

Article



Optical and Spectroscopic Properties of Lorenzenite, Loparite, Perovskite, Titanite, Apatite, Carbonates from the Khibiny, Lovozero, Kovdor, and Afrikanda Alkaline Intrusion of Kola Peninsula (NE Fennoscandia)

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Abstract: This manuscript deals with the analysis of significant rare earth elements (REE) minerals such as eudialyte, lorenzenite, loparite, perovskite, titanite, apatite, and carbonates. These minerals are found in the rocks of the Khibiny, Lovozero, Afrikanda, and Kovdor massifs (the Paleozoic hotspot activity in the Kola-Karelian Alkaline Province is estimated at about 100,000 km²). Performed microscopic analyses that demonstrated their structure and optical features (dimming, interference colors, relief). Single-crystal analysis using XRD methods, SEM-EDS, and spectroscopic (FTIR) studies allowed the characteristics of described minerals: Lorenzenite in Lovozero probably crystalized after loparite have small additions of Nb, La, Ce, Pr, and Nd. Loparite and perovskite have the addition of Ce, Nb, and Ta. The same dopants have titanite probably crystalized after perovskite. Calcite in these massifs had the addition of Ce and Sr, the same as in fluorapatite, which was found in these rocks too. All of the analyzed minerals are REE-bearing and can be considered as deposits.

Keywords: lorenzenite; perovskite; loparite; titanite; apatite; carbonates; Khibiny; Lovozero; Kovdor; Afrikanda; alkaline intrusions; NF Fennoscandia

1. Introduction

The Kola-Karelian Alkaline Province is a unique world complex containing about forty different intrusions of ultramafic alkaline rocks with rare rock and mineral types [1–4]. In the Khibiny, about 10% [5] of all known minerals have been discovered. The minerals lorenzenite, loparite, perovskite, titanite, apatite, and carbonate, among others, are found in these rocks and are admixtures in the discussed rocks. Rare earth inclusions have been found in these minerals, which both enrich their crystal structure and form inclusions and distinct phases. Lorenzenite is a mineral that occurs in the alkaline rocks of the Khibiny and the Lovozero intrusions. Loparite, on the other hand, is found in the urtite formations of the Lovozero and Kovdor rocks. Besides these minerals, apatite is also found in whole rocks of described massifs and is accompanied by minerals such as titanite containing REE admixtures. In addition to these minerals, perovskite and carbonate (contain admixtures of Sr and Ce) are found in Afrikanda in ultramafic-alkaline rocks [6–12]. Lorenzenite, loparite, and Perovskite are relatively rare, and their occurrences in the world are limited, and the optical and spectroscopic characteristics of these minerals are relatively unknown. The authors in this paper decided to introduce the properties of these minerals in this paper by



Citation: Huber, M.; Kamiński, D.; Czernel, G.; Kozlov, E. Optical and Spectroscopic Properties of Lorenzenite, Loparite, Perovskite, Titanite, Apatite, Carbonates from the Khibiny, Lovozero, Kovdor, and Afrikanda Alkaline Intrusion of Kola Peninsula (NE Fennoscandia). *Crystals* 2022, *12*, 224. https://doi.org/10.3390/ cryst12020224

Academic Editors: Dinadayalane Tandabany and Alessandro Chiasera

Received: 12 December 2021 Accepted: 30 January 2022 Published: 4 February 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). presenting the original results of SEM-EDS, FTIR, and single-crystal X-ray studies of these minerals. The purpose is to present the properties of the minerals mentioned above found in the Murmansk District. Below are the characteristics of the study region, the individual intrusions from which samples were taken, and the properties of the minerals in question.

2. Study Area

The NE Fennoscandia region is where more than a dozen diverse intrusions of alkalinebasic rocks are located. This is one of many intrusions connected with the hotspots in the early Paleozoic [1–19], of the alkaline continental magmatism such as the Khibiny, Lovozero, Turiy, Niva, and Salmagora massifs, and many others, and it contains the most original cumulate magma [1–3]. These intrusions form several concentric belts exposed in the region of Murmansk District, Karelia, Finland (and several in the Arkhangelsk region). The outermost of them are composed of ultramafic-alkaline rocks (Afrikanda, Kolvitza region, Lesnaya Varaka, and Ozernaya Varaka) [4,6] of carbonatites (Kovdor, Sokli, and Patyan Vaara) [9,10] and alkaline rocks (Turiy, Khibiny, Lovozero, and Selbyavr) [12,13]. The complex of these intrusions also includes numerous vein formations [1] and kimberlites of the Terski Bereg and Arkhangelsk regions [20–23]. These rocks are intruded in Archean and Paleoproterozoic formations of magmatic and metamorphic character, which are the basement of the Baltic Shield of the Eastern European Platform [24,25]. They were formed due to the impact of a hotspot that occurred between 465–364 million years ago [18], forming the Kola-Karelian Alkaline Province (Figure 1). Some of these intrusions are under the Pleistocene sediments [26,27].



Figure 1. Kola-Karelian Alkaline Province with intrusions localizations (after [22], changed by author).

Most of them are central intrusions usually composed of concentric rings of rocks forming the metasomatized contact zone and internal zones of magmatic derivatives. These sequences are more numerous in large massifs such as Khibiny and Lovozero. An ore zone (Khibiny) [28–30] and zones of pegmatites and vein formations (Khibiny, Lovozero) usually appear there [31–37]. There are elevated amounts of rare earth elements (Ce) [31–38]. The share of these elements is variable, but their occurrences sometimes cause enrichment in these elements of the rock-forming minerals of the discussed massifs or the form of solid inclusions and separate phases.

3. Geology of the Khibiny, Lovozero, Afrikanda, and Kovdor Massifs

The Khibiny massif is a concentric Early Paleozoic intrusion of alkaline rocks, along with the Lovozero intrusion. Khibiny is the largest alkaline rock massif in the NE Fennoscandia region, having an area of 1300 km² (Lovozero 587 km²). The age of these massifs is 385–375 Ma [31–37]. The Khibiny Massif is built of concentrically arranged rock formations in the form of belts, which can be divided into four sequences [25,38–45]. The outermost is composed of so-called massive khibinites or alkali-feldspathic syenites. The inner one (Figure 2) is composed of similarly formed porphyritic foyaites with the presence of biotite, phlogopite, and pegmatites, seen in the nested form [31–37]. Pegmatites are often characterized by the presence of many rare minerals [31,33].



Figure 2. Generalized geological sketch of the Khibiny, Lovozero, Afrikanda, and Kovdor massifs (after [11,39] changed by authors). Rocks abbreviations: Khibiny: CH1-massive syenites, CH2-rischorites, CH3-ore zone, CH4-carbonatites, CH5-surrounded rocks; Lovozero: LV1-syenites, LV2-lujavrites, jovites, LV3-ijolites, LV4-porphyrites, LV5-surrounded rocks; Afrikanda: AF1-contact zone phenites, AF2-melteigites, AF3-pyroxenites, AF4-olivinites with perovskite-magnetite ore, AF5-surrounded rocks; Kovdor: KV1-contact zone phenites, KV2-foidoites, KV3-pyroxenites and olivinites, KV4-magnetite ore, KV5-Precambrian bSasement.

Between these formations is an ore zone (third sequence) formed by titanitic nephelinites. The fourth sequence is formed by veins and dikes cutting the above concentric system, including porphyrites, syenite pegmatites, and melteigites [29]. Carbonatites are also present in the eastern region of the massif [38]. The formations of the zones mentioned above in the area of Lake Vudiavr, Vudiavrchorr hills, Tachtarvumchorr, Yudychvumchorr, Kukisvumchorr, and Malaya Belaya Valley were investigated by the authors (Figure 2, [1,5]).

The Lovozero massif is an intrusion of rocks similar to Khibiny, localized several kilometers to the east. However, they differ significantly in their composition and prevalence of accessory minerals as well as in the directional texture of the rocks dominant in the Lovozero massif. It is an intrusion with an age of 370–359 Ma constituting the second-largest massif in the NE Fennoscandia region after Khibiny [40–44]. This massif is composed of several zones of alkaline rocks, forming concentrically arranged circles. The first outer one is mainly made of trachytes and metasomatized porphyrites. The second, inner one is made of lujavrites accompanied by other foyaites. These rocks are interspersed with various vein rocks and pegmatites forming the third zone of the discussed massif. The rocks were sampled in the western (in the Aluaiv Mt. area) and northern part of the massif (in the Karnasurt and Flora Mts. area, Figure 3) [42].



Figure 3. Macro photographs of the typical rocks from Khibiny: Massive syenite with eudialyte (eud) crystals with nepheline (nph), orthoclase (afs), apatite (ap), aegirine (aeg), ilmenite (ilm), and titanite (ttn) (**A**); Melasyenite (malinite) with titanite, aegirine, eudialyte, and nepheline (**B**).

Afrikanda intrusion is located in the southern part of the Kola Peninsula in the NE part of the Scandinavian Peninsula [45–48]. It is located on the southern shore of Lake Imandra, 35 km south of Khibiny and about 10 km from Polarnye Zori town. It constitutes a single hill with several peaks. The massif has a small area of 6.4 km^2 [11]. It is a Paleozoic intrusion dated by the U-Pb method at 379 ± 5 Ma [1]. It shows similar age to other intrusions in the Kola Peninsula region [8]. It shows an isometric shape with numerous apophyses of pyroxenites. It is characterized by a distinct zone-ring structure. Analyzing the geological structure of the Afrikanda massif (Figure 4), two zones can be distinguished in it, the outer and the inner. The outer ring is made of melteigites. The inner zone comprises various alkaline and ultramafic rocks: olivinites, pyroxenites, and carbonatites (Figure 4). The discussed intrusion represents a complex of ultramafic and alkaline formations, which show the occurrence of clinopyroxene-perovskite association with olivines, orthopyroxenes, as well as magnetite, titanomagnetite, rutile, and titanite. Olivines usually have a significant proportion of magnesium and iron and minor admixtures of nickel. As a result of residual crystallization, pegmatites were formed, in which garnet-schorlomite occurs. Along with the subsequent stages of formation of these rocks, there are processes of their metasomatic transformation (phenitization, amphibolization, and saussuritization). Phenitization causes the appearance of apatite, nepheline. These rocks also show the effects of hydrothermal interactions highlighted by the presence of Cu, Zn, Pb sulfides, and sulfates such as barite [45].



Figure 4. Microphotograph of typical rocks from the Lovozero massif. Massive syenite with visible aegirine crystals and eudialyte, apatite, nepheline, and loparite (**A**); Foyaite with visible apatite, zonal eudialyte, albite and orthoclase, and associated aegirine and loparite (**B**).

The Kovdor massif occurs in the southwestern part of the Murmansk District, in the vicinity of the Finnish border. It is an intrusion composed of concentrically arranged rocks, with an area of 25 km² [49–54]. The age of this massif is determined to be 382 ± 3 Ma [55]. The massif includes Lake Kovdor and a mining town of the same name. This intrusion is composed of ultramafic and alkaline rocks, which are arranged in several circles. The outermost one is formed by syenites and melilites found in the marginal zone. In the next one, these rocks transition into pyroxenites, among which olivine is also found [49–54]. These rocks are located in the central part of the massif. They are interspersed with carbonatites (calcite phoscorites, dolomite phoscorites, calcite-dolomite phoscorites, and manetitites) in which magnetite is the main component. In these rocks, apart from carbonates and magnetite, there are also diopside, olivine, nepheline, apatite, and many rare minerals such as loparite, perovskite, baddeleyite, and others. Accompanying these rocks are phlogopite crystals, the aggregates of which sometimes reach considerable sizes. In weathering zones, phlogopite transforms into vermiculite. In the zones of fractures and tectonic faults, there are breccias cemented with apatite [54]. Like Afrikanda, this intrusion is a complex of ultramafic and alkaline rocks. In this intrusion, there are also zones of derivatives crystallizing in the form of large-crystalline pegmatites with phlogopite, diopside, accompanied by magnetite, and carbonates. In the contact zone of the intrusion, one can observe strong phenitization of rocks forming transition zones where apatite and melilites can be found. In the discussed intrusion, there are also numerous dispersed sulfides forming polymetallic phases of multistage hydrothermal crumbling. However, the proportion of these phases is relatively small.

