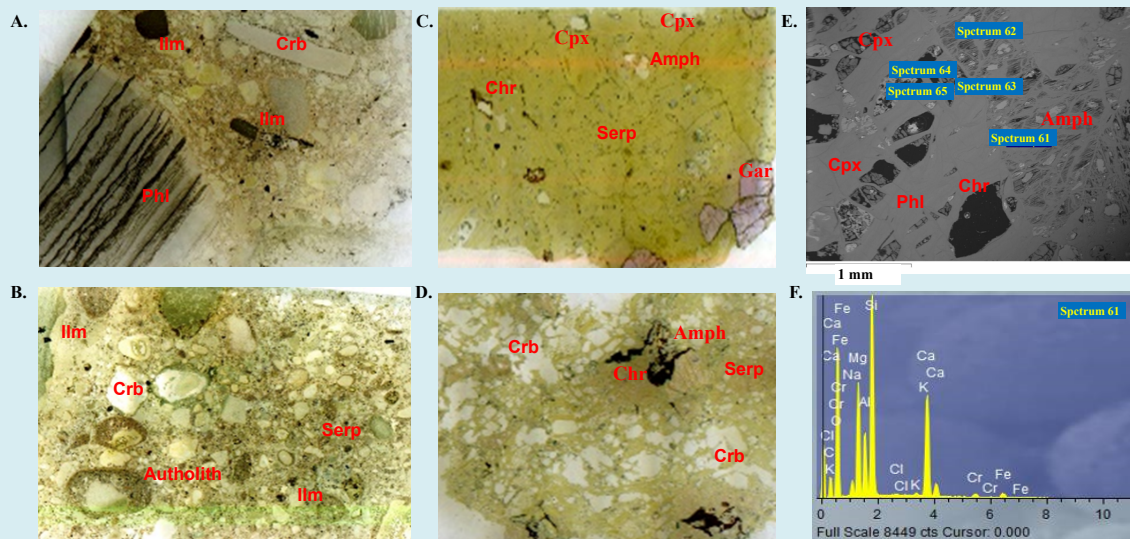


Figure 3: Scanned images of A. Kimberlite from the Leningrad pipe. B. Kimberlite from the Lorik pipe. C. Garnet peridotite xenolith. D. Spinel peridotite with the amphibole and phlogopite. E. Spinel peridotite. F. Spectrum of amphibole. Minerals: Amph- amphibole, Cpx-c inopyroxene. Chr-chromite, Ilm- ilmenite, Carb- carbonate, Serp- serpentine.

Materials and Methods

The pipe was sampled by Oleinnikov OB and Nikishov KN during field works in the 1980th. The samples were preliminarily studied by Babushkina SA using microscopy and electron microprobe analyses (EPMA). They were obtained on partly serpentized xenoliths and washed concentrates from the kimberlite debris [30-32]. In the thin sections, it is clear that amphiboles are in intergrowth with the Cr-spinels sometimes with the ilmenites and apatites, and Cr- rutiles. The electron microscope analyses show that they are in intergrowth and have inclusions of barite and Sr - carbonates as well as various sulfides (Figure 3) (pentlandite, chalcopyrite, pyrrhotite) (see supplementary file 1) (SF1).

Petrography of Kimberlites from Leningrad and Lorik Pipe

The kimberlites from the Leningrad pipe belong to two types: tuffitic kimberlites and autholithic breccias. In the tuffitic kimberlites (Figure 3A), the debris are angular and their amount prevails on the deep-seated mantle material. In autholithic breccia (Figure 3A), the xenocrysts are dominating. Olivine with $Mg\# (=Mg/(Mg+FE))$ 0.85-0.92) are dominating, pyroxenes, the Ca-perovskites, apatites, amphibolies, ilmenites, magnetites, biotites, phlogopites, serpentines and chlorites as well as carbonatites are common (supplementary file3.) In the Lorik pipe (Figure 3B) also compiled by autholithic breccia, the major mineralogy is similar but it contains also barites, zircons, zirconolite, Cr-rutiles similar to the kimberlites from Priazovie [34-36].

In leningrad kimberlites the Cr- diopsides are relatively rare but Cr-bearing amphiboles of various compositions are frequent.. They are found in xenoliths and xenocrysts and are abundant in the concentrates.

The rare diamonds in the Leningrad pipe [6,7,32]. Correspond to low temperatures 1075–1175°C according to the N content and $\delta^{13}C\text{‰} = -4$ which is heavier than for kimberlites in YKP and worldwide ($\delta^{13}C\text{‰} = -5.5$) suggesting the growth from the fluid [9].

The Lorik and Svetlana pipes contain much less tuffitic material and amphiboles are not common among the xenocrysts.

Common type of mantle xenolith in Leningrad pipe are garnet (Gar) (Figure C) and spinel (Sp) harzburgites (Figure 3D) though the spinel type prevails. with amphiboles (Amph) commonly associated with the clinopyroxenes (Cpx), Cr-spinels (Chr) ilmenities (Ilm) and are often in the intergrowth with the phlogopites (Phl). inclusions of the apatites, Cr-rutiles, barites Sr - carbonates and various sulfides were detected by electron microscope (Figure 3E,F). The orthopyroxene (Opx) and olivine (Ol) are mostly substituted. The sulfides like chalcopyrite, nickeline, keilite, millerite, pentlandite, pyrite, smythite, villamaninite occur in intergranular space. The deepest edinites and richterites were not found in thin sections and occur only in the concentrates.

Methods of Analyses

Electron microprobe (EPMA) analysis: These mineral grains were analyzed in the Analytic Center of IGM SM RAS in Camebax Micro and Jeol JXA8320 apparatus according to the published procedure [35,36]. Electron beam 1 micron; accelerating voltage -15 kV; beam current -15 nA; 15 seconds counting time. The relative standard deviation did not exceed 1.5%; the precision was close to 3-5% 2 sigma error. Altogether it was analyzed about 2100 grains (Gar-670, Cpx-142, Amph- 498; Ilm - 420; Chr -380) in addition the analyses of S. Babushkina made in IGDPM SB RAS using Jeol JSM-6480LV microprobe for Leningrad (1220), Svetlana (390) and Lorik pipes (235).

Electron microscope analysis: The detailed mineral compositions of ~ 420 grains in thin sections (370) and epoxy mounts (50) were studied using a MIRA 3 LMU scanning electron microscope with an attached INCA Energy 450 XMax 80 microanalysis energy-dispersive system (SEM-EDS) at the X-ray Laboratory of the Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences [37,38].

Inductively coupled mass spectrometry with laser ablation (LA ICP MS): Mineral grains (77) of the kimberlite indicator minerals (KIM) from the concentrate of Leningrad pipe garnets (Gar) (31) and Cpx (18) Ol (2), Amph (69) were analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in Nikolaev Institute of Inorganic Chemistry SB RAS using aniCAP Q mass spectrometer (Thermo Scientific) and an NWR 213 (New Wave Research), Nd YAG: UV 213 nm laser ablation system (analyst N.S.Medvedev). Detection limit ~10⁻⁷ and the standard deviation of the measurements for most isotopes was about 10-25% [32]. In total 54 isotopes of elements were analyzed. The NIST 612, 610 SRM were used as the standards. For the internal control 24Mg, 29Si, 39K, 47Ti, 55Mn, 52Cr and 44Ca isotopes were used to check agreement with EPMA analyses. The 44Ca, 29Si, 24Mg, isotopes were used for the normalization of the calculated values. Additionally, garnets and clinopyroxenes from samples 315-254, 315-167 and 315-73 analyzed in MRAC Belgium by solution ICP-MS [39] were used as internal standards. All data are presented in tables of the supplementary files (SF1-3).

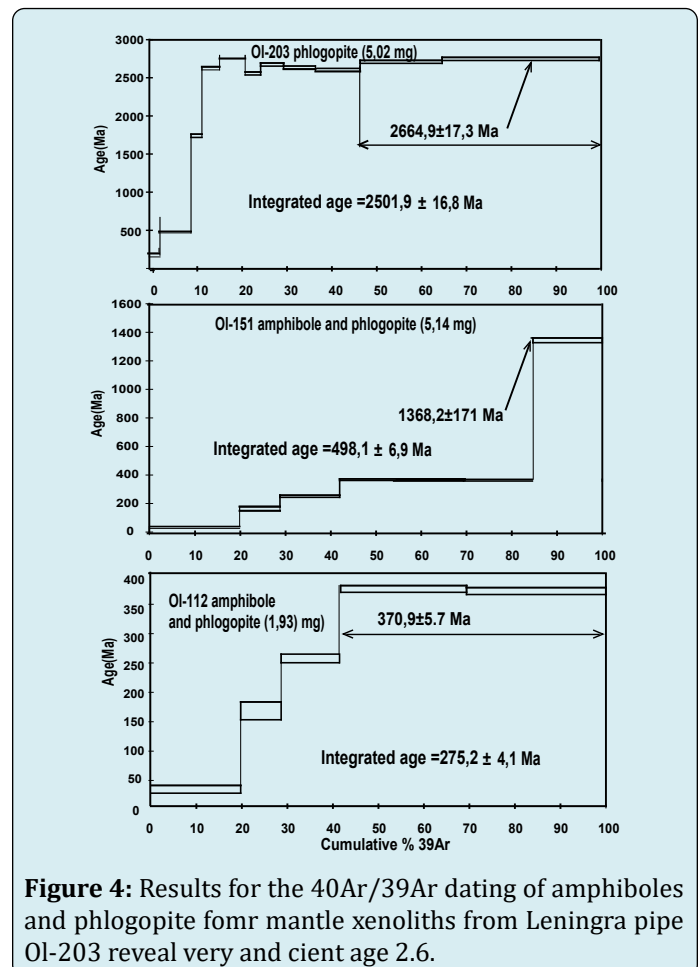
40Ar/39Ar isotopic dating of minerals from xenoliths: Age samples of aillikites estimated by 40Ar/39Ar age using the method described in detail by Travin, et al. [40]. Quartz ampoules with samples were irradiated in the Cd-coated channel of a reactor (BBP-K type) at the Tomsk Polytechnic Institute. The gradient of the neutron flux did not exceed 0.5% of the sample size. Step-heating experiments were carried out in a quartz reactor with an external heater. The blank for 40Ar (10 min at 1200°C) was not higher than 5×10⁻¹⁰ cm³. Ar was purified using Ti and ZrAl SAES getters. The isotopic composition of Ar was measured on a Micromass Noble Gas 5400 mass spectrometer (analyst Yudin DS).

