

## THE KOVDOR PHLOGOPITE DEPOSIT, KOLA PENINSULA, RUSSIA

NATAL'YA I. KRASNOVA<sup>§</sup>

*Geological Institute of the Earth's Crust, St. Petersburg University, University Emb. 7/9, St. Petersburg, 199034, Russia*

### ABSTRACT

The Kovdor phlogopite deposit, one of the largest on Earth, occurs in the northwestern part of the Kovdor carbonatite-bearing alkaline-ultrabasic complex, Kola Peninsula, Russia. The Main phlogopite lode is situated in the central part of a semicircular zone of phlogopite-rich rocks; its morphology is similar to some bodies of granitic pegmatites, hosted in granites, and has a zonal structure. The rocks of the marginal part are monomineralic and consist of giant crystals (up to 2 m across) of diopside, whereas near the center are zones of forsterite–phlogopite, forsterite and apatite rocks. A microtextural study of the phlogopite-bearing bodies shows a regular pattern of spatial arrangement of the main minerals. All grew from the contacts of individual vein-like bodies toward the center. The chemical composition of the main rock-forming minerals (forsterite, phlogopite, diopside) is characterized by lower contents of Ti and Fe compared to the compositions of those minerals in olivinites, but are relatively enriched compared to the same minerals in phoscorites and carbonatites. Gas extracted from phlogopite and apatite shows that hydrogen is an important component in the inclusions. Thermometric data suggest that the formation of the main minerals in the deposit took place at a high temperature, in the range 800–900°C, whereas hydrostatic pressure in the system barely exceeded 2000 bars. On the basis of its shape, structure, features of mineral growth and crystallization sequence, the Main phlogopite lode may be regarded as a peculiar alkali-ultrabasic pegmatite.

*Keywords:* phlogopite, alkaline rocks, carbonatite, alkali-ultrabasic pegmatite, Kovdor complex, Kola Peninsula, Russia.

### SOMMAIRE

Le gisement de phlogopite de Kovdor, un des plus larges sur terre, est situé dans le secteur nord–ouest du complexe alcalin-ultrabasique à carbonatite de Kovdor, péninsule de Kola, en Russie. La zone principale à phlogopite est située au centre d'un arc semi-circulaire de roches riches en phlogopite; sa morphologie ressemble à certains massifs de granite pegmatitique mis en place dans un socle granitique, et elle possède une structure zonée. Les roches de la bordure sont monominérales et contiennent des cristaux géants (jusqu'à 2 m) de diopside, tandis que près du centre, on trouve des roches à forstérite–phlogopite, forstérite et apatite. Une étude microtexturale des accumulations de phlogopite a mis en évidence une disposition régulière dans l'espace des minéraux principaux. Toutes les espèces ont avancé à partir de la bordure de ces accumulations en forme de veines vers le centre. Les principaux minéraux (forstérite, phlogopite, diopside) contiennent moins de Ti et de Fe que les mêmes minéraux dans les olivinites, mais ils en contiennent plus que les mêmes minéraux dans les phoscorites et les carbonatites. La fraction gazeuse extraite de la phlogopite et de l'apatite contient l'hydrogène comme composant important. Les données thermométriques font penser que les minéraux principaux du gisement ont cristallisé à une température élevée, dans l'intervalle 800–900°C, tandis que la pression sur le système dépassait à peine 2000 bars. De par sa forme, sa structure, les aspects de la croissance cristalline et la séquence de cristallisation, la zone minéralisée en phlogopite prend l'allure d'une pegmatite alcaline-ultrabasique assez particulière.

(Traduit par la Rédaction)

*Mots-clés:* phlogopite, roches alcalines, carbonatite, pegmatite alcaline et ultrabasique, complexe de Kovdor, péninsule de Kola, Russie.

<sup>§</sup> E-mail address: ikrasn@comset.net

## INTRODUCTION

The Kovdor phlogopite deposit, located in the Kola Peninsula, was discovered in 1960 and mined since 1963 (Ternovoy *et al.* 1969). It is one of the largest on Earth. The production of coarse-grained phlogopite (formerly used as an electric insulator) resulted in the accumulation of colossal piles composed essentially of micaceous tailings. These tailings undoubtedly still have practical importance. The recent recommendation to use phlogopite as an effective fertiliser with a prolonged positive effect on the fertility of soils (Vasilieva *et al.* 2000) gives a new outlook for the future development of the Kovdor mining-industrial complex. Such prospect, undoubtedly, will cause renewed interest in the geology of this deposit. Several aspects are summarized here.

The geological features of the Kovdor deposit and its genesis have been discussed in detail in the literature. Two major models have been proposed, one involving metasomatic activity (Ternovoy 1972, 1977, Ternovoy *et al.* 1969, Dyad'kina & Orlova 1976), and the other involving precipitation of the main rock-forming minerals from a melt or a supercritical solution (Krasnova 1972). The author participated in the geological and mineralogical studies of the deposit, firstly in the mine between 1963 and 1973, and later she documented some of geological relationships observed in the open pit from its opening in 1979. Some of these observations shed light on the structural features of the deposit, as well as the formation and paragenesis of the phlogopite.

## GEOLOGICAL SETTING

In the Upper Silurian – Late Devonian Kovdor alkaline-ultrabasic complex (420–360 Ma), phlogopite-rich rocks form a semicircular zone 1 km wide, which borders the ultrabasic core to the north (Fig. 1). The age of most alkaline rock series of the Kola Peninsula was determined to be Late Devonian (Kramm *et al.* 1993). The phlogopite-rich unit includes olivinite (“olivinite”, not dunite, is used to emphasize the presence of titaniferous magnetite, not chromian spinel, as the major opaque phase in these rocks), olivine–pyroxene rocks and pyroxenite (melteigite), which were transformed to phlogopite and diopside to various degrees. Phlogopite generally occurs as isolated platy crystals or grains, although there are veins and lenses of phlogopite and phlogopite + diopside that grade into the enclosing rocks. The phlogopite deposit occurs in the northwestern part of the arc made up of phlogopite-rich rocks. The deposit is represented by steeply northwesterly dipping rocks consisting of forsterite + phlogopite + diopside in pegmatitic masses and coarse-grained veins and nests in which the size of all rock-forming minerals varies from 5–10 cm to 1–2 m. The footwall of the deposit at its southern contact is composed of olivinite transformed to phlogopite and diopside, whereas the hanging wall at the northern contact consists of melilite,

monticellite, garnet–amphibole and diopside–amphibole rocks that belong to the turjaitic series of the Kovdor complex.

The Main phlogopite lode is situated in the central part of the arcuate zone and is made up of bodies composed of giant crystals (up to 2 m across) of diopside, forsterite–phlogopite, forsterite and apatite-dominant rocks. These rocks form a complex assemblage in a non-exposed dome-like body, with numerous vein-like branches in its lower part (Fig. 2). The morphology of the lode is similar to that of some granitic pegmatites, and resembles a jellyfish in shape, with numerous vein-like, downward pointing tentacles. Large phlogopite-bearing bodies have sharp contacts with surrounding coarse-grained forsterite – diopside – phlogopite rocks (Fig. 3).

In order to evaluate the structural relationship of the deposit to the rest of the massif, a detailed study was made of the fracture patterns associated with the deposit itself, both within and outside of the complex. Aerial photographs of the Kovdor massif (Krasnova & Sokolova 1978) indicate that the entire phlogopite-enriched zone is related to semicircular faults. These faults bound the arcuate zone, and demarcate the position of a sunken block, 500 m thick. The general dip of the phlogopite bodies toward the contact of the intrusion suggests that the faulting is similar to periclinal fractures (Nevsky 1971), which were probably formed during the emplacement of ring grabens, as is schematically shown in Figures 1a and 1b. Faulting was accompanied by the formation of a system of feather joints, to which most pegmatite bodies are related. Two of the main joints coincide with L (Lagerklufften) and S (Langenklufften) types (after Cloos 1923) of primary (prototectonic) fissures in the intrusion. This relationship was proven by structural measurements of fissure orientation carried out in all accessible outcrops and mines. The localization and the complex morphology of the Main lode are best explained by the subsidence of large blocks along the zone of annular faults (Figs. 1, 2).

