

Article

Three-D Mineralogical Mapping of the Kovdor Phoscorite-Carbonatite Complex, NW Russia: III. Pyrochlore Supergroup Minerals

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Received: 30 May 2018; Accepted: 26 June 2018; Published: 28 June 2018



Abstract: The pyrochlore supergroup minerals (PSM) are typical secondary phases that replace (with zirconolite–laachite) earlier Sc-Nb-rich baddeleyite under the influence of F-bearing hydrothermal solutions, and form individual well-shaped crystals in surrounding carbonatites. Like primary Sc-Nb-rich baddeleyite, the PSM are concentrated in the axial carbonate-rich zone of the phoscorite-carbonatite complex, so their content, grain size and chemical diversity increase from the pipe margins to axis. There are 12 members of the PSM in the phoscorite-carbonatite complex. Fluorine- and oxygen-dominant phases are spread in host silicate rocks and marginal carbonate-poor phoscorite, while hydroxide-dominant PSM occur mainly in the axial carbonate-rich zone of the ore-pipe. Ti-rich PSM (up to oxycalciobertholite) occur in host silicate rocks and calcite carbonatite veins, and Ta-rich phases (up to microlites) are spread in intermediate and axial magnetite-rich phoscorite. In marginal (apatite)-forsterite phoscorite, there are only Ca-dominant PSM, and the rest of the rocks include Ca-, Na- and vacancy-dominant phases. The crystal structures of oxycalciobertholite and hydroxynatrobertholite were refined in the $Fd\bar{3}m$ space group with R_1 values of 0.032 and 0.054 respectively. The total difference in scattering parameters of B sites are in agreement with substitution scheme ${}^B\text{Ti}^{4+} + {}^Y\text{OH}^- = {}^B\text{Nb}^{5+} + {}^Y\text{O}^{2-}$. The perspective process flow diagram for rare-metal “anomalous ore” processing includes sulfur-acidic cleaning of baddeleyite concentrate from PSM and zirconolite–laachite impurities followed by deep metal recovery from baddeleyite concentrate and Nb-Ta-Zr-U-Th-rich sulfatic product from its cleaning.

Keywords: pyrochlore supergroup minerals; typochemistry; crystal structure; Kovdor phoscorite-carbonatite complex

1. Introduction

The Kovdor phoscorite-carbonatite complex is the largest source of magnetite, hydroxylapatite and baddeleyite in the NW of Russia [1–4]. Besides, the deposit contains significant amounts of Sc, Ln, Ta, Nb and U concentrated mainly in baddeleyite and the products of its alteration, first of all, in zirconolite and minerals of the pyrochlore supergroup [5–10]. Therefore, it is important to highlight

the fact that all aforementioned rare metals can be produced during chemical cleaning of baddeleyite concentrate [6]. Also, the pyrochlore supergroup minerals are sensitive indicators of mineral formation conditions, and their study can give us important information on subsolidus and postmagmatic evolution of the phoscorite-carbonatite complex.

The general formula of the pyrochlore supergroup minerals (PSM) is $A_{2-m}B_2X_{6-w}Y_{1-n}$, where $m = 0-2$, $w = 0-0.7$ and $n = 0-1.0$; the species are named according to the dominant cation (or anion) of the dominant valence at each site [11,12]. The position *A* can be occupied by Na, Ca, Sr, Pb^{2+} , Sn^{2+} , Sb^{3+} , Y, U, Ba, Fe^{2+} , Ag, Mn, Bi^{3+} , REE, Sc, Th, H_2O , or be vacant. The position *B* can be occupied by Nb, Ta, Ti, Sb^{5+} , W, Al and Mg (as main components), V^{5+} , Sn^{4+} , Zr, Hf, Fe^{3+} and Si (as impurities). The position *X* is occupied mainly by oxygen, but OH and F can also occur here. The position *Y* is occupied usually by OH^- , F^- , and O^{2-} anions (hydroxy-, fluor-, and oxy-compounds correspondingly), but also it can be vacant (keno-compounds) or occupied by water and/or large univalent cations of K, Cs and Rb.

Correspondingly, there are groups of pyrochlore (M^{5+} cations are dominant at the *B* site, and Nb is dominant among them, and O^{2-} is dominant at the *X* site), microlite (M^{5+} cations are dominant at the *B* site, and Ta is dominant among them, and O^{2-} is dominant at the *X* site), roméite (M^{5+} cations are dominant at the *B* site, and Sb is dominant among them, and O^{2-} is dominant at the *X* site), betafite (M^{4+} cations are dominant at the *B* site, and Ti is dominant among them, and O^{2-} is dominant at the *X* site), elsmoreite (M^{6+} cations are dominant at the *B* site, and W is dominant among them, and O^{2-} is dominant at the *X* site), ralstonite (M^{3+} cations are dominant at the *B* site, and Al is dominant among them, and F^- is dominant at the *X* site) and coulsellite (M^{2+} cations are dominant at the *B* site, and Mg is dominant among them, and F^- is dominant at the *X* site). Hereinafter, we will use generic terms pyrochlores, microlites and betafites for Nb-, Ta- and Ti-dominant members of the pyrochlore supergroup, respectively.

Data on the geology and petrography of the Kovdor alkaline-ultrabasic massif and the eponymous phoscorite-carbonatite complex described in [1,2,4,13–16] is summarized in the first article of this series [17] that has shown that spatial distribution of forsterite content, morphology, grain size, composition and alteration products accent concentric zonation of the Kovdor phoscorite-carbonatite complex. This zonation includes marginal (apatite)-forsterite phoscorite, intermediate low-carbonate magnetite-rich phoscorite and axial carbonate-rich phoscorite and carbonatites. Presented in the second article, 3D data on distribution of content, grain size and composition of sulfides helped us to understand the behavior of sulfur-related metals during crystallization and subsolidus evolution of the phoscorite-carbonatite complex. Wide diversity of the pyrochlore supergroup minerals in the Kovdor phoscorite-carbonatite complex [1,4,13,16,18] permits a reconstruction of the latest hydrothermal episodes of the complex formation and draws attention to the economic significance of pyrochlore mineralization.

2. Materials and Methods

For this study, we used 548 samples of phoscorite, carbonatites and host rocks taken from 108 exploration holes drilled at the interval from −80 to −650 m within the Kovdor phoscorite-carbonatite complex [16]. Bulk-rock samples were analyzed in the Tananaev Institute of Chemistry of KSC RAS (Apatity) by means of inductively coupled plasma-mass spectrometry (ICP-MS) performed with an ELAN 9000 DRC-e mass spectrometer (Perkin Elmer, Waltham, MA, USA). For the analyses, the samples were dissolved in a mixture of concentrated hydrofluoric and nitric acids with distillation of silicon and further addition of hydrogen peroxide to a cooled solution to suppress hydrolysis of polyvalent metals [19].

Composition of PSM grains smaller than 20 μm in diameter was determined using a LEO-1450 scanning electron microscope (Carl Zeiss Microscopy, Oberkochen, Germany) with a Quantax 200 energy-dispersive X-ray spectrometer (Bruker, Ettlingen, Germany). The same equipment with 500-pA beam current and 20 kV acceleration voltage was used to obtain back-scattered electron

(BSE) images of thin polished sections. The Image Tool 3.04 (The University of Texas Health Science Center, San Antonio, TX, USA) was used to determine the equivalent circular diameter of studied PSM grains.

Grains larger 20 μm in diameter were then studied using a Cameca MS-46 electron probe microanalyzer (EPMA) (Cameca, Gennevilliers, France) operating in wavelength-dispersive mode at 20 kV and 20–30 nA. The analyzes were performed with the beam size of 5–10 μm and the counting time of 10–20/10 s on peaks/background for every chemical element and every of 5–10 measurement points. Table 1 presents the used standards, detection limits and precisions based on repeated analyses of standards. Fluorine was determined with a Quantax 200 energy-dispersion instrument and standard-less ZAF method, based on a detection limit of 0.5 wt %. Coefficients in crystallochemical formulas were calculated using the MINAL program by D. V. Dolivo-Dobrovolsky [20].

Table 1. Parameters of electron probe microanalyzer (EPMA) analyses.

Element	Detection Limit, wt %	Standard	Element	Detection Limit, wt %	Standard
Na	0.1	Lorenzenite	Y	0.1	Synthetic $\text{Y}_3\text{Al}_5\text{O}_{12}$
Mg	0.1	Forsterite	Zr	0.1	Synthetic ZrSiO_4
Al	0.05	Pyrope	Nb	0.05	Synthetic LiNbO_3
Si	0.05	Wollastonite	Ba	0.05	Barite
P	0.05	Fluorapatite	La	0.05	Synthetic LaCeS_2
K	0.03	Wadeite	Ce	0.05	Synthetic LaCeS_2
Ca	0.03	Wollastonite	Pr	0.1	Synthetic $\text{LiPr}(\text{WO}_4)_2$
Sc	0.02	Thortveitite	Nd	0.1	Synthetic $\text{LiNd}(\text{MoO}_4)_2$
Ti	0.02	Lorenzenite	Ta	0.05	Metallic tantalum
Mn	0.01	Synthetic MnCO_3	Pb	0.05	Synthetic PbSe
Fe	0.01	Hematite	Th	0.2	Thorite
Sr	0.1	Celestine	U	0.2	Metallic uranium

Single-crystal X-ray diffraction studies of oxycalciopyrochlore and hydroxynatropyrochlore were performed at 293 K using a Bruker Kappa APEX DUO diffractometer equipped with the $\text{I}\mu\text{S}$ microfocus source (beam size of 0.11 mm, $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ and operated at 45 kV and 0.6 mA) and a CCD area detector. The intensity data was reduced and corrected for Lorentz, polarization and background effects. The APEX2 software (Bruker-AXS, Billerica, MA, USA, 2014) applied a multi-scan absorption-correction. Crystal structures were refined with the SHELX program [21] and drawn using the VESTA 3 program [22].

Raman spectra of 6 typical PSM were produced using a Jobin-Yvon LabRam HR 800 spectrometer (Horiba, Kyoto, Japan) with a 514 nm laser under the same conditions for each sample. The band component analysis was performed using the OriginPro 8.1 SR2 program [23], with Lorentzian peak function.

Statistical analyses were implemented with the STATISTICA 8.0 (StatSoft) program [24]. Geostatistical studies and 3D modeling were conducted with the MICROMINE 16 program [25]. Interpolation was performed by ordinary kriging. Automatic 3D geological mapping was developed by conversion of rock chemical composition to mineral composition using logical computation [26].

The following abbreviations were used: Ap (hydroxylapatite), Bdy (baddeleyite), Cal (calcite), Cb (carbonate), Clc (clinocllore), Dol (dolomite), Fo (forsterite), Gn (galena), Ilm (ilmenite), Mag (magnetite), Pcl (pyrochlore unspecified), Phl (phlogopite), Po (pyrrhotite), Py (pyrite), Spl (spinel), Srp (serpentine), Str (strontianite), Val (vallerite), and Zrl (zirconolite). Pyrochlore group minerals (PSM): OCP (oxycalciopyrochlore), ONP (“oxynatropyrochlore”), HCP (hydroxycalciopyrochlore), HNP (hydroxynatropyrochlore), HKP (hydroxykenopyrochlore), FCP (fluorcalciopyrochlore), FNP (fluornatropyrochlore) FKP (“fluorkenopyrochlore”); OCB (“oxycalciobetafite”), FCM (fluorcalciomicrolite), HCM (hydroxycalciomicrolite), HKM (hydroxykenomicrolite).

3. Results

3.1. Occurrence and Morphology

The pyrochlore supergroup minerals are common accessories in all rocks of the Kovdor alkaline-ultrabasic massif. The occurrence and content of PSM decrease from host foidolite and diopside–phlogopite to earlier (apatite)–forsterite phoscorite, and then increase to intermediate phoscorite and, finally, to the latest carbonatites (Table 2). In the phoscorite-carbonatite complex, the pyrochlore supergroup minerals result mainly from the alteration of Nb-rich baddeleyite formed in the pipe axial zone due to the substitution $2\text{Zr}^{4+} \leftrightarrow \text{Sc}^{3+}\text{Nb}^{5+}$. On this reason, the pyrochlore areal coincides with that of Sc-Nb-rich baddeleyite (Figure 1). Carbonate-rich phoscorite and carbonatites enriched in PSM form an intensive radioactive anomaly (about 200 m in diameter and >900 m in depth), known as the “Anomalous Zone” [1]. Content of pyrochlore in rocks of the “Anomalous Zone” gradually increases with depth at the account of baddeleyite [27].

Table 2. Pyrochlore supergroup minerals (PSM) occurrence and grain size in the Kovdor massif.

