Aillikites and Alkali Ultramafic Lamprophyres of the Beloziminsky Alkaline Ultrabasic-Carbonatite Massif: Possible Origin and Relations with Ore Deposits

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Abstract: The 650–621 Ma plume which impinged beneath the Siberian craton during the breakup of Rodinia caused the formation of several alkaline carbonatite massifs in craton margins of the Angara rift system. The Beloziminsky alkaline ultramafic carbonatite massif (BZM) in the Urik-Iya graben includes aillites, phlogopite carbonatites and aillikites. The Yuzhnaya pipe (YuP) ~ 645 Ma and the 640–621 Ma aillikites in BZM, dated by 40Ar/39Ar, contain xenoliths of carbonated sulfide-bearing dunites, xenocrysts of olivines, Cr-diopsides, Cr-phlogopites, Cr-spinels (P ~ 4–2 GPa and T ~ 800–1250 °C) and xenocrysts of augites with elevated HFSE, U, Th. Al-augites and kaersutites fractionated from T ~ 1100–700 °C along the 90 mW/m² geotherm. Higher T trend for Al-Ti augites, pargasites, Ti-biotites series (0.4–1.5 GPa) relate to intermediate magma chambers near the Moho and in the crust. Silicate xenocrysts show Zr-Hf, Ta-Nb peaks and correspond to carbonate-rich magma fractionation that possibly supplied the massif. Aillikites contain olivines, rare Cr-diopsides and oxides. The serpentinites are barren, fragments of ore-bearing Ph carbonatites contain perovskites, Ta-niobates, zircons, thorites, polymetallic sulphides and Ta-Mn-Nb-rich magnetites, ilmenites and Ta-Nb oxides. The aillikites are divided by bulk rock and trace elements into seven groups with varying HFSE and LILE due to different incorporation of carbonatites and related rocks. Apatites and perovskites reveal remarkably high LREE levels. Aillikites were generated by 1–0.5% melting of the highly metasomatized mantle with ilmenite, perovskite apatite, sulfides and mica, enriched by subduction-related melts and fluids rich in LILE and HFSE. Additional silicate crystal fractionation increased the trace element concentrations. The carbonate-silicate P-bearing magmas may have produced the concentration of the ore components and HFSE in the essentially carbonatitic melts after liquid immiscibility in the final stage. The mechanical enrichment of aillikites in ore and trace element-bearing minerals was due to mixture with captured solid carbonatites after intrusion in the massif.

Keywords: carbonatite aillikites; mantle; rare metals; metasomatism; subduction; plume

1. Introduction

The aillikitic rock series was recently divided from the ultramafic lamprophyres [1,2]. The special feature of aillikites is that they are intermediate between carbonatites, kimberlites and alkaline lamprophyres. They form a rather long compositional series, with a wide range of mineral compositions.
Carbonatite alkaline ultramafic complexes of various types are common within continental plate settings [2–8] but plume-related complexes may be found in various environments. They are commonly located in the continental margins like Siberia and Greenland [9,10] (Figure 1) or in global rift zones like Brazil [11,12]. Very often, various ultramafic and mafic lamprophyric rocks including alnöites and aillikites are associated with the ultramafic rocks like kimberlites type I and II [13]. However, aillikites are a separate carbonatite-rich alkaline ultramafic rocks series [1,13]. Sometimes ultramafic lamprophyres trace the convergent margins including subduction zones [14].

The time span for the aillikites in magmatic evolution of the Earth is very wide. Alkaline lamprophyres associated with carbonatites appeared around 2.6 Ga [15] which corresponds to the re-arrangements of mantle convection and the onset of the wide appearance of alkaline mantle rocks [16,17]. Early Proterozoic lamprophyres in the Fennoscandian shield [18] are associated with carbonatites and aillikites associated with the 1.1 By kimberlite plume event in India [5] and in South Africa [19]. Many aillikites and carbonatite complexes trace the last events of the Rodinia breakup into the Northern group of continents [20,21]. Aillikites also accompany most plume events in Paleozoic time in Devonian [22,23] as well as Permo-Triassic superplume [24,25] and in later plume events in Late Cretaceous [26,27] and Eocene [28] periods.

The origin of the aillikitic lamprophyres is suggested to be 1–3% melting of carbonated metasomatic mantle of MARID type [29]. Experiments show that aillikite magmas may appear at pressures of 6–3 GPa from the alkaline- and carbonate-rich sources [30].

![Figure 1. Location of the carbonatitic complexes on the Siberian craton.](image)

Aillikites often carry mantle xenocrysts and xenoliths especially those associated with the kimberlites [29] but detailed studies of these mantle rocks with isotopic compositions and trace element distributions were not yet published. The special explorations devoted to the differences of the aillikites that accompanied the kimberlites and carbonatite massifs were also not yet published, and the influence of the geodynamic settings on the mineralogy and rock compositions was not yet determined.

The relationships of carbonatite-ultramafic complexes with subduction [1,2,14], mantle convection and plume events [1,2,20–29,31,32] have been widely discussed. However, the nature of ore concentrations in the mantle level is not clear. Most authors agree that they are associated with mantle metasomatism related to modern or ancient subduction [1–29,31,32].

In Siberia, aillikites were discovered in the Chadobets uplift [30] and in the Tomtor carbonatite massif [33]. We also checked the series of alkaline lamprophyres rocks in dykes and necks in and near the Beloziminsky massif (BZM) [34–46] in the foothills of the Eastern Sayan mountains and found that they are typical aillikites, but were previously described by alnöites [34–37] and melilitites [42].
The great difference of the BZM series of aillikite is their high enrichment in trace elements and different ore components determined by their close relationships with the carbonatites, which are the main sources of REE, and contain essential amounts of rare metals (Ta, Nb) and others, chalcophile (Pb, Cu, Zn, etc.) and siderophile elements (Fe, Mn) [34–46].

This study is only a brief description of results obtained in IGM Novosibirsk for 50 BZM aillikite samples. In this paper we gave only general outlook of the problems connected with the lamprophyres of the massif. The detailed mineralogical database of >1200 mineral analyses obtained with the electronic microprobe and microscopes and new, more detailed mineralogy will be described in other publications as well as the detailed division into petrographic and genetic groups. A new database has about 50 more bulk rock ICP MS analyses and isotopic investigations is in preparation.