All analytic data are represented in the supplementary data file 5.

Results

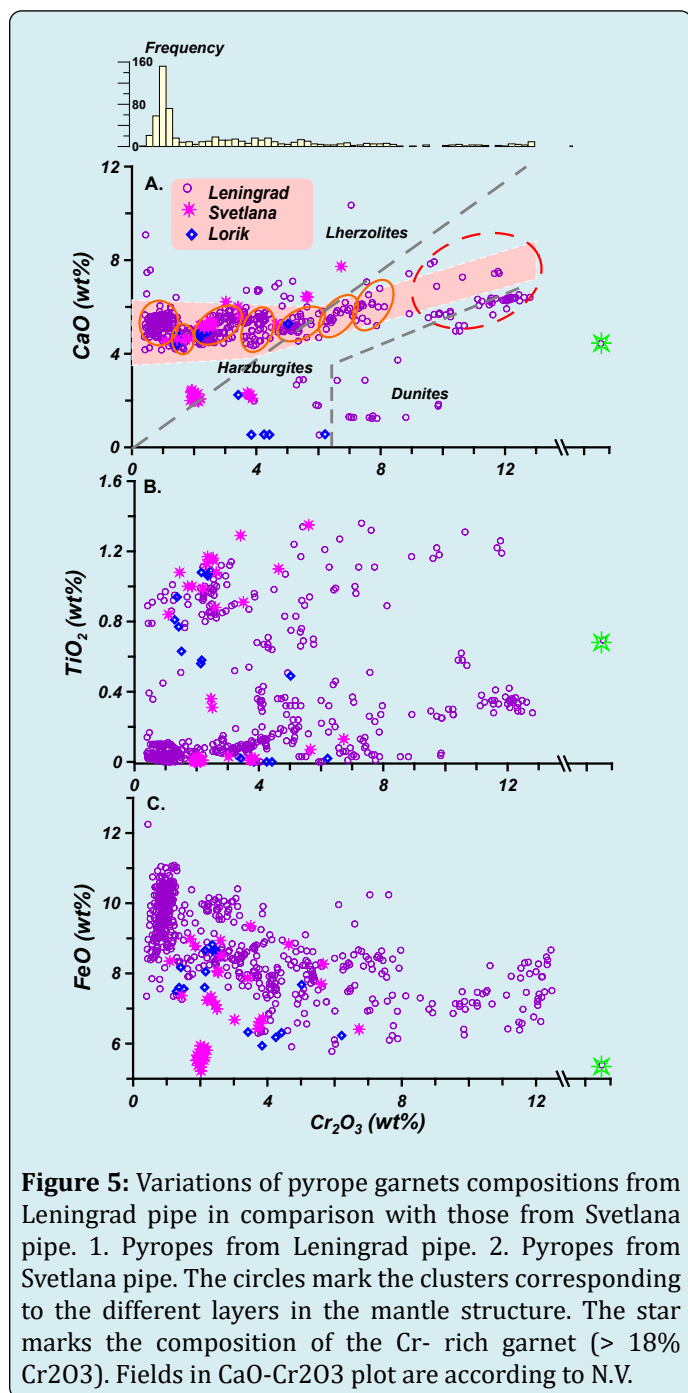
Ar-Ar ages for Amphiboles and Phlogopite from Mantle Xenoliths

The results of the dating of the phlogopite grains and amphiboles occurred in the intergrowth with the Phl are shown in Figure 4. The phlogopite from the spinel lherzolite 2665 Ma corresponding to the final stage of the craton formation. Similar age was determined for the Phl from Udachnaya [41]. The age of the intergrowth of the Amph-Phl from the sample Ol-151 is splitting. The high temperature part with the age 1368 Ma may be referred to the the global activation of the plume and accretion magmatism activity found in many World regions [42] including Siberia [43]. Younger plateau ~ 380-400 Ma corresponds to Devonian plume magmatism. Small plateau ~210 Ma refer to Triassic plume stage. The sample Ol-112 give 370 Ma plateau – Devonian plume age. The younger 160 Ma corresponds to the Jurassic stage of kimberlite volcanism [1-4].



Mineralogy

Garnets: Pyrope garnets were plotted on the CaO - Cr₂O₃ diagram (Figure 5A) covering the intervals from 0.2 to 12.5 wt.% Cr₂O₃. But there is one value at 18.8 wt.% Cr₂O₃ locating within the harzburgite field. The majority of the analyses locate within the lherzolite field according to Sobolev, et al. [44-47]. They are grouped into 8 clusters (Figure 5). Small number <30 of analyses are located within the dunitic field Sobolev et al. [38].



The huge number belongs to the low Cr varieties as is seen in the Cr₂O₃ histogram. They have the steep trend of the FeO rise together with CaO but have very low TiO₂ content (Figure 5B). Several clusters of the dunitic sub- Ca garnets were also detected starting from 2 wt.% Cr₂O₃. Garnets with Cr₂O₃ > 9% are plotting within the harzburgite field including the highest value 18 wt.% Cr₂O₃. Pyroxenitic garnets are rather scarce and occur mainly in the middle part of the diagram. The TiO₂ enrichment from 0.8 to 1.5 wt.% with Cr₂O₃ is found mainly in the low Cr part of the diagram. Comparing published diagrams of garnets and for Svetlana and Lorik pipe [7] those from Leningrad pipe are less abundant and diamond-bearing associations because the capturing interval is shifted to the low-pressure values.

The pyrope - almandine eclogitic garnets are widely distributed. They show the variations in Fe from 12 to 32 wt.% FeO and are separated into two intervals. According to the TiO₂ - Na₂O ratios they belong to the eclogitic non-diamondiferous assemblage.

Clinopyroxenes: The Cr -diopsides from the Leningrad pipe are formed the trend in FeO - TiO₂- Na₂O, Al₂O₃, Cr₂O₃ diagrams to 4 wt.%. In the MgO-Na₂O classification diagram. All Cpx belong to group A (Figure 6A). The Cr₂O₃ and Na₂O are rising to 4 wt. % at 2.5 FeO wt.% (Figure 6B-E) referring to metasomatic trend common abundant in Phl and Amph xenoliths [10,11]. We divided Cpx into 4 groups. The middle part of the diagram with the higher Ti, Cr, corresponds to H₂O metasomatism.

Amphiboles. For the classifications, we used the scheme based on the silica content [40] (Figure 7), the precise names may be found in the spreadsheets (SF1) [41]. The amphiboles from Leningrad pipe form nearly continuous trend from Cr-bearing pargasitic hornblendes to pargasites, edinites, kataforites and later to Na-K and potassic richterites. The typical K richterites (Figure 7A,B) are changed to Fe- rich richterites. Trend cover practically all ranges of mantle amphiboles.

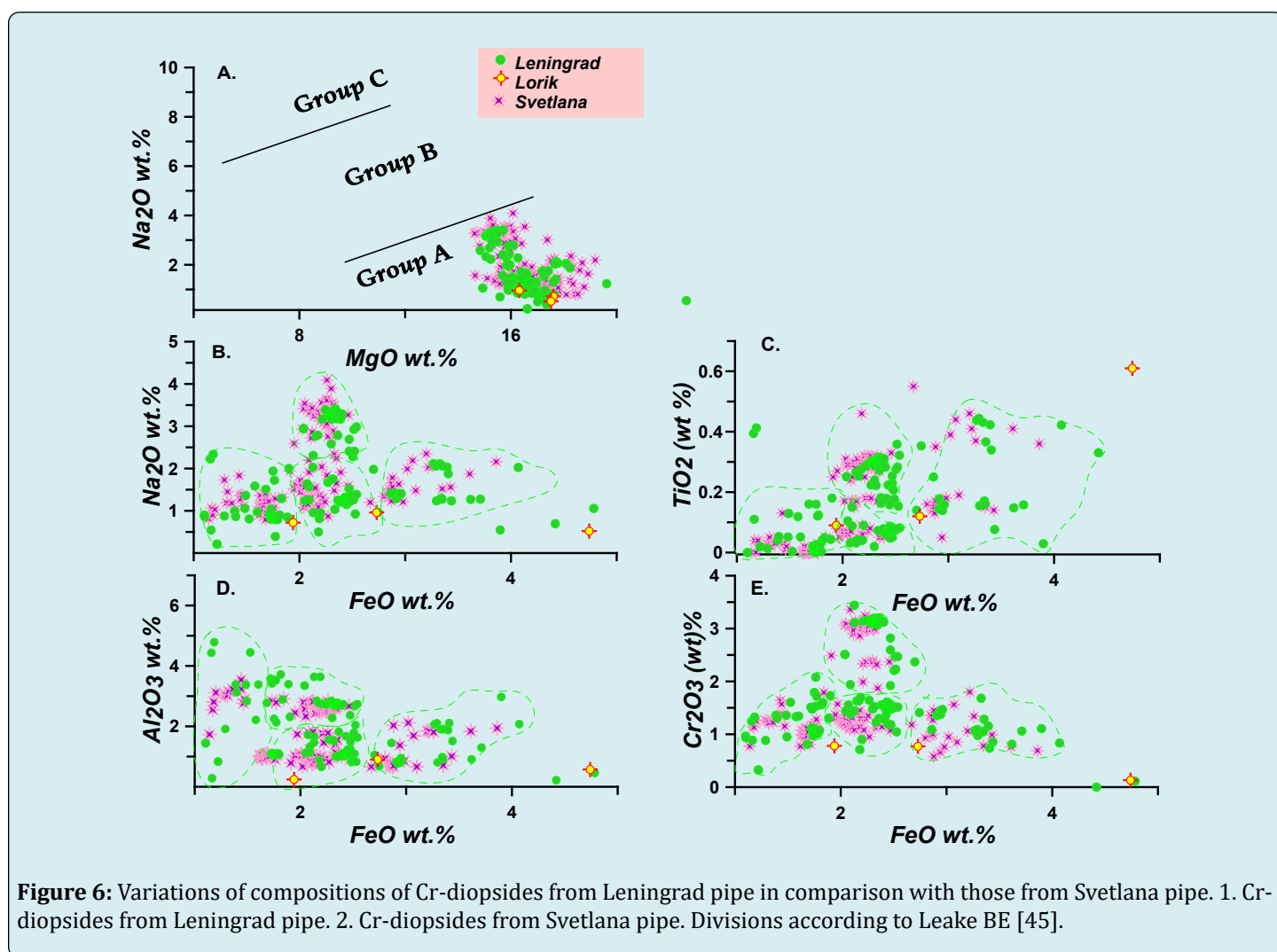
In addition, we subdivided the Fe- rich varieties that occurred among the high silica-rich and low silica varieties. The abundance of the Cr (Figure 7A) is rising in the middle part as in amphiboles from Daldyn -Alakit region [10,11] but TiO₂ in Leningrad amphiboles are lower (Figures 7C & 7J). The amphiboles from the Zarnitsa pipe also essentially differ from K- rich and sodic richterites from the Daldyn area [12-15]. The end members are characterized by the essential increase in Fe especially richteritic varieties (Figure 7D). Leningrad amphiboles are also essentially more sodic than those from Daldyn -Alakit fields. The electron microscope allowed us to determine the halogen content of the amphiboles from xenoliths and intergrowth. They all contain

chlorine (0.1-0.3 wt.%) and no F at al.