The spatial relationship between the phlogopite deposit and the large faults recognized at Kovdor can be used as an exploration tool to search for lodes in other alkali-ultramafic intrusions.

GEOLOGICAL STRUCTURE  
OF THE MAIN PHLOGOPITE LODGE

The Main phlogopite lode, 250 × 100 m in size at the +174 m mine level, has the shape of an ellipsoid. According to Ternovoy *et al.* (1969), it is zoned, with its marginal part composed of giant crystals of diopside up to 1–2 m in size (Di “shell”). Near the center are the zones of pegmatitic forsterite + phlogopite, forsterite and apatite (Ap) rocks. The geological relationships of the Main lode, revealed by structural mapping and interpretation of photographs of the mine walls, show that mineralogical zoning only occurs in those bodies whose

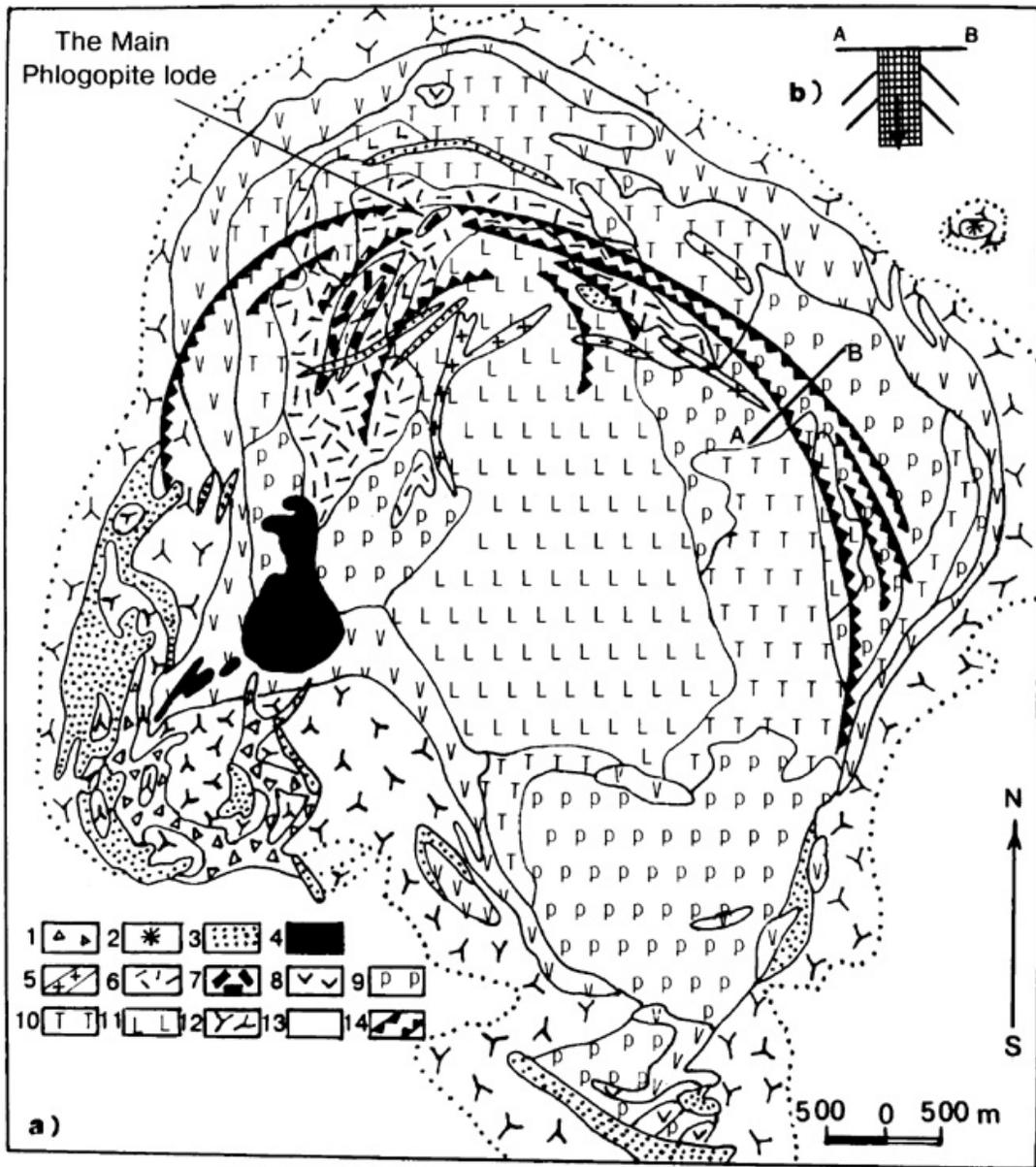


FIG. 1. a) Geological map of the Kovdor massif, after Ternovoy *et al.* (1969), with modifications by the author. Symbols: 1 apatite-“francolite” complex, 2 alkaline rocks of the Kovdor complex, 3 calcite carbonatite, 4 phoscorite complex, 5 feldspar-bearing ijolite dykes, 6 fine- and medium-grained forsterite – diopside – phlogopite rocks, 7 coarse-grained and pegmatitic forsterite – diopside – phlogopite rocks, 8 ijolite, 9 pyroxenite, jacupirangite, melteigite, 10 turjaite, melilitolite, 11 olivinite, 12 fenite, 13 Archean granite-gneiss, gneiss, 14 semi-circular faults. b) Sketch of the periclinal fractures accompanying block subsidence.

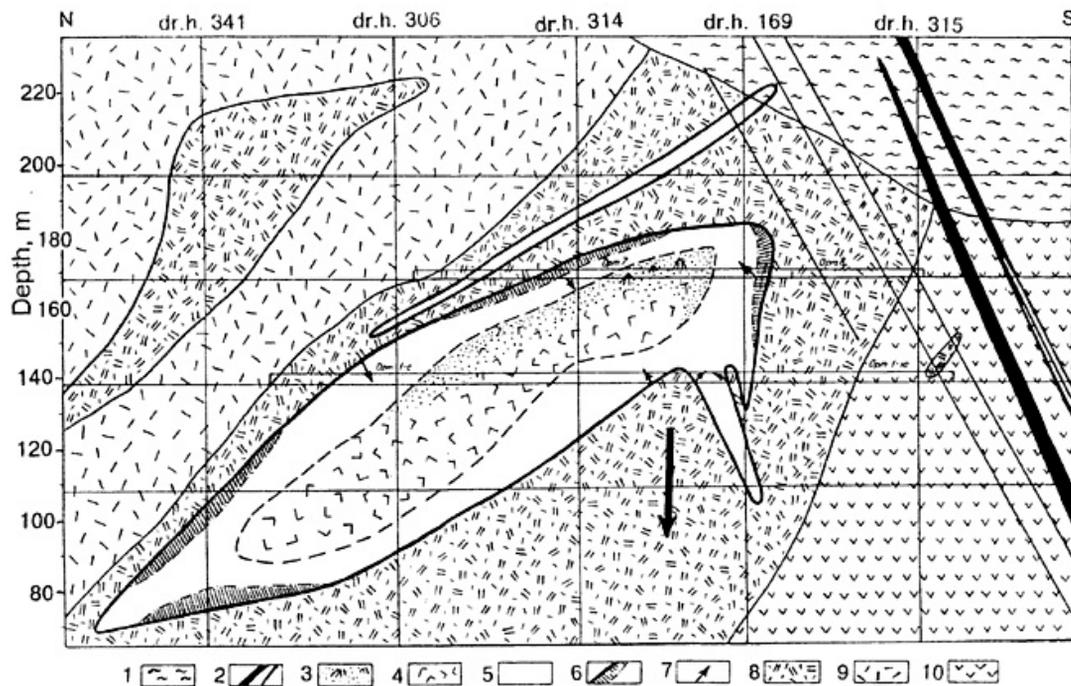


FIG. 2. A geological section of the Main phlogopite lode at Kovdor. Symbols: 1 disintegrated rocks, 2 veins and dykes of feldspar-bearing ijolite, 3 segregations of apatite, 4 forsterite, 5 pegmatitic forsterite-phlogopite rock, 6 pegmatitic diopside rock, 7 the projections of vectors of maximum rate of growth of phlogopite crystals (average), 8 coarse-grained and 9 medium-grained diopside-phlogopite-olivine rock, 10 olivinite. Large arrow: assumed direction of subsidence of block.

