Rippite, $K_2(Nb,Ti)_2(Si_4O_{12})(O,F)_2$, a New K-Nb-Cyclosilicate from Chuktukon Carbonatite Massif, Chadobets Upland, Krasnoyarsk Territory, Russia

Victor V. Sharygin 1,2,3,* 1, Anna G. Doroshkevich 1,4, Yurii V. Seryotkin 1,3, Nikolai S. Karmanov 1, Elena V. Belogub 5,6, Tatyana N. Moroz 1, Elena N. Nigmatulina 1, Alexander P. Yelisseyev 1, Vitalii N. Vedeniapin 1 and Igor N. Kupriyanov 1,3

1 V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of the RAS, 3 Acad. Koptyuga pr., 630090 Novosibirsk, Russia; doroshkevich@igm.nsc.ru (A.D.); yuvs@igm.nsc.ru (Y.V.S.); krm@igm.nsc.ru (N.S.K.); moroz@igm.nsc.ru (T.N.M.); helena@igm.nsc.ru (E.N.N.); eliseev@igm.nsc.ru (A.P.Y.); vvn@igm.nsc.ru (V.N.V.); spectra@igm.nsc.ru (I.N.K.)
2 ExtraTerra Consortium, Institute of Physics and Technology, Ural Federal University, 19 Mira str., 620002 Ekaterinburg, Russia
3 Department of Geology and Geophysics, Novosibirsk State University, 1 Pirogov str., 630090 Novosibirsk, Russia
4 Geological Institute, Siberian Branch of the RAS, 6a Sakhyanova str., 670047 Ulan-Ude, Russia
5 South Urals Federal Research Center of Mineralogy and Geoecology, Uralian Branch of the RAS, 456317 Miass, Russia; belogub@mineralogy.ru
6 South Urals Federal Research Center of Mineralogy and Geoecology, Uralian Branch of the RAS, 456300 Miass, Russia

* Correspondence: sharygin@igm.nsc.ru; Tel.: +7-383-330-80-84

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Abstract: Rippite $K_2(Nb,Ti)_2(Si_4O_{12})(O,F)_2$, a new K-Nb-cyclosilicate, has been discovered in calcio-carbonatites from the Chukotukon massif (Chadobets upland, SW Siberian Platform, Krasnoyarsk Territory, Russia). It was found in a primary mineral assemblage, which also includes calcite, fluorocalciopyrochlore, tainiolite, fluorapatite, fluorite, Nb-rich rutile, olekminskite, K-feldspar, Fe-Mn–dolomite and quartz. Goethite, francolite (Sr-rich carbonate–fluorapatite) and psilomelane (romanëchite ± hollandite) aggregates as well as barite, monazite-(Ce), parisite-(Ce), synchysite-(Ce) and Sr-Ba-Pb-rich keno/hydropyrochlore are related to a stage of metasomatic (hydrothermal) alteration of carbonatites. The calcite–dolomite coexistence assumes crystallization temperature near 837 °C for the primary carbonatite paragenesis. Rippite is tetragonal: $P4bm$, $a = 8.73885(16)$, $c = 8.1277(2)$ Å, $V = 620.69(2)$ Å$^3$, $Z = 2$. It is closely identical in the structure and cell parameters to synthetic $K_2Nb_2(Si_4O_{12})O_2$ (or KNbSi$_2$O$_7$). Similar to synthetic phase, the mineral has nonlinear properties. Some optical and physical properties for rippite are: colorless; Mohs’ hardness—4–5; cleavage—(001); density (meas.)—3.17(2) g/cm$^3$; density (calc.)—3.198 g/cm$^3$; optically uniaxial (+); $\omega = 1.737-1.739$; $\epsilon = 1.747$ (589 nm). The empirical formula of the holotype rippite (mean of 120 analyses) is $K_2[Nb_{1.09}Ti_{0.09}Zr_{0.01}][Si_{4}O_{12}](O_{1.75}OH_{0.12}F_{0.01})$. Majority of rippite prismatic crystals are weakly zoned and show Ti-poor composition K$_2$O$^{5+}$ + O$^{2-}$ → (Ti,Zr)$^{4+}$ + F$^{1-}$. The content of a hypothetical end-member $K_2Ti_2[Si_4O_{12}]F_2$ may be up to 17 mol. % Rippite represents a new structural type among $[Si_4O_{12}]$-cyclosilicates because of specific type of connection of the octahedral...
chains and [Si₄O₁₂]⁶⁻ rings. In structural and chemical aspects it seems to be in close with the labuntsovite-supergroup minerals, namely with vuoriyarvite-(K), K₂(Nb,Ti)₂(Si₄O₁₂)(O,OH)₂·4H₂O.

**Keywords:** rippite; new mineral; K-Nb-cyclosilicate; synthetic K₂Nb₂(Si₄O₁₂)O₂; calciocarbonatite; Chuktukon massif; Chadobets upland; Krasnoyarsk Territory

1. **Introduction**

The natural analog of the tetragonal synthetic phase KNbSi₂O₇, a new structural type among natural K-Nb-cyclosilicates, named rippite, was discovered in calciocarbonatites of the Chuktukon massif, Chadobets upland, SW Siberian Platform, Krasnoyarsk Territory, Russia [1,2].

Synthetic K₂Nb₂(Si₄O₁₂)O₂ (or KNbSi₂O₇) is actively studied since 1990 [3]. The melting point for K₂Nb₂(Si₄O₁₂)O₂ is 1180 °C. No phase transition was found in K₂Nb₂(Si₄O₁₂)O₂ between room temperature and melting point [4]. It is rather inert and chemically stable and is not dissolved in inorganic acids except HF. All studies on KNbSi₂O₇ are mainly focused on its nonlinear optical property [3–15]. Single crystals, ceramics, glass-ceramics, and glass of KNbSi₂O₇ and similar compositions in the systems SiO₂–GeO₂–Nb₂O₅–K₂O have been fabricated [3–12]. The synthesis of glasses and glass-ceramics in the system SiO₂–Nb₂O₅–K₂O has shown that K₂Nb₂(Si₄O₁₂)O₂ may be appeared in the 510–735 °C temperature range in glass/melt [4,6,8–10,13,14]. The KNbSi₂O₇ phase has very high optical nonlinearity with its second harmonic generation (SHG) signal greater than that for α-quartz [14,15]. The study of ferroelectric-dielectric properties has shown that K₂Nb₂(Si₄O₁₂)O₂ is a ferroelectric material with low dielectric permittivity range [4,14]. The isostructural compound K₂Ta₂(Si₄O₁₂)O₂, which may has nonlinear properties, was also synthesized [16].

Rippite, K₂(Nb,Ti)₂(Si₄O₁₂)O(O,F), was approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) as a new mineral species in June 2016 (IMA 2016-025) [1]. The mineral is named in the honor of German Samuilovich Ripp (1935 year of birth, Ulan-Ude, Buryatia, Russia). He is a leading expert on carbonatite petrogenesis, including carbonatite magmatic activity in Eastern Siberia, carbonatite mineralogy, geochemistry and stable isotope geochemistry and rare metal mineralization associated with carbonatites. He has performed detailed studies for carbonatite occurrences in Transbaikalia (Yuzhnoe, Khaluta, Arshan, Pogranichnoe, Veseloe), Eastern Sayan (Belaya Zima) and Mongolia (Mushugai-Khuduk) [17–28]. The holotype specimen of rippite-containing carbonatite from drillhole N 546 (193.5 m deep, author number 546–193.5) of the Chuktukon massif, Siberia, Russia has been deposited in the Central Siberian Geological Museum at the V.S. Sobolev Institute of Geology and Mineralogy (IGM), Siberian Branch of the RAS, Novosibirsk 630090, Russia, catalogue number XIII-347/1).

In this paper, we provide a detailed description of rippite. Some data on rippite-bearing calciocarbonatites of the Chuktukon massif were reported in the previous publications [1,2,9–35].

2. **Brief Geological Background for the Chuktukon Massif**

The Chadobets alkaline complex is located within the Chadobets upland (basin of the Chadobets River, Krasnoyarsk Territory, Russia) at the southwestern part of the Siberian craton (Figure 1) [36]. The upland is 2000 km² in size and occurs at the intersection of two Neoproterozoic grabens being a part of the Angara-Kotuy large-scale rift system [29,37–39]. The Chadobets alkaline ultramafic carbonatite complex is conventionally subdivided into the Chuktukon alkaline ultramafic carbonatite massif (southern part of the upland) and the Terina alkaline massif (silicate rocks, northern part of the upland). In addition, the Chadobets upland also includes dikes of ultramafic lamprophyres (aillikite–damtjernite series). Carbonatites and their weathering species of the Chuktukon massif host major reserves of Nb and REE [40–42]. The U-Pb and Ar-Ar ages for the Chadobets ultramafic alkaline rocks and
carbonatites are between 252 and 231 Ma [30,31,43]. For comparison, the Ilbokich aillikite–damtjernite lamprophyre series, which is located nearby the Chadobets upland, has 392 Ma age [43–45].