Chromites: The chromites from the Leningrad pipe and WUF kimberlites are forming several trends in variational to Cr_2O_3 - plots (Figure 8). The plot Cr_2O_3 - Al_2O_3 is linear as usual but mainly for varieties with Cr_2O_3 40 wt.%. In the corner with high Cr_2O_3 values, there is continuous clouds at the joining of the ulvospinel magnesio-chromite and Fe-chromite trends in Cr_2O_3 - Al_2O_3 - TiO_2 - FeO plots (Figures 8A-8C). In the Cr_2O_3 - FeO plot there are three separate trends, revealing different isomorphous substitutions and oxygen fugacity's regime. Most of the values are from the diamond stability field and essential part close to the field of diamond inclusions.

The Cr_2O_3 -MnO plot shows the higher values for the Leningrad pipe compared to the Lorik and Svetlana pipe.

Ilmenites: The ilmenites from the Leningrad pipe give a long compositional trend on TiO_2 and MgO but there are many low-Mg values and an essential amount of compositions are plotting outside from the typical kimberlitic and typical SCLM values [48,49]. The Cr rich varieties are typical for the high-temperature mantle metasomatites of protokimberlitic melts [10,11,49]. The two Al_2O_3 levels possibly mark magmatic impulses (Figure 9). The MnO is reaching in several varieties 12 wt.% and many grains have 2- 4 wt.% which is not common for the typical protokimberlitic systems.



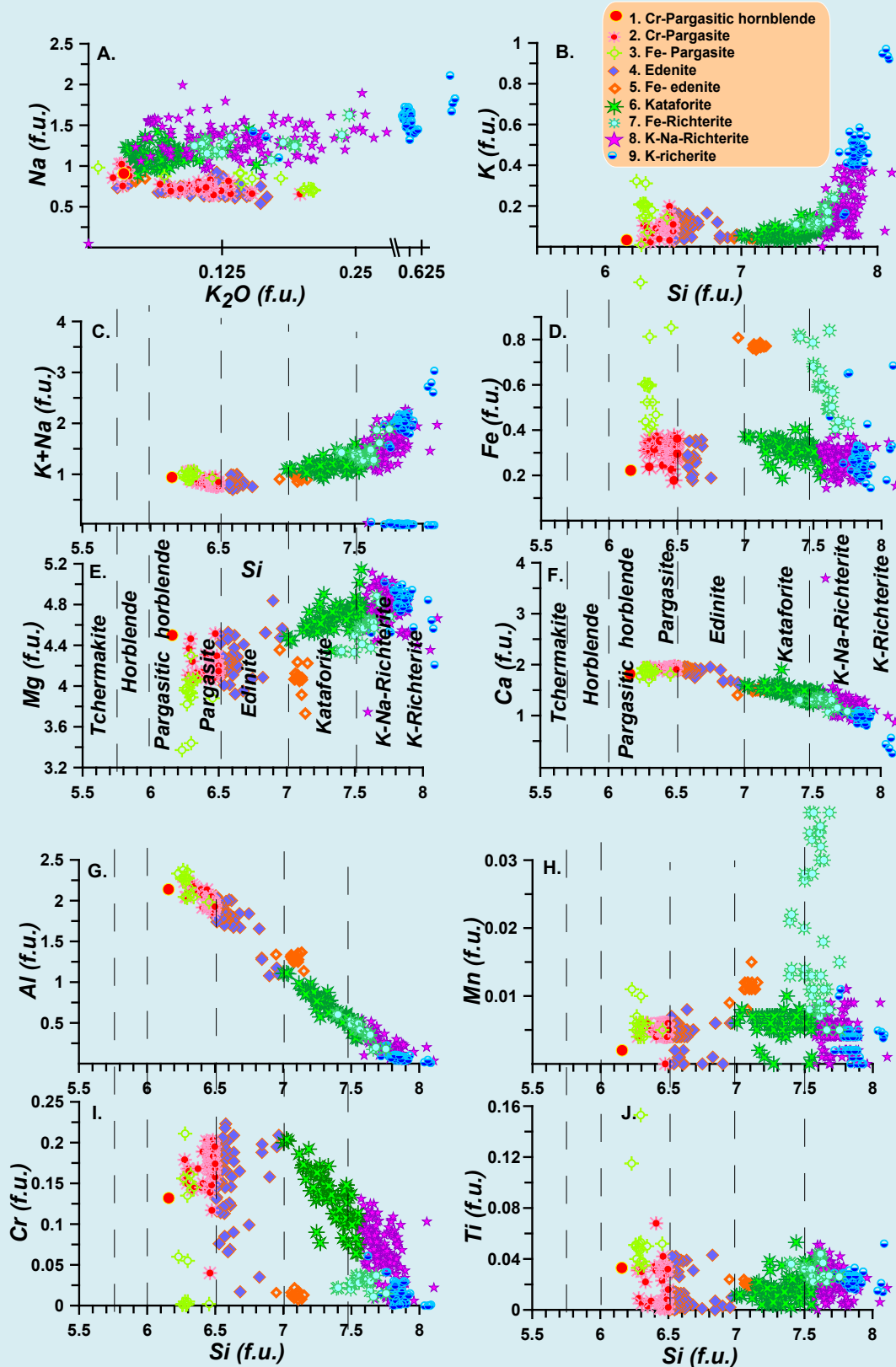


Figure 7: Variations of Cr-amphiboles from Leningrad pipe on the classification diagram [46,47].

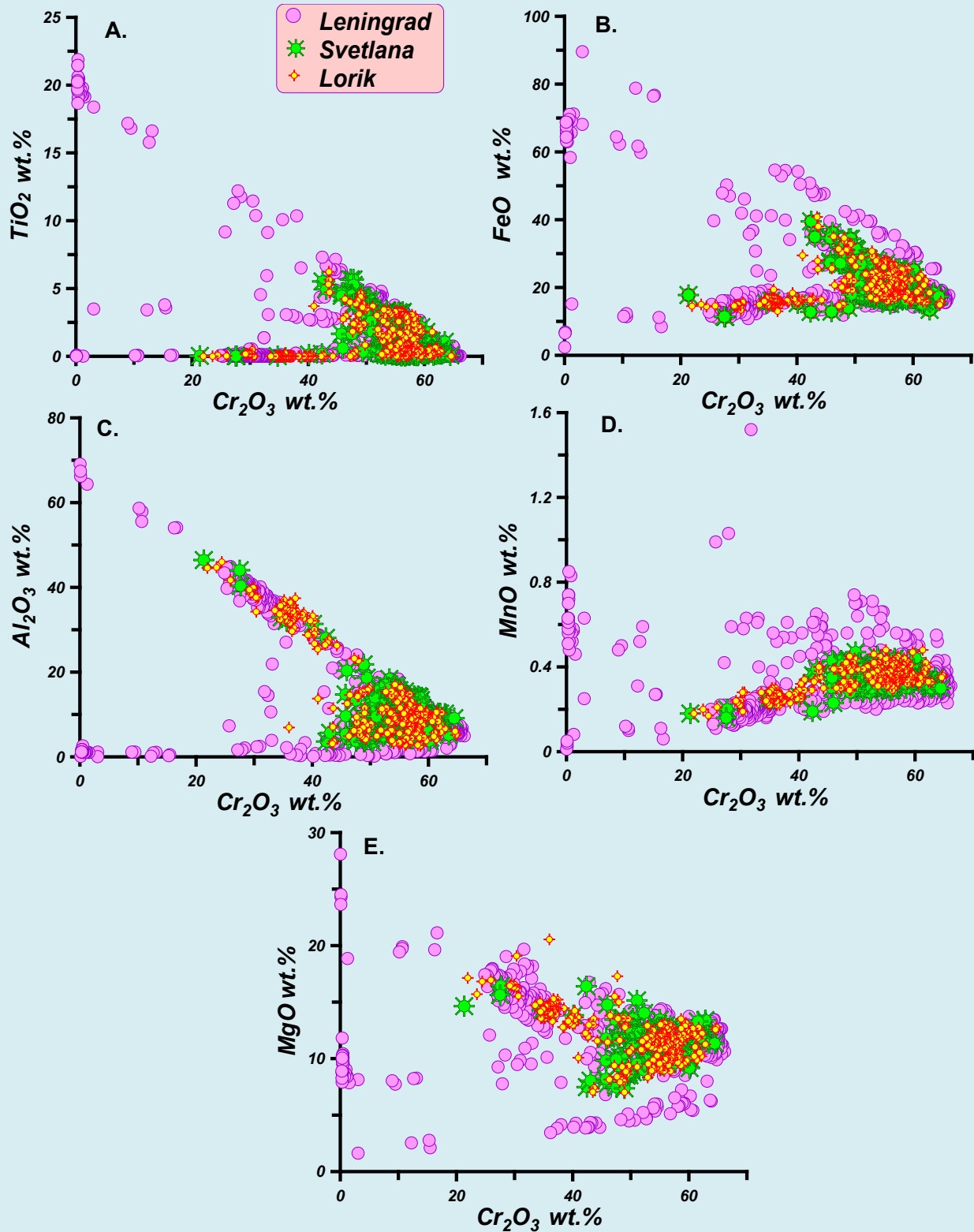
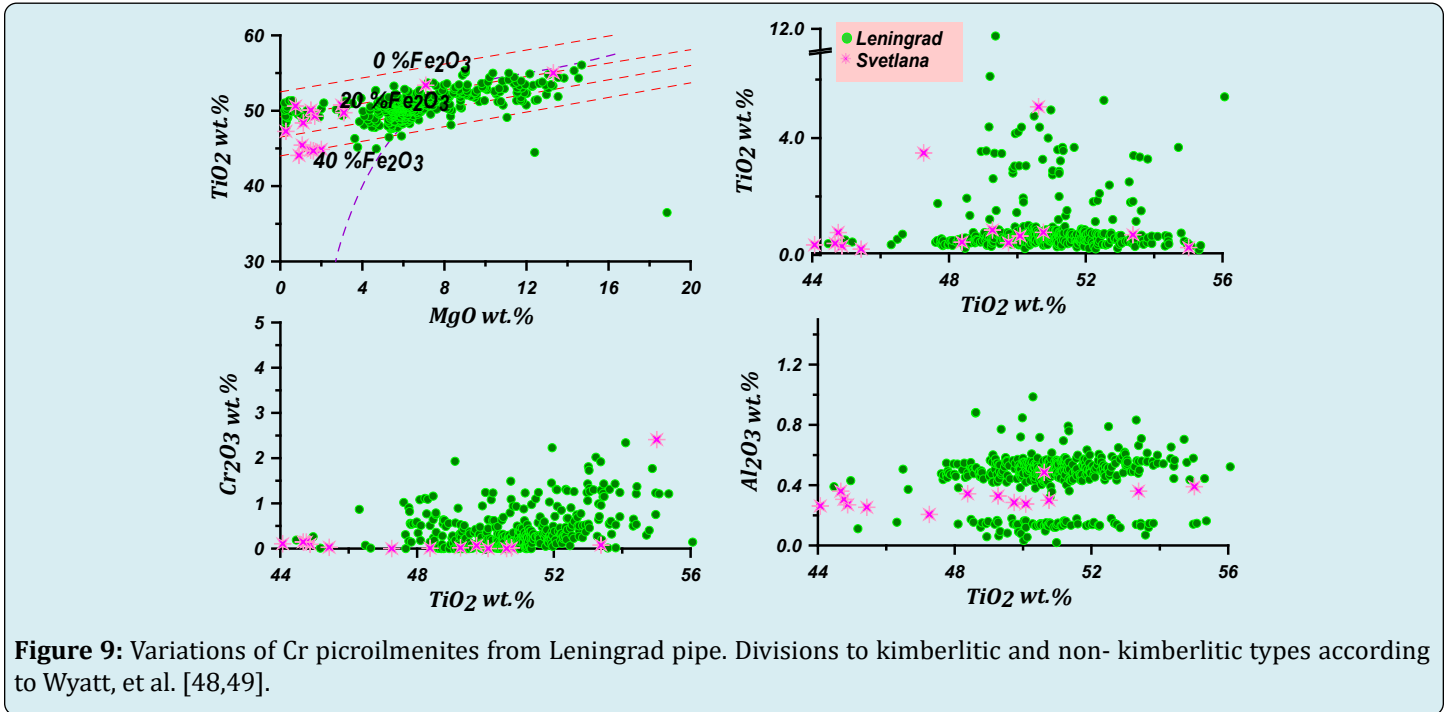