thickness is more than 20–30 m (Fig. 2). Thinner bodies, as a rule, are not zoned (Fig. 3).

In all zones, the rock-forming minerals form large crystals, commonly  $\geq 1$ –2 m long (Figs. 3–5). Zones of finer grain-size are found near selvages of phlogopite bodies (Fig. 3). The crystals began to grow from the contacts of bodies toward their center, just as is observed in geodes.

The apatite-rich zone is situated in the apical part of the lode (Fig. 2). The same applies to apatite segregations occurring in small pegmatitic bodies (Fig. 6). Except for granular segregations, apatite is commonly found as parallel and radiating columnar aggregates, which are invariably directed from the contacts to the center of the lode or pegmatitic body (Figs. 2, 6). The apatite-rich rocks contain irregular segregations of phlogopite, diopside, magnetite and forsterite infilling the interstices between idiomorphic, prismatic crystals of apatite. These rocks are highly radioactive owing to the presence of accessory thorianite.

Monomineralic olivine rocks, so-called “forsterites” in the Russian literature (Fo “kernel”), form the central zone of the differentiated pegmatitic bodies. At the contact of these rocks with the phlogopite-forsterite or diopside-phlogopite-forsterite zones, large frag-

ments of diopside, phlogopite and olivine crystals in a forsterite matrix are found. These fragments show signs of crushing, deformation and replacement by forsterite. At the contact with the forsterites, green phlogopite is replaced by brown-red tetra-ferriphlogopite, and amphibole (tremolite-richterite) + calcite take the place of diopside (Fig. 5). Amphibole crystals form parallel and fibrous aggregates, with the fibers oriented normal to the contact with diopside; zones of white calcite separate amphibole aggregates. Relics of a thin network of magnetite, which is typical of the diopside, also are found in the amphibole-rich zones, which confirms the metasomatic nature of these zones.

Fairly thin veinlets (on average, 2–4 cm) essentially consisting of forsterite branch from the forsterite zone, and cut much larger crystals of the external zones, firstly diopside and phlogopite. The central part of the forsterite veinlets, and especially at the wider parts, consists of calcite, apatite, along with tetra-ferriphlogopite, clinohumite, serpentine, among other minerals.

The various zones found in the differentiated pegmatitic bodies usually exhibit gradual transitions. Some of the zones, for instance the Di “shell” or the Fo “kernel”, may lack zoning. Some parts of large bodies of phlogopite and of the veins are not zoned. All of the

FIG. 3. Vein-like body of non-differentiated pegmatitic forsterite – diopside – phlogopite rock in coarse-grained olivinite in which metasomatism has produced phlogopite and diopside. Adapted from a photograph of the mine walls, as were Figures 4 and 5; 1, 2, ..., 7, scale in meters; Fo: forsterite, Phi: phlogopite, Di: diopside, Am: amphibole, Cal: calcite, Ap: fluorapatite. Arrows: crystal-growth direction.

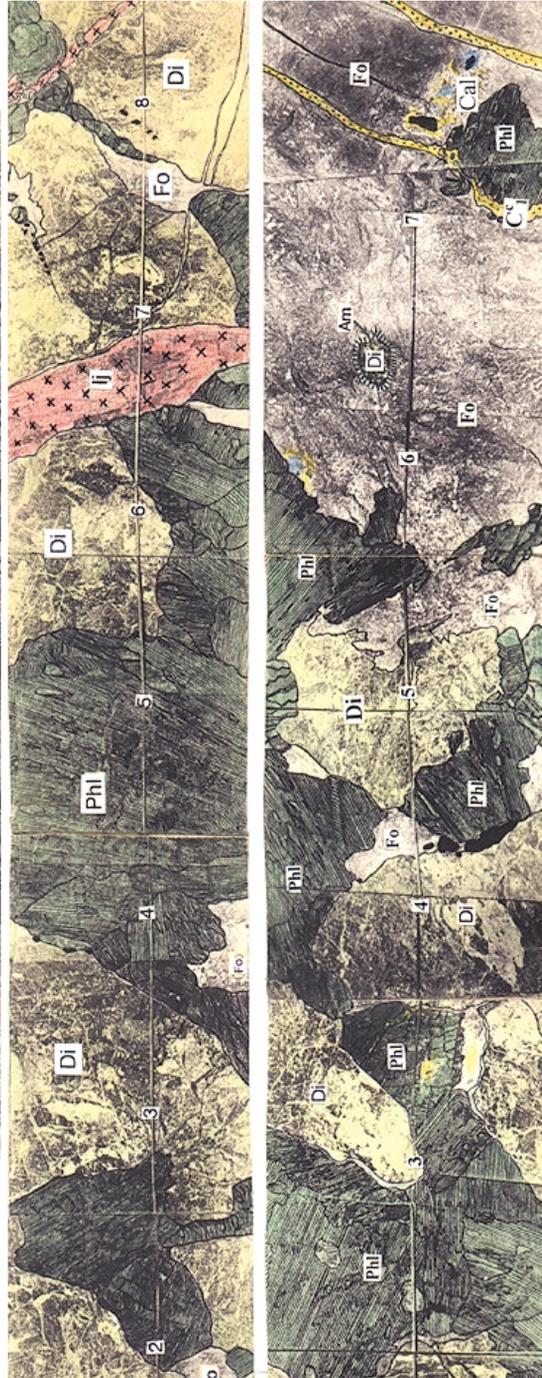
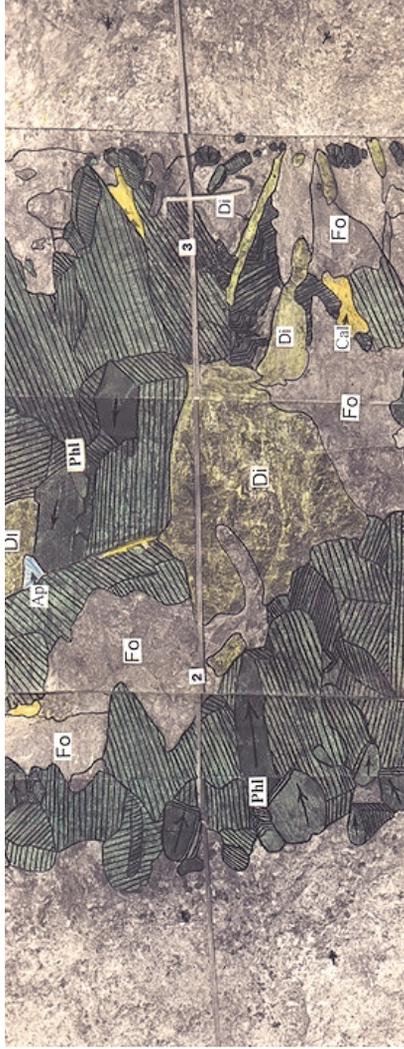


FIG. 4. Pegmatitic forsterite – diopside – phlogopite rocks. Symbols are the same as in Figure 3. Crosses: dyke (pink) of feldspar-bearing ijolite (Ij).  
 FIG. 5. Pegmatitic forsterite – diopside – phlogopite rocks. Symbols are the same as in Figure 3. Dots: carbonatites (yellow; C<sub>1</sub>). Black: magnetite.

