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Rare earth elements in phoscorites and carbonatites of the Devonian Kola Alkaline Province, Russia: examples from Kovdor, Khibina, Vuoriyarvi and Turiy Mys complexes

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Abstract

The Devonian (ca. 385-360 Ma) Kola Alkaline Province includes 22 plutonic ultrabasic-alkaline complexes, some of which also contain carbonatites and rarely phoscorites. The latter are composite silicate-oxide-phosphate-carbonate rocks, occurring in close space-time genetic relations with various carbonatites. Several carbonatites types are recognized at Kola, including abundant calcite carbonatites (early- and late-stage), with subordinate amounts of late-stage dolomite carbonatites, and rarely magnesite, siderite and rhodochrosite carbonatites. In phoscorites and early-stage carbonatites the rare earth elements (REE) are distributed among the major minerals including calcite (up to 490 ppm), apatite (up to 4400 ppm in Kovdor and 3.5 wt.% REE_2O_3 in Khibina), and dolomite (up to 77 ppm), as well as accessory pyrochlore (up to 9.1 wt.% REE_2O_3) and zirconolite (up to 17.8 wt.% REE_2O_3). Late-stage carbonatites, at some localities, are strongly enriched in REE (up to 5.2 wt.% REE_2O_3 in Khibina) and the REE are major components in diverse major and minor minerals such as burbankite, carbocernaite, Ca- and Ba-fluocarbonates, ancylite and others. The rare earth minerals form two distinct mineral assemblages: primary (crystallized from a melt or carbohydrothermal fluid) and secondary (formed during metasomatic replacement). Stable (C-O) and radiogenic (Sr-Nd) isotopes data indicate that the REE minerals and their host calcite and/or dolomite have crystallized from a melt derived from the same mantle source and are co-genetic.

Keywords: Rare earth elements, Rare earth minerals, Phoscorites, Carbonatites, Kola Alkaline Province

1. Introduction

According to the International Union of Pure and Applied Chemistry, the rare earth metals are Sc, Y and the lanthanoids (La to Lu) (IUPAC, 2005). In mineralogy, usage of the term “rare earth elements” is usually restricted to the lanthanoids and yttrium (e.g., Henderson, 1996; Chakhmouradian and Wall, 2012) and this convention is used in this contribution.

The rare earth elements (REE) are present in various igneous, sedimentary and metamorphic rocks in highly variable amounts, e.g. from below 1 ppm in mantle rocks to several wt.% in carbonatites, and occur as trace elements in rock-forming minerals (substituting predominantly Ca) or form REE minerals *sensu stricto* (Chakhmouradian and Wall, 2012 and references herein). Alkaline silicate rocks, either A-type granitoids or peralkaline undersaturated syenites, and carbonatites show the strongest enrichment in REE and, unsurprisingly, the major productive and potentially productive REE deposits are found in these rocks, e.g., Bayan Obo in China, Mountain Pass in USA, Mt. Weld in Australia, Lovozero and Tomtor in Russia, Strange Lake in Canada (Möller, 1986; Orris and Grauch, 2002; Castor and Hedrick, 2006; BGS, 2011; Kynicky et al., 2012; Mariano and Mariano, 2012; Chakhmouradian and Zaitsev, 2012). Because of their importance for 21st century industry (Chakhmouradian and Wall, 2012; Hatch, 2012) rare earth demand and prices have been rising and they are the subject of intensive exploration world-wide.

Russia could become an important supplier of REE in the future. According to the official information from the Ministry of Natural Resources and Environment of the Russian Federation, demonstrated resources of REE in Russia on 1st January 2011 are 18.3 Mt REE_2O_3 and inferred resources are 9.5 Mt REE_2O_3 (Khramov, 2011). Mineral deposits of REE include Lovozero (nepheline syenites and foidolites: resources 7.1 Mt REE_2O_3, average ore content 1.12 wt.% REE_2O_3) and Khibina (also spelt Khibiny, apatite-nepheline rocks: resources 5.5 Mt REE_2O_3, average ore content 0.40 wt.% REE_2O_3), both located in the Kola Peninsula. Other deposits, located in Siberia, are Seligdar (metamorphosed apatite-carbonate rocks, often incorrectly described as carbonatites: resources 4.4 Mt REE_2O_3, average ore content 0.35 wt.% REE_2O_3) and Belaya Zima (carbonatites: resources 1.6 Mt REE_2O_3, average ore content 0.9 wt.% REE_2O_3). However, Lovozerskiy GOK mining company is the only current active producer of REE-bearing ore from the Lovozero complex: 1.28 Mt of loparite ore containing approximately 2300 tons REE_2O_3 was mined in 2010. Actual production of rare earth elements is even smaller, with just 1500 tons REE_2O_3 produced by the Solikamsk Magnesium Plant in 2010. Between 2001 and 2009 REE production varied between 1600 (in 2004) and 3800 (in 2001) tons REE_2O_3.

There are also several promising REE deposits which have been explored during recent years (Khramov, 2011), including the Tomtor carbonatite complex in Yakutia, Russia (e.g., Bagdasarov, 1997; Tolstov and Gunin, 2001; Frolov et al., 2003; Seltmann et al., 2010) with demonstrated ore resources of 1.18 Mt (for Nb_2O_5 cutoff grade 3.5 wt.%), and average content 9.53 wt.% REE_2O_3, 0.595 wt.% Y_2O_3, 0.048 wt.% Sc_2O_3 and 6.71 wt.% Nb_2O_5.

The Kola Peninsula has the potential to become one of a major suppliers of REE through the development of mining of several deposits: (1) eudialyte-bearing nepheline syenites from Lovozero (about 600 Mt ore resources with 0.6 wt.% REE_2O_3 and 3.2 wt.% ZrO_2), (2) perovskite-bearing carbonatitic, alkaline and ultramafic rocks from Afrikanda (up to 1000 tons REE_2O_3 annually as a by-product of perovskite mining), (3) zircon-bearing alkaline rocks from Sakhariok (about 3 Mt ore resources with 0.2 wt.% REE_2O_3, predominantly yttrium and heavy REE, and 0.8 wt.% ZrO_2), and (4) phoscorites and carbonatites in alkaline-ultrabasic complexes that form the Kola Alkaline Province (Petrov, 2004; Afanasev, 2011; Khramov, 2011).

The Kola Alkaline Province (northern Karelia, Kola Peninsula in Russia and north-eastern Finland) includes twenty two complexes consisting of various ultrabasic and alkaline rocks - olivinites, clinopyroxenites, diverse melilititic (turjaites, uncompahgrites, okaites) and diopside-nepheline rocks (melteigites, ijolites, urtites), and nepheline syenites, that range in age from ca. 385 to 360 Ma (Fig. 1) (Kukharenko et al., 1965; Gerasimovsky et al., 1974; Bulakh and Ivanikov, 1984; Bulakh et al., 2004; Kramm and Sindern, 2004; Reguir et al., 2010; Rukhlov and Bell, 2010; Arzamastsev et al., 2013). Carbonatites are known to occur in fourteen localities and six of these also contain phoscorites. These complexes have been intensively studied during the last eighty years due to their economic importance, particularly at Khibina (apatite deposits), Kovdor (baddeleyite-apatite-magnetite deposit) and Lovozero (loparite deposit) (Petrov, 2004). For example, Kovdor is the only currently active producer of baddeleyite concentrate in the world with shipment of about 8 000 tons in 2012 (EuroChem, 2012).

Recently, Kola carbonatites(±phoscorites)-bearing complexes have been also subject to several in-depth academic studies, including elucidating the origin and differentiation of ultrabasic/alkaline magmas, and their conditions of crystallization and late-stage alteration (Kramm et al., 1993; Kramm and Kogarko, 1994; Bulakh and Ivanikov, 1996; Ivanikov et al., 1998; Verhulst et al., 2000; Arzamastsev et al., 2000; Chakhmouradian and Zaitsev, 2002, 2004; Zaitsev and Chakhmouradian, 2002; Bell and Rukhlov, 2004; Sindern et al., 2004; Wall and Zaitsev, 2004a; Downes et al., 2005; Lee et al., 2006; Ivanyuk et al., 2010; Nivin, 2011; Arzamastsev and Arzamastseva, 2013). One of prominent features of the Kola carbonatites is their diverse mineralogy, particularly for accessory and minor minerals. In addition to typical carbonate and silicate carbonatitic minerals (i.e. calcite, dolomite, forsterite, phlogopite, tetraferriphlogopite, diopside), these rocks contain unique assemblages of a range of primary and subsolidus Nb and Zr minerals (pyrochlore, zirconolite, zirkelite, lueshite, catapleiite), rare earth minerals (burbankite, carbocernaite, ancylite, cordylite, kukharenkoite, mckelveyite) (e.g., Bulakh et al., 1998a, b, 1999, 2000; Kapustin, 1980; Zaitsev et al., 1996, 1998; Chakhmouradian and Mitchell, 1998; Krivovichev et al., 1998; Subbotin et al., 1999; Chakhmouradian and Williams, 2004; Wall and Zaitsev, 2004b). Even noble metal mineralization is known in carbonatites and phoscorites from Kovdor (Rudashevsky et al., 2004).

In this paper we present a review and discussion on previously published REE data, as well as new geochemical and mineralogical data for the REE and their minerals in Kola phoscorites and carbonatites, particularly from the Kovdor and Khibina complexes.

2. Phoscorites and carbonatites

2.1. Phoscorites

Phoscorites are a rare rock type: compared with carbonatites, which are known from 527 localities worldwide (Woolley and Kjarsgaard, 2008a, b), phoscorites occur in just 21 complexes, mainly in Kola (Russia and Finland) and Maymeicha-Kotui provinces (Russia), with single examples known also from Africa and America (e.g., Phalaborwa in South Africa, Catalão in Brazil) (Russell et al., 1954; Borodin et al., 1973; Vartiainen, 1980; Egorov, 1991; Yegorov, 1993; Krasnova et al., 2004a; Ribeiro et al., 2005; Cordeiro et al., 2010). Phoscorite is a plutonic rock, consisting of magnetite, forsterite, apatite, diopside, phlogopite, tetraferriphlogopite, magnesio-arfvedsonite, richterite, calcite and dolomite in various proportions, occurring in close spatial, time and genetic relationships with carbonatites (Zaitsev and Bell, 1995; Amelin and Zaitsev, 2002; Krasnova et al., 2004b).

Phoscorites, and associated carbonatites, form multi-phase intrusions with several mineralogical varieties for both rocks. The best studied and described in scientific literature are the phoscorites from the Kovdor ultrabasic-alkaline complexes (Krasnova et al., 2004b and references therein). Geological mapping of the active mining quarry (about 2.3 to 1.6 km in diameter and 300 m depth) and an intensive drilling program have shown the distribution of phoscorites and carbonatites to occur over 3.5 km^2 and to a depth of about 1.7 km. At least nine mineralogical varieties of phoscorites, grouped into three stages according to their relative time of formation, are known at Kovdor (Krasnova and Kopylova, 1988; Krasnova et al., 2004b). The observed diversity of phoscorites is due to significant variations in contents of forsterite, magnetite, apatite, phlogopite, tetraferriphlogopite, calcite and dolomite.

Phoscorites from other Kola localities can be forsterite-free, and they contain diopside or aegirine (Turiy Mys, Seblyavr and Khibina), and some of them are enriched in phlogopite (Sokli and Khibina), and magnesio-arfvedsonite and richterite (Vuoriyarvi) (Lapin, 1979; Bulakh and Ivanikov, 1984; Zaitsev, 1996; Karchevsky and Moutte, 2004; Lee et al., 2004).

These observed variations in mineralogy are well illustrated by whole-rock compositions of phoscorites from Kovdor, Turiy Mys, Vuoriyarvi and Khibina, particularly for the major components. Figure 2 illustrates the wide ranges in SiO_2, Fe_2O_3, CaO, P_2O_5, K_2O and Na_2O (Tables 1-2, Supplementary Table 1). The extreme heterogeneity of phoscorites, both in content of minerals and grain sizes, makes it difficult to obtain a representative sample for each rock variety. Therefore only relatively small samples (0.1-1.0 kg) were analysed, and the observed compositional data may reflect small-scale variation in the phoscorite mineralogy.

2.2. Carbonatites

Kola carbonatites are variable in their mineralogy, and all carbonatite mineralogical varieties (with the exception of alkaline nyerereite-gregoryite carbonatites) are known here. These varieties include calcite, dolomite, ankerite, kutnahorite, magnesite, siderite and rhodochrosite carbonatites (Kukharenko et al., 1965; Kapustin, 1980; Bulakh and Ivanikov, 1984; Zaitsev and Polezhaeva, 1994; Zaitsev, 1996; Zaitsev et al., 1998, 2004). Carbonatites, as well as phoscorites, typically form complex intrusions with calcite carbonatites as the youngest intrusive phase and dolomite-ankerite (rarely magnesite, siderite and rhodochrosite) carbonatites as the latest rocks in succession of carbonatite formation. Carbonatites, particularly those from Kola, are often divided into “early-“ and “late-stage” carbonatites. Both terms were introduced by Kapustin (1980), and they reflect differences in geological position, mineralogy, geochemistry and formation mechanism of the carbonatites.

The Kola carbonatites are polygenetic in origin, and are represented by plutonic magmatic (at Kovdor), magmatic-carbohydrothermal (at Khibina) and magmatic-carbohydrothermal-metasomatic rocks (at Sallanlatvi) (Bukah and Ivanikov, 1984; Zaitsev, 1996; Zaitsev et al., 2004). The final stage in carbonatite evolution is crystallization of carbonate-zeolite rocks that form cross-cutting veins, where the minerals have crystallized from hydrothermal solutions and also partially replace wall rocks (Zaitsev, 1996; Zaitsev et al., 1998).

Carbonatite dykes with calcite phenocrysts, fine-grained dolomite-calcite groundmass and quench textures at dyke margins are known from Kandalaksha and Turiy Mys (Bukah and Ivanikov, 1984; Ivanikov et al., 1998). Some dykes contain significant amounts of fluorite. Poorly studied are the carbonatitic rocks from Kontozero palaeovolcanic complex, where interbedded calcite carbonatite lavas and pyroclastic rocks form a 1000 m thick deposit in a caldera depression (Pyatenko and Saprykina, 1976; Pyatenko and Osokin, 1988).

The major chemical compositions (CaO, MgO, FeO and MnO) of the Kola carbonatites (Tables 1-2, Supplementary Table 2) are shown on Figure 3, and all compositional carbonatite types (calcio-, magnesio-, ferro- and manganocarbonatites) are clearly distinguished one from another.

2.3. Succession of phoscorite-carbonatite formation

The results of geological mapping and drill-core investigation of multi-stage phoscorite-carbonatite complexes, such as at Kovdor, Vuoriyarvi, Seblyavr, Turiy Mys and Khibina, and the geochemical data indicate a great diversity in these rocks that differ in relative time formation, mineralogy and geochemistry (e.g., Kukharenko et al., 1965; Lapin, 1979; Bulakh and Ivanikov, 1984; Subbotin and Subbotina, 2000; Wall and Zaitsev, 2004a). At least 15 rock varieties have been distinguished among Kola phoscorites and carbonatites (Table 3). Of note is that the precise geochronology, using various mineral and isotopic systems, suggests relatively short time periods for the various phoscorite-carbonatite formations. For example, no age differences were detected for the emplacement of the various phoscorites and carbonatites at the Kovdor complex, with the best estimate of phoscorite-carbonatite crystallization given as 378.64 ± 0.23 Ma (Amelin and Zaitsev, 2002).

3. Rare earth elements in phoscorites and carbonatites

Numerous mineralogical studies and some limited geochemical data have been published for Kola phoscorites and carbonatites, and these studies show the existence of two rock groups with quite different REE contents and REE distribution between coexisting minerals (Kukharenko et al., 1965; Borodin et al., 1973; Samoilov, 1984; Verhulst et al., 2000; Dunworth and Bell 2001; Lee et al., 2004).

The first group includes phoscorites, early-stage calcite carbonatites and some of late-stage dolomite-ankerite carbonatites (e.g., at Kovdor, Turiy Mys). These rocks are characterized by low REE contents (with an upper level of approximately 1800-2000 ppm in phoscorites, and 1500-2200 ppm in carbonatites), and with the REE concentrated in the major rock-forming minerals, calcite and apatite, as well as accessory pyrochlore and zirconolite. Rare earth minerals *sensu stricto* are typically absent, but carbocernaite was observed as exsolution lamellae in calcite from early Khibina carbonatites, and burbankite was identified as a daughter mineral in inclusions in magnetite from the Sallanlatvi calcite carbonatites (Zaitsev et al., 2004).

The second group is late-stage carbonatites (calcite, dolomite, ankerite, kutnahorite, magnesite, siderite and rhodochrosite), where the concentration of REE oxides reaches several weight percent (up to 5.2 wt.% REE_2O_3) – the best examples are at Khibina, Vuoriyarvi, Sallanlatvi and Seblyavr. These rocks contain various major and minor minerals in which the REE occupy an individual crystallographic site and form a distinct mineral species (Kukharenko et al., 1965; Kapustin, 1980; Bulakh et al., 1998b; Subbotin et al., 1999; Zaitsev et al., 1998; Wall and Zaitsev, 2004b).

