

Review

Occurrence and Petrogenesis of Phoscorite-Carbonatite Complexes in the Kola Alkaline Province, Arctic

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Abstract : Although phoscorites and carbonatites form only a minor proportion of the earth's crustal rocks, these unusual rocks and their intimate relation are of both academic and economic importance. Rare metal (Nb, Zr, Ta) and REEs mineralizations are in close relation with the differentiation of these phoscorite-carbonatite complexes (PCCs). Recent integrated petrological and geochemical data on PCCs in the Kola Alkaline Province, Arctic, indicate that phoscorites and associated carbonatites are differentiated from common 'carbonated silicate parental magma'. Various hypotheses for the genesis of phoscorite-carbonatite complexes have been proposed during the last half-century. A simple magmatic fractionation scheme can not explain the chemical and mineralogical characteristics of phoscorite and conjugate carbonatite. Instead, the hypotheses involving liquid immiscibility and coeval accumulation processes are favored to explain the mineralogical and geochemical characteristics of phoscorite and carbonatite association.

Key words : Phoscorite-carbonatite complex, rare metal mineralization, Kola Alkaline Province.

1. Introduction

The Kola Alkaline Province (KAP) of the northeastern Baltic Shield, Arctic is one of the few regions in the world where Paleozoic alkaline-ultramafic or alkaline magmatism is well-developed (Woolley 1989; Kogarko *et al.* 1995). Typical products of this magmatism are olivinites, pyroxenites, melilitites, melteigite-ijolite-urtites, alkaline syenites, phoscorites and carbonatites, which have intruded into the late Archean continental crust and are often closely associated within a single massif (Kukharensko *et al.* 1965; Kogarko *et al.* 1995).

More than 20 massifs of Paleozoic alkaline-ultramafic and alkaline rocks occur in the KAP, sixteen of which contain carbonatites (Fig. 1). A characteristic feature of Kola carbonatites in most complexes is their close relation with phoscorites, which consist essentially of apatite-magnetite and silicates (forsterite and/or phlogopite), and basically share the same mineral paragenesis as accompanying carbonatites (Fig. 2). Actually, rocks of the phoscorite

series are rare in other carbonatite complexes in the world. Even if they occur, for example, at Phalaborwa, the type locality of phoscorite, in South Africa, or at Jacupiranga in Brazil, they are not generally considered to be of the rock type to be singled out within the family of carbonatites and related rocks.

The close association of carbonatites with phoscorites and the genetic relationship between them are one of the most interesting problems of carbonatite petrology, but less investigated, despite being extremely important economically because these PCCs are closely accompanied by diverse mineralizations, rich in rare metals (Zr, Nb, Ta), noble metals (Ag, Au), platinum group elements (PGE) and rare earth elements (REEs). In Kovdor massif, they are the main industrial targets containing huge amounts of magnetite, phlogopite and apatite ores.

Until the early 1990's, studies for phoscorite and carbonatite associations have been done mainly on PCCs in the KAP and Maimecha-Kotuy Province in the northern Siberian platform by Russian geologists, and basically focused on field and petrographic investigations. However, over the last ten years, many western geologists have paid

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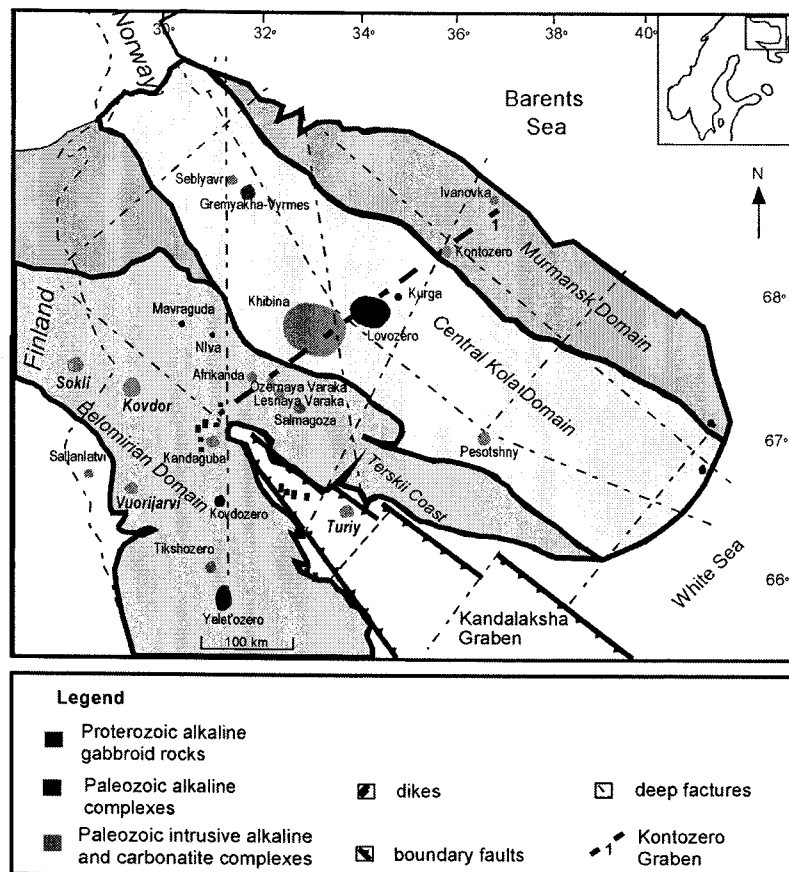


Fig. 1. Map of the Kola Alkaline Province showing the location of the Proterozoic and Paleozoic alkaline intrusions (modified from Bell *et al.* 1996).

attention to the genesis of phoscorite-carbonatite pairs in the KAP from both geochemical and economic points of view because PCCs are recognized as main reservoirs for gigantic rare metal deposits. In Korean petrological society, the attention on PCCs has increased since several years ago because one Fe-REE deposit in the Hongcheon area, Kyeonggi massif, seems to have been formed during the latest differentiation process of phoscorite-carbonatite magma (Lee *et al.* 2002). The occurrence of rare minerals and the close association of Fe deposits with carbonatite in the Hongcheon area are petrologically very similar to late-stage products in the evolution of PCCs (Balaganskaya, personal communication). However, the term of 'phoscorite' has not been well introduced to the Korean petrological society.

