

## Article

# Origin of the Middle Paleoproterozoic Tikshezero Ultramafic-Alkaline-Carbonatite Complex, NE Fennoscandian Shield: Evidence from Geochemical and Isotope Sr-Nd-Hf-Pb-Os Data

Maria Bogina <sup>1,\*</sup>, Boris Belyatsky <sup>2</sup> , Evgenii Sharkov <sup>1</sup>, Alexey Chistyakov <sup>1</sup> and Robert Krymsky <sup>2</sup>

<sup>1</sup> Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry, Russian Academy of Sciences, 119109 Moscow, Russia; esharkov@mail.ru (E.S.); chist\_1970@mail.ru (A.C.)

<sup>2</sup> A.P. Karpinsky Russian Geological Research Institute, 199106 St. Petersburg, Russia; bbelyatsky@mail.ru (B.B.); robert\_krymsky@yahoo.com (R.K.)

\* Correspondence: lekhta@mail.ru



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**Abstract:** This article reports new geochemical, Sr-Nd-Hf-Pb and Re-Os data on the rocks of the Middle Paleoproterozoic (1.99 Ga) Tikshezero ultramafic-alkaline-carbonatite complex confined to the northeastern margin of the Karelian Craton. We focus on the poorly studied silicate rocks. Based on petrographic and geochemical research, the silicate rocks are subdivided into two groups: an ultramafic-mafic series depleted in REE, and other incompatible elements and an alkaline series enriched in these elements. Isotope studies showed that all rocks have juvenile isotope signatures and were likely derived from a primitive OIB-type mantle source with possible contributions of the subcontinental lithospheric mantle (SCLM). Insignificant crustal contamination is recorded by Pb and Os isotopic compositions. The incompatible element enrichment in the alkaline rocks and depletion in ultramafic-mafic rocks of the mildly alkaline series with allowance for insignificant crustal contamination confirm their derivation from different primary melts. However, a narrow range of Sr, Nd, Hf, and Pb isotope compositions and compact clusters in  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $\epsilon\text{Nd}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon\text{Hf}$ - $\epsilon\text{Nd}$  isotope diagrams indicate their origination from a common mantle source. A model of subsequent two-stage melting is being most consistent with the geochemical data for this complex.

**Keywords:** ultramafic-alkaline-carbonatite complex; Karelian Craton; Middle Paleoproterozoic; Sr-Nd-Hf-Pb-Os isotopes; lithosphere mantle

## 1. Introduction

Alkaline-ultramafic carbonatite massifs are made up of a compositionally contrasting series: ultramafic (dunite, peridotite, wehrlite, pyroxenite, and others), alkaline (foidolites, alkaline gabbro, nepheline syenite) series, and carbonatites. Each series has a distinct petrographic and trace-element composition. It is generally accepted that the formation of these massifs is related to the mantle plume activity and usually occurs in an intracontinental rift setting [1,2], being a part of large igneous provinces. However, details of their genesis, parental magmas, and mutual relationships remain a hotly debatable problem [3–6]. Recent studies showed that some of these intrusions were derived from a single alkaline picritic or nephelinitic magma through differentiation and fractionation [7], whereas others were produced from different sources [8]. At the same time, most attention is usually focused on carbonatites, which occupy only insignificant part of the massifs, but have significant ore potential. Silicate rocks received either little attention, or have even remained beyond the scope of the studies, which made it impossible to solve the above-mentioned genetic problems.

Ultramafic-alkaline-carbonatite complexes were emplaced mainly during the Phanerozoic, and are much less developed in the Precambrian. In Archean, there are very few intrusive alkaline rocks. They compose small bodies, dikes and stocks of lamprophyric dikes and syenites sometimes associated with carbonatites. They are 2.68–2.70 Ga in age and developed on the Canadian Shield (Ontario, Northwest Territories, Kaminak Lake), Western Australia (Yilgarn Craton), Fennoscandian Shield (Karelian Craton), and southeast Greenland [9]. The oldest alkaline complex known in Africa is the 2460-Ma Awsard pluton made up mainly of syenites. Ancient Hogenkal pyroxenite-carbonatite complex known in Tamil Nadu, southern Indian Shield, was dated around 2415 Ma [10,11]. The peculiar feature of these massifs is their two-component or even mono-component composition: carbonatites and syenites, carbonatites and pyroxenites, or carbonatites alone (e.g., Silinjärvi massif in the Baltic Shield). The next Precambrian manifestation of the alkaline and carbonatite magmatic activity worldwide occurred around 2.0 Ga. The best-known manifestations of this age are, for example, the 2.06 Ga Ninakri and Phalaborwa complexes in Africa [12], the 2.03–2.06 Ga ultramafic lamprophyres and carbonatites from the Eastern Goldfields Superterrane, Yilgarn craton [13–15], and numerous complexes in North America, e.g., the Gargill Complex at 1.9 Ga, the Borden Complex at 1.87, and the Spanish River Complex (1.84 Ga) [2]. At the Fennoscandian Shield, this magmatism occurred mainly within an interval of 2.08–1.92 Ga and is represented by ~2.08 Elet’ozero massif [16], the ~2.0 Ga Tiksheozero massif [17] and the 1.8 Ga Gremyakha–Vyrmes massif [18–20], as well as carbonatite and kimberlite occurrences, e.g., 1.92 Ga Kimozero kimberlites [21–23] and 2.02 Ga Laivajoki and Kortejärvi carbonatites [24]. Some massifs of this age already show more diverse compositions, with the appearance of ultramafic alkaline varieties. In this respect, the Tiksheozero massif is of most interest, since it is the Earth’s oldest massif consisting of almost the entire rock spectrum from ultramafic and mafic rocks of the mildly alkaline series through jacupirangites and foidolites to syenitic varieties and carbonatites. At the same time, in spite of the ancient age and restriction to the boundary with the Belomorian mobile belt, this complex was only locally subjected to insignificant alteration and metamorphism near fault zones, but mainly retained its primary mineralogy, geochemistry, and isotope signatures. Correspondingly, its study could provide insights into mantle sources and genesis of ancient alkaline rocks early in the Earth history. Previous works on this complex focused on carbonatites, whereas silicate rocks remained practically unstudied. This work reports first geochemical and Sr-Nd-Hf-Pb-Os isotope-geochemical data on silicate rocks of this complex, which allowed us to resolve the most controversial problem of these massifs—relationships between silicate rocks of the mildly alkaline and alkaline series, to decipher their sources, and to propose models for the formation of this complex.

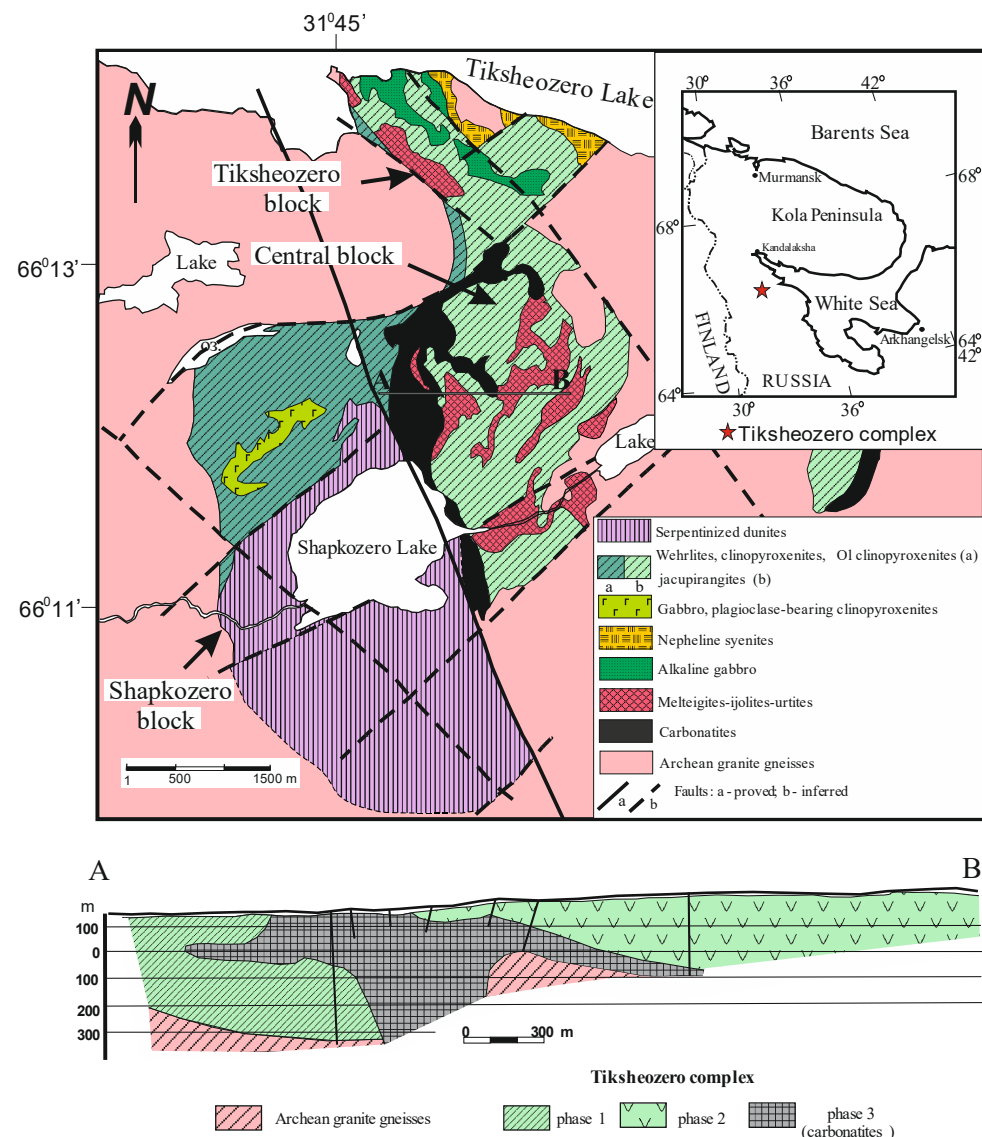
## 2. Geology

The Tiksheozero ultramafic-alkaline-carbonatite complex (24 km<sup>2</sup>) is confined to the northwestern margin of the Archean Karelian Craton, northeastern Fennoscandian shield. The geochronological dating of the carbonatites yielded an age around 1.99 Ga [25–28].

The Tiksheozero complex is restricted to the Svecofennian mobile belt, which was activated in 1.94–1.75 Ga and caused the wide development of fault tectonics, which was accompanied by the shearing and metamorphism of rocks under amphibolite and greenschist facies conditions [29].