3.1. REE as trace elements

Trace element (including REE) geochemistry of phoscorite is poorly studied. Only a few compositional data are available since the first description of phoscorites by Russell et al. (1954), not only for Kola rocks, but also for phoscorites from other localities (e.g., Kravchenko and Bagdasarov, 1987; Kogarko et al., 1997; Cordeiro et al., 2010).

The average REE_2O_3 content in Kola phoscorites was estimated as 0.266 wt.% by Kukharenko et al. (1965), and a small number of recently published analyses for Kovdor and Sokli phoscorites show a wide range in REE content, from 48 to 1144 ppm (Verhulst et al., 2000; Lee et al., 2004).

Our new compositional data for the Kola phoscorites are based on 22 analyses for Kovdor rocks, 27 analyses for Vuoriyarvi, 16 analyses for Turiy Mys and 3 analyses for Khibina (Supplementary Table 1). For comparison, three phoscorite samples from the Phalaborwa complex were also analyzed for major, minor and trace elements. Table 4 shows variations in REE contents of various phoscorite varieties within each studied complex. Overall, the REE content varies from 8 ppm in forsterite-magnetite phoscorite (from Kovdor) to 1950 ppm in biotite-aegirine-apatite phoscorite (from Khibina). The Kovdor phoscorites contain 8-521 ppm REE, whereas higher REE values are observed for Turiy Mys and Vuoriyarvi (26-976 and 69-1860 ppm, respectively), and the highest level of REE is in Khibina rocks (1931-2479 ppm). Phoscorites from Phalaborwa, which are mineralogically similar to Kovdor, contain 1111-1335 ppm REE, close to the value of 1256 ppm published by Hornig-Kjarsgaard (1998) for a single phoscorite sample from Phalaborwa.

Low concentrations of REE are typical for phoscorites enriched in silicate minerals and magnetite, e.g. Turiy Mys diopside-bearing phoscorites (26 ppm REE), Kovdor forsterite-magnetite (up to 51 ppm) and forsterite-dolomite-magnetite phoscorites (28 ppm). Much higher levels of REE are common for calcite- and/or apatite-bearing phoscorites (apatite-forsterite-magnetite and calcite-apatite-forsterite-magnetite varieties), with REE enrichment in the tetraferriphlogopite-bearing phoscorites, e.g. 483-521 ppm at Kovdor, 1141-1860 ppm at Vuoriyarvi and 976 ppm at Turiy Mys. Apatite-rich and magnetite-free phoscorites from the Khibina complex have the highest concentrations of REE (1931-2479 ppm).

All Kola phoscorites are characterized by a strong enrichment in light REE with La concentration factor (La_{CN} = La concentration in phoscorite/La concentration in chondrite) between 7.6 and ca. 1500 (1700-2100 for Khibina phoscorites). Excluding samples enriched in magnetite and silicates with low REE content, the La_{CN} value always exceeds 100. Heavy REE are present only at low levels, and Lu_{CN} values for some Kola phoscorites are 0.8-6.3 (Kovdor), 2.0-6.7 (Turiy Mys, with 23.2 in a single sample), 2.0-28.7 (Vuoriyarvi) and 19-22 (Khibina). Chondrite normalized rare earth element distributions (Fig. 4) indicate highly fractionated patterns with $(La/Lu)_{CN}$ ratios typically 25-80 for calcite- and apatite-poor phoscorites, increasing in tetraferriphlogopite-bearing phoscorites to $(La/Lu)_{CN}$ = 42-212.

In contrast to phoscorites, carbonatites, including those from Kola, are much better studied and a greater amount of compositional data, including those for the REE, has been published (e.g. Eby, 1975; Möller et al., 1980; Samoilov, 1984; Hornig-Kjarsgaard, 1998). Carbonatites are characterized by large variations in REE contents, e.g. data for eight carbonatite complexes from Europe, America and Africa range from 600 to 6000 ppm REE (Hornig-Kjarsgaard, 1998). There are several carbonatite complexes with anomalously high concentrations of REE (> 1 wt.% REE_2O_3), for example, the Tomtor dolomite-ankerite carbonatites with 1.3-3.0 wt.% REE_2O_3 (Bagdasarov, 1997), Sarnu calcite carbonatite with ca. 5.5 wt.% REE_2O_3 (Wall et al., 1993), and Arshan carbonatites with up to 9.8 wt.% REE_2O_3 (Ripp et al., 2000).

The Kola carbonatites contain both REE-poor and REE-rich rocks. All early-stage carbonatites, in terms of Kapustin (1980), are REE-poor rocks, and late-stage carbonatites are characterized by highly variable contents of REE (Supplementary Table 2).

The early carbonatites are calcitic in composition and contain the same non-carbonate minerals as the co-existing phoscorites. The concentrations of REE in the carbonatites vary from 153 ppm (Turiy Mys carbonatites with tetraferriphlogopite) to 1441 ppm (Vuoriyarvi carbonatites with tetraferriphlogopite) (Table 5). Khibina and Sallanlatvi carbonatites are relatively enriched in REE, with ca. 2000 and 467-3049 ppm respectively. However, while rare earth enrichment at Khibina is a primary feature, those Sallanlatvi rocks that are relatively enriched in REE show evidence for hydrothermal alteration accompanied by the formation of secondary REE-rich mineral(s) (Zaitsev et al., 1998, 2004).

Late-stage Kola carbonatites are diverse rocks with a wide variety of major and minor minerals in different complexes (Table 3), and they also display large variations in REE (Table 5). Low levels of REEs are typical for dolomite (±ankerite) carbonatites from Kovdor and Turiy Mys (72-244 and 38 ppm respectively), and also for the magnesite- and siderite-bearing carbonatites from Sallanlatvi (1191-4887 and 124-597 ppm respectively), these values being similar to those observed in early-stage calcite carbonatites.

As in phoscorites, the Kola carbonatites are characterized by strong enrichments in light REE with La_{CN} ratios of 47-829 in Kovdor carbonatites, 35-764 (Turiy Mys), 406-2547 (Vuoriyarvi), 62-4975 (Sallanlatvi) and 1917 (Khibina). Heavy REE contents are typically low with Lu_{CN} ratios of 0.8-9.1 in Kovdor carbonatites, 1.2-12.6 (Turiy Mys), 1.9-18.9 (Sallanlatvi) and 19.4 (Khibina). The $(La/Lu)_{CN}$ ratio in carbonatites from Kovdor, Turiy Mys, Vuoriyarvi and Khibina ranges from 9.3 to 117, with higher values (up to 1230) in the hydrothermally altered Sallanlatvi carbonatites (Fig. 5).

3.1.1. REE in major and minor minerals

Clearly, the REE contents in phoscorites and carbonatites depend on the mineral components of the rock, and variations in the proportions of calcite and apatite strongly influence the observed values. Both calcite and apatite are known to contain REE as trace elements, and apatite can indeed accommodate high concentrations of REE (Eby, 1975; Yegorov, 1984; Hughes et al., 1991; Hornig-Kjarsgaard, 1998; Bühn et al., 2001). Other minerals that play an important role in the REE distribution in phoscorites and carbonatites are the accessory Nb and Zr bearing minerals (e.g., pyrochlore group minerals, zirconolite, calzirtite) that can contain considerable amounts of REE (Williams, 1996; Subbotin and Subbotina, 2000; Chakhmouradian and Williams, 2004).

Available data suggest that silicate minerals, such as forsterite, mica- and pyroxene-group minerals in phoscorites and carbonatites, can also incorporate REE to some degree (from 8 ppm in forsterite up to 529 ppm in biotite) (Eby, 1975; Kravchenko and Bagdasarov, 1987; Shramenko et al., 1992), and presence of REE was also reported for magnetite (10-208 ppm) (Bulakh and Ivanikov, 1984; Kravchenko and Bagdasarov, 1987; Viladkar and Pawaskar, 1989).

Recently, Reguir et al. (2008, 2009, 2012) reported major- and trace-element compositions of magnetite, phlogopite, pyroxene- and amphibole-group minerals using EPMA and laser ablation ICP-MS analysis from various carbonatite localities worldwide. They found that the REE were present in phlogopite only at low concentration levels, typically up to 3 ppm, and rarely up to 10 ppm (Reguir et al., 2009). Pyroxene- and amphibole-group minerals show a relatively higher degree of REE enrichment compared with phlogopite (Reguir et al., 2012). Clinopyroxene, diopside, aegirine–augite and aegirine can accommodate up to 151 ppm REE, but can also contain as low as 0.4 ppm. A diverse variety of amphibole-group minerals occuring in carbonatites (tremolite, magnesiohastingsite, richterite, magnesio-arfvedsonite, ferri-winchite) also contain variable amounts of REE that range from 0.5 ppm in sodic amphiboles to 1070 ppm in calcic amphiboles. However, mass-balance calculations show that pyroxene- and amphibole-group minerals do not play a significant role in the total whole rock budget of REE as these minerals accumulate only up to 3% of the total REE (Reguir et al., 2012).

These spatially-resolved analyses indicate that the high concentrations of REE determined on bulk samples are more likely to reflect the presence of micro-inclusions in the analyzed samples than to be the intrinsic concentrations of REE in silicate minerals. The REE also cannot be considered as substituting components in magnetite (see review of magnetite composition in carbonatites by Reguir et al. (2008)), and these observed values are probably due to the presence of inclusions of minerals such as zirconolite and/or pyrochlore in the analysed bulk samples.

More compositional data are available for calcite, dolomite and apatite from phoscorites and carbonatites. However, much of the published data, particularly between 1965 and 2000, were obtained for bulk mineral samples and sample contamination cannot be excluded. The probable contamination effect is supported by the observed wide range in REE contents in minerals from the same locality, and even from same outcrop. Total concentration of REE in calcite range from 170 to 2140 ppm (e.g., Eby, 1975; von Maravic and Morteani, 1980; Möller et al., 1980; Hornig-Kjarsgaard, 1998), and dolomite is also characterized by varying contents of REE from 64 to 1280 ppm (e.g., Kukharenko et al., 1965; Balashov and Pozharitskaya, 1968; Khomyakov and Semenov, 1971; Möller et al., 1980; Hornig-Kjarsgaard, 1998; Viladkar and Pawaskar, 1989). Laser ablation ICP-MS analyses of carbonates from the Spitskop carbonatites suggests that REE concentrations are much lower in carbonate minerals: 22-73 ppm in calcite and 51-58 ppm in dolomite (Ionov and Harmer, 2002). However, one of analysed samples revealed extremely high REE content in calcite (1377-3030 ppm).

Among the major and minor minerals in phoscorites and carbonatites, apatite shows the highest capacity to accommodate the REE (e.g., Kukharenko et al., 1965; Kapustin, 1980; von Maravic and Morteani, 1980; Yegorov, 1984; Hogarth, 1989; Hornig-Kjarsgaard, 1998, Bühn et al., 2001; Krasnova et al., 2004a). Typically, the REE contents of apatite from phoscorites and carbonatites vary between 0.05 and 1 wt.% REE_2O_3, rarely reaching 1.5-2.0 wt.%. Typically the REE concentrations in apatite increase from early to late formed phoscorites and carbonatites (e.g. Yegorov, 1984; Krasnova et al., 2004a). An exception is apatite reported from the Oka and Otjisazu calcite carbonatites where this mineral contains 2.6-3.4 wt.% REE_2O_3 and 3.1-4.9 wt.% REE respectively (Hornig-Kjarsgaard, 1998; Bühn et al., 2001), and an anomalously REE-rich apatite was described from Oka melilite-calcite carbonatites containing 7.2 and 10.9 wt.% REE (Hughes et al., 1991).

3.1.1.1. REE in Kovdor phoscorites and carbonatite minerals

To produce a comprehensive data set for the Kovdor phoscorites and carbonatites, we have used laser ablation ICP-MS analysis to determine the concentrations of trace elements, including REE, in major and minor minerals, including forsterite, phlogopite, tetraferriphlogopite, magnetite, calcite, dolomite and apatite, from nine varieties of the Kovdor phoscorites and carbonatites (Table 1, Supplementary Table 3).

Forsterite, phlogopite, tetraferriphlogopite and magnetite in all of the phoscorite and carbonatite samples studied contain individual REE at levels below detection limits (Supplementary Table 4). For most of the elements the lower detection limit is 0.15-0.05 ppm, and, in rare cases, 0.5-0.4 ppm. This suggests that previously published relatively high concentrations for these minerals from phoscorites and carbonatite, including Kovdor, which were determined in bulk samples, do not actually represent REE accommodated into the crystal structure of these minerals, but are likely to result from the presence of inclusions of micro-crystals of REE-bearing minerals in forsterite, phlogopite and magnetite.

Prior to LA ICP-MS analyses of calcite, dolomite and apatite, all samples were investigated using cathodoluminescence (CL) and scanning electron microscopy (SEM) to establish any heterogeneity within each crystal and to select only those with no sign of secondary alteration.

Cathodoluminescence studies revealed several features: (1) calcite in phoscorites and carbonatites is typically characterized by a uniform CL colour with variations in yellow, orange and red. However, calcite grains with well-developed zoning were observed in one phoscorite sample (Fig. 6a, b); (2) dolomite also displays a uniform colour with only a few grains displaying minor zonation; (3) nearly all apatite crystals are strongly zoned from core to rim (Fig. 6c), and SEM observation shows that the apatite crystals are typically characterized by fine oscillatory-type zoning.

Calcite from the Kovdor phoscorites and carbonatites show relatively small variations in REE compared to published data (see above), ranging from 231 and 490 ppm REE (Table 6, Fig. 7). Coexisting phoscorite-carbonatite pairs (calcite-rich phoscorite and calcite carbonatites) have different levels of REE in calcite from each phoscorite and carbonatite pair. In early formed rocks (with minor phlogopite) calcite from phoscorite displays enrichment in REE over calcite from carbonatite (357-490 versus 231-265 ppm respectively), whereas in late formed rocks (with minor tetraferriphlogopite) calcite in phoscorite is depleted in REE compared with calcite from carbonatite (373-420 versus 440-479 ppm).

REE distribution patterns within all the analysed calcite crystals are similar with increasing REE contents from core to rim (Table 6). Calcite from three samples have similar differences in REE content between crystal core and rim (31-47 ppm REE), whereas calcite from phoscorite with phlogopite is characterized by a greater difference of 133 ppm. Calcite is enriched in light REE relative to heavy REE and there is a positive relationship between total REE content and La/Lu_{CN}

ratio with highest degree of fractionation (78.3-97.3) observed in calcite with the highest REE content (Fig. 7).

Compared to calcite, dolomite contains less REE with total contents in various phoscorites and carbonatites ranging from 19 and 139 ppm (Table 7, Fig. 7). Accessory dolomite from calcite phoscorites and carbonatites, and dolomite from the dolomite phoscorites and carbonatites contain similar amounts of REE: 20-61 and 19-77 ppm respectively. An exception is one crystal in dolomite carbonatite that contains 139 ppm REE in the crystal core.

Core-to-rim REE distributions in dolomite from various phoscorites and carbonatites do not display any particular trend, and REE concentrations can either increase or decrease from core to rim, or be unchanged. Dolomite is also enriched in light rare earths over heavy rare earths with La/Lu_{CN} ratios between 107 and 233 in dolomite from calcitic rocks and 50-112 in dolomite from dolomitic phoscorites and carbonatites (Fig. 7).

As expected, apatite in both phoscorites and carbonatites from Kovdor has significantly higher REE contents than calcite or dolomite. Apatite contains between 181 ppm REE in dolomite phoscorite and 4404 ppm REE in calcite carbonatite with tetraferriphlogopite (Table 8, Fig. 7). The highest contents of REE (4260-5980 ppm La+Ce+Pr+Nd+Sm) were determined by electron microprobe analyses of apatite from dolomite carbonatite.

The REE concentration in apatite in a series of successively formed phoscorites and carbonatites does not show gradational changes; instead it displays a stepwise change (Fig. 7). However, the average calculated content of REE in apatite (Table 9) has a tendency to increase from early formed rocks (apatite-forsterite±magnetite phoscorite) to late dolomite carbonatite (with the exception of dolomite phoscorites). These data support early observations for REE distributions in apatite from early and late formed Kovdor phoscorites and carbonatites (Zaitsev and Bell, 1995).

REE contents for apatite from the Kovdor phoscorites and carbonatites are similar to those from other Kola localities (e.g., Karchevsky and Moutte, 2004; Lee et al., 2004; Zaitsev at al., 2004). Only apatite from the Khibina phoscorites and carbonatites is characterised by REE enrichments, with 0.1-1.2 wt.% REE_2O_3 in apatite from phoscorites and early-stage carbonatites, and 1.4-3.5 wt.% REE_2O_3 in apatite from late-stage carbonatites (Supplementary Table 5).

3.1.2. REE in accessory minerals

Several accessory minerals in phoscorites and carbonatites contain REE as minor and sometimes major components. These accessory minerals are primarily complex oxides of Nb and Zr, pyrochlore-group minerals (pyrochlore, uranpyrochlore, strontiopyrochlore), perovskite-group minerals (perovskite, lueshite, loparite), zirconolite, zirkelite and calzirtite (e.g. Kukharenko et al., 1965, Kapustin, 1980; Pozharitskaya and Samoilov, 1972; Borodin et al., 1973; Bulakh and Ivanikov, 1984; Hogarth, 1989; Bulakh et al., 1999; Chakhmouradian and Zaitsev, 1999; Subbotin and Subbotina, 2000, Chakhmouradian and Williams, 2004; Zaitsev et al., 2004).