The detailed geology of the Chadobets alkaline ultramafic carbonatite complex was described by Kirichenko et al. [36]. The sequence of the Chukutkon rocks, from the earliest to the youngest, was established by field observations (drillholes description) and comprises alkaline ultramafic rocks, calciocarbonatites and, finally, damtjernites [36]. Alkaline ultramafic rocks (aillikites–damtjernites, olivine melilitites, peridotites and others) of the first emplacement phase form small plugs (up to 1–1.5 km$^2$), dykes and sills ranging in thickness up to 100–120 m. Carbonatites also form small plugs (up to 4 km$^2$), dykes and sills (up to 20 m thick). Damtjernites are presented by pipes (up to 0.5 km$^2$), crosscutting early phases of alkaline ultramafic rocks and carbonatites and typically containing their xenoliths and fragments of the country sedimentary rocks. All rocks of the Chukutkon massif are altered in different degree by hydrothermal and weathering processes [36]. The detailed petrography and mineralogy of the Chadobets alkaline rocks were summarized in [29,30,32,36,43,46,47].

3. Analytical Methods

Double-polished sections of calciocarbonatites (~50–100 µm in thickness) and individual rippite grains from the Chukutkon massif were used for optical examination in transmitted and reflected light and for other studies. The individual rippite crystals were selected from residue after dissolution of carbonatite samples in the diluted HCl or acetic acid.

The identification of all minerals in the Chukutkon calciocarbonatites was based on energy-dispersive spectra (EDS), back-scattered electron (BSE) images and elemental mapping (EDS system), using a TESCAN MIRA 3MLU scanning electron microscope equipped with an INCA Energy 450 XMax 80 microanalysis system (Oxford Instruments Ltd., Abingdon, UK) at the IGM, Novosibirsk, Russia. The SEM-EDS analyses of minerals were operated at an accelerating voltage of 20 kV and a probe current of 1 nA in high-vacuum mode and at an accumulation time of 20–40 s.
The synthetic compounds, pure metals and minerals were used as reference standards for the elements: SiO$_2$ (Si and O), Al$_2$O$_3$ (Al), diopside (Mg and Ca), albite (Na), orthoclase (K), Ca$_2$P$_2$O$_7$ (P), BaF$_2$ (Ba and F), Cr$_2$O$_3$ (Cr), Cs$_2$Re$_2$Cl$_6$ (Cl), LaPO$_4$ (La), CePO$_4$ (Ce), SrF$_2$ (Sr), metallic Nb, Ti, Ta, Zr, Fe, Mn, Zn and V. Matrix effects were corrected using the XPP algorithm, implemented in the software of the microanalysis system. Metallc Co served for quantitative optimization (normalization to probe current and energy calibration of the spectrometer).

Electron microprobe analyses (EMPA-WDS) of rippite and related carbonatite minerals were done at the IGM, using a JEOL JXA-8100 electron microprobe (Jeol Ltd., Tokyo, Japan). Grains (sizes >5 μm) previously analyzed by SEM-EDS were selected for this purpose. The operating conditions were as follows: beam diameter of 1-2 μm, accelerating voltage of 20 kV and a beam current of 10–15 nA, counting time of 10 (5 + 5) s (for most elements). Accumulation time for analyzing of F (using LDE crystal) in rippite was 40 s (20 s—counting of background; 20 s—counting of peak for F), detection limit for F was 308 ppm (0.03 wt %). Synthetic fluorophogopite (Si, Al, F, Mg), orthoclase (K), LiNbO$_3$ (Nb), zircon (Zr), rutile (Ti), Ta$_2$O$_5$ (Ta), diopside (Ca), Fe-rich pyrope (Fe), Ba-silicate glass (Ba), Sr-silicate glass (Sr) and albite (Na) were used as standards during measuring. The precision of analysis for major elements was better than 2% relative. The detection limits for elements were (in ppm): Si—181; Ti—132; Nb—295; Zr—405; Ta—400; Al—168; Fe—28; Mg—188; Ca—123; Sr—844; Na—128; K—115.

Data reduction was performed using a PAP routine (Pouchou & Pichoir, 1985). Overlap corrections were done for the following elements: SiKα—SrLa, SiKα—TaMa and FeLa—FKa.

The contents of some light trace elements (Be, Li, B), F and H$_2$O in rippite of the Chuktukon carbonatite were analyzed by secondary-ion mass spectrometry (SIMS) on a Cameca IMS-4f ion probe at the Analytical Centre of the Yaroslavl Branch of the Institute of Physics and Technology (YBIPT), Yaroslavl, Russia. For the analysis, grains larger than 20 μm and previously analyzed by EMPA-WDS and SEM-EDS were selected. Analysis of trace elements was carried out by the energy filter method; the operating conditions were as follows: primary O$^-$ beam—20 μm, I = 2–4 nA, energy offset—100 eV, and energy slit—50 eV. Concentrations of elements were determined from the ratios of their isotopes to $^{30}$Si, using calibration curves for standard samples [48]. The hydrogen content was determined from the $^1$H mass together with trace elements. Low background content of H$_2$O (0.03 wt %) in the mass spectrometer was achieved by storing the samples for 24 h in high-vacuum. The NIST SRM610 glass was used as external standard [49].

The trace element composition of rippite was also determined by laser ablation ICP-MS at the Friedrich-Alexander University, Erlangen-Nürnberg, Germany. The instrumentation includes an Agilent 7500ii inductively coupled plasma mass spectrometer combined with an ESI New Wave UP193-FX laser ablation system. Samples were ablated at plasma power of 1350 W in an atmosphere of pure He (0.65 L/min) and Ar (1.10 L/min) as gas carriers. In addition, Ar was used as the plasma (14.9 L/min) and auxiliary gas (0.9 L/min) plasma immediately after the ablation cell. Analyses were conducted in spot mode, each analysis lasting 80 s, including 20 s of background acquisition (laser off) followed by 60 s of ablation. A beam 10–50 μm in diameter (2.7 J/cm$^2$) with a laser frequency of 16 Hz was used. The NIST SRM610 standard [49] was used to calibrate the weights of determined elements. The contents of minor elements were compared to those measured on an electron microprobe. Trace element concentrations were calculated with the GLITTER software [50].

The Raman spectra for rippite were recorded on a LabRAM HR 800 mm (HORIBA Scientific Ltd., Kyoto, Japan) spectrometer equipped with a 1024 pixel LN/CCD detector and coupled to an Olympus BX40 confocal microscope (objective ×100) at the IGM. A semiconductor laser emitting at 514.5 nm with a nominal power output of 50 mW was used for excitation. In each case, a 200 μm confocal hole and integrated. Most spectra were recorded between 100 and 1200 cm$^{-1}$, and some spectra were made for the 100–4000 cm$^{-1}$ and 3000–4000 cm$^{-1}$ region. The monochromator was calibrated using the 520.7 cm$^{-1}$ Raman line of elemental Si. A Bruker Vertex 70 FTIR spectrometer equipped with a Hyperion 2000 microscope at the IGM was used for measurements of rippite in the IR region (powder KBr pellets and individual crystals putted on KBr plate). Pellets for infrared absorbance measurements
were obtained by pressing a mixture of about 1 mg of powdered rippite diluted in 400 mg of dried KBr. Spectra over 4000–370 cm\(^{-1}\) range were obtained by of 23 scans with a resolution of 2 cm\(^{-1}\). Interferences from KBr and air were cancelled by subtracting their spectra from the sample spectrum.

The second harmonic generation test (non-linear properties) were provided for rippite using diode pumped solid-state laser DTL-399QT (laser YLF:Nd\(^{3+}\); pulse duration—7–10 ns; energy—100 microjoule; focusing with 50 mm lens; basic frequency 1052 nm was separated by IRG-3 filter) at the IGM. A JSM 6510 LV scanning microscope equipped with Gatan Chrome CL 4UV at the IGM was used for the cathodoluminescence (CL) images (\(V = 10\) kV, quality 1024 \(\times\) 1024) of rippite.

Crystallographic studies of rippite were done at Novosibirsk State University, Novosibirsk, Russia. X-ray powder diffraction data were collected using Stoe IPDS 2T diffractometer (MoK\(\alpha\), \(\lambda = 0.71073\) Å, Gandolfi geometry). Single-crystal X-ray studies were carried out using an Oxford Diffraction Xcalibur Gemini diffractometer (MoK\(\alpha\), \(\lambda = 0.71073\) Å).

The main results are presented in Figures 1–15 and Tables 1–9. Some data are given in Supplementary section (Table S1 and Figures S1–S7).

![Figure 2](image_url)

**Figure 2.** General view and mineral relations for calciocarbonatite from the Chuktukon massif (holotype sample for rippite, 546–193.5), ordinary light and back-scattered electron (BSE) images. Symbols: “Goethite”, Gt—aggregate of goethite and other Fe-oxy/hydroxides; “Francolite”, Ap—Sr-rich carbonate-fluorapatite; “Psilomelane”, Psl—psilomelane aggregate (romanèchite + hollandite + others); Cc—calcite; Mnz—monazite-(Ce); Tai—tainiolite; Brt—barite; Rip—rippite; Pcl—fluorcalciopyrochlore; Dol—Fe–Mn–rich dolomite; Rt—rutile (Nb\(_2\)O\(_5\)—2.2–14.7 wt %; Fe\(_2\)O\(_3\)—0.3–3.9 wt %); Str—strontianite; Kfs—K-feldspar; Qtz—quartz; Zeol—K-Ca-zeolite (?).
Figure 3. Discrete crystal fragments and intergrowths of rippite from the Chuktukon calciocarbonatite, ordinary light and BSE images (holotype sample 546–193.5). The rock fragments were partially or completely dissolved by diluted HCl acid. Some faces of rippite crystals are partially covered by quartz.