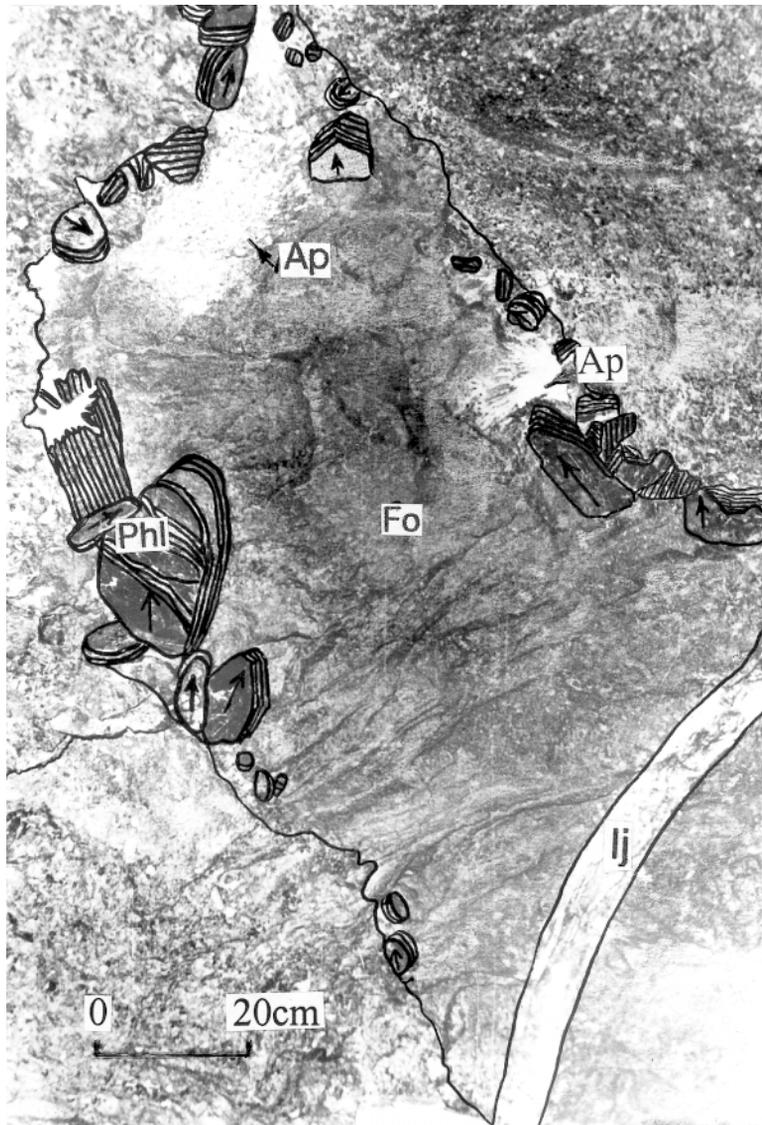


FIG. 6. Apatite segregation in the apical part of a small pegmatitic body of phlogopite-bearing rock.

bodies of ultra-coarse and pegmatitic rocks in the ore zone can be considered to be genetically related. All the zones of the Main phlogopite lode are cut by feldspar-bearing ijolite dykes (Figs. 4, 6), and calcite (Fig. 5) and dolomite carbonatites.

#### PECULIAR GROWTH-RELATED FEATURES AND COMPOSITION OF ROCK-FORMING MINERALS

In the Kovdor phlogopite deposit, 28 minerals have been found. Rimskaya-Korsakova & Sokolova (1964)

recognized three generations of phlogopite, differing from each other in color (Fig. 7) and physical properties, and in mineral associations. The optical characteristics of these micas were shown in more detail by Homenko *et al.* (1991). Typical brown-green phlogopite (generation 1) has a silver tint on the cleavage plane, caused by the presence of tiny gas inclusions. Less common is the phlogopite of generation 2, which is emerald-green in color. Mica of the third generation is represented by tetra-ferriphlogopite. The chemical composition and selected optical characteristics of these

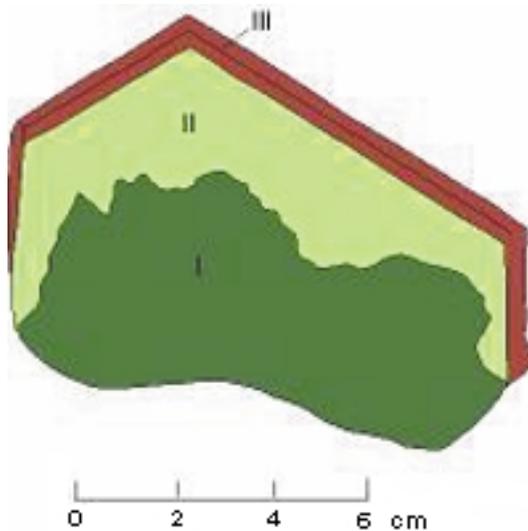


FIG. 7. The interrelation of three generations of phlogopite: 1 brown-green, 2 emerald-green and 3 brown-red tetra-ferriphlogopite.

three groups of micas are shown in Table 1. The concentration of  $\text{Fe}_2\text{O}_3$  in mica of generation 1 varies from 2.1 to 3.1 wt.%, that of  $\text{FeO}$ , from 3.5 to 4.1 wt.%, and that of  $\text{TiO}_2$ , from 0.8 to 1.1%; F amounts to 0.2 wt.%. This phlogopite is characterized by a lower content of Ti and Fe than the phlogopite typically found in olivinite (e.g., Kukharensko *et al.* 1965). Results of many chemical and spectroscopic analyses have demonstrated the limited variability in chemical composition of the phlogopite of generation 1. Only a decrease in the Ba content from 1.1% BaO in the core zone of large crystals to 0.8–0.6% in the external zones was documented. The phlogopite of generation 2 has less  $\text{Fe}^{3+}$  (2.1–2.3%  $\text{Fe}_2\text{O}_3$ ),  $\text{Fe}^{2+}$  (1.50%  $\text{FeO}$ ), Ti (0.3–0.4  $\text{TiO}_2$ ) and Ba (0.3–0.6 BaO), but more F (0.2–0.3 wt.%). Tetra-ferriphlogopite is the most diverse in chemical composition. The name of this mica reflects the deficiency of Al in the tetrahedral positions and its replacement by  $\text{Fe}^{3+}$ . The amount of Al in the first and second generations of phlogopite is usually not less than 14.3 wt.%  $\text{Al}_2\text{O}_3$ , whereas in tetra-ferriphlogopite, it may decrease to 0.9 wt.%, with a corresponding increase in  $\text{Fe}^{3+}$  up to 14.5 wt.%  $\text{Fe}_2\text{O}_3$ .