Natural Sequence of Rock Formation, after [4]	Proportion of Samples with Identified PSM, %	Median Equivalent Circle Diameter of Grains (Min–Max), μm	Mean Nb Content in Baddeleyite, wt %
Foidolite	14	16 (8–30)	0.22
Diopside and phlogopite	22	39 (3–400)	0.28
(Apatite)–forsterite phoscorite	9	40 (5–200)	0.08
Low-carbonate magnetite-rich phoscorite	21	50 (1–1090)	0.17
Calcite-rich phoscorite and phoscorite-related carbonatite	38	60 (4–535)	0.38
Vein calcite carbonatite	60	55 (1–400)	0.66
Vein dolomite carbonatite and magnetite-dolomite-serpentine rocks	47	40 (6–340)	0.39
Total	31	50 (1–1090)	

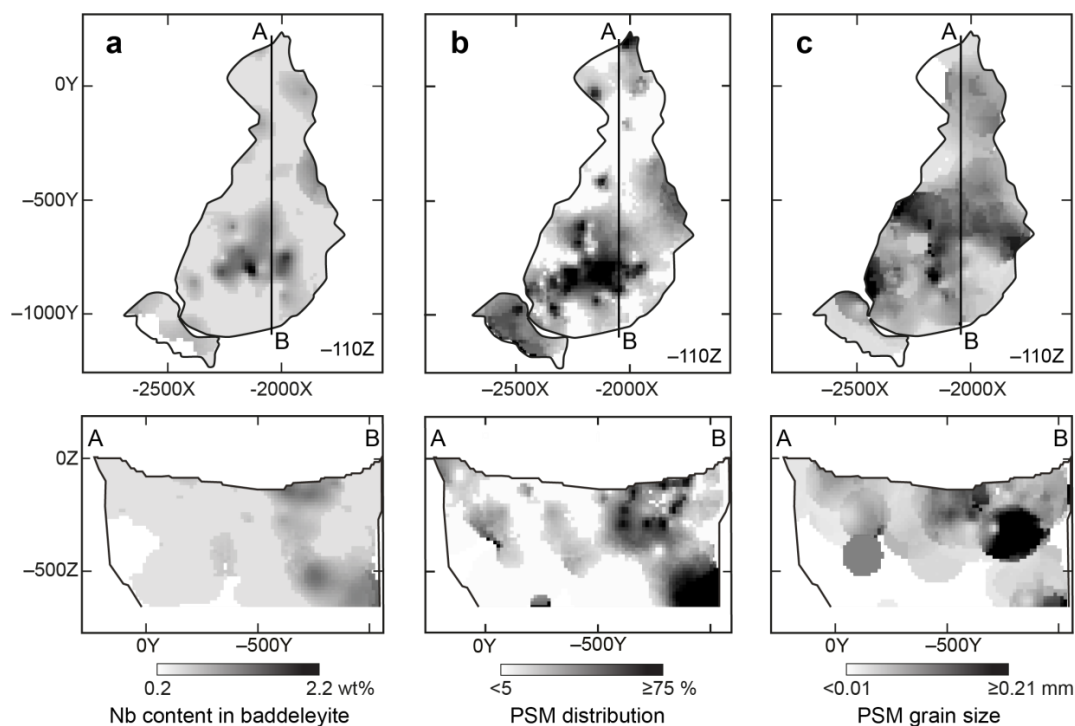


Figure 1. Distributions of Nb in baddeleyite (a), PSM-bearing rocks (b) and average size of PSM grains in a sample (c) within the Kovdor phoscorite-carbonatite complex.

The pyrochlore group minerals, namely oxycalciopyrochlore (OCP), oxynatropyrochlore (ONP), hydroxycalciopyrochlore (HCP), hydroxynatropyrochlore (HNP), hydroxykenopyrochlore (HKP), fluorcalciopyrochlore (FCP), fluornatropyrochlore (FNP) and fluorkenopyrochlore (FKP), are common in foidolite, diopsidite, phlogopitite, phoscorite and carbonatite (OCP, HCP and HNP are predominant). Minerals of microlite and betafite groups play a subordinate role, mainly, as separate parts of PSM inhomogeneous crystals. Oxycalciobetafite (OCB) and its cation-deficient analogue occur in phoscorite and carbonatite of the ore-pipe intermediate and axial zones; while fluorcalciomicrolite (FCM), hydroxycalciomicrolite (HCM) and hydroxykenomicrolite (HKM) are found only in calcite-rich phoscorite and calcite carbonatite.

Within the phoscorite-carbonatite complex, the equivalent circle diameter of the analyzed PSM grains widely varies from 1 to 1000 μm (see Table 2) increasing from host foidolite and diopsidite to marginal (apatite)-forsterite phoscorite, and then to intermediate low-carbonate magnetite-rich phoscorite and axial calcite-rich phoscorite and carbonatite (see Figure 1c). In fact, the PSM grain size is proportional to their content in the rock: in PSM-poor rocks, there are small (up to 100 μm in diameter) separate grains of these minerals; while PSM-rich rocks contain irregularly-shaped and lens-like segregations, bands and veinlets of much larger (up to 1 mm in diameter) crystals of the pyrochlore supergroup minerals.

The morphology and microstructure of pyrochlore particles show different aspects, such as irregularly shaped and rounded grains (Figure 2a,b), idiomorphic octahedral, cubic, cubooctahedral and truncated octahedral crystals (Figure 2c–e), poikilitic and skeletal (meta)crystals (Figure 2e,f), veinlets and filling of fractures (Figure 2g), rims around baddeleyite and lueshite grains followed by partial pseudomorphs (Figure 2h), epitaxial intergrowth with baddeleyite (Figure 2i), as well as the finest inclusions in exsolved titanomagnetite. In all rocks of the phoscorite-carbonatite complex, there are zoned PSM crystals with primary regular zonation corresponding to crystal shape, secondary irregular zoning caused by mineral alteration, and both of these zoning types, which is typical for PSM from carbonatites [28]. The primary zoning is caused usually by increases of Ca, Ta, Ti, Zr and F contents from the crystal core to rim at the expense of Na, Th, U, REE, Nb and (OH) amounts. Secondary zoning appears, first of all, due to leaching of Na, Ca and F from marginal parts of metamict grains of U-Th-rich PSM. Sometimes, separate zones of one crystal are formed by different minerals of the pyrochlore supergroup (see Figure 2f).

Irregularly shaped and drop-like yellowish-brown pyrochlore grains dominate in host silicate rocks and carbonate-poor phoscorite (see Figure 2a); while in carbonate-rich phoscorite and related carbonatite, they also form dark brown truncated octahedral crystals, sometimes with baddeleyite relics (see Figure 2e,i). In calcite carbonatite veins, there are reddish-brown to creamy and yellow octahedral, cubic, truncated octahedral and cubooctahedral crystals of pyrochlores (see Figure 2c), and their close intergrowth with baddeleyite and zirconolite [1,4,29,30]. In vein dolomite carbonatite, yellow to brown truncated octahedral to cubic pyrochlore crystals (see Figure 2d) occur in voids in typical association with zircon and endemic phosphates [1,27,31,32]. Betafite group minerals occur as separate irregularly shaped, drop-like and ellipsoidal grains (up to 100 μm) or form marginal zones of pyrochlore crystals (see Figure 2d) and rims around baddeleyite grains. Microlite group members form marginal zones of pyrochlore crystals and inclusions (up to 20 μm in diameter) in zirconolite, titanomagnetite and exsolution ilmenite.

Like PSM, minerals of the zirconolite–laachite series are typical products of baddeleyite alteration; however, they can also replace pyrochlores (Figure 3a). Besides, grains of U-Th-rich kenopyrochlores are often replaced/rimmed by pyrite (Figure 3b) and valleriite (Figure 3c) and sometimes by strontianite (Figure 3d), probably, due to radiolytic splitting of water into hydrogen peroxide and molecular hydrogen. In particular, with radiation dose growth, a water solution of H_2SO_4 (below 200 °C) becomes significantly rich in H_2 due to H_2O_2 [33,34], and this, probably, causes precipitation of sulfides around the radiation source.

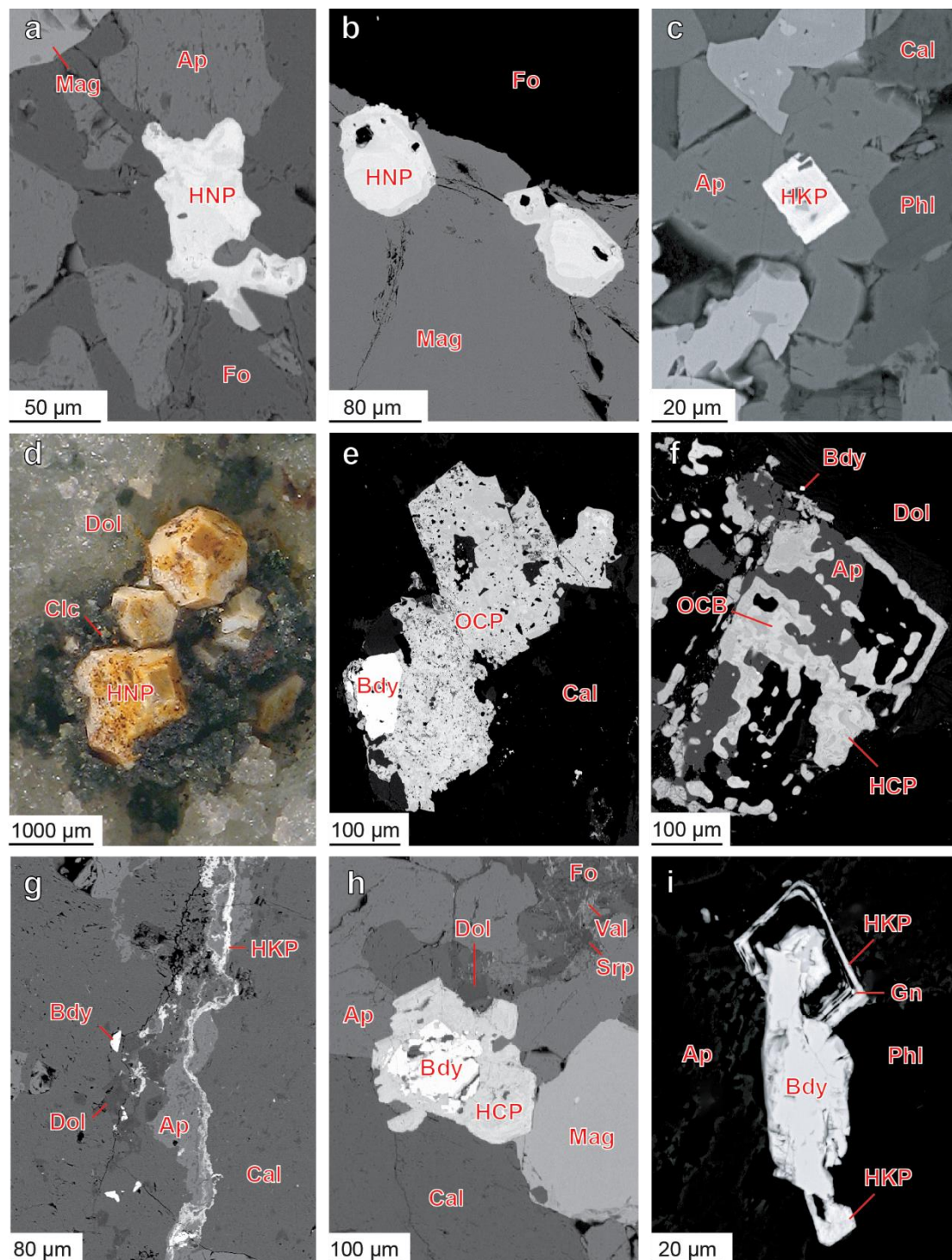


Figure 2. Typical PSM morphology: (a) irregularly shaped grain of hydroxycalcipyrochlore in forsterite-magnetite phoscorite 987/2.1; (b) drop-like grains of oxycalcipyrochlore in calcite-magnetite-apatite-forsterite phoscorite 987/99.6; (c) cubic crystal of hydroxykenopyrochlore in vein calcite carbonatite 963/61.3; (d) truncated octahedral crystals of hydroxynatropyrochlore in dolomite carbonatite K-017-4; (e) poikilitic metacrystal of oxycalcipyrochlore from calcite-magnetite-forsterite phoscorite 917/318.5; (f) skeletal crystal of oxycalcibetafite-hydroxycalcipyrochlore in magnetite-dolomite-serpentine rock 987/198.0; (g) veinlets of hydroxykenopyrochlore in vein calcite carbonatite 989/57.8; (h) hydroxycalcipyrochlore crystal with baddeleyite relics in calcite-magnetite-apatite-forsterite phoscorite 986/49.6; (i) epitaxial overgrowth of hydroxykenopyrochlore on baddeleyite in calcite-apatite-forsterite phoscorite 1009/186.6. Macrophoto (d) and back-scattered electron (BSE) images of thin polished sections (the rest). Mineral abbreviations are in Section 2.

