

## A NEW TYPE OF SCANDIUM MINERALIZATION IN PHOSCORITES AND CARBONATITES OF THE KOVDOR MASSIF, RUSSIA

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### ABSTRACT

Scandium mineralization of a new genetic type has been discovered in the Kovdor alkaline-ultrabasic massif, Kola Peninsula, Russia. It is represented by a new mineral, juonniite, simplified formula  $\text{CaMgSc}(\text{PO}_4)_2(\text{OH})\cdot 4\text{H}_2\text{O}$ , occurring in low-temperature hydrothermal assemblages in the phoscorite – carbonatite complex of the Kovdor massif. The mineral forms spherulites up to 0.8 mm in diameter and is associated with late carbonates and hydrous phosphates. Juonniite occurrences are confined to a linear reactivated fault, which intersects phoscorites and carbonatites. Metasomatism of phoscorites caused almost a two-fold enrichment in Sc in clinohumite-bearing units. Late hydrothermal solutions affected cataclastic clinohumite-bearing phoscorites along the fault zone; the subsequent dissolution of sulfides and Sc-bearing minerals (*e.g.*, forsterite, baddeleyite, pyrochlore-group minerals, *etc.*) was accompanied by mobilization of traces of Sc, most likely in the form of carbonate and sulfate. Fluorapatite-bearing carbonatites with abundant cavities provided the necessary conditions for the precipitation of scandium in the form of a hydrous phosphate, juonniite.

**Keywords:** scandium, carbonatites, phoscorites, clinohumite, cataclasis, mineralization, juonniite, hydrothermal alteration, Kovdor massif, Kola Peninsula, Russia.

### SOMMAIRE

Nous documentons un nouveau genre de minéralisation en scandium, découvert dans le massif alcalin et ultrabasique de Kovdor, dans la péninsule de Kola, en Russie. Cet enrichissement se manifeste par la présence de la nouvelle espèce juonniite, dont la formule simplifiée serait  $\text{CaMgSc}(\text{PO}_4)_2(\text{OH})\cdot 4\text{H}_2\text{O}$ , dans des assemblages hydrothermaux de faible température des phoscorites et carbonatites du massif de Kovdor. Le minéral se présente en sphérules atteignant 0.8 mm de diamètre; il montre une association avec les carbonates et les phosphates hydratés tardifs. Les incidences de juonniite se limitent à une faille linéaire réactivée, à son intersection avec les phoscorites et carbonatites. Une métasomatose des phoscorites a mené à un dédoublement de la teneur en Sc des unités contenant la clinohumite. Des solutions hydrothermales tardives ont affecté les zones broyées à clinohumite dans les phoscorites le long de la faille. La dissolution de sulfures et de minéraux porteurs de scandium (*e.g.*, forstérite, baddeleyite, minéraux du groupe du pyrochlore) a causé une mobilisation de traces de Sc, probablement sous forme de carbonate et de sulfate. Les cavités abondantes des carbonatites à fluorapatite ont fourni les conditions nécessaires pour la précipitation du scandium sous forme de juonniite, phosphate hydraté.

(Traduit par la Rédaction)

**Mots-clés:** scandium, carbonatites, phoscorites, clinohumite, cataclase, minéralisation, juonniite, altération hydrothermale, massif de Kovdor, péninsule de Kola, Russie.

### INTRODUCTION

The only occurrence of a scandium mineral from the Kola region was described from a granitic pegmatite located in the central part of the Kola Peninsula (Voloshin *et al.* 1991); there, thortveitite was found as a single inclusion ~30 µm across in garnet – ilmenite aggregate. The garnet is associated with ilmenorutile, which also contains fine inclusions of Sc-bearing

ixiolite. In carbonatites associated with alkaline-ultrabasic rocks, scandium mineralization is known only in dolomitic carbonatites of Fen, Norway, where thortveitite occurs as inclusions 3–5 µm across in association with Sc-bearing columbite and ilmenorutile (Åmli 1977).

A low-temperature Sc-rich association of an essentially new genetic type has been discovered in the Kovdor phoscorite – carbonatite complex. Late

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dolomitic carbonatites with abundant cavities were found to contain juonniite, a new hydrous phosphate of Ca, Mg and Sc of the overite group (Liferovich *et al.* 1997). The environments of juonniite mineralization, to be described here, provide new insight into the geochemistry and metallogeny of scandium.

#### BRIEF DESCRIPTION OF THE KOVDOR MASSIF

Discovered in 1932, the Kovdor massif and its iron ore and phlogopite deposits have been investigated in detail (Kukharensko *et al.* 1965, Ternovoi 1977, Kogarko *et al.* 1995). This massif is the largest of the Caledonian alkaline-ultrabasic complexes of the Fennoscandian Shield. It is located in a zone of Paleozoic tectonic activity, in which most massifs of this kind are concentrated.

The Kovdor massif, emplaced in the gneisses of the Late Archean White Sea Group, is surrounded by a rim of fenite up to 500 m in width. The subvertical contacts of the intrusion, according to geophysical data, continue down to a depth of more than 15 km. The intrusion is concentrically zoned (Fig. 1). The main phases are olivinite – pyroxenite in the central part, and ijolite – melteigite in the marginal zone. Nepheline pyroxenites, turjaites, melilite- and monticellite-rich rocks and rocks of the phoscorite – carbonatite complex also are abundant. Coarse-grained and pegmatite-like rocks with phlogopite, diopside and olivine are exploited in a phlogopite deposit in the northern part of massif, and its crust of weathering is a vermiculite deposit.