Figure 4. Relations between fluorcalciopyrochlore and rippite in the Chuktukon calciocarbonatites, BSE images. Symbols: Rip—rippite; Pcl—fluorcalciopyrochlore; HPcl—Ba-Sr-Pb-rich hydro-/kenopyrochlore; Cpx—Ca-Na-rich clinopyroxene; Cc—calcite; Ru—rutile; Tai—tainiolite; Qtz—quartz; Brt—barite. For some details see Figures S1 and S2.
**Figure 5.** Rippite crystals partially resorbed by quartz (BSE images) and elemental maps for area with Ti-rich composition (holotype sample 546-193.5). Rip—rippite; Qtz—quartz.

**Figure 6.** Variations of ZrO$_2$ versus Nb$_2$O$_5$ and TiO$_2$ in rippite (in wt %).
Figure 7. Compositional variations of rippite (in apfu).
Figure 8. Cathodoluminescence images of rippite crystals.

Figure 9. The short-wave edge of the rippite transmission spectra at 300 (curve 1) and 80 K (curve 2). In the insert: the Tauc plot for the case when the edge shape is determined by direct allowed electronic transitions. The band gap $E_g$ for rippite is 4.37 and 4.50 eV at 300 and 80 K, respectively.
Figure 10. IR spectrum of rippite in the 350–1700 and 3000–3700 cm$^{-1}$ ranges (powder KBr pellet).

Figure 11. FTIR oriented spectra of rippite in the 3000–3800 cm$^{-1}$ range (single crystal on KBr plate).
Figure 12. Oriented Raman spectra for single crystal of rippite.

Figure 13. Raman spectra for a zoned rippite crystal showing dependence of some bands on chemical composition. For some details see Figures 5 and 8 and Table 2 and Table S1.
Figure 14. The crystal structure of rippite in (001) (a) and (110) (b) projections. Large green balls—K; small red balls—O.

Figure 15. The crystal structure of the synthetic K$_2$(NbO)$_2$Si$_4$O$_{12}$ (KNbSi$_2$O$_7$) [15].
Table 1. List of minerals found in the Chuktukon calciocarbonatites.

| Mineral                              | Formula                        | Mineral                              | Formula                        |
|--------------------------------------|--------------------------------|--------------------------------------|--------------------------------|
| Pyrite                               | FeS₂                           | Ancylite-(Ce)                        | (Ce,La,Nd)Sr(CO₃)₂(OH)·H₂O     |
| Fluorite                             | CaF₂                           | Daqingshanhite-(Ce)                  | (Sr, Ca, Ba, Sr, Ca, La) CO₃(S, O, F)×₂ |
| Neighborite                          | NaMgF₃                         | Quartz                               | SiO₂                          |
| Parascandolaite                      | KMgF₃                         | Rutile                               | TiO₂                          |
| Fluorapatite                         | Ca₅(PO₄)₂F                    | Baddeleyite                          | ZrO₂                          |
| Carbonate-fluorapatite               | (Ca,Sr,Na)₃(PO₄,CO₃)₃F        | Thorianite                           | ThO₂                          |
| Monazite-(Ce)                        | (Ce,La,Nd)PO₄                  | Hematite                             | Fe₂O₃                         |
| Ferrohagendorfite                    | NaCaFe₂⁺(PO₄)₃(OH)             | “Nb-Fe³⁺-zirconolite”                | (Ca, Na)₂(Nb, Ti)₂O₆F         |
| Florencite-(Ce)                      | (Na,REE)Ca₁.₅(Sr, Ba)₃(PO₄)(OH) | Fluorocalcio-pyrochlore              |                               |
| “Sr-Ba-Ca-REE-phosphate”             | (Na,REE)Ca₁.₅(Sr, Ba)₃(PO₄)(OH) | Hydroxykenopyrochlore                |                               |
| “Na-Ca-Fe-Mn-phosphate”              | Na₄.₈Ca₃(Fe, Mn)₃(PO₄)₄        | Hydroxyplumbopyrochlore              |                               |
| “Na-REE-Ca-Sr-Ba-phosphate”          | Na₁.₆REE₀.₆(Ba, Sr, Ca)₀.₆(PO₄)O |                               |                               |
| “Ba-Sr-Ca-REE-H₂O-aluminophosphate”  | (Ba, Sr, Ca, REE)Al(PO₄) nH₂O  |                               |                               |
| Churchite-(Y)                        | Y(PO₄)₂ 2H₂O                    | Goethite                             | α-FeOOH                        |
| Anhydrite                            | CaSO₄                           | “Hydrogoethite”                      | 3Fe₂O₃·4H₂O                    |
| Barite                               | BaSO₄                           | Bernalite                            | Fe(OH)₃ nH₂O                   |
| Celestine                            | SrSO₄                           | Ferrihydrite                         | Fe³⁺/Fe⁴⁺O₁₄(OH)               |
| Calcite                              | CaCO₃                           | Hollandite                           | Ba(Mn⁴⁺⁺₈Mn³⁺⁺₂)O₁₆            |
| Strontianite                         | SrCO₃                           | Romanechite                          | (Ba, H₂O)₂(Mn⁴⁺⁺, Mn³⁺⁺)O₁₀    |
| Dolomite                             | CaMg₃(CO₃)₂                    | K-feldspar                           | KAlSi₃O₈                      |
| Ankerite                             | Ca(Fe²⁺⁺₃⁺, Mg, Mn)(CO₃)₂       | Diopside                             | CaMg₃Si₂O₆                    |
| Skeletalite                          | Sr(Sr, Ca, Ba, Ca)CO₃₂          | Aegirine                             | NaFe³⁺⁺Si₂O₆                   |
| Nyereite                             | Na₂Ca(CO₃)₂                    | Tainiolite                           | KMg₂Li(Si₃O₁₀)F₂               |
| Shortite                             | Na₂Ca₂(CO₃)₃                   | Rippite                              | K₂(Nb, Ti)₂(Si₄O₁₂)O(O, F)     |
| Synchysite-(Ce)                      | Ca(Ce, La, Nd)(CO₃)₂F          | Zircon                               | ZrSiO₄                        |
| Parisite-(Ce)                        | Ca(Ce, La, Nd)(CO₃)₂F          | Thorite                              | ThSiO₄                        |
| Burbankite                           | (Na, Ca)₃(Sr, Ba, Ce)₃(CO₃)₅   | Kaolinite                            | Al₃(Si₄O₁₂)(OH)₄               |
| Khanneshite                          | (Na, Ca)₃(Sr, Sr, Ce, Ca)₃(CO₃)₅ | “K-Ca-zeolite”                       | K₃Ca₅(Al₃Si₆O₂₀)·7·8H₂O      |

New author’s data and data from [1, 2, 29–35] were used. The names in inverted commas mean poorly identified phases.
Table 2. Chemical composition (EMPA-WDS, wt %) of rippite from the Chuktukon calciocarbonatite (holotype sample 546-193.5), Chadobets upland, Siberia, Russia.

| Component | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-----------|---|---|---|---|---|---|---|---|---|
| Grain Nb3-1 | Nb3-18 | Nb3-13 | Nb3-23 | Nb4-28 |
| Position c | or | c | m | r | or | or | c | r | c | r | inc | Ideal |
| n          | 120 | sd | Range  | 22 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 5 |
| SiO₂       | 40.28 | 0.23 | 40.07–41.02 | 40.17 | 40.07 | 40.92 | 40.17 | 40.26 | 40.54 | 40.63 | 41.02 | 40.25 | 40.34 | 40.09 | 40.21 | 40.13 | 40.23 | 40.27 | 40.03 |
| TiO₂       | 1.11 | 0.06 | 0.15–4.41 | 0.52 | 0.15 | 4.05 | 0.58 | 1.18 | 2.01 | 3.02 | 4.41 | 0.45 | 1.39 | 0.26 | 0.74 | 0.57 | 0.82 | 0.91 | 0.00 |
| ZrO₂       | 0.37 | 0.26 | 0.05–1.28 | 0.17 | 0.26 | 0.35 | 0.85 | 0.68 | 0.82 | 0.61 | 0.14 | 0.42 | 0.96 | 0.26 | 0.63 | 0.33 | 0.80 | 0.26 |
| Nb₂O₅      | 42.30 | 1.61 | 38.23–44.00 | 43.37 | 43.81 | 38.20 | 42.51 | 41.81 | 40.61 | 39.28 | 37.87 | 43.30 | 41.29 | 42.55 | 43.06 | 42.25 | 42.72 | 44.28 |
| Na₂O       | 0.01 | 0.02 | 0.00–0.06 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 | 0.02 | 0.02 | 0.03 |
| K₂O        | 15.77 | 0.09 | 15.68–16.07 | 15.72 | 15.71 | 16.03 | 15.74 | 15.77 | 15.89 | 15.86 | 16.07 | 15.74 | 15.80 | 15.71 | 15.76 | 15.71 | 15.74 | 15.69 |
| F           | 0.32 | 0.22 | 0.09–0.95 | 0.13 | 0.15 | 0.91 | 0.25 | 0.37 | 0.56 | 0.69 | 0.95 | 0.15 | 0.50 | 0.19 | 0.38 | 0.30 | 0.32 | 0.28 | 0.00 |
| H₂O        | 0.18 | 0.05 | 0.12–0.26 | 0.18 | 0.20 | 100.34 | 100.15 | 100.46 | 100.10 | 100.07 | 100.43 | 100.13 | 100.46 | 100.33 | 100.28 | 100.12 | 100.27 | 100.12 | 100.18 | 100.20 | 100.00 |
| O-F        | 0.01 | 0.02 | 0.00–0.06 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Sum        | 100.20 | 0.20 | 100.09 | 100.07 | 99.99 | 99.92 | 100.19 | 99.84 | 100.06 | 100.27 | 100.07 | 100.04 | 100.11 | 99.99 | 100.08 | 100.00 | 100.00 | 100.00 | 100.00 |