The present paper introduces the term of 'phoscorite' and the occurrence of PCCs first, and then reviews the petrographical results performed on several PCCs in Kola (Sokli, Kovdor, Vuorijarvi and Turiy Mys) over the last

fifty years, and finally discusses the genetic relationship between phoscorite and associated carbonatite, mainly on the basis of recently obtained mineralogical and geochemical data on the Sokli PCC (Lee 2002).

2. What is phoscorite?

According to the IUGS recommendations (Le matre *et al.* 1989), phoscorite is defined as plutonic ultramafic phosphate-oxide-silicate rock that occurs in spatial and temporal association with carbonatite. The term 'phoscorite' was derived from the name of the company, the *Phosphate Development Corporation*, and refers to olivine-apatite-magnetite rock confined to the central region containing the carbonatite body of the Phalaborwa ijolite-carbonatite complex, South Africa (Russell *et al.* 1954).

Camaforite is another name for phoscorite, used by some Russian authors; the name is an acronym for Calcite-Apatite-Magnetite-Forsterite (Borodin *et al.* 1973). The

definition is thus somewhat restrictive compared to that of phoscorite. This term is considered inadequate by authors who consider that the carbonate in phoscorites is an interstitial or secondary phase (Yegorov 1980). Moreover, even including carbonate as a constituent in the definition, the term camaforite seems to be narrow because the silicate of the phoscoritic rocks is not necessarily forsterite (for example, apatite-diopside-magnetite rock is considered a type of phoscorites by many authors). Also, oxide is not necessarily magnetite alone, but oxides commonly include titanomagnetite or ilmenite. Other terms also used by authors to refer to rocks equivalent to phoscorites are: 'carbonatitoid', for all carbonate-poor rocks associated with carbonatites, or simply 'ore' (Kukharensko *et al.* 1965) to designate all magnetite-rich rocks or even apatite-rich rocks.

As for the status of calcite (more generally carbonate) in phoscorite, Krasnova *et al.* (in preparation) proposed another definition of phoscorite, which is very similar to the IUGS definition, which adds carbonate as an essential constituent.

The main minerals of phoscorites considered to be crystallized from a melt are olivine, magnetite, apatite, calcite and/or dolomite. The various mineral contents produce large varieties of the phoscorite rock series such as forsterite, magnetite, phoscorite (*sensu stricto*), nelsonite and apatite. Other minerals include mica (phlogopite, biotite and tetraferriphlogopite), pyroxene (diopside and aegirine), amphibole (hastingsite, tremolite and richterite) and ilmenite. Pyrochlore, baddeleyite, calzirtite, zircon and zirconolite are typical as accessory minerals.

The average chemical compositions of phoscorites and carbonatites, on the basis of the formation stage, in the Sokli complex are given in Table 1 (Lee 2002). Compared with associated carbonatites in the same stage, phoscorites are enriched in most major elements except Ca as well as rare metal elements (Ta, Nb and Zr). This result indicates that phoscorites are intimately associated with other rare metal minerals such as pyrochlore, baddeleyite, calzirtite, zircon and zirconolite.

3. Occurrence of phoscorite and carbonatite complex (PCC) in Kovdor

Although phoscorite-carbonatite association is comparatively rare in other carbonatite complexes in the world, it is relatively abundant in the Kola, Maimecha-Kotuy and Aldan provinces in Russia. The various phoscorite-carbonatite rock associations are found in the Sokli (Finland), Kovdor,

Table 1. Average compositions of the main rock types in the Sokli complex.

Rock type	C1	P1	C2	P2	C3	P3	D4	D5
N.A.	6	7	8	9	8	7	8	7
wt. %								
SiO ₂	4.99	16.57	2.63	16.43	2.51	14.96	0.27	0.71
TiO ₂	0.26	0.98	0.22	1.84	0.21	2.27	0.02	0.06
Al ₂ O ₃	0.32	1.00	0.35	2.36	0.25	1.72	0.03	0.04
Fe ₂ O ₃ *	7.44	24.45	5.71	38.14	5.33	42.47	2.88	7.15
MnO	0.25	0.70	0.25	0.52	0.30	0.54	0.52	0.69
MgO	6.82	20.81	3.90	13.79	4.57	13.93	17.55	14.39
CaO	42.23	15.62	46.37	11.40	45.66	9.59	33.18	29.56
Na ₂ O	0.07	0.14	0.07	0.37	0.14	0.28	0.03	0.07
K ₂ O	0.20	0.83	0.32	2.19	0.32	2.10	0.05	0.08
P ₂ O ₅	4.13	2.60	3.69	5.33	3.24	4.11	1.08	0.33
Nb ₂ O ₅	0.009	0.012	0.059	0.578	0.116	0.888	0.031	0.060
ZrO ₂	0.056	0.348	0.038	0.266	0.031	0.146	0.008	0.019
La ₂ O ₃	0.028	0.014	0.026	0.022	0.031	0.020	0.014	0.569
Ce ₂ O ₃	0.063	0.035	0.057	0.061	0.066	0.057	0.027	0.797
SrO	0.407	0.149	0.539	0.146	0.611	0.151	0.619	1.991
BaO	0.055	0.109	0.088	0.131	0.069	0.070	0.037	2.250
LOI	31.39	15.66	34.27	6.01	34.60	6.04	42.34	38.99
ppm								
Sc	24	70	17	44	20	35	10	14
V	50	191	54	565	58	478	14	5
Cr	3	3	3	25	5	14	3	6
Co	d.l.	d.l.	2	60	2	38	3	39
Ni	d.l.	d.l.	d.l.	37	3	19	6	2
Cu	d.l.	d.l.	5	537	19	153	32	232
Zn	56	233	48	377	43	404	24	686
Ga	6	20	5	63	7	83	2	3
Rb	d.l.	21	5	75	5	73	d.l.	d.l.
Sr	3446	1258	4616	1278	5242	1345	5270	16890
Y	56	32	44	40	50	30	20	18
Zr	414	2577	279	1974	232	1080	62	142
Nb	61	88	413	3957	847	6250	217	418
Ba	488	976	787	1177	620	630	334	19882
La	241	119	221	191	264	169	117	4843
Ce	539	297	488	520	559	483	232	6810
Eu	11	6	10	11	11	9	4	20
Yb	3	3	3	3	3	3	1	1
Ta	9	18	17	200	39	138	3	2
Pb	3	4	3	12	6	15	3	8
Th	35	24	38	391	55	764	12	112
U	6	2	7	120	24	29	d.l.	d.l.