Figure 8: Variations of Cr-spinelides from Leningrad pipe in comparison with those from Lorik and Svetlana pipes.



Thermobarometry

Single grain thermobarometry: For the reconstructions based on the KIM minerals from the concentrate, we used the system of the published thermobarometers for the major peridotitic minerals: clinopyroxenes (Cpx), orthopyroxenes (Opx), garnets (Gar), chromites (Chr), ilmenites (Ilm) [50-52]. For the Cpx in the peridotitic system, jadeite – diopside barometer [37,44-46] is used. The corrected Jd- Cpx barometry is used also for the omphacites in the eclogitic system [50]. The modified Cr- garnet barometer [50,51] is used for pyrope garnets. The eclogite garnet barometer gives appropriate results for the Ca-, Na-bearing garnets using the dependence of Na in garnet from pressure with FeO varying from 12 to 30 wt.% [50]. For the Cr-spinels and chromites, we calibrated their dependence of Cr# (=Cr/Cr+Al) on pressure separately in garnet and spinel mantle facies [52]. The barometer is in combination with the spinel-olivine thermometer of Taylor, et al. [53] where the $Fe\# = Fe / (Fe + Mg)$ for the coexisting olivine ($Fe\#Ol$) is calculated from $Fe\#$ for ilmenites ($Fe\#Ilm$) and $T^{\circ}C$ by the empirical equations.

The oxygen fugacity: The oxygen fugacity of the Gudmundsson G and Wood B [54] in the monomineral version was used to estimate the fO_2 for garnets. The fO_2 for ilmenite and chromite were calculated according to [53] in monomineral version. For the ortho- and clinopyroxenes the polynomial approximations [55] based in garnet estimates [54] were used.

All these thermobarometers are combined in the PT

program Ter55 written in FORTRAN-70 [56].

Monomineral Amphibole Thermobarometry

The experimental high-pressure works give the stability of the Ca- amphiboles commonly to 3.0-3.5 GPa [21] and pargasitic to 4.0-4.5 GPa [22] while for the richterites the stability field was found to 8.5 GPa [23]. But a recent study shows that pargasites are stable to 10 GPa [24].

Existing thermobarometers for Ca- amphiboles allow to work in low-pressures [18-22] varieties. The first author developed a new thermobarometric method [57] using the KD accounting Si-Al and K, Na-Ca re-distributions and the influence of other components and equations in analogy with the universe clinopyroxene barometer [50]. In this paper, this method was essentially improved. Using experiments to 8 GPa [22-24] and was checked using the material from the kimberlite xenoliths [10-17,29] for cross-correlations of PT estimates for different minerals.

As the thermometer, the method of Ravna K [58-64] based on the Fe-Mg (accounting Ca and other components) distribution between garnet and amphibole is used. It was transformed to the monomineral version. We added the corrections to the published version (Figure 10). The list of the used papers see in SF5.

The equations of the amphibole thermo barometer are given in the appendix.

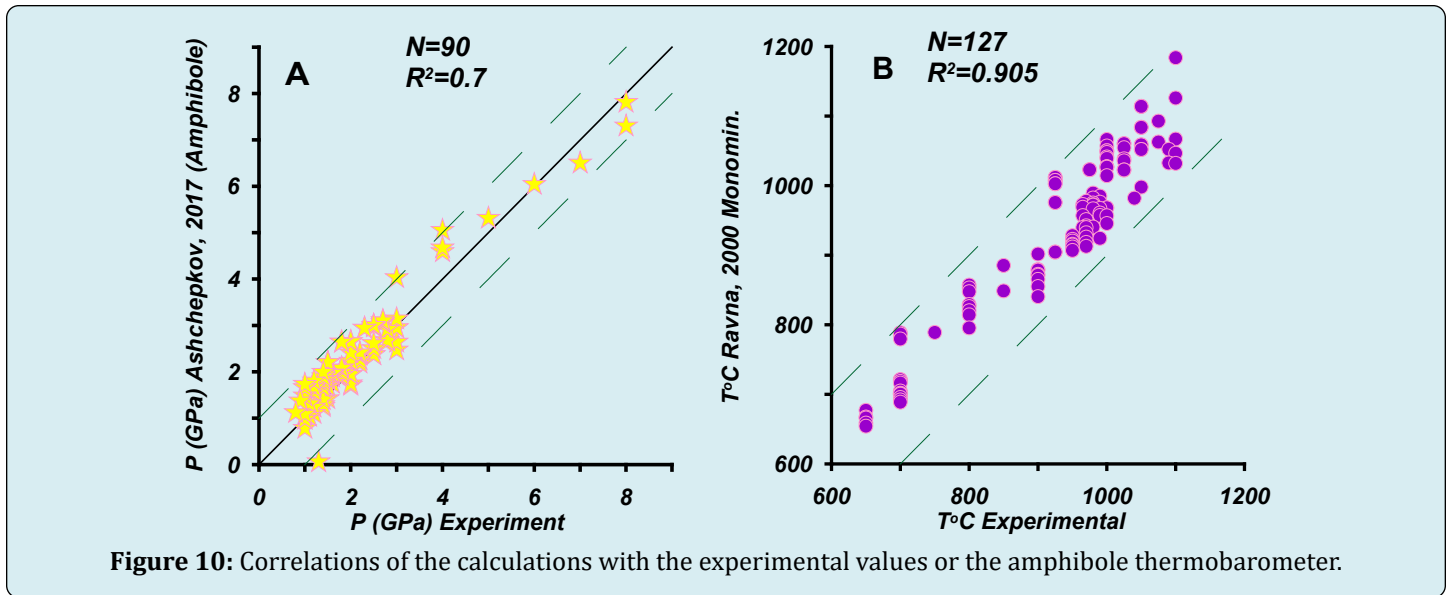


Figure 10: Correlations of the calculations with the experimental values or the amphibole thermobarometer.

Reconstruction of Mantle Sections Beneath the West Ukukit Kimberlite Field

The complex nature of the processes in the mantle lithosphere beneath the Leningrad pipe is visible in the PT diagram with the very rather complex geotherm branches (Figure 11).

The garnets are forming a wide PT field that is located in the lower part starting from 6 between 40 and 35 mw/m^2 conductive geotherm and in the upper part near 2.0 GPa, it is slightly above 45 mw/m^2 geotherm. From 6 GPa and deeper there is a wide scattered convective branch traced together by the Ilm and Gar PT estimates. The additional convective branch is traced by the garnets from 4 to 5.5 GPa just at the diamond – graphite transitions [65-69].

Amphiboles of different types trace practically all geotherm branches formed by Cpx and garnets. The low pressure are covering the 2.5-0.8 GPa interval and are divided into relatively high - Al-rich hornblendes and lower -Al - pargasites varieties. The edinites are tracing the middle part of the SCLMin pressure interval from 2.5 to 4.5 GPa. The kataforites and richterites are deeper and are found in 4.5-6 GPa interval. Their PT split to high-temperature (HT) and LT branches which close to those formed by Cpx's and pyrope's PT estimates. The K-Na richterites give high-temperature (LT) geotherm which is correspondent to those of pyrope diamond inclusions [70]. In addition, The Fe-enriched richterite varieties give the deviations to the high-temperature convective branch traced by ilmenites and HT garnets. The general feature of PT conditions for amphiboles is their division to HT and LT branches in all pressure intervals (Figure 11). The general feature of PT conditions for amphiboles is their division to HT and LT branches in all

pressure intervals. In the SCLM mantle beneath Leningrad pipe, West Ukukit field, Yakutia, the thermobarometry for garnets, Cpx, Chr, Amph allows us to identify seven horizons corresponding to paleo subduction slabs [71,72] (Figure 11). The oxidation state of the pyrope garnets is common and form the trend between 1-10% CO_2 . The eclogitic and pyroxenitic Cr-low garnets are more oxidized and close to QMF buffer (Quartz-Magnetite= Fayalite) [68,69,71]. The chromites are the same in general but at 3-2 GPa they are anomalously reduced. The part of the clinopyroxenes is following to pyrope trend. But the those located within 6.5-4 GPa intervals are more oxidized and are plotting near the boundary Enstatite- Magnetite- Olivine- Garnet = Diamond (EMOG/D) [68,69] buffer to 0 QMF. The ilmenites reflecting the conditions of the picroilmenites shows FO2 values following EMOG/D buffer, in general, being more oxidized at the lithosphere base.