The study was carried out for the least altered magmatic rocks, which, however, show traces of greenschist facies metamorphism expressed in the partial replacement of magmatic clinopyroxenes and amphiboles by secondary fibrous actinolite. Host rocks are Archean granite gneisses and Early Paleoproterozoic granites. The massif is very poorly exposed and was mapped mainly using drilling and geophysical data. It forms an NS-trending lopolithic body divided by faults into the Shapkozero, Central, and Tiksheozero blocks (Figure 1). The Shapkozero Block (250 m thick) consists mainly of alternating serpentized

dunites, wehrlites, clinopyroxenites, and subordinate olivine gabbro and ferrogabbro of the mildly alkaline series [17,30,31].



**Figure 1.** Geological scheme of the Tikshezero Complex (modified after [30]), its geographical position (inset), and geological cross-section along line A-B.

The Central Block consists of alkaline clinopyroxenites (jacupirangites), foidolites (melteigites-ijolites-urtites). Its thickness reaches 500 m, decreasing in margins to 50–70 m [31]. This block also comprises a large carbonatite body intruding all above mentioned rocks, which is confirmed by the presence of fragments of all rock varieties of the massif and xenoliths of host Archean rocks in breccia at the contact of the carbonatite body. The carbonatites caused strong contact metasomatic alterations with formation of carbonate-silicate metasomatites in the outercontact. The Tikshezero Block extends along Lake Tikshezero and is separated from the Central block by NE-trending en-echelon faults. Its thickness is 300–400 m. It is mainly made up of jacupirangites, as well as alkali gabbro and foidolites, which are intruded by small bodies of nepheline syenites, as well as foidolite dikes.

It is generally accepted that the massif was formed in three phases [17,30]: (1) ultramafic-mafic rocks of mildly alkaline series (dunites, wehrlites, clinopyroxenites, and gabbro); (2) mainly alkaline rocks: jacupirangites and foidolites (ijolites, melteigites, urtites), alkali

gabbro, and nepheline syenites; (3) calcitic carbonatites and associated contact-metasomatic silicate-carbonate rocks. Direct geological relations between the first and second intrusive phases are absent.

### 3. Materials and Methods

The least altered samples were collected from outcrops, except for carbonatites, which were taken from cores. Silicate rocks were sampled from three blocks of the Tikshezero Complex: (1) Shapkozero, (2) Central, and (3) Tikshezero. They represent all major rock types of the mildly alkaline and alkaline series, and carbonatites.

Major elements were determined by XRF at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry of the Russian Academy of Sciences (IGEM RAS) (Analyst A.I. Yakushev). Trace elements were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) at the Institute of Microelectronics Technology and High Purity Materials of the Russian Academy of Sciences, Chernogolovka, Russia (analyst V.K. Karandashev) following the technique described in [32].

The whole-rock Sr, Nd, and Pb isotope composition was measured on a Triton (Thermo) solid-phase multi-collector mass spectrometer in a static mode at the Isotope Research Center of the A.P. Karpinsky Russian Geological Research Institute (VSEGEI, Saint Petersburg, Russia). The values used for normalization were  $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$  and  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ . The decomposition of silicate samples and separation of elements were performed through a standard method of ion exchange column chromatography. The blank values during the analysis did not exceed 0.01 ng for Sm, Nd, Pb, and 0.01 and 0.05 for Rb and Sr, respectively. The element contents were determined by isotope dilution using a calibrated isotope tracer. The isotopic compositions of the standards were JNdi-1:  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512105 \pm 0.000004$  and SRM987  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710245 \pm 0.000011$ . The error of the corresponding isotope ratio is given at 95% significance level in absolute values ( $2\sigma$ , abs) or percentages ( $2\sigma$ , %).  $^{87}\text{Sr}/^{86}\text{Sr}_i$  and  $^{143}\text{Nd}/^{144}\text{Nd}_i$  are the initial isotope composition of corresponding sample at the time of its origin (2000 Ma).

The Re-Os isotope systematics of whole-rock samples were investigated at the Isotope Research Center of VSEGEI (contents of Re and Os were determined by the isotope dilution method). A 300 mg specimen of mixed  $^{185}\text{Re}$ - $^{190}\text{Os}$  isotope tracer was added to finely ground (2 g) samples. After the addition of 3 mL 11N HCl, the mixtures were frozen at  $-20^\circ\text{C}$  and kept for 30 min; then 7 mL 14N  $\text{HNO}_3$  was added. Then, samples were decomposed in 90-mm quartz vessels placed in an HPA-S furnace for 12 h at a constant temperature of  $300^\circ\text{C}$  and a pressure of 120 bars. The Os and Re were separated using the protocol [33]. The sample solution after HPA-S was transferred to a Savillex PFA 60 mL vial with 1 mL bromine and stirred for 30 min. The rhenium isotope composition and concentration were measured on an ICP-MS ELEMENT-2 (Thermo). The rhenium solution in the 3% nitric acid was analyzed on multiplier in dynamic mode at low resolution ( $\Delta M = 300$ ) using quartz nebulizer, the Ni cones, and the peristaltic pump. The argon plasma conditions are: cooling gas 15.5 L/min, sample gas 1.03 L/min, auxiliary gas 1.02 L/min, power 1031 W. A standard sample bracketing method was used for mass-bias correction. Each measurement consists of 44 scans on 1.5 s. The precision of measurements of  $^{185}\text{Re}/^{187}\text{Re}$  was better than 0.5%. The Os isotope composition was measured on a Triton (Thermo) solid-state multicollector mass spectrometer in the static regime of negative-ion current recording on the Faraday cups. The measured  $^{192}\text{Os}/^{188}\text{Os}$  ratios were corrected (to eliminate the influence of instrumental mass fractionation) to the natural value (3.092016). The technique is described in detail by [34]. The total blanks were 70 pg Re and 1 pg Os. The average values of measurement of UB-N serpentinite standard were as follows: Re =  $0.2218 \pm 0.0064$  ppb, Os =  $3.65 \pm 0.12$  ppb,  $^{187}\text{Re}/^{188}\text{Os} = 0.292 \pm 0.014$ ,  $^{187}\text{Os}/^{188}\text{Os} = 0.127176 \pm 0.000091$  ( $n = 4$ ). These results agree with the published data [35].

## 4. Results

### 4.1. Petrography

The detailed description of petrography and microprobe composition of minerals of the Tikshezero Complex are given in our previous paper [17].

Dunites are black massive medium to coarse-grained, almost monomineralic rocks consisting of highly serpentinized olivines (Fo<sub>88–90</sub>) and accessory alumochromite (Cr<sub>2</sub>O<sub>3</sub> 40 wt %).

Wehrlites (samples A-13-28, A-13-29, A-13-32) are dark massive medium-grained rocks made up of subhedral and irregularly shaped olivine (40–65 vol %, Fo<sub>78–79</sub>) and diopside (30–55 vol %, Wo<sub>46–48</sub>En<sub>44–46</sub>Fs<sub>7–8</sub>), with small subhedral intergrowths of magnetite and ilmenite in interstices.

Olivine clinopyroxenites (sample T4, Figure 2) and clinopyroxenites (sample T18, Figure 2) are massive, inequigranular fine-to-medium grained rocks. Clinopyroxenites almost completely consist of diopside (Wo<sub>43–47</sub>En<sub>44–49</sub>Fs<sub>7–10</sub>) from a few to over 4–5 mm in size. Olivine in the olivine clinopyroxenites (Fo<sub>76–81</sub>) is variably serpentinized and occurs as single grains between Cpx grains. Common accessory minerals are Fe-Ti oxides and sulfides, mainly pyrite. In ore clinopyroxenites, the content of interstitial Fe-Ti oxides widely varies from 5–10% to 60–70% in net-textured areas. In the plagioclase-bearing clinopyroxenites, plagioclase (up to 20 vol %, An<sub>60–63</sub>) occurs interstitially. It also forms clusters of small grains among Cpx (Wo<sub>46–48</sub>En<sub>42–43</sub>Fs<sub>11–12</sub>) and scarce irregularly shaped grains (Fo<sub>64–67</sub>) from a few to 6–7 mm in size. Coronitic textures are developed at the contact between olivine and Fe-Ti oxides. Gabbro (sample T23) occurs in the central part of the Shapkozero Block, where it is alternated with plagioclase-bearing clinopyroxenite. It is a fine to medium-grained rock with gabbroic texture, consisting of diopside (~ 60 vol %, Wo<sub>47</sub>En<sub>41</sub>Fs<sub>12</sub>), plagioclase (~ 30 vol %, An<sub>51–54</sub>) and Fe-Ti oxides (intergrowths of magnetite and ilmenite, up to 10 vol %), with scarce olivine grains (Fo<sub>60</sub>).

Jacupirangites (samples T15, A-13-32B, 834, Figure 2) are fine to medium-grained rocks consisting mainly (up to 70 vol %) of fassaite (Wo<sub>50–52</sub>En<sub>33–35</sub>Fs<sub>13–16</sub>, TiO<sub>2</sub> up to 3 wt % and Na<sub>2</sub>O-0.67–1.85 wt %) from a tenth of a mm to 2–3 mm. Olivine (Fo<sub>55</sub>) sometimes occurs as single irregularly shaped grains. Interstitial nepheline (Na/K = 5.3–6.7) accounts for up to 10 vol %. Fe-Ti oxides (up to 10 vol %) occur as evenly distributed small grains. Kaersutite (TiO<sub>2</sub>-up to 5.5 wt %) forms grains up to 1–2 mm and large oikocrysts with inclusions of Cpx and Fe-Ti oxides. There are also scarce biotite (#Mg 0.65) and accessory F-apatite.