C1, C1 calcite carbonatite; C2, C2 calcite carbonatite; C3, C3 calcite carbonatite.

P1, P1 phoscorite; P2, P2 phoscorite; P3, P3 phoscorite.

D4, D4 dolomite carbonatite; D5, D5 dolomite carbonatite.

N.A., number of analysis; d.l., below detection limit; *total Fe as Fe₂O₃.

Vuorijärvi and Turij Mys (Russia) carbonatite complexes of the KAP. These complexes also include diverse ultramafic-alkaline rocks from olivinites through ijolite-melteigites to alkaline syenites.

Most complexes at the KAP have been studied mainly through extensive drilling campaigns, with the exception of the Kovdor massif, because the large areas are covered with thick glacial drift. The Kovdor massif (380-360 Ma, Kramm *et al.* 1993) has numerous 'artificial outcrops' and is thoroughly studied owing to the open pit mining operations (magnetite, phlogopite, apatite, etc.). Subsequently, a multi-stage evolution has been established in detail in the phoscorite-carbonatite complex.

The Kovdor massif is a complex, multiphase and concentric intrusion (Fig. 3; Kukhareno *et al.* 1965; Kogarko *et al.* 1995). It intrudes Archean gneisses and granitic gneisses of the Belomorian group. The main rock types are, from the oldest to youngest, ultramafic rocks (olivinite and pyroxenite), turjaites and melilitolites, rocks

of the ijolite-melteigite series, phoscorite and carbonatite complex and nepheline syenites. These various ultramafic and alkaline silicate rocks are believed to have been formed from several batches of a carbonated olivine melanephelinite parental magma by a mechanism involving fractional crystallization and magma mixing or contamination (Kukhareno *et al.* 1965; Veksler *et al.* 1998a; Verhulst *et al.* 2000).

In the SW of the complex, a stock of phoscorite and carbonatite has been emplaced. At least six stages are distinguished in the Kovdor PCC, and each stage typically includes phoscorite-carbonatite pairs with the same mineral assemblage and mineral composition (Fig. 2; Krasnova and Kopylova 1988; Balaganskaya 1994). One of the characteristic features of the Kovdor PCC is the occurrence of various kinds of breccias (Balaganskaya 1994), which clearly separate the successive intrusive stages.

Phoscorites of the Kovdor massif vary widely in the

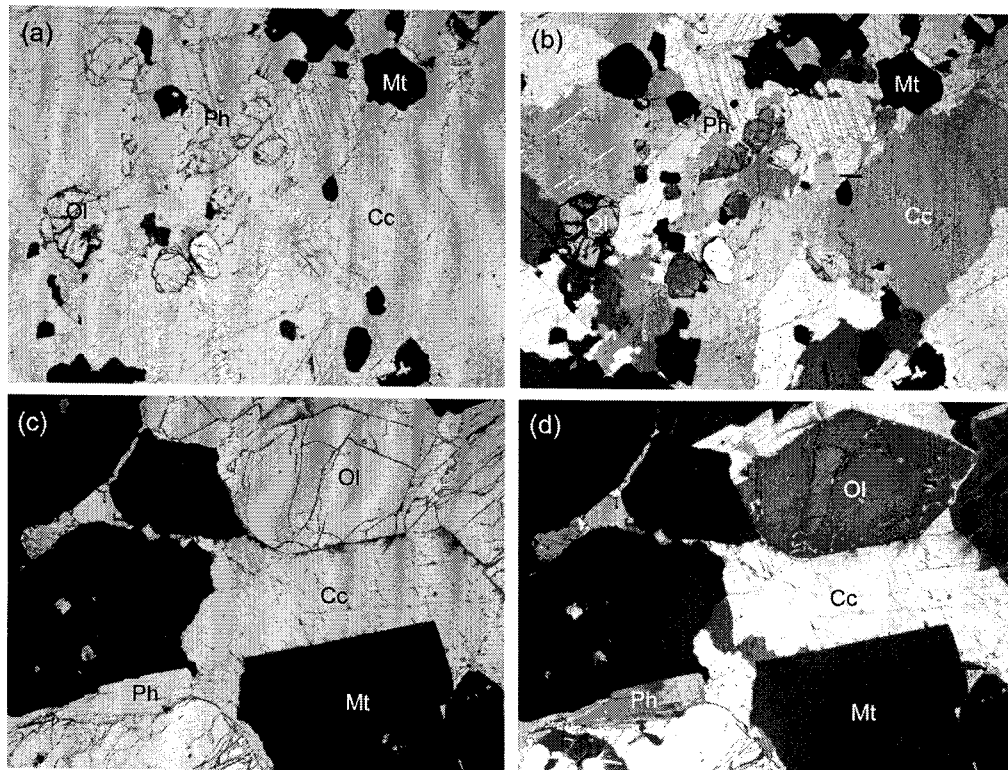


Fig. 2. Petrographic features of stage 2 phoscorite and carbonatite pair in the Kovdor PCC. (a) C2 calcite carbonatite (open), (b) C2 calcite carbonatite (cross), (c) P2 phoscorite (open) and (d) P2 phoscorite (cross). The widths of all photomicrographs are 6 mm. Note that phoscorite and carbonatite in the same stage basically share the same mineral assemblage. Olivine and magnetite usually occur as major euhedral minerals, whereas phlogopite occurs as subhedral to anhedral grains. Modal proportion of phlogopite is relatively small in early stages. Abbreviations: Ol, olivine; Ph, phlogopite; Mt, magnetite; Cc, calcite.