2. Geological Situation

There are several carbonatite ultramafic complexes in the marginal zones of the Siberian craton [6,21,25,33,47–52] (Figure 1) One of the interesting objects with the complex plume-subduction nature is the Beloziminsky massif (BZM) [34–46] which has various metallogenic specialization in Ta, Nb, REE and P, and a wide range of components including Th and U. It was involved in exploration despite its distant location (140 km) from the railway. Concentrate of ore minerals was extracted from the excavated weathering crust in an open pit in the 1990s. The main source of these elements are carbonatites and ijolites of late ankerite carbonatite phases. There are four main types of ores: (1) polymetallic galena-sphalerite-chalcopyrite; (2) parsite-bastnäsite-monazite; (3) apatite-magnetite-pyrochlore; and (4) apatite-pyrochlore-columbite [35–38]. In the quarry, deposits of Ta-bearing Ti-magnetites with other high field strength elements (HFSE) with Mn were explored.

Formation of the massif, like many other similar alkaline and carbonatitic massifs on the boundary of the Siberian continent, are associated with the global Angara-Taimyr rift structure [27,46], formed during the last stages of the supercontinent Rodinia breakup [46,48–52]. Paleo reconstructions for Siberia show that BZM massif is associated with the Srednezimisky and Bolshetagninsky massifs (Figure 2) [10].

![Figure 2](image_url) **Figure 2.** Paleo reconstruction for the Vendian (Neoproterozoic III) time of the Northern continents [16–19]. Carbonatite massifs: 1—Zhidoysky; 2—Beloziminsky; 3—Sredneziminsky; 4—Bolshetagninsky; 5—Arbarastakh; 6—Srednetatarsky; 7—Tatarsky; 8—Ingili; 9—Kiysky (redrawn from [10] with the additions).

The massifs are located in East Sayan foothill within the Urik-Iya graben intruding Lower Proterozoic terrigenous rock series (Figure 3) [35]. The BZM massif consists of ijolite-melteigite, carbonatite rock series and ultramafic lamprophyre (aillikite) intrusions [35,44] (Figure 4). The late-stage carbonatite rocks are dolomite, calcite and final ankerite carbonatite varieties.

Ultramafic rocks (dykes and stocks) with abundant phlogopite, carbonates, Ti-magnetite and rarer pyroxene, olivine and amphibole are found in two positions. The relics of the early bodies are
located at the NE core part of the massif [35,36]. The first one is represented by mafic variety described as melilitite, alnöites or nephelineite [34–44], but melilitite occurs rarely in this rock series, which are characterized by fine or cryptic groundmass structure (Figure 5a). The second group are the youngest diopside-phlogopite dykes emplaced near the border and becoming more common in prevailing NNE direction of Proterozoic terrigenous strata. They contain a lot of serpentinite xenoliths with Cr-spinels and abundant sulfide.

Figure 3. Geological scheme of the Nizhnesayansky alkali ultramafic carbonatite complex including Beloziminsky, Sredneziminsky; Bolshetagninsky massifs (redrawn from [35]).

Figure 4. Geological scheme of Beloziminsky massif: (from [35]). 1—early aillikites (alnöites), 2—late aillikite dykes, 3—Phl-forsterite-diopside carbonatites (aillikites), 4—Middle Proterozoic schists, 5—Middle Proterozoic amphibolites, 6—melteigite-ijolites, 7—calcite carbonatites; 8—calcite-dolomite carbonatites, 8—amphibole-calcite carbonatites, 9—ankerite carbonatites; 10—nepheline (Ne) syenites; 11—parisite-bastnäsite-monazite ores, 12—faults.
A series of olivine, diopside, phlogopite-bearing essentially carbonatitic rocks with giant grained phlogopites and xenoliths of carbonatites (Figure 5b) form the lenses concordant with the concentric fracturing within the massif cutting the carbonatites. In our opinion, also corresponding to ultramafic lamprophyres and according to SiO\textsubscript{2}-CO\textsubscript{2} contents, they are close to aillikites compared with the average compositions of these rocks [1]. These magmatic breccias contain fragments of carbonatites sometimes with ore minerals (Figure 5b). Fresh grains of olivines, Cr-spinels, ilmenites and grossular or almandine garnets also are common.

Upstream in the Belaya Zima river 15 km SW of BZM there is a neck of lamprophyric breccia called the Yuzhnaya pipe (YuP) with Mg' (Mg number) ~ 0.7 (sample 799-1) containing xenocrysts of Cr-diopside, Ti-augites, olivines, amphiboles (kaersutite, pargasite), and xenoliths of serpentinized Spl-bearing dunites [52] with sulfides and Cr-spinels (20–25% Cr\textsubscript{2}O\textsubscript{3}). These rocks of YuP were considered to be melilitites or alnöites [52] but in all diagrams, they are closer to aillikites than alnöites (see Figures 9 and 10).

At a distance of ~1 km upstream from the YuP, a substantially carbonatite dyke is exposed containing monticellite, pyroxenes and mica xenocrysts (sample 799-2), with debris of glimmerites and carbonatites containing fluorite. Another ultramafic dyke near the mouth of the Chernaya Zima river contains xenocrysts of augite (3–9 wt% Al\textsubscript{2}O\textsubscript{3}), amphibole, chromite, mica and rarer olivine (Mg’ ~0.84–0.88). One more large Bushkanai aillikitic (alnöitic) dyke [53] is situated 9 km west of BZM contain Cr-diopsides and olivines (Figure 3).