Phoscorites (baddeleyite – apatite – magnetite ores) and calcitic and dolomitic carbonatites have a variable composition and occur in the southwestern segment of the massif as a stock intruded between pyroxenite and ijolite units (Fig. 2). The stock is bordered by fine-grained apatite – phlogopite – forsterite rocks, which are considered to be silicate rocks metasomatized by the fluid phase of the phoscorite – carbonatite intrusion (Ternovoi 1977). The position of the phoscorites is controlled by the junction of at least two major linear faults, complicated by a series of ring-type, conical and radial faults (Dunaev 1982). The stock, extending in the N–S direction for 1500 m, is asymmetrically zoned with a multiple-phase, telescoped core of phoscorite. The width of the stock in outcrop ranges from 150 to 800 m, reaching its maximum in an area of intersection of the ore-controlling faults. The stock has been traced by drilling down to a depth of 2 km. At depth, the orebody narrows and dips steeply to the south. The Kovdor phoscorites experienced various postmagmatic processes, such as metasomatic alteration, cataclasis, and weathering. These rocks are characterized by significant variations in the ratio of constituent minerals: forsterite, magnetite, apatite, calcite, dolomite and phlogopite. Apatite – forsterite – magnetite and forsterite – magnetite rocks and their calcite-bearing analogues are predominant. Figure 2 illustrates the distribution of the major litholo-

gies in the stockwork. All the rocks contain green phlogopite and early light-colored baddeleyite (baddeleyite I), the average abundance of which is about 0.1 – 0.2 wt.%.

In the center of the southern part of the phoscorite stock, there are bodies of clinohumite-bearing phoscorite (Fig. 3) that are considered to have resulted from metasomatism of apatite – forsterite – magnetite – calcite phoscorites. Metasomatism is manifested by intensive replacement of forsterite by clinohumite, crystallization of late calcite and red tetra-ferriphlogopite, which forms a pseudomorph by replacement after early green phlogopite, the formation of late generations of accessory minerals of Zr and Nb (dark secondary baddeleyite II, uranoan pyrochlore, zirconolite), sulfide enrichment of rocks, and the appearance of amphibole and chlorite. The metasomatism also resulted in the increase of the natural radioactivity of the rocks.

In the same part of the phoscorite stock, carbonatites form a network of subvertical veins intersecting the clinohumite-bearing phoscorites. The carbonatites are massive, light-colored rocks of variable composition, including calcitic and dolomitic varieties. The location of dolomitic carbonatites and zones of brecciation and cataclasis in the phoscorites is controlled by a long-lived NE- and N-trending faults (Fig. 2). The carbonatite veins and the phoscorites affected by cataclasis and hydrothermal alteration in the fault zones (particularly in the central and eastern parts of the phoscorite – carbonatite complex: Fig. 2) contain numerous cracks and cm-size cavities. The cavities in some cases account for 10–15% of a rock's volume. They contain late hydrothermal minerals, among which are rare hydrous phosphates of Mg, Fe<sup>2+</sup>, Ca, Sr, Ba, Al, Zr and Sc: juonniite, goyazite, gorceixite, collinsite, bobierite, baričite, vivianite, kovdorskite, rimkorolite, strontio whitlockite, hydroxylapatite, catapleite and hydrous minerals of Zr and Nb. Juonniite occurs just within the zones with cavernous dolomitic veins, which are spatially associated with the fault zone and cross-cut the stock-like bodies of clinohumite-bearing phoscorites (Fig. 2).

#### ANALYTICAL METHODS

All rock types of the Kovdor massif and the phoscorite – carbonatite complex, as well as main rock-forming and some accessory minerals, were analyzed for Sc. Scandium contents below 100 ppm were determined by a quantitative spectral analysis. Duplicates of rocks and minerals, analogous to the analyzed samples in each set, were used as standards. The Sc contents in these analytical standards were determined by instrumental neutron-activation analysis (INAA) in two independent laboratories: the GEOCHI, Moscow, and the University of Massachusetts at Lowell. An analytical accuracy of scandium measurements in the range of 8–12% relative was attained.