4. Materials and Methods

Rock samples were collected by the author during numerous field investigations between 1999 and 2021. During this time, the discussed massifs were visited, and geological documentation of the samples was also done. In the Khibiny massif, the Malaya Belaya valley regions, Takhtarvumchorr region, Kukisvumchorr, and the massifs surrounding Lake Vudiavr were studied. In the Lovozero region, these were the Aluaiv and Karnasurt Mts. slopes in the western part of the massif and the Flora region in the northern part. In the Afrikanda area, rocks were sampled in the main quarry and several smaller ones in this intrusion. In the Kovdor area, samples were taken corresponding to the most important rock types discussed in the main quarry area. The selected rocks were targeted for thin section preparations to determine further the characteristics of the minerals discussed. Subsequently, these minerals were subjected to analyses using a Leica DM2500P polarizing optical microscope and examination with a Scanning Electron Microscope Hitachi SU6600, with an EDS attachment. These samples were analyzed under low vacuum (10 Pa), 15 kV beam diameter of 02 µm. A total of 3711 mineral analyses were performed in the microprobe (at Khibiny 676, at Lovozero 1338, at Kovdor 888, and Afrikanda 869, respectively). Next, the selected minerals were separated and analyzed with single-crystal X-ray diffraction. Data were collected on a Rigaku diffractometer (Rigaku, Tokyo, Japan) with CuK α radiation (λ = 1.54184 Å) at 293 K. Crystallographic refinement and data collection as well as data reduction, and analysis was performed with the CrysAlisPro 1.171.39.27b (Rigaku Oxford Diffraction, Tokyo, Japan) [56]. Selected single crystals were mounted on the nylon loop with oil. Structures were solved by applying direct methods using the SHELXS-86 program and refined with SHELXL–2018/3 [56–60] in Olex2 software [57]. These samples were also examined with the FTIR technique. Samples were measurement using Shimadzu FTIR spectrophotometer equipped with an ATR accessory, QATR-S (wide-band diamond crystal). Apodization Function: Happ-Genzel, Detector: DLATGS. Every single spectrum was obtained from 25 records at 2 cm⁻¹ resolution ranging from 250 to 2000 cm⁻¹. The elaboration of a spectrum was carried out using Grams 9.1 program. Optical and microscopic studies were performed in the Department of Geology, Soil Science, and Geoinformation of the Institute of Earth and Environmental Sciences, and crystal-chemistry studies were performed in the Department of Crystallochemistry, Faculty of Chemistry, Maria Curie-Skłodowska University in Lublin. FTIR analysis was performed in the Department of Biophysics, University of Life Sciences in Lublin.

5. Results

5.1. Petrology of Selected Massifs

To better describe the mineralogy of the phases discussed in the title, the main features of the most important rocks of the massifs are briefly presented: Khibiny, Lovozero, Afrikanda, and Kovdor.

5.1.1. Khibiny

In the Khibiny massif, these are massive syenites, melasyenites, porphyritic foyaites, and apatite-nepheline ores. Massive syenites-khibinites are usually grayish-greenish rocks with a coarse crystalline structure and compact, disorderly texture (Figure 3A). Large crystals of orthoclase and albite are visible along with other minerals of the rock, filling the space, touching each other. They are accompanied by needle-shaped aegirine crystals, which form sheaves, radial clusters, sometimes interspersed with feldspar. Next to these minerals, riebeckite appears. Along with these minerals, nepheline with characteristic cube-shaped crystals and apatite forming an admixture occurs in the rock. Large crystals of eudialyte, usually cherry red, can also be seen in the rock. Arfvedsonite, astrophyllite, and lorenzenite are found as accessory minerals. Ore minerals are represented by ilmenite and titanite (up to 10% by volume) less frequently, loparite, pyrite, magnetite. Melasyenites (malinites) are a variety of rocks that form vein formations and usually have fine crystalline structures and linear textures (Figure 3B). They are also distinguished from the above syenites by the increased presence of mafic minerals. There is much more aggirine in the matrix of these rocks, but sometimes augite aegirine, arfvedsonite, aenigmatite, ilmenite, and titanite are found. Occasionally there is also a large admixture of hematite. Porphyritic foyaites, on the other hand, are gray-pink rocks with a coarse-crystalline, porphyritic

structure and a compact, disorderly texture. The matrix of these rocks consists of orthoclase, nepheline, and apatite crystals.

Next to these minerals, eudialyte is sometimes visible in the rocks. It is interspersed with needles of aegirine, which also occurs in the spaces between the discussed crystals. It is accompanied by biotite. Aenigmatite, arfvedsonite, and phlogopite are also present. Ore minerals are represented by titanite, ilmenite, as well as pyrite and titan-rich magnetite. Nepheline-apatite-titanite ores are brown-greenish-pink rocks with a coarse crystalline structure and compact, disorderly texture. The matrix in this rock are crystals of apatite and nepheline in different proportions co-occurring with each other. They are also accompanied by titanite, sometimes forming a matrix mineral in the rock. Titanite in these rocks usually shows a zonal structure. Along with these minerals, aegirine and ilmenite are also leading minerals. The accessories minerals such as aenigmatite and arfvedsonite were also found.

5.1.2. Lovozero

The Lovozero Massif contains mainly massive syenites, lujavrites, foyaites, jovites, and porphyrites. Massive syenites are gray-green rocks with a fine crystalline structure and a compact, disorderly texture (Figure 4A). Larger phenocrysts of microcline accompanied by plaques of albite and apatite embedded in a finer matrix (or groundmass matrix) of the rock are visible. Between these crystals, one can see nepheline and aegirine. Next to them, the eudialyte is also visible. Accessory minerals visible are titanite, loparite, lovozerite, and many other minerals. They are accompanied by ore minerals such as titanite, ilmenite, and pyrite. Apatite is usually enriched in cerium, while titanite is in niobium, thorium, and cerium. Lujavrites are gray-green rocks with red speckles with a medium crystalline structure, an extremely linear texture, which is emphasized by femic minerals. The rock matrix is formed by aggirine crystals, giving the rock its linearity. They are accompanied by augite and aenigmatite. Between these crystals, apatite, albite, and eudialyte are visible, forming red "dots" in the rock. Between these minerals, there is also loparite and ilmenite. Accessory minerals are present in small additions, including pyrite, chalcopyrite, and zircon. Foyaites are grayish rocks of medium crystalline structure with a compact and linear texture. In this rock, the matrix is formed by aegirine needles between nepheline and microcline crystals (Figure 4B). Next to these minerals apatite, albite sometimes single crystals of small eudialyte are visible. They are accompanied by ilmenite, loparite, riebeckite. Also, single crystals of zircon can be seen. There are varieties rich also in murmanite, a characteristic pink mineral that occurs in these rocks. Jovites are rocks with a greenish color, porphyritic structure, and linear texture. These rocks are similar to the foyaites described above, with a larger amount of leucocratic minerals occurring in them. The rock matrix consists of microcline, nepheline forming large crystals interlayered with aegirine. Next to them, eudialyte and ilmenite may also occur. In these rocks may occur loparite and titanite. Porphyries are gray-green rocks with porphyritic structure and compact, disorderly texture. The rock matrix is built by aegirine needles together with albite, microcline, nepheline. These are generally fine-crystalline minerals. Next to them, there are large, euhedral crystals of eudialyte, lorenzenite, epistolite, astrophyllite, loparite, and narsarsukite. As a rule, these crystals have a skeletal character; except for a certain border made of the phase that builds the discussed minerals, the interior is filled with numerous fractures forming the rock matrix. Small druses filled with euhedral crystals of eudialyte, lorenzenite, and aegirine can be found in these rocks.

5.1.3. Afrikanda

In the Afrikanda massif, there are pyroxenites and olivinite accompanied by magnetitites as well as melteigites, pegmatites, and carbonatites. Pyroxenites and olivine pyroxenites are black or black-greenish rocks, with a coarse and very coarse crystalline structure, compact, disorderly, less frequently miarolitic texture. The rock matrix is formed by large crystals of pyroxene (diopside, augite, and aegirine), sometimes reaching several centimeters in size; next to these crystals, there are also large aggregates of phlogopite reaching several centimeters in size. Between these minerals, the common hornblende is seen accessory. They are accompanied by biotite, apatite, magnetite, and perovskite. The accessory is also epidote, chlorite, sulfides (pyrite, chalcopyrite, chalcopyrite, sphalerite), and sulfates (barite). Sometimes, there are druses filled by euhedral diopside, magnetite, perovskite, and carbonates in the discussed rocks. Olivinites are black-green rocks with a fine crystalline structure, disorderly texture (Figure 5B). The matrix of these rocks is built by olivines, often serpentinized, and next to them, one can see small admixtures of diopside, nepheline, and apatite. Magnetite-perovskite magnetites are metallic-black, coarse-crystalline, granular rocks with a compact, disorderly texture (Figure 5A). The matrix of these rocks is formed by magnetite, which is close together with large crystals reaching up to 1 cm in size. It is accompanied by perovskite with polysynthetic associations, sometimes with an admixture of Ce-rich perovskite (knopite). Apart from these minerals, sometimes single crystals of orthopyroxene, carbonates, titanite are found in the discussed rocks. Accessories are pyrite, chalcopyrite, pentlandite. Melteigites: these are pink-greenish rocks with a coarse crystalline structure, compact, disorderly structure. The matrix of these rocks consists of orthopyroxene crystals (bronzite), sometimes accompanied by olivine (serpentinized). These minerals occur in the matrix of nepheline and sodalite. Apatite and microcline titanite are also visible next to them. Carbonatites are light gray rocks, occurring mainly in the form of veins, druses, and small accumulations accompanying magnetite-perovskite ores and other rocks (e.g., pyroxenites and peridotites). They have a coarse crystalline structure, compact, disorderly texture. They are composed mainly of calcite and dolomite and, in smaller amounts, strontianite. Between these crystals, there sometimes appear very well-formed (self-shaped) titanites, perovskite, magnetite, and also diopside, hornblende, phlogopite. Pegmatites are rocks distinguished primarily by their large crystalline structure of the rock. The matrix of these rocks consists of albite with microcline and also phlogopite, epidote, and chlorite. The feldspars are often sericitized. In these rocks, there is a rare schoolmite garnet, sometimes reaching several cm in size. The accessory is titanite, magnetite, and ilmenite.



Figure 5. Microphotography of typical rocks from the Afrikanda massif. Perovskite magnetite magnetities with diopside (cpx), magnetite (mag), and perovskite (prv) (**A**); olivinite with olivine (ol) serpentinized crystals (srp), magnetite, and perovskite (**B**).

5.1.4. Kovdor

In the Kovdor massif, syenites are the rocks of the contact zone. They have a coarsely crystalline, poikilitic, compact, disorderly texture. The rock matrix is filled by aggregates of

aegirine and diopside accompanied by large crystals of nepheline and orthoclase. They are accompanied by apatite and small amounts of magnetite. Melilites are also found among these rocks. These rocks have a coarse crystalline structure, compact texture, sometimes porphyritic. The matrix of these rocks consists of melilite crystals in contact with each other. Next to these minerals, there is nepheline and apatite. Single magnetite crystals, phlogopite aggregates, and carbonates can also be seen in the rock. In the central part, these rocks transform into pyroxenites. Pyroxenites have a coarse-crystalline, porphyritic structure with a compact, disorderly texture. They are dominated by diopside accompanied by hypersthene. These minerals are usually large, compactly contacting each other. In the spaces between them, magnetite has crystallized, subordinately also hercynite. Single crystals of olivine and small aggregates of phlogopite can also be seen in these rocks. Between these phases, apatite and calcite are also sporadically present in the rock. Olivinites are rocks that accompany pyroxenites. They have a fine crystalline structure and a compact and disorderly texture (Figure 6A). They are composed mostly of olivine, sometimes bearing traces of serpentinization visible in the marginal zones of the crystals. In their vicinity, one can see magnetite, usually of small size. Next to olivine, there are also crystals of diopside and aggregates of phlogopite. Sometimes single specimens of nepheline, apatite, and carbonates can be found in the spaces between these minerals. Phoscorites and associated magnetitites can be found in the central part of the intrusion. Phoscorites are coarsely crystalline rocks with a compact, disorderly texture (Figure 6B). They are characterized by the presence of various carbonates. These are crystals of calcite, dolomite, or carbonates doped with iron and other elements (e.g., strontium). In addition to these carbonates, the rock contains euhedral crystals of diopside, which occur together with aggregates of phlogopite. Magnetite crystals are also found in these rocks, sometimes in significant amounts forming transitions to magnetitites. They are also accompanied by baddeleyite, monazite, and loparite in small amounts. Next to mafic minerals, one can also see small crystals of apatite and nepheline. Hematite and sulfides (pyrite and chalcopyrite) also occur accessorily. In tectonic zones, there is also a breccia cemented with apatite. Next to apatite and carbonates, there is vermiculite, sometimes forming quite large aggregates. It is accompanied by magnetite, nepheline, and hematite.