Formula based on 8 cations:

| Si        | 4.000 |
| Ti        | 0.083 |
| Zr        | 0.018 |
| Nb        | 1.899 |
| K + Na    | 2.000 |
| F         | 0.101 |
| OH        | 0.118 |

End–members, mol. %:

| K₂Nb₂(SiO₄)₂O₂ | 0.95 |
| K₂Ti₂(SiO₄)₂(F,OH)₂ | 0.05 |

Notes: n—number of analyses; Ta₂O₅, BaO, SrO, FeO, Al₂O₃, MgO, MnO and CaO are below detection limits (<0.005 wt %). 1—average composition of holotype rippite; 2—average composition for crystals used for SIMS (determination of H₂O and F); 3–7—individual crystals (see Figures 5, 8 and 12, Figures S6 and S7); 8 (inc)—from secondary inclusions in fluorcalcipyrochlore (Figure 4); 9—ideal composition K₂Nb₂(SiO₄)₂O₂; c, m, r and or—core, middle, rim and outermost rim of crystals.
Table 3. Representative compositions (EMPA-WDS, wt %) of rippite from other Chuktukon calciocarbonatites, Chadobets upland, Siberia, Russia.

| Sample | 514-231 | 514-231 | 549-192 | 549-192 | 549-192 | 549-192 |
|--------|---------|---------|---------|---------|---------|---------|
| Grain  | R8-5    | R8-4    | R9-Rip2 | R9-Rip3 | R5-7    | R5-3    |
| Position | c    | r    | c    | r    | c    | r    | or    | inc | inc |
| SiO₂     | 40.20 | 40.30 | 40.31 | 40.43 | 40.19 | 40.44 | 40.10 | 40.35 | 41.04 | 40.17 | 40.75 |
| TiO₂     | 0.37  | 0.91  | 1.10  | 1.56  | 0.30  | 1.81  | 0.46  | 1.69  | 4.27  | 0.80  | 3.39  |
| ZrO₂     | 0.24  | 0.28  | 0.69  | 0.43  | 0.63  | 0.55  | 0.17  | 0.43  | 0.40  | 0.52  | 0.36  |
| Nb₂O₅   | 43.54 | 42.68 | 42.00 | 41.62 | 43.26 | 41.15 | 43.39 | 41.40 | 37.80 | 42.52 | 39.00 |
| Na₂O    | 0.07  | 0.00  | 0.00  | 0.04  | 0.05  | 0.05  | 0.04  | 0.03  | 0.03  | 0.03  | 0.06  |
| K₂O     | 15.64 | 15.81 | 15.80 | 15.78 | 15.67 | 15.76 | 15.67 | 15.78 | 16.04 | 15.71 | 15.89 |
| F       | 0.11  | 0.12  | 0.50  | 0.29  | 0.23  | 0.51  | 0.34  | 0.57  | 0.74  | 0.55  | 0.84  |
| Sum     | 100.17| 100.20| 100.41| 100.15| 100.33| 100.27| 100.17| 100.25| 100.31| 100.31| 100.29|
| O-F₂    | 0.05  | 0.05  | 0.21  | 0.12  | 0.10  | 0.22  | 0.14  | 0.24  | 0.31  | 0.23  | 0.35  |
| Sum     | 100.12| 100.15| 100.20| 100.03| 100.23| 100.05| 100.02| 100.01| 100.00| 100.07| 99.94 |

Formula based on 8 cations:

| Si        | 4.002 | 3.998 | 4.000 | 4.001 | 4.000 | 4.000 | 4.000 | 3.999 | 4.001 | 4.000 | 4.000 |
| Ti        | 0.027 | 0.068 | 0.082 | 0.116 | 0.022 | 0.134 | 0.034 | 0.126 | 0.313 | 0.060 | 0.250 |
| Zr        | 0.011 | 0.019 | 0.034 | 0.021 | 0.031 | 0.027 | 0.008 | 0.021 | 0.019 | 0.025 | 0.017 |
| Nb        | 1.959 | 1.914 | 1.884 | 1.862 | 1.947 | 1.840 | 1.957 | 1.855 | 1.666 | 1.914 | 1.731 |
| K + Na    | 2.000 | 2.001 | 2.000 | 2.000 | 2.000 | 1.999 | 2.001 | 2.000 | 2.000 | 2.001 | 2.001 |
| F         | 0.036 | 0.036 | 0.158 | 0.090 | 0.073 | 0.160 | 0.107 | 0.179 | 0.227 | 0.174 | 0.261 |

End-members, mol. %:

| K₂Nb₂(Si₄O₁₂)O₂ | 0.98  | 0.96  | 0.94  | 0.93  | 0.97  | 0.92  | 0.98  | 0.93  | 0.83  | 0.96  | 0.87  |
| K₂Ti₂(Si₄O₁₂)(F,OH)₂ | 0.02  | 0.04  | 0.06  | 0.07  | 0.03  | 0.08  | 0.02  | 0.07  | 0.17  | 0.04  | 0.13  |

Ta₂O₅, BaO, SrO, FeO, Al₂O₃, MgO, MnO and CaO are below detection limits (<0.005 wt %). c, m, r and or—core, middle, rim and outermost rim of crystals; inc—from secondary inclusions in fluorcalcio.pyrochlore. For samples: 514—number of drillhole; and 231—depths in drillhole. See Figure 4 and Figures S1–S4.
Table 4. Major and trace element composition of individual grains of rippite from the Chuktukon calcio-carbonatite (holotype sample 546-193.5), Chadobets upland, Siberia, Russia.

| Component | 1 | 2 | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|-----------|---|---|----|----|----|----|----|----|----|----|
| Grain     |  5-1Rp | 5-2Rp | Rp-1 | Rp-2 | Rp-3 | Rp-4 | Rp-5 | Rp-6-1 | Rp-6-2 | Rp-7 |
| n         | 2 | 2 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 2 |
| SiO₂, wt % | 40.31 | 40.32 | 40.16 | 40.19 | 40.15 | 40.17 | 40.20 | 40.19 | 40.15 | 40.11 |
| TiO₂      | 0.65 | 0.83 | 0.87 | 0.62 | 0.44 | 0.45 | 0.49 | 0.69 | 0.39 | 0.23 |
| ZrO₂      | 0.21 | 0.32 | 0.20 | 0.22 | 0.18 | 0.30 | 0.15 | 0.17 | 0.05 | 0.08 |
| Nb₂O₅     | 42.88 | 43.22 | 42.75 | 43.17 | 43.48 | 43.37 | 43.48 | 43.1 | 43.69 | 43.87 |
| Na₂O      | 0.00 | 0.04 | 0.00 | 0.03 | 0.03 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 |
| K₂O       | 15.57 | 15.67 | 15.74 | 15.70 | 15.73 | 15.70 | 15.75 | 15.75 | 15.70 | 15.71 |
| F         | 0.23 | 0.11 | 0.16 | 0.10 | 0.12 | 0.09 | 0.15 | 0.10 |
| H₂O       | 0.16 | 0.17 | 0.25 | 0.17 | 0.14 | 0.13 | 0.26 | 0.12 |
| Sum       | 99.61 | 100.34 | 100.10 | 100.21 | 100.39 | 100.29 | 100.33 | 100.12 | 100.40 | 100.21 |
| O-F₂      | 0.10 | 0.05 | 0.07 | 0.04 | 0.05 | 0.04 | 0.04 | 0.06 |
| Sum       | 99.61 | 100.34 | 100.00 | 100.16 | 100.32 | 100.25 | 100.28 | 100.08 |
| Li, ppm   | 0.36 | 0.37 | 0.22 | 0.31 | 0.11 | 0.05 | 0.11 | 0.13 |
| Be        | 0.01 | 0.03 | 0.04 | 0.01 | 0.01 | 0.03 | 0.02 | 0.01 |
| B         | 0.85 | 0.45 | 0.96 | 0.22 | 0.35 | 0.45 | 2.80 | 1.1 |
| P         | 22 | 23 | 16 | 16 | 201 | 153 | 1.31 | 0.70 |
| Ca        | 7.1 | 9.4 | 1.61 | 0.56 | 0.95 | 1.00 | 26 | 12 |
| Sr        | 42 | 0.24 | 0.03 | 0.03 | 0.25 | 0.26 | 22 | 36 |
| Hf        | 7.3 | 11.3 | 0.05 | 0.10 | 0.61 | 0.35 |
| Notes: n—number of analyses; Al₂O₃, MgO, MnO and CaO are below detection limits (<0.005 wt %). 1–2—SEM-EDS + LA-ICP-MS [32]; 3–10—SEM-EDS + SIMS (with determination of H₂O and F, author’s data).
Table 5. X-ray powder diffraction data for rippite (MoKα = 0.71073 Å, Gandolfi geometry, I > 1).