TABLE 1. CHEMICAL COMPOSITION OF ROCK-FORMING MINERALS, PHLOGOPITE DEPOSIT, KOVDOR COMPLEX, KOLA PENINSULA, RUSSIA

N°	Phlogopite, generation				Diopside		Tremolite-richterite		Clinohumite	
	1 308	2 41-42	3 13/169	5473	1 53	2 39	1 2004	2 6037	8679	1562
$\text{SiO}_2$ wt%	37.90	39.08	41.30	38.42	52.18	53.72	40.59	55.62	36.70	36.45
$\text{TiO}_2$	1.11	0.38	0.46	0.44	0.58	0.20	1.16	0.57	1.60	4.40
$\text{Al}_2\text{O}_3$	15.61	15.56	9.35	0.88	1.57	0.31	14.05	0.46	n.d.	n.d.
$\text{Fe}_2\text{O}_3$	2.14	2.11	4.13	14.51	1.90	0.89	5.58	3.41	n.d.	n.d.
$\text{Cr}_2\text{O}_3$	0.03	-	0.03	-	-	-	-	-	-	-
$\text{FeO}$	4.14	1.50	3.32	2.47	1.84	1.50	3.55	1.08	3.87	6.52
$\text{MnO}$	0.09	0.02	0.12	0.14	0.09	0.08	0.09	0.14	0.64	0.32
$\text{MgO}$	23.60	25.95	26.40	25.03	16.53	17.44	16.50	22.52	55.12	50.70
$\text{CaO}$	n.d.	0.04	n.d.	0.49	24.74	25.43	12.51	5.11	n.d.	n.d.
$\text{NiO}$	0.18	-	0.22	-	-	-	-	-	-	-
$\text{BaO}$	0.98	0.30	-	-	0.30	-	-	0.02	-	-
$\text{K}_2\text{O}$	9.51	9.06	9.93	10.40	0.04	0.18	1.52	1.12	n.d.	n.d.
$\text{Na}_2\text{O}$	0.75	0.93	0.58	0.59	0.28	0.20	2.63	6.59	n.d.	n.d.
$\text{Rb}_2\text{O}$	0.03	-	0.03	-	-	-	-	-	-	-
$\text{H}_2\text{O}^+$	4.12	4.43	3.72	6.47	0.28	0.21	1.90	2.40	1.30	1.28
$\text{H}_2\text{O}^-$	n.d.	0.42	n.d.	0.24	0.20	0.02	0.10	0.18	n.d.	n.d.
$\text{F}^-$	0.22	0.34	1.04	0.09	0.02	-	0.12	0.66	1.89	1.34
$\text{Cl}^-$	0.04	-	0.03	-	-	-	-	-	-	-
sub-total	100.45	100.12	100.66	100.17	100.55	100.62	100.30	99.88	101.12	101.01
-O=F <sub>2</sub>	0.09	0.14	0.43	0.04	0.01	-	0.05	0.28	0.79	0.56
total	100.36	99.98	100.23	100.13	100.54	100.62	100.25	99.60	100.33	100.45
$n_z$	} 1.605	} 1.594	} 1.600	} 1.642	1.710	1.700	1.678	1.628	1.666	1.698
$n_m$					1.688	1.675	1.670	1.621	1.644	1.674
$n_p$	1.566	1.556	1.562	1.608	1.680	1.669	1.659	1.611	1.631	1.665
2V	1–2°	2–3°	4°	10°	60°	59°	-88°	n.d.	60°	61°

n.d.: not detected; dash, not analyzed.

All phlogopite and diopside samples and sample 6037 were analyzed by V.F. Filonova, Central Chemical Laboratory of the North-West Geological Survey, St. Petersburg. Sample 2004 was analyzed by R.I. Ryzhova, Chemical Laboratory of the Department of Mineralogy, St. Petersburg State University. Samples 8679 and 1562 were analyzed by V.A. Moleva, Chemical Laboratory of the Institute of Geology of Ore Deposits, Petrography and Geochemistry (IGEM), Moscow.

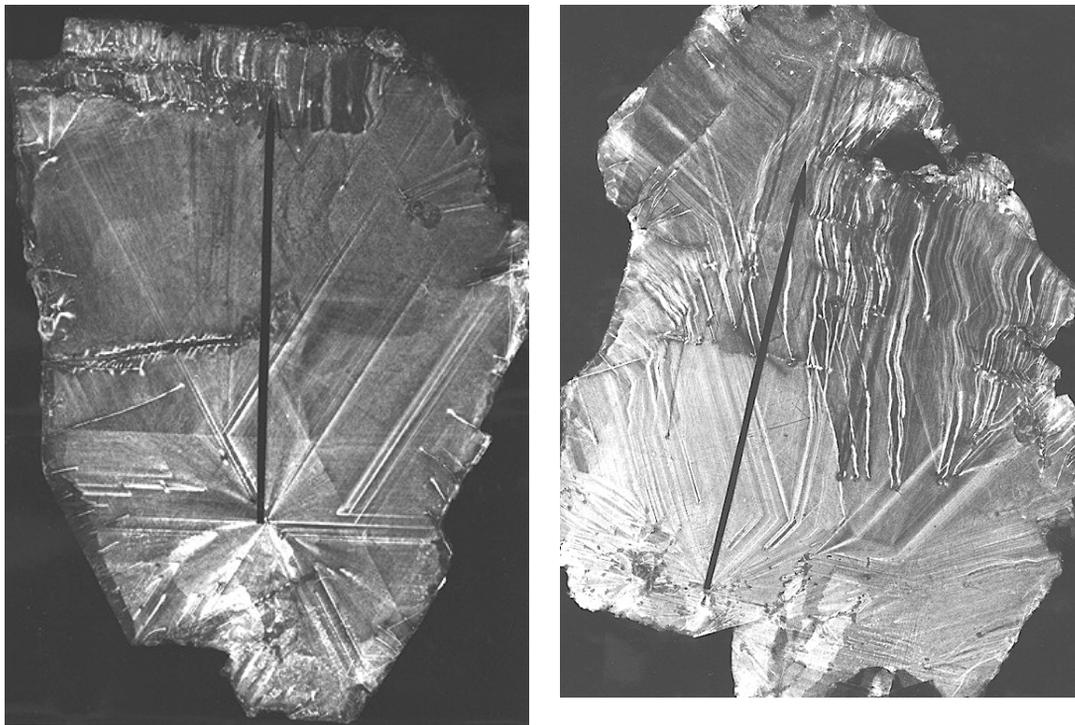


FIG. 8. The asymmetrically zoned phlogopite crystal with typical patterns on the cleavage plane. Arrow shows the projection of the vector showing maximum rate of crystal growth. The long axis of the plate is 9 cm on the left, and 13 cm on the right.

The phlogopite of generation 1 contains geometrical patterns (Fig. 8) caused by the concentration of gas inclusions along the axes of screw and edge dislocations (Rimskaya-Korsakova *et al.* 1967). These patterns, easily discernible on the cleavage planes, along with observed zoning in color, can be used to determine the direction of predominant growth (Krasnova *et al.* 1970). The macro- and microstructural study of the phlogopite-bearing bodies shows a distinct regular character in the spatial arrangement of the main minerals (Phl, Di and Fo) and, above all, a typical asymmetry in the growth of the phlogopite (Fig. 8).

Orientation measurements of approximately 3000 growth vectors, projected on the cleavage planes of mica, show that all phlogopite crystals grew in the direction from the contacts of pegmatitic vein-like bodies toward their center (Figs. 2, 3, 6, arrows). Moreover, the (001) plane of mica crystals is oriented subperpendicular to the contacts of bodies. The *c* axes of the prismatic diopside and apatite crystals, and partly those of forsterite, exhibit an orientation perpendicular to the walls of the pegmatite bodies. On the basis of these facts, the whole lode seems to have been formed from the selvages to the center. The main zones in the differentiated parts of the bodies developed in the same direc-

tion. Such directed growth of individuals in the Main lode implies a concentration gradient that existed until the forsterite zone was formed. This gradient could be maintained either by thermal differences or by replenishment by pegmatite-forming melts from the axial zones of large fissures.