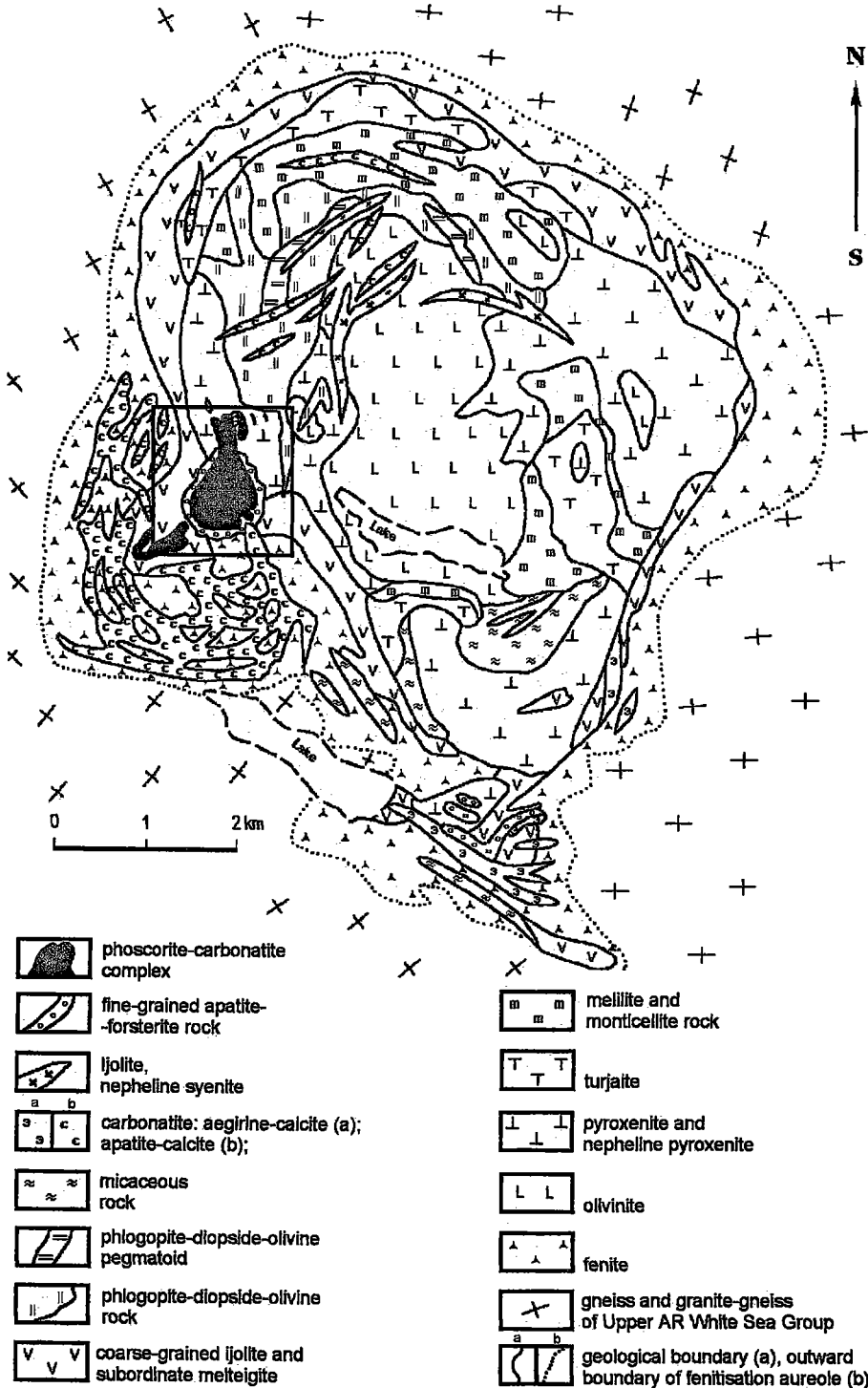


FIG. 1. Geological map of the Kovdor massif, after Ternovoi (1977), with some additions. The square area shows the outlie of Figure 2.