At Kovdor the rare earth-bearing minerals are pyrochlore, uranpyrochlore and zirconolite (e.g. Kukharenko et al., 1965; Kapustin, 1980; Strelnikova and Polezhaeva, 1981; Williams, 1996; Subbotin and Subbotina, 2000; Chakhmouradian and Williams, 2004). It is quite common to observe pyrochlore and zirconolite in association with baddeleyite, and their order of formation (baddeleyite → zirconolite → pyrochlore) is clearly seen in Figure 8.

New data based on 72 microprobe spot analyses of pyrochlore-group minerals indicate the presence of several distinct compositions occurring in various phoscorite and carbonatite varieties (Table 10):

(1) REE- and Ta-rich pyrochlore in calcite-forsterite-magnetite phoscorites, with 13.2-20.7 wt.%, Ta_2O_5 and 4.7-9.1 wt.% REE_2O_3;

(2) REE-poor, Ta-rich uranpyrochlore in phoscorites and carbonatites containing tetraferriphlogopite (5.8-18.1 wt.% Ta_2O_5, 11.6-21.1 wt.% UO_2 and 0.5-1.3 wt.% REE_2O_3;

(3) REE-poor, Ta-rich pyrochlore with bariopyrochlore rims in dolomite-forsterite-magnetite phoscorites and with similar amounts of rare earths in both minerals (0.6-1.0 wt.% REE_2O_3);

(4) REE-bearing, Ba-rich pyrochlore in dolomite carbonatites, with 1.1-3.4 wt.% REE_2O_3.

Pyrochlore-group minerals contain only light REE (La, Ce, Pr, Nd and rarely Sm) at levels above the limit of detection (0.1 wt.% oxides).

Zirconolite in Kovdor phoscorites and carbonatites was found only in calcite-bearing rocks, and 41 microprobe spot analyses reveal the presence of three mineral varieties on the basis of their Nb and REE contents (Table 11):

(1) REE- and Nb-rich zirconolite in calcite-forsterite-magnetite phoscorites, zirconolite containing 18.4-22.8 wt.% Nb_2O_5 and 9.5-17.8 wt.% REE_2O_3;

(2) low Nb and low REE zirconolite in calcite carbonatites with forsterite and phlogopite (3.7 wt.% Nb_2O_5 and <0.05 wt.% REE_2O_3);

(3) Nb-rich zirconolite (15.8-22.2 wt.% Nb_2O_5) with moderate contents of REE_2O_3 (2.5-6.3 wt.%). This variety occurs in phoscorites and carbonatites containing tetraferriphlogopite.

In addition to light REE, zirconolite also accommodates detectable levels of middle to heavy REE (Gd, Dy and Er).

3.1.3. REE distributions between minerals

Mass-balance calculations of REE distribution between various rocks and minerals in ultrabasic-alkaline rocks complexes with phoscorites and carbonatites were originally published by Kukharenko et al. (1965) (see Table 1.3 in Bulakh et al. (2004)). These authors showed that REE are concentrated in ultrabasic and alkaline rocks to the extent of 93.7% of the whole-complex budget, and only 0.3% of REE are present in phoscorites and 6.0% in carbonatites. The calculated average total bulk concentration of REE in Kola carbonatitic complexes is 1570 ppm.

Bulk geochemistry of carbonatites and phoscorites, as well as individual mineral compositions, indicate that apatite and calcite are the major hosts for REE, with other possible significant hosts being perovskite and pyrochlore (Balashov and Pozharitskaya, 1968; Borodin et al., 1973; Eby, 1975; Bulakh and Ivanikov, 1984; Kravchenko and Bagdasarov, 1987; Hornig-Kjarsgaard, 1998). The contribution of apatite and calcite to the whole-rock REE budget is variable with 51-86% for apatite and 9-48% for calcite. Silicate minerals, pyroxenes and amphiboles, can accumulate up to 3% of total rare earths (Reguir et al., 2012).

The distribution of REE between major, minor and accessory minerals in the Kovdor phoscorites and carbonatites has been calculated for five typical varieties of phoscorites and three varieties of carbonatites (Table 1, Supplementary Table 3). Mass-balance calculations (Table 12) were based on mineralogy, whole-rock compositions and average content of REE in minerals estimated on the basis of internal zonation observed from CL and BSE images.

Calculations show that in phoscorites the REE are primarily concentrated in apatite, which is the host for between 68.5-97.9 % of total REE content in these rocks. An exception is the calcite-forsterite-magnetite phoscorites where the major mineral concentrator of REE is calcite (76.7 % of total REE), with apatite accumulating only 2.9 % of total REE. Dolomite is not an essential REE host in calcite-bearing varieties of phoscorites (0.1-0.5 % of total REE), but it is an important carrier of REE in dolomite phoscorites, where the dolomite contributes 20.8 % REE.

Among the accessory minerals pyrochlore plays a significant role in REE budget in some phoscorites varieties. The modal proportion of pyrochlore is only 0.02-0.18 wt.%, but enrichment of REE in pyrochlore leads to an accumulation of 4.2-16.6 % of the total REE. In calcite-forsterite-magnetite phoscorite, pyrochlore concentrates 5.7 times more REE than apatite, and in calcite phoscorites with tetraferriphlogopite its contribution to the REE budget is comparable with that of calcite.

In carbonatites the principal hosts for REE are carbonates, calcite and dolomite, with lesser contribution from apatite. Carbonates in calcite carbonatites accumulate between 60.6 and 97.5 % of total REE with apatite hosting 1.6-31.7 %. In dolomite carbonatite with minor magnetite, forsterite and phlogopite nearly all the REE are present in dolomite, with this mineral contributing 96.9 % of the total REE. Accessory zirconolite in carbonatite with tetraferriphlogopite is a minor host for REE and contains 6.8 % of total REE.

3.2. REE as major elements

Strong enrichment in REE has been documented for several Kola carbonatites, including Khibina, Vuoriyarvi, Seblyavr and Sallanlatvi complexes. This enrichment is reflected in the mineralogy of these carbonatites and particularly in the presence of a variety of REE minerals (e.g. burbankite group minerals, Ca and Ba fluocarbonates, ancylite (e.g. Wall and Zaitsev, 2004b and references herein). However, only a few compositional data are published for REE-rich carbonatites from Kola apart from La, Ce and Nd in Khibina rocks (Zaitsev et al., 1998) and a single complete REE dataset for Sallanlatvi carbonatite (Zaitsev et al., 2004).

New analytical data for the Khibina late-stage carbonatites are given in Table 2. The Khibina carbonatites as well as phoscorites are heterogeneous rocks with variable amounts of major, minor and trace minerals (Zaitsev, 1996; Zaitsev et al., 1998, 2012). Their heterogeneity leads to significant variations in the content of elements that are usually described as ’trace’ elements, such as Sr, Ba and REE (Table 2). Contents of REE at Khibina carbonatites vary from 3001 ppm (0.35 wt.% REE_2O_3) to 44411 ppm (5.20 wt.% REE_2O_3).

Although both light REE and heavy REE minerals are known from Khibina (Voloshin et al., 1990, 1992; Zaitsev et al., 1998), the latter ones are rare, and all carbonatites are strongly enriched in light rare earths with La_{CN} value up to 70658 (Fig. 9). The Khibina carbonatites, however, are also relatively enriched in heavy rare earths with Lu_N values between 48 and 63, which is significantly higher for the Lu_{CN} in the Sallanlatvi REE carbonatites (4.3) (Fig. 9).

REE patterns in the Khibina carbonatites show significant differences, especially in the light rare earth distribution, between early formed calcite carbonatites (containing burbankite) and the latest rhodochrosite-ankerite carbonatites with Ca and Ba fluocarbonates. La/Ce_{CN} and La/Nd_{CN} ratios range from 1.54-2.03 and 4.02-7.84 for burbankite-bearing carbonatites to 0.85-1.16 and 1.75-2.67 for fluocarbonate-bearing carbonatites. This can be explained by (1) variations in the proportion of major REE minerals (burbankite vs. synchysite, cordylite and kukharenkoite) in the various carbonatites; (2) the occurrence of heavy REE-bearing mckelveyite group minerals in the latest carbonatite variety; and (3) transition from magmatic to (carbo)hydrothermal conditions of carbonatite formation (Zaitsev et al., 1998).

3.2.1. REE minerals

Important carriers of rare earth elements in carbonatites are REE minerals *sensu stricto*. Approximately 45 REE minerals have been reported from carbonatites worldwide, with the Kola carbonatites probably the most diverse REE-bearing rocks, in which 26 REE minerals have been studied in detail, including first mineral descriptions of carbocernaite, hydroxyl-bastnäsite, kukharenkoite and anzaite (Wall and Zaitsev, 2004b and references herein). The principal and most widespread REE minerals at Kola are alkali carbonates (burbankite group minerals, carbocernaite), Ca±Ba fluocarbonates (bastnäsite, synchysite, cordylite, kukharenkoite), hydrous carbonates (ancylite), phosphates (monazite), oxides (loparite, niobo-aeschynite) and silicates (britholite, cerite). Late-stage carbonatites from Khibina, Vuoriyarvi, Sallanlatvi and Seblyavr contain rare earth minerals as major and minor components (Fig. 10), whereas in carbonatites from Kovdor, Turiy Mys, Afrikanda, Lesnya varaka, Salmagora and Kandaguba the rare earth minerals occur only as accessory components.

The REE minerals, in Kola carbonatites and elsewhere, form three distinct mineral assemblages, these are: (1) primary magmatic minerals (burbankite and Ca fluocarbonates group minerals); (2) subsolidus hydrothermal-metasomatic minerals (ancylite ± Ca-Ba fluocarbonates); and (3) low-temperature secondary minerals (monazite) (Wall and Zaitsev, 2004b; Chakhmouradian and Zaitsev, 2012 and references herein). Observations from geological settings, mineral assemblages, studies of melt and fluid inclusions, as well as experimental studies, indicate a wide range of crystallization temperatures for the REE minerals from ca. 750 to 25 ºC (Wall and Zaitsev, 2004b).

The first REE minerals to crystallize in the Kola carbonatites are the burbankite group minerals, i.e. burbankite or calcioburbankite and they typically form crystals up to several cm in size. These carbonatites are best described as pegmatitic carbonatites. Where burbankite group minerals are present in carbonatites it is common to observe complex replacement of these minerals, resulting in the formation of partial and full pseudomorphs. Subsolidus mineral assemblages, formed after burbankite group minerals, include a variety of REE-Sr-Ba rich minerals including carbocernaite, ancylite, synchysite, strontianite, baryte, with other minerals in varying proportions. The occurrence of pseudomorphs is an indication of substantial hydrothermal and metasomatic alteration of carbonatites by late-stage fluids.

With the exception of the mckelveyite-group of minerals that occur in the Khibina and Vuoriyarvi carbonatites, all REE minerals in the Kola carbonatites are strongly enriched in light REE. Ce is the principal light REE, however, a La-rich mineral (ancylite-(La)) is also known from the Sallanlatvi carbonatites (Zaitsev et al., 2004). Mckelveyite, ewaldite and donnayite are Y and heavy REE rich minerals that occur in the latest stage of crystallization of carbonatite rocks (Voloshin et al., 1990, 1992; Zaitsev et al., 1998). Enrichment of carbonatites in heavy REE is not common, and only a few localities contain xenotime as an accessory mineral (Wall et al., 2008).

4. Origin of Kola phoscorites and carbonatites

The mechanism of carbonatite formation has been under discussion for many decades. These mineralogically and compositionally diverse rocks have been considered to be magmatic (e.g. Tuttle and Gittins, 1966; Le Bas, 1977; Egorov, 1991), hydrothermal-metasomatic (e.g. Kukharenko et al., 1965; Pozharitskaya and Samoilov, 1972) or polygenetic in origin (e.g. Bulakh and Ivanikov, 1984; Bagdasarov, 1992). Field geological observations, coupled with mineralogical and petrographical data suggest that some of Kola multi-stage carbonatite (±phoscorite) complexes (e.g. Khibina, Seblyavr, Vuoriyarvi, Sallanlatvi) are polygenetic, with phoscorites and early carbonatites formed from a magmatic melt, and late-stage carbonatites crystallized from carbohydrothermal fluids (Zaitsev, 1996; Bulakh et al., 1998b, 2000; Zaitsev et al., 2004). Metasomatic replacement of primary minerals in carbonatites and reactions with host rocks are also important during carbonatite formation. In a recent review of carbonatites Mitchell (2005) concluded that "...there must be carbonatites and carbonatites and carbonatites…", i.e. carbonatites are rocks of different formation.

An explanation of the origin of carbonatites is also not straightforward. Current thinking indicates that the source of carbonate-bearing melts is lithospheric and/or asthenopheric mantle. A few carbonatites are considered to have crystallized from a carbonatite melt derived directly from the mantle, and at Kola Peninsula these rocks can be represented by the Early Kandalaksha dyke complex (Bell and Rukhlov, 2004 and references herein). However, the majority of carbonatites, including the Kola Alkaline Province, occur in a space-and-time association with diverse ultrabasic and alkaline silicate rocks (e.g. Kukharenko et al., 1965; Woolley, 2003) that implies some kind of genetic relationship between them. The occurrence of carbonatites in ultrabasic-silicate complexes might be explained by carbonate–silicate liquid immiscibility or by crystallization from a residual melt after fractional crystallization. The source in both cases is carbonated silicate magma originating from partial melting of phlogopite±amphibole carbonate-bearing lherzolite (Bell and Rukhlov, 2004 and references herein).

Studies of stable and radiogenic isotopes in Kola carbonatites, phoscorites and associated silicate rocks show wide variations in their $\delta^{13}C$ and $\delta^{18}O$ values, and initial $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios. This variability has been attributed to mantle heterogeneity, or magma mixing originating from distinct mantle sources (HIMU, EMI, FOZO), with subsequent high and low temperature alteration (e.g. Kramm and Kogarko, 1994; Zaitsev and Bell, 1995; Zaitsev et al., 1997, 2002; Demény et al., 2004; Bell and Rukhov, 2004; Lee et al., 2006). The majority of isotopic analyses were undertaken on bulk samples from phoscorites and carbonatites with low REE content, and only burbankite group minerals, in addition to their pseudomorphs, were investigated in Khibina and Vuoriyarvi (Zaitsev et al., 1997, 2002). Within each complex the C–O and Sr–Nd isotopic data are similar for primary burbankite group minerals and co-existing calcite or dolomite hosts, e.g. for the Khibina minerals $\delta^{13}C$(V-PDB) = -6.4 to -5.8 ‰, $\delta^{18}O$(V-SMOW) = 7.3 to 7.7 ‰, $(^{87}Sr/^{86}Sr)_{370}$ = 0.70390–0.70404 and $(^{143}Nd/^{144}Nd)_{370}$ = 0.51230–0.51235. This observation indicates a deep mantle source for elements in these REE minerals and their host carbonatites in each complex, and their co-genetic relationship.

Strong REE enrichment in carbonatites could be a result of either: (1) immiscibility between silicate and carbonate melts, or (2) multi-stage fractional crystallization of a primary carbonated magma. Numerous experimental studies of immiscibility for carbonate-silicate system (see review by Veksler et al., 2012) have shown that in the carbonate-silicate system, the REE partition coefficients (D) are less than 1 and decrease sharply from light (~0.7) to heavy (~0.07) REE. The addition of water to carbonatite melt only results in small increases of D values, up to ~1.05 for La and ~0.25 for Lu. These results, combined with data from studies of crystallized melt inclusions in carbonatitic minerals, lead to the conclusion that "… plutonic carbonatites carrying economical deposits of Nb, Zr and REE rare-metal ores cannot be produced by carbonate–silicate immiscibility" (Veksler et al., 2012, p. 37), and "… they are probably formed as residual liquids by fractional crystallization" (Veksler et al., 1998, p. 2104). In contrast, distribution coefficients (*D*'s) for REE are very high in systems involving hydrous salt melts, containing significant amount of Cl, S, P or F. The highest values were observed for fluoride–silicate system with *D* values of 215 for La and 93.6 for Lu. Thus, a carbonatite system, enriched in 'salt' components (S, P, F and Cl), is likely to dissolve significant amounts of REE during an immiscible separation from a silicate melt.

Compared to carbonatites, much less information is available to explain the origin and formation of phoscorites. Phoscorites are essentially melanocratic, silica-bearing analogues (enriched in Si, P and Fe) of carbonatites and they display similar geological, mineralogical and geochemical characteristics to those of carbonatites (Krasnova et al., 2004a and references herein). Phoscorites crystallized from mantle-derived melts, and processes such as cumulation, fractional crystallization and liquid immiscibility may play important roles during their formation and evolution. The limited experimental data available are insufficient to establish whether phoscorites formed via fractional crystallization or liquid immiscibility (Klemme, 2010), and future studies are clearly needed to fully understand these exotic rock types.