3. Samples

We collected samples of the Yuzhnaya pipe from large blocks exposed near the pipes and the other dykes outcropping in the riverbanks. We sampled material of one of the drilling stores containing only ultramafic lamprophyres from the BZM near the Belaya Zima settlement. Collected ~270 samples were at first divided into several groups according to the petrographic and mineralogical compositions and studied by analytic methods. The major first group include the samples which are close to the YuP in texture (Figure 5a; Figure 6a,b) and contain macroscopic dark inclusions of the serpentine (altered ultramafic xenoliths) and Cr-diopsides, they also occur more rarely in the massif. Another group composed of the several varieties have similar cryptic groundmass structure and porphyroclasts of amphiboles and clinopyroxenes. The third large group includes rocks with pegmatoid structures and giant-grained phlogopites (Figure 5b).
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Figure 6. Photos of the aillikites in thin sections (1—parallel and 2—crossed nicols) of samples BZ726 (a,b), 799-1 (c–f), BZ732 (g,h), BZ742 (i,j). (a) The aillikite has a porphyritic, lamprophyre structure. The pyroxene grains (Cpx) are deformed, with wavy extinction of phlogopite (Phl) grains, among the fine-grained serpentine-chlorite-carbonate-phlogopite groundmass with a thin rash of magnetite. (b) Phlogopite (Phl) phenocrysts are in the (carbonate Ca-chlorite–Cl-phlogopite) bulk of aillikite. (c) The aillikite has a porphyric structure. Pyroxene phenocryst (Cpx) and partially deformed phlogopite phenocrysts (Phl). Relatively large grains are olivines which are replaced by serpentine (Srp), with a thin rash of magnetite (Mag) inside the grains and in large quantities along the edges of the grains (grains encircled by magnetite). The bulk is carbonate, phlogopite, magnetite, chlorite (d). There is a fragment of olivine grain replaced by serpentine (Srp), in the marginal part of which magnetite (Mag) is widely developed. On the right are phlogopite (Phl) phenocrysts. (e) Phenocrysts of pyroxene (Cpx) and phlogopite (Phl) among the carbonate-chlorite-phlogopite-magnetite mass. (f) There are phenocrysts of pyroxene (Cpx), phlogopite (Phl) with fragments olivine grains substituted by serpentine (Srp). The bulk is represented by chlorite, carbonate, phlogopite, magnetite. (g) Phenocrysts of phlogopite (Phl) with wavy extinction in the bulk consisting of carbonate, phlogopite, magnetite, epidote or millerite. (h) There are pyroxenes (Cpx) which are replaced by an epidote. In the center, between the grains of pyroxene is calcite (Cal). The bulk is carbonate, phlogopite, chlorite, magnetite. (i) Large phenocrysts of pyroxene (Px) (with a poikilitic structure) and phlogopite (Phl) in a fine-grained polymineral mass consisting of phlogopite, magnetite, carbonate, and chlorite. (j) There is a contact of aillikite with a carbonatite melt (Cb). Along the boundary are clusters of magnetite (Mag). Photos of the aillikites in thin sections (crossed nicols). Fine grained aillikite with Phl (a,b); fine grained aillikite with Phl, apatite rimmed by magnetite (c); twinned phlogopite grain with apatite inclusions.
4. Methods

Mineral compositions were analyzed by the wavelength-dispersive analysis using an electron microscopes and Jeol Superprobe in Analytic Sobolev V.S. Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia (standard conditions) using 15 kV acceleration voltage and 15 nA beam current in epoxy mounts. Minerals and rocks were analyzed in thin sections according to the procedure of [28,54]. The relative standard deviation does not exceed 1.5%; the precision was close to 0.02–0.01% for minor elements.

The detailed mineral composition of ~800 grains 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 (analysts Ashchepkov I.V., Karmanov N.S., Belyanin D.S.)

The bulk rock compositions were measured by X-ray fluorescence method (XRF) using BRA-135F apparatus in glasses prepared for XRF by the melting of rock powder with Li-tetraborate.

More than 80 mineral grains from 15 aillikite samples were analyzed by laser ablation in Nikolaev’s IIC SB RAS using the mass spectrometer anICAP Q (Thermo Scientific) with the Nd UV laser NWR 213 (New Wave Research) (analyst N.S. Medvedev). As standards the NIST 610-612 SRF were used. We used for the second standard garnets and clinopyroxenes sample 313-73 analyzed by solution ICP MS in MRAC Belgium [55]. The method has a detection limit ~10^{-7} (0.1 ppm) and standard deviation of the measurements for most isotopes was about 7–15%.

The trace elements of bulk rock compositions of 12 samples were analyzed twice, at first in glasses by laser ablation ICP MS using the method described above, and then they were analyzed in solution under standard conditions with a Thermo Finnigan Element 2 single-collector at low (LR)-300, medium (MR)-4000, and high (HR)-10000 M/∆M resolution. The measurement results and instrumental drift were checked against international standards BHVO-1, STM-1. The glasses obtained by fusion with LiBO2 were dissolved in ultra-pure HNO3 to prepare sample solutions.

The age of aillikites estimated by 40Ar/39Ar age using the method was described in detail by Travin et al. [56]. 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 (analysts Travin A.V., Yudin D.S.).

5. Age

Dated by the 40Ar/39Ar method, aillikite and ultramafic bodies display a range of ages from 645 to 622 Ma (Figures 7 and 8, Table S1). The Yuzhnaya pipe [43] has been dated at 645 Ma (Figure 7) which coincides with the age of the carbonatites from the other massifs in South Eastern and Western Siberia massifs [4,46,50]. A regression through barely distributed points of YuP with very low 39Ar/40Ar values provides an age of 666 ± 18 Ma (Figure 7) Yet, this ‘isochron’ is of doubtful geological significance in view of the 204 ± 20 value of 36Ar/40Ar that suggests there might be partial loss of radionic 40Ar*. At any rate, such an age of ca. 666 for the YuP could refer to the separation of a local melted zone within the mantle which gave the melt for the YuP. The early phase YuP was dated by Rb/Sr isochron as Early Proterozoic [42]. Our 40Ar/39Ar age of YuP at ca. 645 Ma is slightly older than age of the carbonatites of the BZM massif (640–645 Ma) [38,39]. All analytic data are given in the supplementary data files.

Aillikite breccias in BZM represent by essentially phlogopite-bearing varieties with abundant carbonatites yielded reveal ages ranging from ca. 622 Ma to 640 Ma divided in three intervals 621–627, 630–633 and 640 Ma (Figures 7 and 8) with a tendency of increasing carbonatite component in younger rocks. Carbonate-rich aillikitic dykes located at 10–15 km distance from BZM appears to be younger as inferred from the plateau age of ca. 584 Ma (total gas age 595 Ma, Figure 7).
worldwide [1–22, 26–29] often contain lamprophyres sometimes close to aillikites [1, 2].

Phl. The BZM aillikites are enriched in alkalis and alumina but depleted in TiO

composition from 232 samples worldwide [1] practically coincides with the composition of some Chadobets uplift [31, 33], Scotland [23], Greenland [20, 27] and Eastern India [28]. The average aillikite

6.1. Major Element Compositions

The series of the ultramafic alkaline carbonatite complexes in Central Asia [33–44, 47–52] and worldwide [1–22, 26–29] often contain lamprophyres sometimes close to aillikites [1, 2].

Rock compositions of studied lamprophyres vary greatly from 14 wt% SiO

Figure 7. Results for the 40Ar/39Ar dating of YuP (a, b) and carbonatite phlogopite-bearing dyke (c) located nearby.

Figure 8. Results for the 40Ar/39Ar dating of lamprophyre dykes and stocks inside the BZM.