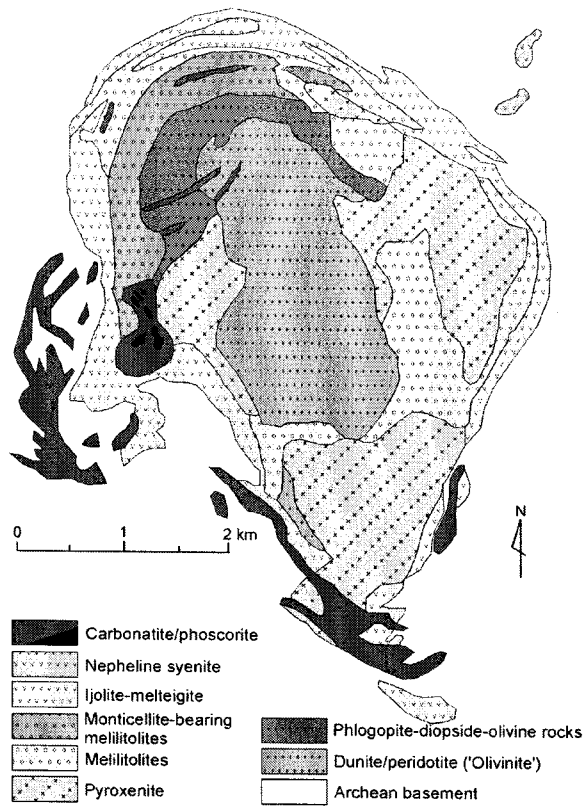


Fig. 3. Geological map of the Kovdor massif in the Kola Alkaline Province (after Ternovoy *et al.* 1969).

relative abundance of their rock-forming minerals: Forsterite-Magnetite (FM), Apatite-Magnetite (AM), Apatite-Forsterite-Magnetite (AFM), Calcite-Forsterite-Magnetite (CFM), Calcite-Magnetite (CM) and other varieties can be observed (Krasnova and Kopylova 1988) and are conventionally named by Russian investigators using abbreviations composed of the capitalized first letters of their prevailing minerals. Calcite carbonatites form veins, vein-like bodies and lenses, and the two late stages of dolomite carbonatites cut calcite carbonatites and phoscorites (Krasnova and Kopylova 1988).

The detailed map of the Magnetite open pit by Krasnova and Kopylova (1988) clearly shows how the phoscorites and carbonatites are associated, and that most structures (internal banding and contacts) are subvertical (Fig. 4). There is a zonal distribution of the early, and most important in volume, 'venue' of phoscorites: the zoning comprises an external zone, composed of AF rocks (Apatite-Forsterite phoscorite), located on contacts with the host ijolite series rocks, through AFM rocks (Apatite-Forsterite-Magnetite phoscorite), then to CFM rocks (Calcite-Forsterite-Magnetite

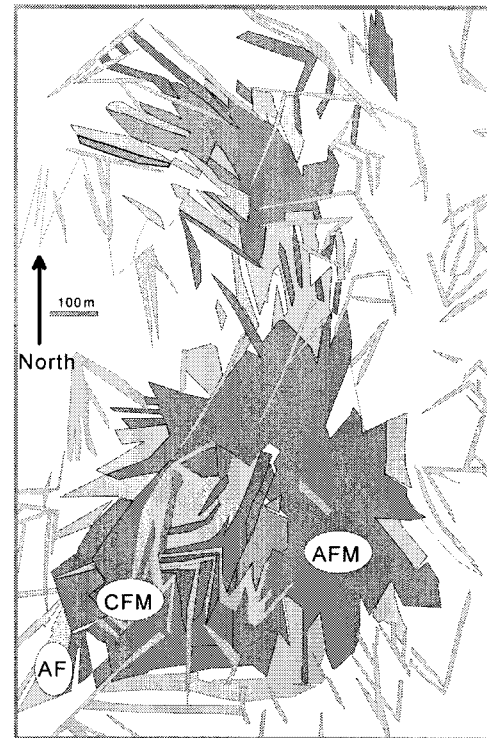


Fig. 4. Geological map of the Kovdor phoscorite-carbonatite complex (after Krasnova and Kopylova 1988).

phoscorite), and finally CM rocks (Calcite-Magnetite phoscorite). Although these four main minerals are present throughout the sequence, there is the following evolution in the dominant minerals: Apatite > Forsterite > Magnetite > Calcite.

4. General trends in the differentiation of PCC

Many PCCs commonly show two-stage sequences, with the emplacement of early phoscorites-carbonatites which form the bulk of the complex, followed by an intrusion of a smaller volume of phoscorites-carbonatites in the center, distinguished by the presence of tetraferriphlogopite and the enrichment of pyrochlore and other rare metal minerals. This sequence is typically found at Kovdor and Phalaborwa (where the late phoscorite is called 'transgressive foskorite') as well as at Sokli, Vuorijärvi and Turij Mys in the KAP. Silicate and magnetite contents generally decrease in later