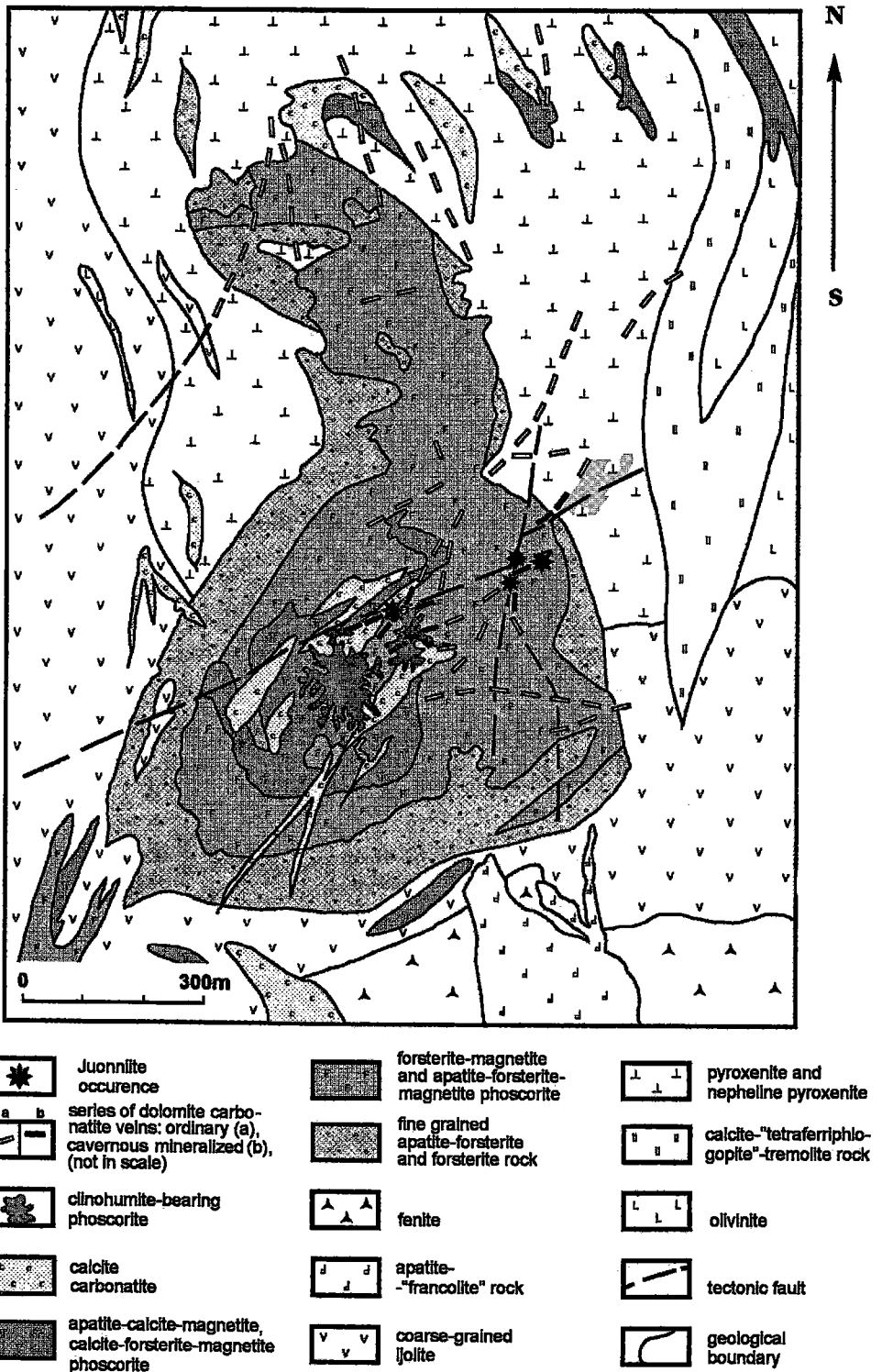


FIG. 2. Geological sketch-map of the Kovdor phoscorite-carbonatite (ore) complex, after Ternovoi (1977), with some additions.

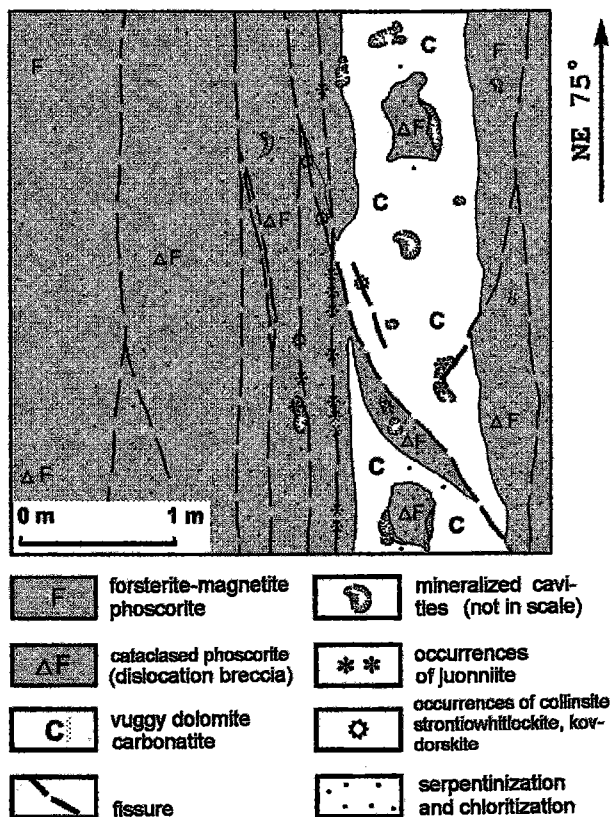


FIG. 3. A sketch-map of one of the localities of juonniite mineralization. A plan of the surface bench (mine horizon: 35 m, eastern part of the Kovdor iron-deposit).

The minerals containing more than 100 ppm Sc were analyzed with a Cameca MS-46 electron microprobe at an accelerating voltage of 20 kV (30 kV for Sr) and a sample current of 15–30 nA. Apatite (for Ca and P), forsterite (Mg), thortveitite (Sc), lorenzenite (Ti), synthetic  $\text{MnCO}_3$  (Mn), hematite (Fe), metallic niobium (Nb), baddeleyite (Zr), celestine (Sr) and barite (Ba) were used as standards.

Concentrates of baddeleyite, the main Sc-bearing mineral, from various types of phoscorites also were analyzed for Sc, using the X-ray fluorescence spectrometer VRA-20.

#### SCANDIUM IN ROCKS AND MINERALS OF THE KOVDOR MASSIF

The geochemical characteristics of the Kovdor massif conform with the generally recognized features of alkaline-ultrabasic carbonatite-bearing massifs (Kukharensko *et al.* 1965, 1971, Eby 1973). The Sc contents in the main types of rocks and some minerals are given in Tables 1–4. Scandium is strongly enriched in pegmatitic phlogopite- and diopside-rich rocks,

phoscorites (especially clinohumite-bearing varieties) and in mineralized vuggy dolomitic veins. In other types of silicate rocks and carbonatites, only low concentrations of Sc are revealed. It should be noted that the common dolomitic carbonatites that are not affected by hydrothermal alteration are the poorest rocks in terms of Sc (Table 1).