6. Whole-Rock Compositions

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Rock compositions of studied lamprophyres vary greatly from 14 wt% SiO2 from Phl carbonatite to 42 wt% SiO2 (close to ijolites) (Figure 9, Table S2). The variations of SiO2 and major elements are similar to aillikites of Labrador [7, 13, 57] and other regions such as the Tomtor massif [6, 47, 58, 59], Chadobets uplift [31, 33], Scotland [23], Greenland [20, 27] and Eastern India [28]. The average aillikite composition from 232 samples worldwide [1] practically coincides with the composition of some aillikites from BZM but many of the latter are richer in alkalis and Al2O3 (higher modal proportion of Phl. The BZM aillikites are enriched in alkalis and alumina but depleted in TiO2 compared to Labrador aillikites [7, 13, 29, 57].
6. Whole-Rock Compositions

6.1. Major Element Compositions

We divided the studied collection into 7 groups according mainly to their bulk rock compositions accounting the trace element compositions, supported by the mineralogy. The first group is represented by composition of the YuP and two close compositions from BZM with Mg# ~70 ± 5 and relatively low alkalis with some dominance of K2O. The rocks of the second group are rare. They are the most SiO2-rich samples with low CaO content and as well most of other components. The contents of K2O ~6 wt% and ~40 wt% SiO2 attesting that these are practically monomineralic phlogopite rocks. The third group is very similar to the first group and differs mainly in the higher content of alkalis both K2O and sometimes extremely high Na2O. These features suggest that they are aillikites rich in mica and alkali pyroxenes. The fourth group is the early emplaced carbonatitic group with 12–15 wt% SiO2. It is lower in all oxides except for CaO and MgO. Group 5 is enriched in Al2O3, FeO and alkalis due to the abundance of magnetite and Ti-biotites. Groups 6 and 7 have similar silica content ~20–25 wt% and differ mainly in the abundance of P and Na2O, K2O determined by mica, pyroxenes andapatite within the rocks. The sixth group is more enriched in alkalis, alumina and TiO2.

The groups determined on the diagram only partly coincide with the clots of concentrations of components vs Mg# (Figure 10). The reasons are described in discussion. In the diagram of Mg’ vs major components, the trends look smoother. We consider that the primary melts are the varieties between Mg’ 0.63 and 0.79 because they correspond to the equilibrium with the dominant values of mantle olivines (Mg’ = 0.9 and 0.93) (Figure 10). We calculated the equilibrated olivine compositions using a partition coefficient (KD) of olivine—melt close to 0.33 [60]. According to this division, almost all BZM lamprophyres are located within the primary melts field or from the metasomatized mantle spreading commonly to 0.84 in Mg’Ol (or 0.57 for the parental melts).

The variations of the bulk rock compositions in time (Figure 11) show the vast variations. The major tendency is general degrease of the MgO and increase of CaO, TiO2, alkalis (carbonatite component) in time.

Figure 9. Variations of bulk rock compositions of BZM aillikites in comparison with the Labrador aillikites [7,13,29,57] and Tomtor lamprophyres [6,47,58,59].
We divided the trace element patterns of studied aillikites into 7 groups which are supported by the bulk rock grouping.

The variations in La/Yb \( n = 7–12 \). La varies from 200 to 500 relative to the primitive mantle (PM) [61].

All the REE patterns of bulk rock compositions of aillikites (close to YuP) are inclined, with variations in La/Yb, \( n = 7–12 \). La varies from 200 to 500 relative to the primitive mantle (PM) [61] (Figure 12, Table S2). We divided the trace element patterns of studied aillikites into 7 groups which are supported by the bulk rock grouping.

The first group of the most primitive patterns of aillikites corresponds to the typical spectra of garnet-bearing mantle peridotites [55,62], with peaks in Nb, Th, but low Hf. In the second panel (with the flat hump at Gd-Pr) along the bent pattern is similar to clinopyroxene (second panel) with the flat hump at Gd-Pr along the bent pattern is similar to clinopyroxene.

This grouping is supported by the measurements of the radiometry for these rocks regulated by Tomtor [47,58,59]. According to this division, Group 1 is enriched in Al \(_2\)O\(_3\), FeO and alkalis due to the abundance of magnetite and Ti-biotites.

Group 2 is enriched in LILE. The fifth group have intermediate enrichment in La-500-80/C\(_1\) but high Nb and Ba, Th, U and very weak minima in Zr, Hf, Ta, U and are more enriched in alkalis, alumina and TiO\(_2\).

Groups 6 and 7 have similar silica content ~20–25 wt% and differ mainly in the abundance of P and LILE. The fifth group have intermediate enrichment in La-500-80/C\(_1\) but high Nb and Ba, Th, U and have very weak minima in Zr, Hf, Ta, U and are more enriched in alkalis, alumina and TiO\(_2\).
pronounced in Sr, Pb. Very similar samples were found within the massif and as well in Buskanay dyke [53]. This group is suggested to be primary melts (Group 1). The second group (second panel) with the flat hump at Gd-Pr-along the bent pattern is similar to clinopyroxene patterns from garnet-bearing mantle peridotites [55,62], with peaks in Nb, Th, but low Hf. In the third group, some REE patterns of carbonatites have sharply increased La-1000-2000/C1 and HFSE (Nb >> Ta); and lower Zr and Hf (Zr >> Hf). The fourth group of rocks have sharply inclined and highly enriched REE patterns with LREE ~ 10000/C1 and peaks of Th and Nb, but relatively lower LILE. The fifth group have intermediate enrichment in La-500-80/C1 but high Nb and Ba, Th, U and varying Hf, Ta, U. The sixth group are phlogopite-enriched rocks with the lowest REE (La-50/C1) with flattened HREE patterns and enrichment of Rb, Cs, Zr, Ta, Nb, and lower Th-U. The seventh group are similar carbonatites but lower in phlogopites. They contain Nb, Na, Zr mainly as the inclusions of Ta- niobates and Zr-Na, Ta oxides (Figure 12).

This grouping is supported by the measurements of the radiometry for these rocks regulated by the abundance of U and Th and proved by the more presentative study of >50 TRE bulk rock compositions (Zhmodik et al., in preparation). The reasons of the variations are described in discussion.

Figure 12. REE and TRE spectra of bulk composition of aillikites and carbonatites from BZM. Aillikites outside massif (a), aillkites in BZM (b), Phl carbonatities and aillikites (c). Normalized to primitive mantle [62] and chondrite C1.
7. Compositions of the Minerals

7.1. Variations of Major Elements in Minerals

We mainly studied the mineralogy of the primary rocks such YuP and similar rocks in BZM but mineral compositions from other groups were also included (Table S3).