5. Conclusions

Carbonatites, and to a lesser degree phoscorites, are relatively common rocks in the Devonian Kola ultrabasic-alkaline complexes. These rocks are always the latest to crystallize in complex ultrabasic and alkaline plutonic massifs. With 10 minerals (calcite, dolomite, apatite, forsterite, diopside, phlogopite, tetraferriphlogopite, magnesio-arfvedsonite, richterite and magnetite) as major rock-forming minerals, carbonatites and phoscorites form multi-stage complexes with mineralogically diverse rock types that were formed during relatively short periods of time (Wall and Zaitsev, 2004a).

Compositionally, Kola phoscorites are enriched in silica, iron and phosphorus to varying degrees, with some rock types containing significant proportions of primary carbonate components. Carbonatites are rocks with mainly calcium carbonate composition, with some varieties enriched in magnesium, iron and phosphorus, but rarely in manganese. Many of these rocks are characterised by enrichment in certain trace elements including zirconium, niobium and tantalum. Although only phoscorites and carbonatites from Kovdor are currently mined, other complexes, including those at Vuoriyarvi, Seblyavr, Sallanlatvi and Turiy Mys have been intensively studied and contain potential deposits for future mining exploitation (Petrov, 2004; Afanasev, 2011).

Rare earth elements are also typical components in the phoscorites and carbonatites, and their concentrations vary from a few tens of ppm to several weight per cent. Low contents of REE are observed in phoscorites rich in silicate minerals and magnetite, whereas high REE are common for some late-stage carbonatites. In rocks where no REE minerals *sensu stricto* are present, the REE are concentrated in minerals such as apatite and calcite, with smaller amounts accumulated by pyrochlore and zirconolite. By comparing REE compositional data for Kola carbonatites and using the presence (or absence) of certain REE minerals in the carbonatites, it is possible to establish a threshold for the content of REE at 2000-3000 ppm, above which REE minerals are likely to be present. Various REE minerals that occur in the Kola carbonatites are represented by: (1) primary magmatic and (2) secondary hydrothermal-metasomatic minerals (Wall and Zaitsev, 2004b). Isotopic geochemistry of primary and secondary REE minerals, as well as their host carbonates, indicates a mantle source for carbon, oxygen, strontium and neodymium in these minerals (Zaitsev et al., 1997, 2002). Additionally, all isotopic data, including those for silicate rocks, suggest the involvement of several mantle components to generate the primary melts from which the Kola complexes were crystallized (Kramm and Kogarko, 1994; Zaitsev and Bell, 1995; Bell and Rukhlov, 2004).

All available geological, mineralogical and geochemical (including isotopic) data for carbonatite(±phoscorites)-bearing complexes that form the Kola Alkaline Province have been recently summarised by Bell and Rukhlov (2004), Chakhmouradian and Zaitsev (2004), Demény et al. (2004), and Arzamastsev and Arzamastseva (2013). These authors postulated the origin of the primary melts to be the result of a low degree of partial melting of either pargasite-bearing lherzolite (Fig. 11, for details see Chakhmouradian and Zaitsev, 2004) or phlogopite-bearing (±amphibole) garnet lherzolite, with the formation of carbonatites at a particular locality through either crystal fractionation, liquid immiscibility or direct partial melting of mantle material. The route to REE-enrichment in the Kola carbonatites was probably through fractional crystallization of a mantle-derived carbonated silicate melt, less probably a carbonate melt but cannot have been through conventional carbonate-silicate immiscibility. Immiscible separation may become a viable mechanism if it can be shown that substantial ’salt‘ components rich in S, P, F or Cl were present.

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Table 1
Major (wt.%) and trace elements (ppm) composition of the Kovdor phoscorites and carbonatites.

Rock	AF	AFM	CFM	Cc	CFM tphl	Cc tphl	DMF	Dc	Dc
Index	Ph 1	Ph 2	Ph 3	C 1	Ph 4	C 2	Ph 5	C 3a	C 3b
Sample	AZ2000-20	AZ2000-22	7307/3	57/249	4046	AZ2000-26	720/78	3/99	6/99
SiO_2	32.38	10.28	12.69	1.38	7.66	0.77	4.28	2.43	<0.01
TiO_2	0.09	0.47	0.27	0.03	2.66	0.07	0.31	0.09	<0.01
Al_2O_3	0.22	1.33	3.16	0.52	0.65	0.08	2.42	1.35	0.01
Fe_2O_3	9.30	47.51	45.97	8.56	59.10	1.91	64.55	23.16	1.83
MnO	0.27	0.35	0.37	0.16	0.45	0.12	0.41	0.23	0.32
MgO	41.84	16.75	18.08	5.07	11.02	2.95	12.29	17.42	20.42
CaO	9.68	14.20	10.44	45.68	10.51	51.10	6.02	22.09	31.07
Na_2O	0.08	0.10	0.12	0.09	0.07	0.07	0.16	0.11	0.11
K_2O	0.12	0.06	1.29	0.28	0.72	0.12	0.51	0.65	0.04
P_2O_5	7.04	10.45	0.09	0.16	3.97	2.41	1.18	0.05	0.29
CO_2	1.00	<0.01	9.08	37.09	3.96	39.78	6.99	32.99	46.36
Total	102.01	101.51	101.56	99.02	100.77	99.37	99.13	100.58	100.44
Sc	9.61	58.5	90.2	24.8	63.7	19.2	58.5	23.7	9.63
V	44.1	398	434	48.8	1142	20.7	401	138	3.60
Cr	81.6	2.11	0.50	1.90	0.25	5.24	0.53	1.17	2.45
Cu	25.1	67.7	32.4	28.9	3089	117	116	17.1	10.6
Rb	3.23	1.93	57.1	4.64	33.5	2.12	13.8	15.8	<0.10
Sr	361	502	1226	2729	1990	7987	502	1406	3802
Y	7.02	7.63	4.78	15.1	8.39	23.3	1.41	1.63	6.75
Zr	409	1682	1583	637	698	398	930	414	139
Nb	19.1	41.2	128	7.75	453	153	59.8	27.8	6.03
Ba	78.5	24.9	1331	141	154	147	383	440	93.3
Hf	13.6	54.4	52.7	19.7	0.79	10.8	30.4	12.0	3.67
Ta	1.57	8.02	24.3	1.46	61.6	23.8	13.1	5.60	<0.10
Pb	2.22	2.64	1.36	3.28	4.67	13.1	4.23	1.80	3.96
Th	2.89	4.88	2.98	0.17	85.6	11.9	3.18	2.98	5.80
U	0.23	0.31	0.55	0.03	69.9	34.5	0.40	0.14	0.25
La	37.2	32.1	31.2	43.0	57.4	157	6.44	11.2	43.7
Ce	72.5	70.5	56.3	81.9	135	300	13.0	18.9	80.5
Pr	8.72	9.17	6.20	9.22	17.4	35.3	1.41	1.98	8.65
Nd	30.4	33.3	20.5	33.5	64.3	117	5.06	6.09	27.5
Sm	4.76	5.45	2.96	5.17	9.41	16.7	0.73	0.82	3.91
Eu	1.27	1.43	0.87	1.55	1.92	4.49	0.22	0.26	1.01
Gd	3.91	4.5	2.55	4.48	5.78	13.3	0.71	0.74	3.03
Tb	0.43	0.51	0.27	0.54	0.71	1.56	<0.05	0.08	0.33
Dy	1.79	2.19	1.17	3.17	3.45	6.02	0.44	0.34	1.44
Ho	0.28	0.35	0.19	0.52	0.39	1.05	<0.05	0.06	0.24
Er	0.64	0.77	0.47	1.45	0.95	2.26	0.19	0.13	0.56
Tm	0.07	0.08	0.05	0.18	0.08	0.36	<0.05	0.02	0.07
Yb	0.38	0.48	0.48	1.12	0.47	1.36	0.20	0.15	0.35

Lu	0.05	0.06	0.05	0.15	0.03	0.19	<0.05	0.02	0.05

AF – apatite-forsterite phoscorites, AFM – apatite-forsterite-magnetite phoscorites, CFM – calcite-forsterite-magnetite phoscorite, Cc – calcite carbonatite, CFMtphl - calcite-forsterite-magnetite phoscorites with tetraferriphlogopite, Cctphl – calcite carbonatite with tetraferriphlogopie, DMF – dolomite-magnetite-forsterite phoscorite, Dc – dolomite carbonatite. Rock indexes are from Zaitsev and Bell (1995).

Table 2

Major (wt.%) and trace elements (ppm) composition of the Khibina phoscorites and carbonatites.

Rock	Phoscorites			Carbonatites				
Index	AAB	AAB	AAB	C I	C II-1	C II-1	C II-3	C II-3
Sample	632B/1935	632B/1940	32B/1975	632B/1934	632B/1522.4	633/477.7	603/89	6034/90.0
SiO_2	16.47	19.88	14.80	4.81	0.36	0.64	1.88	2.09
TiO_2	1.84	3.76	2.11	0.64	0.03	0.03	0.02	0.08
Al_2O_3	3.32	4.84	3.03	0.88	0.19	0.25	0.69	0.70
FeO	11.85	12.68	13.42	4.99	3.46	3.79	19.14	22.97
MnO	0.46	0.54	0.45	0.37	1.08	1.56	12.78	12.60
MgO	2.54	2.39	2.36	1.20	0.45	0.41	3.97	2.35
CaO	21.20	23.45	21.56	46.50	46.26	32.52	12.13	18.40
Na_2O	0.62	0.45	0.56	0.36	0.63	3.09	0.21	0.25
K_2O	4.31	5.67	3.86	1.45	0.01	0.09	0.55	0.69
P_2O_5	4.95	7.62	2.97	1.25	0.03	0.02	0.11	0.91
S	0.61	0.40	0.90	0.32	0.70	0.73	1.59	1.12
F	0.43	0.59	0.27	0.09	0.04	0.06	0.21	0.12
Cl	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.01
-O=S,F,Cl	0.49	0.45	0.56	0.20	0.37	0.39	0.88	0.61
Total	78.12	81.83	75.73	62.67	52.88	42.82	52.42	61.68
Sr	7858	4571	6493	13449	28494	63819	5533	7017
Ba	908	1124	1024	1343	10565	13102	28374	1280
Li	41.0	42.9	33.3	11.4	0.69	4.34	17.2	6.41
Be	1.02	1.09	1.24	0.38	0.04	0.08	2.09	0.86
V	357	246	395	99.1	4.80	4.00	153	128
Ni	6.11	7.12	13.0	5.11	6.97	7.55	2.03	3.45
Cu	9.85	12.6	21.5	12.3	11.1	13.3	17.5	10.2
Zn	295	322	302	81.1	181	59.9	3413	3854
Rb	248	325	285	61.4	0.29	2.12	18.3	21.2
Y	60.0	68.0	63.5	72.7	110	144	66.4	125

Zr	50.6	79.4	70.1	40.3	<1	<2.5	4.80	14.6
Nb	257	1376	436	105	13.9	4.80	199	129
Mo	0.67	2.02	0.40	0.29	3.51	3.67	72.9	156
Cd	0.52	0.36	0.69	0.45	1.80	1.12	0.65	2.02
Sn	2.25	2.98	2.62	1.36	0.44	3.93	3.01	3.99
Sb	0.10	0.23	0.22	0.29	0.79	0.35	1.09	3.21
Cs	3.87	5.76	4.52	0.93	<0.04	<0.1	<0.05	<0.05
Ta	2.36	22.6	5.96	0.69	<0.1	<0.25	2.45	0.64
Tl	0.29	0.40	0.42	0.10	0.12	0.07	0.76	0.72
Pb	23.0	9.94	36.1	15.2	62.9	125	1837	526
Th	29.8	24.3	53.5	17.3	32.7	139	169	98.9
U	180	36.2	350	41.9	0.18	<0.4	3.74	1.26
La	490	504	405	454	856	16746	4876	2833
Ce	1026	1168	911	933	1432	21254	14785	6333
Pr	114	139	105	105	134	1652	1726	675
Nd	400	509	384	371	420	4210	5501	2092
Sm	49.9	65.9	49.6	49.1	53.9	284	415	185
Eu	12.7	17.0	12.8	12.8	15.0	58.1	69.5	36.6
Gd	29.2	38.2	28.9	29.4	35.6	115	95.7	71.6
Tb	3.48	4.47	3.54	3.62	4.77	11.0	8.13	6.88
Dy	15.9	19.6	16.4	17.0	23.7	44.1	27.6	30.4
Ho	2.46	2.95	2.57	2.80	4.05	6.27	3.46	4.76
Er	5.57	6.45	5.94	6.80	10.6	15.0	8.19	11.6
Tm	0.641	0.714	0.707	0.851	1.40	1.82	1.05	1.52
Yb	3.65	3.83	4.12	5.04	9.16	11.3	7.65	8.86
Lu	0.492	0.481	0.562	0.699	1.27	1.60	1.22	1.25

Carbonatite data for major elements, Sr and Ba are from Zaitsev et al. (2008). AAB –apatite-aegirine-biotite phoscorite, C I – calcite carbonatite with biotite, aegirine and apatite, C II-1 – calcite carbonatite with burbankite, C II-3 – rhodochrosite-ankerite carbonatite with synchysite (Zaitsev, 1996).

Table 3
General succession of formation of the Kola phoscorites and carbonatites.

Stage	Variety	Phoscorite	Carbonatite	Complex
Phoscorite-carbonatitic	1	apatite-phlogopite-diopside, magnetite-diopside, apatite-diopside-magnetite	calcite with diopside and phlogopite	Seblyavr, Turiy Mys
	2	apatite-aegirite-biotite	calcite with aegirine	Khibina
	3	apatite-forsterite		Kovdor
	4	apatite-forsterite-magnetite, forsterite-magnetite	calcute with forsterite, magnetite and phlogopite	Kovdor, Vuoriyarvi, Seblyavr, Turiy Mys
	5	calcite-forsterite-magnetite with phlogopite	calcite with forsterite, magnetite and phlogopite	Kovdor, Vuoriyarvi, Turiy Mys
	6	calcite-forsterite-magnetite with tetraferriphlogopite	calcite with tetraferriphlogopite	Kovdor, Vuoriyarvi, Seblyavr, Turiy Mys
	7	calcite-dolomite-richterite-magnetite	calcite with tetraferriphlogopite, magnesio-arfvedsonite or richterite	Vuoriyarvi, Turiy Mys, Kovdor
	8	dolomite-forsterite-magnetite, dolomite-magnetite	dolomite with forsterite and phlogopite	Kovdor
Late carbonatitic	9		calcite with burbankite (secondary ancylite after burbankite)	Khibina, Vuoriyarvi, Sallanlatvi
	10		dolomite with burbankite (secondary ancylite after burbankite)	Vuoriyarvi, Seblyavr, Sallanlatvi
	11		calcite-dolomite/ankerite, ankerite with burbankite or synchysite	Khibina, Vuoriyarvi
	12		magnesite-dolomite with ancylite	Sallanlatvi
	13		siderite-ankerite with ancylite	Sallanlatvi
	14		ankerite-rhodochrosite with synchysite or cordylite	Khibina
	15		siderite with ancylite	Sallanlatvi, Khibina

Table 4
Variations in REE concentrations in Kola phoscorites (ppm).

Complex	Kovdor	Turiy Mys	Vuoriyarvi	Khibina	Phalaborwa
Phoscorites, all varieties	8-521	26-976	69-1860	1301-1950	1111-1335
diopside-magnetite		26			
aegirine-apatite-biotite				1931-2479	
apatite-forsterite	162				
forsterite-magnetite	8-51				
apatite-forsterite-magnetite	161-501	212-762			
calcite-forsterite-magnetite	37-123		69-365		
apatite-calcite-forsterite-magnetite	100	782	753-1072		1111-1335
calcite-magnetite	15-121				
forsterite-magnetite with tetraferriphlogopite	99	37-173	221-314		
calcite-magnetite with tetraferriphlogopite		340	159-467		
apatite-forsterite-magnetite with tetraferriphlogopite	298-417		813-1164		
calcite-forsterite-magnetite with tetraferriphlogopite	483-521	976	560-1860		
calcite-apatite with tetraferriphlogopite			1573		
forsterite-dolomite-magnetite	28				

Table 5
Variations in REE concentrations in Kola carbonatites (ppm).

Complex	Kovdor	Turiy Mys	Vuoriyarvi	Sallanlatvi	Khibina	Afrikanda
Carbonatites, all varieties	72-789	38-817	401-2581	124-34145	1991-44411	1437
Early-stage						
calcite with forsterite, phlogopite, diopside or aegirine	185-679	210-817	401-1102	467-3049	1991	1437
calcite with tetraferriphlogopite	548-789					
and richterite		153-526	573-1441			
Late-stage						
calcite				34145	3001-44411	
dolomite-ankerite	72-244	38	2442-18782*	1257-13270		
magnesite-dolomite				1191-4887		
siderite				124-597		
Mn-ankerite-Fe-rhodochrosite					12292-27526	

* – including data by E.G. Balaganskaya (2004, pers.comm.).

Table 6
Trace-elements (ppm) composition of calcite from Kovdor phoscorites and carbonatites.