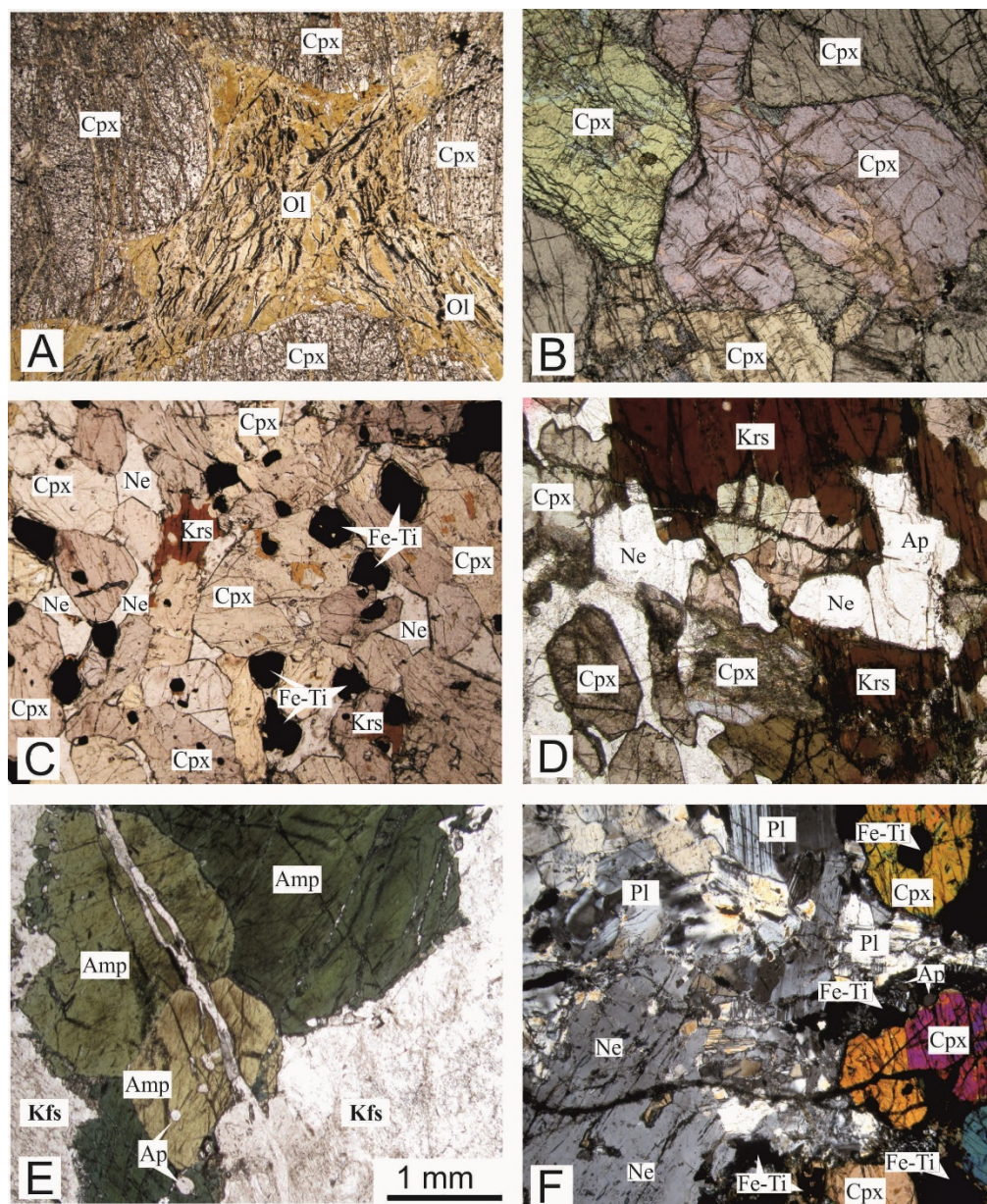
Foidolites (sample T32, Figure 2) are represented by medium-grained feldspar-free clinopyroxene-nepheline rocks of the melteigite (nepheline 30–40 vol %)-ijolite (Ne-40–60%)-urtite (Ne > 60 vol %) series. Major minerals are clinopyroxene (Ti augite Wo<sub>47–56</sub>En<sub>32–37</sub>Fs<sub>9–17</sub> in melteigite-ijolite and Wo<sub>50–53</sub>En<sub>26–34</sub>Fs<sub>13–23</sub> in urtites) and nepheline. Among subordinate minerals are greenish brown pargasite-kaersutite amphiboles, forming both interstitial grains and large (up to 1 cm) oikocrysts with chadacrysts of clinopyroxene and more rarely, nepheline, as well as magnesian biotite (#Mg = 65–68) and Fe-Ti oxides. Accessory minerals are apatite and titanite, as well as finely disseminated sulfides, and carbonate material.

Alkaline gabbro (sample T32a) is a fine- to medium-grained rock formed by greenish diopside (Wo<sub>50–52</sub>En<sub>33–35</sub>Fs<sub>13–17</sub>) and plagioclase (An<sub>47–52</sub>), which occur as subprismatic and irregularly shaped grains up to 1–2 mm approximately in equal amounts and compose up to 70 vol %. Nepheline grains (Na/K ~ 6) up to 2 mm in size account for >10 vol %. Fe-Ti oxides (intergrowths of ilmenite and magnetite) with Fe-rich biotite (#Mg = 0.38–0.44) account for ~ 20 vol %. Accessory F-apatite is observed more frequently as small inclusions in biotite.

Nepheline syenites (samples 27–15 and T46, Figure 2) are massive medium-grained leucocratic rocks. A major mineral is K-feldspar (40–65%), consisting of hatched microcline and mainly K-Fsp with albite micropertthites. Nepheline (up to 25 vol %) occurs as large (up to 5–6 mm) grains. Mafic minerals (<20 vol %) are represented by 2–3 mm grains and



aggregates of 1–2 mm grains of pargasitic amphibole with dark green to light brown green pleochroism. Accessory minerals are represented by Fe-Ti oxides observed as scarce grains in amphiboles, F-apatite, and titanite.



**Figure 2.** Microphotos of the rocks of the Tiksheozero Complex. (A) wehrlite (sample T2), (B) clinopyroxenite (T18), (C) Jacupirangite (T15), (D) ijolite (T32), (E) nepheline syenite (T46), (F) alkaline gabbro (T32a). (A–E) in transmitted light, parallel nicols; (F) crossed nicols. Mineral abbreviations: (Ol) olivine, (Cpx) clinopyroxenite, (Pl) plagioclase, (Amp) amphibole, (Krs) Kaersutite, (Ne) Nepheline; (Kfs) K-feldspar, (Fe-Ti) ilmenite-magnetite intergrowths, (Ap) apatite.

Carbonatites are fine to medium-grained inequigranular rock. Calcite of intricate shape composes up to 80 vol %. F-apatite (up to 10 vol %) from 0.05 to 0.5 mm was found as inclusions in and between carbonates. Remaining minerals are magnetite and phlogopite (#Mg = 0.8) and alkaline amphibole (richterite-cataphorite) frequently forming aggregates surrounded by Fe-Mg carbonate. Magnetite is observed as scarce fine inclusions in calcite and large grains (up to 0.55 mm) of intricate shape.

Amphibole-carbonate, amphibole–phlogopite–carbonate rocks, as well as sodalite–alkaline–amphibole rocks with cancrinite, aegirine, andradite, and titanite are developed in the outercontact of carbonatite bodies. The rocks have patchy or banded appearance, which is determined by the alternation of accumulations of finely crystalline mafic minerals and leucocratic minerals including calcite, sodalite, cancrinite, sometimes albite and K-feldspar.

#### 4.2. Whole-Rock Geochemistry

Based on major element compositions, the rocks of the massif were subdivided into four groups [17]: (1) highly silica-undersaturated ultramafic alkaline rocks (jacupirangites, foidolites); (2) silica-undersaturated alkaline rocks (alkaline gabbro, nepheline syenite); (3) carbonatites and carbonate-silicate rocks; (4) ultramafic-mafic rocks of the mildly alkaline series (dunites, wehrlites, clinopyroxenites, gabbro). Representative analyses of the rocks are given in Table 1.