Two pipes from the SW part of the field also contains KIM used for the thermobarometric reconstructions. Both of them contains mainly chromates. The chromites from the Lorik and Svetlana pipes show the low-temperature conditions at the lithosphere base at 6 GPa which is followed by the advective trend to 3 GPa (Figure 12). The pyrope garnets are represented mainly by the sub-calsic varieties tracing low-temperature geotherm. In the upper part, the geotherm is composed of the PT estimates for the wehrilitic garnets and Ti-rich Cr-spinels. Pyrope garnets mostly give the 3-4 GPa interval and are sharply divided into sub-calsic and pyroxenitic varieties. The latter show the conditions up to 7.5 GPa referring to 40 mw/m^2 . The clinopyroxenes trace all parts of the geotherm for garnets and Cr-spinels. They also create the relatively Fe-rich hot branch at 6.0 GPa commonly associated with deformed peridotites.

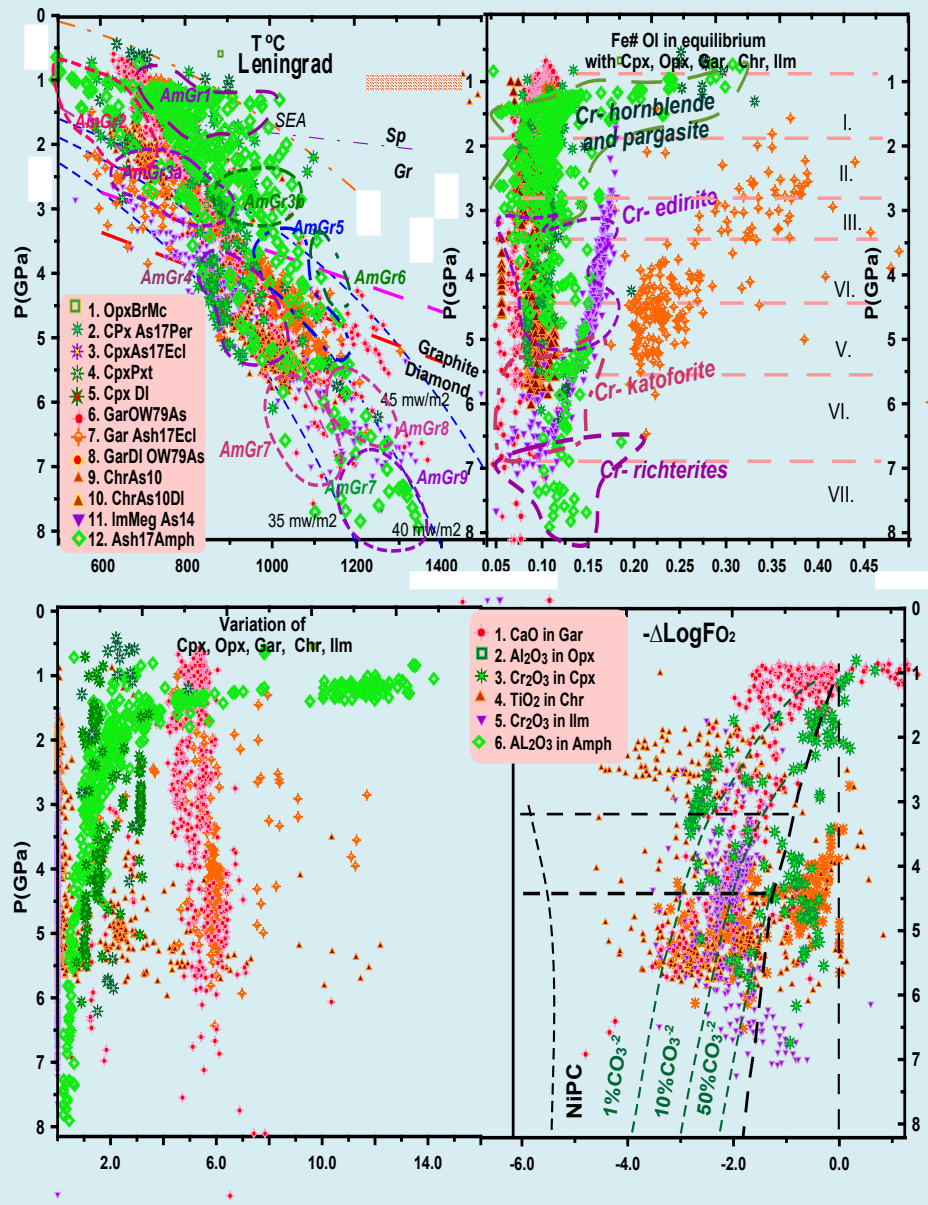


Figure 11: PTxfO₂ diagram for the minerals xenocrysts from Leningrad pipe. Signs: 1. Opx: ToC [59]-P(GPa)[60]. 2. Cpx: ToC - [61] - P(GPa) - [50] (for Cr -diopsides); 3. The same for pyroxenites and Fe- Cr -diopsides. 4. The same for eclogites and pyroxenites; garnet: 5. ToC [62] -P(GPa) [50]. 6. [58]- [44] for eclogites; chromite: 7. ToC [63] -P(GPa) [52]; 8. Ilmenite megacrysts: 7. ToC [53]- P(GPa)[52]; Amphibole: 9. ToC -P[58] -P (GPa) [51] corrected. The horizontal dashed line at 3.5 and 4.5 GPa corresponds to the Graphite-Diamond boundary [65,66] at 35 and 40 mWm⁻² respectively. Conductive geotherms [67] The field for P-FO₂ diagrams and lines of CO₃⁻ concentration in melts are from [68,69].

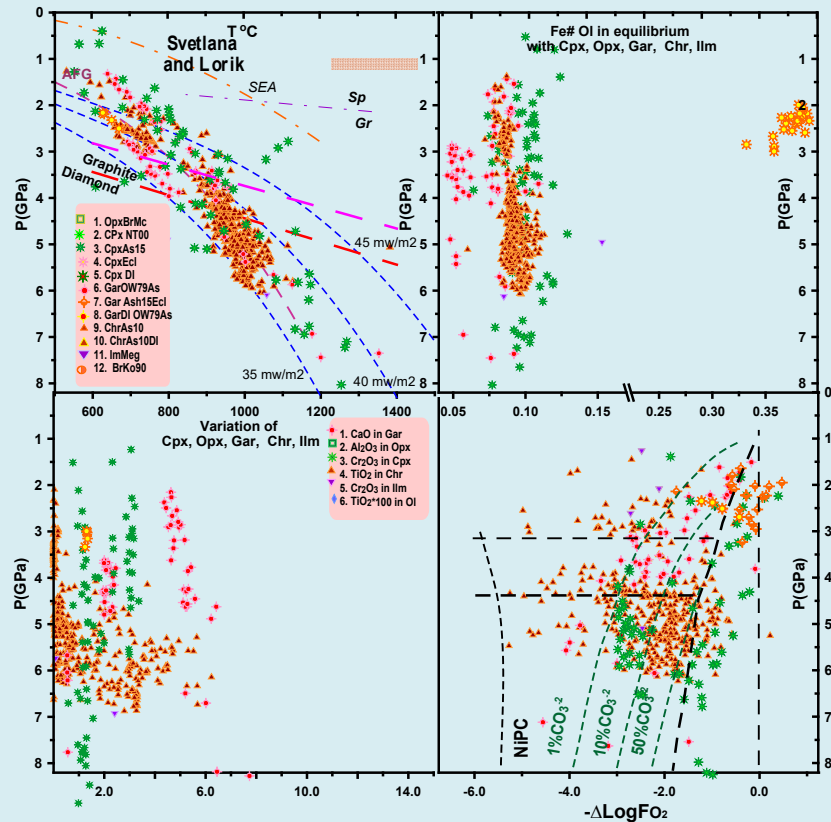


Figure 12: PTXfO₂ diagram for the minerals xenocrysts: a) Lorik pipe; b) Svetlana pipe. Symbols are the same as in Figure 11.

Geochemistry of the minerals

Garnets: We divided garnets into 7 groups according to trace element patterns. The group with the highest REE level at 100/CI (Chondrite Iruma) [73] refer to the crust granulites and they show deep minimums in high field strengthen elements (HFSE). Analyzed peridotitic garnets from the Leningrad pipe of the prevailing lherzolitic type reveal mostly regular semi-round (concave upward) rare earth elements (REE) patterns with the low LREE level. Common lherzolites (GLh) in the spider diagram for trace elements (SDTR) reveal the evident elevations in Zr-Hf typical for the metasomatic phlogopite bearing mantle and rather high Ta, Nb, U and Th. The trace element (TRE) spider diagrams show not very low minima in Sr, Pb and deep in Ba and low large ion lithophile elements (LILE) except for Rb. Harzburgitic garnets (GrHz) display small minima in MHREE and essentially lower all incompatible elements from the left part. The depleted harzburgites GrHrD show also lower LREE part and all incompatible elements. Garnets from dunites (GrDun) show and moderately low levels of incompatible elements and HFSE and some of them show even elevated levels of LILE. There are two types of pyroxenitic garnets. The 1st one GrPxt1 reveal the hump in the REE pattern and the SDTR show the high incompatible element level including HFSE

with the peak at U. the second GrPxt2 display the flattened REE and slightly elevated LREE and LILE while HFSE are slightly lowered (Figure 13).