| h  | k  | l  | d<sub>calc</sub> (Å) | d<sub>obs</sub> (Å) | I  | h  | k  | l  | d<sub>calc</sub> (Å) | d<sub>obs</sub> (Å) | I  |
|----|----|----|----------------------|---------------------|----|----|----|----|----------------------|---------------------|----|
| 0  | 0  | 1  | 8.127                | 8.161               | 4  | 1  | 5  | 0  | 1.713                | 1.712               | 19 |
| 1  | 1  | 0  | 6.177                | 6.205               | 100| 2  | 4  | 2  | 1.697                |                      |    |
| 1  | 1  | 1  | 4.917                | 4.943               | 11  | 3  | 4  | 1.637                | 1.639               | 14 |
| 0  | 2  | 0  | 4.367                | 4.383               | 83  | 1  | 5  | 2  | 1.579                | 1.580               | 18 |
| 0  | 2  | 2  | 4.063                | 4.082               | 90  | 4  | 4  | 0  | 1.544                | 1.546               | 13 |
| 1  | 2  | 0  | 3.906                | 3.914               | 46  | 1  | 2  | 5  | 1.501                | 1.502               | 11 |
| 0  | 2  | 1  | 3.847                | 3.850               | 18  | 3  | 5  | 0  | 1.498                |                      |    |
| 1  | 2  | 1  | 3.521                | 3.530               | 87  | 0  | 4  | 4  | 1.487                | 1.491               | 7  |
| 1  | 1  | 2  | 3.395                | 3.405               | 40  | 1  | 4  | 4  | 1.466                | 1.469               | 5  |
| 2  | 2  | 0  | 3.088                | 3.096               | 59  | 0  | 6  | 0  | 1.456                | 1.460               | 5  |
| 0  | 2  | 2  | 2.975                | 2.985               | 81  | 4  | 4  | 2  | 1.443                | 1.446               | 8  |
| 1  | 2  | 2  | 2.816                | 2.822               | 70  | 2  | 4  | 4  | 1.408                | 1.410               | 11 |
| 1  | 3  | 0  | 2.762                | 2.768               | 99  | 2  | 6  | 0  | 1.381                | 1.383               | 6  |
| 2  | 2  | 2  | 2.459                | 2.466               | 7   | 2  | 3  | 5  | 1.350                | 1.351               | 3  |
| 2  | 3  | 0  | 2.423                | 2.426               | 3   | 1  | 5  | 4  | 1.310                | 1.309               | 16 |
| 2  | 3  | 1  | 2.322                | 2.324               | 6   | 2  | 6  | 2  | 1.308                |                      |    |
| 0  | 2  | 3  | 2.302                | 2.293               | 9   | 0  | 4  | 5  | 1.304                |                      |    |
| 1  | 3  | 2  | 2.284                |                    | 3   | 6  | 0  | 1.302                | 1.301               | 11 |
| 0  | 4  | 0  | 2.184                | 2.187               | 3   | 0  | 2  | 6  | 1.294                |                      |    |
| 1  | 4  | 0  | 2.119                | 2.120               | 16  | 4  | 4  | 4  | 1.229                | 1.233               | 3  |
| 0  | 4  | 1  | 2.109                |                    | 4   | 6  | 0  | 1.211                | 1.211               | 5  |
| 1  | 4  | 1  | 2.050                | 2.036               | 26  | 3  | 5  | 4  | 1.206                |                      |    |
| 0  | 0  | 4  | 2.032                |                    | 2   | 7  | 0  | 1.200                | 1.206               | 5  |
| 2  | 4  | 0  | 1.953                | 1.955               | 44  | 0  | 6  | 4  | 1.183                | 1.184               | 3  |
| 1  | 3  | 3  | 1.934                |                    | 4   | 6  | 2  | 1.161                | 1.161               | 2  |
| 1  | 1  | 4  | 1.930                | 1.930               | 23  | 3  | 7  | 0  | 1.147                | 1.148               | 6  |
| 0  | 4  | 2  | 1.924                |                    | 2   | 6  | 4  | 1.142                |                      |    |
| 0  | 2  | 4  | 1.842                | 1.841               | 13  | 3  | 7  | 2  | 1.104                | 1.104               | 3  |
| 3  | 3  | 2  | 1.837                |                    | 3   | 5  | 5  | 1.102                |                      |    |
| 2  | 3  | 3  | 1.806                | 1.810               | 5   | 3  | 6  | 4  | 1.096                | 1.098               | 2  |
| 2  | 4  | 2  | 1.760                | 1.762               | 25  | 0  | 8  | 2  | 1.054                | 1.058               | 3  |

The strongest diffraction lines are given in bold.

Table 6. Data collection and structure refinement details for rippite.

| Crystal Data | |
|---------------|----------------------------------|
| Unit cell dimensions (Å) | a = 8.73885(16), c = 8.1277(2) |
| Space group | P4bm (No. 100) |
| Volume (Å³) | 620.69(2) |
| Z | 2 |
| Chemical formula | K₂(Nb₁.₉₃T₁₀.₀₅Zr₀.₀₂)[Si₄O₁₂]O(O₀.₉₃F₀.₀₇) |

| Intensity Measurement | |
|-----------------------|--------------------------|
| Crystal shape | Fragment of prismatic crystal bounded by cleavage on (001) |
| Crystal size (mm) | 0.30 × 0.24 × 0.14 |
| Diffractometer | Oxford Diffraction Xcalibur Gemini |
| X-ray radiation | Mo Kα |
| X-ray power | 50 kV 30 mA |
| Monochromator | Graphite |
| Temperature | 293 K |
| Detector to sample distance | 85 mm |
### Table 6. Cont.

#### Intensity Measurement

| Measurement method | Omega scan |
|-------------------|------------|
| Radiation width   | 1°         |
| Time per frame    | 5 s        |
| Max. θ°-range for Data collection | 32.04 |
| Index ranges      | −6 ≤ h ≤ 12, −12 ≤ k ≤ 11, −11 ≤ l ≤ 9 |

| No. of measured reflections | 3667 |
| No. of unique reflections  | 949  |
| No. of observed reflections (I > 2σ(I)) | 834 |

#### Refinement of the structure

| No. of parameters used in refinement | 63 |
| Rint                              | 0.0269 |
| Flack x parameter                 | 0.15(16) |
| R1, I > 2σ(I)                      | 0.0360 |
| R1 all Data                       | 0.0429 |
| wR2 on (I^2)                      | 0.0980 |
| GoodF                             | 1.109 |
| Δρ min (e Å^−3)                    | −0.814 close to K1 |
| Δρ max (e Å^−3)                    | 0.855 close to Nb1 |

### Table 7. Atom coordinates, Ueq (Å^2) values, and occupancies for rippite.

| Atom   | Occupancy | x     | y     | z           | Ueq   |
|--------|-----------|-------|-------|-------------|-------|
| Nb1    | Nb0.96Ti0.03Zr0.01 | 0.0   | 0.0   | 0.23217(13) | 0.0255(2) |
| Nb2    | Nb0.96Ti0.03Zr0.01 | 0.0   | 0.0   | 0.73373(12) | 0.0237(2) |
| K1     |           | 0.32254(8) | 0.82254(8) | 0.0003(3) | 0.0216(2) |
| Si1    | 1         | 0.12425(14) | 0.62425(14) | 0.3080(2) | 0.0139(3) |
| Si2    | 1         | 0.12401(13) | 0.62401(13) | 0.69906(18) | 0.0076(3) |
| O1     | 1         | 0.4240(4) | 0.2895(4) | 0.2361(4) | 0.0182(8) |
| O2     | 1         | 0.4229(5) | 0.2877(5) | 0.7680(3) | 0.0158(9) |
| O3     | 1         | 0.0      | 0.0     | −0.0020(14) | 0.0200(11) |
| O4     | 1         | 0.0      | 0.0     | 0.4943(17) | 0.0229(12) |
| O5     | 1         | 0.1204(3) | 0.6204(3) | 0.4974(8) | 0.0203(7) |
| O6     | 1         | 0.5      | 0.0     | 0.2356(8) | 0.0156(14) |
| O7     | 1         | 0.5      | 0.0     | 0.7679(7) | 0.0138(17) |

### Table 8. Anisotropic displacement parameters (Å^2) for rippite.

| Atom   | U^11   | U^22   | U^33   | U^12   | U^13   | U^23   |
|--------|--------|--------|--------|--------|--------|--------|
| Nb1    | 0.0105(2) | 0.0105(2) | 0.0555(5) | 0.0 | 0.0 | 0.0 |
| Nb2    | 0.0114(2) | 0.0114(2) | 0.0483(5) | 0.0 | 0.0 | 0.0 |
| K1     | 0.0237(3) | 0.0237(3) | 0.0176(4) | −0.0041(3) | 0.0004(6) | 0.0004(6) |
| Si1    | 0.0141(5) | 0.0141(5) | 0.0133(7) | −0.0007(6) | −0.0001(4) | −0.0001(4) |
| Si2    | 0.0098(4) | 0.0098(4) | 0.0032(6) | 0.0005(5) | −0.0002(4) | −0.0002(4) |
| O1     | 0.0189(16) | 0.0109(14) | 0.0247(15) | −0.0009(13) | −0.0029(12) | −0.0022(12) |
| O2     | 0.0217(19) | 0.0147(18) | 0.0110(14) | −0.0043(15) | −0.0001(11) | −0.0035(11) |
| O3     | 0.0161(12) | 0.0161(12) | 0.028(3) | 0.0 | 0.0 | 0.0 |
| O4     | 0.0194(13) | 0.0194(13) | 0.030(3) | 0.0 | 0.0 | 0.0 |
| O5     | 0.0264(9) | 0.0264(9) | 0.0080(14) | −0.0090(12) | −0.0054(18) | −0.0054(18) |
| O6     | 0.0139(18) | 0.0139(18) | 0.019(3) | 0.005(3) | 0.0 | 0.0 |
| O7     | 0.017(2) | 0.017(2) | 0.007(3) | 0.007(3) | 0.0 | 0.0 |
### Table 9. Bond lengths (Å) for rippite.