Figure 6. Microphotographs of typical rocks from the Kovdor massif. Olivinite with visible crystals of olivine and apatite and nepheline (**A**); phoscorites with visible calcite (cal), phlogopite (phl) nepheline, and crystals of magnetite (**B**).

5.2. Structures of the Discussed Minerals

Lorenzenite is chocolate brown, forming nice crystals up to several cm in size. Both single euhedral specimens of 2–3 cm in size and smaller, usually darker, can be observed. These are usually euhedral crystals found in porphyrites.

These minerals in the Lovozero massif usually have a skeletal character (Figure 7A). Their outer boundaries are formed properly, while in the middle, they have numerous inclusions of ambient minerals cemented by the substance of the phase in question. In the Khibiny massif, lorenzenite is found less frequently among syenite rocks. It forms single small crystals in the vicinity of titanite and other mafic minerals.



Figure 7. Macro photographs of the minerals discussed: lorenzenite (**A**), loparite (**B**), perovskite (**C**), titanite (**D**), apatite (**E**), and eudialyte (**F**).

Loparite in the discussed rocks forms small crystals with a metallic silver-steel luster. It usually forms polysynthetic twins (Figure 7C). This is evident both in the shape of the discussed crystals showing twinned adhesions. In the rocks of the Lovozero massif, these crystals are euhedral similarly in the Khibiny massif. The Kovdor rocks show farreaching corrosion and have a strongly developed boundary. In Afrikanda, they rarely occur, accompanying perovskites by filling the spaces between these minerals, crystallizing on their walls as a form of epitaxy.

Perovskite macroscopically forms crystals with a metallic luster and steel-gray color, up to 1 cm in size. It forms euhedral crystals with numerous twinned adhesions, occurring as admixtures in pyroxenites and other Afrikanda rocks (Figure 7B). In megnetitites, they form nested ore-like accumulations, filling 80% of the volume of these rocks. At Kovdor, they are usually heavily corroded, as is loparite, accompanying magnetites in phoscorites. At Khibiny, they infrequently occur in the vicinity of femic minerals such as titanite and pyroxene.

Titanite usually has strongly elongated crystals reaching several mm in size, colored in chocolate brown (Figure 7D). In the Khibiny massif, it forms large crystals, sometimes with a visible sector structure. In syenitic rocks, it forms numerous admixtures together with ilmenite. In the ore zone, it forms rock-forming accumulations, together with nepheline, apatite, and femic minerals, forming admixtures. In these rocks, it is often twinned. In malinites, it occurs in anhedral form, crystallizing between crystals of aegirine, arfvedsonite, nepheline, and apatite. In the Lovozero massif, titanite occurs less frequently, accompanying femic minerals and often having an anhedral shape. In the Afrikanda massif, titanite occurs adjacent to perovskite, where it forms xenomorphic crystals together with carbonates. At Kovdor, titanite occurs accessorily in the form of small admixtures in the rocks in question.

Apatite usually has sugary light green or pink crystals. It forms minor accessory admixtures in all the discussed rocks of the Khibiny, Lovozero, Afrikanda, and Kovdor massifs. These minerals usually have a euhedral shape, are small in size, and co-occur with other phases in the discussed rocks (Figure 7E).

Carbonates form anhedral crystals, forming carbonatite veins cutting the Afrikanda pyroxenites. They are also present in minor admixtures in Afrikanda pyroxenite rocks, occurring between clinopyroxene and magnetite crystals. Small admixtures of carbonates were also found in the Khibiny massif stuck in the space between aegirine and titanite, nepheline. At Lovozero, calcite is much less common. In addition, at Khibiny, there are zones of carbonatite breccias in the northeastern part of the massif. At Kovdor, the carbonates form complexes of phoscorites rocks, where they occur in significant amounts co-occurring with magnetite, apatite, pyroxenes, olivine, phlogopite, and other minerals. These carbonates are represented by calcite, dolomite, less frequently ankerite, siderite, and strontianite. The latter often occurs as admixtures and inclusions in other carbonates, also accompanying phosphates.

Eudialyte crystals usually have a cherry-red to light blood-red color (Figure 7F). In rocks of the Khibiny massif, they usually form anhedral crystals crystallizing between nepheline, apatite, and femic minerals. In the vein varieties of malinites (melasyenites) they usually form crystals that have a sector structure. In the Lovozero Massif, these crystals are more intensely red and sometimes have euhedral forms (in porphyrites) where they crystallize similarly to Lorenzenite forming euhedral, skeletal crystals with numerous fractures in the center.

5.3. Optical Properties of the Discussed Minerals

Lorenzenite in the thin section is a mineral with visible positive relief, this relief is the highest of all the minerals discussed. It has straw-brown colors showing dichroism. In polarized light, it has interference colors on the borderline of the 2nd order (Figure 8A,B).

Loparite in a thin section has the same high positive relief as lorenzenite (Figure 8C,D). It shows a brown-orange coloration, and under polarized light, the sector structure and polysynthetic twins are visible. Interference colors are of the 3rd order, but because this mineral is dark, these colors are not well visible and on the matrix of other minerals forming more intense interference colors.

Perovskite also has high positive relief, in the thin section forming brown colored crystals, in polarized light, it shows a gray-blue color on the border between the colors of 3rd order. Polysynthetic twinning can be seen in it (Figure 8E,F).



Figure 8. Microphotographs of minerals by polarization microscopy in transmitted light (1N: (**A**,**C**,**E**,**G**,**J**,**M**)) and polarized light (Nx: (**B**,**D**,**F**,**H**,**I**,**K**,**L**,**N**,**O**)): lorenzenite (**A**,**B**); loparite (**C**,**D**); perovskite (**E**,**F**); titanite (**G**–**I**); eudialyte (**J**–**L**); apatite (**M**,**N**); and calcite (**O**).

Titanite is a well-known mineral. In the rocks of the discussed massif, it has a positive relief although much smaller than the minerals discussed above. In a thin section, it shows a trace color in straw-brown tones. In polarized light, it dims obliquely and has interference colors of the 3rd order of a brown character, showing sector structure and twins (especially in Khibiny rocks, Figure 8G–I).

Carbonates are mainly represented by calcite, less frequently ankerite dolomite, siderite, or strontianite. They form small crystals with positive relief. In a thin section, they are colorless, while in polarized light, they show interference colors of the third-order (Figure 8O). These minerals form their rocks in the Kovdor massif, where they are a rockforming component of calcite and dolomitic phocorites. In the thin section, a domain structure is often visible, emphasized by a change in the direction of optical alignment in the carbonate. In Afrikanda rocks, they form small nests in pyroxenites and adjacent to perovskite in magnetitites. They also form mineral veins, where calcite is mainly present and is sometimes admixed with strontianite. In the Khibiny and Lovozero massifs, they usually represent a minor admixture of strontianite, although, at Khibiny, they also form carbonatite breccias in the northeastern region of the intrusion.

Eudialyte in the thin section is usually colorless, although it shows a slight pinkishcherry coloration in some rocks of Khibiny or Lovozero (Figure 8J–L). This crystal under polarized light is colored dark gray, sometimes showing a slight pleochroism in the colors of the borderline 1st order (dark purple-blue). Numerous twining, zonal, or sector structures of these crystals are then visible.

Apatite forms crystals with a small positive relief, in polarized light, it is usually dark gray. In most of the discussed rocks, it forms euhedral crystals occurring both in the vicinity of leucocratic minerals (with nepheline and feldspar) and in the form of inclusions accompanying femic minerals. In the Kovdor and Afrikanda massifs, it accompanies pyroxenes and olivines in the Khibiny and Lovozero massifs it occurs in titanite (Figure 8M,N).

5.4. Spectroscopic Properties of the Discussed Minerals

All the minerals in question were examined spectroscopically. Lorenzenite was examined from the 'Flora' exposure area in the northern part of Lovozero, loparite from the Aluaiv area in the northwestern parts of Lovozero, perovskite was examined from rocks at Afrikanda, titanite from the ore zone at Khibiny. Calcite was examined from the Afrikanda carbonatite veins, eudialyte was examined from the Kukisvumchorr area in Khibiny and the Aluaiv area in Lovozero. Fluoroapatite, on the other hand, as well as titanite, are from the Khibiny ore zone. FTIR spectroscopic spectra are shown in Figure 9. In the spectrum of lorenzenite, bands at 893 and 829 cm⁻¹ were observed, which correspond to stretching vibrations of the Si-O group, bands at 728, 688, and 308 cm^{-1} , which can be related to stretching vibrations of the Ti-O group, vibrations at 509 cm⁻¹ corresponding to bending vibrations of the Na-O group, and vibrations at 417 cm^{-1} correspond to bending vibrations of the Si-O group (Figure 9A). In the case of loparite (Figure 9B) and perovskite (Figure 9B), some similarity spectra were found in the region of 433–441 cm^{-1} indicating bending vibrations, in the case of loparite, the bending vibrations of the Ti-O group were noted at 326 cm^{-1} , while for loparite, it was 367 cm^{-1} . Ti-O stretching vibrations are seen in the region at 664 cm⁻¹ for the examined perovskite, while in loparite, these vibrations were not noted. In the group of minerals, perovskite-loparite-tausonite group of minerals, such types of vibrations may not be evident everywhere as described in [61]. In loparite vibrations in the region, 503 cm^{-1} are visible, which can be connected with torsional vibrations for Nb-O.

Vibrations in the region of 710 cm⁻¹ in perovskite can be connected with Ca-O stretching vibrations and in loparite 811 and 727 cm⁻¹ for Ce-O group and Ca-O, Na-O groups. Unexplained remains a band in Perovskite in the region of 1245 cm⁻¹, which can come from carbonate suffix in this mineral. The examined titanite crystal (Figure 9C) has a band in the region of 845 cm⁻¹, which may be related to Si-O stretching vibrations, and in the region of 688 cm⁻¹, characteristic of stretching vibrations of TiO₆ octahedra. In the region of 554 cm⁻¹ and 372 cm⁻¹, bands corresponding to Si-O bending vibrations were found, and for 334 cm^{-1} , bending vibrations of the Ti-O group. Some deviations from the standard results [62] may be related to the substitution of small amounts of Th, Nb, Ce in place of Ca, Ti. In the case of the calcite spectra (Figure 9D), three large peaks were found at 1215 cm⁻¹, characteristic of the stretching vibrations of the carboxyl group, 660 cm^{-1} , and 490 cm^{-1} , and a small peak at 875 cm^{-1} probably related to the vibrations of the Ca-O bridge [63] and possible substitutions of Sr-O, and Ce-O, which occur in small amounts in the Afrikanda crystals discussed. Spectra of Eudialyte (Figure 9E) have been overlaid on spectra of samples from Khibiny and Lovozero. They show great similarity to each other. There are bands in the range of 764 cm^{-1} and 708 cm^{-1} , which correspond to tetrahedral vibrations. The bands in the range 519 cm⁻¹, 474 cm⁻¹, and 432 cm⁻¹ are from the stretching vibrations of Zr-O and Fe-O bridges [64]. From 301 to 311 cm⁻¹, there are stretching vibrations of tetrahedral groups. The slight differences in the vibrations of the eudialyte from Khibiny and Lovozero may be related to slight differences in the substitutions with Mn, Fe, Na, and Ca ions. For hydroxyl and chlorine groups, vibrations are recorded from 3200 cm^{-1} to 3700 cm^{-1} [64], which was not captured during the measurement. The examined fluorapatite from Khibiny (Figure 9F) shows a band at 890 cm⁻¹, characteristic of bending vibrations between oxygen and fluorine, and bands in the range 821 cm^{-1} , 755 cm⁻¹ associated with Ca-O stretching vibrations. The bands at 474 cm⁻¹, 371 cm^{-1} , and 340 cm^{-1} may be responsible for the bending vibrations of the Ca-O group and the phosphate group [65].