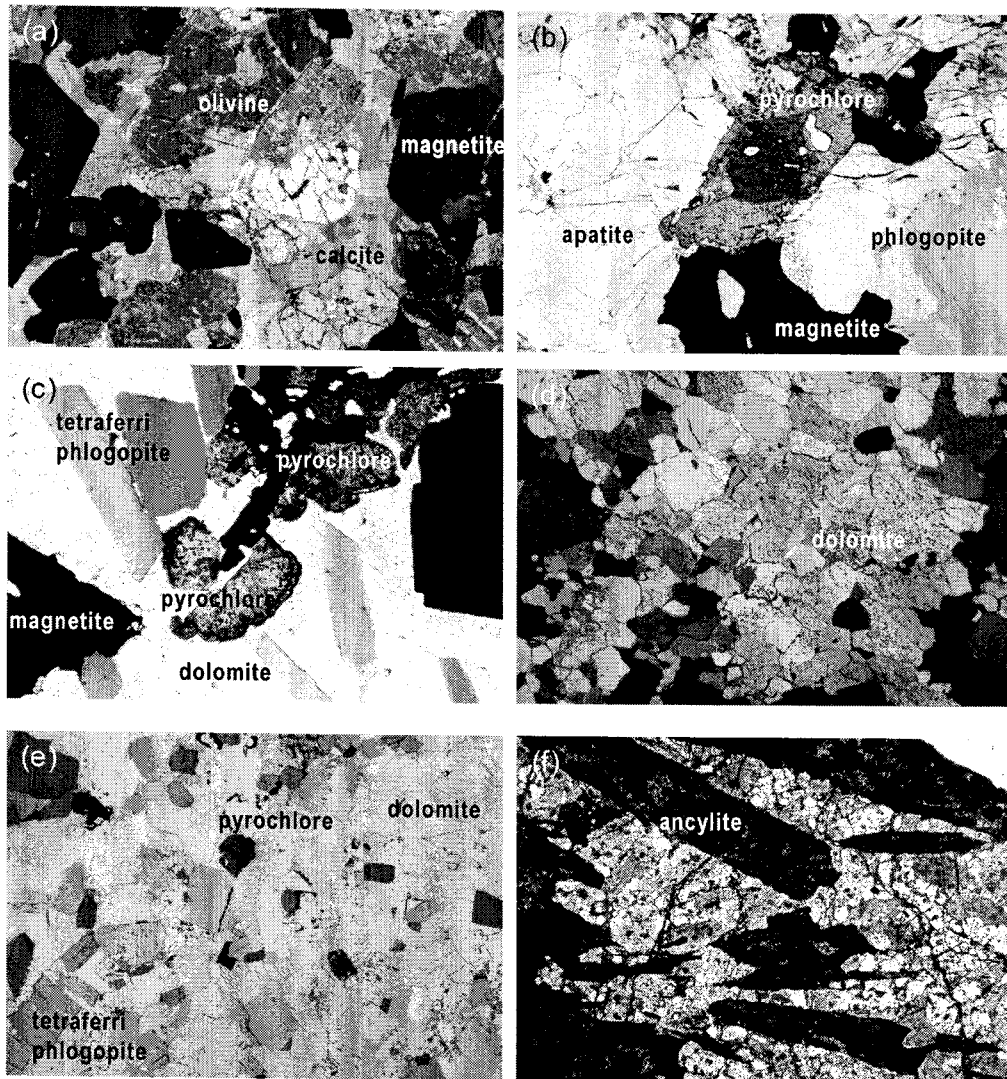


Fig. 5. Microscopic features of the Sokli phoscorites and carbonatites according to the evolutionary stages. (a) P1C1 rocks mainly consist of euhedral magnetite, olivine and calcite with subordinate apatite and phlogopite. Baddeleyite is the only Nb-Zr mineral (stage 1 phoscorite, cross, width = 1.3 mm), (b) Modal proportion of apatite and phlogopite in P2C2 rocks increases. U-Ta rich red pyrochlore begins to crystallize (stage 2 phoscorite, open, width = 2.5 mm), (c) Ce-Th rich yellow pyrochlore and euhedral tetraferriphlogopite are characteristic minerals in P3C3 rocks (stage 3 phoscorite, open, width = 2.5 mm), (d) Pure dolomitic D4 carbonatite (stage 4 dolomite carbonatite, cross, width = 1.3 mm), (e) Euhedral tetraferriphlogopite is the main silicate mineral in D5 dolomite carbonatite (stage 5 dolomite carbonatite, open, width = 6.3 mm) and (f) Ancyrite ($\text{SrCe}(\text{CO}_3)_2$) in D5 (stage 5 dolomite carbonatite, open, width = 6.3 mm).

stages, which consist of small volumes of carbonatite dikes, evolving from pure dolomitic carbonatite toward dolomite carbonatite and/or ferrocarbonatite containing Sr-Ba-REE-rich carbonates and rare phosphate minerals. The change of mineral paragenesis of the Sokli PCC from stage to stage illustrates well these evolutionary trends (Fig. 5).

5. The origin of PCC: metasomatic vs magmatic

The emplacement and differentiation of PCC have long been considered metasomatic processes, particularly by Kukhareenko *et al.* (1965) in their reference work on Caledonian complexes. For example, Epshteyn and Danil'chenko (1988) presented the following arguments for a metasomatic

origin for PCC, based mainly on observations at the Kovdor complex: (1) presence of spatial zoning of the 'apatite-magnetite deposit' with phoscorites in periphery, and a decrease in the number of minerals and a tendency toward monomineralic calcite in the inner zone; (2) occurrence of relics of host rocks in marginal parts and relics of rocks of the preceding zone in each succeeding zone; (3) dependence of mineral composition of the 'frontal part' on the composition of the host rocks (for example, phlogopite rocks appear only at the contact with nepheline pyroxenite due to inheritance of inert alumina).

Since the 1980's, numerous arguments against the metasomatic origin of the phoscorites have been suggested. The main arguments supporting the idea of a magmatic origin for PCC can be summarized as follows:

(1) phoscorites have sharp intrusive contacts with their host rocks; (2) mineral compositions of phoscorites and carbonatites are independent of those of country rocks; (3) absence of contact alterations, except for zones interpreted to have been formed by reaction or contamination processes; (4) presence of 'intra ore breccias' showing magmatic structures with xenoliths of olivinites, pyroxenites, melteigites, etc. suspended in a matrix of phoscorite-carbonatite composition (Balaganskaya *et al.* 2001); (5) thermometric investigation on melt and fluid inclusions in minerals gives a large range of temperatures from 800-900°C in early phoscorite and carbonatite pairs to 200-300°C in late carbonatites (Veksler *et al.* 1998a). This evidence leads to the conclusion that metasomatic origin for PCC is unreasonable because a metasomatic system cannot be maintained across such a high and actually reverse temperature gradient. Thermometric data, together with occurrence of magmatic breccias thus played an important role in firmly establishing the magmatic origin of the phoscorite-carbonatite system.

6. Genetic relationship between phoscorite and carbonatite

The question of the relation between phoscorite and carbonatite has been addressed by several authors, especially concerning the Kola complexes (Lapin 1982; Balaganskaya 1994; Zaitsev and Bell 1995). Until the period 1970-1980, a 'metasomatist' point of view was dominant in Russian literature. To account for the global organization of the phoscorites as a series of zones around a core composed of carbonatite dykes, phoscoritic rocks of the Kola complexes were long considered metasomatic rocks resulting from the progressive equilibration of infiltrating carbonate-rich

fluids with the host pyroxene-nepheline rocks.