| Bond                  | Value (Å)  |
|-----------------------|------------|
| Nb1–O3                | 1.903(12)  |
| Nb1–O1 (4×)           | 1.956(4)   |
| Nb1–O4                | 2.131(13)  |
| mean                  | 1.976      |
| Nb2–O4                | 1.946(13)  |
| Nb2–O2 (4×)           | 1.993(4)   |
| Nb2–O3                | 2.148(12)  |
| mean                  | 2.011      |
| Si1–O5                | 1.541(7)   |
| Si1–O1 (2×)           | 1.614(4)   |
| K1–O2 (2×)            | 2.874(4)   |
| K1–O7                 | 2.894(4)   |
| Si1–O6                | 1.590(4)   |
| mean                  | 1.603      |
| Si2–O2 (2×)           | 3.2171(3)  |
| K1–O3 (2×)            | 3.009      |
| Si2–O5                | 1.632(2)   |
| mean                  | 1.623      |

### 4. Mineralogy and Petrography of Calciocarbonatites from the Chuktukon Massif

The Chuktukon calciocarbonatites are fine- and medium-grained rocks with massive, spotty and banded textures (Figure 2), sometimes contain vugs which are filled with euhedral calcite, barite and/or quartz. Some species are medium to highly altered. The primary mineral assemblage includes calcite, fluorcalcioyicrohlore, rippite, tainiolite, fluorapatite (up to 2.3 wt % SrO), fluoroite, Nb-rich rutile (up to 17 wt % Nb₂O₅, up to 5.1 wt % Fe₂O₃), K-feldspar, dolomite, ancylite-(Ce), strontianite, olekminskite, sulfides, aegirine, quartz and zircon. Calcite is speckled with dolomite spots and fine disseminations of ancy tile-(Ce), strontianite, and olekminskite. The SrO concentration in calcite is up to 0.8 wt % [29]. Minerals found in all species of calciocarbonatites are listed in Table 1. The chemical compositions of some minerals are considered in previous works [1,2,29–35]. In general, rippite is the second main mineral to concentrate Nb in the Chuktukon calciocarbonatites [1,2,29,32], and its content in some rocks may be equal and even higher rather than that of pyrochlore.

Strontianite, daqingshanite-(Ce), ferrohagendorfite, barite, burbankite–khanneshite, Na-Ca carbonates (nyerereite, shortite), thorite, anhydrite, hematite, baddeleyite, zirconolite-group minerals, unidentified Na-REE-Ba-Ca-rich and Na-Fe-rich phosphates, and Na-rich hydrated carbonate occasionally appear in multiphase or monomineralic inclusions in fluorapatite, fluorcalcioyicrohlore, zircon and calcite of the Chuktukon calciocarbonatites [30,34,35]. The secondary multiphase inclusions from the cores of zircon are carbonate-rich in composition and multiphase: calcite + dolomite or alkali-rich carbonates (nyerereite + shortite + burbankite) [30,34].

Aggregates of “francolite” (Sr-rich carbonate-fluorapatite with up to 7 wt % SrO), “goethite” (goethite + “hydrogoethite” + other Fe-oxides/hydroxides) and “psilomelane” (romanechite ± hollandite) are common in various quantities for all calciocarbonatite species (Figure 2). Barite, quartz, Ca-REE-fluorcarbonates (parisite-(Ce), synchysite-(Ce)), monazite-(Ce), Sr-Ba-Pb-rich hydro-/kenopyrochlores and above aggregates are related to a stage of metasomatic (hydrothermal) alteration of the calciocarbonatites. They occur interstitially among grains of primary minerals and/or form networks of microveinlets. In addition, goethite forms complete pseudomorphs after euhedral pyrite and prismatic grains (up to 1 cm) of an unidentified mineral, which commonly contains inclusions of calcite and tainiolite (Figure 2) [33].

Detailed studies of the petrography and mineralogy of the highly altered calciocarbonatite are given in [32,40]. These rocks are composed of relict minerals (calcite, fluorcalcioyicrohlore, rippite, rutile, and zircon) and minerals formed during alteration. The rocks are fine-grained, banded, and patchy-striped, which is expressed as alternating bands and spots of goethite and rare earth minerals. The groundmass is composed of an aggregate of “goethite” and kaolinite. Florencite-(Ce), monazite-(Ce), “psilomelane” aggregate, churchite-(Y), and daqingshanite-(Ce) are minor and accessory minerals.
"Goethite" aggregate from hydrothermally altered carbonatites contains up to 2.2 wt % of Nb2O5 [32]. Florencite-(Ce) and monazite-(Ce) occur as irregularly shaped grains, up to 0.3 cm in size, as well as aggregates of micron-sized grains of intricately shaped patches, as well as network of vein-like segregations. Typically, both minerals have a porous internal structure. Churchite-(Y) forms radially fibrous 2–5 mm aggregates and individual 2–3 mm crystals. A network of “psilomelane” (microveinlets) dissects the rocks [29]. The petrographic observations of different types of the Chuktukon calcio carbonatites have shown that rippite is very resistant to alteration/weathering processes. In addition to holotype sample 546–193.5 (Figure 2) this mineral was also found as minor component in calcio carbonatites (including highly altered samples) from 180–200 m depths of neighboring drillholes.

5. Morphology, Optical and Physical Properties of Rippite

Rippite commonly forms elongated prismatic crystals (up to 0.5–2 mm) and their intergrowths in carbonate matrix (Figures 2 and 3), rarely in the “goethite” or “francolite” aggregates. The major forms are prism {100} and pinacoid {001}. Twinning is none observed. The mineral is colorless and it may be confused with fluorapatite due to elongated crystals.

The color of the powdered mineral is white. Rippite has vitreous luster and weak fluorescence. The second harmonic generation test indicated nonlinear optical properties of the mineral. Under laser the weak glow of rippite powder was steady and green that was comparable with colour characteristics of the reference sample (LiIO3). Cleavage is very perfect on (001) and perfect to distinct on (100); parting is none observed, fracture is stepped to uneven across cleavage (Figure 3). The Mohs’ hardness of rippite is 4–5, micro-indentation hardness is VHN50 = 210–487 kg/mm2, mean (n = 19)—307 kg/mm2. The density measured by flotation in the Clerici liquid (HCOOTl + Tl2[OOCCH2COO]) is 3.17(2) g/cm3. Density calculated from unit-cell dimensions and results of electron-microprobe analyses assumes 3.198 g/cm3. Rippite is optically uniaxial (+); ω = 1.737–1.739; ε = 1.747 (589 nm). The optical orientation is X = c. No dispersion and pleochroism were observed. The mineral is not soluble in concentrated HCl and H2SO4 that is comparable with the synthetic phase. The Gladstone–Dale’s compatibility factor for the holotype rippite is 0.005 (superior).

Fluorcalciopyrochlore octahedra and tainiolite blades occasionally occur as inclusions in rippite, and vice versa rippite (± quartz and other phases) sometimes fills the fissures in fluorcalciopyrochlore crystals (Figure 4, Figures S1 and S2). Such relationships indicate that rippite is later Nb-mineral than fluorcalciopyrochlore and crystallized together with tainiolite or later (Figure 4, Figures S1–S3). Most of rippite grains are partially resorpted by quartz especially along cleavage planes and even replaced by quartz in the outer parts of some crystals (Figures 3–5, Figures S3–S5). “Goethite” impregnation is common of some grains occurring in altered carbonatite samples. In general, rippite is resistant to low-temperature alteration or weathering, but may be partially replaced by quartz (plus rutile and other phases) during carbonatite crystallization (Figure 5 and Figures S3–S5).

6. Chemical Composition of Rippite

6.1. SEM and EMPA data

Majority of rippite prismatic crystals are homogeneous in composition and unzoned or weakly-zoned that is virtually invisible in the elemental SEM maps (Figures S3, S6 and S7). The contrast zonation is only fixed for rare grains with narrow Ti-rich outermost zone. Those core-to-rim variations are well indicated in the Nb and Ti elemental maps (Figure 5). In general the chemical composition of the mineral is close to the ideal structural formula K2Nb2(Si4O12)O2 (Tables 2 and 3). The empirical formula of the holotype rippite (sample 546-193.5, mean of 110 analyses) is K2(Nb1.90Ti0.09Zr0.01)(Si4O12)(O1.78OH0.12F0.10) (Table 2). Most of grains from holotype and other samples show compositions poor in TiO2 (<0.7–1.0 wt %) and F (<0.5 wt %), K2(Nb1.93Ti0.05Zr0.02) [Si4O12](O1.93F0.07) (Tables 2 and 3). Raman, IR and SIMS data indicate very low content of H2O or
(OH)-groups in such grains (see text below). High contents of TiO$_2$ (up to 4.4 wt %) and F (up to 1.0 wt %) are common of the outermost zone in some grains, up to K$_2$(Nb$_{1.67}$Ti$_{0.32}$Zr$_{0.01}$)[Si$_4$O$_{12}$](O$_{1.67}$F$_{0.33}$) (Table 2, Figure 5). The ZrO$_2$ amount is up to 1.3 wt %. However, there is no any clear correlation ZrO$_2$ with TiO$_2$ and Nb$_2$O$_5$ (Figure 6). All above-mentioned data strongly suggest the incorporation of (Ti,Zr) and F in the structure of rippite via the isomorphism Nb$^{5+}$ + O$^{2-}$ $\rightarrow$ (Ti,Zr)$^{4+}$ + F$^{1-}$ (Figure 7). The content of a hypothetical end-member K$_2$Ti$_2$[Si$_4$O$_{12}$]F$_2$ may be up to 17 mol. % (Table 2). The database of chemistry for all rippite grains is given in Supplementary Table S1.