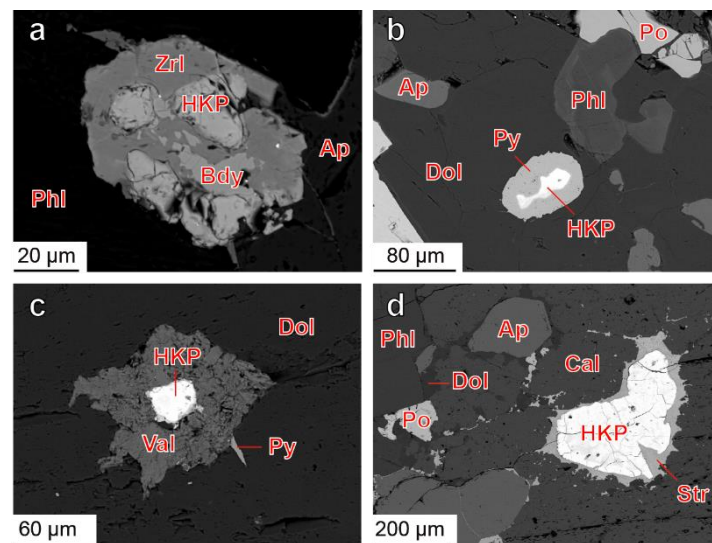


Figure 3. Typical products of hydroxykenopyrochlore low-temperature alteration: **a**—replacement of baddeleyite and hydroxykenopyrochlore by zirconolite in dolomite carbonatite 964/148.2; **b**—relic of hydroxykenopyrochlore within pyrite grain in phlogopitite 948/31.4; **c**—radiated aggregate vallerite around hydroxykenopyrochlore grain in vein calcite carbonatite 943/54.7; **d**—hydroxykenopyrochlore grain rimmed by strontianite in phoscorite-related calcite carbonatite 974/115.6. BSE-images of polished thin sections. Mineral abbreviations are in Section 2.

3.2. Chemical Composition

Table 3 shows the results of precision EPMA analyses conducted on 12 different members of the pyrochlore supergroup found in the Kovdor massif, and Table 4 presents statistical data on the PSM composition in different rocks of this massif. Most of the analyzed grains (92%) correspond to Ca-, Na- and vacancy-dominant members of the pyrochlore group and the rest 8% are represented by minerals of microlite and betafite groups (about 4% of each). Pyrochlores occur in all rocks of the Kovdor massif (Figure 4), and microlites and betafites co-exist with pyrochlore in the central part of the phoscorite-carbonatite complex.

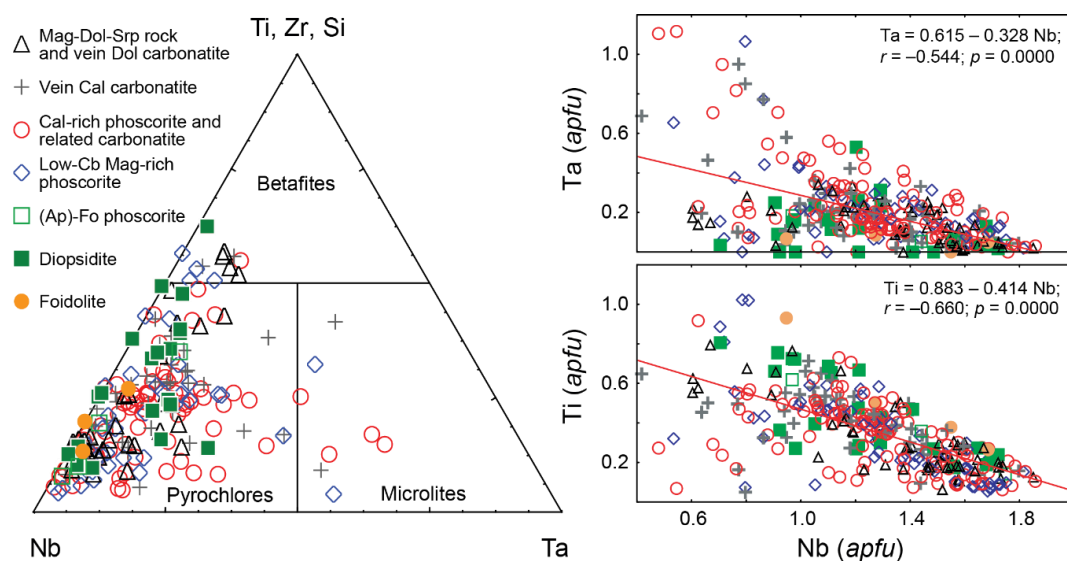


Figure 4. The Kovdor PSM classification diagram [11] and relations between Nb, Ta and Ti contents.

Table 3. Precision microprobe analyses of pyrochlore supergroup minerals (wt %) (see abbreviations above) and the corresponding crystallochemical formulas calculated on the basis of $B = 2$, $X = 6$ and $Y = 1$ atoms per formula unit (*apfu*).

PSM	OCP	ONP	HCP	HNP	HKP	FCP	FNP	FKP	HCM	HKM	FCM	OCB
Sample	1010/243.7	987/67.2	1010/243.7	972/86.9	987/2.1	901/109.9	987/198.0	974/50.6	901/109.9	981/520	973/533.3	957/141.0
F, wt %	1.51	bd	2.00	0.09	0.03	1.99	2.48	2.31	0.42	0.43	2.47	bd
Na ₂ O	3.59	5.12	7.31	8.03	0.89	3.45	9.90	bd	0.51	0.66	3.46	bd
MgO	bd	bd	bd	bd	bd	bd	bd	bd	bd	0.24	0.29	bd
Al ₂ O ₃	0.21	bd	bd	bd	bd	0.11	bd	bd	0.19	bd	bd	bd
SiO ₂	bd	0.19	bd	bd	0.35	bd	bd	bd	bd	1.62	bd	bd
CaO	13.70	8.83	15.18	10.05	8.47	15.78	8.60	8.58	9.80	4.41	11.33	12.30
TiO ₂	3.50	6.71	1.92	3.83	8.32	0.90	5.66	4.36	1.03	5.00	1.00	16.07
MnO	bd	bd	bd	bd	bd	bd	bd	bd	bd	0.35	bd	bd
Fe ₂ O ₃	2.09	1.16	0.83	bd	1.70	0.32	bd	1.62	0.50	2.23	7.01	4.60
ZrO ₂	bd	1.32	0.73	bd	1.29	bd	bd	bd	bd	1.09	7.68	bd
Nb ₂ O ₅	42.34	31.49	60.82	56.72	32.21	53.79	57.11	43.72	17.95	19.34	11.26	21.24
BaO	bd	bd	bd	bd	bd	bd	bd	bd	bd	7.12	bd	bd
La ₂ O ₃	bd	bd	0.17	bd	bd	bd	bd	bd	bd	0.46	bd	3.59
Ce ₂ O ₃	1.37	0.34	1.60	3.01	0.45	2.88	2.63	1.45	0.65	3.07	bd	6.70
Pr ₂ O ₃	bd	bd	bd	bd	bd	bd	bd	bd	bd	0.51	bd	bd
Nd ₂ O ₃	0.41	0.13	0.11	bd	0.10	bd	bd	bd	bd	1.03	bd	bd
Ta ₂ O ₅	12.76	16.25	7.35	7.48	14.81	6.59	3.20	11.23	53.29	33.39	51.21	7.80
PbO	bd	bd	bd	bd	0.88	bd	bd	bd	bd	bd	bd	bd
ThO ₂	14.35	1.48	bd	4.66	2.57	1.33	3.67	bd	8.09	6.11	bd	22.92
UO ₂	0.45	24.64	bd	3.84	20.86	0.01	4.94	26.90	5.62	bd	bd	bd
–O=F ₂	0.64	bd	0.84	0.04	0.01	0.84	1.04	0.97	0.18	0.18	1.04	bd
Total	95.64	97.67	97.18	97.67	92.91	86.31	97.16	99.20	97.86	86.86	94.66	95.22
Ca, <i>apfu</i>	1.08	0.74	1.02	0.71	0.67	1.24	0.60	0.67	0.88	0.36	0.83	0.97
Na	0.51	0.79	0.89	1.02	0.13	0.49	1.24	–	0.08	0.10	0.46	–
Ba	–	–	–	–	–	–	–	–	–	0.21	–	–
Mn	–	–	–	–	–	–	–	–	–	0.02	–	–
La	–	–	–	–	–	–	–	–	–	0.01	–	0.10
Ce	0.04	0.01	0.04	0.07	0.01	0.08	0.06	0.04	0.02	0.09	–	0.18
Pr	–	–	–	–	–	–	–	–	–	0.01	–	–
Nd	0.01	–	–	–	–	–	–	–	–	0.03	–	–
Pb	–	–	–	–	0.02	–	–	–	–	–	–	–
Th	0.24	0.03	–	0.07	0.04	0.02	0.05	–	0.15	0.11	–	0.38
U	0.01	0.43	–	0.06	0.34	–	0.07	0.44	0.10	–	–	–
vac	0.10	–	0.05	0.07	0.79	0.17	–	0.85	0.76	1.06	0.71	0.38
ΣA	2.00	2.00	2.00	2.00	2.00	2.00	2.02	2.00	2.00	2.00	2.00	2.00
Nb	1.41	1.13	1.72	1.68	1.07	1.79	1.67	1.45	0.68	0.68	0.35	0.70
Ta	0.26	0.35	0.13	0.13	0.30	0.13	0.06	0.22	1.21	0.71	0.95	0.16
Ti	0.19	0.40	0.09	0.19	0.46	0.05	0.27	0.24	0.06	0.29	0.05	0.89

Table 3. Cont.

PSM	OCP	ONP	HCP	HNP	HKP	FCP	FNP	FKP	HCM	HKM	FCM	OCB
Zr	—	0.05	0.02	—	0.05	—	—	—	—	0.04	0.26	—
Si	—	—	0.02	—	0.03	—	—	—	—	0.12	—	—
Fe ³⁺	0.12	0.07	0.04	—	0.09	0.02	—	0.09	0.03	0.13	0.36	0.25
Al	0.02	—	—	—	—	0.01	—	—	0.02	—	—	—
Mg	—	—	—	—	—	—	—	—	—	0.03	0.03	—
ΣB	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
* O ^{2−}	6.00	6.00	5.86	5.94	5.36	6.00	5.83	5.80	5.74	4.24	4.00	5.91
* (OH) [−]	—	—	0.14	0.06	0.64	—	0.17	0.20	0.26	1.76	2.00	0.09
ΣX	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
* O ^{2−}	0.36	0.54	—	—	—	0.20	—	—	—	—	—	0.50
* (OH) [−]	0.29	0.46	0.72	0.98	0.99	0.34	0.49	0.47	0.89	0.93	0.47	—
F [−]	0.35	—	0.28	0.02	0.01	0.46	0.51	0.53	0.11	0.07	0.53	—
ΣY	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.50

* Calculated values. bd—below detection limit.

Table 4. The PSM mean composition in rocks of the Kovdor massif (mean $\pm$ standard deviation (SD)/min–max, *apfu*).

Rock	Foidolite	Diopsidite and Phlogopitite	(Ap)-Fo Phoscorite	Low-Cb Mag-Rich Phoscorite	Cal-Rich Phoscorite and Related Carbonatite	Vein Calcite Carbonatite	Vein Dol Carbonatite and Mag-Dol-Srp Rock
<i>n</i>	3	20	4	51	92	44	39
Ca	0.5 $\pm$ 0.2 0.29–0.67	0.6 $\pm$ 0.4 0.12–1.59	0.8 $\pm$ 0.4 0.38–1.14	0.7 $\pm$ 0.3 0.10–1.24	0.6 $\pm$ 0.3 0.08–1.61	0.5 $\pm$ 0.2 0.13–1.00	0.6 $\pm$ 0.3 0.09–1.11
Na	0.6 $\pm$ 0.5 0.00–0.90	0.4 $\pm$ 0.4 0.00–1.02	0.3 $\pm$ 0.3 0.00–0.70	0.3 $\pm$ 0.3 0.00–0.96	0.3 $\pm$ 0.4 0.00–1.32	0.2 $\pm$ 0.4 0.00–1.37	0.4 $\pm$ 0.4 0.00–1.31
Mn	—	0.00 $\pm$ 0.01 0.00–0.03	0.02 $\pm$ 0.05 0.00–0.09	0.01 $\pm$ 0.03 0.00–0.10	0.01 $\pm$ 0.02 0.00–0.10	0.01 $\pm$ 0.03 0.00–0.18	0.01 $\pm$ 0.02 0.00–0.08
Ni	—	—	0.01 $\pm$ 0.01 0.00–0.03	—	—	—	—
Ba	—	—	—	0.00 $\pm$ 0.01 0.00–0.04	0.03 $\pm$ 0.09 0.00–0.55	0.02 $\pm$ 0.07 0.00–0.36	0.02 $\pm$ 0.07 0.00–0.36
Sc	—	—	—	0.00 0.00–0.03	—	—	—
Cu	—	—	—	—	—	—	0.00 $\pm$ 0.01 0.00–0.08
Sr	—	—	0.1 $\pm$ 0.1 0.00–0.19	0.02 $\pm$ 0.05 0.00–0.26	0.04 $\pm$ 0.08 0.00–0.36	0.03 $\pm$ 0.07 0.00–0.29	0.1 $\pm$ 0.1 0.00–0.30
Y	—	0.01 $\pm$ 0.04 0.00–0.17	—	0.01 $\pm$ 0.03 0.00–0.16	0.01 $\pm$ 0.03 0.00–0.18	0.00 $\pm$ 0.03 0.00–0.18	—
La	0.05 $\pm$ 0.01 0.03–0.06	0.02 $\pm$ 0.02 0.00–0.06	0.01 $\pm$ 0.01 0.00–0.02	0.02 $\pm$ 0.05 0.00–0.25	0.01 $\pm$ 0.02 0.00–0.07	0.02 $\pm$ 0.02 0.00–0.06	0.01 $\pm$ 0.02 0.00–0.06

Table 4. Cont.