The pyroxene quadrilateral (Figure 13) [63] shows that all minerals have very wide compositional ranges formed at conditions from 1200 to 600 °C and less.

Clinopyroxenes (Cpx) from YuP were divided into 3 groups. Cpx from the most representative group 1 (Gr1) forms a trend from 5 to 12 wt% FeO with a joint increase in FeO, TiO₂, Al₂O₃, Na₂O and a decrease in CaO, MgO. Group 2 Cr-diopsides with the lowest FeO (~3–4 wt%) and Cr₂O₃ content (0.2–2 wt%) and widely varying Na₂O and Al₂O₃ are similar to the xenogenic mantle material (peridotite metasomatites in subduction-related settings) [64] and most lower in Al₂O₃ Cr-diopsides are close to dunites in carbonatite-ultrabasic massifs [65] (Figure 14).

Close to YuP Cpx are Cr-diopsides from Bushkanai dyke, but more Fe-rich varieties are close to Gr1. The 3rd group of alumina-enriched augites up to fassaites, with intermediate Mg’ and sharply varying TiO₂ and Al₂O₃ and low Na₂O. Among the clinopyroxenes from the BZM, Cr-diopsides occur rarely and they are slightly more Fe-rich than in YuP (Figure 14).

All minerals from carbonatites and ijolites BZM in general are much more Fe-rich (not in the diagrams) [38,39].

The amphiboles of pargasite-kaersutite type (Mg’ ~ 0.56) are close in Mg’ with the most Fe-rich pyroxenes (Figure 13).

![Figure 13. Pyroxene quadrilateral for aillikite minerals [63] of BZM, YuP and aillikites and carbonatite dykes located in Belaya Zima river basin. The compositions of olivines, amphiboles, phlogopites and magnolites are projected and do not correspond the isotherms.](image)

Phlogopites. We plotted together the compositions YuP and BZM with the addition of the minerals from Labrador aillikites [7,12,28,57]. According to Giuliani [66], different area in FeO-Al₂O₃ and TiO₂-Al₂O₃ may be attributed to aillikites, kimberlites, orangeites and lamproites. The phlogopites from YuP are essentially more Mg-rich and plot in the aillikite field trending to alnöites as well BZM phlogopites are more Fe rich and tends to alnöites. (Figure 15). Cr-phlogopites with 0.5–1.7 wt% Cr₂O₃ and Mg’ = 0.88–0.85 are probably in equilibrium with Cr-diopsides, but the Ti-biotites with Mg’ ~ 0.55–0.54 are in equilibrium with Fe-rich amphiboles (Figures 13 and 15).

The olivine compositions from the Yuzhnaya pipe and from BZM aillikite are quite variable. Those with Mg’ from 0.89 to 0.84 have very low CaO content. Two groups of olivines from the BZM show much higher CaO content to 0.4 wt%, suggest Ca-rich carbonatitic melts. Another group contains MnO to 4–6 wt%, are found in aillikites enriched in carbonatitic material. Where ilmenites and magnetites contain MnO to 10 wt% (Figure 16).

Ilmenites from BZM plot in the Fe₂O₃-rich field. They are highly variable in TiO₂. Some varieties are enriched in Nb₂O₃ to 9 wt%, V₂O₃ to 7 wt% and in ZrO₂ to 1.3 wt% and have notable Al₂O₃ to 1.3 wt%.
There are essentially MnO-rich (to 30 wt.% varieties; the other group have ~10 wt.% MnO (Figure 17). Mn-rich ilmenites are common in kimberlites [11].

Figure 14. Variations of clinopyroxene compositions from aillikites of YuP, BZM and Bushkanai dyke [53].

Figure 15. Variations of phlogopite compositions from BZM. The fields and arrows after [66].
7.2. Rare Elements of Minerals from Yuzhnaya Pipe

The patterns of rare elements in minerals from YuP were determined using grains selected from the heavy minerals separates (Table S4). Cr-diopsides (Gr1) have peaks of Y, Zr and very high Ba, Th, U, Nb, Ta. Al-augites (Gr3) show highest REE level, inclined and slightly concave patterns with very high Sr, Ba peaks and elevated HFSE. The concentrations of U, Th became lower more rapidly than REE and higher HFSE concentration [38,39] (Figure 18b).

In general, the patterns of the minerals of aillikites essentially differ from the patterns of minerals from basaltic derivatives, for example of Vitim pyroxenites [55]. The spider diagrams have strong peaks at Zr, Hf, Ta, sometimes at Ba, and smaller one at Y. (Figure 18c).
The clinopyroxenes of high-Al group have asymmetric bell-shaped REE patterns typical of basaltic derivatives, for example of Vitim pyroxenites [55]. The spider diagrams have strong peaks at Zr, Hf, Ta, sometimes at Ba, and smaller one at Y. (Figure 18c).

For the kaersutites and pargasites, the REE patterns are essentially higher and slightly less inclined compared to those of Al-augites with higher peaks of Zr, Hf, Nb, Ba, Rb, Sr (Figure 19b).

**Figure 18.** REE patterns and TRE spider diagrams of minerals of aillikites of Yuzhnaya pipe: for Cr-diopsides and Al-augites (a); for Ti-augites (b) for kaersutites and Ti biotites (c). Normalized to primitive mantle [61] and chondrite C1 [68].

7.3. **The Spectra of Rare Elements in Minerals of Aillikites of BZM**

In those aillikites from the BZM that have a high carbonatite component, the REE levels are often much higher (Figure 19). Carbonate clots and nests in such aillikites contains the minerals that concentrate REE, Th, U, Ta, Nb, and most often they are perovskite and apatite. The abundance of ore minerals and trace element concentrators and their diversity is much higher in carbonatites [37,38].
The trace element patterns of Ti-biotites are flat and slightly LREE-rich and often show Eu, Sr, Pb maxima. They have relatively high Nb, Ta and slightly lower Zr and Hf. Perovskites in ore aillikites from BZM show very high level of REE and especially LREE enrichment (to 100000-10000 /C1), and HREE 100 times less. They show the minima of HFSE, with the exception of Nb, as well as for LILE (Figure 19a). The second generation phlogopites are very rich in Ba and in REE, due to tiny fluid inclusions (Figure 19b).