**Table 1.** Compositions of rocks of the Tikshezero Complex (oxides in wt %, elements, in ppm).

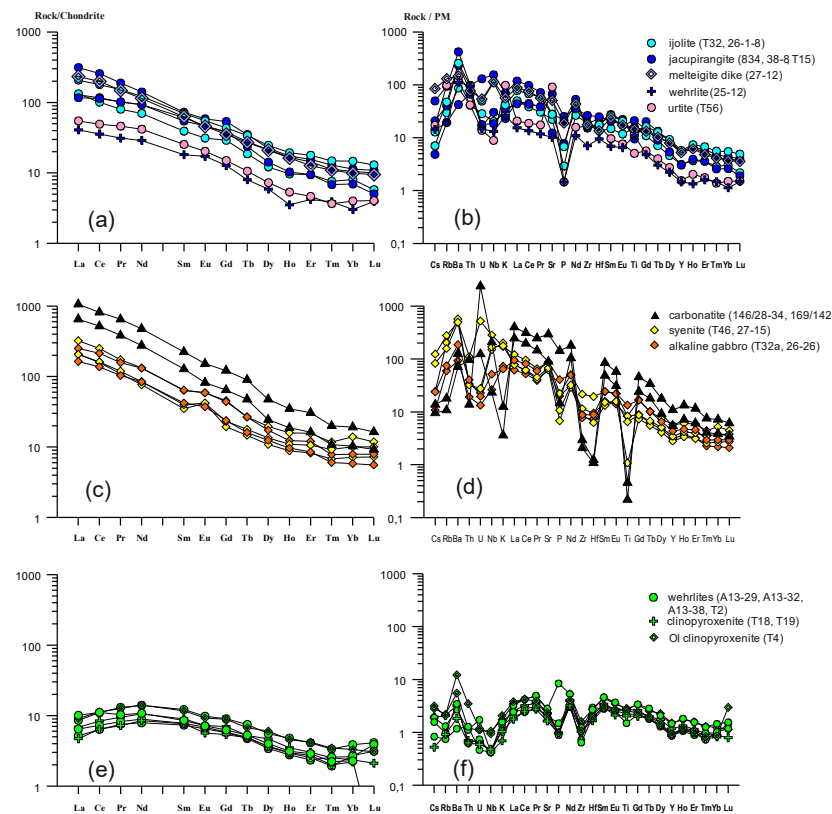
|                                | 1          | 2          | 3          | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11     | 12    | 13            | 14             | 15      |
|--------------------------------|------------|------------|------------|-------|-------|-------|-------|-------|-------|-------|--------|-------|---------------|----------------|---------|
| Samples                        | A<br>13-32 | A<br>13-28 | A<br>13-29 | T18   | T4    | T15   | 834   | T32   | T32a  | T46   | 835    | 839   | 146/28–<br>34 | 146/96–<br>107 | 169/142 |
| SiO <sub>2</sub>               | 47.89      | 47.14      | 48.74      | 50.05 | 46.61 | 38.04 | 40.67 | 42.41 | 41.09 | 51.25 | 40.2   | 34.61 | 0.91          | 9.41           | 1.43    |
| TiO <sub>2</sub>               | 0.54       | 0          | 0.45       | 0.55  | 0.57  | 4.23  | 1.9   | 2.23  | 1.63  | 0.21  | 1.98   | 0.95  | 0.04          | 0.22           | 0.09    |
| Al <sub>2</sub> O <sub>3</sub> | 2.29       | 1.46       | 1.64       | 2.25  | 2.21  | 9.29  | 9.43  | 8.8   | 24.27 | 23.1  | 13.66  | 15.33 | 0.20          | 0.76           | 0.37    |
| Fe <sub>2</sub> O <sub>3</sub> | 10.01      | 10.0       | 9.76       | 6.06  | 10.41 | 17.54 | 13.39 | 12.59 | 8.67  | 4.99  | 12.77  | 7.48  | 3.52          | 22.72          | 3.80    |
| MnO                            | 0.13       | 0.15       | 0.13       | 0.095 | 0.158 | 0.204 | 0.23  | 0.227 | 0.114 | 0.131 | 0.21   | 0.08  | 0.18          | 0.41           | 0.33    |
| MgO                            | 21.41      | 26.03      | 22.58      | 18.79 | 21.33 | 8.6   | 12.22 | 10.28 | 2.8   | 0.51  | 7.07   | 7.98  | 1.47          | 7.07           | 3.57    |
| CaO                            | 15.03      | 12.24      | 14.76      | 19.51 | 15.69 | 16.5  | 12.96 | 15.86 | 8.79  | 2.42  | 13.11  | 12.17 | 54.43         | 35.28          | 48.80   |
| Na <sub>2</sub> O              | 0.22       | 0.21       | 0.32       | 0.29  | 0.40  | 1.71  | 3.8   | 3.11  | 9.02  | 8.28  | 6.67   | 10.14 | 0.16          | 0.84           | 0.12    |
| K <sub>2</sub> O               | 0.03       | 0.04       | 0.05       | 0.02  | 0.05  | 0.67  | 2.05  | 1.21  | 2.11  | 5.82  | 0.97   | 1.47  | 0.07          | 0.52           | 0.25    |
| P <sub>2</sub> O <sub>5</sub>  | 0.17       | 0.03       | 0.02       | 0.02  | 0.02  | 0.16  | 0.44  | 0.14  | 0.41  | 0.14  | 0.72   | 0.11  | 2.96          | 3.04           | 0.30    |
| L.O.I.                         | 2.7        | 2.87       | 1.99       | 1.64  | 2.04  | 2.49  | 2.27  | 2.26  | 0.64  | 1.8   | 2.1    | 9.27  | 35.42         | 21.17          | 40.79   |
| Mg#                            | 80.9       | 83.7       | 82.1       | 86.0  | 80.2  | 49.2  | 64.3  | 61.7  | 39.0  | 16.8  | 52.3   | 67.8  | 42.7          | 35.7           | 62.6    |
| V                              | 173        | 118        | 135        | 111   | 145   | 810   | 316   | 261.5 | 161   | 3.82  | 197    | 128   | 88.1          | 356.2          | 32.6    |
| Cr                             | 2205       | 1913       | 1840       | 1437  | 878   | 28.2  | 200   | 478   | 24.6  | 3.7   | 138.17 | 7.19  | 5.48          | 0.83           | 44.72   |
| Co                             | 89         | 100        | 105        | 48.9  | 72.8  | 81.6  | 80    | 44.6  | 29.9  | 8.27  | 57.3   | 29.3  | 10.5          | 32.67          | 18.20   |
| Ni                             | 591        | 855        | 694        | 540   | 501   | 146   | 308   | 163.6 | 41.5  | 5.65  | 39.25  | 17.03 | 10.6          | 9.62           | 153.24  |
| Rb                             | 0.59       | 0.79       | 0.45       | 1.3   | 1.3   | 11.7  | 56    | 28.44 | 35.7  | 121.8 | 12.39  | 46.54 | 6.45          | 35.10          | 10.79   |
| Sr                             | 56         | 41         | 39         | 45.4  | 55.1  | 245   | 560   | 550.7 | 1258  | 1232  | 2044   | 424   | 5843          | 2977           | 1778    |
| Y                              | 6.3        | 3.7        | 4          | 5     | 6.5   | 23.2  | 24    | 24.68 | 13.5  | 12.05 | 24     | 27    | 46.70         | 30.61          | 23.31   |
| Zr                             | 12.84      | 7.6        | 6.7        | 12.8  | 16.7  | 192   | 160   | 175.3 | 81    | 93.77 | 87     | 123   | 30.86         | 319            | 21.94   |
| Nb                             |            |            |            | 0.28  | 0.69  | 19.9  | 102   | 72.8  | 17.3  | 99.07 | 27.33  | 8.46  | 15.3          | 109            | 138     |
| Ba                             | 23         | 18         | 7.7        | 21.3  | 36.4  | 280   | 2788  | 1700  | 613   | 3768  | 1619   | 1739  | 470           | 215            | 829     |
| La                             | 2.1        | 1.3        | 1.6        | 1.7   | 2.2   | 31.4  | 77    | 50.7  | 40    | 50.75 | 81     | 70    | 259           | 132            | 159     |
| Ce                             | 7          | 4.1        | 4.6        | 5.3   | 7.2   | 74.5  | 164   | 114.2 | 87.6  | 101.2 | 159    | 156   | 521           | 284            | 331     |
| Pr                             | 1.3        | 0.72       | 0.79       | 0.9   | 1.2   | 9.8   | 18    | 14.61 | 10    | 10.52 | 19     | 20    | 62.6          | 34.1           | 36.9    |
| Nd                             | 6.6        | 3.7        | 4.2        | 5     | 6.7   | 44.2  | 67    | 57.82 | 39.7  | 36.25 | 76     | 84    | 225           | 125            | 131     |
| Sm                             | 1.9        | 1.1        | 1.2        | 1.4   | 1.8   | 9.4   | 11    | 10.73 | 6.5   | 5.37  | 12     | 15    | 34.4          | 20.0           | 19.7    |
| Eu                             | 0.57       | 0.38       | 0.4        | 0.42  | 0.54  | 2.6   | 3.4   | 3.19  | 2.2   | 2.41  | 4.4    | 4.5   | 8.83          | 5.13           | 4.76    |
| Gd                             | 1.8        | 1.2        | 1.2        | 1.4   | 1.8   | 7.8   | 11    | 8.88  | 4.9   | 3.95  | 8.67   | 9.92  | 24.81         | 14.85          | 13.15   |
| Tb                             | 0.28       | 0.18       | 0.18       | 0.2   | 0.25  | 1     | 1.3   | 1.27  | 0.6   | 0.55  | 1.17   | 1.35  | 3.36          | 1.95           | 1.78    |
| Dy                             | 1.4        | 0.86       | 0.92       | 1.2   | 1.5   | 5.4   | 5.7   | 6.27  | 3.2   | 2.76  | 5.58   | 6.7   | 12.04         | 7.65           | 6.19    |
| Ho                             | 0.27       | 0.16       | 0.17       | 0.2   | 0.26  | 0.94  | 0.98  | 1.1   | 0.55  | 0.5   | 0.94   | 1.09  | 1.98          | 1.33           | 1.06    |
| Er                             | 0.68       | 0.39       | 0.42       | 0.5   | 0.7   | 2.38  | 2.6   | 2.96  | 1.4   | 1.36  | 2.4    | 2.71  | 5.08          | 3.46           | 2.69    |
| Tm                             | 0.086      | 0.066      | 0.049      | 0.065 | 0.088 | 0.29  | 0.33  | 0.38  | 0.15  | 0.17  | 0.28   | 0.31  | 0.51          | 0.38           | 0.28    |
| Yb                             | 0.64       | 0.43       | 0.45       | 0.39  | 0.54  | 1.74  | 1.9   | 2.42  | 1     | 1.18  | 1.67   | 1.81  | 3.16          | 2.39           | 1.69    |
| Lu                             | 0.1        | 0.1        | 0.079      | 0.054 | 0.077 | 0.25  | 0.28  | 0.33  | 0.14  | 0.18  | 0.22   | 0.21  | 0.41          | 0.33           | 0.23    |
| Hf                             | 0.76       | 0.83       | 0.56       | 0.6   | 0.78  | 6.6   | 5.1   | 4.96  | 2.1   | 1.77  | 2.16   | 2.97  | 0.35          | 1.11           | 0.30    |
| Pb                             | 1.2        | 2.2        | 1.5        | 0.58  | 1.4   | 3.8   | 7.8   | 4.48  | 1.6   | 9.92  | 5.47   | 51.63 | 7.24          | 2.72           | 2.10    |
| Th                             | 0.049      | 0.088      | 0.1        | 0.056 | 0.1   | 5.3   | 7.8   | 7.6   | 1.5   | 2.71  | 3.57   | 71.6  | 7.68          | 4.82           | 1.10    |
| U                              | 0.015      | 0.035      | 0.009      | 0.014 | 0.022 | 0.34  | 2.6   | 1     | 0.27  | 0.46  | 0.41   | 0.39  | 2.51          | 2.34           | 48.46   |

Note: ultramafic-mafic series: (1–3) wehrlites, (4) pyroxenite, (5) Ol clinopyroxenite; alkaline series: (6,7) jacupirangite, (8) ijolite, (9) alkaline gabbro, (10) syenite; (11,12) carbonate-silicate rock, (13–15) carbonatites. Analyses (1–3) were taken from Report No. 18123/2. “Development and Improvement of a New Method of Local Uranium-Lead Dating of Ore-Bearing Igneous Rocks and Wall-Rock Metasomatites using Pyrochlore as Mineral Geochronometer to Improve Efficiency of Prospecting and Exploration Works. State Contract No. K41.2014.014, dated 31 October 2014.

The ultramafic-mafic rocks of the mildly alkaline series are mainly represented by wehrlites, clinopyroxenites, olivine clinopyroxenites, with minor gabbros. The rocks are characterized by relatively low SiO<sub>2</sub> (from 43.89 to 51.93 wt %) at high MgO (from 17.79 to 24.57 wt %), high Ni (from 540 to 855 ppm) and ultrahigh Cr (878 to 2072 ppm), and low TiO<sub>2</sub> contents (0.42–0.79 wt %). Gabbro differs in having lower MgO (12.29–16.47 wt %), Ni (219–261 ppm), Cr (354–882 ppm), and higher TiO<sub>2</sub> (1.36–1.69 wt %). The ultramafic-mafic



rocks are depleted in LREE, show weak to moderate HREE fractionation, at low REE level (5–10 chondrites:  $((\text{La}/\text{Yb})_N = 2.62\text{--}5.6; (\text{La}/\text{Sm})_N = 0.61\text{--}1.65; (\text{Gd}/\text{Yb})_N = 2.45\text{--}2.95))$  and no Eu anomaly. In the spidergram, they show negative P and Zr anomalies and positive Ba and Nd anomalies (Figure 3).