6.2. LA-ICP-MS and SIMS Data

Trace elements were measured by LA-ICP-MS for Ti-poor compositions of rippite from the Chuktukon calciocarbonatite. The REE and trace element concentrations are consistently low (<220 ppm in total) (Table 4). The substantial amounts (>2–5 ppm) are common of P (22–23 ppm), Ca (16 ppm), Ba (153–205 ppm), V (12–26 ppm), Sc (7.1–9.4 ppm), Hf (22–36 ppm) and Ta (7.3–11.3 ppm) (Table 4).

The contents of some light trace elements (Be, Li, B), F and H$_2$O in low-Ti rippite were analyzed by SIMS (Table 4). The results indicate very low concentration of light elements (<5 ppm) and H$_2$O (0.09–0.23 wt %). The content of F is consistent with EMPA-WDS data.

7. Optical Studies for Rippite

7.1. Cathodoluminescence

The CL images for single rippite crystals show green colour and very complex history during their growth (Figure 8). However, the individual zones and regions fixed in the CL images are weakly documented by the BSE images and elemental maps and do not reflect the variations in chemical composition (Figure 8, Figures S6 and S7). In general, the stages of nucleation, chaotic growth, dissolution and further growths may be observed in the CL images of individual rippite grains (Figure 8).

7.2. Transmission Spectra

The color of the powdered rippite is white and its crystals are almost colorless. Figure 9 shows the short-wave edge of the optical transmission spectra obtained for a crystal of about 150 × 150 mm$^2$ and about 100 mm thick, at 300 and 80 K. It is seen that the crystal becomes transparent from a wavelength of about 275 nm in the UV region of the spectrum. The Tauc analysis [51] indicates that the spectra are straightened in coordinates ($\alpha^2(h\nu)$ = f(h$\nu$), where $\alpha$ is the absorption coefficient and h$\nu$ is the photon energy. This is evidence that the shape of the fundamental absorption edge is determined by the direct allowed band-to-band electronic transitions. The position of the intersection points of straight lines with the abscissa axis determines the values of the band gap at 300 and 80 K: $E_g$ = 4.37 and 4.50 eV, respectively. Under the action of laser radiation with a wavelength of 1052 nm, second-harmonic radiation (526 nm) is generated in the rippite powder. The intensity of the second harmonic is comparable to that obtained from the powder of the reference sample, a well-known nonlinear optical crystal, lithium iodate (LiIO$_3$), for which the second-order nonlinear susceptibility is $\chi^{(2)}$ = 4.1 ± 0.4 pm/V [52].

Rippite has a weak fluorescence and, in addition, its samples show spontaneous luminescence in the range of 100—400 K when heated or cooled at a rate of ~30 deg/min. This glow is typical for pyroelectrics [53] and indicates the absence of an inversion center in the structure. Indeed, rippite with a structure with a point group of 4mm belongs to one of the 10 crystallographic groups with a pyroelectric effect: 1, 2, 3, 4, 6, m, mm, mm2, 3m, 4mm and 6mm [54]. Such crystals have electric polarization even in the absence of an external electric field (spontaneous polarization). Pyrolyuminescence is the result of modifications in the atomic polarization in the crystal volume as temperature changes [53]. Flashes of light are the result of an electrical breakdown in pyroelectric fields, the intensity of which reaches hundreds of kV/cm.
7.3. Infrared and Raman Spectroscopy

Tetragonal rippite and its synthetic analog are related to space group $P4_{2}bm$ (No. 100), its point group is $C_{4v}$ (4mm). Symmetry-representation analysis gives 105 modes of vibrations for rippite, which can be divided as $21A_{1} + 16A_{2} + 12B_{1} + 17B_{2} + 39E$, where $20A_{1} + 38E$ vibrations are infrared active, $20A_{1} + 12B_{1} + 17B_{2} + 38E$ vibrations are Raman active, and $16A_{2}$ vibrations are inactive in both regions. Acoustic modes $A_{1} + E$ are not included here. Among these, the silicate tetrahedrons will share the following internal vibrations $5A_{1} + 4B_{1} + 5B_{2} + 9E$. External vibrations include translation and SiO$_4$ libration modes. Their irreducible representations can be expressed as: $8A_{1} + 7B_{1} + 8B_{2} + 18E$ and $7A_{1} + 4B_{1} + 4B_{2} + 11E$, respectively. The $C_{4v}$ point groups allow the simultaneous activity of some part of vibrations in both IR and Raman spectra [55]. The number of IR and Raman modes observed for rippite is fat fewer than predicted, because of the low intensity of some modes and orientation effects. Crystals of Ti-poor rippite were mainly used for the IR and Raman spectroscopic studies.

7.3.1. Infrared Spectra

The following absorption bands are more remarkable in the IR spectra of rippite (in cm$^{-1}$): 395, 468, 493, 515, 553, 578, 686, 708, 784, 800, 818, 910, 967, 1087, 1166, 1245, 1388 and 1634 (powder KBr pellet, Figure 10). There are no clear bands in the 3000–4000 cm$^{-1}$ region (Figures 10 and 11).

The strongest absorption band of the IR spectrum of rippite is 967 cm$^{-1}$ (Figure 10) and assigned to be the $v3$ internal stretching mode of the SiO$_4$ tetrahedra. The antisymmetric stretching modes of the Si-O-Si bonds and the stretching vibrations of Si-O of the SiO$_4$ tetrahedra are active between 1300 and 960 cm$^{-1}$; and symmetric stretching vibrational modes of the Si-O-Si bonds lying between 800 and 680 cm$^{-1}$. The latest bands are associated with the presence of bridging oxides (Si-O-Si linkage) in the structure. The stretching modes of the Nb-O bonds in the NbO$_6$ octahedra occur in the 600–800 cm$^{-1}$ range as weak bands and shoulders, considering the stronger force constant of the Si-O bonds than that of the Nb-O ones. The bands below 580 cm$^{-1}$ of the IR spectrum indicate silicon-oxygen bending vibrations and the stretching vibrations arising from K-O bonds. In addition, the IR and FTIR spectra of rippite show very weak and broad bands near 1634 and 3415 cm$^{-1}$ (Figures 10 and 11). However, heating of rippite in powder KBr pellet up to 380 °C and following IR measurements resulted to diminishing of these bands. Consequently, the presence of the substantial bands in the 1600–1700 and 3400–3500 cm$^{-1}$ region in unheated rippite samples may be partially related to absorbed H$_2$O. Nevertheless, we have to mention that our SIMS data indicate low H$_2$O content (0.09–0.23 wt %) in the Ti-poor rippite. Thus, weak bands in the 3000–4000 cm$^{-1}$ range, which may be related to the vibrations of (OH)-groups, unfortunately cannot outline the presence or absence of H$_2$O and as result the true H$_2$O concentration.

7.3.2. Raman Spectra

Main bands in oriented Raman spectra of rippite are (in cm$^{-1}$): 116, 144, 279, 324, 356, 397, 497, 652, 761, 807, 937, 1055 and 1112 (Figure 12). There are no clear bands in the 3000–4000 cm$^{-1}$ region.

In general, bands below 360 cm$^{-1}$ are ascribed to vibrations in polyhedra and octahedra as well as librational vibrations of the Si$_4$O$_{12}$ group. Bands in the 390–700 cm$^{-1}$ region are related to tetrahedral SiO$_4$ bending vibrations ($v4 + v2$). The strongest Raman band at 761 cm$^{-1}$ (Figure 12) is assigned to be the internal stretching mode $v1$ of the SiO$_4$ tetrahedra. The $v3$ modes of the SiO$_4$ tetrahedra seem to be bands in the 900–1200 cm$^{-1}$ region.

In addition, we tried to obtain data for rippite concerning to the dependence between chemical composition and changing in Raman spectra. For this purpose, we used zoned crystal Nb3-18. All spectra were obtained during one analytical session and in same conditions. The most substantial differences are visible for the bands at 934, 395 and 354 cm$^{-1}$ (Figure 13). The increasing of the Ti(+Zr) content in rippite lead to left shifting for the 934 cm$^{-1}$ band and to right shifting for the 395 and
354 cm\(^{-1}\) bands in Raman spectra. Unfortunately, such insufficient deviations (in 1–2 cm\(^{-1}\)) cannot be used for identification of chemical composition for rippite according to Raman spectra.

8. X-ray Crystallography and Crystal Structure of Rippite

The second harmonic generation test for rippite indicated the weak glow of powder, which was steady and green. The reference sample (Li\(\text{IO}_4\)), which is used in nonlinear optics, showed the same colour characteristics. All this strongly assumes a noncentro-symmetrical structure for rippite.

X-ray powder diffraction data for rippite (in Å for MoK\(\alpha\)) are given in Table 5. Unit cell parameters refined from the powder data using STOE Win XPOW 2.21 program package are as follows: tetragonal symmetry; space group \(P4bm\); \(a = 8.735(3)\) Å; \(c = 8.127(5)\) Å; \(V = 620.1(4)\) Å\(^3\); \(Z = 2\).