Rock	Foidolite	Diopsidite and Phlogopitite	(Ap)-Fo Phoscorite	Low-Cb Mag-Rich Phoscorite	Cal-Rich Phoscorite and Related Carbonatite	Vein Calcite Carbonatite	Vein Dol Carbonatite and Mag-Dol-Srp Rock
Ce	0.07 ± 0.03 0.05–0.10	0.10 ± 0.08 0.00–0.37	0.04 ± 0.05 0.00–0.08	0.06 ± 0.07 0.00–0.38	0.06 ± 0.05 0.00–0.19	0.08 ± 0.05 0.00–0.20	0.06 ± 0.04 0.00–0.16
Pr	–	–	–	–	0.00 0.00–0.01	–	–
Nd	–	0.01 ± 0.02 0.00–0.04	0.01 ± 0.02 0.00–0.03	0.01 ± 0.01 0.00–0.06	0.01 ± 0.01 0.00–0.07	0.02 ± 0.02 0.00–0.08	0.01 ± 0.02 0.00–0.07
Pb	–	–	–	0.01 ± 0.04 0.00–0.28	0.01 ± 0.01 0.00–0.04	–	–
Th	0.2 ± 0.1 0.06–0.33	0.07 ± 0.09 0.00–0.35	0.06 ± 0.05 0.00–0.12	0.1 ± 0.1 0.00–0.48	0.06 ± 0.05 0.00–0.25	0.04 ± 0.05 0.00–0.20	0.05 ± 0.05 0.00–0.25
U	0.1 ± 0.1 0.00–0.22	0.2 ± 0.1 0.00–0.41	0.1 ± 0.1 0.00–0.27	0.2 ± 0.2 0.00–0.57	0.2 ± 0.2 0.00–0.43	0.2 ± 0.1 0.00–0.44	0.1 ± 0.1 0.00–0.43
A	1.4 ± 0.3 1.11–1.57	1.3 ± 0.5 0.57–2.10	1.3 ± 0.4 0.93–1.85	1.4 ± 0.4 0.51–2.14	1.4 ± 0.4 0.63–2.14	1.1 ± 0.4 0.41–2.03	1.4 ± 0.5 0.65–2.14
Nb	1.5 ± 0.2 1.27–1.69	1.2 ± 0.3 0.71–1.72	1.4 ± 0.3 0.97–1.75	1.2 ± 0.3 0.53–1.79	1.2 ± 0.3 0.35–1.86	1.1 ± 0.3 0.42–1.80	1.3 ± 0.4 0.55–1.72
Ti	0.4 ± 0.1 0.27–0.50	0.5 ± 0.2 0.18–0.81	0.3 ± 0.2 0.14–0.62	0.4 ± 0.3 0.05–1.17	0.4 ± 0.2 0.05–0.92	0.4 ± 0.2 0.09–0.71	0.4 ± 0.2 0.16–0.80
Ta	0.05 ± 0.04 0.00–0.09	0.1 ± 0.1 0.00–0.53	0.08 ± 0.07 0.03–0.18	0.2 ± 0.2 0.00–1.21	0.3 ± 0.2 0.00–1.12	0.2 ± 0.2 0.02–0.95	0.13 ± 0.09 0.00–0.34
Fe	0.07 ± 0.07 0.00–0.14	0.08 ± 0.08 0.00–0.32	0.13 ± 0.06 0.08–0.20	0.12 ± 0.08 0.00–0.40	0.10 ± 0.07 0.00–0.45	0.12 ± 0.08 0.00–0.40	0.10 ± 0.06 0.00–0.28
Al	–	–	–	0.01 ± 0.03 0.00–0.21	0.00 ± 0.01 0.00–0.10	–	0.01 ± 0.02 0.00–0.08
Zr	–	0.01 ± 0.05 0.00–0.16	–	0.02 ± 0.05 0.00–0.24	0.04 ± 0.07 0.00–0.36	0.1 ± 0.1 0.00–0.36	0.1 ± 0.1 0.00–0.39
Mg	–	0.00 ± 0.02 0.00–0.08	0.04 ± 0.07 0.00–0.15	0.02 ± 0.06 0.00–0.32	0.01 ± 0.03 0.00–0.14	0.03 ± 0.05 0.00–0.21	0.03 ± 0.05 0.00–0.19
Si	–	0.1 ± 0.2 0.00–0.54	–	0.02 ± 0.06 0.00–0.31	0.02 ± 0.05 0.00–0.34	0.02 ± 0.05 0.00–0.23	0.01 ± 0.03 0.00–0.18
P	–	–	–	–	0.00 ± 0.01 0.00–0.10	–	0.01 ± 0.04 0.00–0.18
B	2	2	2	2	2	2	2
K	–	–	–	0.00 ± 0.02 0.00–0.13	0.01 ± 0.02 0.00–0.15	–	0.00 ± 0.01 0.00–0.03
F				0.2 ± 0.2 0.00–0.71	0.1 ± 0.1 0.00–0.53	0.1 ± 0.2 0.00–0.53	0.2 ± 0.3 0.00–0.51
Nb/(Nb + Ta)	0.96 ± 0.03 0.93–1.00	0.91 ± 0.09 0.69–1.00	0.94 ± 0.06 0.84–0.98	0.9 ± 0.1 0.43–1.00	0.9 ± 0.1 0.30–1.00	0.8 ± 0.1 0.38–0.98	0.90 ± 0.07 0.73–1.00
Ti/(Nb + Ta + Ti)	0.3 ± 0.1 0.13–0.48	0.3 ± 0.1 0.09–0.52	0.2 ± 0.1 0.07–0.35	0.2 ± 0.1 0.03–0.57	0.2 ± 0.1 0.03–0.52	0.2 ± 0.1 0.03–0.38	0.2 ± 0.1 0.04–0.49
Ca/(Ca + Na)	0.5 ± 0.3 0.26–1.00	0.7 ± 0.3 0.31–1.00	0.7 ± 0.2 0.58–1.00	0.6 ± 0.2 0.17–1.00	0.7 ± 0.2 0.08–1.00	0.8 ± 0.3 0.05–1.00	0.6 ± 0.2 0.26–1.00

Over 92% of the analyzed PSM are represented by O- and (OH)-dominant phases, and the rest are fluorine-dominant. Fluorine shows positive correlations with Ca and Nb and negative correlations with Ti and U (Figure 5). Correspondingly, fluorine-dominant phases occur mainly among calciopyrochlores; while natropyrochlores, betafites and microlites are usually represented by hydroxyl-dominant and sometimes oxygen-dominant phases. As for pyrochlore, Ca-dominant phases prevail in $\approx 45\%$ of the analyzed samples; about 20% of the samples include Na-dominant pyrochlore, and the rest are formed by kenopyrochlore (Figure 6a) as a result of heterovalent substitutions: $2\text{Ca}^{2+} \rightarrow \text{Na}^+\text{REE}^{3+}$, $2\text{Ca}^{2+} \rightarrow \square \text{U}^{4+}$, $\text{Ca}^{2+}\text{O}^{2-} \rightarrow \text{Na}^+(\text{OH})^-$, etc. Simultaneously, Nb is replaced with Ta and Ti up to the formation of microlite and betafite.

In about 35% of the analyzed PSM, the sum of cations in the A-position does not exceed 1 apfu (see Figure 6a). Kenopyrochlores occur in 59% of the analyzed samples of vein calcite carbonatite, 45% of diopsidite and phlogopitite samples, 25% of phoscorite samples, and 23% of vein dolomite carbonatite samples. The deficit of cations in the A-position is caused by both the presence of high-charge cations of U^{4+} , Th^{4+} , REE^{3+} instead of Na^+ and Ca^{2+} ($4\text{Na}^+ \leftrightarrow 3\square \text{U}^{4+}$, $3\text{Ca}^{2+} \leftrightarrow \square 2\text{REE}^{3+}$, etc.), and cation loss during pyrochlore metamictization and hydration. The last processes are typical for pyrochlore with >15 wt % of $(\text{U,Th})\text{O}_2$, and accompanied by destruction of the mineral crystal structure and leaching of Na, then Ca, and finally REE, U and Th (Figure 6b). In kenopyrochlore, uranium is a predominant high-charge cation; while Th-dominant phases occur much rarely (Figure 6c). Rare-earth elements are represented mainly by light lanthanides La through Nd, with total average content of La and Ce of about 87%. The highest REE content in pyrochlore is typical for host diopsidite and phlogopitite, as well as vein calcite carbonatite.

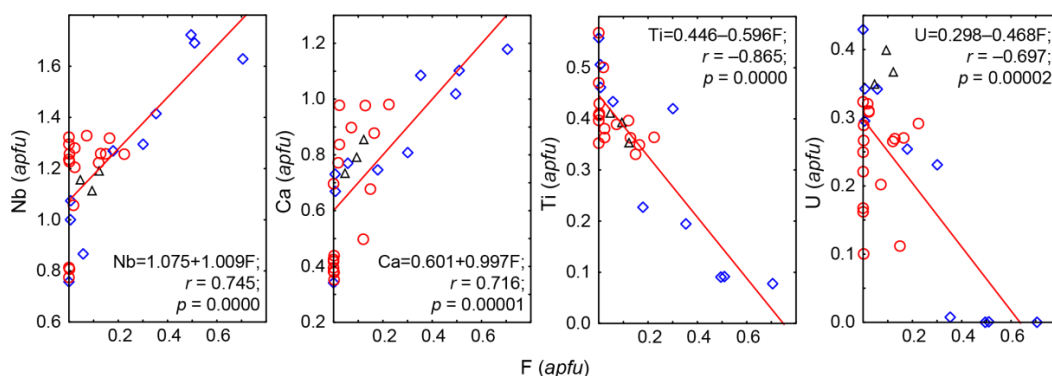


Figure 5. Nb, Ti, Ca and U content vs. fluorine amount in PSM.

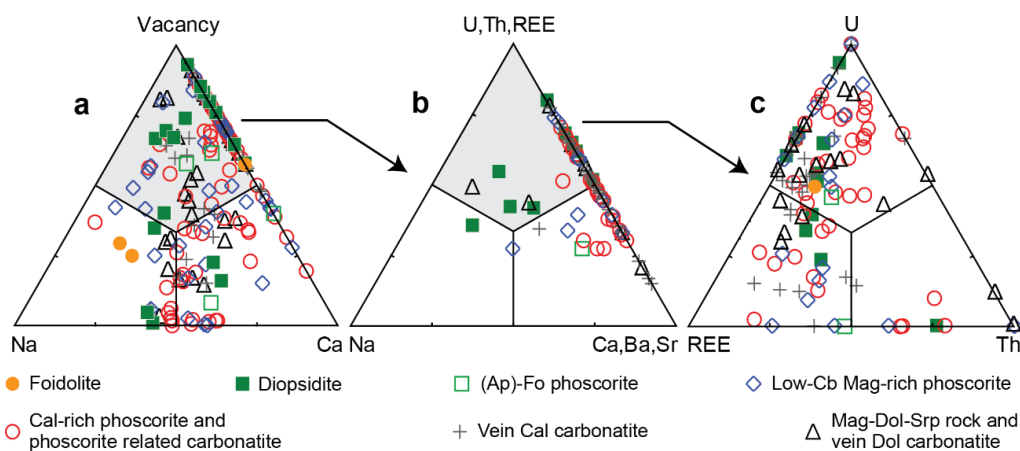


Figure 6. Relations between cations and vacancies in the A-site of the Kovdor PSM (a—all samples, b—kenopyrochlores, c—kenopyrochlores enriched in high-charge cations).

To determine the chemical evolution of the PSM in natural rock sequence, we implemented factor analysis of 314 PSM compositions using the method of principal components (with normalization and varimax rotation of factors) (Table 5). The resultant factors enable us to specify five schemas of isomorphic substitutions (elements with high factor loadings are bolded): (1) $\text{Na}^+\text{Ca}^{2+}\text{Nb}^{5+} \leftrightarrow \text{U}^{4+}\text{Ti}^{4+}$; (2) $(\text{Th}^{4+}, \text{REE}^{3+}) \leftrightarrow \text{U}^{4+}$; (3) $\text{Na}^+\text{Nb}^{5+} \leftrightarrow \text{Sr}^{2+}\text{Zr}^{4+}$; (4) $\text{Nb}^{5+} \leftrightarrow (\text{Ta}^{5+}, \text{Fe}^{3+})$; (5) $\text{Ca}^{2+} \leftrightarrow \text{Ba}^{2+}$. Correspondingly, in the natural sequence of the Kovdor rocks (Figure 7), content of Ba, Sr, U, Ta, Fe and Zr in PSM gradually increases due to Na, Ca, REE, Th and Nb (F2–F5), while higher contents of Ti, U and vacancies are observed in host silicate and calcio-carbonatite rocks (F1).

Table 5. Result of factor analysis of PSM composition.