**Figure 3.** REE and trace-element distribution patterns for rocks of the Tikshezzero Complex. Concentrations are normalized to chondrite and primitive mantle after [36]. (a,b) highly silica-undersaturated ultramafic alkaline rocks (jacupirangites, foidolites) (group 1); (c,d) silica-undersaturated alkaline rocks (alkaline gabbro, nepheline syenite) (group 2) and carbonatites (group 3); (e,f) ultramafic-mafic rocks of the mildly alkaline series (dunites, wehrlites, clinopyroxenites) (group 4). Data on samples T18, T19, 26-1-8, 38-8, 27-12, 25-12, T56, 26-26 are taken from [17].

Compared to the mildly alkaline ultramafic-mafic rocks, the highly silica-undersaturated ultramafic alkaline rocks are characterized by the insignificant variations at lower  $\text{SiO}_2$  content (39.21 to 43.85 wt %), higher  $\text{Na}_2\text{O}$  predominating over  $\text{K}_2\text{O}$ , lower  $\text{MgO}$  (7.37 to 12.57 wt %), higher  $\text{TiO}_2$  (1.96–4.35 wt %) and  $\text{P}_2\text{O}_5$  (up to 0.61 wt %), and much lower Ni (417.7 to 21.45 ppm) and Cr contents (478 to 9.57 ppm). All the rocks are characterized by the elevated contents of Ba, LREE, and Ti. They have fractionated REE patterns with moderate to high LREE enrichment relative to HREE ( $((\text{La}/\text{Yb})_N = 12.19\text{--}27.50; (\text{La}/\text{Sm})_N = 1.54\text{--}4.31$  and  $(\text{Gd}/\text{Yb})_N = 3.62\text{--}5.47)$ ). Spidergrams show a deep negative P anomaly, negative Nb anomaly, depletion in Th and U, a positive Ba anomaly, and shallow Zr-Hf anomaly (Figure 3).

The silica-undersaturated rocks (alkaline gabbro and melasyenite) are the most evolved rocks. Compared to the alkaline ultramafic rocks, they have higher  $\text{SiO}_2$  (from 41.52 to 52.91), at lower  $\text{MgO}$  (from 6.87 to 0.53), lower Ni (5.65 to 96.5) Cr (3.70 to 24.6), and  $\text{TiO}_2$  (0.57 to 2.85). The rocks show LREE enrichments ( $((\text{La}/\text{Yb})_N = 18.97\text{--}31.87; (\text{La}/\text{Sm})_N = 3.57\text{--}3.90; (\text{Gd}/\text{Yb})_N = 3.20\text{--}5.59)$ ) and their REE patterns are close to those of the most evolved rocks of the ultramafic alkaline rocks, which suggests their genetic affinity. They reveal a positive Ba anomaly, insignificant to deep P anomaly, as the highly silica-undersaturated ultramafic alkaline rocks, but differ from them in the appearance of a negative Zr-Hf



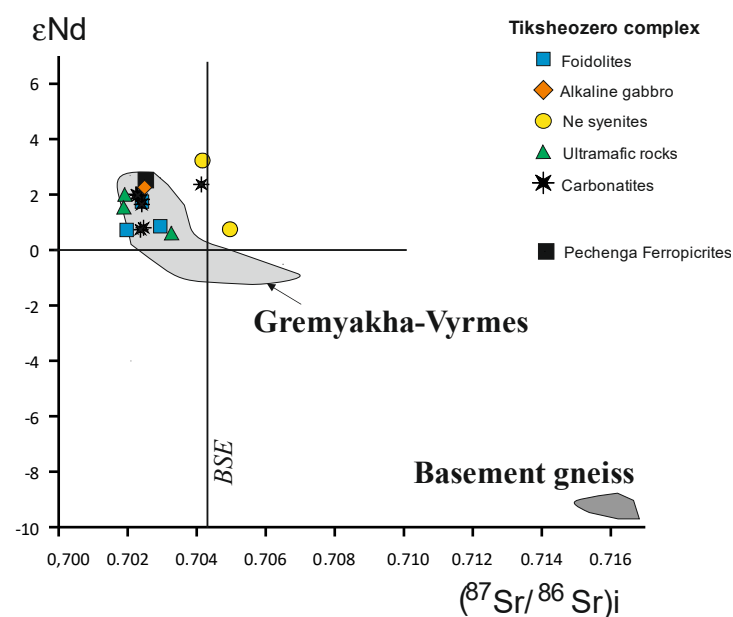
anomaly (Figure 3). Rocks from alkaline ultramafic rocks to nepheline syenites show an increase of  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ , at decrease of  $\text{TiO}_2$ ,  $\text{CaO}$ , and  $\text{Mg}\#$ .

Carbonatites are characterized by the highest contents of LREE and LILE, most fractionated REE patterns ( $(\text{La}/\text{Yb})_{\text{N}} = 26\text{--}106$ ;  $(\text{La}/\text{Sm})_{\text{N}} = 3.9\text{--}5.0$ ;  $(\text{Gd}/\text{Yb})_{\text{N}} = 4.1\text{--}9.7$ ), and deep K, Zr-Hf, Ti anomalies.

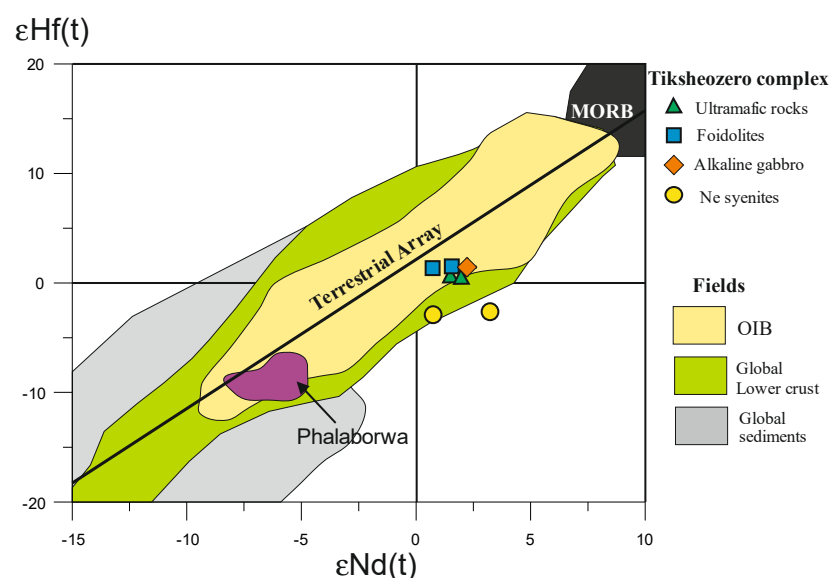
#### 4.3. Isotope Composition

##### 4.3.1. Sr-Nd-Hf Isotope Composition

The results of whole-rock Sr, Nd, and Hf isotope analysis are shown in Tables 2 and 3 and plotted in the  $\epsilon\text{Nd}$ - $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon\text{Hf}$ - $\epsilon\text{Nd}$  diagrams (Figures 4 and 5).



**Figure 4.** Sr–Nd isotope diagrams for rocks of the Tikshezero massif. Fields for the Gremyakha–Vyrmes massif and Basement gneiss are shown after [18].



**Figure 5.** Hf–Nd isotope diagrams for rocks of the Tikshezero massif. Fields of MORB, OIB, global lower crust and sediments are from [38,39]. The Terrestrial Array is from [40]. Field for the Phalaborwa massif is shown after [39]. For symbols, see Figure 4.