Single-crystal X-ray studies were carried out on a fragment of low-Ti rippite grain and gave the following results: tetragonal symmetry; space group \(P4bm\); \(a = 8.7388(2)\) Å; \(c = 8.1277(2)\) Å; \(V = 620.69(2)\) Å\(^3\); \(Z = 2\). The crystal structure was studied for Ti-poor rippite \(K_2(Nb_{1.93}Ti_{0.05}Zr_{0.02})[Si_4O_{12}]O(OH)_{0.93}F_{0.07}\). It was solved by direct methods and refined on the basis of 949 independent reflections (836 reflections with \(l \geq 2\alpha(l)\)). The factor \(R_1\) for the crystal structure is 0.036. Crystallographic data for rippite are given in Tables 6–9. The crystal structure is shown in Figure 14. Rippite is closely identical in the crystal structure to synthetic compound \(K_2Nb_2(Si_4O_{12})O_2\) (or \(KNbSi_2O_7\)) [3–5,15] (Figure 15).

The Nb\(^{5+}\) cations occupy two sites, which also contain minor amounts of Ti\(^{4+}\) and Zr\(^{4+}\). The Nb sites are surrounded by six O atoms in octahedral coordination. The corner-shared NbO\(_6\) octahedra form chains running parallel to a four-fold symmetry axes. The chains are coupled together by four-membered Si\(_4\)O\(_{12}\) rings so that each octahedron shares four corners with four SiO\(_4\) tetrahedra belonging to four different Si\(_4\)O\(_{12}\) rings. Each Si\(_4\)O\(_{12}\) ring shares its terminal O atoms with eight NbO\(_6\) octahedra of four neighboring chains linking them in the 3D heteropolyhedral framework. The four-membered rings are in the plane \([110]\); at that each ring is connected with two neighboring Nb-octahedra of one chain via shared O-atoms forming heteropolyhedral four-membered rings (Figure 14b). Positions of K\(^+\) are situated in channels which extend through the structure in the [001] direction. K\(^+\) cations are coordinated by twenty O atoms in a form of a two-capped pentagonal prism. Low content of F does not give possibility to determine its structural position.

It is should be noted that rippite is structurally related to cyclosilicates with [Si\(_4\)O\(_{12}\)]\(^8−\) four-membered single rings. In structural and chemical aspects it seems to be in close with the labunsovite-supergroup minerals, namely with vuoriyarvite-(K), \(K_2(Nb, Ti_2)(Si_4O_{12})(O, OH)_2 \cdot 4H_2O\) (vuoriyarvite group, space group \(Cm\), \(a = 14.692\) Å, \(b = 14.164\) Å, \(c = 7.859\) Å, \(Z = 4\); \(\beta = 117.87^\circ\), \(V = 1445.74\) Å\(^3\)) [56–60]. However, rippite is nominally free in H\(_2\)O and (OH)-groups. In addition, the connection of the octahedral chains and [Si\(_4\)O\(_{12}\)]-rings is quite different in the crystal structure of rippite (this work) and the labunsovite-supergroup minerals [56–60]. Unlike rippite the four-membered tetrahedral rings in the structure of vuoriyarvite-(K) are oriented perpendicularly to the NbO\(_6\)-chains and two neighboring Nb-octahedra in one chain are connected by shared O-atoms with edge of the SiO\(_4\)-tetrahedron. It led to considerable deformation of the octahedral chain. In general, we suggest that the rippite-related structure is a new structural type among cyclosilicates with the [Si\(_4\)O\(_{12}\)]\(^8−\) single rings.

The compound \(K_4(NbO)_2[Si_8O_{21}]\) is somewhat close in element suite, chemistry and structure to rippite and synthetic \(K_2(NbO)_2Si_4O_{12}\) [61,62]. It was synthesized in the hydrothermal system K\(_2\)O-Nb\(_2\)O\(_5\)-SiO\(_2\)-H\(_2\)O (\(T = 450–500^\circ\)C; \(P = 1000–1200\) bar) and its composition is (EMPA, in wt %): SiO\(_2\)–51.10; NbO\(_2\)–28.80; K\(_2\)O–20.84 [61]. Unlike rippite and its synthetic analog this phase has complex modulated structure and triclinic symmetry: space group \(P-1\); \(a = 33.92(2)\) Å, \(b = 10.950(6)\) Å, \(c = 7.737(4)\) Å, \(\alpha = 76.42(4)^\circ\), \(\beta = 72.10(5)^\circ\), \(\gamma = 89.81(5)^\circ\), \(V = 2650.8\) Å\(^3\) [62]. In addition, \(K_4(NbO)_2[Si_8O_{21}]\) is characterized by a relatively low nonlinear polarization in comparison with \(K_2(NbO)_2Si_4O_{12}\) owing to the low concentration of the isolated NbO\(_6\) octahedra in its structure [63].
In contrast with this K-Nb-silicate, rippite and synthetic $K_2(NbO_2)Si_4O_{12}$ display a strong non-linear effect, as the NbO$_6$ octahedra are linked in columns (Figures 14 and 15).

9. Discussion and Concluding Remarks

In general the detailed studies for the Chukutkon calcioarbonatites (Chadobets upland, Krasnoyarsk Territory, Russia) gave the possibility of describing the chemical composition and crystal structure for a new mineral, rippite $K_2(Nb,Ti)(Si_4O_{12})(O,F)_{12}$, which belongs to a new structural type among the $[Si_4O_{12}]$-cyclosilicates and is close to the labuntsovite supergroup. This mineral is related to primary phases, which were crystallized after fluorcalciopyrochlore, the main carrier of Nb in the calcioarbonatites. The primary carbonatite paragenesis may be formed at temperatures near and below 837 °C according to the calcite-dolomite thermometer. The synthesis in the system SiO$_2$-Nb$_2$O$_5$-K$_2$O has indicated that the $K_2Nb_2(Si_4O_{12})O_2$ phase may be stable in the 510–735 °C temperature range [4,6,8–10,13,14].

Rippite is the second main mineral to concentrate Nb in the Chukutkon calcioarbonatites [1,2,29,32]. The presence of this mineral should be into account in processing schemes of carbonatitic Nb-ores, as in some rock species the modal contents of pyrochlore and rippite may be equal. The weathered carbonatites are the basis of the Chukutkon niobium-rare earth elements ore deposit, which is very promising for development in eastern Siberia in a future [40–42]. It is quite possible that unweathered calcioarbonatites will be also involved in processing schemes. In general, it is concerning not only to the Chukutkon calcioarbonatites, but and to other pyrochlore-rich carbonatites around the world [64]. At present rippite was found only in calcioarbonatites of the Chukutkon massif. However, we are not sure that this mineral is endemic for the Chukutkon rocks and may be also occur in other pyrochlore-containing carbonatites worldwide.

It should be noted that the mineral phase with ratio of the main components (K:Nb:Si) similar to rippite has been described as minute inclusions in late apatite aggregates from calcioarbonatites of the Araxá alkaline-carbonatite complex, Brazil [65]. According to chemistry (SiO$_2$—37.9–39.3 wt %; Nb$_2$O$_5$—34.7–37.6 wt %; TiO$_2$—0.3–1.6 wt %; K$_2$O—14.2–14.4 wt %) and low total sums this mineral was identified as nenadkevichite (labuntsovite supergroup). Probably further studies will clearly outline whether the Araxá mineral is rippite or it is vuoriyarvite-K (labuntsovite supergroup).

The discovery of rippite also highlights some problems in the synthesis and growth of high-quality crystals suitable for industrial purposes. It is known that synthetic analog of rippite is a good material for nonlinear optics [3–14]. Ideal and large single crystals of KNb$_2$Si$_2$O$_7$ (near 1 cm) of high optical quality, which are valid for industrial purpose, are still rarity [14]. The mineral association of rippite-containing calcioarbonatites may be a key in understanding of favorable conditions for synthesis of the perfect KNb$_2$Si$_2$O$_7$ crystals (Ca-rich carbonate environment).

The compositional study of rippite strongly suggests the incorporation of (Ti,Zr) and F in the structure via the isomorphism Nb$^{5+}$ + O$^{2-}$ → (Ti,Zr)$^{4+}$ + F$^{1-}$. As a result the content of a hypothetical end-member $K_2Ti_2[Si_4O_{12}]F_2$ in rippite may be up to 17 mol. %. Unfortunately, there are no any data about synthesis of $K_2Ti_2[Si_4O_{12}]F_2$ or $K_2Zr_2[Si_4O_{12}]F_2$, which may be isostructural with $K_2Nb_2[Si_4O_{12}]O_2$ and $K_2Ta_2[Si_4O_{12}]O_2$ [3–5,16]. It is quite possible that Ti- and Zr-counterparts or their intermediate compositions with $K_2Nb_2(Si_4O_{12})O_2$ will have higher nonlinearity rather than pure $K_2Nb_2(Si_4O_{12})O_2$. From other side the minimal doping of the $K_2Nb_2(Si_4O_{12})O_2$ compound by Ti or Zr may lead to good conditions for single crystal fabrication.

It should be also mentioned that rippite has been successfully used as a geochronometer. The Ar-Ar age estimated for rippite from the Chukutkon calcioarbonatite (sample 546-193.5) is 231.1 ± 2.7 Ma [31].

Supplementary Materials: The following figures are available online at http://www.mdpi.com/2075-163X/10/12/1102/s1: Figure S1: Secondary polymineral inclusions with rippite in fluorcalciopyrochlore, Chukutkon calcioarbonatite, BSE images and elemental maps; Figure S2: Inclusions of fluorcalciopyrochlore in rippite, Chukutkon calcioarbonatite, BSE images and elemental maps; Figure S3: Relationship of rippite with tainiolite in the Chukutkon calcioarbonatite, BSE images and elemental maps; Figure S4: The outer zone in a rippite crystal and its replacement by quartz with formation of the TiO$_2$ phase (rutile ?), Chukutkon calcioarbonatite,
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