Diopside, containing about 130 ppm Sc, is the dominant host of Sc in pegmatite-like phlogopite – diopside – forsterite rocks. The main rock-forming minerals of phoscorites and carbonatites, phlogopite, apatite, calcite and dolomite, contain less than 10 ppm Sc. Magnetite, forsterite and clinohumite contain up to 110 ppm Sc. Accessories of Zr and Nb in these rocks are more significantly enriched in Sc. The dominant host of Sc in the common phoscorites is baddeleyite I (Table 2), which contains on average 0.06 wt.%  $\text{Sc}_2\text{O}_3$  according to 50 electron-microprobe analyses (including the data of Polyakov & Polezhaeva 1991). According to the results of X-ray-fluorescence analysis, this value lies within the range 0.10–0.18 wt.%  $\text{Sc}_2\text{O}_3$  (Table 3).

The late baddeleyite (II) from clinohumite-bearing phoscorites contains on average 0.26 wt.%  $\text{Sc}_2\text{O}_3$

TABLE 1. SCANDIUM CONTENT OF ROCKS OF THE KOVDOR MASSIF, AS DETERMINED BY QUANTITATIVE SPECTROGRAPHIC ANALYSIS

	Ranges	Average	Amount of runs	Factor of concentration *
<b>Main rock types of the massif</b>				
Olivinites	5 - 14	8	6	0.5
Pyroxenites	12 - 47	28	22	1.8
Nepheline pyroxenites	6 - 26	14	8	0.9
Phlogopite-olivine-diopside pegmatites	78 - 110	95	4	6.1
Micaeous rocks	5 - 30	8	5	0.5
Jiolite-meltnigites	5 - 17	7	14	0.4
Turjaita, smecticalite and malilita rocks	11 - 32	20	12	1.3
Vermiculite rocks	22 - 60	35	6	2.2
<b>Rocks of the Kovdor phoscorite-carbonatite complex</b>				
Fenites	8 - 22	14	3	0.9
Fine-grained apatite-forsterite rocks	13 - 37	24	17	1.5
<b>Phoscorites:</b>				
Forsterite-magnetite	30 - 95	67	21	4.3
Apatite-forsterite-magnetite	21 - 110	49.8	71	3.2
Calcite-forsterite-magnetite	20 - 77	48	8	3.1
Apatite-calcite-magnetite	19 - 56	40.5	13	2.6
Clinohumite-bearing varieties	43 - 170	80.8	32	5.2
Calcite-strotaferrillogopiteo-tranomite	47 - 68	52	4	3.3
Serpentinized phoscorites from submeridional zone of cataclasis	50 - 120	89	22	5.7
<b>Carbonatites:</b>				
Calcite	7 - 54	30	29	1.9
Dolomitic	11 - 17	14	6	0.9
Mineralized cavernous dolomitic veins and phoscorite from their exocontacts	12 - 190	**	8	-
Apatite-«ferricolite» rocks	7 - 50	21	8	1.3

Values are quoted in ppm. \* Calculated as a ratio of average content to content of Sc in the lithosphere, according to Borisenko & Polikashina (1991). \*\* Not averaged because of great dispersion of abundances recorded.

according to 16 electron-microprobe analyses, and 0.27–0.34 wt.% Sc<sub>2</sub>O<sub>3</sub> according to the X-ray fluorescence results (Tables 2, 3). Accessory zirconolite and uranoan pyrochlore also are noticeably enriched in Sc (Table 2). The clinohumite-bearing variety of phoscorite stands out for having a higher Sc content than the others owing to enrichment by late generation of accessory minerals of Zr and Nb. In addition, increased concentrations of Sc

TABLE 2. CHEMICAL COMPOSITION OF Sc-BEARING ACCESSORY MINERALS OF PHOSCORITES OF THE KOVDOR MASSIF, AS DETERMINED BY ELECTRON-MICROPROBE ANALYSIS

	Phoscorites		Clinohumite-bearing phoscorites				
	Baddeleyite-I	Baddeleyite-II	Zirconolite	Uranopyrochlore	U-bearing pyrochlore		
Nb <sub>2</sub> O <sub>5</sub>	-	-	0.98	0.73	-	1.15	6.10
MgO	-	-	0.62	0.80	-	-	-
CaO	-	0.03	12.23	11.70	2.34	2.81	9.42
MnO	-	-	0.25	0.27	-	0.17	-
FeO	-	0.07	7.54	7.64	1.97	1.94	0.76
SrO	-	-	-	-	2.13	0.54	0.37
BaO	-	-	-	-	6.78	0.12	-
PbO	-	-	-	-	0.75	0.69	2.54
Sc <sub>2</sub> O <sub>3</sub>	0.03	0.14	0.07	0.56	0.08	0.07	0.05
La <sub>2</sub> O <sub>3</sub>	-	-	0.25	0.29	-	-	-
Ce <sub>2</sub> O <sub>3</sub>	-	-	1.25	1.86	-	0.77	-
Ni <sub>2</sub> O <sub>3</sub>	-	-	0.97	1.31	-	0.23	-
TiO <sub>2</sub>	-	0.08	0.21	18.26	18.40	5.92	10.29
ZrO <sub>2</sub>	98.14	97.64	95.31	95.20	31.39	29.83	2.26
HfO <sub>2</sub>	2.21	2.17	2.08	1.85	0.38	0.40	-
ThO <sub>2</sub>	-	-	-	2.50	2.54	1.01	1.77
UO <sub>2</sub>	-	-	-	-	-	18.23	15.42
Nb <sub>2</sub> O <sub>5</sub>	-	1.66	1.43	20.03	19.39	35.59	43.71
Ta <sub>2</sub> O <sub>5</sub>	-	-	0.28	1.06	1.23	12.02	7.59
Total	100.38	99.98	99.27	99.69	97.79	96.51	91.65*
							92.44**
							98.63

Values are quoted in wt.%. \* Includes 2.58% SiO<sub>2</sub>. \*\* Includes 1.05% K<sub>2</sub>O.