Figure 19. REE patterns and TRE spider diagrams of minerals from aillikites of Beloziminsky massif: for micas low in TRE (a); for micas high in TRE (b); for amphiboles (c); perovskites (d); apatites (e). Normalization to primitive mantle [61] and chondrite C1 [68].
Amphiboles are characterized by almost linear and slightly concave REE patterns with La levels at 100-100/C1. They have high LILE especially Ba, Rb and Nb peaks (Figure 19c).

In carbonatites apatites have mostly concave downward in HMREE part, probably because BZM carbonatites contain early crystallized grossular garnets that have convex MREE patterns (Figure 19d). Grossular garnets exist more rarely in aillikites.

Since perovskite grains are very small, we often analyzed them in serpentines, carbonates and micas and some diagrams show mixed patterns. Therefore, many analyzed aggregates give patterns enriched in LILE, and minima of HFSE, U, Th which is typical for carbonates (Figure 19d).

Apatite shows inclined REE patterns with a concave HMREE part, often with Eu minima. Some of them are depleted in HFSE, but for others the level of Zr, Hf is close to most of REE and TRE. There are patterns low in Th, U, LILE and some very high in Ta (Figure 19e). The intergrowths of apatite with mica are also characterized by the concave arc shaped REE patterns and high contents of LILE and depressions in Zr, Hf and increased Nb, Ta and Sr levels.

8. Mineral Thermobarometry

The PT conditions of the xenocrysts from aillikite dykes from the surroundings and within massif combined with the data for the pyroxenes and amphiboles were calculated using single grain thermobarometry [69–73]. For the Cr-diopsides we used the method of P.Nimis [67]. The PT conditions for the Cr spinels were calculated according to [70,71]. For the typical xenocrysts of Ti augites and high Al pyroxenes the method [71] was used. For the amphiboles, the single grain method [73] was used. Several fields appeared on the diagram (Figure 20).

![Figure 20](image-url)

Figure 20. PT conditions for xenocrysts of aillikites BZM defined according to the mono-mineral thermobarometry for Cr-diopsides [69] and other pyroxenes [70–72]; for amphiboles [73] and for Cr-spinels [70].

The first field calculated using xenocryst of Cr-diopsides and chromites using thermobarometric methods [69,71] is located along the high-temperature continental geotherm (45 mW/m²) in the range of 4–2.2 GPa, referring to conditions of the garnet peridotite mantle facies.

The second field calculated with the single grain pyroxene thermobarometry [72] for xenocrysts of low-alumina clinopyroxenes at the beginning Cr-bearing clinopyroxenes [69] and continued by Mg-augites give the PT trajectory close to the convective geotherm of South-East Australia [62] (SEA) ranging from 2.4 to 0.2 GPa (Figure 20). The third area of clotting of the PT points near the Moho, appears to be consistent with a pause in melt ascent during formation of channels. Crystallization of the low-temperature amphiboles in the pressure range 0.5–1 GPa is related to the crust conditions. The higher temperature...
advective path fourth from mantle to Moho condition is estimated using Cpx from Bushkanai dykes and Cpx from the BZM massif. The fifth field composed with Al-augites and amphiboles (up to 1200 °C) corresponds to crustal conditions.

9. Discussion

9.1. Reasons for Variations of Bulk Rock Compositions

Bulk rock major element compositions of many of BZM aillikites shows the high deviation from the primitive group 1 mainly due to deviations in SiO$_2$ regulated by carbonate or serpentine admixtures. Some of them are rich in carbonates. Cognate carbonates occur in all rocks but in most cases, these are xenogenic carbonates (or fragments of carbonatites), which contain also abundant ores and TRE-rich minerals.

Several Mg-rich varieties contain xenoliths of mantle rocks such as serpentinites containing chromites, sulfides and phlogopites also mainly carbonatized. In addition, small amount of varieties which are lower in Mg may relate to melts mixed with the later carbonatites captured as xenoliths. Thus the primary variations in the mantle sources and probably accompanied by differentiation are accompanied by the admixture of several sources: Mg-rich dunites, carbonatites, phlogopites (K$_2$O), sulfides and suggested subduction-related metasomatites which could include the mature crust sediments with the concentrators of TRE-monazites, zircons, ilmenite, rutiles, MnO oxides etc. And the plume source could essentially influence the melt compositions by addition of TiO$_2$, PGE, Ni and other magmaphile elements.

Trace element compositions. High inclination of the REE patterns of primitive BZM melts indicates their formation within the garnet facie of the upper mantle. The TRE spiderdiagrams of YuP and similar rocks are close to the alkaline basalts, minettes, even kimberlites suggesting which occurs by low degree melting with (1–0.1%) of primitive mantle source [61] in a presence of volatiles proved by high content of LILE elements and Sr, Pb peaks.

Trace element spider diagrams for bulk rock compositions (Figure 18) allowed us to separate the aillikites into 7 groups, which are related to the groups divided in the TAS diagram. The spider diagrams for the rocks of the BZM are more enriched in REE and TRE than aillikites from Aillik Bay Labrador [7,13]. As well, K$_2$O is regulated mainly by phlogopites and Na$_2$O by the carbonates and clinopyroxenes, whereas CaO is mainly determined by calcite abundance. The high in CaO and CO$_2$ (and H$_2$O) are often closer to carbonatites.

Enrichment in TRE is mainly determined mainly by differences in the compositions of accessory minerals such as zircons, perovskites, Ta-niobates, thorites andapatites etc., which mainly are segregated in the carbonate-rich portions of the rocks. Their content is lower in phlogopite-dominated where apatites are more common than monazites and perovskites. The Ti-magnetites sometimes very enriched in Nb, Mn, also influence the compositions for CaO-rich rocks.

Comparing groups 1 and 3 (Figure 18a), it is clear that the latter is enriched in trace elements due to addition of amphiboles and perovskites. The REE-enrichment of group 4 is due to the high concentration of REE in the apatite. The peaks in Th in Group 2 (Figure 18b) may be the only results of contamination with some Th minerals as monazites or together with the zircons. In contrast, the high abundance of the HFSE such as Nb, Ta together with the high LILE may be result of the high abundance of late-formed perovskites (Figure 12c).

Possible fractionation processes including precipitations of olivines and pyroxenes should take place which is proved by the trends of the clinopyroxenes and their high variations. The modeling of the partial melting and fractionation will be in discussed in future publications.