Clinopyroxenes: The clinopyroxenes were divided into 5 groups. The samples from Gr1Cpx show REE level at 300/CI or more in La and inclined La/Yb_n ~10 patterns. In SDTR the HFSE reveal minimums in and rather low LILE but Th, U are slightly elevated. The Cpx from the Gr2Cpx are lower in La level but are more inclined La/Yb_n ~12- 15. The HFSE are varying and mostly low similar to those in intergrowths with the ilmenites [14]. The Gr3Cpx (pyroxenitic) display higher REE inclination and nearly straight line REE patterns. The SDTR is more smooth and the left part of the diagram (incompatible) is very low. The REE patterns from with lower REE with La_n ~15 concentrations have minima in Ta, Nb and more flat Zr -Hf. The samples from the Gr5Cpx have different REE – one (a) displays very high LREE >100 and La/Yb ratio the second nearly flat pattern at ~10 La_n level typical for spinel facie. But they have very huge U-Th peaks but like those for the carbonates. They have minima in Hf, Pb, Nb and LILE.

One Opx show lowered concave downward inclined REE pattern with La_n at 20. The SDTR display deep minima in Zr, Hf, Nb but elevated Th, U, Sr. And one olivine display also

inclined concave pattern with the minima from Dy to Tm. The right part of the SDTR is lightly inclined but relatively smooth with the minima at Ta but peaks in Pb.

Olivine and Orthopyroxene

Amphiboles: The low-pressure Cr – pargasitic hornblendes (AmGr1) show highly inclined and deeply concave downward REE patterns. All of them have the peaks in Eu reveal rather high LREE level - $La_n \sim 100$ CI and they have essential depressions in HMREE part with the minima near Ho-Dy REE patterns. The SDTR for most of them shows strong peaks in Ba, U and smaller ones in Ba. They reveal HFSE minima except for Y. The more HT varieties (AmGr2a) show similar patterns but much lower in REE and less inclined pattern with the LREE at 50-10/CI and they reveal the minima in Nd and Ta and highly variable foor maximum in Zr Hf. The amphiboles from Gr2b show a much lower LREE level ($La_n \sim 10$ /CI).

The amphiboles (mainly edenites) from AmGr3 are subdivided into 2 subgroups. Groups 3a and 3b have a similar inclination of REE patterns with $(Gd/Yb)_n \sim 5-7$ and slightly bell-like from La to Sm pattern. The MHREE are slightly concave downward from Yb to Ho. The amphiboles of AmGr3a with the higher REE level and $La_n \sim 150$ to 100 reveals the evident Eu minima. The samples from AmGr3B have no Eu anomalies. The TRE spider-diagram for AmGr3a show the minima in Zr-Hf and contrast Nb peaks and minima. Both two groups have moderately depleted LILE group with local Ba and higher U peaks. The AmGr3b have elevated Ta, Nb and slightly elevated Zr, Hf, Y very low Th.

The kataforites AmGr4 reveal similar REE patterns without no Eu anomalies. with the inclined from Nd to Yb part and more flattened from La to Nb part and The level

of $La_n \sim 100-40$ or higher. The spider diagrams have gently decreased from the Nd to Yb part with the small fluctuation in Hf and Sr. The definite feature is a strong Nb peak and They have Th trough rather low U and elevated LILE. The REE patterns from AmGr5 are show bell-like spreading in LREE part and the same inclined branch from Sm to Yb as the previous. An opposite they reveal very high U and deep Nb trough but high Ta.

The same Am.Gr6 are similar as previous but have lower REE they show troughs in Th, U.

The high-pressure amphiboles K-Na richterites typically reveal higher inclinations compared to all previous groups $(Gd/Yb)_n \sim 20-30$ with the minima in HMREE near Er-Tm.

The amphiboles from AmGr7 corresponding to the low-temperature geotherm reveal nearly straight-line REE patterns with the very high level of LREE ($La_n \sim 1000$ /CI) with the Eu minima and flattened HREE part for samples from AmGr7b. One spectrum of AmGr7b for the Na- richterite shows a less inclined REE patterns and small depression from La to Eu.

The samples from the Gr8Am reveal lower REE highly inclined REE ($La_n \sim 100-60$ /CI) and $(Sm/Yb)_n \sim 70-50$ display with the more flattened right and left parts. They have strong U, Ta, Sr peaks and elevated Rb, Hf, Zr, Y and minimums in Nb.

The more HT group AmGr9 reveal less enriched in REE and nearly conform patterns. They display the same peaks in Ba, U (for most) Ta, Sr, Zr, Hf and small in Y and negative in Th. One sample shows negative Ta and positive Th anomalies.

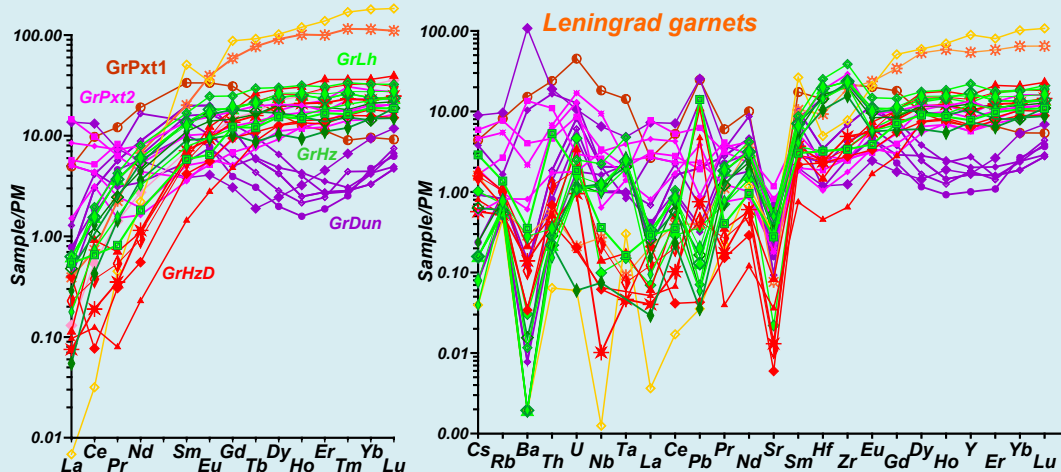


Figure 13: REE patterns and TRE spider diagrams for the pyrope garnets from Leningrad pipe. Normalization REE to [73] and TRE spider diagrams to [74].

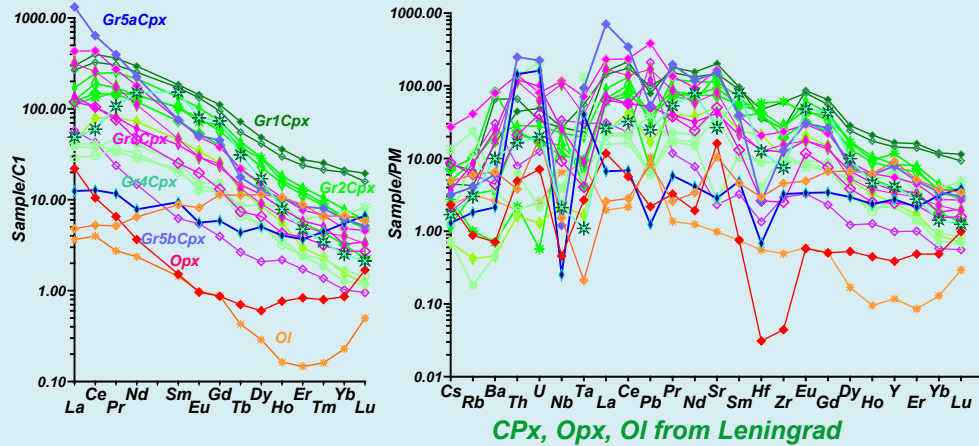


Figure 14: REE patterns and TRE spider diagrams for the clinopyroxenes, orthopyroxenes and olivine from Leningrad pipe. Normalization is the same as in Figure 13.

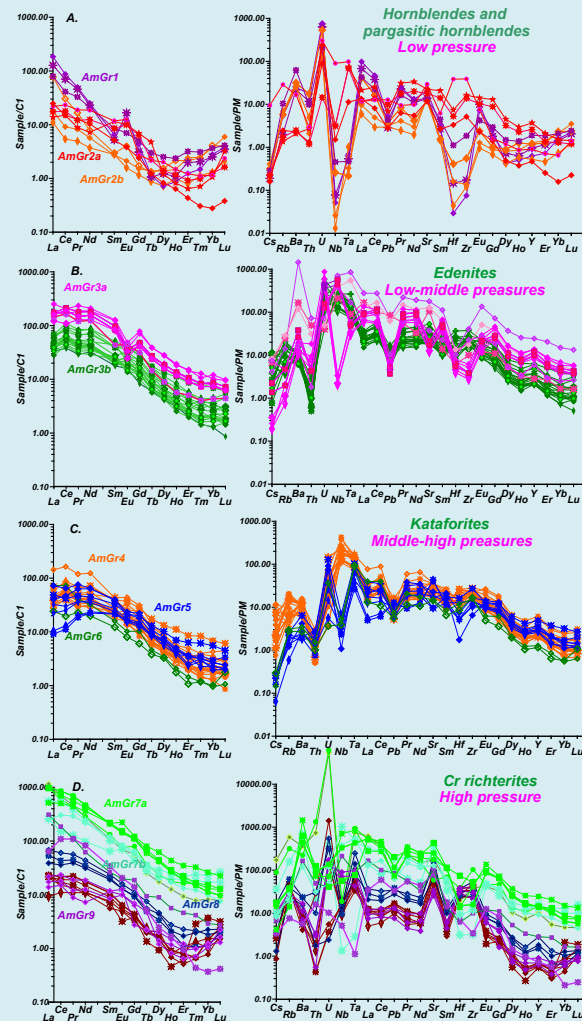


Figure 15: REE patterns and TRE spider diagrams for patterns for amphiboles from Leningrad pipe: a) low-pressure hornblendes and other Ca- amphiboles; b) low-middle-pressure pargasites; c) middle- high - pressure pargasites edenites; d) high-pressure Cr- richterites. Normalization is the same as in Figure 13.

Discussion

The Mineralogy as the Factor of the Diamond Grade and Geodynamic Conditions

The mineralogy of the Leningrad pipe, in general, is similar to pipes of the Devonian kimberlites from YKP [75,76] showing the long range of the Cr_2O_3 -CaO in the lherzolitic field and extending to 18.2% Cr_2O_3 belonging to the harzburgitic field which is one of the highest in the YKP. It suggests the very deep source of this pipe like those from the Mir [67], Nakyn [77] or Zarnitsa [13]. Unfortunately, like some other large pipes including the Zarnitsa, the prevailing breccias capture mainly the upper part of the mantle section without diamonds. The pipe has the polyphased structure, which is visible not only from the observations of the kimberlite relationships in the pipe but also supported by the complex chromite and ilmenite trends in the variation diagrams. The majority of the chromites are rather high chromium that also expands the perspectives of the diamond grade. A rather high amount of the almandine-pyrope garnets refer to the eclogites and HP varieties according to the thermobarometry may be diamondiferous. It suggests that similar rocks may be source of placers which contain beautiful diamonds [78-80].