TABLE 3. CONCENTRATION OF Sc AND SELECTED ELEMENTS IN THE BADDELEYITE FRACTION OF VARIOUS ROCKS, KOVDOR MASSIF, AS DETERMINED BY X-RAY FLUORESCENCE ANALYSIS

Sc <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	HfO <sub>2</sub>	ThO <sub>2</sub>	UO <sub>2</sub>	Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>
<b>Apatite-forsterite rocks</b>						
0.10	0.32	1.06	0.015	0.015	0.56	0.07
0.14	0.07	1.40	<0.003	0.009	0.26	0.06
<b>Phoscorites</b>						
0.10	0.05	1.34	<0.003	0.006	0.24	0.07
0.17	0.05	1.35	0.004	0.012	0.33	0.07
0.14	0.06	1.08	0.007	0.040	0.51	0.07
0.18	0.06	1.38	0.006	0.012	0.44	0.09
<b>Clinohumite-bearing phoscorites</b>						
0.35	0.37	1.25	0.022	0.640	1.76	0.54
0.27	0.26	1.43	0.005	0.095	0.82	0.16
0.34	0.45	1.20	0.081	0.750	2.45	0.37

Values are quoted in wt.%.

are found in serpentinized phoscorites from the N–S-trending zone of cataclasis, situated in the eastern part of the mineralized complex (Fig. 2).

Juonniite is the dominant host of Sc in the vuggy dolomitic veins and their exocontacts. Juonniite, CaMgSc(PO<sub>4</sub>)<sub>2</sub>(OH)·4H<sub>2</sub>O, is a newly described hydrous phosphate of the overite group (Liferovich *et al.* 1997). The mineral forms brown translucent spherulites up to 0.8 mm in diameter (Fig. 4), which consist of closely clustered lamellar crystals. The mineral occurs in cavities in association with late carbonates, sulfides, hydrous phosphates and silicates. Locally, juonniite is replaced by X-ray-amorphous phases containing about 3 wt.% Sc<sub>2</sub>O<sub>3</sub>. The content of Sc in juonniite ranges between 11.9 and 14.4 wt.% Sc<sub>2</sub>O<sub>3</sub> according to the electron-microprobe data on a few tens of samples. An increase of Sc content toward the external part of the spherulites is commonly observed. Spatial relationships with other minerals in the hydrothermal assemblage indicate that juonniite is one of latest minerals, but it formed earlier than strontio whitlockite, clinochlore, pyrite, and cubanite. A noticeable concentration of Sc in the other minerals of the hydrothermal assemblage of the vuggy mineralized rocks has not been detected. In late calcite, dolomite, hydroxylapatite and other hydrothermal phosphates, Sc does not exceed 10 ppm. In secondary Fe- and Mg-bearing silicates (amphibole, chlorite, serpentine), the abundance of Sc is 2.5–3 times less than in primary forsterite and clinohumite.

The accessory phases baddeleyite (both generations), zirconolite and uranoan pyrochlore were corroded, dissolved or transformed to other minerals species in zones of intense hydrothermal alteration. An example of baddeleyite corrosion is shown in Figure 5. Thereafter, Zr precipitated, probably in the form of zircon. A late generation of zircon relative to baddeleyite and zirconolite is identified in the clinohumite-bearing phoscorites from the exocontact of the vuggy dolomitic veins. At some stage of the hydrothermal process, the newly crystallized zircon also became unstable, and was replaced by catapleite. The latter is common in cavities



FIG. 4. Spherulite of juonniite on crystals of kovdorskite. Scanning electron micrograph. Width of field of view: 400  $\mu\text{m}$ .

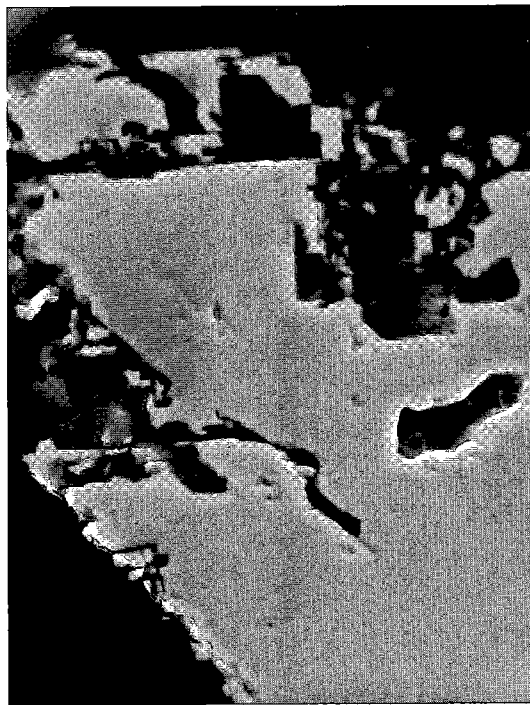


FIG. 5. Corroded crystal of baddeleyite within aggregates of late calcite from clinohumite-bearing phoscorites. Scanning electron micrograph. Width of field of view: 95  $\mu\text{m}$ .

with juonniite and other minerals of the hydrothermal assemblage. Under hydrothermal conditions, uranoan pyrochlore was replaced by common Ca–Na-pyrochlore and, later, by Ba-bearing pyrochlore. In zones of intense

hydrothermal alteration of phoscorites and dolomite carbonatites, there is only one Nb-bearing mineral, which is close to ternovite (Subbotin *et al.* 1997) in composition. Except for zircon, which in some cases contains noticeable Sc (Table 4), the level of Sc in these late minerals is below the limit of detection.