Since the 1980's, numerous arguments, shortly reviewed in the above chapter, were found in favour of a magmatic origin of phoscorites. The magmatic origin is now widely accepted; several scenarios have been suggested to explain the strong contrast in bulk composition between phoscorites and carbonatites.

Most authors who studied these questions in some detail (e.g., Lapin 1982; Lapin *et al.* 1983; Balaganskaya 1994) noted that phoscorites and carbonatites appear to be pairs of conjugate rock types that share common mineral characteristics at each stage in their evolutionary trend.

The close relationship between the two rock types of a given stage suggests that they were derived from a common 'phoscoritic' magma; a carbonated silicate melt enriched in Fe(Ti)P. From a magmatic point of view, the chemical contrast between phoscorite and carbonatite may result from (1) solid-liquid (magmatic fractionation), (2) solid-solid (coeval accumulation) and (3) liquid-liquid (liquid immiscibility) separations or from a combination of these processes.

Magmatic fractionation

Traditional magmatic fractionation may produce phoscorite and carbonatite in a single magma chamber through differentiation crystallization or accumulation of early crystallizing phases. However, normal differentiation cannot explain the same mineral assemblage and most similar mineral compositions between phoscorite and conjugate carbonatite in the same evolutionary stage, but is only suitable for explaining the chemical and mineralogical differences of phoscorite-carbonatite pairs between the two different stages.

Considering the simple accumulation process, it can produce phoscorites as cumulative rocks and carbonatites as residual liquids; alternatively, carbonatites may also represent cumulative rocks crystallized from residual liquids. If one of them had been produced by simple accumulation, there should be differences in mineral compositions between early cumulates and rocks representing later differentiates or cumulates from them. However, as described in an earlier chapter, this is not the case of PCCs in the KAP.

Coeval accumulation process

It is also possible that carbonatites and phoscorites are not fractionated one from the other, but coeval crystallization products, more or less cumulative, from the same magma. If this is the case, their distribution in the field as

separate entities would result from a purely physical segregation operating at the site of emplacement. When a batch of 'phoscoritic' magma rises, cools and begins to crystallize, it can produce a crystal mush. Then, during emplacement, physical processes (gravity settling, filter pressing and/or elutriation) operate and sort the components of the mush according to density, grain size and shape.

This kind of segregation, well known in silicate systems, may introduce some peculiarities in carbonatitic, especially in the phoscoritic system. First, the low viscosity of the interstitial melts and the strong contrasts in physical properties (density, grain size) of the main minerals (apatite, olivine, magnetite and calcite) in the carbonate-rich magmatic system may produce an extensive sorting among early-crystallizing minerals of a crystal mush and thus lead the system to be highly sensitive to the segregation process. Secondly, although the database lacks an estimate of the density of phoscoritic magmas, it is probable that this density is intermediate between those of a carbonatite magma and a silicate magma, and significantly higher than that of calcite due to high contents of Si and Fe. This segregation process of a phoscoritic magma, as it rises through the conduits, will produce three terms: 1) a calcite 'floated cumulate', entrapping small amounts of fine-grained apatite, olivine and magnetite, 2) possibly an intermediate material, enriched in melt, and 3) a phoscoritic cumulate, enriched in coarse-grained olivine, magnetite, and apatite aggregates. According to this mechanism, both carbonatite and phoscorite should be highly cumulative, coeval crystallization products, from a common magma.

This process can explain the common crystallization history observed in phoscorite-carbonatite pairs in the KAP (Lee 2002), but has difficulty in accounting for the compositional gap between the two rock types; bulk compositions of the two rock types are clearly different, and the rocks having middle compositions are not to be found. What would be expected in this hypothesis is a layered cumulate having variable contents of calcite, magnetite and silicates and a gradual transition of carbonatite into phoscorite: a layered cumulate is indeed observed in some carbonatites, but it does not grade into the phoscorite compositions.

Liquid immiscibility

Another possible process of differentiation, considered by some authors (e.g., Lapin 1982), is that carbonatitic and phoscoritic materials differentiate from each other through liquid immiscibility, in which case the rocks observed are crystallization products from two conjugate

liquids that were produced by unmixing from the parental 'phoscoritic melt'. This process easily explains the chemical gap and different mineralogical records in the late stage of phoscorites and conjugate carbonatites.

Liquid immiscibility is a process that is often called for in discussions on carbonatite genesis (Ferguson and Currie 1971; Koster Van Groos 1975; Hamilton *et al.* 1979; Foley 1984; Le Bas 1977, 1987, 1989; Kjarsgaard and Hamilton 1988, 1989; Baker and Wyllie 1990; Lee and Wyllie 1996, 1997). Since Koster van Groos and Wyllie (1963), the experimental database on liquid immiscibility has been largely extended, but experiments are generally devoted to Si-Al-Na-K-Ca systems, generally highly enriched in alkalis and low in Fe-P. These simple systems cannot be applied directly to phoscoritic systems enriched in Fe-P-Ti. Relatively high contents of Fe, Ti and P found in phoscoritic systems can lead to another type of immiscibility between a melt enriched in Si and alkalis and a melt enriched in Fe, Ti, P and Ca (Philpotts 1982).

Various partition coefficients for carbonate/silicate melt are found in the literature (Jones *et al.* 1995; Brooker 1998; Veksler *et al.* 1998b). Some are obtained at low pressure (Veksler *et al.* 1998b, at 800-900 bars), and others at high

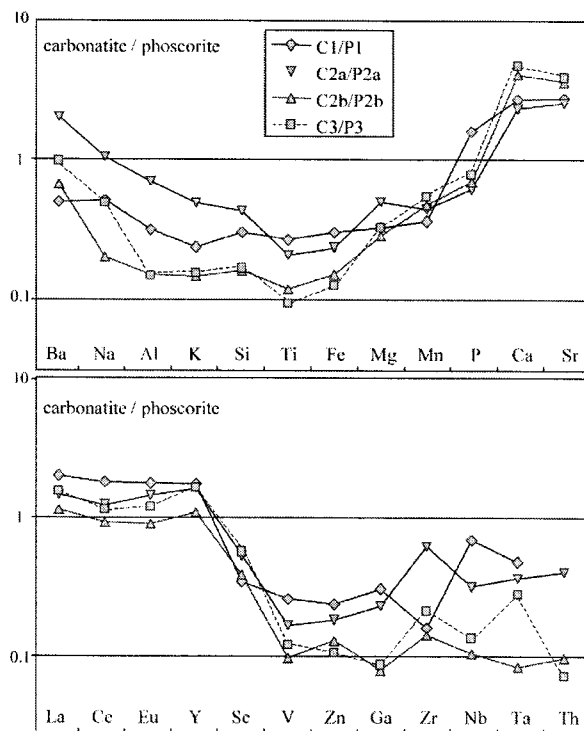


Fig. 6. Differences of element concentrations between carbonatite and conjugate phoscorite in the Sokli complex (Data from Lee 2002).