The chemical composition of other main minerals of the phlogopite lode, diopside, amphibole (tremolite-richterite), clinohumite, apatite, magnetite and ilmenite-geikielite lamellar inclusions, are represented in Tables 1-3. Diopside of the first generation forms coarse-grained and giant crystals, and is dark green in color. This diopside does not vary much in chemical composition; the amount of the hedenbergite component is about 10 mol.%. Diopside 2 is associated with calcite and tetra-ferriphlogopite, commonly forms idiomorphic, short prismatic crystals, 1-3 cm long. The color of this diopside is yellow-green, and its chemical composition corresponds to almost pure diopside. Amphibole forms a reaction rim around large crystals of diopside, or fragments thereof (Fig. 5), at the contact with forsterite, forsterite veins and carbonatites. The most common amphibole is needle-like tremolite-richterite, light blue-green in color. It contains 2.5-2.7 wt.%  $\text{Na}_2\text{O}$ , 1.5-1.9 wt.%  $\text{H}_2\text{O}^+$  and 0.1-0.4 wt.% F. Near the carbonatite

TABLE 2. CHEMICAL COMPOSITION OF FLUORAPATITE, KOVDOR PHLOGOPITE DEPOSIT

	4052	270		4052	270
P <sub>2</sub> O <sub>5</sub> wt. %	40.97	41.33	H <sub>2</sub> O*	0.51	0.44
CaO	55.18	54.81	insoluble rest	0.20	0.35
CO <sub>2</sub>	n.d.	0.69	F <sup>-</sup>	1.32	1.18
SrO	0.22	0.18	total	99.54	99.82
MnO	0.25	0.25	-O=F <sub>2</sub>	0.55	0.50
MgO	0.06	0.25	total	98.99	99.32
REE <sub>2</sub> O <sub>3</sub>	0.65	0.05			
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.09	n <sub>o</sub>	1.644	1.643
Na <sub>2</sub> O	0.18	0.19	n <sub>e</sub>	1.638	1.639
K <sub>2</sub> O	0.00	0.01	n <sub>o</sub> - n <sub>e</sub>	0.006	0.004

n.d.: not detected. Analyst: Z.V. Vasilyeva, Chemical Laboratory of IGEM, Moscow.

contacts, this amphibole in some cases becomes almost white and asbestiform, enriched in Mg (22.5 wt.% MgO), Na (6.6 wt.% Na<sub>2</sub>O), H<sub>2</sub>O (2.4 wt.%), F (0.7 wt.%) and depleted in Ca, Fe and Ti (Table 1, No. 6037, tremolite-richterite). Clinohumite commonly replaces forsterite along the contacts with carbonatites; some euhedral crystals of clinohumite occur in the carbonate segregations or carbonatites and are invariably associated with serpentine. The clinohumite varies from red to dark red in color, owing to increasing of Ti (1.6 → 4.4 wt.% TiO<sub>2</sub>) and Fe (3.9 → 6.5 wt.% FeO) contents. Both amphibole and clinohumite reaction zones are 0.5–5 cm thick, which reflects the minor role of metasomatism during the formation of forsterites and carbonatites.

Chemical analyses of the medium-grained apatite (Table 2, No 4052) and euhedral prismatic crystals of apatite (No 270) show the presence of low amounts of Sr (0.2 wt.% SrO), variable content of rare-earth elements (0.1–0.6% of the respective oxides) and constant values for F (1.2–1.3 wt.%). The contents of Sr, REE and F in apatite from the phlogopite deposit are higher than those in apatite from typical phosphorites and calcite carbonatites, but lower than in apatite from ijolites and rare-metal-enriched calcite – forsterite – magnetite ores containing tetra-ferriphlogopite.

Two generations of magnetite can be distinguished. Magnetite of the first generation forms large (3–10 cm), mostly anhedral crystals (Figs. 4, 5), which are associated with phlogopite 1. This magnetite is rich in Ti (Table 3, No 6029–1, 4.57 wt.% TiO<sub>2</sub>), Al (1.87% Al<sub>2</sub>O<sub>3</sub>) and Mg (3.53% MgO). Magnetite 1 includes lamellar intergrowths of ilmenite–geikielite due to exsolution (Table 3, No 6417/1), containing up to 11.6 wt.% MgO. Some isolated inclusions in magnetite 1 were shown to be a manganian ilmenite (No 6417/1a), with 10.79 wt.% MnO. Magnetite of generation 2 rims the first generation of magnetite or occurs as octahedral crystals and is invariably associated with serpentine. This magnetite is relatively close to the end-member composition (Table 3, No 6029–2) and devoid of intergrown ilmenite or spinel.

TABLE 3. CHEMICAL COMPOSITION OF MAGNETITE AND ILMENITE, KOVDOR PHLOGOPITE DEPOSIT

	Magnetite		Ilmenite*	
	Type 1 6029-1	Type 2 6029-2	6417/1	6417/1a
SiO <sub>2</sub> wt. %	0.20	0.46	-	-
TiO <sub>2</sub>	4.57	2.29	55.55	53.86
Al <sub>2</sub> O <sub>3</sub>	1.87	0.29	-	-
Fe <sub>2</sub> O <sub>3</sub>	60.89	68.17	1.72**	n.d.
V <sub>2</sub> O <sub>5</sub>	0.03	0.10	-	-
Cr <sub>2</sub> O <sub>3</sub>	0.10	0.31	-	-
FeO	28.02	26.35	27.24**	33.24
NiO	0.23	0.09	-	-
CoO	0.03	0.03	-	-
CuO	0.01	0.01	-	-
MnO	0.59	0.56	3.87	10.79
MgO	3.53	1.01	11.62	0.84
CaO	0.01	0.01	-	-
ZnO	0.10	0.07	n.d.	1.27
P <sub>2</sub> O <sub>5</sub>	0.03	0.05	-	-
S	0.03	0.01	-	-
total	100.24	99.81	100.00	100.00

n.d.: not detected; dash: not analyzed. Analyst: V.F. Filonova, Central Chemical Laboratory of the North-West Geological Survey, St. Petersburg.

\* Electron-microprobe analyses, scanning electron microscope SEM-501 (with an energy-dispersion system for semiquantitative analyses). Analyst: A.R. Nesterov, laboratory of the University of St. Petersburg.

\*\* Proportions of FeO and Fe<sub>2</sub>O<sub>3</sub> calculated on the basis of 3 atoms of oxygen and 2 cations.

The gas fraction extracted from phlogopite and apatite samples using the milling method (Table 4) is mainly hydrogen. The highest amount of H<sub>2</sub> was found in phlogopite 1, the richest in gas inclusions. A lower H<sub>2</sub> content is detected in inclusion-poor phlogopite 2, and the least H<sub>2</sub> content is observed for inclusion-free phlogopite 3.

#### THE CONDITIONS OF FORMATION OF THE DEPOSIT

Special attention was given to a definition of the physicochemical conditions of formation of deposit. The

TABLE 4. ANALYSES OF GAS EXTRACTED FROM PHLOGOPITE AND APATITE, KOVDOR PHLOGOPITE DEPOSIT

	Number	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	He
Phlogopite 1	8748	241.58	n.d.	n.d.	0.12	n.d.	n.d.	0.13
Phlogopite 1	V	136.28	1.95	0.12	n.d.	n.d.	n.d.	n.d.
Phlogopite 2	18	101.18	1.25	0.20	0.52	n.d.	n.d.	n.d.
Phlogopite 3	8677	0.55	n.d.	n.d.	0.007	0.0002	n.d.	n.d.
Phlogopite 3	17	0.21	1.85	0.08	n.d.	-	-	-
Apatite	36	1.17	n.d.	n.d.	0.11	0.008	0.0005	0.09
Apatite	38	0.56	n.d.	0.007	0.007	0.004	0.0004	0.29

n.d.: not detected; dash: not analyzed.