Variables	Factor Loadings				
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Na	−0.828	0.164	−0.135	0.059	−0.165
Ca	−0.740	0.129	−0.117	−0.182	−0.298
U	0.594	0.624	−0.214	0.034	−0.174
Th	0.213	−0.628	−0.279	0.075	0.033
REE	0.235	−0.726	0.073	−0.111	−0.265
Ba	0.021	0.032	0.128	0.035	0.742
Mn	0.288	0.132	−0.330	−0.026	0.452
Sr	0.103	−0.016	0.620	−0.243	0.315
Vacancy	0.818	−0.199	0.167	0.078	0.241
Nb	−0.652	−0.107	−0.186	−0.657	0.131
Ta	0.064	0.314	−0.130	0.779	−0.010
Ti	0.832	−0.015	−0.001	0.010	−0.256
Zr	0.256	0.108	0.760	0.152	−0.113
Fe	−0.017	−0.303	0.028	0.626	0.083
Expl. Var	3.638	1.627	1.328	1.575	1.233
Prp. Totl	0.260	0.116	0.095	0.113	0.088

Marked factor loadings exceed 0.5. Expl. Var—single factor variance explained, Prp. Totl—percentage of the total variance explained.

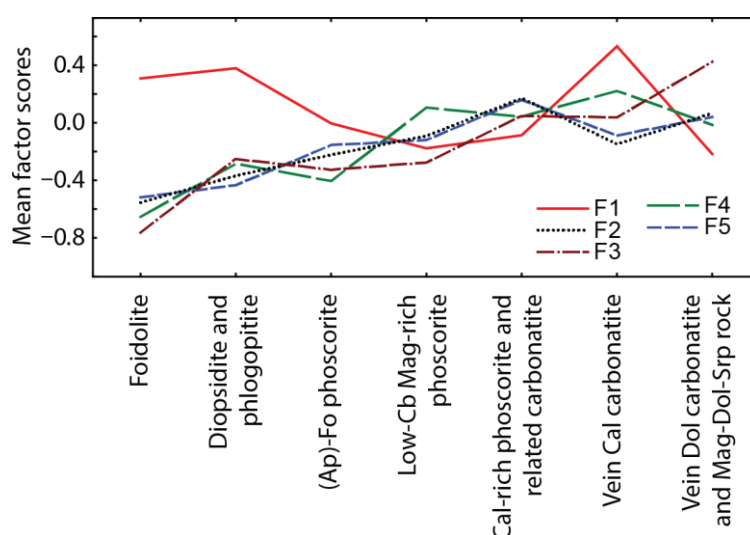


Figure 7. Changes of mean factor scores reflected PSM composition (see Table 5) in natural sequence of the Kovdor rocks.

All above substitutions cause complex zonation of the ore-pipe in terms of the PSM composition (Figure 8): marginal (apatite)-forsterite phoscorite contains Th-REE-rich (keno)pyrochlore and betafite, intermediate low-carbonate magnetite-rich phoscorite comprises pyrochlore with medium content

of basic cations, and axial calcite-rich phoscorite and carbonatites accumulate (keno)pyrochlore, (keno)microlite and betafite comparatively enriched in U, Fe, Zr, Ba and Sr.

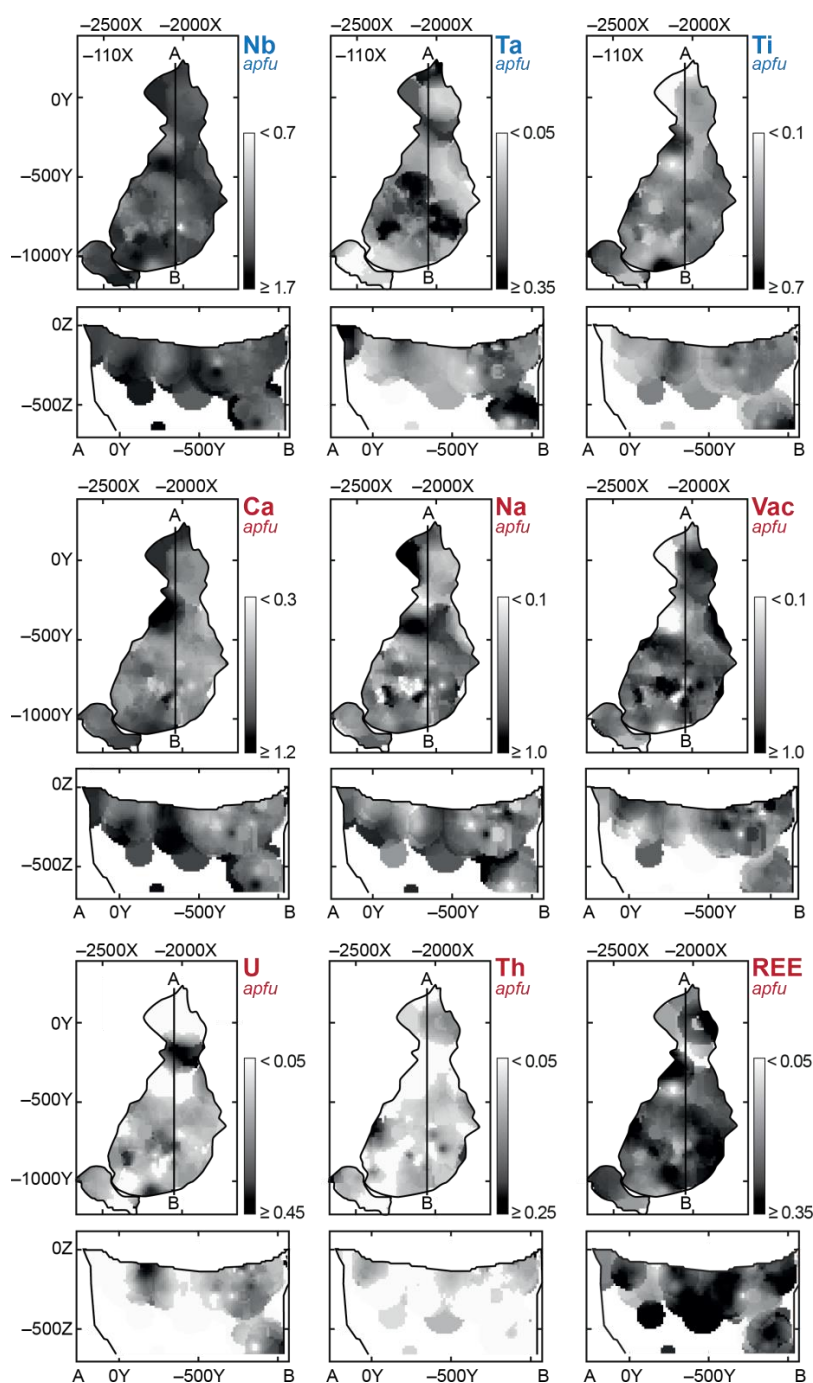


Figure 8. Distribution of the PSM basic constituents in the Kovdor phoscorite-carbonatite complex.

In the unaltered PSM crystals from diopside, phlogopite, phoscorite and calcite carbonatite, there are irregular variations of chemical composition between separate zones, without any clear trends from cores to margins. However, in host foidolite, marginal zones of pyrochlore crystals are constantly enriched in Ca, Na, Th and Nb in comparison with REE-U-Ta-Ti-rich cores, and the latest dolomite carbonatite, pyrochlore grains have Na-Nb-dominant cores and Ca-U-Zr-rich margins. Besides, U-Th-rich (keno)pyrochlore grains often have secondary zonation due to leaching of A-cations

and then *B*-cations from the grain marginal parts. Fluorine content increases from the core to rim in fresh pyrochlore crystals (Figure 9a). The PSM alteration under the influence of self-irradiation causes loss of fluorine (Figure 9b); therefore, the content of fluorine in the PSM is directly proportional to the amounts of Ca and Nb, and inversely proportional to the content of U and Th (see Figure 5).

X-ray powder diffraction of the Kovdor PSM showed good crystallinity of U/Th-poor calcio- and natropyrochlores; while all analyzed kenopyrochlores became amorphous. Therefore, a single-crystal X-ray study was performed only for low-vacant pyrochlore.

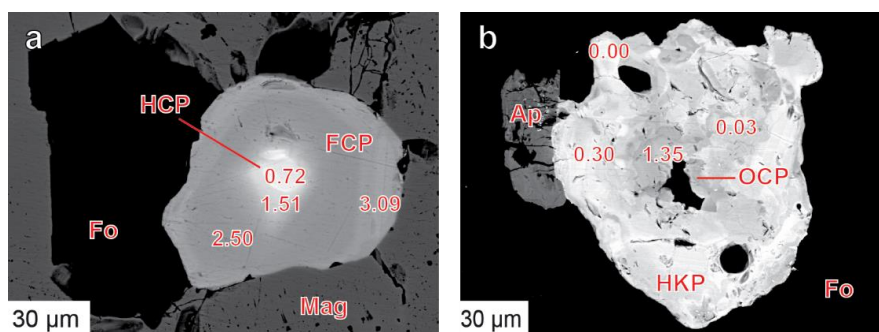


Figure 9. Zonal crystals of pyrochlore: (a) primary zonation of hydroxycalcio-pyrochlore–fluorcalcio-pyrochlore crystal from magnetite-forsterite phoscorite 1010/243.7; (b) secondary zonation in grain of oxycalcio-pyrochlore–U-rich hydroxykeno-pyrochlore from magnetite-forsterite phoscorite 987/2.1. BSE-images of thin polished sections with indicated fluorine contents. Mineral abbreviations are in Section 2.

3.3. Crystal Structure

Single-crystal X-ray diffraction data were obtained for well-crystalline oxycalcio-pyrochlore 917-318.5 (see Figure 2e) and hydroxynatropyrochlore K-017-4 (see Figure 2d). A quadrant of three-dimensional data was collected with frame widths of 1° in ω , and with 220 s in the range 2θ 6.8° – 55° . Scattering factors were calculated from initial model with all Ca and Na at *A*, all Nb and Ti at *B*, O at O1, and O at Y1 site. All cation site-occupancies are given in accordance with electron-microprobe-determined values (normalized on a basis of 2*B* cations per formula unit), the O-populated sites (O1 and Y1) was set at full occupancy.

Table 6 shows data collection and refinement parameters for the single-crystal X-ray experiments. Atom coordinates, displacement parameters and site occupancies are given in Table 7, and bond lengths in Table 8. Anisotropic displacement parameters are attached in Supplementary Materials (CIF data is available).

Crystal structures of oxycalcio-pyrochlore 917/318.5 and hydroxynatropyrochlore K-017-4 (Figure 10) were refined in the $Fd\bar{3}m$ space group with R_1 values of 0.032 and 0.054, respectively. Octahedral *B* site has scattering 39.7 and 33.2 *epfu*, respectively, which agrees well with occupancies $(\text{Nb}_{0.965}\text{Ti}_{0.02}\text{Ta}_{0.15})_{1.00}$ and $(\text{Nb}_{0.65}\text{Ti}_{0.32}\text{Mg}_{0.02}\text{Ta}_{0.01})_{1.00}$. The calculated scattering factor values of 22.1 and 18.7 *epfu* for the *A* site slightly exceed the observed values of 18.7 and 15.3 *epfu*, probably, due to variation of Th- and U-content. In the crystal structure of oxycalcio-pyrochlore 917/318.5 and hydroxynatropyrochlore K-017-4, eight-coordinated *A* sites are predominately occupied by calcium and sodium, respectively, and their final occupancies are $(\text{Ca}_{0.59}\text{Na}_{0.25}\text{Y}_{0.09}\text{Fe}_{0.02}\text{Th}_{0.02}\text{Ce}_{0.02}\text{La}_{0.01})_{1.00}$ and $(\text{Na}_{0.49}\text{Ca}_{0.20}\square_{0.13}\text{Fe}_{0.06}\text{Sr}_{0.06}\text{Th}_{0.04}\text{U}_{0.02})_{1.00}$ respectively. The mean A1–O bond ranges from 2.530 to 2.533 Å, which is more suitable for ideal Ca–O distance 2.54 Å than for ideal Na–O distance 2.60 Å [35]. For hydroxynatropyrochlore K-017-4, displacement parameters for the Y site are slightly higher than those for oxygen, and are consistent with its occupancy by (OH)-groups (Table 7); while for oxycalcio-pyrochlore 917-318.5, displacement parameters for Y1 and O1 are almost equal.

Based on the structure refinement, crystal-chemical formulas of oxycalcio-pyrochlore 917/318.5 and hydroxynatropyrochlore K-017-4 can be determined as $^A(\text{Ca}_{1.18}\text{Na}_{0.50}\text{Y}_{0.18}\text{Fe}_{0.04}\text{Ce}_{0.04}\text{Th}_{0.04}\text{La}_{0.02})_{2.00}$

$^B(\text{Nb}_{1.93}\text{Ti}_{0.04}\text{Ta}_{0.015})_{2.00}\text{O}_{6.00}^{\text{Y}}(\text{O}_{0.78}\text{OH}_{0.22})_{1.00}$ and $^A(\text{Na}_{0.98}\text{Ca}_{0.40}\square_{0.26}\text{Fe}_{0.12}\text{Sr}_{0.12}\text{Th}_{0.08}\text{U}_{0.04})_{2.00}^B(\text{Nb}_{1.30}\text{Ti}_{0.64}\text{Mg}_{0.04}\text{Ta}_{0.02})_{2.00}[\text{O}_{4.98}\text{OH}_{1.02}]_{6.00}^{\text{Y}}(\text{OH}_{0.61}\text{F}_{0.39})_{1.00}$ respectively. According to the structural data, the common difference in scattering parameters of the B site (39.7 and 33.2 *epfu*) lies in agreement with the substitution scheme $^B\text{Ti}^{4+} + ^{\text{Y}}\text{OH}^- = ^B\text{Nb}^{5+} + ^{\text{Y}}\text{O}^{2-}$. For oxycalcipyrochlore 917/318.5, lower means of Y1 site displacement parameters reflect lesser content of (OH)-groups as compared to hydroxynatropyrochlore K-017-4.