pressure (Brooker 1998, 10 kbar), but pressure does not seem to affect the general pattern. With an increasing degree of immiscibility, the compositional contrast increases. However, in most experiments with the exception of a series of runs by Brooker (1998), the relative order of preference does not change. The carbonate/silicate melt partition coefficients generally show the following order: for major elements, Al < Si < Ti < Fe < Mg < K < Na < Ca < F < P < CO₂, and for trace elements, Hf < Zr < Ta < Tm < Er < Y < Tb < Nb < Sm < Nd < Sr < Ba with some minor inversions between elements exhibiting similar behavior.

In the case of the Sokli complex, the global compositional differences between phoscorites and carbonatites are likely to match apparently with the general patterns obtained from these experiments, with a strong partition of Al, Si, Fe, Zr, Hf, Ta and Nb toward phoscorites (Fig. 6). However, it is not always consistent with experimental results. If such immiscibility between phoscorite and carbonatite liquids had occurred, it would be apparent in differences occurring in some interelement ratios (e.g., Zr/Nb or K/Al) that are known to be very sensitive to that process (Jones *et al.* 1995; Brooker 1998; Veksler *et al.* 1998b). The geochemical data of the Kola phoscorites and associated carbonatites do not show any significant differences in terms of these interelement ratios (Lee 2002).

However, this experimental misfit is still not conclusive because the individual roles of Fe, Si, P and carbonates in driving immiscibility are not fully understood. It should be noted that Fe(Ti)-enrichment in phoscorites is even more important than Si-enrichment, hence the relationships between a Fe-rich and a carbonate-rich system should be investigated in detail. P partitions much more strongly toward a carbonate melt in silicate-carbonate pairs, in which such a system has lower concentrations of Fe and P (Jones *et al.* 1995), than it does in its orientation toward silicate melt, but P is also an essential component of Fe-Ti-rich melts that are immiscible with silicate melts (Philpotts 1982), hence the potential effect of Fe on P partitioning needs to be evaluated.

7. Conclusions

Various hypotheses for the genesis of phoscorite-carbonatite complexes have been proposed during the last half-century. Recent mineralogical and petrological studies on PCCs in the KAP clearly show that phoscorites and associated carbonatites are differentiated from common 'carbonated silicate parental magma' and preclude the

simple idea that phoscorites are cumulates and carbonatites residual liquids. Instead, the hypotheses involving liquid immiscibility and coeval accumulation processes are favored to explain the mineralogical and geochemical characteristics of the phoscorite and carbonatite association. However, further work must be carried out as part of a more systematic study on mineralogy, petrology and geochemistry of PCCs, together with experimental studies on chemical and physical separation processes of phoscorite and associated carbonatite, in order to establish a more advanced petrogenetic model for PCC.

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References

- Balaganskaya, E.G. 1994. Breccias of the Kovdor phoscorite-carbonatite deposit of magnetite and their geological meaning. *Zapiski Vserossiyskogo Mineralogicheskogo Obshchestva*, 2, 24-36 (in Russian).
- Balaganskaya, E., N.I. Krasnova, and R. Liferovich. 2001. Brief description of Kovdor ultramafic-alkaline complex with carbonatites and associated mineral deposits. p. 25-78. In: *Formation, Exploration and Exploitation of Economic Deposits Associated with Mantle Carbon: Euro-Carb Workshop Excursion Guide*, eds. by S. Gehor, R. Liferovich and F. Wall. University of Oulu, Oulu.
- Barker, D.S. and P.J. Wyllie. 1990. Liquid immiscibility in a nephelinite-carbonatite system at 25 kbars and implications for carbonatite origin. *Nature*, 346, 168-170.
- Borodin, L.S., A.V. Lapin, and A.G. Kharchenkov. 1973. *Rare-metal bearing camaforites*. Nauka, Moscow, 176 p (in Russian).
- Brooker, R.A. 1998. The effect of CO₂ saturation on immiscibility between silicate and carbonate liquids: an experimental study. *J. Petrol.*, 39, 1905-1915.
- Epshteyn, Ye.M. and N.A. Danil'chenko. 1988. A spatial-genetic model of the Kovdor apatite-magnetite deposit, a carbonatite complex of the ultramafic, ijolite and carbonatite rock association. *Int. Geol. Rev.*, 30, 981-993.
- Ferguson, J. and K.L. Currie. 1971. Evidence of liquid immiscibility in alkaline ultrabasic dikes at Callander Bay, Ontario. *J. Petrol.*, 12, 561-585.
- Foley, S.F. 1984. Liquid immiscibility and melt segregation in the alkaline lamprophyres from Labrador. *Lithos*, 17,