9.2. Reasons of Variations of Mineral Compositions

The groups of the pyroxenes are determined not only the variations of the chemistry of parental melts but also depends on thermobarometric conditions [63,69–73].
The trend for Gr1 reflects the interaction of mantle rocks with the very Mg-rich melts or fluids because interaction with plume and subduction-related melts should essentially increase Fe', Ti and Al, which is visible for the xenocrysts of Cr-diopsides from Bushkanai dyke [53]. The Gr2 Cpx of joint increase of magamphile FeO, TiO₂, represents the fractionation trend which is formed by the rising fractionation trends during the creation of the magmatic channels like for most alkali basalts [55]. It is controlled mainly by joint Cpx-Oi crystallization. This is proved by the thermobarometric estimates (Figure 20). The Gr3 dominated by Al-rich fassaite according to thermobarometry was formed in relatively shallow depths (see Figure 20). Late xenocrysts of Fe-rich amphiboles from YuP according to thermobarometry were probably formed near Moho or in shallow conditions the crust [72,73]. The path fourth represents the path of late mainly plume-related melts from ailikite of the massif and Bushkanai dyke, corresponding conditions of the last melt portion sub-adiabatically ascending from the region of interaction to the Moho. The melts that created the fifth series were silicate-carbonatite or substantially carbonatitic. Their intrusion above the Moho caused the appearance of magma chambers where stratified intrusions with Al-augites and amphiboles (up to 1200 °C) generated the syenitic and layered alkaline silicate carbonatitic magmas probably due to interaction with the crust. They possibly have supplied the BZM and generated series of contrast rocks (Figure 21).

![Figure 21. Scheme of PT evolution mantle melts according to thermobarometry.](image)

The series of the of the phlogopites and biotites show the trend between the aillikites (carbonate + phlogopite) and lamproites (phlogopites +olivine) source (Figure 15).

Olivines with high Mg' and low CaO are probably xenogenic. Those higher CaO content to 0.4 wt% are rather high temperature or were formed from the Ca-rich melts. The olivines contain MnO to 4–6 wt%, probably due to mixing with carbonatitic material which is enriched in crustal subduction components (Figure 16).

The reasons of the ilmenite variations reflect relatively high oxygen conditions (Figure 17) and the high Mn, Zr and Nb varieties reflect the various sources of BZM carbonatite-silicate melts.

*The trace elements of minerals.* The Cpx from YuP show high difference between Gr1 Cr diopsides with have very high REE levels with the concave pattern evidences about the LREE from the fluids and also abundance of subduction-related components U, Ba, Sr [74–77] (Figure 18). The Gr2 augites show the signs of fractionation with conformable patterns of REE and TRE spider diagrams. The peaks in HFSE suggest the contaminations of the parental melts in concentrators such as ilmenites or perovskites
from mantle metasomatises. Very REE-enriched patterns of Al-rich augites and Eu anomalies suggest a possible origin from the carbonatite melt in relatively low-pressure conditions in Moho or crust.

Calculated with the partition coefficients (Kd) for the silicate melts [78] for melts in equilibrium with CPX gives to high level of La and other REE to $10^6$ relative to chondrite C1. Using the carbonatite Kd [79] the calculated compositions which enrich the melts of Gr4 have low HFSE and LILE should be essentially evolved carbonatic melts. But calculated melts in equilibrium with Cr-diopsides (Gr1) and Ti-augites are much higher in these components especially in Ba and have concave downward patterns and one order higher La/Yb ratios (Figure 22) which suggests possibly participation of high density fluid [80] having such ratios.

In BZM massif observed very high level of REE and HFSE (Figure 19) is determined by the high concentrations of incompatible elements in the evolved carbonatites melt pockets. Abundance of melt and fluid inclusions in the late silicate minerals determines also strong LREE-enrichment associated with abundance of volatiles.

![Figure 22](image-url)

**Figure 22.** REE and TRE spectra of the melts in equilibrium with the Cpx from YUP Gr1-2 calculated with the partition coefficients after [79]. Normalized to primitive mantle [61] and chondrite C1 [68].

### 9.3. Problems of Origin of Aillikites and Ultramafic Lamprophyres

The origin of aillikites cover huge range of interrelated problems including subduction and fluid metasomatism [64,65,74], magmatic plume melts interaction [81], partial melting of the mantle [68], magmatic evolution, including fractionation [82] and suggesting wall rock assimilation (AFC) [83] and possible magmatic immiscibility at the mantle level [30,78] which all together determine the wide series and a rather unstable composition of the aillikite rock series.

Genesis of Belaya Zima aillikites in carbonatite massif and other similar massifs in Southern Siberia [6,21,34–46,48–53] and worldwide [1–3,7,8,10,12,13,27–29,57,79,81,84–86] are widely discussed. The aillikites occur in three, major groups: 1—as part of alkaline ultrabasic carbonatite complexes [1–3,10–12,15,79,80,86] or massifs, 2—in association with the kimberlites [5,7,13,29,57,87–89], or form independent intrusions [23,27] and they differ in compositions in mineralogy. The first group is closer to carbonatites and enriched in TRE and REE and apatite (phosphorus) and HFSE. The second group is more enriched in Mg and TiO₂ and the third series appears to be more alkaline.

In turn, aillikites from carbonatite ultramafic massifs differ from the silicate-carbonatites P-rich rocks called phoscorites [89–93] that are found in many carbonatite massifs. Phoscorites do not contain any chrome-rich minerals and have high FeO (more than 20 wt%) and low Mg" [90–92]. Our studied aillikite rock series have no pyrochlore-group minerals, typical of carbonatites of the BZM [38,39] but
contains a lot of Cr minerals. Phoscorites and other carbonatites have been suggested to be immiscible melts, which may be derived from the primary homogeneous alkali carbonatite-silicate melt [30] which possibly occur at the crust level during carbonatitic magma differentiation abundance in P is possibly the critical factor of such immiscibility. Such phoscorites are evidently higher in REE [91–94] which distributed to apatites.

Experimental evidence of such of carbonates immiscibility [95–99] exists for relatively shallow pressures 75–100 MPa [97] in the crust show that such magmas do not contain high concentration of ore components.

9.4. Mantle Roots of the Alkaline Ultramafic Carbonatitic Massifs in Southern Siberia

In mantle conditions, liquid immiscibility and separation of carbonates was experimentally obtained for relatively low temperatures 1100 °C at pressures 3–5 GPa [30,79,100] and more, which are similar to the conditions for Cr-bearing inclusions in Yuzhnaya pipe, which corresponds exactly to the region of mantle xenolith and inclusions capture in Torngat, Labrador [7,29,57] and BZM. Similar or slightly higher pressures were determined for the aillikites of Scotland [23] and Eastern Antarcctica [89].