5.5. Single Crystals Analysis Results

The same crystal samples as in the spectroscopic analyses were examined, along with an eudialyte from Khibiny. Lorenzenite crystallizes in an orthorhombic—dipyramidal H-M Symbol (2/m 2/m 2/m) Space Group: P bcn [66]. The investigated crystal cell parameters from the 'flora' exposure in the Lovozero massif are a = 8.7035(9) Å, b = 5.2266(5) Å, c = 14.476(1) Å, Z = 4; V = 658.51 Å3 Den(Calc) = 3.44. Some minor differences in the cell parameters may be related to the La, Ce, Nd substitutions found in the micro-area studies. The crystal structure of lorenzenite is shown in Figure 10A. Some minor differences in the cell parameters may be related to the bad quality of the Lorenzenite crystals. Therefore, it cannot be excluded that the structure contains trace amounts of La, Ce, and Nd substitutions found in the micro-area studies.

The analysis of loparite showed that it crystallizes in isometric-hexoctahedral H-M system Symbol (4/m -3 2/m) Space Group: P m-3m [67]. The studied parameters of the Aluaiv slope crystal from the Lovozero massif are: a = 3.891(1) Å, Z = 1; V = 58.94 Å3 Den(Calc) = 4.79. The deviations from the standard data are related to the loparte-perovskite-tausonite crystallization system. The loparite-tausonite member crystallizes in a similar arrangement, while the loparite-perovskite cell arrangement differs (see text below). The substitutions of Nb, Ti, and Ce, Ca in the crystal structure modify the arrangement in which this mineral crystallizes. The crystal structure of the examined loparite is shown in Figure 10B. Both micro-area studies and spectroscopic analyses demonstrated this.

The situation is similar for perovskite. These crystals crystallize in an orthorhombic dipyramidal H-M Symbol (2/m 2/m) Space Group: P nma [68]. The elemental cell parameters of the studied crystal from Afrikand are: a = 5.4530(5), b = 7.660(3) Å, c = 5.397(1) Å, Z = 4; V = 225.45 Å3, Den(Calc) = 4.03. The differences in the studied values and the benchmark values are explained similarly for loparite, since Afrikanda is Ce-rich perovskite and, in addition, some Nb doping and probably also Fe were also found in the perovskite structure. An image of the crystal structure of perovskite is shown in Figure 10C.

Titanite crystallizes in the monoclinic—prismatic H-M system Symbol (2/m) Space Group: P 21/a [69]. The elemental cell parameters of the studied titanite from the Khibiny massif (ore zone) are as follows: a = 6.5605(5) Å, b = 8.7123(6) Å, c = 7.0698(5) Å, Z = 4; beta = 113.885° V = 369.48 Å3 Den(Calc) = 3.55.





Figure 9. FTIR spectra of the described minerals: Lorenzenite (**A**), Perovskite (black, (**B**)), Loparite (green, (**B**)), Titanite (**C**), Calcite (**D**), Eudialyte from Khibiny (black, (**E**)), Eudialyte from Lovozero (green, (**E**)), and apatite (**F**).

Some slight differences in the cell constant c and angle β in the studied crystal compared to the standard are probably due to substitutions of Nb and W, in place of Ti, found in these crystals. The crystal structure of titanite from Khibiny is illustrated in Figure 10D.

Calcite from carbonatite veins in the Afrikanda massif was studied. Calcite crystallizes in a trigonal-hexagonal Scalenohedral H-M Symbol (3 2/m) Space Group: R 3c [70]. Some admixtures of strontianite (crystallizing in the Orthorhombic-Dipyramidal H-M Symbol (2/m 2/m 2/m) Space Group: Pmcn [70]) and Ce admixtures in the calcite crystal structure found in the micro-area. The crystal structure of calcite is visualized in Figure 10E.

The mineral eudialyte is a part of the eudialyte group, in which numerous substitutions of Na, Ce, La, Sr, Mn, Ti, and Fe [64] can occur, this also influences the nature of the elementary cell of this crystal. The studied eudialyte crystallizes in trigonal-hexagonal scalenohedral H-M Symbol (32/m) Space Group: R -3m [71]. Its elemental cell parameters are: a = 14.2508(2) Å, c = 30.0846(5) Å, Z = 12; V = 5291.19 Å3, Den(Calc) = 3.67. And are consistent within error with the reference structures from [71]. The eudialyte crystals studied in the microarray, along with their given formulas, are in the text below. An illustrated eudialyte elemental cell from the Khibiny massif is illustrated in Figure 10G.



Figure 10. Results of the crystal structure of described minerals: lorenzenite (**A**), loparite (**B**), perovskite (**C**), titanite (**D**), calcite (**E**), apatite (**F**), and eudialyte (**G**).

Apatites are minerals that have numerous substitutions. It may be hydroxyapatite, fluorapatite, chlorapatite, carbonate-rich apatite, while Ca be replaced by La and Ce. In the Khibiny massif, fluorapatite is the most common (visible in the examined structure), although carbonate and chlorine admixtures are also found. The studied apatite crystal from the ore zone in the Khibiny massif crystallizes in the Hexagonal—Dipyramidal H-M Symbol (6/m) Space Group: P 63/m [72], and has the following elemental cell parameters: a = 10.0103(3) Å, c = 8.3924(3) Å, Z = 2; V = 728.30 Å3 Den(Calc) = 3.20. The sizes in the c direction deviate significantly from the reference structure. The crystal structure of Khibiny fluorapatite is illustrated in Figure 10F.

5.6. Results of SEM-EDS Analyses

5.6.1. Lorenzenite

This mineral has been found in rocks of the Lovozero and Khibiny massifs [73–77]. At Lovozero, it occurs mostly among porphyrites, where it forms euhedral crystals together with eudialyte, astrophyllite, epistolite, and murmanite. Analyses in the SEM-EDS (Figure 11A) showed that this mineral contains small amounts of niobium. In the boundary zones of the crystal, numerous small inclusions of phosphates containing La, Ce, Pr, Nd, and loparite, also containing some of U, were found. In the Khibiny rocks, it was found as an admixture, accompanying rocks of the ore zone; these minerals co-occur with titanite and pyroxenes. Lorenzenite in these rocks has an anhedral shape and is generally small and strongly corroded. Details are shown in Table A1 in the Appendix A.

5.6.2. Loparite

This mineral has been found in all the discussed massifs, although it occurs in them in different proportions [78–85]. In the Lovozero massif, it is relatively common, occurs as an accessory mineral, and is a rock-forming mineral in some pegmatites. In Lovozero rocks, it usually has a euhedral shape and is visible against other minerals. The results of the analysis in the Lovozero loparite SEM-EDS showed that it contains admixtures of uranium and strontium. The mineral also has niobium in it. In the Khibiny Massif, loparite occurs much less frequently. It has been found, inter alia, in the ore zone, where it accompanies apatite-nepheline rocks in the vicinity of titanite. It is typically small in size and corroded. Analysis in the SEM-EDS (Figure 11B) showed that loparite from Khibiny is sometimes slightly doped with strontium. In the Kovdor rocks, loparite is relatively common as a minor admixture. It co-occurs with magnetite, which is often intergrown with perovskite, and with femic minerals such as pyroxene and phlogopite. SEM-EDS analysis has shown that some of these minerals are admixed with Ta and U, and also Th and Cd. Small admixtures of barite are also found in their vicinity. In Afrikanda rocks, loparite is a rare mineral, co-occurring with perovskite and Ce -rich perovskite as minor associated phases.

The results of the SEM-EDS analyses for loparite are shown in Table A2 in the Appendix A. The results of the analyses are shown in Table A3 in the Appendix A.

5.6.3. Perovskite

This mineral has been found in all massifs discussed [46–48,81]. In Afrikanda, it occurs mostly in rocks (derivatives in magnetitites and pyroxenites). The crystals found there are numerous, large, euhedral. Studies in the SEM-EDS (Figure 11C) have shown that it is doped with Ce, Th, Nb, and sometimes W. In the Kovdor massif, perovskite is also relatively abundant accompanying magnetites, growing on these crystals and in the form of admixtures in femic minerals. In the Khibiny massif, it rarely occurs, as a small admixture in rocks of the ore zone co-occurring with titanite. The same is true in the Lovozero massif, where small amounts of this crystal have been studied in jovite rocks (04LV12). These minerals in this massif have numerous admixtures of Nd, Th, and sometimes also Ce and Th [86].

5.6.4. Titanite

This mineral occurs in all discussed massifs [73–75,86,87]. The Khibiny massif sometimes forms significant accumulations, especially in the ore zone, where it can occur as a rock-forming mineral together with arfvedsonite and aegirine in intercalations with apatite-nepheline ore. In other rocks, it is often present along with ilmenite and less often with magnetite. The titanite specimens examined in the SEM-EDS (Figure 11D) often show admixtures of Nb, Ta, and, less frequently, W. Moreover, inclusions of lanthanide-containing phases are common in these minerals. The same is true for titanite from the Lovozero massif, where it is less common, although it occurs along with ilmenite in syenites, lujavrites, and jovites. When examined in the SEM-EDS, it has abundant admixtures of Nb, Th, Ce, and occasionally Nd, as evidenced by SEM-EDS analyses. Among the Afrikanda rocks, titanite sometimes co-occurs with perovskite, forming a phase of a secondary character, while in the rocks of the Kovdor massif, it is a rare phase. The results of analyses in the SEM-EDS of this mineral can be found in Table A4 in the Appendix A.

5.6.5. Calcite

Calcite occurs in all of the discussed massifs in varying proportions. Most of these minerals are found in Kovdor, where they root their rocks (phoscorites) [4,10–13,49–52,88–93]. In this massif, it is usually calcite, sometimes admixed with iron and manganese. Along with calcite, there is also dolomite forming dolomite phoscorites. In the Afrikanda massif, carbonates are represented mainly by calcite. It forms carbonatite veins and nests among pyroxenites and other rocks. Studies of the SEM-EDS showed that there are numerous admixtures of lanthanum and cerium, and less frequently strontium (Figure 11G). In the Khibiny massif, calcite is an accessory mineral and is less common in alkaline rocks except in zones in the northeastern part of the massif where carbonatites and carbonatite breccias occur. The studied calcite from Khibiny has a large admixture of strontium (strontianite). In the Lovozero massif, as in Khibiny, carbonates generally occur less frequently as accessory minerals in some alkalic rock types. The studied rock samples are dominated by a large admixture of strontium similar to Khibiny. The results of the analyses in the carbonate micro-area can be found in Table A7 in the Appendix A.

5.6.6. Eudialyte

Eudialyte occurs in rocks of the Khibiny and Lovozero massifs [94–97]. At Khibiny, eudialyte is an accessory mineral to many different rocks, as it is at Lovozero. Detailed analyses in the SEM-EDS (Figure 11F) showed little variation in the occurrence of zircon, manganese, and occasionally doped titanium contents in these minerals (can be found in Table A6 in the Appendix A).

5.6.7. Apatite

Apatite crystals co-occur in rocks in all discussed massifs [52,77,89]. At Khibiny, they form rock-forming accumulations in the ore zone, where nepheline-apatite rocks occur. In addition to these rocks, apatite is also present in all varieties of agpatite rocks found there, usually as an accessory mineral. Analyses in the SEM-EDS (Figure 11E) showed that hydroxyapatite sometimes dominates with a small admixture of fluorine less frequently chlorite. The same is true for the Lovozero massif, where apatite also occurs frequently as an accessory mineral. Studies in the SEM-EDS also indicate the occurrence of hydroxyapatite admixed with fluorine, rarely chlorine. In addition, admixtures of lanthanum, cerium, strontium less frequently silver are found in this mineral. In the Afrikanda massif, apatite forms an accessory mineral representing as above hydroxyapatite and fluorapatite. In the case of the Kovdor rocks, apatite sometimes forms their breccias, filling their spaces. These are usually phases of apatite, growing in a concentric form on crumbs of phoscorite breccia. Apart from these zones, apatite also occurs as accessory crystals in rocks, usually as hydroxyapatite and less frequently as fluorapatite. Micro-area studies have shown that barite inclusions are also sometimes present in this mineral. The results of micro-area analyses of this mineral can be found in Table A5 in the Appendix A.



Figure 11. Example EDS spectra of the studied minerals: Lorenzenite (**A**), loparite (**B**), perovskite (**C**), titanite (**D**), apatite (**E**), eudialyte (**F**), and carbonates (**G**). The elemental contributions to each phase are discussed in the text.