**Table 2.** Whole rock Rb-Sr and Sm-Nd isotopic data for the Tiksheozero complex.

| Sample     | Rock                                          | Rb (ppm) | Sr (ppm) | $^{87}\text{Rb}/^{86}\text{Sr}$ | $^{87}\text{Sr}/^{86}\text{Sr} \pm 2\sigma$ | Sm (ppm) | Nd (ppm) | $^{147}\text{Sm}/^{144}\text{Nd}$ | $^{143}\text{Nd}/^{144}\text{Nd} \pm 2\sigma$ | $(^{87}\text{Sr}/^{86}\text{Sr})_i$ | $\epsilon_{\text{Nd}(t)}$ |
|------------|-----------------------------------------------|----------|----------|---------------------------------|---------------------------------------------|----------|----------|-----------------------------------|-----------------------------------------------|-------------------------------------|---------------------------|
| T18        | clinopyroxenite                               | 1.08     | 44.5     | 0.06984                         | $0.703273 \pm 22$                           | 1.30     | 4.62     | 0.16943                           | $0.512358 \pm 7$                              | 0.701261                            | 1.6                       |
| A13-29     | peridotite                                    | 0.48     | 38.7     | 0.03559                         | $0.703436 \pm 33$                           | 1.20     | 4.37     | 0.16616                           | $0.512326 \pm 7$                              | 0.702411                            | 1.8                       |
| A13-32     | peridotite                                    | 0.60     | 56.5     | 0.03092                         | $0.703833 \pm 15$                           | 1.70     | 6.26     | 0.16384                           | $0.512249 \pm 6$                              | 0.702942                            | 0.9                       |
| T4         | olivine<br>pyroxenite                         | 1.10     | 40.1     | 0.07909                         | $0.704247 \pm 15$                           | 1.57     | 5.76     | 0.16434                           | $0.512249 \pm 3$                              | 0.701968                            | 0.7                       |
| 27–15      | nepheline<br>syenite                          | 93.3     | 1303     | 0.20711                         | $0.710930 \pm 4$                            | 6.01     | 38.8     | 0.09369                           | $0.511320 \pm 4$                              | 0.704964                            | 0.7                       |
| T46        | syenite                                       | 108      | 1064     | 0.29325                         | $0.712614 \pm 5$                            | 5.24     | 37.0     | 0.08570                           | $0.511341 \pm 3$                              | 0.704166                            | 3.2                       |
| T32a       | alkaline<br>gabbro                            | 37.7     | 1406     | 0.07763                         | $0.704723 \pm 3$                            | 8.42     | 51.5     | 0.09891                           | $0.511466 \pm 3$                              | 0.702487                            | 2.3                       |
| T32        | ijolite                                       | 31.6     | 591      | 0.15442                         | $0.706339 \pm 5$                            | 10.8     | 59.1     | 0.11005                           | $0.511573 \pm 5$                              | 0.701891                            | 1.5                       |
| T15        | jacupirangite                                 | 12.1     | 257      | 0.13505                         | $0.705809 \pm 3$                            | 9.77     | 46.8     | 0.12610                           | $0.511809 \pm 2$                              | 0.701919                            | 2.0                       |
| 206/97     | carbonatite                                   | 46.9     | 4000     | 0.03392                         | $0.703220 \pm 8$                            | 21.3     | 139      | 0.09294                           | $0.511374 \pm 6$                              | 0.702243                            | 2.0                       |
| 146/28–34  | carbonatite                                   | 6.20     | 6115     | 0.00293                         | $0.702542 \pm 4$                            | 35.9     | 240      | 0.09065                           | $0.511283 \pm 4$                              | 0.702458                            | 0.8                       |
| 169/42     | carbonatite                                   | 11.4     | 1816     | 0.01820                         | $0.702933 \pm 7$                            | 19.5     | 135      | 0.08770                           | $0.511296 \pm 2$                              | 0.702409                            | 1.8                       |
| 101/13     | carbonatite                                   | 2.73     | 3096     | 0.00255                         | $0.704208 \pm 4$                            | 1.04     | 3.14     | 0.19981                           | $0.512800 \pm 4$                              | 0.704135                            | 2.4                       |
| 206/74     | carbonatite                                   | 15.3     | 3971     | 0.01112                         | $0.702614 \pm 5$                            | 44.5     | 282      | 0.09524                           | $0.511403 \pm 4$                              | 0.702294                            | 2.0                       |
| 146/96–107 | carbonatite<br>silicate-<br>carbonate<br>rock | 37.4     | 3136     | 0.03448                         | $0.703364 \pm 13$                           | 20.6     | 133      | 0.09358                           | $0.511318 \pm 3$                              | 0.702370                            | 0.7                       |
| 835        | carbonate<br>rock                             | 13.8     | 2037     | 0.01962                         | $0.702972 \pm 4$                            | 9.58     | 60.3     | 0.09608                           | $0.511397 \pm 4$                              | 0.702407                            | 1.6                       |
| 41–3–5     | melteigite                                    | 62.1     | 1260     | 0.14255                         | $0.710389 \pm 23$                           | 5.61     | 33.7     | 0.10071                           | $0.511482 \pm 4$                              | 0.706282                            | 2.1                       |

**Table 3.** Whole rock Re-Os and Lu-Hf isotopic data on the Tiksheozero complex.

| Sample | Re (ppb) | Os (ppb) | $^{187}\text{Re}/^{188}\text{Os}$ | $^{187}\text{Os}/^{188}\text{Os} \pm 2\sigma$ | $(^{187}\text{Os}/^{186}\text{Os})_i$ | YOs | Lu (ppm) | Hf (ppm) | $^{176}\text{Lu}/^{177}\text{Hf}$ | $^{176}\text{Hf}/^{177}\text{Hf} \pm 2\sigma$ | $\text{Hf}_i$ | $\epsilon$ |
|--------|----------|----------|-----------------------------------|-----------------------------------------------|---------------------------------------|-----|----------|----------|-----------------------------------|-----------------------------------------------|---------------|------------|
| T18    | 0.193    | 0.694    | 1.343                             | $0.1926 \pm 7$                                | 0.1471                                | 30  | 0.06     | 0.60     | 0.01420                           | $0.282143 \pm 59$                             | 0.281603      | 3.3        |
| T4     | 0.213    | 0.322    | 3.234                             | $0.2944 \pm 5$                                | 0.1848                                | 63  | 0.08     | 0.80     | 0.01420                           | $0.282138 \pm 57$                             | 0.281598      | 3.2        |
| 27–15  | 0.178    | 0.057    | 16.999                            | $1.1802 \pm 27$                               | 0.6043                                | 433 | 0.26     | 2.68     | 0.01377                           | $0.282002 \pm 18$                             | 0.281478      | −1.1       |
| T46    | 0.065    | 0.028    | 12.735                            | $1.2415 \pm 19$                               | 0.8100                                | 614 | 0.15     | 1.80     | 0.01183                           | $0.281932 \pm 8$                              | 0.281482      | −0.9       |
| T32a   | 0.979    | 0.080    | 79.782                            | $2.9277 \pm 42$                               | 0.2246                                | 98  | 0.14     | 2.10     | 0.00946                           | $0.281954 \pm 7$                              | 0.281594      | 3.0        |
| T32    | 6.12     | 0.157    | 207.779                           | $1.0073 \pm 14$                               |                                       |     | 0.33     | 4.96     | 0.00945                           | $0.281932 \pm 39$                             | 0.281572      | 2.3        |
| T15    | 2.53     | 0.144    | 147.282                           | $5.8657 \pm 176$                              | 0.8756                                | 672 | 0.25     | 6.60     | 0.00538                           | $0.281765 \pm 30$                             | 0.281561      | 1.8        |

The rocks mainly show extremely narrow initial  $^{87}\text{Sr}/^{86}\text{Sr}$  range varying from unradiogenic and weakly radiogenic values of 0.7019 to 0.702942 in ultramafic rocks of the mildly alkaline series to more radiogenic values of 0.704166–0.704964 in nepheline syenite. Carbonatites, on average, are characterized by the unradiogenic Sr ratio around 0.702. Some rocks have near-chondritic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio ( $<0.702$ ), which is likely related to the late-stage Rb influx and a shift of the Rb/Sr ratio. All rocks are characterized by slightly positive  $\epsilon\text{Nd}$  values. In the ultramafic rocks of the mildly alkaline series,  $\epsilon\text{Nd}$  shows narrow variations (from +0.72 to +1.77), completely falling within a range for rocks of the alkaline series from +0.75 to more radiogenic +3.2 in the nepheline syenite.  $^{87}\text{Sr}/^{86}\text{Sr}$  shows no correlation with  $^{143}\text{Nd}/^{144}\text{Nd}$ . DM Nd model ages calculated according to [37] vary from 2142 to 2781 Ma for ultramafic rocks of the mildly alkaline series and from 2150 to 2315 Ma in the rocks of the alkaline series.

The  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios vary from 0.2815 to 0.2816, at  $\epsilon\text{Hf}$  varying from +2.25 to 3.33. As for Sr, exceptions are syenites with a slightly negative  $\epsilon\text{Hf}$  from  $-0.94$  to  $-1.09$ .

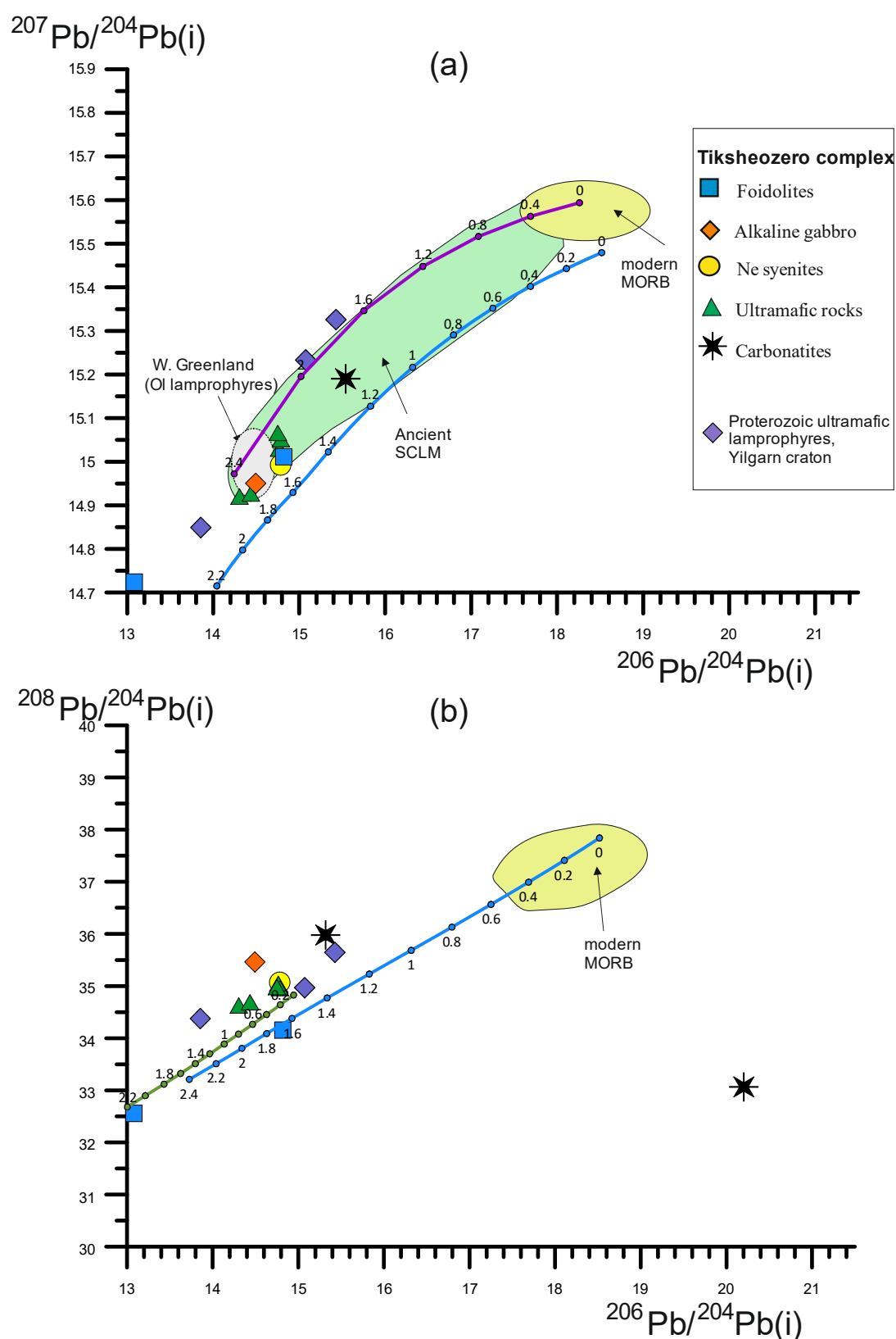
#### 4.3.2. Pb Isotope Composition

Pb isotope data are listed in Table 4. The Pb, Th, and U contents in the studied rocks vary, respectively, from 0.58 to 9.92, from 0.056 to 7.60, and from 0.014 to 1.0 ppm, respectively. Note that the rocks of the alkaline series show much higher contents of Th, Pb, and U.