Rock	CFM (Ph 3)				Cc (C 1)		
Sample	7307/3				57/249		
Analysis	core	mantle	mantle	rim	core	mantle	rim
Sc	3.91	4.19	4.88	6.06	18.4	22.9	18.9
Mn	420	472	435	431	919	880	1006
Sr	4847	4966	5126	5017	4340	5420	4858
Y	13.8	13.9	14.9	17.3	18.7	19.1	19.6
Ba	128	131	135	143	133	164	153
La	100	106	112	134	56.9	61.7	66.8
Ce	169	172	187	240	101	106	117
Pr	16.6	17.2	19.3	21.6	10.7	14.2	12.6
Nd	51.3	55.1	60.5	67.4	42.9	44.0	44.3
Sm	6.28	6.99	7.39	8.55	6.21	5.94	6.53
Eu	1.91	2.00	2.14	2.39	2.27	2.39	2.15
Gd	5.10	5.61	6.09	7.05	5.87	7.01	6.38
Tb	0.55	0.71	0.72	0.74	0.68	0.78	0.71
Dy	2.97	3.48	3.67	3.78	3.59	4.67	3.55
Ho	0.49	0.55	0.61	0.67	0.67	0.62	0.78
Er	1.22	1.32	1.39	1.54	2.00	1.58	1.87
Tm	0.16	0.17	0.18	0.20	0.25	0.30	0.29
Yb	0.94	1.03	1.09	1.14	1.60	1.60	1.65
Lu	0.14	0.14	0.15	0.17	0.20	0.20	0.24
Total REE	357	372	402	490	234	251	265
La/Ce$_{CN}$	1.54	1.59	1.55	1.44	1.46	1.51	1.48
La/Nd$_{CN}$	3.86	3.79	3.65	3.93	2.61	2.77	2.97
La/Yb$_{CN}$	76.42	73.82	73.70	84.32	25.42	27.63	29.05
La/Lu$_{CN}$	78.34	81.15	80.02	86.68	30.83	32.68	29.83

$_{CN}$ – chondrite normalized, data for chondrite are from Sun and McDonough (1989).

Table 6 (continued).

Rock	CFM tphl (Ph 4)			Cc tphl (C 2)		
Sample	4046			AZ2000-26		
Analysis	core	mantle	rim	core = mantle		rim
Sc	8.99	8.17	8.54	14.8	15.7	15.6
Mn	741	801	731	950	997	952
Sr	6751	6205	6498	8812	9325	9265
Y	13.8	13.8	15.6	18.5	17.8	18.4
Ba	544	520	526	319	358	362
La	112	105	122	119	128	131
Ce	172	181	196	203	219	222
Pr	17.1	17.8	19.7	21.5	22.5	23.0
Nd	52.2	55.6	61.0	69.1	74.7	75.2
Sm	6.06	6.77	7.38	9.61	9.70	9.77
Eu	1.78	2.01	2.05	2.61	2.74	2.64
Gd	4.76	5.13	5.70	6.30	6.85	6.34
Tb	0.63	0.68	0.72	0.79	0.80	0.79
Dy	2.80	3.15	3.22	4.05	3.95	4.08
Ho	0.46	0.51	0.53	0.66	0.63	0.66
Er	1.16	1.26	1.18	1.41	1.44	1.51
Tm	0.14	0.15	0.16	0.18	0.19	0.18
Yb	0.90	1.01	0.95	1.06	0.98	1.08
Lu	0.15	0.13	0.16	0.15	0.14	0.14
Total REE	373	380	420	440	472	479
La/Ce$_{CN}$	1.68	1.50	1.61	1.52	1.51	1.53
La/Nd$_{CN}$	4.24	3.72	3.93	3.41	3.39	3.44
La/Yb$_{CN}$	89.46	74.61	91.88	81.03	93.75	86.76
La/Lu$_{CN}$	82.71	84.73	79.25	84.24	96.44	97.28

Table 7

Trace-elements (ppm) composition of dolomite from Kovdor phoscorites and carbonatites.

Rocks	CFM (Ph 3)		Cc (C 1)	CFM tphl (Ph 4)		Cc tphl (C 2)	
Sample	7307/3		57/249	4046		AZ2000-26	
Analysis	core	mantle				core	rim
Mn	868	901	1444	1236	1332	1316	1308
Sr	2422	2415	1694	2727	2800	3932	4020
Y	0.88	1.26	1.04	0.62	0.96	1.24	1.18
Ba	1.68	2.03	10.0	20.4	25.0	15.6	15.9
La	11.0	14.8	4.90	7.24	10.7	14.0	13.7
Ce	22.4	30.8	9.78	13.4	19.9	28.9	26.7
Pr	2.27	2.95	1.03	1.20	1.94	2.88	2.60
Nd	6.49	9.49	3.32	3.48	5.96	8.63	8.42
Sm	0.78	1.13	0.46	0.37	0.68	1.05	0.98
Eu	0.22	0.31	0.15	0.10	0.20	0.28	0.25
Gd	0.57	0.81	0.40	0.26	0.49	0.73	0.66
Tb	0.06	0.08	0.05	0.04	0.06	0.07	0.06
Dy	0.27	0.33	0.26	0.15	0.21	0.30	0.29
Ho	0.04	0.04	0.04	0.02	0.04	0.04	0.05
Er	0.07	0.11	<0.10	0.06	0.07	0.08	0.10
Tm	0.01	0.01	<0.02	0.01	0.01	0.01	0.01
Yb	0.07	0.07	0.04	0.05	0.06	0.06	0.07
Lu	<0.01	0.01	<0.02	<0.01	0.01	0.01	0.01
Total REE	44.2	60.9	20.4	26.3	40.3	57.1	53.9
$\mathrm{La/Ce}_{CN}$	1.27	1.24	1.29	1.40	1.39	1.25	1.32
$\mathrm{La/Nd}_{CN}$	3.33	3.06	2.91	4.11	3.55	3.20	3.20
$\mathrm{La/Yb}_{CN}$	113.26	142.79	87.79	115.15	130.32	164.01	133.55
$\mathrm{La/Lu}_{CN}$		137.16			130.95	233.73	149.10

$_{CN}$ – chondrite normalized, data for chondrite are from Sun and McDonough (1989).

Table 7 (continued).

Rock	DFM (Ph 5)			Dc (C 3a)			
Sample	720/78			3/99			
Analysis	core	rim	rim	mantle	rim	core	rim
Mn	1842	1920	1625	1771	1726	1974	2039
Sr	1741	1956	1873	1765	2019	2156	2092
Y	1.06	1.74	1.50	2.92	1.32	4.32	1.54
Ba	11.9	5.10	4.74	107	19.6	130	34.5
La	5.69	9.34	11.24	21.3	11.0	41.9	12.0
Ce	11.5	20.0	21.2	38.5	19.4	66.2	22.1
Pr	1.18	1.87	2.07	3.33	1.84	6.17	2.08
Nd	3.91	6.32	6.72	10.3	5.59	18.6	6.57
Sm	0.53	0.86	0.92	1.30	0.79	2.31	0.80
Eu	0.15	0.25	0.24	0.38	0.19	0.59	0.23
Gd	0.45	0.57	0.65	1.05	0.55	1.69	0.64
Tb	0.06	0.08	0.08	0.12	0.06	0.17	0.07
Dy	0.24	0.44	0.35	0.65	0.28	0.85	0.31
Ho	0.04	0.07	0.06	0.10	0.05	0.15	0.06
Er	0.09	0.17	0.12	0.21	0.16	0.31	0.13
Tm	0.01	0.02	0.02	0.03	0.02	0.05	0.01
Yb	0.07	0.14	0.09	0.19	0.14	0.27	0.10
Lu	0.01	0.02	0.01	0.03	0.02	0.04	0.01
Total REE	23.9	40.1	43.8	77.4	40.1	139	45.1
La/$\mathrm{Ce}_{\mathrm{CN}}$	1.28	1.21	1.37	1.43	1.47	1.63	1.41
La/$\mathrm{Nd}_{\mathrm{CN}}$	2.87	2.91	3.30	4.07	3.89	4.43	3.62
La/$\mathrm{Yb}_{\mathrm{CN}}$	55.83	48.55	87.15	82.28	54.96	112.39	88.42
La/$\mathrm{Lu}_{\mathrm{CN}}$	70.54	47.82	93.21	86.52	62.86	112.38	100.95

Table 8
Trace-elements (ppm) composition of apatite from Kovdor apatite-forsterite phoscorite (Ph 1).

Sample	AZ2000-20					
Analysis	core	core	mantle	rim	rim	core=rim
CL colour	green	green	light yellow	yellow	yellow	dark yellow
Mg	93.0	190	430	483	1022	773
Sc	1.40	1.41	1.57	1.65	1.55	1.59
Mn	78.1	62.0	116	119	141	145
Sr	2867	3427	3641	3470	2984	2177
Y	83.3	57.5	50.9	47.5	39.1	26.4
Ba	14.8	1.69	6.77	2.86	8.34	5.87
Th	1.19	5.73	8.87	9.88	9.61	9.18
U	<0.02	<0.02	0.02	<0.02	0.31	0.43
La	642	438	346	316	253	118
Ce	1419	985	983	856	703	274
Pr	123	83.6	88.0	77.7	68.0	33.4
Nd	412	267	303	270	243	120
Sm	57.0	37.3	43.2	39.0	34.0	18.2
Eu	15.2	9.89	11.1	9.92	8.95	4.92
Gd	46.0	34.0	35.5	33.0	28.1	15.2
Tb	4.88	3.42	3.54	3.29	2.77	1.65
Dy	22.8	15.8	15.3	14.3	12.0	7.77
Ho	3.51	2.46	2.31	2.08	1.80	1.16
Er	7.32	5.27	4.62	4.37	3.67	2.53
Tm	0.79	0.62	0.47	0.49	0.35	0.27
Yb	3.89	3.30	2.30	2.29	1.85	1.30
Lu	0.44	0.42	0.27	0.26	0.22	0.16
Total REE	2758	1886	1839	1629	1360	598
La/Ce_{CN}	1.17	1.15	0.91	0.95	0.93	1.11
La/Nd_{CN}	3.07	3.24	2.25	2.31	2.05	1.93
La/Yb_{CN}	118.37	95.37	108.11	98.86	97.87	65.08
La/Lu_{CN}	155.75	110.93	139.52	128.16	125.11	78.83

$_{CN}$ – chondrite normalized, data for chondrite are from Sun and McDonough (1989).

Table 8 (continued).
Trace-elements (ppm) composition of apatite from Kovdor apatite-forsterite magnetite phoscorite (Ph 2).

Sample	AZ2000-22							
Analysis	core	mantle	rim	core	mantle	rim	core	rim
CL colour	red	yellow	green	red	yellow	green	red	yellow
Mg	526	583	400	452	495	196	497	509
Sc	<2.92	<2.30	<2.11	1.83	1.64	1.31	1.68	1.97
Mn	107	135	108	114	152	67.8	142	163
Sr	1674	2014	1993	1920	2193	2226	2001	2201
Y	25.2	30.1	33.3	29.7	31.4	38.7	32.2	30.2
Ba	8.63	3.89	<0.26	9.43	2.71	0.24	9.24	4.08
Th	4.66	9.66	9.87	10.1	7.61	9.81	6.86	9.74
U	0.12	0.27	0.31	0.29	0.16	0.31	0.17	0.30
La	71.0	123	131	88.4	131	163	98.4	124
Ce	162	273	285	215	324	425	236	323
Pr	22.0	35.2	37.5	27.3	38.5	46.6	30.3	37.3
Nd	85.6	132	141	103	142	169	115	137
Sm	14.1	20.5	22.3	17.4	22.4	26.2	18.8	21.3
Eu	4.11	5.51	5.86	4.81	5.98	7.00	5.20	5.59
Gd	12.2	16.7	17.6	15.5	18.2	21.6	16.4	17.4
Tb	1.42	1.80	1.93	1.64	1.97	2.33	1.80	1.84
Dy	7.25	8.90	9.25	8.73	9.39	11.59	9.16	8.94
Ho	1.11	1.33	1.46	1.38	1.46	1.72	1.41	1.38
Er	2.48	2.90	3.11	3.10	3.16	3.95	3.20	2.85
Tm	0.25	0.29	0.32	0.31	0.32	0.41	0.36	0.32
Yb	1.42	1.54	1.61	1.52	1.71	2.25	1.73	1.51
Lu	0.17	0.19	0.20	0.21	0.20	0.28	0.20	0.19
Total REE	385	623	658	488	700	880	537	682
La/Ce$_{\mathrm{CN}}$	1.13	1.16	1.18	1.06	1.05	0.99	1.08	0.99
La/Nd$_{\mathrm{CN}}$	1.63	1.83	1.83	1.68	1.82	1.90	1.69	1.79
La/Yb$_{\mathrm{CN}}$	35.79	57.42	58.11	41.83	54.93	51.89	40.85	58.74
La/Lu$_{\mathrm{CN}}$	45.45	68.19	68.58	45.31	69.68	61.86	53.94	70.69

Table 8 (continued).
Trace-elements (ppm) composition of apatite from Kovdor calcite-forsterite magnetite phoscorite (Ph 3).

Sample	7307/3						
Analysis	core	rim	core	rim	core	mantle	rim
CL colour	red-yellow	yellow	yellow	yellow	red-yellow	yellow	yellow-green
Mg	580	568	582	609	744	509	665
Sc	1.37	1.49	1.36	1.47	1.94	1.67	1.70
Mn	114	117	106	111	135	103	123
Sr	3375	2713	2757	2551	3465	3245	3281
Y	43.0	34.9	28.7	26.8	43.9	48.1	40.2
Ba	13.8	7.15	10.1	8.58	15.1	8.68	12.0
Th	19.8	9.64	12.7	11.0	20.3	10.1	15.4
U	0.49	0.23	0.34	0.30	0.52	0.26	0.38
La	328	238	217	187	379	426	324
Ce	919	736	611	515	1094	1167	899
Pr	99.1	73.5	63.7	54.5	108	117	94.8
Nd	365	268	227	196	397	420	341
Sm	53.8	39.2	32.6	28.1	56.6	60.4	50.1
Eu	13.6	9.88	8.02	7.13	14.1	15.2	12.4
Gd	36.4	24.4	20.5	19.1	35.7	38.2	31.5
Tb	3.77	2.82	2.31	2.03	3.85	4.03	3.40
Dy	15.6	12.3	10.1	8.86	16.2	17.5	14.5
Ho	2.14	1.68	1.35	1.21	2.15	2.38	1.90
Er	3.72	3.08	2.49	2.33	3.87	4.31	3.54
Tm	0.36	0.29	0.24	0.22	0.37	0.40	0.34
Yb	1.59	1.28	1.19	0.94	1.61	1.72	1.44
Lu	0.16	0.15	0.12	0.13	0.19	0.19	0.15
Total REE	1843	1411	1198	1022	2112	2275	1778
La/Ce_{CN}	0.92	0.83	0.92	0.94	0.89	0.94	0.93
La/Nd_{CN}	1.77	1.75	1.88	1.88	1.88	2.00	1.88
La/Yb_{CN}	147.93	133.46	130.64	141.98	168.35	178.05	161.31
La/Lu_{CN}	216.04	165.79	191.67	155.18	208.56	243.82	224.87

Table 8 (continued).
Trace-elements (ppm) composition of apatite from Kovdor calcite carbonatite (C 1).

Sample	57/249				
Analysis	core	rim		core	rim
La	139	152	Mg	983	1094
Ce	339	371	Sc	<2.38	<1.18
Pr	43.6	47.4	Mn	155	167
Nd	170	181	Sr	2243	2655
Sm	27.9	28.6	Y	37.1	39.0
Eu	7.65	7.96	Ba	5.38	7.92
Gd	24.2	24.0	Pb	0.67	0.72
Tb	2.42	2.53	Th	3.25	2.70
Dy	11.4	12.1	U	0.27	0.26
Ho	1.77	1.79			
Er	3.47	3.54			
Tm	0.36	0.38			
Yb	1.87	1.86			
Lu	0.23	0.22			
Total REE	772	834			
La/Ce$_{CN}$	1.06	1.06			
La/Nd$_{CN}$	1.61	1.65			
La/Yb$_{CN}$	53.37	58.45			
La/Lu$_{CN}$	64.27	73.29			

Table 8 (continued).
Trace-elements (ppm) composition of apatite from Kovdor calcite-forsterite-magnetite phoscorite with tetraferriphlogopite (Ph 4).

Sample	4046						
Analysis	core	rim	core	rim	core	rim	rim
CL colour	blue	green	blue	green	blue	green	green
Sc	<2.45	<1.56	<1.21	<1.88	<1.57	<1.49	<1.37
Mn	79.8	75.5	79.7	79.9	74.2	72.7	73.1
Sr	4449	3595	4239	4199	4158	3699	3657
Y	62.1	46.7	60.6	44.5	57.2	45.1	44.9
Ba	18.1	12.6	16.7	11.4	16.2	11.4	10.9
Th	12.8	10.1	14.5	1.13	12.7	6.18	3.61
U	0.10	0.09	0.14	0.38	0.14	0.08	0.05
La	611	345	644	404	575	356	368
Ce	1436	838	1520	1083	1349	865	910
Pr	170	106	171	118	156	107	107
Nd	588	388	585	410	534	384	383
Sm	79.1	54.9	75.5	54.3	69.7	53.0	52.7
Eu	19.7	13.8	18.9	13.7	17.2	13.5	13.2
Gd	59.7	40.0	63.0	45.0	58.6	49.9	48.2
Tb	6.87	4.82	6.25	4.49	5.79	4.38	4.30
Dy	22.5	16.2	21.1	14.9	19.4	15.2	14.8
Ho	2.96	2.22	2.86	2.01	2.63	2.10	2.03
Er	5.63	4.14	5.28	3.59	4.89	3.80	3.66
Tm	0.53	0.38	0.50	0.33	0.48	0.38	0.36
Yb	2.60	1.86	2.45	1.54	2.36	1.83	1.69
Lu	0.27	0.18	0.25	0.17	0.26	0.20	0.19
Total REE	3005	1815	3117	2155	2794	1856	1909
La/Ce_{CN}	1.10	1.06	1.09	0.96	1.10	1.06	1.04
La/Nd_{CN}	2.05	1.75	2.17	1.94	2.12	1.83	1.89
La/Yb_{CN}	168.93	132.72	188.74	187.74	175.01	139.90	156.34
La/Lu_{CN}	241.64	203.78	272.70	248.23	237.94	193.47	210.44

Table 8 (continued).
Trace-elements (ppm) composition of apatite from Kovdor calcite carbonatite with tetraferriphlogopite (C 2).