6. Discussion

The discussed minerals are important components of rocks in the Khibiny, Lovozero, Kovdor, and Afrikanda massifs. Their presence indicates multi-stadial crystallization processes occurring in the discussed intrusions [98–106]. Perovskite is the mineral of the earliest crystallization that occurs mainly in the Afrikanda massif, less frequently in Kovdor, and is a rare mineral in the Khibiny and Lovozero massifs. In contrast, REE-rich phases such as knopite and loparite are phases that crystallized somewhat later in the crystallization phase of the contaminated melt. It is evidenced by the petrographic features, where in the microscopic image, knopite occurs mostly in the outer parts of perovskite or the crack zones of this crystal. SEM-EDS studies showed numerous Nb and Sr substitutions in perovskite, which was also confirmed by single crystals analysis and FTIR studies. In turn, loparite occurs in rocks in an accessory form, crystallizing together with alkaline phases such as eudialyte and lorenzenite. In carbonatite rocks, loparite has a corroded character which may mean that under changing conditions, it was disintegrated. This hypothesis may be supported by the fact that loparite and perovskite occur at Khibiny, mainly as an admixture among femic minerals, most often together with titanite. In addition, analysis of titanite from Khibiny and Lovozero indicates that it often has Nb admixtures as in loparite. The crystallizing phases in the Loparite-Perovskite-Tausonite series have many dopants indicating some contribution of these members to the loparite structure. Their microanalysis and single-crystals, as well as FTIR studies, indicate a small admixture of Nb and Ti, and Ce and Ca in the crystal structure modify the arrangement in which this mineral crystallizes. Titanite occurs much more frequently at Khibiny and Lovozero than at Afrikanda and Kovdor. It is a secondary mineral to perovskite and loparite, which passed to titanite during the impact of secondary processes. In zones of titanite occurrence, one can see relicts of perovskite and loparite, especially in Khibiny. Due to the nature of titanite (usually a secondary mineral after perovskite or loparite), REE dopants are also found in this mineral. Apatite crystallized probably at the same time as loparite. This is evidenced especially by apatites in the ore zone rocks, forming euhedral crystal inclusions along with loparite and perovskite surrounded by titanite. Apatite from the discussed massifs is also rich in REE elements which were identified using SEM-EDS, single-crystals, and FTIR analysis. Minerals such as lorenzenite and eudialyte crystallized in the residual or hydrothermal phase [40,88,93]. This is particularly evident in the porphyrites of the Lovozero massif, where these minerals form skeletal crystals with numerous inclusions of surrounding phases. In the other rocks of the Lovozero and Khibiny massifs, eudialyte usually forms minerals of anhedral character filling the voids in the rocks between mafic phases as well as feldspars. Lorenzenite is present only in a few hydrothermal impact areas like the porphyrites mentioned above. Crystal structure analyses indicated a model crystal structure. However, FTIR studies showed some slight differences between the eudialyte from Khibiny and that from Lovozero. Carbonates in the discussed massifs are usually present in the form of admixtures, although, in Afrikanda, they form their nests and Kovdor rocks. Their position has been the subject of dispute for many researchers, who have emphasized their features indicating both crystallization during the mixing phase of alkali melts with supracrustal material and later [86]. Isotopic studies of these minerals indicate that they were generally formed by fluid crystallization from the Earth's mantle, although some crystallize later, as also evidenced by δ^{13} C values in carbonates [11,89,107] and δ^{34} S sulfides [108–111]. This is also confirmed by data obtained by other researchers. According to Arzamastsev, the age of perovskite from Khibiny is 383 ± 7 Ma, while the age of apatite-nepheline phases is 370 ± 3 Ma, respectively [22]. This indicates the order of crystallization of these phases. Sr-Nd [89] isotopic data indicate a mantle origin of the components of the intrusions in question and subsequent contamination with supracrustal material at the migration stage of these magmas towards the Earth surface and their further evolution during the formation of the intrusions in question. The Afrikanda and Kovdor intrusions have the most primordial character, and the Khibiny and Lovozero intrusions

are the most contaminated [112]. This hypothesis is also supported by the geochemical data and results of helium isotope studies [113,114].

7. Conclusions

The discussed minerals are indicator phases in intrusions of ultramafic and alkaline rocks. Their presence is associated with different phases of the evolution of the melts from which the intrusions were formed in the Kola-Karelian Alkaline Province [7,20,21,115,116]. Their presence and petrographic character indicate the processes of their crystallization, corrosion, and phase formation at the expense of these minerals (e.g., titanite after loparite and perovskite). These minerals in the discussed massifs are carriers of REE elements. They are interesting from a mineralogical as well as deposit point of view. Their optical, spectroscopic features are closely related to the internal structure, optical properties of these minerals, and the form of crystallization. Their presence in alkaline rocks arouses interest and is an important genetic indicator of the studied rocks. The occurrence of these phases in the Khibiny, Lovozero, Afrikanda, and Kovdor intrusions is unique in the world. These massifs are relatively easy to access; moreover, the Khibiny and Lovozero massifs are large, showing the multi-zone nature of the different rocks. This provides the opportunity to observe these minerals macroscopically and study them with modern methods of analysis.

Author Contributions: Conceptualization, M.H.; methodology, M.H., D.K. and G.C.; software, M.H.; validation, M.H., D.K., G.C. and E.K.; formal analysis, M.H.; investigation, M.H.; resources, M.H. and E.K.; data curation, M.H.; writing—original draft preparation, M.H., D.K. and G.C.; writing—review and editing, M.H.; visualization, supervision, and project administration, M.H.; funding acquisition, M.H. and E.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: This statement if the study did not report any data.

Acknowledgments: Authors would like to acknowledge of V. V. Balaganskiy and F. P. Mintrofanov from Kola Science Center of Russian Academy of Sciences, for help us collect minerals and needed informations.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Results of the microanalysis of the lorenzenite crystals.

Sample	0	Na	Si	Ca	Ti	Nb	u
CH20(3)_pt1	46.96	4.58	7.92		9.76		
CH20(6)_pt12	45.19	8.11	12.01		15.97		
CH20(6)_pt13	44.33	8.57	12.67		15.31		
CH20(6)_pt16	43.83	6.99	11.36		16.78		
CH20(6)_pt6	43.37	8.7	13.62		17.85		
CH20(6)_pt7	45.57	8.84	12.75		14.32		
CH20(6)_pt8	45.44	7.6	11.18		13.89		
CH20(6)_pt9	44	7.42	12.06		16.46		
06LV12-(2)_pt1	49.25	11.83	16.07		12.37		
47LV00(2)_pt3	49.67	17.16	15.53		15.86	0.81	
47LV00(5)_pt1	27.81	11.61	13.59		18.25	0.79	
51LV00(2)_pt1	22.33	9.09	15.72	0.88	42.28		
51LV00(2)_pt2	23.77	8.21	16.06	0.92	43.73		
51LV00(2)_pt3	23.52	8.25	16.29		40.73		
51LV00(2)_pt4	24.26	8.46	15.76	0.83	40.12		

Table A1. Cont.

Sample	0	Na	Si	Ca	Ti	Nb	u
51LV00(2) pt5	22.72	8.67	15.84		42.43		
51LV00(3) pt1	35.42	1.15	20.31	3.07	6.03	13.98	
51LV00(3) pt2	22.94	0.59	14 66	2	6.15	19.22	14.5
52LV00(3) pt3	52 27	17.13	16.93	-	12 29	17.22	11.0
$53LV00(0)_{pt0}$	30.47	9.83	16.06	0.6	40.66		
$53LV00(1)_pt1$	26.33	10.15	16.00	0.0	39.04		
$53LV00(1)_pt2$	20.55	10.15	16.14	0.65	38.9		
$53LV00(1)_pt3$ 52LV00(1)_pt4	20.44	10.20	16.42	0.05	27.49		
$55LV00(1)_pt4$ 52LV00(1)_pt4	30.44	0.11	16.42	0.71	21.40		
$55LV00(1)_pt5$ 52LV00(1)_pt6	20.75	9.11	16.40	0.71	31.4 20.07		
53LV00(1)_pt6	30.67	10.1	16.99	0.94	38.87	0.70	10.40
53LV00(2)_pt2	35.12	4.94	20.98	2.44	7.61	8.79	13.46
53LV00(3)_pt4	34.92	8.35	29.79	0.83	3.40		
54LV00(1)_pt1	29.24	3.19	11.99		9.2	25.71	15.67
54LV00(1)_pt2	31.32	4.16	16.95		6.01	16.34	16.16
54LV00(1)_pt3	36.36	8.63	32.68	1.18	2.87		
54LV00(1)_pt5	30.8	9.29	19.44		36.45		
54LV00(1)_pt6	30.07	9.32	18.94		37.45		
54LV00(1)_pt7	29.96	9.18	19.12		37.5		
54LV00(1)_pt8	31.76	9.12	19.27		35.88		
54LV00(2)_pt1	38.19	4.55	19		9.1	22.32	
54LV00(2)_pt3	38.6	4.54	20.33		9.48	19.49	
54LV00(2)_pt6	32.57	9.45	21.16		33.52		
54LV00(2)_pt7	31.82	9.77	19.98		35.07		
54LV00(2) pt8	32.3	9.43	20.38		34.39		
54LV00(3) pt1	30.76	8.92	17.87	0.77	38.38		
54LV00(3) pt2	32.53	8.79	19.91		34.6		
54LV00(3) pt3	33.52	9.17	19.17		33.47		
54LV00(3) pt4	31 21	9.06	17 94	0.65	37 71		
54LV00(3) pt5	36.63	4.39	19	3.53	9.04	17.37	
54LV00(3)_pt6	30.06	3 29	12 79	0.00	8.99	22.61	16 23
54LV00(3)_pt0	30.34	3.95	14.03		6.82	23.96	15 32
541 V00(3) pt8	30.29	3.94	13.18		7 34	23.20	15.8
551 V00(3) pt0	25.93	7.85	16.10		13.65	20.00	15.0
$551V00(1)_{pt1}$	25.93	7.85	16.5		43.65		
$55LV00(1)_pt1$	23.93	7.83	17.54		43.03		
$55LV00(1)_pt2$	20.34	7.02	17.54		41.40		
$55LV00(1)_pt2$	26.34	7.82	17.54		41.40 42 FE		
55LV00(1)_pt3	27.29	8.22	16.96		42.55		
55LV00(1)_pt3	27.29	8.22	16.96	110	42.55		
55LV00(1)_pt4	24.82	7.78	16.93	1.16	36.58		
55LV00(1)_pt4	24.82	7.78	16.93	1.16	36.58		
55LV00(1)_pt5	28.82	7.69	18.67		38.07		
55LV00(1)_pt5	28.82	7.69	18.67		38.07		
56LV00(1)_pt10	21.57	7.3	14.06	0.69	46.98		
56LV00(1)_pt11	20.03	6.9	13.77	0.73	46.19		
56LV00(1)_pt2	24.91	7.8	15.18	0.83	44.61		
56LV00(1)_pt3	24.74	7.86	14.58	0.63	45.68		
56LV00(1)_pt4	23.51	7.17	14.47		48.08		
56LV00(1)_pt5	22.99	6.7	14.06		49.06		
56LV00(1)_pt6	20.96	7.27	14.75		48.88		
56LV00(1)_pt7	20.58	7.41	14.62		47.65		
56LV00(1)_pt8	20.77	7.06	14.39	0.68	45.01		
56LV00(1) pt9	21.88	7.19	14.34	0.73	46.99		
56LV00(2) pt1	30.35	8.79	14.13	0.56	38.7		
56LV(0(2) pt10	31.24	8.81	14.57	0.00	37.83		
56LV(0)(2) pt2	30.72	8.97	14.32	0.63	37.65		
ptz	00.72	0.77	11.02	0.00	07.00		

Sample	0	Na	Si	Ca	Ti	Nb	u
56LV00(2)_pt3	33.41	9.5	13.02	0.89	32.02		
56LV00(2)_pt4	33.75	9.23	12.22	0.94	29.6		
56LV00(2)_pt5	33.58	8.8	12.17	1.39	29.16		
56LV00(2)_pt6	33.78	9.04	12.18	1.06	29.58		
56LV00(2)_pt7	33.58	9.23	12.78	0.71	30.33		
56LV00(2)_pt8	34.45	9.66	13.06	0.41	32.79		
56LV00(2)_pt9	30.68	9.34	14.16		39.07		

Table A2. Results of the microanalysis of the loparite crystals.