All analyses were made in the Gas Laboratory (leader: S.V. Ikorskii) of the Geological Institute, Kola Science Center of the Russian Academy of Sciences, Apatite. Chromathermochemical gas apparatus CTCG-1. Disintegration time: 16 hours for phlogopite, 20 minutes for apatite in vacuum, 10<sup>-2</sup> mm of mercury column. Units: cm<sup>3</sup>/1 kg of mineral.

temperature of equilibration of phlogopite 1 and pyroxene 1 was determined by the phase-equilibrium method based on the distribution coefficient of Mg and Fe between these silicates (Pertchuck 1968). The mole % of the magnesium end-member [Mg/(Mg +  $\Delta$ Fe + Mn) or Mg#] in typical phlogopite 1 varies from 0.87 to 0.88. In the coexisting diopside 1, the Mg# is 0.87 and 0.90, respectively. The calculated temperature of the formation of this mineral association proved to be in excess of 700 and 720°C. The temperatures of partial homogenization of the exsolution products in forsterite were determined experimentally by heating mineral grains in evacuated silica capsules. Exsolution is reflected by ultrafine diopside and skeletal magnetite segregations, which morphologically resemble the inclusions in olivine described by Agaphonov *et al.* (1974). Disappearance of the diopside and changes in the shape of magnetite intergrowths in our experiments started at a temperature not lower than 1050°C. Bearing in mind that the temperature of homogenization of inclusions in exsolution structures in sulfides and oxides commonly exceeds the exsolution temperature by 100–150°C, we assume by analogy that the olivine exsolution may have taken place at a temperature of about 950–900°C. Comparison with the experimental data of Haggerty & Baker (1967), who reproduced the exsolution of clinopyroxene and magnetite from olivine, suggests that the exsolution-related intergrowths could form at a temperature above 820°C.

To estimate the temperature of formation of apatite in the Main lode, trapped inclusions in apatite were investigated. Microscopic studies showed that many primary inclusions contain between three and six phases. In the latter case, the inclusions contain a gas bubble, small amount of liquid and three or four minerals. The liquid + vapor fraction in these inclusions homogenizes to gas at temperatures of between 500 and 700–750°C. These results are consistent with data obtained by decrepitation of inclusions in the same apatite samples. An investigation of the salt composition of the inclusions in apatite by means of the H<sub>2</sub>O-extraction method (Govorov *et al.* 1968) showed the predominance of CaCl<sub>2</sub>. The chemical composition of the solution extracted from one apatite sample is: Ca<sup>2+</sup><sub>0.75</sub> Na<sup>+</sup><sub>0.14</sub> Mg<sup>2+</sup><sub>0.07</sub> K<sup>+</sup><sub>0.04</sub> / Cl<sup>-</sup><sub>0.73</sub> SO<sub>4</sub><sup>2-</sup><sub>0.23</sub> HCO<sub>3</sub><sup>-</sup><sub>0.04</sub>.

## DISCUSSION

According to all the above data, the main minerals (phlogopite, diopside and forsterite) of the Kovdor deposit began to form at a high temperature, 800–900°C, when hydrostatic pressure in the system, according to Kukharevko *et al.* (1965), was approximately 2000 bars. Therefore, it is possible that the phlogopite formed at first from a highly concentrated melt (alkali-ultrabasic pegmatitic residual liquid) and then, at a lower temperature, from a supercritical fluid, which was gradually transformed to a hydrothermal solution. The crystalli-

zation of fluorine-bearing biotite from a melt was experimentally studied by Grigoriev (1938, 1944), and that of phlogopite by Yoder & Eugster (1954). During the hydrothermal stage, minerals such as serpentine, saponite, brucite, vermiculite, barite, sjögrenite, and euhedral calcite and dolomite formed. The roof rocks of the Main phlogopite lode underwent intense metasomatic alteration, followed later by weathering, vermiculitization of phlogopite, serpentinization, oxidation and disintegration of olivine (Fig. 2).

By analogy with the position of phlogopite pegmatite around the phoscorite unit in the Phalaborwa massif (Eriksson 1989, Moore 1984, Verwoerd 1986), it is possible to assume that the phlogopite-bearing rocks at Kovdor also are genetically related to the phoscorite complex. Kukharevko *et al.* (1965) and Ternovoy (1977), in fact, reached such a conclusion. The appearance of forsterite and such minerals as apatite, calcite, magnetite and part of the forsterite at the final stages of development of the pegmatite suggests that the phlogopite deposit formed prior to the appearance of the phoscorite. In the latter, forsterites formed early in the crystallization history; forsterite, apatite, magnetite and calcite are the main rock-forming minerals of all types of phoscorite (Krasnova & Kopylova 1988). This latter interpretation is supported by the fact that the phlogopite of generation 1 and the coarse-grained rocks of the phlogopite complex are cut by thin veinlets of magnetite. The occurrence of xenoliths of phlogopite 1 within the northern part of the magnetite deposit also suggests that the phlogopite complex formed prior to the phoscorite. The formation of both phlogopite and phoscorite complexes followed the emplacement of the alkaline intrusion.

The main process responsible for the phlogopite deposit, in the author's opinion, was successive crystallization of minerals that took place from the margins to the center of relatively closed chambers occupied by magma. The accumulation of apatite in the apical parts of the Main lode (Figs. 2, 6), can be explained by separation of a phosphate liquid from a silicate melt or by the process of gravitational differentiation during crystallization and segregation of the phosphate component in the apical parts of pegmatitic bodies. Flotation of the phosphate globules (or apatite crystals) could be due to their slightly lower density compared to that of the silicate melt, or their flotation could be caused by transportation involving gas bubbles. The immiscible separation of phosphate and silicate liquids in the presence of various alkaline salts has been proven experimentally by many scientists (*e.g.*, Kogarko & Ryabchikov 1969, Melentiev & Delitzin 1969) and probably is widespread in natural silicate systems. Most modern petrologists rely on the phosphate–silicate immiscibility theory to explain the genesis of the well-known apatite deposits at Khibina. A field of such immiscibility exists in the system apatite – nepheline – NaF, which is rather similar to natural associations in the Khibina deposits. The

main reasons for this immiscibility, as these authors proposed, could be the structural incompatibility of ion groups, difference of the surface tension of two liquids, and presence of some salts, *e.g.*, NaF, NaCl, KCl, and LiF.

On the basis of the author's observations at Kovdor, there seems to be no regular order of crystallization within the phlogopite deposit. Although it is possible to outline only a general trend for the formation of zoning in the deposit, each of the individual bodies behaved independently as isolated, partly closed systems. The sequence of mineral crystallization was controlled mainly by the relative contents of the main components in different parts of the system. For instance, in some contact parts of the Main lode, one can observe a zone of diopside (Fig. 2), whereas in others a zone of phlogopite-forsterite rocks (Figs. 2, 6) or apatite segregations (Fig. 6, upper part of photo) are found.

#### CONCLUSIONS

On the basis of shape, structure, peculiar features of mineral growth, crystallization sequences in its different parts, temperature of mineral formation and state of the system, it is possible to regard the Main phlogopite lode as a peculiar alkali-ultrabasic pegmatite. The interpretation of this deposit as a skarn deposit that results from reaction between the carbonate-rich and silicate rocks (Smirnov 1982) does not appear to be consistent with the observations summarized here. Nor are the data consistent with metasomatic processes according to the criteria of Krasnova (1988). The hypothesis of metasomatism as a dominant process during the formation of the Kovdor phlogopite deposit and related rocks, as suggested by Ternovoy (1972, 1977) and Dyad'kina & Orlova (1976), contradicts the observations recorded here. According to these authors, postmagmatic solutions circulated along the arcuate faults and caused the metasomatic zonation of the deposit, reflecting the variable mobility of the main chemical components, and the process of recrystallization followed its formation. The facts do not confirm a metasomatic origin of the Main phlogopite lode. On the contrary, there are many lines of evidence showing that the main minerals grew from the contacts of the bodies to their center from a melt phase, and this process was accompanied by gravitational settling and liquid immiscibility.