There are many signs that the mantle in the northern YKP is more hydrated is higher than in central YKP region.

Comparisons with the Amphiboles Worldwide

The most interesting feature of the Leningrad pipes – the high variations of the Cr-bearing amphiboles, which is the highest in the World among the kimberlitic pipes and any other mantle objects. Commonly amphiboles occur in the highly metasomatized mantle peridotites. The richterites were found in the MARID xenoliths in several pipes from the Kaapvaal craton [29,81-83]. The pargasitic types were described in the peridotite mantle xenoliths from Kimberly pipe [84] and in the xenoliths from Gibeon Kimberlite Province, southern Namibia [85,86]. They were found in the eclogites of Orapa, Roberts Victor [81] and other kimberlite pipes of South Africa [87]. Ca-amphiboles occur in peridotite of many orogenic massifs such as Lherz [25], etc. They are detected in the mantle xenoliths from the alkali basalts in Transbaikal in Bartoy volcanoes [88], in the European Cenozoic basalts including Massif Central [89], Rhon Graben [90] and Pannonian [28], in Victoria Land, Australia [91,92] in Nushan, China [93] and many mantle arc basalt localities [94] other locations of mantle xenoliths.

The breakdown of the amphiboles in the mantle in the island arc environment is the source of the H_2O during the formations of the granites above the deep subduction zones

[95]. The amphibole metasomatism put an essential role in the distribution of the LILE and HFSE components in the mantle [90] due to the high partition coefficients of this mineral [96-100].

Recent researches show that pargasites are stable to 20.5 GPa [24]. The PT stability field is consistent with the conditions of both hot and cold subduction. The richterites are stable to 8.5 GPa and more [23,96].

The presence of the crustal signatures in the geochemical features of the amphibole suggest the strong influence of the subduction material to very high-pressure conditions of the SCLM [100-102]. The abundance of the amphibole is caused by the continental margin environment of the W.Ukukit mantle in ancient times.

Thermobarometry and Mantle Layering, the Geothermal Conditions of the SCLM Beneath West Ukukit Field

The layering of the mantle column is mainly shown by the distribution and variations of the pyrope garnets in the SCLM. In the P-Fe #, diagrams there are several small arrays of the growth of the Fe with the decreasing pressure which probably refer to the primary layering caused by the coupling of the paleo subduction slabs in the Archean time [103]. It is visible in the middle part from 3 to 4.5 GPa. The lithosphere base is probably found at the common position at 6 GPa. The hot garnet geotherm is found from 7.5 to 5.5 GPa marked by ilmenite trend produced by interaction with the protokimberlite system. Heating is found in the middle part where there is a hot branch formed by pyropes along the diamond graphite boundary. In the upper part of SCLM, the heating is pronounced from 3 GPa to Moho. However, several clots of rather low-temperature garnets are found at 7 GPa. The eclogitic garnets are forming two branches in the PT and P-Fe# plots. The Fe# growth during the pressure decrease was probably created during the rise of the melts, which were produced during submerging of the subduction layers to the depth [104,105]. It is proved that even peridotite paleosubducted layers were significantly re-melted [106] and eclogites should be nearly completely melted forming ascending magmatic bodies. On the PT diagram, eclogites are mainly forming the branch near 40 mw/m^2 in the lower and middle part of the mantle column and they reveal low-temperature conditions in the upper SCLM part starting from 4 GPa. Branching for the Cpx geotherm from LT 35 mw/m^2 branch to HT convective branches (advective) from 6 to 4 GPa probably reflect influence of the protokimberlite melts and fertilization processes [107,108]. The most Mg-rich chromite compositions also are distributed in the middle part of the mantle section from 3 to 5 GPa. While in the lower and upper parts of the SCLM, they became more

Fe rich due to interaction with the protokimberlites. in the lower and middle part and probably with basaltic melts in the upper part of the SCLM. The same feature is found for the compositions of the amphiboles which are forming the hot and Fe rich branches in the base of the lithosphere and the upper part starting from 3 GPa.

The ilmenite trends and distribution in the mantle column is complicated. The lower part from 7.5 to 6 GPa is rather high-temperature and Mg-rich and corresponds in the PT conditions to the dunite harzburgite garnets. Probably these are the high-temperature metasomatites at the lithosphere base, which are found in most kimberlite pipes. The deviations to the high Mg-Ilm compositions refer to the metasomatites. However, the major trend is the typical trend of the protokimberlite melt fractionation.

The amphiboles provide the most complex PT conditions. They are sharply divided into three pressure groups. The lower part is correspondent to the 3 clusters. The sodic richterites with the Eu anomalies gives the lowest temperature branches to 35 mw/m² starts from 6.5 GPa and continuing to 4 GPa slightly heating. The possible model is

reactions with rising of the hydrous subduction-related fluid rich melts through the mantle column. The hottest branch is correspondent to the K -richterites and edinites at the lithosphere, which are Fe- Ti, enriched due to reactions with group II kimberlite and heated to the 45 mw/m² geotherm. There are all the intermediate temperature variations. Next hot clots the amphiboles is at 5 - 5.5 GP and this cluster nearly coincides with the hot garnet branch for the pyropes. The next heated branch is near the diamond-graphite boundary. The heated branches are most pronounced between 3-1 GPa. In addition, the heating for amphiboles is from 45 to 90 mw/m² geotherm in the upper part for both Cpx and Amph that corresponds to typical "basaltic" or SEA geotherm [109]. The behaviour of the Al in amphiboles on the P -Variation diagram (for amphiboles Al₂O₃) shows the changes from the LAB level to 3.5 GPa where the Al₂O₃ begin essentially grow up. Starting from 2.2, GPa the Al in amphiboles drastically splits from enriched in al compositions to typical hornblendic with the 10-14 wt.% Al₂O₃.

Using the Cpx, Gar, Chr, Ilm and Amph composition we determined 7 levels in the mantle column beneath the Leningrad pipe.

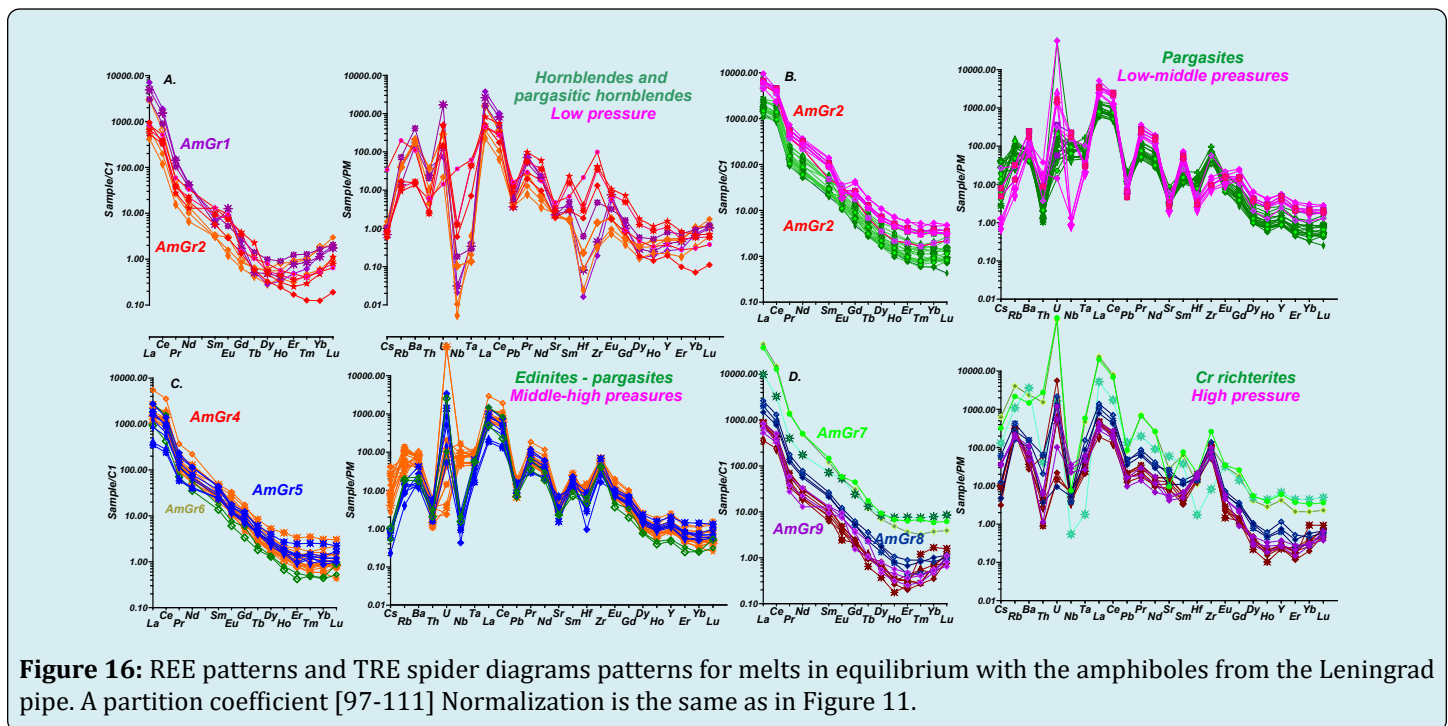


Figure 16: REE patterns and TRE spider diagrams patterns for melts in equilibrium with the amphiboles from the Leningrad pipe. A partition coefficient [97-111] Normalization is the same as in Figure 11.

Geochemistry of Minerals from Mantle Peridotites, Metasomatites and Vein Systems and Relations to Geodynamics

Garnets are splitting by the REE and TRE spectrums to typical lherzolites with the Zr- Hf peaks which mark H₂O metasomatism [75] and tharzburgitic groups with

the different LREE content and probably melting degrees of host rocks. It is clear that dunitic and harzburgitic garnets with relatively low HFSE should be related to the ancient subduction-related processes which commonly reveal elevated Ba, U, Sr, Pb [110] but troughs in the HFSE.. Pyroxenitic garnets type 1-2 with the elevated or high levels incompatible elements but minima in Zr, Hf with the high

levels in all incompatible elements probably have the hybrid nature of mixed subduction related processes. Garnets from the low crust probably refer to the cumulates from the plume basalts.