Sample	0	Na	Ca	Ti	Nb	Pb	u	Ag	Се	Та
13AF15(10) pt1	21.28	2.83	13.43	32.92	3.71				19.09	
06CH(22)_pt1	37.69		1.94	6.65	16.73					
06CH(22)_pt2	35.29		2.11	7.18	17.94					
06CH(22)_pt3	43.3		1.94	6.81	16.43					
10CH02(17)_pt1	37.75	6.12	4.43	31.36	9.15					
10CH02(17)_pt2	46.28	6.58	3.44	23.78	7.9					
10CH02(19)_pt1	33.5	3.68	5.1	37.94	5.11					
01KV(10)_pt1	23.62	2.45	22.56	4.19	33.38					
01KV(11)_pt1	23.73	1.18	27.87		39.13					
01KV(11)_pt2	31.51		37.88	4.98	18.30					
01KV(11)_pt3	26.77		32.57	4.42	23.82					8.25
01KV(12)_pt1	27.13	0.56	26.42	3.55	29.58					
01KV(12)_pt2	25.62	0.66	24.91	3.99	33.94					
01KV(12)_pt3	25.11	0.80	22.65	3.54	37.39					
01KV(12)_pt4	25.50		24.67	3.61	37.55					
01KV(12)_pt5	30.28		29.99		33.96					
01KV(13)_pt1	23.89	1.65	27.75	3.59	33.26					
01KV(13)_pt2	24.54	1.01	26.01	2.07	32.01					5.15
01KV(13)_pt3	24.11	0.64	27.20	3.07	29.7					7.74
01KV(13)_pt4	25.89	1.01	31.96	3.18	27.43					5.24
01KV(13)_pt5	25.20	1.02	32.56	1.50	26.81					4.53
01KV(14)_pt1	23.82		13.29	0.78	18.48					
01KV(14)_pt2	28.47		8.43	3.47	17.01					
01KV(14)_pt3	31.22	0.54	17.79	6.53	15.79					
01KV(14)_pt4	26.09		18.01	2.57	16.65					
01KV(14)_pt5	28.75		17.76	8.1	21.35					
01KV(14)_pt6	28.53		18.46	5.08	21.86					
01KV(15)_pt1	26.89		12.26		24.16					
01KV(15)_pt2	25.57		10.64	1.31	21.61					
01KV(15)_pt3	26.6		11.4		18.7					
01KV(15)_pt4	31.92		13.06	10.26	17.58					
01KV(15)_pt5	28.45		10.72	4.22	17.61					
01KV(16)_pt1	25.17		15.97	2.95	20.11					
01KV(16)_pt2	26.15		18.93	2.96	19.76					
01KV(16)_pt3	23.05		15.42		18.44					
01KV(16)_pt4	25.96		18.37		21.01					
01KV(16)_pt5	30.96		20.74	4.19	22.62					
01KV(18)_pt1	29.11		14.66	7.71	20.16					
01KV(18)_pt2	27.52		15.12	3.06	17.59					
01KV(2)_pt1	24.72	0.98	27.74	3.95	32.68					
01KV(2)_pt2	26.42		27.16		28.17					9.66
01KV(23)_pt1	25.49		23.58		18.44					
01KV(23)_pt2	26.27		24.4	3.05	18.34					

Table A2. Cont.

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Sample	0	Na	Ca	Ti	Nb	Pb	U	Ag	Ce	Ta
01KV(23)_pt3	25.06		24.65	3.66	16.3					
01KV(3)_pt1	25.29	0.84	23.7	3.79	31.36					8.87
01KV(3)_pt2	25.17	0.53	27.18	2.93	28.2					8.12
01KV(3)_pt3	24.39	1.18	24.65	3.85	31.22					7.5
01KV(3)_pt4	25.04	0.78	25.96	3.32	32.59					4.94
01KV(3)_pt5	23.99	1.97	28.4	3.51	30.55					5.27
01KV(3)_pt6	24.11	1.26	27.5	2.97	30.61					6.77
01KV(4)_pt1	25.01		24.64	2.55	24.6					0.95
01KV(4)_pt2	23.66	1.54	25.7	3.41	31.31					6.34
01KV(4)_pt3	25.97	0.47	25.73	5.33	29.8					6.34
01KV(4)_pt4	26.06	0.33	27.11	3.59	28.06					8.95
01KV(4)_pt5	24.23	0.82	25.29	4.87	34.97					
01KV(6)_pt1	24.25	2.25	27.33	2.65	35.66					
01KV(6)_pt2	24.96	1.1	26.61	3.9	30.44					5.56
01KV(6)_pt3	26.68	0.58	27.09	3.93	32.98					
01KV(6)_pt4	26.59	0.71	27.31	4.2	31.58					2.41
01KV(6)_pt5	24.3	1.12	27.13	3.01	27.89			2.65		2.12
01KV(6)_pt6	26.04	1.67	30.96	3.52	28.69					
01KV(8)_pt1	27.13	0.53	27.95	4.94	29.86					
01KV(8)_pt2	27.5		27.4	4.28	28.66					
01KV(8)_pt3	28.51		27.01	5.07	29.23					
01KV(8)_pt4	23.91		23.26		25.71					
N19(1)_pt2	24.62	2.25	29.44	5.15	17.06		13.89			
N19(2)_pt1	21.00		23.27	6.79	23.89		14.09			
N19(2)_pt2	21.91		21.93	5.72	26.24		12.64			
06LV12-	32 43			3 77	34 27		18 98			
(21)_pt1	02.10			0.77	01.27		10.70			
06LV12-	32 43			4 4 5	32 09		192			
(21)_pt2	02.10			1.10	02.07		17.2			
06LV12-	33 79			7 23	38 38		16 16			
(21)_pt3	00.77			1.20	00.00		10.10			
06LV12-	33.8			7.41	34.33		20.82			
(21)_pt4	0010				0 1.00		-0.02			

 Table A3. Results of the microanalysis of the perovskite crystals.

Sample	0	Na	Ca	Ti	Nb	Се	Nd	W	Th
13AF15(1)_pt1	32.07		58.87	4.86					
13AF15(1)_pt10	25.11		28.21	32.92					
13AF15(1)_pt11	31.67		53.28	10.37					
13AF15(1)_pt2	28.43		54.18	13.41					
13AF15(1)_pt3	25.17		28.69	32.61					
13AF15(1)_pt4	17.78	2.19	14.77	42.11		21.75			
13AF15(1)_pt5	24.67		21.32	17.31		25.54			
13AF15(1)_pt6	27.18		20.31	20.98		24.03		2.79	
13AF15(1)_pt7	19.39	0.39	32.62	45.74					
13AF15(1)_pt8	19.07		32.66	47.17					
13AF15(1)_pt9	24.81		27.43	35.05					
13AF15(10)_pt2	22.79	0.56	29.16	42.2					
13AF15(10)_pt3	23.46	0.56	28.32	41.93					
13AF15(10)_pt4	29.79	0.89	24.47	21.98					
13AF15(3)_pt1	30.15		18.78	19.38		22.36			
13AF15(3)_pt10	19.61	0.31	31.21	46.16					
13AF15(3)_pt11	19.83		30.74	47.43					
13AF15(3)_pt12	18.71	0.39	31.31	47.7					

Table A3. Cont.

Sample	0	Na	Ca	Ti	Nb	Се	Nd	W	Th
13AF15(3)_pt13	19.58	0.3	31.24	46.96					
13AF15(3)_pt14	19.83	0.38	30.75	46.85					
13AF15(3)_pt15	20.67		31.08	44.92					
13AF15(3)_pt2	24.71		16.02	19.36		31.11			
13AF15(3)_pt3	27.29		20.31	25.9		18.74			
13AF15(3)_pt4	24.97		21.48	21.23		21.99			
13AF15(3)_pt5	23.44		19.29	18.16		29.99			
13AF15(3)_pt6	41.4		23.43	27.48					
13AF15(3)_pt7	27.39		22.47	19.88		22.44			
13AF15(3)_pt8	23.15		21.29	18.37		27.57			
13AF15(3)_pt9	23.48		20.58	19.46		26.48			
13AF15(4)_pt1	18.37		14.51			29.14		= < 0	
13AF15(4)_pt10	28.44		16.14	11.16		33.06		7.63	
13AF15(4)_pt11	26.78		13.17	12.35		31.83		13.48	
13AF15(4)_pt12	28.37		16.36	13.41		31.67		6.13	
$13AF15(4)_{pt13}$	25.22	0.20	19.8	19.04		25.08			
$13AF15(4)_pt14$ 12 A E15(4) pt15	20.29	0.38	31.26 21.21	45.69					
$13AF15(4)_pt15$ $12AF15(4)_pt16$	19.84	0.24	31.31	46.75					
$13AF13(4)_{pt10}$ 12AF15(4)_pt17	19.79	0.24	32.00 21.62	43.29					
$13AF15(4)_p(17)$ $13AF15(4)_pt18$	19.04	0.41	32.02	40.49					
$13 \pm F15(4) = pt10$ 13 \Delta F15(4) = pt2	25.23	0.41	18 28	15.82		29 49			
13AF15(4) pt2 13AF15(4) pt3	28.9		17 29	17.67		25.49			
13AF15(4) pt4	24.98		15.11	15.88		31.83			2.08
13AF15(4) pt5	25.25		20.62	17.03		26.25			2.00
13AF15(4) pt6	26.82		18.34	18.39		30			
13AF15(4) pt7	28.42		16.46	13.71		34.58			
13AF15(4) pt8	29.5		15.23	12.81		29.65		9.09	
13AF15(4)_pt9	26.6		15.27	9.66		37.61		7.47	
13AF15(5)_pt1	24.54		20.81	10.26		33.49			
13AF15(5)_pt2	25.05		23.75	10.71		27.92			
13AF15(5)_pt3	24.17		18.67	16.51		32.38			
13AF15(5)_pt4	26.45		18.97	17.1		27.51			
13AF15(7)_pt4	29.01	0.73	22.83	21.92					
13AF15(8)_pt10	21.63	0.73	31.98	43.49					
13AF15(8)_pt5	24.39	2.23	20.48	46.76	3.63				
13AF15(8)_pt6	29.33		26.63	7.44		23		10.65	
13AF15(8)_pt7	31.44		53.69	9.73					
13AF15(8)_pt8	32.79	2.27	29.35	6.63					
13AF15(8)_pt9	26.05		31.75	28.7					
06bCH(2)_pt1	20.43	1.1	29.97	42.43					
06bCH(2)_pt2	19.46	0.83	29.77	42.61					
06bCH(5)_pt1	19.15	0.51	30.73	45.46					
06bCH(5)_pt2	21.21	0.42	32.14	41.23					
06bCH(5)_pt3	19.65	0.43	31.6	43.23					
$06bCH(5)_pt4$	19.04	0.66	31.76	43.72					
$06bCH(6)_pt1$	22.34	1.5	28.64	37.80					
06bCH(6) ptl	22.34 20.66	1.5	20.04 32.02	37.00 37.12					
11KV(1) pt2	20.00 23.55	0.55	32.93 29.22	31.13					
$11KV(1)_{pt1}$	25.55	0.62	29.33 28.62	30.15					
$11KV(1)_pt2$ $11KV(2)_pt3$	24.01 26.05	0.00	20.02	20.15 20.80					
$11KV(2)_{pt3}$	23.05	0.05	29.97	29.09 34.86					
$11KV(2) - P^{12}$	22.07	0.79	34 15	35.53					
11KV(2) - P(3) 11KV(2) pt6	24.02	0.86	31.88	33.38					
7bKV(3) nt1	22.11	0.63	29.12	37.56					
·····		5.00		2					

Sample	0	Na	Ca	Ti	Nb	Ce	Nd	W	Th
7bKV(3)_pt2	23.11	0.49	28	37.96					
7bKV(3)_pt3	20.17	0.62	30.34	35.1					
7bKV(3)_pt5	27.34	0.45	23.57	29.01					
7bKV(3)_pt7	24.8	0.43	24.96	33.97					
7bKV(4)_pt1	24.08	0.51	25.2	30.27					
7bKV(4)_pt2	25.54	0.63	24.88	30.51					
7bKV(4)_pt3	23.87		27.44	32.44					
7bKV(5)_pt4	24.43	0.55	26.91	31.46					
7bKV(5)_pt5	26.39	0.59	25.62	31.7					
7bKV(5)_pt6	24.19	0.4	26.38	34.05					
N09kv03(2)_pt2	15.05		6.28	9.05					
N09kv03(2)_pt3	15.64		8.61	7.67					
N09kv03(2)_pt4	12.99		6.24	10.08					
N09kv03(2)_pt6	14.13		7.86	8.3					
04LV12-	32 60			24.16		13.01	13 54		1 88
(29)_pt1	52.09			24.10		15.01	15.54		4.00
04LV12-	33.6			22.18		10.96	16.26		5 51
(29)_pt2	55.0			22.10		10.90	10.20		5.51
04LV12-	16 39		1 47	10 08			16 73		
(29)_pt3	HU. 39		1.4/	17.90			10.75		
04LV12-	37 87			24.42			16 52		8 1 2
(29)_pt6	57.07			27.72			10.52		0.12

 Table A4. Results of the microanalysis of the titanite crystals.