The gas analyses of phlogopite and apatite specimens rich in inclusions show a perceptible role of hydrogen during the formation of the deposit. Such minerals as forsterite, phlogopite of the first and second generations, and magnetite could have formed only under reducing conditions. The system became more oxidized during last stages of the carbonatite formation, when tetraferriphlogopite appeared in the mineral assemblage (Rimskaya-Korsakova & Sokolova 1964).

#### ACKNOWLEDGEMENTS

The author is grateful to A.A. Kukharenko, O.M. Rimskaya-Korsakova, and T.G. Petrov for their help and enlightening discussions during this study, and K. Bell for constructive criticism of an earlier version of this paper. R.F. Martin's comments led to a considerable improvement of the manuscript.

#### REFERENCES

- AGAPHONOV, L.V., CHEPUROV, A.I., LAVRENT'EV, YU.G. & POKACHALOVA, O.S. (1974): Regularly oriented inclusions in olivine from ultrabasites of Koriakiya. *Geol. Geophys.* **6**, 49-60 (in Russ.).
- CLOOS, H. (1923): Das Batholithenproblem. *Fortschr. d. Geol. u. Paläontol.* **1**.
- DYAD'KINA, I.YA. & ORLOVA, M.P. (1976): *Phlogopite Deposits*. Nedra Press, Leningrad, Russia (in Russ.).
- ERIKSSON, S.C. (1989): Phalaborwa, a saga of magmatism, metasomatism and miscibility. In *Carbonatites, Genesis and Evolution* (K. Bell, ed.). Unwin Hyman, London, U.K. (221-254).
- GOVOROV, I.N., FILIPPOVA, T.G. & EFIMOVA, M.I. (1968): Chemical composition and temperature of mineral-forming solutions of rare-metal Far-East deposits, connected with granite intrusions. In *Mineralogical Thermometry and Barometry 1*. Nauka Press, Moscow, Russia (33-46; in Russ.).
- GRIGORIEV, D.P. (1938): Synthesis and the investigation of biotite. *Dokl. Acad. Sci. USSR* **20**(5), 391-393 (in Russ.).
- \_\_\_\_\_ (1944): Synthesis and the investigation of phlogopite. *Dokl. Acad. Sci. USSR* **43**(2), 63-65.
- HAGGERTY, S.E. & BAKER, I. (1967): The alteration of olivine in basaltic and associated lavas. 1. High temperature alteration. *Contrib. Mineral. Petrol.* **16**, 233-257.
- HOMENKO, V.M., PLATONOV, A.N. & KRASNOVA, N.I. (1991): The optical properties of phlogopite of the Kovdor massif. *Izv. Akad. Nauk SSR, Ser. Geologicheskaya* **12**, 94-105 (in Russ.).
- KOGARKO, L.N. & RYABCHIKOV, I.D. (1969): Differentiation of alkaline magmas rich in volatiles. *Geochem. Int.* **6**, 2011-2021.
- KRAMM, U., KOGARKO, L.N., KONONOVA, V.A. & VARTAINEN, H. (1993): The Kola Alkaline Province of the CIS and Finland: precise Rb-Sr ages define 380-360 Ma age range for all magmatism. *Lithos* **30**, 33-44.
- KRASNOVA, N.I. (1972): *Mineralogy and Genesis Questions of the Kovdor Phlogopite Deposit*. Avtoref. Cand. Diss., The University of Leningrad, Leningrad, Russia (in Russ.).

- \_\_\_\_\_ (1988): Diagnostic features of metasomatism. *Int. Geol. Rev.* **30**, 1070-1083.
- \_\_\_\_\_ & KOPYLOVA, L.N. (1988): The geological basis for mineral-technological mapping at the Kovdor deposit. *Int. Geol. Rev.* **30**, 307-319.
- \_\_\_\_\_, PETROV, T.G. & KOCHUROVA, T.L. (1970): An attempt to determine the vectors of greatest rate of crystal growth. *Zap. Vses. Mineral. Obshchest.* **99**, 730-735 (in Russ.).
- \_\_\_\_\_ & SOKOLOVA, V.B. (1978): The tectonics and mechanism of formation of the Kovdor alkaline-ultrabasic intrusive complex. *Vestnik Leningrad Univ.* **6**, 16-21 (in Russ.).
- KUKHARENKO, A.A., ORLOVA, M.P., BULAKH, A.G., BAGDASAROV, E.A., RIMSKAYA-KORSAKOVA, O.M., NEFEDOV, E.I., IL'INSKII, G.A., SERGEEV, A.S. & ABAKUMOVA, N.B. (1965): *The Caledonian Complex of Ultrabasic Alkaline rocks and Carbonatites of the Kola Peninsula and Northern Karelia*. Nedra Press, Moscow, Russia (in Russ.).
- MELENTIEV, B.N. & DELITZIN, L.M. (1969): The problem of liquation in magma. *Dokl. Akad. Nauk SSSR* **186**(1), 191-193 (in Russ.).
- MOORE, A.C. (1984): Orbicular rhythmic layering in the Palabora carbonatite, South Africa. *Geol. Mag.* **121**, 53-60.
- NEVSKY, V.A. (1971): Circular fractures and some data of their formation. *Izv. Akad. Nauk SSSR, Ser. Geol.* **5**, 47-61 (in Russ.).
- PERTCHUCK, L.L. (1968): The effect of temperature and pressure on the equilibrium of natural iron-magnesium minerals. *Int. Geol. Rev.* **11**, 875-901.
- RIMSKAYA-KORSAKOVA, O.M., KRASNOVA, N.I., PETROV, T.G. & POLIKARPOVA V.N. (1967): The nature of patterns, observed on the cleavage planes of some phlogopites. *Zap. Vses. Mineral. Obshchest.* **96**(2), 141-154 (in Russ.).
- \_\_\_\_\_ & SOKOLOVA, E.P. (1964): About iron-magnesium mica with reverse adsorption scheme. *Zap. Vses. Mineral. Obshchest.* **94**, 411-423 (in Russ.).
- SMIRNOV, V.I. (1982): *Geology of Mineral Resources* (4<sup>th</sup> ed.). Nedra Press, Moscow, Russia (in Russ.).
- TERNOVOY, V.I. (1972): Phlogopite-bearing rocks of Kovdor deposit. In *Pegmatites* (P.M. Tatarinov, ed.). Nedra Press, Leningrad, Russia (244-248; in Russ.).
- \_\_\_\_\_ (1977): *Carbonatite Massifs and their Mineral Resources*. Leningrad University Press, Leningrad, Russia (in Russ.).
- \_\_\_\_\_, AFANASYEV, B.V. & SULIMOV, B.I. (1969): *Geology and Exploration of Kovdor Vermiculite-Phlogopite Deposit*. Nedra Press, Leningrad, Russia (in Russ.).
- VASILIEVA, V.V., MATVEEV, I.V., TURCHENKO, S.I. & KRASNOVA N.I. (2000): Second life for phlogopite from Kovdor deposit. *Proc. Russ. Mineral. Soc. (Annual Meeting, St. Petersburg)*, 48-50 (in Russ.).
- VERWOERD, W.J. (1986): Mineral deposits associated with carbonatites and alkaline rocks. In *Mineral Deposits of Southern Africa* (C.R. Anhaeusser & S. Maske, eds.). Geological Society of South Africa, Johannesburg, South Africa (2173-2191).
- YODER, H.S., JR. & EUGSTER, H.P. (1954): Phlogopite synthesis and stability range. *Geochim. Cosmochim. Acta* **6**, 157-185.

*Received January 15, 2000, revised manuscript accepted December 25, 2000.*