TABLE 4. CHEMICAL COMPOSITION OF LATE HYDROTHERMAL MINERALS OF Zr AND Nb FROM ALTERED DOLOMITIC CARBONATITES AND PHOSCORITES OF THE KOVDOR MASSIF, AS DETERMINED BY ELECTRON-MICROPROBE ANALYSIS

	Juonniite	Zircon	Pyrochlore	Ba-bearing pyrochlore	Ternovite-like phase
$\text{Na}_2\text{O}$	-	-	8.94	2.54	-
$\text{K}_2\text{O}$	-	-	-	0.85	-
$\text{MgO}$	12.13	12.11	-	-	4.61
$\text{CaO}$	10.33	12.24	13.65	3.31	0.13
$\text{MnO}$	2.54	0.47	-	0.12	-
$\text{FeO}$	2.11	0.40	-	0.96	0.09
$\text{SrO}$	1.33	0.54	1.14	2.59	-
$\text{BaO}$	1.54	3.53	-	11.55	-
$\text{PbO}$	-	-	0.15	-	-
$\text{Sc}_2\text{O}_3$	11.85	14.37	0.05	-	-
$\text{La}_2\text{O}_3$	-	-	0.35	0.28	-
$\text{Ce}_2\text{O}_3$	-	-	0.99	0.42	-
$\text{Nd}_2\text{O}_3$	-	-	0.20	0.20	-
$\text{SiO}_2$	-	33.08	-	-	-
$\text{TiO}_2$	0.75	-	1.99	2.44	0.07
$\text{ZrO}_2$	-	66.25	0.35	0.85	-
$\text{HfO}_2$	-	1.05	-	-	-
$\text{UO}_2$	-	-	-	0.83	-
$\text{P}_2\text{O}_5$	36.73	36.17	0.18	-	-
$\text{Nb}_2\text{O}_5$	-	-	68.25	62.91	59.28
$\text{Ta}_2\text{O}_5$	-	-	1.76	3.90	0.17
Total	79.31	99.83 *	100.43	97.95	64.35

Values are quoted in wt.%. \* Includes 20%  $\text{H}_2\text{O}$ , determined by the Penfield method.

## DISCUSSION

The main factor leading to Sc mineralization in the Kovdor phoscorites and carbonatites was postcarbonatite tectonic activity followed by hydrothermal alteration of the rocks. These processes were most intense in tectonic zones along NE- and N-trending faults, which affected the dolomitic carbonatite veins and intersected the host phoscorites, mostly the clinohumite-bearing varieties. The zone of juonniite occurrences is traced for at least tens of meters vertically and a few hundreds of meters laterally. Sampling has shown that the zone is lens-shaped or discontinuous, controlled by the structural features of postcarbonatite tectonics. The abundance of juonniite decreases rapidly with distance from the faults in the central and eastern parts of the phoscorite – carbonatite complex.

The probable sources of Sc were baddeleyite, zirconolite and uranoan pyrochlore. Destabilization and

TABLE 5. GENETIC TYPES OF DEPOSITS AND OCCURRENCES OF SCANDIUM MINERALS

	Genetic type	Associated minerals	Occurrences	Importance
<i>Silicate minerals</i>				
Thortveitite	Granitic pegmatites	Garnet, ilmenorutile, monazite, beryl, zircon, Sc-bearing ixiolite	Iveland, Norway Befanamo, Madagascar Karelia; Kola Peninsula	Small deposits Scientific interest only
Bazzite	Metasomatic rocks related to quartz porphyries	Biotite, albite, U-bearing minerals, tourmaline, fluor-carbonates of the rare-earth elements	Kumir, Altai	Middle-size complex Sc-REE-U deposit
	Carbonates of an alkaline-ultrabasic massif	Scandian columbite, niobian rutile, dolomite, ankerite, chlorite quartz, apatite	Fen, Norway	A possible source of scandium
	Voids in granites and pegmatites	Quartz, microcline, chlorite, hematite, calcite	Taveto, Switzerland; Kent, Kazakhstan	Of scientific interest only
	Amazonitic pegmatites	Beryl, quartz, albite	Telemark, Norway	Of scientific interest only
Jervisite cascandite	Cavities in alpine granites	Quartz, orthoclase, albite	Baveno, Italy	Of scientific interest only
<i>Phosphate minerals</i>				
Pretulite	Alpine veins	<i>Goyazite, crandallite, xenotime-(Y) florencite-(Ce)</i> , zircon, apatite, quartz	Styria, Austria	Of scientific interest only
Kolbeckite	Voids in W-Sn-bearing greisens	<i>Goyazite, gorceixite, apatite, vitaniemite, monazite, xenotime-(Y)</i>	Tigrinoe, Sikhote-Alin	Of scientific interest only
	Crust of weathering on phosphorites	Wavellite, <i>crandallite</i> , collinsite, messelite, fairfieldite	Fairfield, Utah U.S.A.	Of scientific interest only
	Crust of weathering on carbonates	<i>Gorceixite, florencite-(Ce)</i> , monazite	Mrima Hill, Kenya	Of scientific interest only
Juonniite	Altered dolomitic carbonates and phoscorites	Dolomite, gypsum, pyrite, manasseite, barite, <i>goyazite, gorceixite, kovdorskite, rimkorolite, bobierite, Sr-rich collinsite, chlorite, talc</i>	Kovdor Kola Peninsula Russia	Of scientific interest only