Sample	0	Si	Ca	Ti	Fe	Nb	Ce	Nd	Th
13AF15(3)_pt16	24.83	10.69	28.92	33.19					
13AF15(3)_pt17	24.84	10.18	27.17	35	1.38				
13AF15(4)_pt19	25.79	11.79	27.16	33.37					
13AF15(4)_pt20	25.08	11.08	28.4	33.65					
13AF15(5)_pt10	25.81	10.06	33.2	26.32					
13AF15(5)_pt5	25.51	10.55	31.27	29.43					
13AF15(5)_pt6	25.91	11.17	30.18	29.56					
13AF15(5)_pt7	25.85	11.09	28.31	31.32					
13AF15(5)_pt8	25.95	10.37	29.66	31.2					
13AF15(5)_pt9	24.94	10.37	30.52	31.72					
13AF15(6)_pt1	24.11	10.1	29.32	35.01					
13AF15(6)_pt2	24.86	11.94	28.05	34.02					
06bCH(5)_pt5	23.4	10.29	31.8	30.53					
06bCH(6)_pt4	37.43	24.43	15.4	6.72					
06bCH(6)_pt5	33.62	28.59	11.08	3.06	1.03				
10CH02(6)_pt4	26.2	11.89	17.06	23.89					
10CH02(7)_pt1	24.11	13.4	24.63	35.42					
10CH02(7)_pt2	24.95	12.92	24.61	34.91					
10CH02(7)_pt3	25.68	12.97	23.8	34.2					
10CH02(7)_pt4	25.18	13.3	24.46	33.83					
10CH02(7)_pt5	25.49	13.87	24.03	33.13					
10CH02(8)_pt4	26.9	14.63	20.28	31.11					
10CH02(8)_pt5	26.31	14.54	23.5	31.03					
10CH02(8)_pt6	26.77	14.32	22.46	31.86					
20aCH02(7)_pt4	29.41	15.66	18.89	25.72					
c(2)_pt1	63.09	13.06	9.33	6.83					
CH20(2)_pt2	64.6	12.15	8.2	5.73					
CH20(2)_pt3	33.93	15.93	21.74	20.54					
CH20(2)_pt4	50.18	15.98	12.41	11.68					

Sample	0	Si	Ca	Ti	Fe	Nb	Ce	Nd	Th
7bKV(5)_pt1	34.91	18.78	17.38	2.63	9.07				
7bKV(5)_pt2	34.06	17.54	16.42	4.09	10.62				
7bKV(5)_pt3	35.23	18.32	17.59	3.21	7.46				
03LV12-	20.25	12.26	14.60	4 1 2		2 62			1.09
(16)_pt1	39.33	15.50	14.09	4.12		2.03			1.90
03LV12-	36 34	14.62	16.02	4 52		1 71	5 10		3.81
(16)_pt2	50.54	14.02	10.02	4.52		1.71	5.19		5.04
03LV12-	28 12	1417	14.02	5.22				2.86	
(17)_pt3	30.43	14.17	14.93	5.25				3.80	
03LV12-	10.06	12.07	14 22	4 51		2.25	2.05		2 97
(17)_pt4	40.90	13.97	14.52	4.51		2.23	5.95		2.07
03LV12-	22.64	15.2	12.6	4 97		2 22	6 73		2.45
(17)_pt6	55.04	15.2	12.0	4.97		2.55	0.75		2.40
Lov1(4)_pt1	54.06	14.01	10.73	14		0.85			
Lov1(4)_pt2	48.82	14.87	13.19	17.82					
LV12(18)_pt3	50.59	13.52	12.03	16.92					
LV12(18)_pt4	41.13	12.42	15.4	22.04					
LV12(20)_pt1	41.66	13.84	15.89	21.66	0.36	0.86			
LV12(20)_pt2	50.81	12.34	2.33	15.51					
LV12(5)_pt2	41.98	14.22	15.64	21.92					
LV12(5)_pt4	46.45	14.09	14.31	19.26					
LV12(7)_pt8	44.45	14.22	13.87	18.83					

Table A4. Cont.

 Table A5. Results of the microanalysis of the apatite crystals.

Sample	С	0	F	Р	Cl	Ca	Sr	Nb	и	La	Ce
13AF15(7)_pt1	2.11	27.12	0.83	11.98		48.21					
13AF15(7)_pt2	1.8	27.33	0.16	12.3		49.51					
13AF15(7)_pt3	1.98	26.85	1.22	12.23		48.35					
13AF15(8)_pt1	2	28.15	0.77	11.63		48.89					
13AF15(8)_pt2	1.79	27.17	0.89	12.32		49.16					
13AF15(8)_pt3	1.94	28.19	0.27	12.08		49.43					
13AF15(8)_pt4	1.9	25.92	0.55	11.92		48.48					
10CH02(11)_pt3	2.15	30.66	1.09	12.03		37.24					
10CH02(12)_pt1	4.84	30.23		12.55		41.7					
10CH02(12)_pt2	4.23	29.33	1.01	12.91		38.25					
10CH02(12)_pt3	6	28.05	1.66	13.67		41.76					
10CH02(13)_pt1	3.17	28.39	1.48	14.16		44.79					
10CH02(13)_pt2	2.33	28.44	1.38	14.34		45.15					
10CH02(13)_pt3	3.33	28.55	1.41	14.46		44.97					
10CH02(13)_pt4	1.94	29.36	1.52	13.76		43.23					
10CH02(13)_pt5	2.08	29.73	1.15	13.13		43.93					
10CH02(13)_pt6	1.61	27.92	1.59	14.59		46.91					
10CH02(13)_pt7	11.76	26.47	1.19	12.42		40.15					
10CH02(14)_pt1	1.05	29.26	1.25	13.95		42.43					
10CH02(14)_pt2	1	28.96	1.36	13.73		42.82					
10CH02(14)_pt3	1.13	28.97	1.44	14.02		43.55					
10CH02(14)_pt4	1.42	28.94	1.81	13.88		44.21					
10CH02(14)_pt5	1.54	29.88	1.6	14.13		42.27					
10CH02(15)_pt1	1.52	29	1.35	13.56		42.57					
10CH02(15)_pt2	1.52	28.63	1.15	14.75		43.17					
10CH02(15)_pt3	2.17	30.19	2.16	12.72		41.92					
10CH02(15)_pt4	2.13	29.12	1.17	13.74		43.75					
10CH02(2)_pt4	2.41	30.99	0.98	11.95		36.07					
10CH02(2)_pt5	3.03	30.02	0.99	11.72		35.96					

Table A5. Cont.

Sample	С	0	F	Р	Cl	Ca	Sr	Nb	U	La	Ce
10CH02(3) pt6	3.97	29.22	0.58	12.04		35.26					
10CH02(3) pt7	2.33	30.72	1.14	12.42		36.78					
10CH02(3) pt8	1.73	30.2	0.93	11.84		37.19					
10CH02(5) pt4	1.92	27.79	1.54	12.96		43.28					
10CH02(5) pt5	3.46	28.04	0.94	12.27		38.4					
10CH02(6) pt3	4.87	27.75	0.89	13.06		41.22					
10CH02(8) pt1	2.07	30.67	1.34	11.89		38.22					
10CH02(8) pt2	2.05	30.49	1.34	12.21		37.33					
20aCH02(6) pt1	0.85	32.96	1.86	12.42		37.73					
20aCH02(6) pt2	0.91	33.35	2.7	12.4		38.06					
20aCH02(6) pt3	1.89	32.66		6.71	0.9	25.53					
CH20(1) pt1	2.54	46.35	5.26	14.1	0.0	31.32					
CH20(1) pt2	2.89	47.36	5.07	14.03		30.66					
CH20(1) pt3	4.23	29.84	2.62	17.18		45.95					
CH20(1) pt4	1.95	43.21	5.2	14.31		35.34					
CH20(1) pt5	6.57	21.97	1.36	13.47		55.41					
CH20(1) pt6	3.6	32.73	3.41	15.72		44.26					
CH20(2) pt1	45.54		5.25	13.17		32.51					
CH20(2) pt2	48.1		2.33	9.99		25.77					
CH20(2) pt3	49.89		5.71	13.75		26.79					
CH20(2) pt4	54.92		7.18	13.64		17.75					
CH20(2) pt5	59.65		10.47	11.6		5.99					
CH20(3) pt1	2.25	14.5	0.87	17.46		64.92					
CH20(3) pt2	1.32	19.43	1.69	17.09		60.48					
CH20(3) pt3	12.6	18.22	0.79	12.28		53.39					
CH20(3)_pt5	2.06	42.86	5.16	13.96		35.96					
CH20(3)_pt6	1.12	37.44	3.62	13.33		44.5					
CH20(3)_pt7	3.28	40.4	2.13	12.46		32.27					
01KV(10)_pt3	4.72	29.1	1	15.42		49.09					
01KV(11)_pt4	2.85	27.85		14.22		55.08					
01KV(12)_pt6		25.13		14.17		57.33					
01KV(14)_pt10	5.22	27.97	0.88	13.07		40.12					
01KV(14)_pt7	4.09	28.8	0.87	14.41		43.33					
01KV(14)_pt8	5.01	29.66		15		42.45					
01KV(14)_pt9	4.35	30.54		14.21		42.7					
01KV(16)_pt6	7.31	30.08	0.63	12.6		39.82					
01KV(18)_pt4	4.49	33.41	3.07	13.34		42.69					
01KV(19)_pt3	4.48	25.64	1.07	13.15		38.46					
01KV(19)_pt4	3.4	26.71	0.31	13.31		42.43					
01KV(19)_pt5	3.75	24.41	0.57	12.47		39.22					
01KV(19)_pt6	7.21	22.86	1.23	8.36		27.78					
01KV(19)_pt7	4.08	27.54		12.8		37.23					
01KV(19)_pt8	4.26	28.73		12.43		38.36					
01KV(19)_pt9	6.14	25.85	0.54	10.92		33.05					
01KV(2)_pt4	2.77	26.78		13.76		56.69					
01KV(21)_pt2	3.02	26.38	0.83	13.45		43.82					
01KV(21)_pt3	3.96	26.36		13.63		41.58					
01KV(21)_pt5	3.84	26.02		12.71		44.65					
01KV(21)_pt6	4.31	28.27		10.72		43.25					
$01KV(4)_{pt8}$	4.67	28.51		14.82		52.79					
01KV(7)_pt1	4.27	26.26	1.17	14.4		50.67					
$01KV(8)_{pt5}$		28.34	1.60	14.57		53.62					
N09kv03(2)_pt38		17.44	1.63	12.88		28.44					
N09kv03(2)_pt39		19.21	1.63	13.84		29.23					
N09Kv03(2)_pt40		15.79	0.92	13.22		28.61					
1NU9KVU3(2)_pt41		16.94		14.12		29.56					

 Table A5. Cont.