**Table 4.** Whole rock Pb isotopic data on the rocks of the Tiksheozero Complex.

| Sample     | $^{206}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$ | $^{207}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$ | $^{208}\text{Pb}/^{204}\text{Pb} \pm 2\sigma$ | $\mu$ | $(^{206}\text{Pb}/^{204}\text{Pb})_i$ | $(^{207}\text{Pb}/^{204}\text{Pb})_i$ | $(^{208}\text{Pb}/^{204}\text{Pb})_i$ |
|------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-------|---------------------------------------|---------------------------------------|---------------------------------------|
| T18        | 15.2628 $\pm$ 6                               | 15.0850 $\pm$ 7                               | 35.5925 $\pm$ 25                              | 1.36  | 14.7677                               | 15.0241                               | 34.9939                               |
| A13-29     | 14.5711 $\pm$ 3                               | 14.9372 $\pm$ 5                               | 35.0633 $\pm$ 16                              | 0.37  | 14.4377                               | 14.9208                               | 34.6388                               |
| A13-32     | 15.0475 $\pm$ 4                               | 15.0778 $\pm$ 5                               | 35.1630 $\pm$ 15                              | 0.72  | 14.7867                               | 15.0458                               | 34.9092                               |
| T4         | 15.0764 $\pm$ 9                               | 15.1000 $\pm$ 14                              | 35.3389 $\pm$ 44                              | 0.89  | 14.7511                               | 15.0600                               | 34.9298                               |
| T46        | 15.7948 $\pm$ 14                              | 15.1169 $\pm$ 14                              | 36.8171 $\pm$ 39                              | 2.78  | 14.7840                               | 14.9925                               | 35.0702                               |
| T32a       | 18.6862 $\pm$ 12                              | 15.4660 $\pm$ 10                              | 42.4144 $\pm$ 28                              | 11.52 | 14.4938                               | 14.9504                               | 35.4612                               |
| T32        | 18.7306 $\pm$ 10                              | 15.4184 $\pm$ 8                               | 45.2211 $\pm$ 29                              | 15.53 | 13.0818                               | 14.7236                               | 32.5574                               |
| T15        | 16.9627 $\pm$ 9                               | 15.2745 $\pm$ 9                               | 44.0853 $\pm$ 31                              | 5.89  | 14.8207                               | 15.0111                               | 34.1553                               |
| A13-30B    | 18.0715 $\pm$ 10                              | 15.3919 $\pm$ 10                              | 40.2044 $\pm$ 35                              | 22.62 | 9.8438                                | 14.3800                               | 30.6050                               |
| 146/28–34  | 30.0826 $\pm$ 8                               | 17.6937 $\pm$ 7                               | 42.0005 $\pm$ 24                              | 27.16 | 20.2029                               | 16.4786                               | 33.0642                               |
| 101/13     | 15.3748 $\pm$ 5                               | 15.2500 $\pm$ 7                               | 36.0519 $\pm$ 25                              | 0.15  | 15.3200                               | 15.2433                               | 35.9777                               |
| 146/96–107 | 41.9784 $\pm$ 29                              | 18.2034 $\pm$ 7                               | 51.9618 $\pm$ 69                              | 84.07 | 11.3954                               | 14.4421                               | 33.3549                               |
| 835        | 17.5658 $\pm$ 8                               | 15.3784 $\pm$ 9                               | 45.9080 $\pm$ 37                              | 5.13  | 15.6995                               | 15.1488                               | 41.0615                               |

Initial Pb isotope compositions of the rocks are shown in the  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  diagrams compared to the evolution curves of depleted and primitive mantle and old lower crust, and SCLM (subcontinental lithosphere mantle) and MORB fields (Figure 6). Carbonatites have strongly radiogenic Pb isotope composition due to the presence of U-bearing minerals, and show a wide scatter. Therefore, the plot shows their initial average Pb isotope composition estimated from 2-Ga isochron. All rocks show strongly unradiogenic initial Pb isotope composition with relatively narrow variations, forming a compact cluster between the depleted mantle [41] and primitive mantle [42] evolution curves in the  $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$  diagram. Exceptions are data points of ijolite T32 and alkaline gabbro T32a, which are displaced to the even more unradiogenic compositions likely owing to the disturbance of their isotope system. In the  $^{208}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$  diagram, data points fall either above the old lower crust curve or in the depleted mantle curve.



**Figure 6.** Initial isotope compositions of the rocks of the Tiksheozero complex in the  $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$  (a) and  $^{208}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$  (b) diagrams. Solid blue and green lines are lead isotope evolution curves for depleted upper mantle and old lower crust, respectively, after [41]. The violet solid line shows the lead evolution curve for primitive mantle after [42]. The Proterozoic ultramafic lamprophyres from the Yilgarn Craton [14] and West Greenland lamprophyres [43] are shown for comparison. The compositional field of the ancient SCLM (subcontinental lithospheric mantle) is from [43]. The compositional fields for MORB and OIB are from [44].



#### 4.3.3. Re-Os Isotope Composition

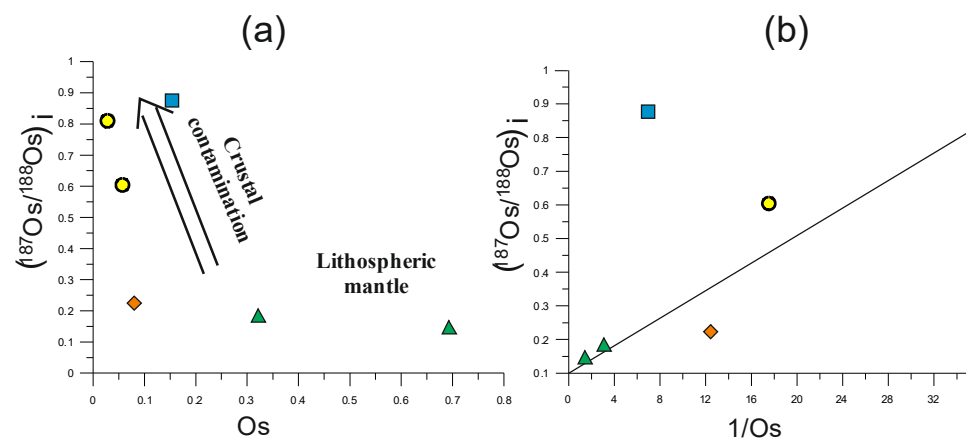
Re-Os isotopes data are given in Table 3. The Re concentrations are mainly less than 0.1 ppb, except for alkaline ultramafic rocks with 6.11 and 2.52 ppb Re. The Os concentrations vary from 0.057 in the most evolved rocks-syenites to 0.694 ppb in pyroxenite. Based on the initial  $^{187}\text{Os}/^{186}\text{Os}$  ratio and  $\gamma$ , the studied rocks also can be subdivided into two groups: (1) ultramafic rocks of the mildly alkaline series with ratios varying from 0.1471 to 0.1848 and  $\gamma$  values from 29 to 62; and (2) rocks of alkaline series with much more radiogenic initial values from 0.6064 to 0.8756 at  $\gamma$  from 432 to 672. The alkaline gabbro has an intermediate value of 0.2246 at  $\gamma = 98$ .

### 5. Discussion

#### 5.1. Crustal Contamination

The addition of small amounts of average continental crust (<10%) with Nd concentrations of 20 ppm, Sr 320 ppm, and Hf 3.7 ppm [45] would not have a strong effect on the contents of incompatible elements and Sr-Nd-Hf isotopic ratios for LILE- and LREE-rich rocks of alkaline series, but likely affects the isotope composition of LREE- and LILE-depleted rocks of the ultramafic rocks of the mildly alkaline series with low Nd contents. The mildly alkaline ultramafic-mafic rocks have low contents of lithophile elements. Correspondingly, their Sr, Nd, and Hf isotope compositions must be more sensitive to crustal contamination. However, their Sr isotope composition is unradiogenic, which coupled with slightly positive  $\epsilon\text{Nd}$  isotope composition suggests crustal contribution, which was likely insignificant for these isotope systems. At the same time, their DM model age is older than that of the alkaline series (2724 Ma). The rocks of the alkaline series have high contents of lithophile elements, which make them insensitive to minor crustal contamination. Correspondingly, they show, in general, slightly more radiogenic  $\epsilon\text{Nd}$  and, a younger average DM model age (2265 Ma). The older DM model age of the ultramafic rocks of the mildly alkaline series likely indicates some contribution of subcontinental lithospheric mantle. At the same time, practically all data points define a sufficiently compact cluster in the field of the Gremyakh-Vyrmes massif, which is close to the Tikshezero massif in age and composition. They also plot closely to the ferropicrites of the Materta subformation, the middle part of the fourth (1.98 Ga Pilgularvi) unit of Pechenga volcanosedimentary structure [18]. It was assumed that the ferropicritic melts close in composition to the Pechenga ferropicrites were parental melts for the ultrabasic rocks of the Gremyaha-Vyrmes massif [18]. At the same time, the most evolved rocks, syenites, have much more radiogenic Sr isotope compositions, which may indicate the more significant contamination of these rocks related to the involvement of high  $^{87}\text{Sr}/^{86}\text{Sr}$  components (likely, gneisses) in their genesis (Figure 4). The Nd-Sr data are coupled with Hf isotope data, which also show a limited variation range of weakly positive values, forming a compact cluster within the OIB field, except for the slightly negative crustal values for syenites (Figure 5). Note that almost coeval Phalaborwa massif was derived from a sharply distinct source, which is interpreted as metasomatized lithospheric mantle or an enriched asthenosphere component [40].

Minor amounts of crustal contamination can significantly change the Os isotopic composition of magma with low Os concentrations [46,47]. The low-Os rocks could be affected by crustal contamination during magma ascent, and, respectively, their  $^{187}\text{Os}/^{186}\text{Os}$  and PGE contents can be used to trace a small degree of crustal contamination. There is a covariation between  $^{187}\text{Os}/^{188}\text{Os}$  and  $1/\text{Os}$ , which suggests some crustal contamination for the studied rocks, which, as for Sm-Nd and Rb-Sr systems, was more expressed for syenites (Figure 7a). Jacupirangite T15 significantly deviates from the general trend, which is likely related to the recent Re addition. In the  $^{187}\text{Os}/^{188}\text{Os}$ –Os diagram (Figure 7b), data points of the ultramafic rocks of mildly alkaline series fall in the range of the lithospheric mantle, which is consistent with their older model age, whereas other data points follow a contamination trend.