- 127-137.
- Hamilton, D.L., I.G. Freestone, J.B. Dawson, and C.H. Donaldson. 1979. Origin of carbonatites by liquid immiscibility. *Nature*, 279, 52-54.
- Jones, J.H., D. Walker, D.A. Picket, M.T. Murrel, and P. Beate. 1995. Experimental investigations of the partitioning of Nb, Mo, Ba, Ce, Pb, Ra, Th, Pa and U between immiscible carbonate and silicate liquid. *Geochim. Cosmochim. Acta*, 59, 1307-1320.
- Kjarsgaard, B.A. and D.L. Hamilton. 1988. Liquid immiscibility and the origin of the alkali-poor carbonatite. *Mineral Magazine*, 52, 43-55.
- Kjarsgaard, B.A. and D.L. Hamilton. 1989. The genesis of carbonatites by immiscibility. p. 388-404. In: *Carbonatites, Genesis and Evolution*. ed. by K. Bell. Unwin Hyman, London.
- Kogarko, L.N., V.A. Kononova, M.P. Orlova, and A.R. Woolley. 1995. Alkaline Rocks and Carbonatites of the World: Part 2. Former USSR. Chapman and Hall, London, 225 p.
- Koster Van Groos, A.F. 1975. The effect of high CO₂ pressure on alkalic rocks and its bearing on the formation of alkalic ultrabasic rocks and the associated carbonatites. *Am. J. Sci.*, 275, 163-185.
- Koster Van Groos, A.F. and P.J. Wyllie. 1963. Experimental data bearing on the role of liquid immiscibility in the genesis of carbonatites. *Nature*, 199, 801-802.
- Kramm, U., L.N. Kogarko, V.A. Kononova, and H. Vartiainen. 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. and L.N. Kopylova. 1988. The geological basis for mineral technological mapping at the Kovdor ore deposit. *Int. Geol. Rev.*, 30, 307-319.
- Kukhareenko, A.A., M.P. Orlova, A.G. Bulakh, E.A. Bagdasarov, O.M. Rimskaya-Korsakova, E.I. Nefedov, G.A. Ilinskiy, A.S. Sergeev, and N.B. Abakumova. 1965. The Caledonian Ultramafic Alkaline Rocks and Carbonatites of the Kola Peninsula and Northern Karelia. Nedra Press, Leningrad, 772 p (in Russian).
- Lapin, A.V. 1982. Carbonatite differentiation process. *Int. Geol. Rev.*, 24, 1079-1089.
- Lapin, A.V. and H. Vartiainen. 1983. Orbicular and spherulitic carbonatites from Sokli and Vuorijärvi. *Lithos*, 16, 53-60.
- Le Bas, M.J. 1977. Carbonatite-Nephelinite Volcanism. Wiley, London, 347 p.
- Le Bas, M.J. 1987. Nephelinites and carbonatites. p. 55-88. In: *Alkaline Igneous Rocks*. eds. by J.G. Fitton and B.G.J. Upton, Geol. Soc. Spec. Publ., 30, Blackwell, London.
- Le Bas, M.J. 1989. Diversification of carbonatite. p. 428-447. In: *Carbonatites, Genesis and Evolution*. ed. by K. Bell, Unwin Hyman, London.
- Lee, H.Y., J.K. Park, and D.H. Hwang. 2002. Petrography of Hongcheon Fe-REE deposits. *J. Petrol. Soc. Korea*, 11, 90-102 (in Korean).
- Lee, M.J. 2002. Minéralogie, pétrographie et géochimie de l'association phoscorites-carbonatites dans le complexe alcalin de Sokli, Finlande. Ph.D. Thesis, Ecole des Mines de Saint-Etienne.
- Lee, W.J. and P.J. Wyllie. 1996. Liquid immiscibility in the join NaAlSi₃O₈-CaCO₃ to 2.5 GPa and the origin of calcic-carbonatite magmas. *J. Petrol.*, 37, 1125-1152.
- Lee, W.J. and P.J. Wyllie. 1997. Liquid immiscibility in the join NaAlSiO₄-NaAlSi₃O₈-CaCO₃ at 1.0 Gpa: implications for crustal carbonatites. *J. Petrol.*, 38, 457-469.
- Le matre, R.W., P. Bateman, A. Dudek, J. Keller, J. Lameyre, M.J. Le Bas, P.A. Sabine, R. Schmid, H. Sörensen, A. Streckeisen, A.R. Woolley, and B. Zanettin. 1989. *A Classification of Igneous Rocks and Glossary of Terms*. Blackwell, London, 193 p.
- Philpotts, A.R. 1982. Compositions of immiscible liquids in volcanic rocks. *Contrib. Mineral. Petrol.*, 80, 201-218.
- Russell, H.D., S.A. Hiemstra, and D. Groeneveld. 1954. The mineralogy and petrology of the carbonatite at Loolekop, eastern Transvaal. *Trans. Geol. Soc. South Africa*, 57, 197-208.
- Ternovoy, V.I., B.V. Afanasiev, and B.I. Sulimov. 1969. Geology and Prospecting of the Kovdor Vermiculite-Phlogopite Deposit. Nedra, Leningrad, 288 p (in Russian).
- Veksler, I.V., T.F.D. Nielsen, and S.V. Sokolov. 1998a. Mineralogy of crystallized melt inclusions from Gardiner and Kovdor ultramafic alkaline complexes: implication for carbonatite genesis. *J. Petrol.*, 39, 2015-2031.
- Veksler, I.V., C. Petibon, G.A. Jenner, A.M. Dorfman, and D.B. Dingwell. 1998b. Trace element partitioning in immiscible silicate-carbonate liquid systems: an initial experimental study using a centrifuge autoclave. *J. Petrol.*, 39, 2095-2104.
- Verhulst, A., E. Balaganskaya, Y. Kimarsky, and D. Demaiffe. 2000. Petrological and geochemical (trace elements and Sr-Nd isotopes) characteristics of the Paleozoic Kovdor ultramafic, alkaline and carbonatite intrusion (Kola Peninsula, NW Russia). *Lithos*, 51, 1-25.
- Woolley, A.R. 1989. The spatial and temporal distribution of carbonatites. p. 15-37. In: *Carbonatites, Genesis and Evolution*. ed. by K. Bell. Unwin Hyman, London.
- Yegorov, L.S. 1980. Rocks of the phoscorite series (apatite-magnetite ores) of the Yessey pluton and some general problems of the petrology, classification and nomenclature of the apatite-olivine-magnetite rocks of ijolite-carbonatite complexes. p. 39-60. In: *Alkaline Magmatism and the Apatite Potential of Northern Siberia*. Leningrad.
- Zaitsev, A. and K. Bell. 1995. Sr and Nd isotope data of apatite, calcite and dolomite as indicators of source, and the relationships of phoscorites and carbonatites from the Kovdor massif, Kola Peninsula, Russia. *Contrib. Mineral. Petrol.*, 121, 324-335.

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