N09kv03(2) pt42 18.11 0.49 11.91 27.99	
N09kv03(2) pt43 17.83 13.16 27.12	
N09kv03(2) pt45 17.52 1.48 13.86 29.42	
N09kv03(2)_pt46 17.9 13.03 27.66	
N09kv03(2) pt47 17.64 12.56 27.81	
N09kv03(2) pt48 18.19 1.43 13.08 27.91	
N09kv03(2) pt49 18.65 0.97 13.06 28.16	
N09kv03(2) pt50 18.04 1.42 13.35 29.67	
N09kv03(2) pt51 17.17 12.93 30.27	
N09kv03(2) pt52 18.99 1.64 12.51 29.79	
N09kv03(2) pt53 17.42 14.4 32.05	
N09kv03(2) pt54 23.99 6.21 22.24	
N09kv03(2) pt55 18.23 16.02 30.71	
N09kv03(2) pt56 21.2 15.29 30.84	
N09kv03(2) pt57 19.38 0.96 14.25 28.81	
N09kv03(2) pt58 19.6 12.41 30.18	
N09kv03(2) pt59 17.9 14.12 29.35	
N09kv03(2) pt60 20.71 1.56 14.9 29.92	
N09kv03(2) pt61 16.36 2.25 12.78 28.51	
N09kv03(2) pt62 19.05 15.28 31.69	
N09kv03(2) pt63 17.97 16.37 27.86	
N09kv03(2) pt64 $17.36 1.05 13.29 28.33$	
N09kv03(2) pt65 17.86 13.71 30.06	
N09ky03(2) pt66 16.66 13.41 29.45	
N09kv03(2) pt67 19.6 16.75 32.04	
N09kv03(2) pt68 17.3 13.59 27.64	
N09kv03(2) pt69 16.65 13.63 27.39	
N09kv03(2) pt70 18.4 1.06 12.26 29.31	
N8KV(1) pt1 2.26 27.97 0.14 13.87 53.19	
N8KV(1) pt2 2.34 28.86 0.47 12.96 52.84	
N8KV(1) pt3 2.29 28.49 0.35 13.14 55.73	
N8KV(1) pt4 2.78 28.57 0.18 12.87 55.34	
06LV21(10) pt1 1.67 32.03 11.46 5.94	24.24
06LV21(10) pt2 3.61 36.51 0.41 6.7 8.32	
06LV21(10) pt3 2.07 32.87 0 7.29 4.84	26.96
06LV21(10) pt4 2.92 34.56 7.36 0.66 5.1	21.08
06LV21(10) pt5 2.95 34.36 11.74 5.28	22.13
06LV21(10) pt6 2.28 31.2 0.52 8.63 4.66	29.7
06LV21(10) pt7 1.82 33.28 0 8.79 5.58	25.18
06LV21(6) pt1 1.8 31.4 9.28 5.77	25.6
06LV21(6) pt2 1.59 30.36 0.03 8.55 0.73 6.61	27.43
06LV21(6)_pt3 1.54 29.78 0 8.84 6.05	27.89
06LV21(6)_pt4 2.07 30.57 0 10.04 6.47	24.96
06LV21(6)_pt5 2.63 30.68 0 8.61 6.42	27.27
06LV21(9) pt1 1.48 32.93 11.01 5.19	23.55
06LV21(9)_pt2 0.95 31.95 0 8.11 4.56	26.42
06LV21(9)_pt3 1.13 32.46 10.86 5.41	25.37
06LV21(9)_pt4 1.28 31.65 10.42 5.38	25.78
06LV21(9)_pt5 1.61 33.28 7.5 4.84	22.21
06LV21(9)_pt6 1.24 33.47 0 9.24 5.18	24.03
06LV21(9)_pt7 1.36 32.78 0 8.86 5.07	25.82
06LV21(9)_pt8 1.28 31.17 0 8.3 3.6	28.88
LV12(11)_pt12 4.81 50.48 12.79 20.54 3.2	
LV12(11)_pt5 4.5 49.28 12.97 23.2 2.13	
LV12(15)_pt2 5.2 42.21 5.6 14.49 25.96 5.37	
LV12(14)_pt3 7.28 42.38 4.48 11.95 20.49 2.55	
55LV00(1)_pt6 3.65 30.53 1.41 10.18 28.04	

Table A5. Con	ıt.
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Sample	С	0	F	Р	Cl	Са	Sr	Nb	U	La	Се
			-								
55LV00(1)_pt7	2.95	28.56	1.71	9.15		31.17					
55LV00(1)_pt6	3.65	30.53	1.41	10.18		28.04					
55LV00(1)_pt7	2.95	28.56	1.71	9.15		31.17					
55LV00(2)_pt1	5.52	41.9		10.02		7.33					
55LV00(2)_pt2	4	29.93	0.61	8.63		15.12					
55LV00(3)_pt1	1.99	18.81		5.55		4.45				13.29	28.74
55LV00(3)_pt3	2.51	22.66		8.72		7.22				13.27	23.05
55LV00(3)_pt4	5.42	30.7		7.19	0.63	6.94					16.07
55LV00(3)_pt7	2.84	34.04		8.81		26.24					
55LV00(3)_pt8	4.28	32.9		3.74		10.47					

 Table A6. Results of the microanalysis of the eudialyte crystals.

Sample	0	Na	Si	Ca	Mn	Fe	Zr
32CH99(3)_pt1	29.31	8.65	26.33	10.38	9.72	2.13	9.19
32CH99(3)_pt2	29.69	8.09	24.92	10.75	6.91	6.99	8.94
32CH99(3)_pt3	28.38	8.57	25.6	10.08	8.23	6.3	9.43
32CH99(3)_pt4	28.93	8.66	26.73	10.27	9.25	2.57	9.41
32CH99(3)_pt5	28.05	7.72	25.12	10.02	10.07	6.47	8.02
32CH99(3)_pt6	27.3	8.9	26.45	11.04	10.66	1.86	10.73
32CH99(3)_pt7	27.99	8.8	27.02	11.27	6.43	3.67	10.57
32CH99(5)_pt1	26.75	7.79	22.82	9.45	5.46	8.1	8.04
32CH99(5)_pt2	27.67	8.56	25.94	11.74	7.48	2.81	9.16
32CH99(5)_pt3	31.25	8.83	28.7	12.38		2.78	9.94
32CH99(5)_pt4	28.12	8.71	27.27	12.38	6.11	2.92	10.22
32CH99(5)_pt5	31.75	9.19	28.29	12.13		2.6	10.83
32CH99(5)_pt6	27.96	8.69	27.18	11.45	7	2.33	9.98
06LV21(10)_pt8	42.69	9	27.46	2.05			3.56
06LV21(14)_pt1	32.48	5.14	28.47	8.57	9.02	1.61	9.67
06LV21(14)_pt2	32.11	5.23	28.95	9.14	8.23	0.52	10.53
06LV21(14)_pt3	30.94	4.19	28.5	9.77	8.86		11.83
06LV21(14)_pt4	32.99	5.34	28.89	7.17	7.1	0	12.37
06LV21(7)_pt1	32.37	4.64		8.53	8	0.04	9.03
06LV21(7)_pt10	32.67	4.92		8.88	6.74		8.43
06LV21(7)_pt2	30.91	3.96		7.93	8.3	0.6	8.65
06LV21(7)_pt3	32.7	4.83		8.31	8.13	0.77	9.18
06LV21(7)_pt4	32.01	4.42		8.55	6.52		10.09
06LV21(7)_pt5	29.54	4.17		8.91	6.55	1.26	11.31
06LV21(7)_pt6	31.21	4.27		8.93	7.29	0.14	9.83
06LV21(7)_pt7	31.74	4.64		8.33	7.01	1.3	10.32
06LV21(7)_pt8	31.6	4.61		7.98	8.78	0	9.55
06LV21(7)_pt9	31.17	4.07		7.63	8.25		9.43
06LV21(8)_pt3	32.03	5.15	27.66	8.21			10.37
06LV21(8)_pt4	31.07	5.02	28.79	8.96		1.38	11.08
53LV00(1)_pt10	34.19	5.67	28.24	6.61	9.18		9.2
53LV00(1)_pt11	32.53	8.38	27.52	7.09	11.61		7.23
53LV00(1)_pt7	34.32	5.23	24.31	6.73	6.44	0	7.51
53LV00(1)_pt8	31.88	7.79	24.3	6.07	6.7	0	7.76
53LV00(1)_pt9	32.88	7.36	27.97	6.3	9.3		10.27
54LV00(2)_pt4	32.59	4.11	16.4	1.84	22.26		9.68
54LV00(2)_pt5	31.53	7.9	26.5	6.92	9.29	6.85	6.2
55LV00(3)_pt10	31.13	6.32	29.76	9.32			8.94
55LV00(3)_pt2	33.13	2.15	27.49	6.84		1.05	15.05
55LV00(3)_pt5	31.46	6.01	28.05	8.18	6.04		8.91
55LV00(3)_pt6	32.42	3.93	26.64	6.19	7.03		13.83

Sample	С	0	Mg	Ca	Fe	Nb	Та	Sr	La	Ce
13AF15(10) pt5	4.92	35.52	1.33	50.73						
13AF15(5) pt11	3.15	32.66		55.68						
13AF15(5)_pt12	3.45	31.68		55.76						
13AF15(6)_pt3	3.31	31.7		57.56						
13AF15(6)_pt4	1.01	22.07	0.24	15.95		5.23	7.87			
13AF15(9)_pt1	4.65	23.95	4.63	6.5	0.34				12.5	34.89
13AF15(9)_pt2	4.26	22.55	4.11	5.23	5.06				12.92	35.31
AF-cc(1)_pt1	1.48	16.74		25.86					15.56	35.84
$AF-cc(1)_pt2$	2.21	27.56		27.95					11.05	24.87
AF-cc(1)_pt3	1.84	22.93		29.86					12.76	27.84
AF-cc(1)_pt4	2.12	21.99		55.63						19.46
AF-cc(1)_pt5	2.39	27.19		53.91						15.74
AF-cc(1)_pt6	1.45	21.59		76.95						
AF-cc(1)_pt7	3.42	38.56		58.02						
AF-cc(1)_pt8	3.45	36.33		60.22						
AF-cc(1)_pt9	2.73	33.94		63.33						
AF-cc(2)_pt1	1.89	20.13		25.84					12.26	33.98
AF-cc(2)_pt2	1.49	14.39		29.52					13.69	38.01
AF-cc(2)_pt3	2.89	32.74		45.52						16.17
AF-cc(2)_pt4	2.18	26.65		71.17						
AF-cc(2)_pt5	3.19	37.94		58.87						
AF-cc(2)_pt6	2.35	30.49		67.16						
AF-cc(2)_pt7	3.22	34.38		62.4						
AF-cc(3)_pt1	1.42	15.78		27.65					12.25	39.06
AF-cc(3)_pt2	1.87	17.47		31.98					12.13	33.1
AF-cc(3)_pt3	2.32	27.49		32.4						32
AF-cc(3)_pt4	1.97	30.04		65.57						
AF-cc(4)_pt1	2.35	24.09		49.75						21.4
AF-cc(4)_pt10	2.6	31.4		65.62						
AF-cc(4)_pt11	3.24	34.63		62.12						
AF-cc(4)_pt15	2.38	30.22		67.41						
AF-cc(4)_pt16	3.44	37.72		58.84						
AF-cc(4)_pt2	2	21.15		50.13						24.8
AF-cc(4)_pt3	1.43	19.19		19.88					14.01	37.99
AF-cc(4)_pt4	1.44	13.2		27.53					15.81	38.2
AF-cc(4)_pt5	1.99	27.68		69.73						
AF-cc(4)_pt6	1.53	18.35		21.19					13.07	38.68
AF-cc(4)_pt7	2.31	27.8		69.88						
AF-cc(4)_pt8	3.48	38.43		58.09						
AF-cc(4)_pt9	2.85	33.68		63.15						
10CH(4)_pt2	5.05	34.55		3.63				13.66	25.36	15.73
01KV(11)_pt5	3.51	38.03		58.46						
$01KV(11)_{pt6}$	3.99	35.85		60.16						
$01KV(13)_pt/$	2.62	27.58	0.00	55.67						
$01KV(13)_{pt8}$	3.89	36.27	0.98	58.86 45.00						
$01KV(13)_{pt9}$	3.8Z	33.92 28 F1	5.58	45.08						
$01KV(4)_pto$	3.27 2 E0	24.0	0.02	52.79						
$01KV(4)_pt9$ 01KV(7) = 12	3.38 2.40	34.9 26 2	1.51	50.22						
$01KV(1)_ptZ$ $01KV(0)_ptZ$	3.49 3.70	30.3 27.47	1.13	51.07						
01KV(9) pts 01KV(9) pts	5.7Z 2.64	27.07 26.32	0.90	52.55						
$V12(1) - \mu 0$	2.04 10.87	20.32	0.04	52.45 41 25				6 37		
LV12(1) pt7	3.82	24.99		34.49				28.86		
	0.04	- 1.//		01.17				-0.00		

 Table A7. Results of the microanalysis of the carbonate crystals.

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