Sample	AZ2000-26			
Analysis	core	rim	core	rim
Sc	<2.29	<1.66	<2.16	<2.00
Mn	89.9	72.1	90.7	75.2
Sr	6337	5839	6302	5738
Y	71.0	58.3	65.5	55.5
Ba	21.8	16.3	23.1	16.0
Th	25.2	1.58	23.3	1.96
U	0.13	0.02	0.15	0.02
La	925	620	862	573
Ce	2145	1532	1986	1446
Pr	237	178	217	166
Nd	839	626	762	579
Sm	109	82.4	99.4	77.9
Eu	26.5	20.6	24.5	19.3
Gd	75.4	57.4	67.9	52.3
Tb	6.58	4.96	5.99	4.80
Dy	27.1	20.6	24.8	19.8
Ho	3.56	2.81	3.25	2.68
Er	6.42	4.99	5.80	4.67
Tm	0.59	0.44	0.51	0.42
Yb	2.51	1.96	2.28	1.87
Lu	0.24	0.22	0.25	0.20
Total REE	4404	3153	4062	2948
La/Ce_{CN}	1.11	1.05	1.12	1.02
La/Nd_{CN}	2.17	1.95	2.23	1.95
La/Yb_{CN}	264.48	227.48	271.30	219.70
La/Lu_{CN}	406.00	303.27	368.28	308.95

Table 8 (continued).
Trace-elements (ppm) composition of apatite from Kovdor dolomite-forsterite-magnetite phoscorite (Ph 5).

Sample	720/78					
Analysis	core	core	mantle	mantle	rim	rim
CL colour	yellow-green	yellow-green	dark red	dark red	yellow	yellow
Sc	4.93	11.6	60.2	62.5	76.9	72.9
Mn	239	319	1088	1139	1298	703
Sr	3635	3324	5116	6503	5069	4101
Y	38.5	33.1	11.7	17.4	12.7	6.76
Ba	14.4	50.6	1432	1411	1207	857
Th	4.42	5.32	0.14	0.34	0.30	0.08
U	0.04	0.05	<0.01	0.01	0.04	<0.01
La	222	203	73.9	118	71.3	47.7
Ce	326	326	134	206	129	86.4
Pr	33.3	32.2	14.2	20.9	13.8	8.73
Nd	106	105	47.0	66.4	45.6	27.5
Sm	14.5	14.2	6.41	8.44	6.18	3.58
Eu	3.95	4.15	1.89	2.53	1.90	1.13
Gd	11.5	11.0	4.90	6.79	5.50	2.84
Tb	1.60	1.40	0.59	0.82	0.63	0.34
Dy	7.77	6.85	2.50	3.69	2.80	1.48
Ho	1.32	1.15	0.47	0.64	0.48	0.24
Er	3.76	2.91	1.02	1.64	1.15	0.58
Tm	0.49	0.39	0.15	0.23	0.16	0.09
Yb	3.39	2.49	1.09	1.63	1.10	0.55
Lu	0.47	0.36	0.17	0.27	0.18	0.09
Total REE	736	712	289	438	279	181
La/Ce_{CN}	1.76	1.61	1.42	1.49	1.43	1.43
La/Nd_{CN}	4.13	3.80	3.10	3.52	3.08	3.41
La/Yb_{CN}	46.96	58.68	48.64	52.16	46.35	62.54
La/Lu_{CN}	50.05	61.36	46.55	47.36	43.55	56.69

Table 9
Variations in REE concentrations (ppm) in apatite from Kovdor phoscorites and carbonatites.

Rock	min - max	average*
apatite-forsterite phoscorite (Ph 1)	598-2758	924
apatite-forsterite-magnetite phoscorite (Ph 2)	385-880	634
calcite-forsterite-magnetite phoscorite (Ph 3)	1022-2275	1744
calcite carbonatite (C 1)	772-834	801
calcite-forsterite-magnetite phoscorite with tetraferriphlogopite (Ph 4)	1815-3117	2386
calcite carbonatite with tetraferriphlogopite (C 2)	2948-4404	3629
dolomite-forsterite-magnetite phoscorite (Ph 5)	181-736	692
dolomite carbonatite (C 3)	4260-5980**	5330**

* - average values were calculated taking into account the relative areas of different CL colour zones,
** - data from microprobe analysis.

Table 10

Representative compositions (wt.%) of pyrochlore-group minerals from the Kovdor phoscorites and carbonatites.

Rock	CFM (Ph3)				CFM tphl (Ph 4)				Cc tphl (C 2)			
Sample	7307/3				4046				AZ2000/26			
Na_2O	4.74	5.16	5.34	5.29	0.09	0.10	0.28	<0.05	0.32	5.02	<0.05	<0.05
MgO	0.03	0.09	0.04	0.10	0.45	0.02	0.38	0.97	<0.03	<0.03	0.95	0.19
Al_2O_3	0.10	0.06	0.06	0.08	0.11	0.04	0.14	0.16	<0.03	<0.03	<0.03	0.03
CaO	15.31	13.29	12.35	12.38	5.62	4.22	10.52	6.91	5.90	12.61	8.56	8.27
TiO_2	0.75	0.64	0.73	0.68	7.08	7.47	8.56	10.31	7.40	7.37	6.03	8.11
MnO	0.08	<0.03	<0.03	0.03	0.53	0.20	0.37	0.28	0.16	0.07	0.08	0.16
Fe_2O_3	0.56	0.66	0.75	0.48	1.54	1.44	1.47	2.90	2.45	<0.03	0.40	3.63
SrO	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	2.42	3.57
Y_2O_3	<0.05	<0.05	0.06	0.10	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
ZrO_2	1.11	1.02	0.99	1.06	1.26	1.24	1.09	5.86	0.23	0.27	0.41	1.92
Nb_2O_5	54.77	51.43	52.71	53.49	37.22	36.18	40.73	30.10	49.23	48.01	44.07	42.90
BaO	<0.05	<0.05	<0.05	<0.05	1.43	0.47	0.13	0.60	<0.05	<0.05	0.65	0.43
La_2O_3	0.79	1.24	1.45	1.61	0.07	<0.05	0.04	0.18	0.06	0.10	0.07	0.11
Ce_2O_3	3.47	4.99	5.62	6.33	0.42	0.32	0.71	0.80	0.33	0.44	0.87	1.01
Pr_2O_3	0.45	0.93	1.32	1.20	<0.05	0.19	<0.05	<0.05	0.05	0.10	<0.05	0.13
Nd_2O_3	<0.05	<0.05	<0.05	<0.05	<0.05	0.15	<0.05	0.33	<0.05	<0.05	0.07	0.36
HfO_2	0.43	0.54	0.18	0.19	0.19	0.37	0.18	0.36	0.14	<0.05	0.15	0.10
Ta_2O_5	14.68	17.24	15.42	13.40	16.34	18.33	8.42	13.07	8.20	6.98	9.77	5.78
PbO	<0.05	<0.05	0.10	<0.05	<0.05	0.78	<0.05	0.27	0.33	0.73	0.81	<0.05
ThO_2	0.15	<0.05	<0.05	<0.05	1.18	1.98	1.14	2.41	0.56	1.20	1.11	1.79
UO_2	0.05	<0.05	<0.05	0.41	20.32	21.02	17.32	18.19	16.91	14.43	17.46	12.10
F	2.03	1.89	1.65	1.89	<0.05	0.17	0.71	<0.05	0.26	1.89	0.30	0.14
-O=F	0.86	0.80	0.70	0.79		0.07	0.30		0.11	0.79	0.13	0.06
Total	98.65	98.37	98.07	97.92	93.85	94.62	91.88	93.71	92.41	98.42	94.14*	91.03**
REE_2O_3	4.71	7.16	8.38	9.14	0.50	0.66	0.75	1.32	0.43	0.64	1.10	1.61

CFM – calcite-forsterime-magnetite phoscorite, CFM tphl – calcite-forsterime-magnetite phoscorites with tetraferriphlogopite, Cc tphl – calcite carbonatite with tetraferriphlogopite. * - including 0.08 wt.% Sm_2O_3, ** - including 0.36 wt.% SiO_2.

Table 10 (continued).

Rock	DFM (Ph 5)				Dc (C 3)					
Sample	720/78				3/99					6/99
Na_2O	5.39	5.42	5.19	0.14	1.28	0.73	2.43	1.59	3.20	1.25
MgO	0.03	0.06	0.05	0.82	0.23	0.05	0.03	0.03	<0.03	0.04
Al_2O_3	0.18	0.29	0.27	0.48	0.15	0.10	0.10	0.11	0.10	0.09
SiO_2	<0.03	<0.03	<0.03	<0.03	0.23	<0.03	0.23	<0.03	<0.03	0.04
CaO	15.42	15.11	15.31	3.63	6.99	8.06	8.41	8.74	6.78	3.74
TiO_2	0.87	0.79	0.78	1.13	3.14	2.75	2.36	2.95	2.43	2.72
MnO	<0.03	<0.03	0.09	0.12	0.04	0.13	0.03	0.11	0.03	0.04
Fe_2O_3	1.49	1.51	1.74	3.26	1.67	2.06	1.45	2.09	0.93	0.24
SrO	<0.05	<0.05	<0.05	<0.05	4.81	3.18	0.82	0.94	0.21	9.04
Y_2O_3	<0.05	<0.05	<0.05	<0.05	0.11	<0.05	0.05	0.09	0.13	0.07
ZrO_2	0.64	0.49	0.75	<0.05	0.15	0.04	0.23	0.21	0.09	<0.05
Nb_2O_5	53.80	47.32	48.81	33.84	56.00	59.03	61.23	59.79	61.41	62.70
BaO	<0.05	<0.05	<0.05	12.18	5.87	7.13	4.28	4.48	4.10	9.66
La_2O_3	0.09	0.09	0.11	0.18	0.21	0.29	0.46	0.67	0.88	0.44
Ce_2O_3	0.48	0.55	0.52	0.82	0.87	1.06	1.40	1.86	2.24	1.34
Pr_2O_3	<0.05	<0.05	<0.05	<0.05	<0.05	0.10	0.15	0.30	0.25	<0.05
HfO_2	<0.05	0.10	0.11	0.12	0.17	<0.05	0.13	<0.05	<0.05	0.19
Ta_2O_5	17.20	24.66	22.32	26.99	3.36	1.96	2.06	2.82	3.42	0.22
ThO_2	3.49	2.56	3.24	3.46	2.95	2.08	3.96	3.17	4.56	1.77
UO_2	<0.05	0.10	0.24	0.28	0.22	0.21	0.18	0.38	<0.05	0.21
F	2.39	2.09	2.10	<0.05	1.22	1.04	2.26	1.83	2.04	0.83
-O=F	1.01	0.88	0.88		0.51	0.44	0.95	0.77	0.86	0.35
Total	100.45	100.23	100.83*	87.53**	89.17	89.54	91.28	91.39	91.94	94.28
REE_2O_3	0.60	0.64	0.74	1.00	1.08	1.45	2.00	2.83	3.37	1.78

DFM – dolomite-forsterite-magnetite phoscorites, Dc – dolomite carbonatite. * - including 0.08 wt.% Nd_2O_3, ** - including 0.06 wt.% PbO.

Table 11
Representative compositions (wt.%) of zirconolite from the Kovdor phoscorites and carbonatites.

Rock	CFM (Ph 3)			Cc (C 1)	CFM tphl (Ph 4)	Cc tphl (C 2)					
Sample	7307/3			57/249	4046	AZ2000-26					
MgO	1.05	1.49	1.37	<0.03	1.06	0.21	0.56	0.68	0.30	0.36	0.51
Al_2O_3	0.18	0.17	0.17	0.21	0.09	<0.03	0.04	0.04	0.03	<0.03	<0.03
CaO	10.83	9.33	5.96	15.06	10.26	13.76	12.10	11.00	12.38	11.96	10.99
TiO_2	14.65	15.94	16.08	39.45	17.04	23.35	17.16	17.87	21.79	20.46	19.61
MnO	0.63	0.67	1.11	0.04	0.38	0.08	0.16	0.18	0.05	0.16	0.17
Fe_2O_3	5.52	5.66	4.99	5.06	0.77	7.81	7.85	8.42	8.20	8.04	8.56
Y_2O_3	0.59	1.08	1.11	<0.05	0.09	0.17	0.18	0.21	0.33	0.28	0.43
ZrO_2	25.32	26.78	23.88	36.58	27.65	30.77	29.16	29.26	30.83	31.16	29.82
Nb_2O_5	22.80	19.55	19.52	3.68	26.35	16.88	22.17	19.58	17.27	18.07	18.20
BaO	0.33	0.52	0.55	0.39	0.80	0.20	0.22	0.14	0.31	0.16	0.25
La_2O_3	1.49	1.48	1.64	0.05	0.39	0.14	0.23	0.36	0.33	0.36	0.33
Ce_2O_3	4.51	4.86	7.21	<0.05	1.47	0.94	1.20	2.03	1.90	2.00	2.53
Pr_2O_3	0.49	0.73	1.09	<0.05	<0.05	0.21	0.27	0.38	0.55	0.45	0.39
Nd_2O_3	1.86	2.96	5.37	<0.05	0.65	0.86	0.98	1.27	1.44	1.62	2.20
Sm_2O_3	0.21	0.34	1.12	<0.05	<0.05	0.15	0.23	0.15	0.33	0.43	0.43
Gd_2O_3	0.38	0.19	0.85	<0.10	<0.10	0.08	0.17	0.23	0.21	0.33	0.31
Dy_2O_3	0.21	0.26	0.52	<0.10	<0.10	<0.10	<0.10	0.17	0.21	0.16	0.09
Er_2O_3	<0.10	0.23	<0.10	0.10	<0.10	0.13	0.13	<0.10	<0.10	0.10	<0.10
HfO_2	1.28	1.29	0.96	0.88	0.28	0.51	0.36	0.57	0.69	0.76	0.78
Ta_2O_5	6.39	5.60	0.85	0.21	7.38	2.23	2.76	2.37	1.14	1.32	1.34
ThO_2	0.11	0.18	1.90	0.12	5.00	1.02	3.33	4.27	0.92	1.11	1.68
UO_2	0.19	0.19	<0.05	0.13	3.14	0.05	0.32	0.29	0.19	0.29	0.58
Total	99.02	99.50	96.25	101.96	102.80	99.55	99.66*	99.47	99.40	99.58	99.25**
REE_2O_3	9.14	11.05	17.78	0.15	2.51	2.52	3.21	4.61	4.97	5.46	6.28

CFM – calcite-forsterite-magnetite phoscorite, Cc – calcite carbonatite, CFM tphl – calcite-forsterite-magnetite phoscorites with tetraferriphlogopite, Cc tphl – calcite carbonatite with tetraferriphlogopite. * - including 0.08 wt.% PbO, ** - including 0.05 wt.% PbO.

Table 12

REE distribution between various minerals in Kovdor phoscorites and carbonatites.

Mineral // Rock	AF (Ph 1)	AFM (Ph 2)	CFM (Ph 3)	CFM tphl (Ph 4)	DFM (Ph 5)	Cc (C 1)	Cc tphl (C 2)	Dc (C 3)
Apatite								
Mineral content, wt.%	16.73	24.84	0.21	9.41	2.81	0.38	5.74	
Average REE content in mineral, ppm	924	634	1744	2386	692	801	3629	
REE mineral share, %	95.2	97.9	2.9	75.5	68.5	1.6	31.7	
Calcite								
Mineral content, wt.%			20.64	9.00		74.56	85.86	
Average REE content in mineral, ppm			458	391		243	463	
REE mineral share, %			76.7	11.8		97.5	60.6	
Dolomite								
Mineral content, wt.%			1.15	0.86	15.16	5.40	4.52	71.80
Average REE content in mineral, ppm			51	33	39	20	54	55
REE mineral share, %			0.5	0.1	20.8	0.6	0.4	96.9
Pyrochlore								
Mineral content, wt.%			0.035	0.168	0.019			0.007
Average REE content in mineral, ppm			59337	7431	6574			17246
REE mineral share, %			16.6	4.2	4.3			2.9
Zirconolite								
Mineral content, wt.%						0.030	0.117	
Average REE content in mineral, ppm						427	38327	
REE mineral share, %						0.1	6.8	
Σ REE budget, %	95.2	97.9	96.7	91.6	93.6	99.8	99.5	99.8
Σ mineral content, wt.%	16.73	24.84	22.03	19.44	17.99	80.37	96.24	71.80

Phoscorites: AF – apatite-forsterite, AFM – apatite-forsterite-magnetite, CFM – calcite-forsterite-magnetite, CFM tphl – calcite-forsterite-magnetite with tetraferriphlogopite, DFM – dolomite-forsterite-magnetite. Carbonatites: Cc – calcite, Cc tphl – calcite with tetraferriphlogopite, Dc – dolomite.