Table 6. Crystal data and structure refinement for oxycalcipyrochlore 917/318.5 and hydroxynatropyrochlore K-017-4.

Mineral Sample	Oxycalcipyrochlore 917/318.5	Hydroxynatropyrochlore K-017-4
Temperature (K)	293(2)	293(2)
Crystal system	cubic	cubic
Space group	$Fd\bar{3}m$	$Fd\bar{3}m$
<i>a</i> (Å)	10.4065(4)	10.3917(4)
Volume (Å ³)	1126.96(14)	1122.16(14)
<i>Z</i>	8	8
ρ_{calc} (g/cm ³)	4.310	3.829
μ (mm ^{−1})	5.508	4.517
<i>F</i> (000)	1378.0	1225.0
Crystal size (mm ³)	0.15 × 0.15 × 0.15	0.13 × 0.13 × 0.13
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 Θ range for data collection (°)	6.782–54.54	6.792–54.62
Index ranges	−8 ≤ <i>h</i> ≤ 13, −7 ≤ <i>k</i> ≤ 11, −12 ≤ <i>l</i> ≤ 13	−9 ≤ <i>h</i> ≤ 9, −12 ≤ <i>k</i> ≤ 13, −13 ≤ <i>l</i> ≤ 10
Reflections collected	602	758
Independent reflections	83 [<i>R</i> _{int} = 0.0433, <i>R</i> _{sigma} = 0.0224]	84 [<i>R</i> _{int} = 0.0981, <i>R</i> _{sigma} = 0.0348]
Data/restraints/parameters	83/0/12	84/0/12
Goodness-of-fit on <i>F</i> ²	1.286	1.173
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0320, <i>wR</i> ₂ = 0.0687	<i>R</i> ₁ = 0.0536, <i>wR</i> ₂ = 0.1346
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0363, <i>wR</i> ₂ = 0.0716	<i>R</i> ₁ = 0.0595, <i>wR</i> ₂ = 0.1497
Largest diff. peak/hole (eÅ ^{−3})	0.63/−0.50	0.93/−1.30

Table 7. Atom coordinates, displacement parameters (Å²) and site occupancies for oxycalcipyrochlore 917/318.5 and hydroxynatropyrochlore K-017-4.

Sample	Site	Occupancy	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}	<i>s.s.</i> (epfu)	<i>s.s.</i> -calc (epfu)
917/318.5	B1	Nb _{0.965} Ti _{0.02} Ta _{0.15}	0	1/2	0	0.014(1)	39.67	41.1
K-017-4	B1	Nb _{0.65} Ti _{0.32} Mg _{0.02} Ta _{0.01}	0	1/2	0	0.021(1)	33.2	34.7
917/318.5	A1	Ca _{0.59} Na _{0.25} Y _{0.09} Fe _{0.02} Th _{0.02} Ce _{0.02} La _{0.01}	−1/4	3/4	0	0.021(1)	18.65	22.11
K-017-4	A1	Na _{0.49} Ca _{0.20} □ _{0.13} Fe _{0.06} Sr _{0.06} Th _{0.04} U _{0.02}	−1/4	3/4	0	0.020(3)	15.3	18.7
917/318.5	Y1 *	O _{0.78} OH _{0.22}	−3/8	5/8	1/8	0.015(3)		
K-017-4	Y1 *	OH _{0.61} F _{0.39}	−3/8	5/8	1/8	0.044(4)		
917/318.5	O1 *	O _{1.00}	−0.0704(5)	5/8	1/8	0.017(2)		
K-017-4	O1 *	O _{0.83} OH _{0.17}	−0.0693(6)	5/8	1/8	0.031(2)		

* Relation of O/(OH, F) is calculated for the formula charge balance.

Table 8. Selected bond distances (Å) for oxycalcipyrochlore 917/318.5 and hydroxynatropyrochlore K-017-4 crystal structures.

Mineral Sample	Oxycalcipyrochlore 917/318.5		Hydroxynatropyrochlore K-017-4	
B1 - O1	1.980(2)	×6	B1 - O1	1.973(2) ×6
A1 - Y1	2.2530(1)	×2	A1 - Y1	2.2499(1) ×2
A1 - O1	2.622(4)	×6	A1 - O1	2.627(5) ×6
<A1 - O>	2.530		<A1 - O>	2.533

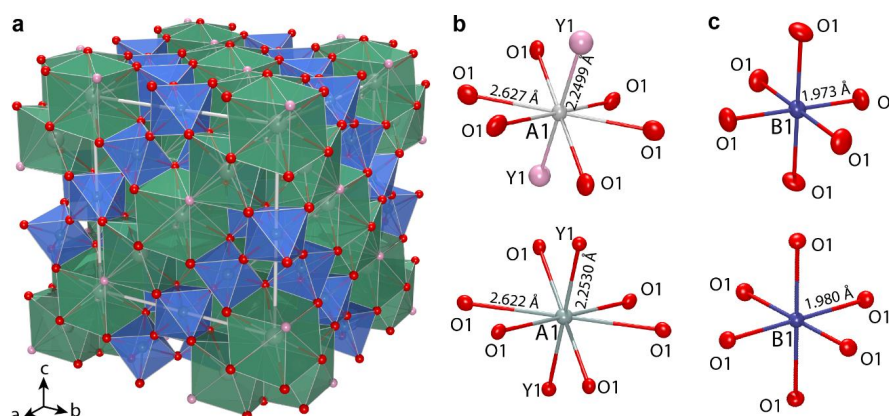


Figure 10. General view of hydroxynatropyrochlore K-017-4 crystal structure (a) and geometry of the coordination polyhedra in the crystal structures of hydroxynatropyrochlore K-017-4 (b) and oxycalcipyrochlore 917/318.5 (c). AO_8 polyhedra are green, BO_6 octahedra are blue, oxygen sites are represented by red circles, Y1 sites are shown as pink circles.

3.4. Raman Spectroscopy

The PSM Raman spectra obtained under the same conditions showed significantly different observed intensities I_{obs} of absorption bands (Figure 11a). The observed intensity of the spectrum depends on mineral crystallinity, which, in turn, gradually decreases with growth of U and Th total content from 0.13 *apfu* in HNP 972/86.9 to 0.47 *apfu* in ONP 966/62.9 (Table 9). For the same reason, the stability of the UTh-rich PSM decreases under the influence of laser beams. Corrected absorption band intensities I were calculated as $I = I_{obs} / (n(\omega) + 1)$, where $n(\omega)$ is the Bose (Einstein factor). Figure 11b shows the results for a zoned HKP-HNP crystal from calcite carbonatite 972/86.9.

The absorption bands (see Table 9) were assigned by analogy with other pyrochlore-like compounds [36–38] taking into account theoretical considerations by McCauley [39] and Arenas et al. [40]. According to McCauley [39], pyrochlore yields six Raman-active modes and one acoustic. These modes involve four vibrations of F_{1u} , F_{2g} , E_g , and A_{1g} symmetry. Theoretical calculations by [40] consider bands in the region of 70–180 cm^{-1} as related to acoustic modes (lattice vibrations or bending modes of O-A-O and stretching modes of A- BO_6). Bands in the region of 250–400 cm^{-1} can be assigned to different modes of A-O vibrations. The most intensive bands are related to bending vibrations of O-B-O bonds (400–680 cm^{-1}) and stretching vibrations of B-O bonds in BO_6 octahedra (680–900 cm^{-1}). Positions of typical absorption bands caused by different stretching vibrations depend on composition of the corresponding polyhedra (Figure 12), which enables us to estimate the content of major impurities using the PSM Raman spectra.

Table 9. The PSM chemical composition, Raman shifts and their assignment.

Sample		972/86.9	979/34.0	987/67.2	989/23.1	972/86.9	966/62.9
PSM		HNP	HKP	OCP	HCP	HKP	ONP
Bands assignment		Raman frequencies (cm^{-1})					
¹ B-O	stretching	894				894	
² B-O	stretching	828	842	786	819	830	836
³ B-O	stretching	734	778	707	777	756	755
⁴ B-O	stretching	681			715	688	
¹ O-B-O	bending	628	637	622	627	631	644
² O-B-O	bending	567	532	539	527	595	540
³ O-B-O	bending			449			
¹ A-O	stretching	354	362	381	390	354	361
² A-O	stretching		260	304	326		257

Table 9. Cont.

Sample		972/86.9	979/34.0	987/67.2	989/23.1	972/86.9	966/62.9
PSM		HNP	HKP	OCP	HCP	HKP	ONP
¹ O-A-O	bending	282			279	253	
A-BO ₆	stretching	180	203	212	221	195	203
² O-A-O	bending		144	164	126	145	142
³ O-A-O	bending	86	91			92	90
Chemical composition (apfu)							
Ca		0.70	0.15	1.21	0.62	0.18	0.78
Na		1.02	0.00	0.78	0.71	0.27	1.03
Ce		0.07	0.12	0.01	0.04	0.07	0.06
Th		0.07	0.03	0.03	0.00	0.05	0.06
U		0.06	0.31	0.43	0.43	0.35	0.41
Nb		1.68	1.03	1.12	1.16	1.21	1.31
Ti		0.19	0.72	0.40	0.46	0.48	0.35
Ta		0.13	0.14	0.35	0.26	0.26	0.34
Fe		0.00	0.08	0.07	0.12	0.05	0.00

OCP is oxycalciopyrochlore, ONP is oxynatropyrochlore, HCP is hydroxycalciopyrochlore, HNP is hydroxynatropyrochlore, HKP is hydroxykenopyrochlore.

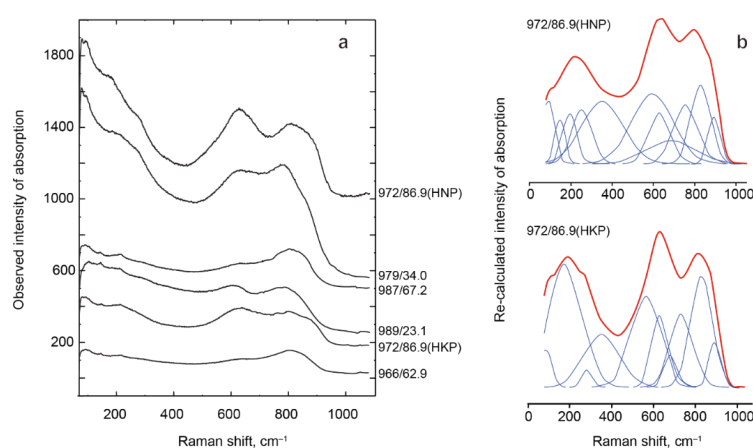


Figure 11. Initial (a) and re-calculated (b) Raman spectra of pyrochlore supergroup minerals. HNP is hydroxynatropyrochlore, HKP is hydroxykenopyrochlore.

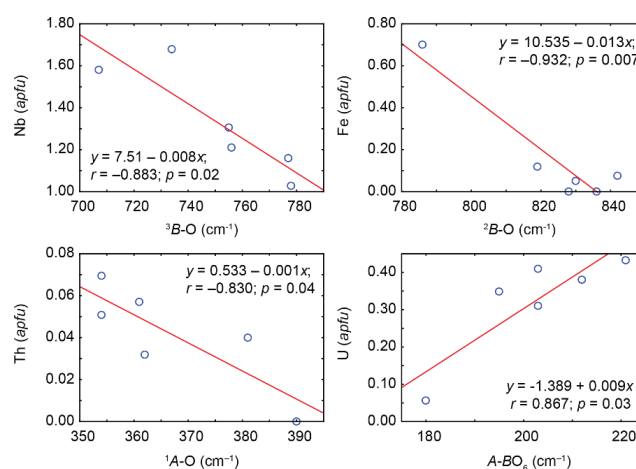


Figure 12. PSM composition vs. position of typical absorption bands in the corresponding Raman spectra.

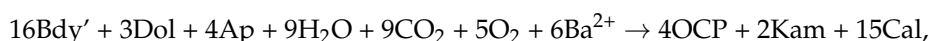
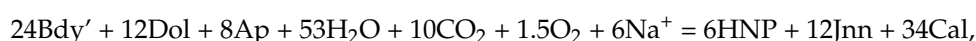
4. Discussion

Within the Kovdor phoscorite-carbonatite complex, the PSM are concentrated in the axial carbonate-rich zone, so their content, grain size and diversity increase from the pipe margins towards its axis (see Figure 1). Besides, in this direction, we observe gradual growth of Ba, Sr, U, Ta, Fe and Zr content in PSM due to Na, Ca, REE, Th and Nb amounts (see Figures 7 and 8). This trend is the reverse of known ranges of carbonate/silicate melt partition coefficients [41–44]: $Al < Si < Ti < Fe < Mg < K < Na < Ca < F < P < CO_2$ (for major elements), and $Hf < Zr < Th < U < Ta < Y < Nb < Nd < Sr < Ba$ (for trace elements). In other words, we can assume that most of the high-field-strength elements (HFSE: Ti, Zr, Hf, Nb, Ta and Y) are predominantly distributed in silicate melt; while alkaline-earth and most of rare-earth elements will be localized in carbonate melt. If we compare the earliest silicate rocks (including forsterite-dominant phoscorite) and the latest carbonatite veins (Table 10), we can see that this assumption is correct.