**Figure 7.** Initial  $^{187}\text{Os}/^{188}\text{Os}$  vs.  $1/\text{Os}$  (a) and vs. Os concentrations (b) diagrams. In (b), the correlation curve was plotted excluding sample with the highest  $(^{187}\text{Os}/^{188}\text{Os})_i$ . For symbols, see Figure 4.

As was demonstrated for the Guli alkaline massif [48], minor crustal contribution can also be traced using Pb isotope ratios. It is known that U/Pb ratio in the mantle and lower crust is low, while the Th/Pb ratio in the lower crust is higher. In the diagram with thorogenic Pb ( $^{208}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ ), data points of the studied rocks, except for two foidolite samples, are displaced above the old lower crust evolution curve (Figure 6), which may serve as the indication of the lower crustal contamination.

### 5.2. Magma Sources

It is seen that whole-rock isotope compositions of the Tiksheozero massif, except for Re–Os composition, show a narrow range and form compact clusters in most diagrams, which indicates their origin from a common or similar source. In two samples with the least radiogenic compositions in the Pb isotope diagram, isotope systems were likely disturbed. In the diagram  $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$  (Figure 6a), data points fall between the lead evolution curves for the primitive and depleted mantle, in the field of subcontinental lithospheric mantle, in the vicinity of the Greenland lamprophyres with very similar age. The close position is occupied by the Australian lamprophyres of the same age. As mentioned above, it was argued that these lamprophyres were derived from subcontinental lithosphere mantle. This suggests some contribution of lithospheric mantle in the studied rocks. The contribution of the subcontinental lithospheric mantle, especially for the ultramafic-mafic rocks, is also seen in Figure 7b.

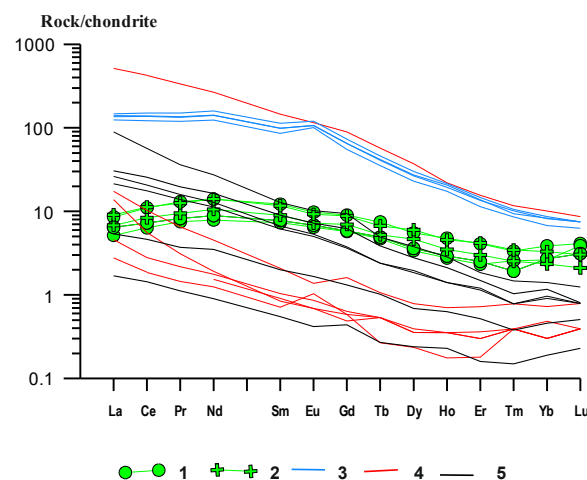
Based on the classification of osmium isotope reservoirs [49], the rocks of the mildly alkaline ultramafic–mafic series correspond to the long-term rhenium-enriched ocean island basalt (OIB)-type plume mantle with  $\gamma\text{Os}$  values from  $-2$  to  $+60$ . Alkaline rocks have much more radiogenic Os compositions, which correspond to the contribution of continental or oceanic crustal reservoirs with  $\gamma > 400$ . The OIB-type source for all rocks, except for syenites, is also determined from Figure 5.

The initial  $^{187}\text{Os}/^{188}\text{Os}$  values vary from 0.14 to 0.81. All these samples are more radiogenic than primitive upper mantle (present day  $^{187}\text{Os}/^{188}\text{Os} = 0.1296$  [50]) and distinct from the depleted MORB mantle ( $^{187}\text{Os}/^{188}\text{Os} = 0.122$ – $0.127$  [51]). The  $^{187}\text{Os}/^{188}\text{Os}$  is within the OIB range of 0.12–0.21 [52,53] for ultramafic rocks and is much more radiogenic in the alkaline rocks.

### 5.3. Relations between Rocks of the Mafic–Ultramafic and Alkaline Series

The relationships between ultramafic-mafic rocks of the mildly alkaline and alkaline series within a single ultramafic–mafic–alkaline complex could be spatial or genetic. For instance, it was demonstrated that the alkaline-carbonatite complex of Jacupiranga (Brazil) was derived from two different but alkaline melts: the dunite-gabbro-syenite massif

was generated from OIB-type alkaline melt, while the clinopyroxenite–ijolite plutonic body was produced from a nephelinite melt [8]. The same model was proposed for the Gremyakha–Vyrmes massif [18], where ultramafic–mafic rocks were argued to have been derived from a ferropicritic melt and ultramafic alkaline rocks from nephelinite melt. The study of the Guli massif [7,54,55] showed that dunites are genetically related to the alkaline rocks, representing their cumulates. However, it is noteworthy that, in all the cases, parental magmas had an alkaline nature. The Tikshezero massif sharply differs from these two massifs in that its ultramafic core and surrounding rocks are ascribed to the rocks of the mildly alkaline series, having no alkaline affinity. It is also very unlikely that the ultramafic–mafic rocks (dunites, wehrlites, pyroxenites) are cumulates to foidolites, alkaline gabbro, and syenites. The ultramafic–mafic rocks of the mildly alkaline series have LREE-depleted pattern and moderately to weakly fractionated HREEs, whereas all rocks of the alkaline series have high to moderate LREE enrichments and usually steeper HREE fractionation (Figure 2). Rocks representing a single fractionation series derived from a common source usually have parallel REE patterns. Of course, the LREE enrichment in alkaline rocks would be caused by significant crustal contamination, but isotope studies did not reveal significant crustal contribution. It is clearly seen that ultramafic cumulates of all aforementioned complexes are LREE enriched (Figure 8), whereas ultramafic cumulates of the Tikshezero massif are LREE depleted. In addition, ultramafic rocks in all mentioned massifs usually contain intercumulus biotite, ilmenite, apatite, perovskite in variable amounts, whereas the ultramafic rocks of the Tikshezero massif contain none these minerals. This suggests that the mafic–ultramafic rocks likely are not related to the rocks of the alkaline series through fractional crystallization of a common primary melt, and were not derivatives of an alkaline magma.



**Figure 8.** Chondrite-normalized REE pattern for ultramafic rocks of the mildly alkaline series of the Tikshezero massif compared to the ultramafic rocks of the Gremyakha–Vyrmes [18]; Guli [54,55], and Jacupiranga [8] alkaline–ultramafic–carbonatite massifs. Normalizing values are from [36]. Symbols: Ultramafic rocks of the mildly alkaline series of the Tikshezero massif: (1) wehrlite, (2) peridotite; (3) Gremyakha–Vyrmes massif; (4) Jacupiranga massif; (5) Guli massif.

At the same time, it is remarkable that the ultramafic–mafic and alkaline rocks overlap in their isotope compositions practically for all studied isotope systems. This suggests that their melts were generated from a common mantle source, but under different conditions.

#### 5.4. Models

Since geological relations between rocks of the alkaline and mildly alkaline series are not observed, we propose two alternative models to explain the origin of silicate rocks of this complex, which are not related by differentiation from a common melt, but were produced from the same mantle source.

- (1) It is generally accepted that magma generation in the mantle plume heads is related to decompressional adiabatic melting. When mantle plumes ascend, as pressure decreases, the temperature eventually exceeds solidus temperature, triggering melting. It is suggested that melting occurred in three stages and was controlled by a temperature decrease as the plume head cooled and by the content of fluid components. The first high-temperature stage caused large-scale adiabatic melting of the plume protolith with generation of basalts of the mildly alkaline series. With further cooling, the temperature gradually decreased and melting was terminated. The resumption of melting was caused by the influx of low-temperature fluids from the plume interior, which decreased solidus temperature and caused melting at lower temperatures. This stage is responsible for the formation of alkaline melts. At the third stage, the decompressional adiabatic melting likely gave way to a local fluid-assisted melting, which was caused by metasomatic reworking of already solidified but hot material. Residual fluids involved in this melting were released during the solidification of the mantle plume head. The traces of such melting are frequently preserved as “melt-pockets” in mantle spinel lherzolite xenoliths from basalts and basanites [56–58].
- (2) An alternative model suggests a successive two-stage melting of a plume. During the first stage, the low-degree melting of an upwelling plume at great depths caused the formation of alkaline rocks, with the extraction of incompatible elements from the source. Further plume ascent and pressure decrease resulted in the higher-degree melting of the same source already depleted in incompatible elements and, respectively, the formation of the depleted ultramafic-mafic series. These processes were likely accompanied by some interaction with the lithospheric mantle, as recorded in the Pb and Os isotope systems. The same sequence of events is interpreted at the early magmatic evolution in the plume-related Parana-Etendeka province, where the low-degree melting was triggered by the initial impact of the Tristan plume and produced alkaline magmatism, which was followed by tholeiitic magmatism some 6 Ma later [59].

## 6. Conclusions

- (1) Based on our petrographic and trace-element study, the silicate rocks of the Tikshezero Complex can be subdivided into two large groups: ultramafic–mafic series depleted in REE and other incompatible elements and rocks of alkaline series enriched in these elements.
- (2) The majority of rocks have mainly juvenile isotope signatures evident from unradiogenic Sr and Pb isotope compositions and slightly positive initial  $\epsilon_{\text{Nd}}$  and  $\epsilon_{\text{Hf}}$  values and were likely derived from a primitive OIB-type mantle source with a possible contribution of subcontinental lithosphere mantle.
- (3) Pb and Os isotopic data indicate that the studied rocks experienced limited but detectable crustal contamination en route to the surface.
- (4) Obtained data indicate that the mafic–ultramafic rocks of the mildly alkaline series are not comagmatic to the alkaline rocks of the complex. The incompatible element enrichment in the alkaline rocks and depletion in the ultramafic-mafic rocks of the mildly alkaline series coupled with isotope evidence for insignificant crustal contamination are consistent with their derivation from different parental melts.
- (5) The rocks, with few exceptions, fall in a narrow range of initial Sr, Nd, Hf, and Pb isotope composition and define compact clusters in  $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $\epsilon_{\text{Nd}}$ – $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon_{\text{Hf}}$ – $\epsilon_{\text{Nd}}$  isotope diagrams, which suggests their derivation from a similar, or more likely, a common mantle source, but at different conditions.
- (6) Two alternative models are proposed to explain the origin of the silicate rocks of the Tikshezero Complex. The second model is preferred, because it is highly consistent with geochemical and isotope data.

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