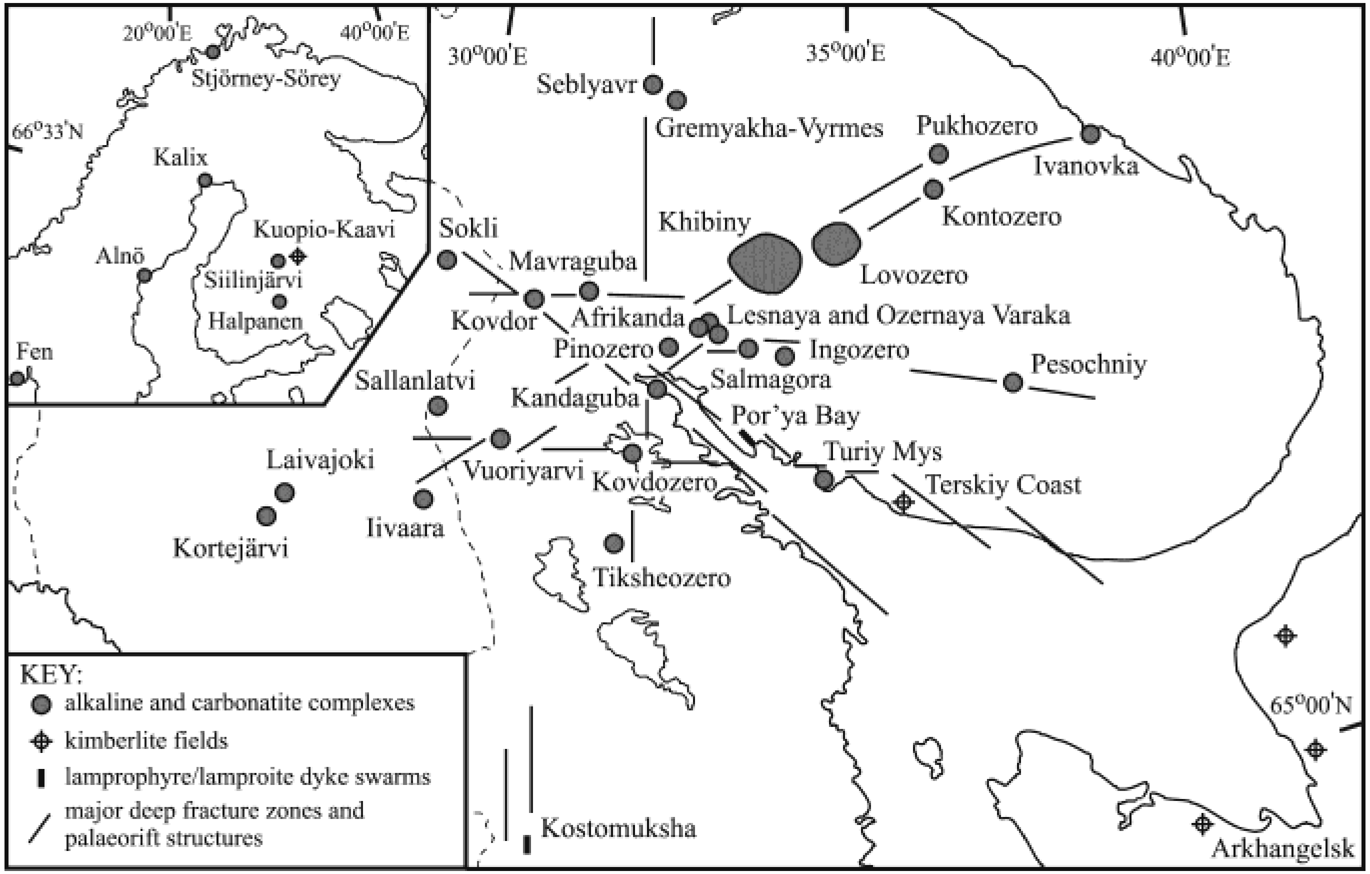

Fig. 1. Simplified map of the Kola province showing the distribution of ultrabasic-alkaline-carbonatite complexes, kimberlites, lamproites and lamprophyres (after Bell and Rukhlov, 2004 - reproduced with the kind permission of the Mineralogical Society of Great Britain and Ireland). Pinozero and Pukhozero are small outcrops of dykes.

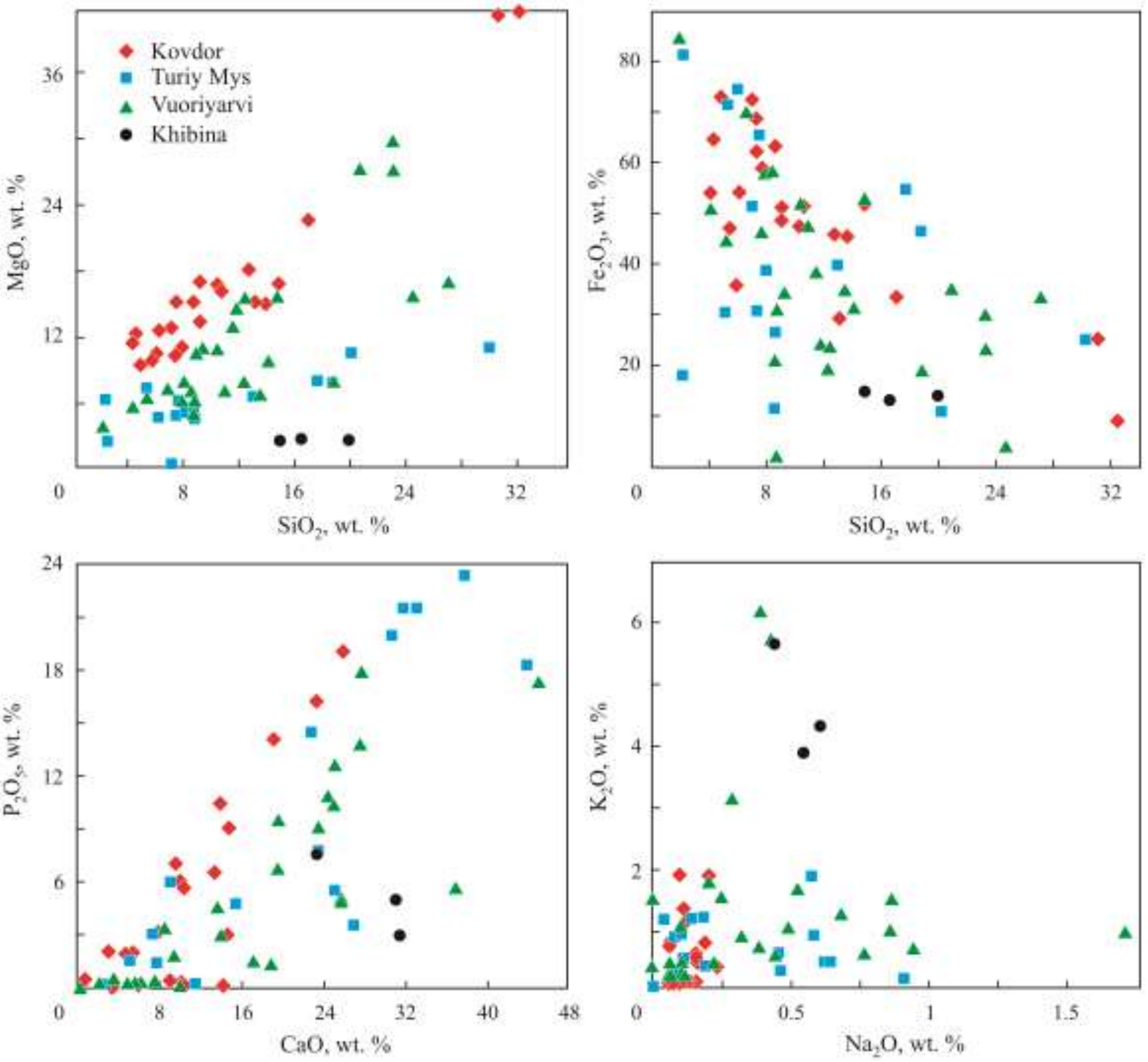

Fig. 2. Composition of phoscorites from Kovdor, Turiy Mys, Vuroriyarvi and Khibina complexes.

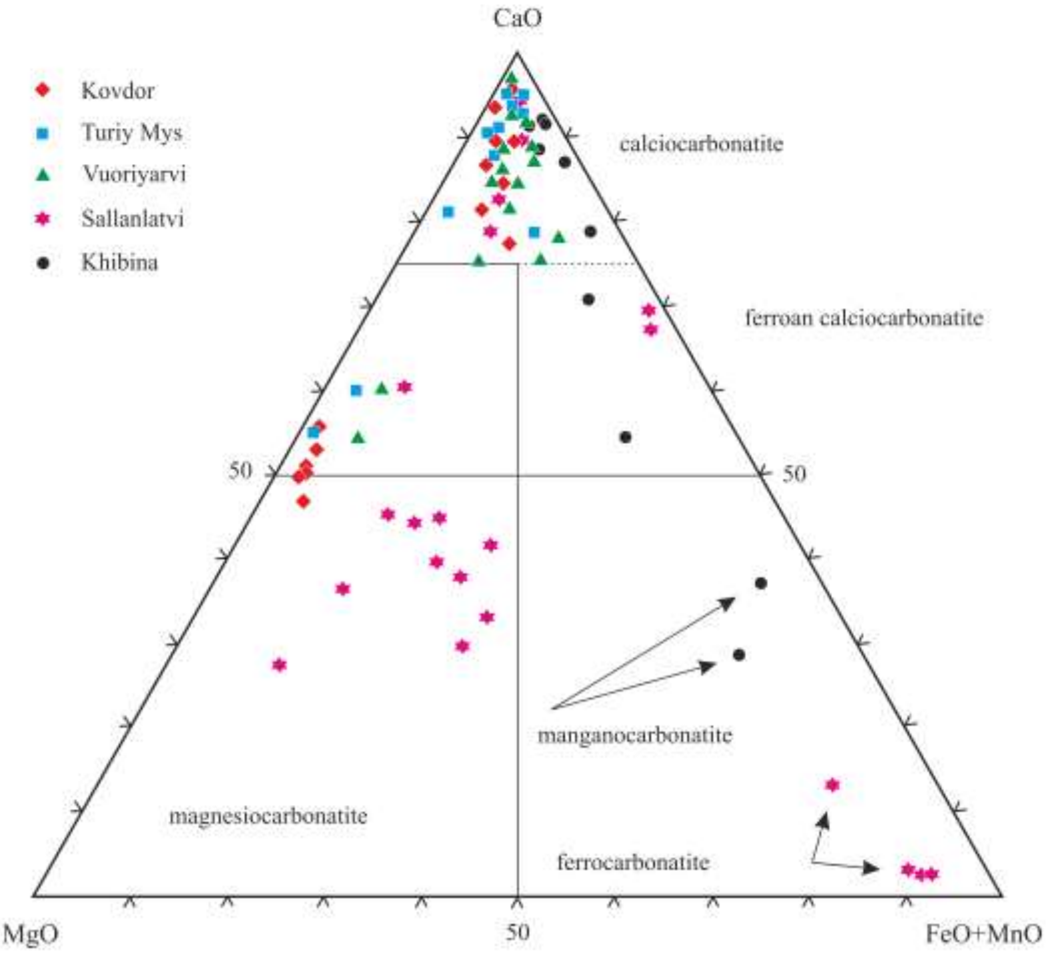

Fig. 3. Composition of carbonatites from Kovdor, Turiy Mys, Vuoriyarvi, Sallanlatvi and Khibina complexes.

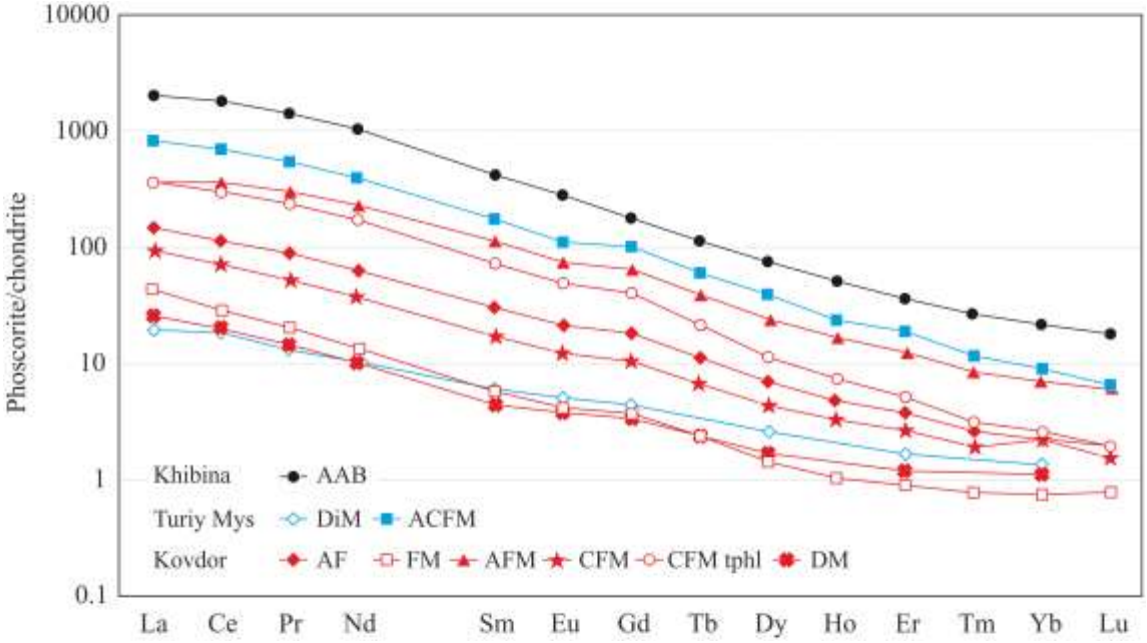

Fig. 4. Chondrite-normalized REE patterns in phoscorites from Kovdor, Turiy Mys and Khibina complexes. Phoscorites: AAB – apatite-aegirine-biotite, DiM – diopside-magnetite, ACFM – apatite-calcite-forsterite-magnetite, AF – apatite-forsterite, FM – forsterite-magnetite, AFM – apatite-forsterite-magnetite, CFM – calcite-forsterite-magnetite, CFM tphl – calcite-forsterite-magnetite with tetraferriphlogopite, DM – dolomite-magnetite. Chondrite values are from Sun and McDonough (1989).

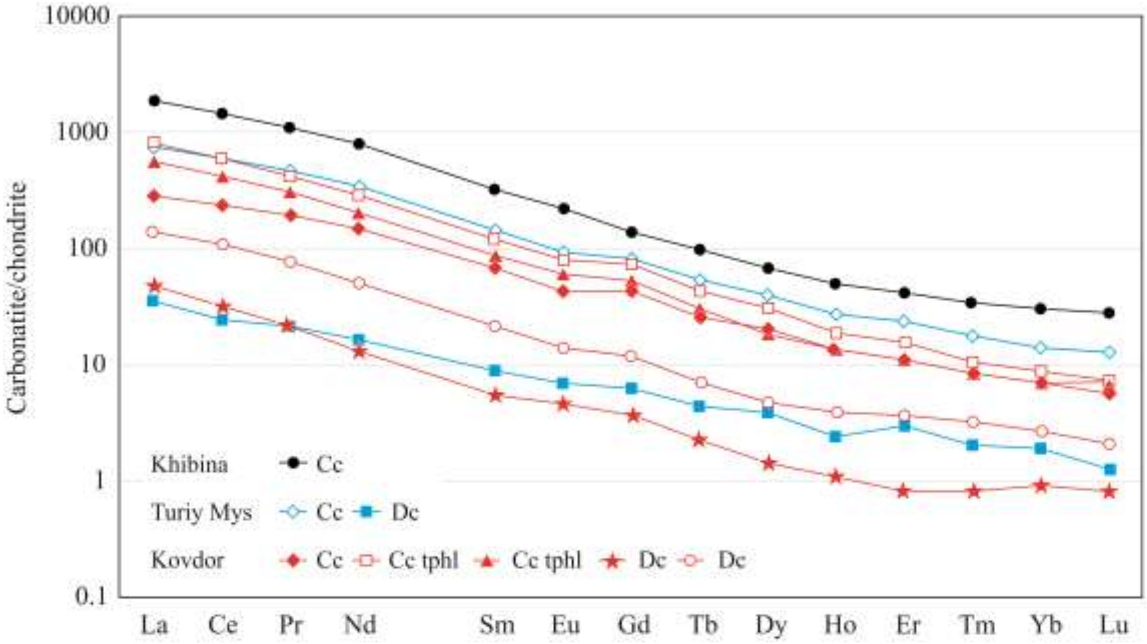

Fig. 5. Chondrite-normalized REE patterns in calcite and dolomite carbonatites without REE minerals from Kovdor, Turiy Mys and Khibina complexes. Cc – calcite carbonatite, Cc tphl – calcite carbonatite with tetraferriphlogopite, Dc – dolomite carbonatite. Chondrite values are from Sun and McDonough (1989).