Table 10. Mean contents of the main rock constituents in the Kovdor phoscorite-carbonatite complex.

Rock	Host Silicate Rock	(Ap)-Fo Phoscorite	Low-Cb Mag-Rich Phoscorite	Cal-Rich Phoscorite and Related Carbonatite	Vein Cal-Carbonatite
<i>n</i>	23	11	59	34	9
Al ₂ O ₃ , wt %	5.19	1.25	1.44	0.54	0.20
SiO ₂	41.91	25.60	7.00	5.06	0.73
TiO ₂	0.94	0.19	0.45	0.36	0.04
Fe ₂ O ₃ tot	9.71	11.28	42.07	28.09	5.61
MgO	14.11	31.93	13.05	10.38	2.95
K ₂ O	1.59	0.40	0.12	0.12	0.14
Na ₂ O	1.97	0.20	0.13	0.16	0.13
CaO	17.32	10.20	13.60	24.79	45.50
F	0.04	0.11	0.14	0.13	0.08
P ₂ O ₅	0.18	5.84	10.48	6.70	3.22
CO ₂	0.42	0.40	0.40	3.27	9.62
Hf, ppm	7.21	5.17	31.63	21.43	1.37
Zr	237.19	192.78	1270.64	799.99	47.52
Th	4.37	3.12	3.75	3.70	4.01
U	0.85	0.35	0.43	0.65	0.41
Ta	8.33	5.62	15.08	17.65	5.65
Y	4.60	9.45	11.22	12.72	24.77
Nb	78.03	24.27	52.32	62.76	14.64
Nd	32.58	36.27	49.20	79.08	125.72
Sr	434.41	731.49	628.25	1680.81	5067.39
Ba	173.34	229.95	130.74	262.78	464.52

However, the highest concentrations of Zr, Hf, Ta and F as well as the local maximum of Nb content characterize magnetite-rich phoscorite, and can be caused by initial concentration of HFSE in Mg-Al-Ti-rich magnetite. Magnetite exsolution produces ScNb-rich baddeleyite (Figure 13) as a co-product of spinel and ilmenite–geikielite [45], and later alteration of such baddeleyite with fluorine-bearing hydrothermal solutions enriches them in Zr, Nb and Sc. When the concentration of HFSE in the solution reaches a critical level, the PSM start crystallizing. One part of the PSM is formed in situ as rims around baddeleyite grains, and the other part is crystallized as individual crystals in carbonatites that act as a geochemical barrier for $Nb(OH)_3F_2$, $Ta(OH)_3F_3^+$ and other HFSE complexes [46,47]. Besides zirconolite–laachite, the typical PSM associated minerals in carbonate-rich rocks include Sc-phosphates juonniite and kampfite [27,48]:



where Ap—hydroxylapatite; Bdy'—ScNb end member of baddeleyite, $Sc_{0.5}Nb_{0.5}O_2$; Cal—calcite, Dol—dolomite; Jnn—juonniite, $CaMgScP_2O_8(OH) \cdot 4H_2O$; Kam—kampfite, $Ba_3Mg_{1.5}Sc_4(PO_4)_6(OH)_3 \cdot 4H_2O$; HNP—hydroxynatropyrochlore, $NaCaNb_2O_6(OH)$; OCP—oxycalcipyrochlore, $Ca_2Nb_2O_7$.

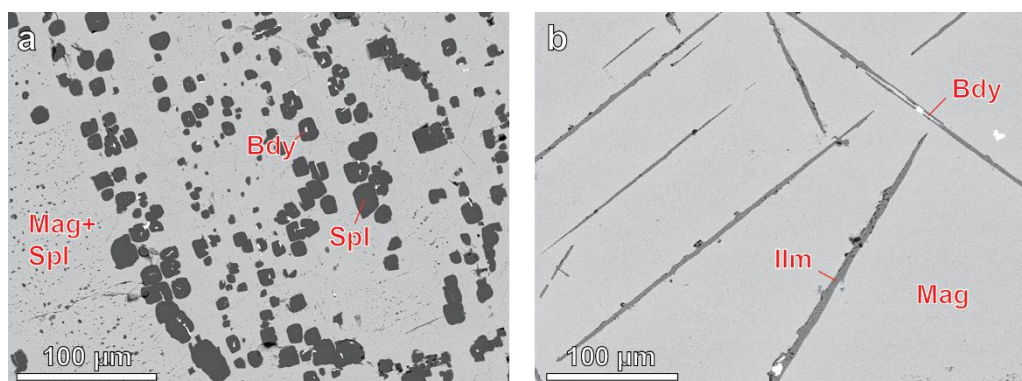


Figure 13. Particles of baddeleyite within exsolution inclusions of spinel and ilmenite in magnetite from calcite-magnetite-apatite phoscorite 956/138.9 (a) and magnetite-forsterite phoscorite 987/2.1 (b). Mineral abbreviations are in Section 2.

Since Sc-Nb-rich baddeleyite and U-Ta-rich PSM of the ore-pipe axial zone contain most of the Kovdor's Nb, Ta, U, as well as a major part of Sc, this “Anomalous” zone can be regarded as a complex rare-metal deposit [6–8]. Prevailing close intergrowths of Sc-rich baddeleyite and U-rich kenopyrochlore significantly complicate the production of a high-quality baddeleyite concentrate. A perspective approach for the deposit development includes selective mining of “anomalous ore”, sulfur-acidic cleaning of baddeleyite concentrate from pyrochlore and zirconolite impurities (Figure 14a), followed by deep metal recovery from baddeleyite concentrate (Figure 14b) and Nb-Ta-Zr-U-Th-rich sulfatic product of its cleaning [49–51].

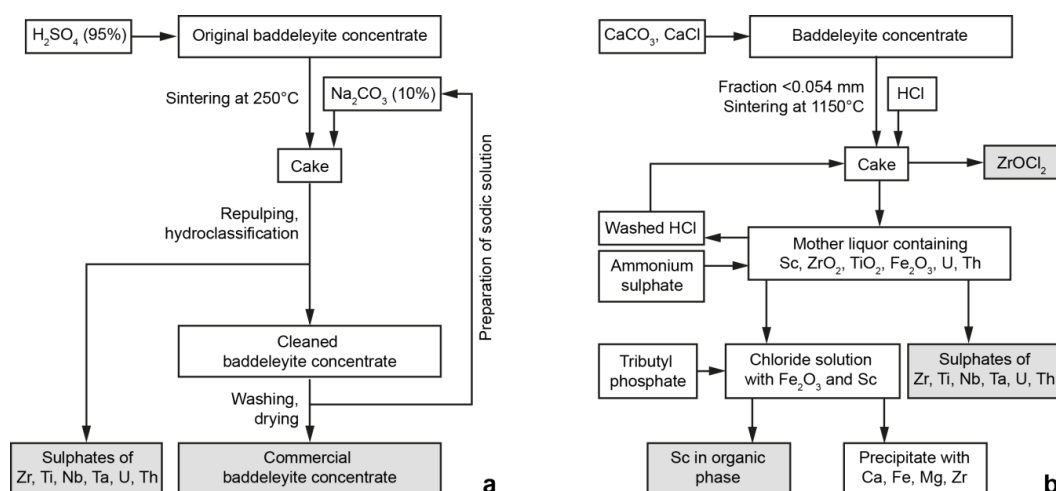


Figure 14. Process flow diagrams of the PSM-bearing baddeleyite concentrate acidic cleaning (a, after [49]) and deep processing (b, after [50,51]). Gray rectangles show final products.

5. Conclusions

According to mineralogical, geochemical, crystallochemical and spectroscopic data obtained for the PSM from the Kovdor phoscorite-carbonatite complex, we can make the following conclusions:

- (1) High-temperature magmatic magnetite is a primary concentrator of Zr, Ti, Nb and Sc in the Kovdor phoscorite-carbonatite complex. The magnetite exsolution under cooling produces spinel and ilmenite-geikielite inclusions containing, in turn, the smallest baddeleyite particles. Besides, separate baddeleyite crystals are crystallized within and around magnetite grains due to their self-cleaning from listed impurities. The content of Nb and Sc in baddeleyite gradually increase

from marginal (apatite)-forsterite phoscorite to axial carbonate-magnetite-rich phoscorite and carbonatite, which is made possible following formation of apo-baddeleyite Nb-Sc-minerals including PSM;

- (2) The PSM are secondary minerals that replace (together with zirconolite-laachite) grains of Sc-Nb-rich baddeleyite and use them as seed crystals. Content, grain size and chemical diversity of PSM increase from the pipe margins to axis against the background of a gradual decreasing of temperature of subsolidus processes. In particular, Ca-(Nb,Ti)-F-rich PSM are spread in marginal (apatite)-forsterite phoscorite, Na-(Nb,Ta)-OH-rich phases occur mainly in intermediate low-carbonate magnetite-rich phoscorite, and U-(Nb,Ti)-OH-rich PSM are localized in axial carbonate-rich phoscorite and carbonatites. Subsolidus PSM crystals usually have primary zoning, with increases of Ca, Ta, Ti, Zr and F contents from core to rim at the expense of Na, Th, U, REE, Nb and (OH) amounts;
- (3) In addition to comparatively high-temperature subsolidus PSM, there are hydrothermal (Na,Ca)-OH-rich pyrochlores that form well-shaped crystals in voids and fractures (in characteristic association with low-temperature Sc-phosphates). Primary zoning of hydrothermal PSM crystals is characterized by growth of U and F contents at the expense of Na, Ca and (OH) amounts. Besides, high U and Th contents cause radiation destruction of the PSM crystal structure, with the following loss of Na, Ca and F under the influence of hydrothermal solutions and the formation of corresponding secondary zoning.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/8/7/277/s1>.

Author Contributions: G.Y.I. and N.G.K. designed the experiments, took samples, performed statistical investigations, and wrote the manuscript. V.N.Y. took and prepared samples and carried out mineralogical investigations. Y.A.P. and A.V.B. took BSE images and performed electron microscope investigations. A.O.K. performed geostatistical investigation, built 3D models, drew maps and took samples. T.L.P. performed crystallographic investigations and formulated crystal-chemical conclusions. V.N.B. performed Raman spectroscopy. J.A.M. carried out petrographical investigations and reviewed the manuscript. All authors discussed the manuscript.

Funding: The research is supported by the Russian Science Foundation, Grant 16-17-10173.

Acknowledgments: Samples were taken during exploration of deep levels of the Kovdor deposit implemented by JSC Kovdorskiy GOK in 2007–11. X-ray crystal studies were carried out with the equipment provided by the X-ray Diffraction Centre of Saint-Petersburg State University. The authors would like to thank I.R. Elizarova for ICP-MS analyses of bulk-rock samples. The anonymous reviewers helped us to considerably improve this paper.

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

References

1. Ivanyuk, G.Y.; Yakovenchuk, V.N.; Pakhomovsky, Y.A. *Kovdor*; Laplandia Minerals: Apatity, Russia, 2002; ISBN 5900395413.
2. Krasnova, N.I.; Balaganskaya, E.G.; Garcia, B. Kovdor—Classic phoscorites and carbonatites. In *Phoscorites and Carbonatites from Mantle to Mine: The Key Example of the Kola Alkaline Province. Mineralogical Society Series 10*; Wall, F., Zaitsev, A.N., Eds.; Mineralogical Society: London, UK, 2004; pp. 99–132. ISBN 0-903056-22-4.
3. Afanasyev, B.V. *Mineral Resources of Alkaline-Ultrabasic Massifs of the Kola Peninsula*; Roza Vetrov Publishing: Saint-Petersburg, Russia, 2011. (In Russian)
4. Ivanyuk, G.Y.; Kalashnikov, A.O.; Pakhomovsky, Y.A.; Mikhailova, J.A.; Yakovenchuk, V.N.; Konopleva, N.G.; Sokharev, V.A.; Bazai, A.V.; Goryainov, P.M. Economic minerals of the Kovdor baddeleyite-apatite-magnetite deposit, Russia: Mineralogy, spatial distribution and ore processing optimization. *Ore Geol. Rev.* **2016**, *77*, 279–311. [[CrossRef](#)]
5. Kalashnikov, A.O.; Konopleva, N.G.; Pakhomovsky, Y.A.; Ivanyuk, G.Y. Rare earth deposits of the Murmansk Region, Russia—A review. *Econ. Geol.* **2016**, *111*, 1529–1559. [[CrossRef](#)]
6. Kalashnikov, A.O.; Yakovenchuk, V.N.; Pakhomovsky, Y.A.; Bazai, A.V.; Sokharev, V.A.; Konopleva, N.G.; Mikhailova, J.A.; Goryainov, P.M.; Ivanyuk, G.Y. Scandium of the Kovdor baddeleyite-apatite-magnetite deposit (Murmansk Region, Russia): Mineralogy, spatial distribution, and potential resource. *Ore Geol. Rev.* **2016**, *72*, 532–537. [[CrossRef](#)]