Compilation of data from Åmli (1977), Mellini *et al.* (1982), Voloshin *et al.* (1991), Solodov *et al.* (1991), Egorov *et al.* (1993), Lapin (1995) and Bernhard *et al.* (1998). Minerals of the crandallite group, invariably associated with Sc phosphates in hydrothermal and epithermal assemblages, are printed in italics.

replacement of these minerals by later zircon, cata-pleiite, and pyrochlore resulted in a release of Sc in amounts sufficient for the onset of juonniite mineralization. The breakdown of rock-forming minerals such as forsterite and clinohumite resulted in an additional transfer of Sc to hydrothermal solutions. It should be noted that juonniite is not present in the rocks that are well away from the clinohumite-bearing altered phoscorites.

Possible agents of transport of Sc could be  $\text{SO}_4^{2-}$  or  $\text{CO}_3^{2-}$ , which most likely were present in solutions. The solubility of carbonates and sulfates of Sc and the insolubility of its phosphates under low-temperature hydrous conditions are well known (Shakhno *et al.* 1976, Borisenko & Polikashina 1991). Sulfides, mainly

pyrrhotite, as well as fluorapatite are present in dolomite carbonates and host phoscorites, generally in minor amounts. Active hydrolysis of sulfides took place in zones of cataclastic rocks, predominantly in dolomitic carbonates. This fact is confirmed by the presence of numerous cavities in mineralized veins of dolomitic carbonates. The cavities locally contain corroded relics of sulfides, but more commonly are filled with a fine sooty mixture of iron and manganese oxides, phosphates of Mg and Fe, gypsum, barite and magnetite. Such mixtures are not found in cavities in zones of more intense circulation of solutions. Owing to the hydrolysis of sulfides, sulfate anions were transferred to circulating hydrothermal solutions, which, according to Bulakh & Ivanikov (1984), were originally enriched in  $\text{CO}_2$ . In



addition, the initial granular fluorapatite is everywhere replaced by a fine brown aggregate of hydroxylapatite, which contains 2–2.5 wt.% less phosphorus. Taking into account these findings, scandium appears to have been transported in solution from altered phoscorites as a soluble carbonate or sulfate (or both) and to have precipitated from solutions in the presence of phosphorus in vuggy dolomitic carbonatites and their exocontacts. Thus, the vuggy carbonatite veins served as a phosphatic barrier on the migration paths of scandium, and this resulted in the formation of a unique hydrothermal assemblage with the hydrous phosphate of scandium, juonniite.

The temperature of formation of Sc mineralization can be estimated only approximately. According to thermometric tests of fluid inclusions in rock-forming minerals, phoscorites formed at 690–900°C, and carbonatites, at 640–755°C (Kharlamov *et al.* 1981). The upper temperature of postcarbonatite hydrothermal veins is about 400°C (Bulakh & Ivanikov 1984). The spatial relationships of minerals in the hydrothermal assemblage from mineralized dolomitic veins indicate that juonniite crystallized after kovdorskite, but before bobierrite. Because these mineral species contain molecules of H<sub>2</sub>O and the loss of hydration water leads to destruction of their structures, we used results of thermal analyses of kovdorskite and bobierrite to estimate roughly the temperature range of juonniite crystallization. As kovdorskite and bobierrite break down at temperatures of 230° and 160°C, respectively, the temperature of formation of juonniite cannot exceed 230°C.

The occurrence of juonniite in the Kovdor phoscorite – carbonatite complex is a new type of scandium mineralization (Table 5). It originated owing to a set of favorable factors, the most notable being the enrichment of Zr- and Nb-bearing accessories in Sc, a spatial coincidence of scandium-enriched varieties of phoscorites and a stockwork of late dolomitic carbonatites affected by faults and postcarbonatite solutions, and the instability of Sc-bearing minerals, sulfides and fluorapatite under hydrothermal conditions.

This study and data from the literature attest to the existence of a stable paragenetic relationship between phosphates of Sc and the crandallite-group minerals in hydrothermal and exogenic conditions (Table 5). Probably, hydrous phosphates of aluminum and scandium crystallize in hydrous solutions under similar conditions. It is likely that the occurrence of crandallite-group minerals in low-temperature mineral assemblages can be indicative of potentially increased concentrations of Sc and of the presence of scandium phosphates.

The scandium mineralization discovered in the Kovdor massif makes it possible to consider phoscorite – carbonatite complexes of alkaline-ultrabasic massifs as potential sources of scandium. Large differentiated central-type massifs with carbonatites and clinohumite-bearing phoscorites, such as at Kovdor, Vuoriyarvi, Seblyavr, Sökli, and Palaborwa, are the most promising in this respect.

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