The clinopyroxenes reveal quite variable tendencies. One Cpx from Sp lherzolites demonstrate high Th-U peaks typical of carbonatitic melts [112] but the other with. The Cpx from garnet facies also reveals controversial tendencies. Two of them have elevated Rb and Sr, elevated Th but low U what probably means the influence of potassium bearing fluids. The trough in Zr and Hf combines with the strange Sr peak for olivine. These features are suggesting the influence of the evolved carbonatite melts Gr1, Gr5. The typical the clinopyroxenes with the high REE level and Th, U, Sr Gr1Cpx, Gr3 Cpx, Gr5 Cpx probably are related to the alkali-carbonatitic melt. Gr4- should relate to early-stage protokimberlitic melts and Gr4Cpx have mixed signatures. The inclination is commonly regulated by the Cpx/Gar ratios in the source which is higher for the pyroxenites,

Most of the low-pressure hornblende amphiboles show concave REE patterns have the concave downward patterns which mean the fluid type crystallization as it is found for the boninites and anomalies of Eu suggesting the participation of Pl bearing crust material in the source of fluids. They could be created from the amphibolization for the pre-existing eclogites or directly due to the substitution of the clinopyroxenes [113]. The low- middle-pressure amphiboles show rather high La/Yb_n ratios which suggest the crystallization in presence of garnets or/ and participation of the LREE rich fluids in the origin of the parental melts. High Ba and elevated U and essentially high Na/K ratios support the presence of Na- subduction-related fluids [109] as well as the very deep HFSE anomalies with the varying Ta- Nb which is typical for the rutiles having different partition coefficients for the Nb and Ta [110]. The edinites and pargasites from the middle-pressure interval reveal the serious difference in the geochemistry. The edinites from the low-temperature branch have minima in Eu, which suggest the higher oxidation stage they have higher Rb, Ba T and display minima in Zr Hf and Nb but elevated Ta. The pargasites demonstrate the lower REE and TRE values and practically no Eu and HFSE anomalies and even peak in Ta and as well lower Ba, Th, U than pargasites and high Sr and Pb. This probably meant the participation of the rather high temperature melts in their origin because the higher the temperature the low are the REE and as well (La/Yb)_n ratios The fan-like spreading REE part of the patterns suggest the participation of the partial melts from the peridotite source with the different Ga/Cpx ratios in the source [74]. The most high-pressure richterites are very different. Those with high REE and inclination (La/Yb)_n, LILE and all other incompatible components and minimum in Ta [101] suggest low degree melting and high

Ga/Cpx ratio in the substrate [74].

The compositions of the melts reconstructed with the KD for the amphiboles [97-99] reveal very high LREE patterns and concave in the MREE part (Figure 16). The levels of the HFSE are mostly low but there are some varieties rather high in Zr which is probably evidence about the participation of the H₂O rich melts/fluids in their generation. They are not close to boninites but somewhat similar [113,114]. Most probably such amphiboles generation matters were fluids.

The halogens in the amphiboles of all types are represented only by chlorine which supported the idea of the influence of the subducted related fluids [113-117]. Commonly the fluorine is more compatible in Ca- amphiboles than chlorine [115]. The abundance of sulfides, apatites, barite also support the idea about the subduction-related metasomatism.

Model of the mantle evolution of the SCLM beneath the Ukukit field and the role of the subduction.

The SCLM beneath Ukukit have rather contrast layering typical of Siberian Craton [66] and the formation of the mantle beneath the Ukukit field (Figures 11-12) is not different from the central parts of the craton. The model suggests the hot subduction at the presence of superplume which caused the floating of essentially melted peridotite – eclogite slab and joining it to craton keel from beneath [72,75,103]. The alternative model suggests the stacked subducted slabs [75].

Presence of the Phl with the 2.6 Ga referring to the most andvient mertasomatic H₂O bearing metasomatic processes recorded in the mantle xenoliths in the World proves the common model of the appearance of water in the mantle at the last stages of the continents grows, The other two peaks 400 -380 Ma and 160 Ma both may be referred to the plume Kimberlite magmatic and even to the protokimberlite stage (latest one).

The essential difference is the broad development of amphiboles, which means the later very vast interaction with the subducted related melts, which were enriched in the LILE and sometimes U, Th, HFSE (Figure 15) due to participation of the continental material in the subducted material. It is difficult to imagine the abundance of primary amphiboles in essentially heated Early Archean mantle. The contrasting behaviour of Ta and Nb is regulated by the rutile partition coefficients likely for primary eclogites. Though it could occur because they were found in the Archean mantle eclogites [110]. And it was suggested they were the source of the archaic crust [118]. But mostly metasomatized eclogites are related to later events [119,120]. They were subjected to

the melting and are mostly magmatic bodies rising through the lower part of mantle columns [121].

The hydrated mantle may occur in the continental arc environment where H₂O together with Cl, S, P could provide essentially influence the primary mantle peridotites and eclogites [118]. The subduction-related fluids passed through the all mantle column and caused vast perturbations. Subduction and Na and K (siliceous) types of fluids percolated through the mantle with abundant eclogites causing amphibolization through the whole mantle column. The plumes produced hybridism and more smooth patterns. The presence of the different types of amphibole suggests that it was subjected to multistage fluid interaction of both Na and essentially type which suggests the changes of the type of subduction-related processes. The HT amphiboles appeared as a result of the interaction of the hydrated mantle with the plumes in several stages. The huge compositional variation amphiboles from the Leningrad pipe nearly cover all types of mantle amphiboles [13]. The pressure interval for the amphiboles nearly covers all types of mantle amphiboles determined for the new version of the amphibole thermobarometry [51] (see appendix) support the experimental data [120-134] and presence of amphiboles in diamond inclusions [135] and deepest metasomatites [128,136,137]. And as we can see from the Leningrad kimberlite xenocrysts they form continuous series in the thick lithospheric mantle beneath Sibeian [138] and possibly other cratons. Earlier it was suggested that in the northern part of Siberian craton mantle lithosphere is not thick [139] and even delaminated, but the examples from Leningrad and all studied pipes prove that it was very thick even in Jurassic and Triassic impulses of kimberlite magmatism, which suppose that it possible to find high in diamond grade pipes in the Northern part of Siberian craton.

Conclusion

1. Leningrad pipe contains a huge number (>500 EPMA analyses) of various amphiboles (9 groups according to geochemistry) from Cr - pargasitic hornblendes through Cr- pargasites, edinites, kataforites to Cr - richterites referring to the different PT conditions from lithosphere base to the Moho. This suggests high H₂O activity in the mantle column and the relatively low-temperature nature of mantle metasomatites.
2. The geochemistry reveals the vast variations of the TRE and REE spectra. The low-pressure Cr - pargasites have the signs of fluid interaction with the melt/fluids with the concave REE patterns and peaks of Ba, HFSE minima reflecting high oxygen fugacity. The Eu anomalies suggests the crust material participation. The HFSE enrichment possibly suggests the interactions with the evolved essentially carbonatitic plume mostly protokimberlite melts.
3. The chemistry of pyropes (18 wt. % Cr₂O₃) suggests their deep probably asthenospheric origin.
4. Complex geotherms and trends of amphiboles, chromites and ilmenites and variable geochemistry of minerals suggests the multistage interaction with the subduction-related and later plume melts.

Supplementary Materials

The following are available online at

Author Contributions

Conceptualization, I.A.; methodology I.A., S.B., O.O. and N.M.; software, I.A.; validation, I.A., S.B., O.O, N.M.; formal analysis, I.A., S.B.,N.K and N.M; investigation, I.A., S.B., O.O, N.M, N.K; resources, I.A.; data curation, I.A., S.B., O.O. and N.M.; writing—original draft preparation, I.A.; writing—review and editing, I.A.; visualization, I.A.; supervision, I.A., O.O.; project administration, I.A.; funding acquisition, I.A. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

The data for Siberian craton and many of published paper may be found in Research Gate <https://www.researchgate.net/profile/Igor-Ashchepkov>

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Conflicts of Interest

The authors declare no conflict of interest.

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Appendix A. Amphibole Thermobarometer Equations

Barometer

$$X_{Fe3am} = \frac{Fe + Mn + Mg + Ca - 4}{(Al + X_{Fe3am} + 2 * Ti) * 0.75 * (Na + K) / Ca}; \quad x_{AMKd} = Si^{*1} /$$

$$P = 0.0575 * (4 + (K / (Na + K) * 1.5 * Mg) / Fe + 4.25 * (0.85 * Na + 1.10 * K) / Ca) * x_{aMkD} * ToK^{*0.75} /$$

$$(1 + 7 * Fe) - Ln(1273 / (ToK)) * 2.5 * (3.8 * Mg - Al * 2.3) + 3 * Ti) + 12 * Cr + 2 * K) + 25 - 0.04 * Ti * ToK - Ca * (ToK - 750) / 300; \quad P = P * 0.9 + 5 + 1.55 * Ti$$

Thermometer: Ravna, 2000 Gar-Amphibole (monomineral version)

$$Ca_{Gar} = 0.1958 * Ca_{Am} + 0.1889; \quad Mg_{Gar} = 0.475 * Mg_{Am} - 0.5753 + 0.0035 * P; \quad Fe_{Gar} = 1.125 * Fe_{Am} - 0.1132 - 0.0001 * P$$

$$Z = Ca + Fe + Mg; \quad Fe_{Gar} = Fe_{Gar} * 3 / Z; \quad Mg_{Gar} = Mg_{Gar} * 3 / Z$$

$$Ca_{Gar} = Ca_{Gar} * 3 / Z; \quad x_{581} = Ca / 3; \quad x_{561} = Mn / 3 * x_{KD} = (Fe / Mg)_{Gar} * (Mg / Fe)_{Am}$$

$$T = (1504 + 1784 * (x_{581} + x_{561})) / (Ln(x_{KD}) + 0.720)$$

Corrections: $T = T - (52 - SiO_2) * 35 + 50 + 5 * Ti;$
 $T = T + (P - 50) * 2.5 - 20$

Where P – pressure in kbar; T – ToK.

The method is realized in the PT program written in FORTRAN 77 [55].

The results of the calibration and the correlations of the calculations with the experimental values are represented on the diagram (Figure 10).