7. Epshteyn, E.M. Genesis of Kovdor apatite-magnetite ores. Reports on Mineralogy and Geochemistry for 1968. *Tr. VIMS* **1970**, *218–224*. (In Russian)
8. Zhuravleva, L.N.; Berezina, L.A.; Gulin, E.N. Peculiarities of the geochemistry of rare and radioactive elements in apatite-magnetite ores of ultrabasic-alkaline complexes. *Geochemistry* **1976**, *10*, 1512–1532. (In Russian)
9. Zaitsev, A.N.; Williams, C.T.; Jeffries, T.E.; Strekopytov, S.; Moutte, J.; Ivashchenkova, O.V.; Spratt, J.; Petrov, S.V.; Wall, F.; Seltmann, R.; Borozdin, A.P. Rare earth elements in phoscorites and carbonatites of the Devonian Kola Alkaline Province, Russia: Examples from Kovdor, Khibina, Vuoriyarvi and Turiy Mys complexes. *Ore Geol. Rev.* **2014**, *61*, 204–225. [\[CrossRef\]](#)
10. Bazai, A.V.; Goryainov, P.M.; Elizarova, I.R.; Ivanyuk, G.Y.; Kalashnikov, A.O.; Konopleva, N.G.; Mikhailova, J.A.; Pakhomovsky, Y.A.; Yakovenchuk, V.N. New data on REE resource potential of the Murmansk Region. *Vestn. Kola Sci. Cent.* **2014**, *4*, 50–65. (In Russian)
11. Atencio, D.; Andrade, M.B.; Christy, A.G.; Giere, R.; Kartashov, P.M. The pyrochlore supergroup of minerals: Nomenclature. *Can. Mineral.* **2010**, *48*, 673–698. [\[CrossRef\]](#)
12. Atencio, D.; Andrade, M.B.; Bastos Neto, A.C.; Pereira, V.P. Ralstonite Renamed Hydrokenoralstonite, Coulsellite Renamed Fluornatrocoulsellite, and Their Incorporation Into the Pyrochlore Supergroup. *Can. Mineral.* **2017**, *55*, 115–120. [\[CrossRef\]](#)
13. Kukharenko, A.A.; Orlova, M.P.; Bulakh, A.G.; Bagdasarov, E.A.; Rimskaya-Korsakova, O.M.; Nefedov, E.I.; Ilyinsky, G.A.; Sergeev, A.S.; Abakumova, N.B. *Caledonian Complex of Ultrabasic, Alkaline Rocks and Carbonatites of Kola Peninsula and Northern Karelia (Geology, Petrology, Mineralogy and Geochemistry)*; Nedra: Moscow, Russia, 1965. (In Russian)
14. Kapustin, Y.L. *Mineralogy of Carbonatites*; Amerind Publishing: New Delhi, India, 1980.
15. Rimskaya-Korsakova, O.M.; Krasnova, N.I. *Geology of Deposits of the Kovdor Massif*; St. Petersburg University Press: Saint-Petersburg, Russia, 2002. (In Russian)
16. Mikhailova, J.A.; Kalashnikov, A.O.; Sokharev, V.A.; Pakhomovsky, Y.A.; Konopleva, N.G.; Yakovenchuk, V.N.; Bazai, A.V.; Goryainov, P.M.; Ivanyuk, G.Y. 3D mineralogical mapping of the Kovdor phoscorite-carbonatite complex (Russia). *Miner. Depos.* **2016**, *51*, 131–149. [\[CrossRef\]](#)
17. Mikhailova, J.A.; Ivanyuk, G.Y.; Kalashnikov, A.O.; Pakhomovsky, Y.A.; Bazai, A.V.; Panikorovskii, T.L.; Yakovenchuk, V.N.; Konopleva, N.G.; Goryainov, P.M. Three-D mineralogical mapping of the Kovdor phoscorite-carbonatite complex, NW Russia: I. Forsterite. *Minerals* **2018**, *8*, 260. [\[CrossRef\]](#)
18. Williams, T.C. The occurrence of nbiobian zirconolite, pyrochlore and baddeleyite in the Kovdor carbonatite complex, Kola Peninsula, Russia. *Mineral. Mag.* **1996**, *60*, 639–646. [\[CrossRef\]](#)
19. Rosstandart FR.1.31.2016.25424. The Method for Determining the Content of Rare-Earth Elements (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), Sodium, Aluminum, Potassium, Calcium, Titanium, Iron, Thorium and Uranium in Apatite Mineral Raw Materials and Phosphogypsum by Inductively Coupled Plasma Mass Spectrometry. Available online: http://www.fundmetrology.ru/06_metod/2view_file.aspx?id=25424 (accessed on 27 June 2018).
20. Dolivo-Dobrovolsky, D.D. MINAL, Free Software. Available online: <http://www.dimadd.ru> (accessed on 8 July 2013).
21. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276. [\[CrossRef\]](#)
23. OriginLab Corporation. OriginPro 8.1 SR2 2010. Available online: www.OriginLab.com (accessed on 27 June 2018).
24. StatSoft Inc. Statistica 8. Available online: www.statsoft.ru (accessed on 27 June 2018).
25. Micromine Pty Ltd. Micromine 16.1. Available online: www.micromine.com (accessed on 27 June 2018).
26. Kalashnikov, A.O.; Ivanyuk, G.Y.; Mikhailova, J.A.; Sokharev, V.A. Approach of automatic 3D geological mapping: The case of the Kovdor phoscorite-carbonatite complex, NW Russia. *Sci. Rep.* **2017**, *7*. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Ivanyuk, G.Y.; Yakovenchuk, V.N.; Panikorovskii, T.L.; Konoplyova, N.G.; Pakhomovsky, Y.A.; Bazai, A.V.; Bocharov, V.N.; Krivovichev, S.V. Hydroxynatropyrochlore, (Na, Ca, Ce)₂Nb₂O₆(OH), a new member of the pyrochlore group from the Kovdor phoscorite-carbonatite pipe (Kola Peninsula, Russia). *Mineral. Mag.* **2018**. [\[CrossRef\]](#)

28. Hogarth, D.D.; Williams, C.T.; Jones, P. Primary zoning in pyrochlore group minerals from carbonatites. *Mineral. Mag.* **2000**, *64*, 683–697. [[CrossRef](#)]
29. Rims kaya-Korsakova, O.M.; Dinaburg, I.B. Baddeleyite in massifs of ultrabasic and alkaline rocks of the Kola Peninsula. *Mineral. Geochem.* **1964**, *1*, 13–30. (In Russian)
30. Kirnarsky, Y.M.; Afanas'ev, A.; Men'shikov, Y.P. Accessory Th-rich betafite from carbonatites. In *Materialy po Mineralogii Kol'skogo Poluostrova (Data on the Mineralogy of the Kola Peninsula)*; Nauka: Leningrad, Russia, 1968; Volume 6, pp. 155–163. (In Russian)
31. Osokin, A.S. Accessory rare-metal mineralization of carbonatites of a certain massif of alkaline-ultrabasic rocks (the Kola Peninsula). *Mineral. Geochem.* **1979**, *6*, 27–38. (In Russian)
32. Strelnikova, L.A.; Polezhaeva, L.I. Accessory minerals of pyrochlore group from carbonatites of some alkali-ultrabasic massifs. In *Substantial Composition of Alkaline Intrusive Complexes of the Kola Peninsula*; KolFAN: Apatity, Russia, 1981; pp. 81–88. (In Russian)
33. Yamada, R.; Nagaishi, R.; Hatano, Y.; Yoshida, Z. Hydrogen production in the γ -radiolysis of aqueous sulfuric acid solutions containing Al_2O_3 , SiO_2 , TiO_2 or ZrO_2 fine particles. *Int. J. Hydrog. Energy* **2008**, *33*, 929–936. [[CrossRef](#)]
34. Dolin, P.I.; Ershler, B.V. Radiolysis of water in the presence of H_2 and O_2 due to reactor radiation, fission fragments and X-radiation. In *Investigations in Chemistry, Geology and Metallurgy. Reports of Soviet Delegation at the International Conference on the Peaceful Uses of Atomic Energy*; AN SSSR: Geneva, Switzerland, 1955; pp. 293–319. (In Russian)
35. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767. [[CrossRef](#)]
36. Seikh, M.M.; Sood, A.K.; Narayana, C. Electronic and vibrational Raman spectroscopy of $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ through the phase transitions. *Pramana* **2005**, *64*, 119–128. [[CrossRef](#)]
37. Bahfenne, S.; Frost, R.L. Raman spectroscopic study of the antimonate mineral roméite. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2010**, *75*, 637–639. [[CrossRef](#)] [[PubMed](#)]
38. Maczka, M.; Knyazev, A.V.; Kuznetsova, N.Y.; Ptak, M.; Macalik, L. Raman and IR studies of $\text{TaWO}_{5.5}$, ASbWO_6 ($A = \text{K, Rb, Cs, Tl}$), and $\text{ASbWO}_6 \cdot \text{H}_2\text{O}$ ($A = \text{H, NH}_4, \text{Li, Na}$) pyrochlore oxides. *J. Raman Spectrosc.* **2011**, *42*, 529–533. [[CrossRef](#)]
39. McCauley, R.A. Infrared-absorption characteristics of the pyrochlore structure. *J. Opt. Soc. Am.* **1973**, *63*, 721. [[CrossRef](#)]
40. Arenas, D.J.; Gasparov, L.V.; Qiu, W.; Nino, J.C.; Patterson, C.H.; Tanner, D.B. Raman study of phonon modes in bismuth pyrochlores. *Phys. Rev. B* **2010**, *82*, 214302. [[CrossRef](#)]
41. Jones, J.H.; Walker, D.; Pickett, D.A.; Murrell, M.T.; Beattie, P. Experimental investigations of the partitioning of Nb, Mo, Ba, Ce, Pb, Ra, Th, Pa, and U between immiscible carbonate and silicate liquids. *Geochim. Cosmochim. Acta* **1995**, *59*, 1307–1320. [[CrossRef](#)]
42. Brooker, R.A. The effect of CO_2 saturation on immiscibility between silicate and carbonate liquids: An experimental study. *J. Petrol.* **1998**, *39*, 1905–1915. [[CrossRef](#)]
43. Veksler, I.V.; Petibon, C.; Jenner, G.A.; Dorfman, A.M.; Dingwell, D.B. Trace Element Partitioning in Immiscible Silicate-Carbonate Liquid Systems: An Initial Experimental Study Using a Centrifuge Autoclave. *J. Petrol.* **1998**, *39*, 2095–2104. [[CrossRef](#)]
44. Lee, M.J.; Lee, J.I.; Garcia, D.; Moutte, J.; Williams, C.T.; Wall, F.; Kim, Y. Pyrochlore chemistry from the Sokli phoscorite-carbonatite complex, Finland: Implications for the genesis of phoscorite and carbonatite association. *Geochem. J.* **2006**, *40*, 1–13. [[CrossRef](#)]
45. Ivanyuk, G.; Kalashnikov, A.; Pakhomovsky, Y.; Bazai, A.; Goryainov, P.; Mikhailova, J.; Yakovenchuk, V.; Konopleva, N. Subsolidus Evolution of the Magnetite-Spinel-Ulvöspinel Solid Solutions in the Kovdor Phoscorite-Carbonatite Complex, NW Russia. *Minerals* **2017**, *7*, 215. [[CrossRef](#)]
46. Timofeev, A.; Migdisov, A.A.; Williams-Jones, A.E. An experimental study of the solubility and speciation of niobium in fluoride-bearing aqueous solutions at elevated temperature. *Geochim. Cosmochim. Acta* **2015**, *158*, 103–111. [[CrossRef](#)]
47. Timofeev, A.; Migdisov, A.A.; Williams-Jones, A.E. An experimental study of the solubility and speciation of tantalum in fluoride-bearing aqueous solutions at elevated temperature. *Geochim. Cosmochim. Acta* **2017**, *197*, 294–304. [[CrossRef](#)]

48. Yakovenchuk, V.N.N.; Ivanyuk, G.Y.Y.; Pakhomovsky, Y.A.A.; Panikorovskii, T.L.L.; Britvin, S.N.N.; Krivovichev, S.V.V.; Shilovskikh, V.V.V.; Bocharov, V.N.N. Kampelite, $\text{Ba}_3\text{Mg}_{1.5}\text{Sc}_4(\text{PO}_4)_6(\text{OH})_3 \cdot 4\text{H}_2\text{O}$, a new very complex Ba-Sc phosphate mineral from the Kovdor phoscorite-carbonatite complex (Kola Peninsula, Russia). *Mineral. Petrol.* **2017**, *4*, 1–11. [CrossRef]
49. Lokshin, E.P.; Lebedev, V.N.; Bogdanovich, V.V.; Novozhilova, V.V.; Popovich, V.F. Method of Baddeleyite Concentrate Cleaning; Patent RU-2139250, 1998. Available online: <https://patents.google.com/patent/RU2139250C1/ru> (accessed on 27 June 2018).
50. Lebedev, V.N.; Lokshin, E.P.; Mel'nik, N.A.; Shchur, T.E.; Popova, L.A. Possibility of Integrated Processing of the Baddeleyite Concentrate. *Russ. J. Appl. Chem.* **2004**, *77*, 708–710. [CrossRef]
51. Lebedev, V.N. Extraction and refining of scandium upon the processing of baddeleyite concentrates. *Theor. Found. Chem. Eng.* **2007**, *41*, 718–722. [CrossRef]



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