Primitive aillikites in BZM often have a very high Mg’ ~ 0.69 YuP and more for many other varieties which for silicate magmas is very high, almost close to komatites or boninites [101]. Only some olivines Mg’ ~ 0.89 are in equilibrium, the others as well as Cpx with Mg’ ~ 0.85–0.8 are more Fe-rich and fractionated. All Cr-bearing Al-rich Cpx, kaersutites and Ti–micas are derived from different melt portions and are xenocrysts. Consequently, magmas may originally have been less Mg-rich and then dissolved magnesium material (olivines or dunites). The probability of assimilation is very high, because carbonated dunite xenoliths in YuP are abundant and apparently influenced the bulk composition of the rock.

9.5. Processes in Mantle Source for BZM and Evolution of Aillikite Melts

There are three main hypotheses of the origin for aillikites and related rocks: (1) melting of carbonated peridotites [100,102]; (2) assimilation of carbonated phlogopite metasomatites [30,100,103,104] by plume silicate melts; (3) mixing of carbonatites with silicate melts in the mantle or assimilation of mantle material by carbonatites [3,30,100]. Presence of carbonates in melt inclusions from YuP [52,105–107] in olivines as well for other massifs [108] supports the first two suggestions rather than the third because olivine is not on the liquidus of carbonatites. For the alkaline carbonatite complexes there are many evidences of the action of plume melts [3,10,13,21,28,81,102,109] and melting the phlogopite metasomatized and carbonated mantle [100].

In the PT diagram (Figures 20 and 21), the source mantle region shows a heated conductive geotherm. But the heating to SEA geotherm may be the only product of the heating by plume and upwelling of the melts to 2.5 from 4 GPa, further creating a fractionation path along the SEA. The next array 3 on the diagram possibly refers to the rapid fractionation of amphiboles and clinopyroxenes and then crystallization of the groundmass pyroxenes. The geochemistry of the mantle minerals shows very high enrichments of the YuP xenocrysts in REE and TRE elements (Figure 18). The sulfide components were present in the dunite inclusions.

The fields 4 and 5 on the diagram refer to the more rapid ascent of the later plume melts to the Moho and then formation of the shallow mantle magma chamber where differentiation of the primary magmas could occur and separation of the relatively enriched fluids and fractional crystallization and finally creation of the ultramafic carbonatite complex. The large silicate masses possibly were left by magma in the intermediate magma chambers in the lower crust (Field 5) and further moved mainly carbonatitic melts in several stages. Later phases in the massif are much more enriched in TRE compositions (Figure 18).

The time span of about 25 Ma for the evolution of the aillikites in BZM and overall time > 65 Ma provide evidence for the long developing of the carbonatite ultramafic massifs comparable with the common periodicity of the plumes and tectonic geological processes close to 65 Ma [109,110].
9.6. The Source of the Ore Substance

The Cu-Zn ores as well as Ta-Nb, Th-U and REE specialization and high MnO content evidences about the complex origin of the ore components in BZM. High alkalis, carbonates, high \( \text{H}_2\text{O} \) associated with Ba, Sr, U, Pb, Zn, Cu, Au, Ag are often considered to be a subduction-related fluid metasomatism [64,74,76,77,111,112]. However, the rare earths and elements such as Nb, Ta, Zr, Hf, Ti, are not commonly attributed to subduction [3,8,14,74,76] though the remobilization of the subducted crustal sediments can be a possible source of HFSE and other elements [2,76]. All these elements are concentrated in the perovskites and may be the result of re-melting of specific metasomatic fronts, which occur around essentially carbonatitic melts such as protokimberlites [112]. The source of the phosphorus is also debatable [89,91,113]. The partition of the components between the silicate and immiscible carbonatite liquid also may be the reason of the enrichment in HFSE, P and other elements [76,85,90,91]. Breakdown of the silicate magma and carbonatite at depth of about 4.0 GPa and in crust conditions [30,70] may contribute to the concentration of ore material.

Such processes of interaction of plumes and metasomatized mantle were the reason of formation of ultramafic carbonatite complexes worldwide [1–5,7,8,11–14,18,22,26,29,32,38,39,57,81,86,89,109] and in Siberia [4,34–56,58,59,105–107,110]. An additional source can be considered the transfer of some components (LREE, LILE) by fluxes of volatiles, or melts that are saturated in volatiles [77,107,108,111]. One of the effective mechanisms of concentration of ore components, including rare-metals and radioactive elements, is multi-stage small degrees melting of carbonated mantle and crystallization with the formation of a metasomatic front, abundant in carbonates, perovskite, apatite, along with ilmenite and mica [112]. Such metasomatites are suggested to be associated with protokimberlite melts, which are essentially carbonatitic in final stage near 4.0 GPa [30,100]. But in the final stages, decarbonation reactions cause increased concentrations of the REE and TRE in fluids [114].

Presumably, a group of carbonate metasomatites with high REE and TRE content melted, which arose due to the contamination of allilikes with perovskite and ilmenite and Ba-Sr mica. Additional differentiation at the level of Moho and in shallow chambers with separation into carbonatite and silicate components after significant crystallization differentiation should lead to the concentration of rare elements in carbonatites especially if they contain phosphorus [76,85,90–94]. There is a separation of the association into two groups: (1) with apatite and micas with Ba-Sr-LREE specialization and (2) the perovskite and minerals of U-Th, Ta-Nb, Zr-Hf in association with carbonates. It indicates the participation of different types of melts and volatiles in the process of ore formation. However, it can be assumed that deep carbonatite melts associated with the plume or superplume could also be substantially enriched with Ti and other HFSE. There was high oxidation of the magma in the final stage because magnetite is one of the most widespread minerals in the allilikes in massif. Hence the allilitic and carbonatitic magmas essentially differed in oxidation stage from the initial magmatic conditions [113].

10. Conclusions

1. Aillikites from BZM complex containing primary mantle material as xenocrysts are characterized by a wide range of compositions from ijolites to Phl carbonatites.
2. The mantle xenocrysts give the pressures of the aillikite origin >4.0 GPa and the PT path corresponding to convective 90 mW/m² geotherm and probably separate magma chambers near Moho and above.
3. Deep-seated minerals in mantle level were originally enriched in HFSE and LILe.
4. Additional enrichment of aillikites in ore minerals occurred due to mixing with carbonatites.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/10/5/404/s1, Table S1: Measurements of Ar isotopic compositions; Table S2: Bulk rocks major and TRE composition; Table S3: EPMA minerals, electron microscope analyses of minerals; Table S4: TRE in minerals.

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