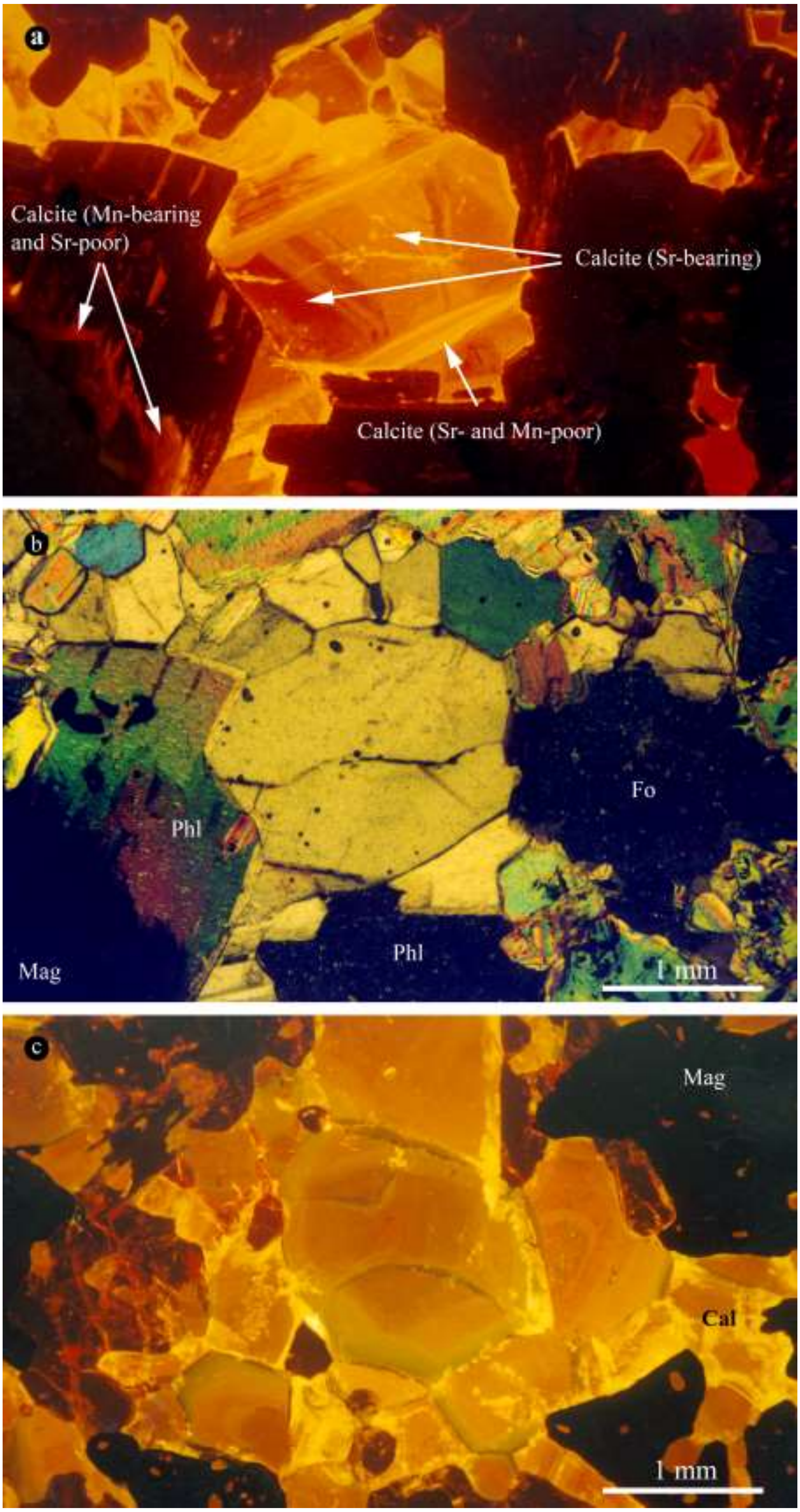

Fig. 6. Zoned calcite (a-b) and apatite (c) crystals in Kovdor phoscorites. (a) and (c) – cathodoluminescence images, (b) - cross-polarized light image of (a).

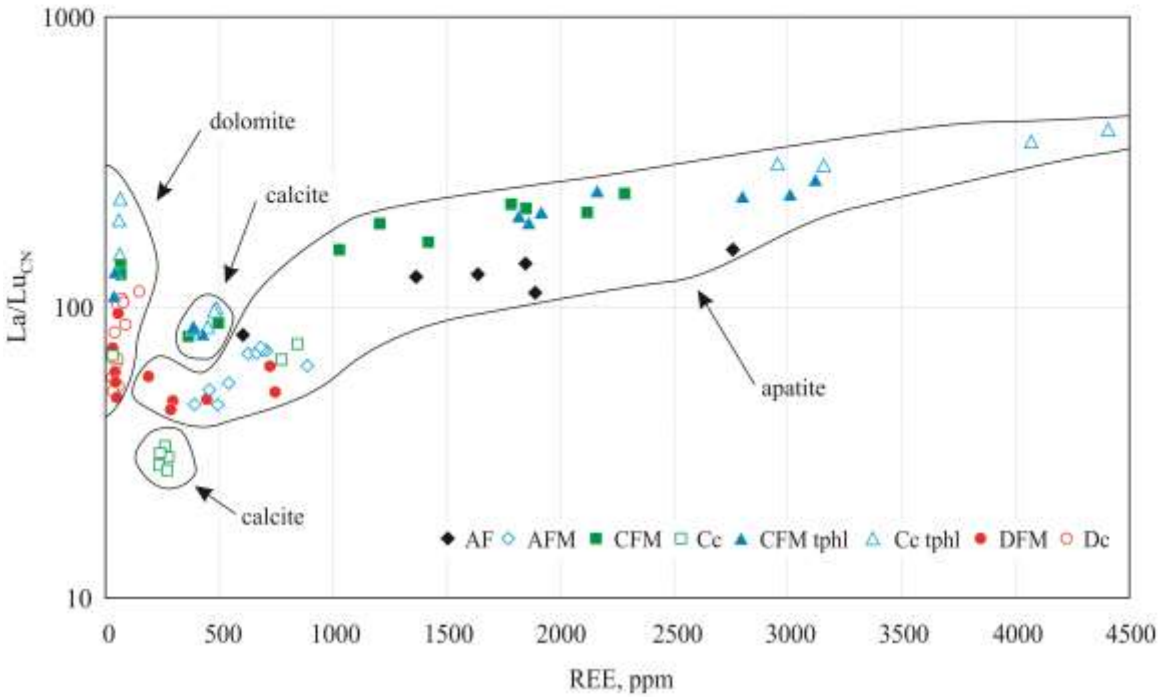

Fig. 7. Relationship between total REE contents and La/Lu$_{CN}$ ratios in calcite, dolomite and apatite from Kovdor phoscorites and carbonatites. Phoscorites: AF – apatite-forsterite, AFM – apatite-forsterite-magnetite, CFM – calcite-forsterite-magnetite, CFM tphl – calcite-forsterite-magnetite with tetraferriphlogopite, DFM – dolomite-forsterite-magnetite. Carbonatites: Cc – calcite, Cc tphl – calcite with tetraferriphlogopite, Dc – dolomite. Chondrite values are from Sun and McDonough (1989).

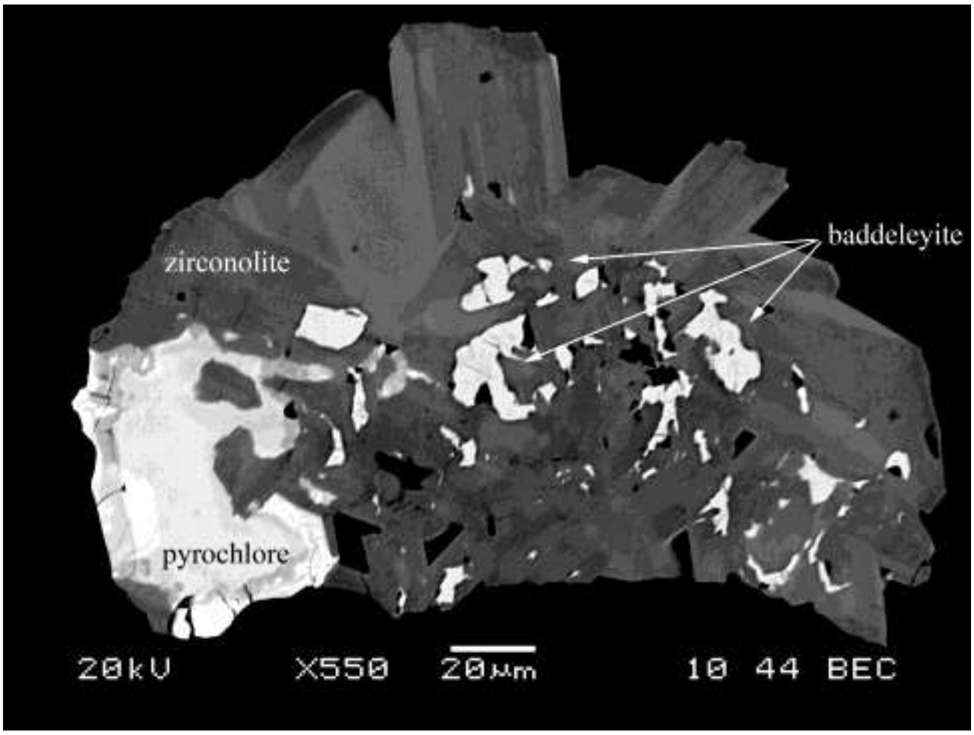

Fig. 8. Baddeleyite-zirconolite-pyrochlore relationship in Kovdor calcite carbonatite with tetraferriphlogopite. Back-scattered electron image.

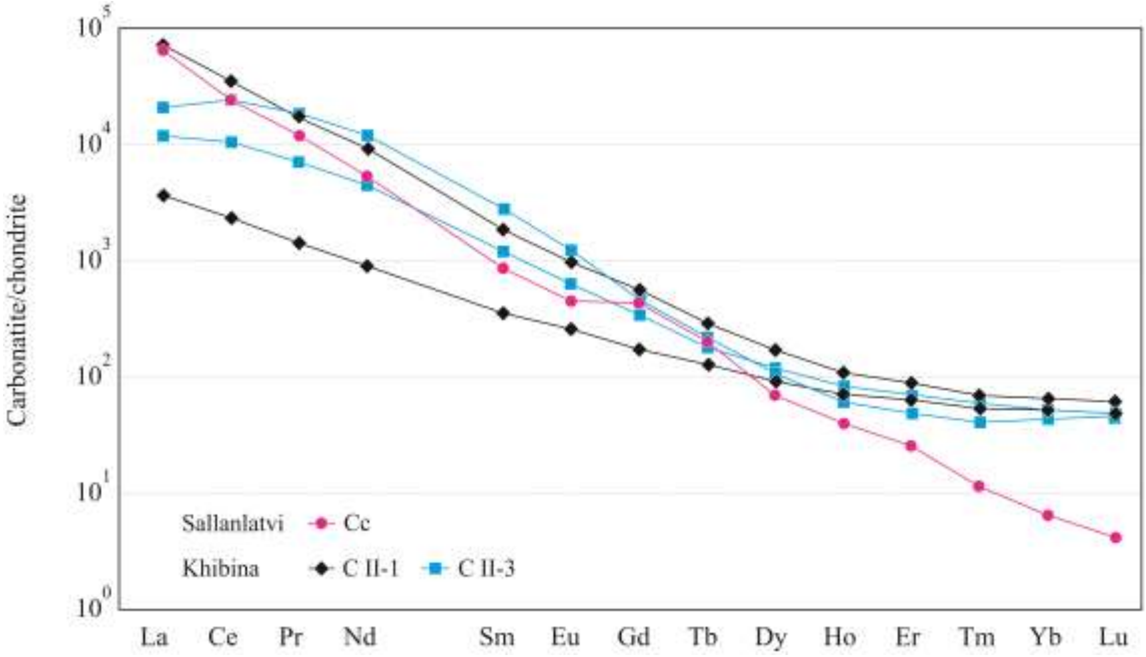

Fig. 9. Chondrite-normalized REE patterns in late-stage carbonatites with REE minerals from Khibina and Sallanlatvi complexes. C II-1 – calcite carbonatite with burbankite, C II-3 – rhodochrosite-ankerite carbonatite with synchysite, Cc – calcite carbonatite with ancylite. Chondrite values are from Sun and McDonough (1989).

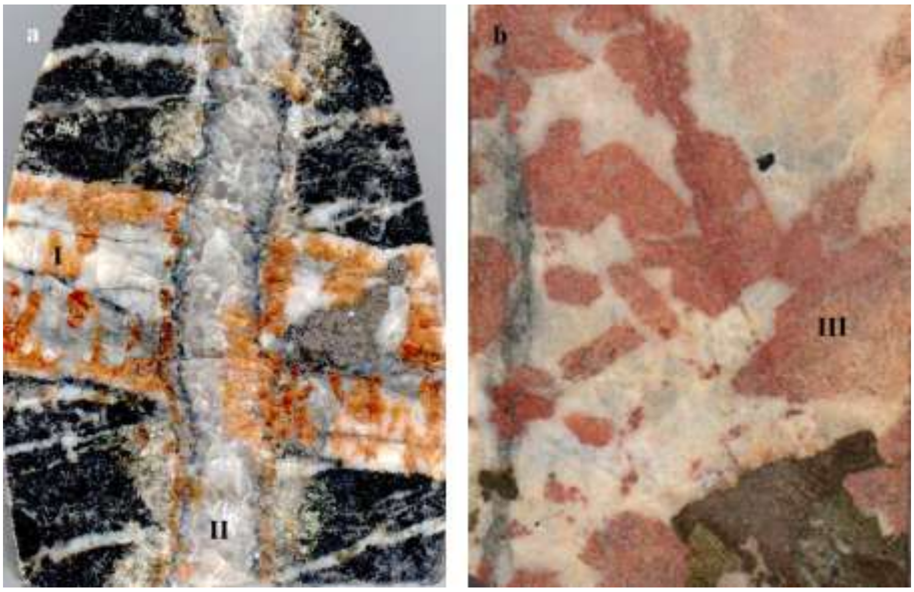

Fig. 10. Khibina REE-rich calcite carbonatites, (a) cross-cutting relations between carbonatite with burbankite (I) and carbonatite with bastnäsite and synchysite (II), (b) baryte-strontianite-synchysite pseudomorphs (III) after burbankite. Size of each sample is 4 x 5.26 cm.

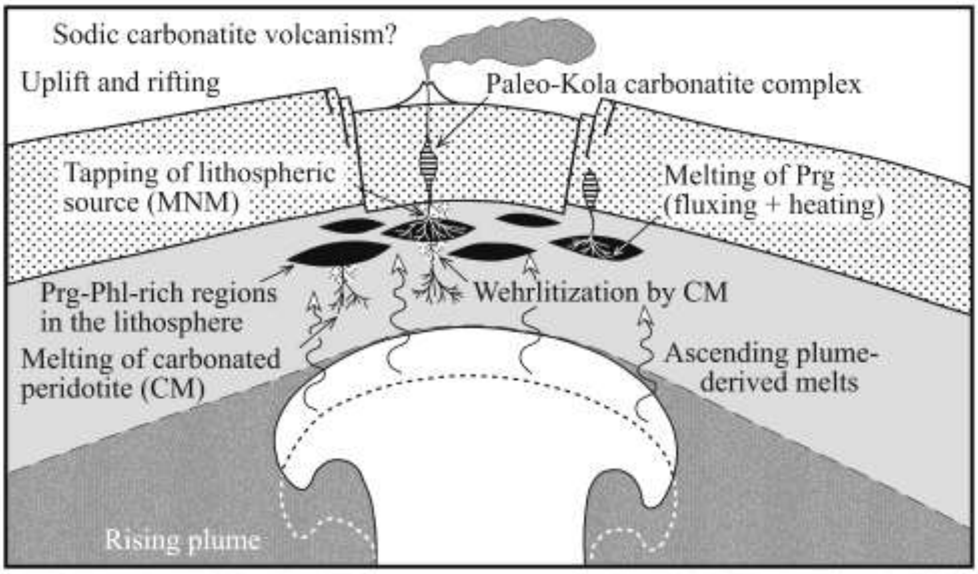

Fig. 11. Illustration of the mantle-plume model of formation of Kola ultrabasic-alkaline-carbonatite complexes (after Chakhmouradian and Zaitsev, 2004 - reproduced with the kind permission of the Mineralogical Society of Great Britain and Ireland).

Supplementary Tables

Analytical methods

Whole-rock analyses

Kovdor, Turiy Mys, Vuoriyarvi and Phalaborwa complexes

Whole rock compositions were measured, on powders ground with an agate mortar, by X-ray fluorescence (Phillips PW1404) for major elements on fused glass disks, and by ICP-AES (Jobin Yvon JY138 Ultrace) and ICP-MS (PE-Elan 6100) for trace elements after standard multi-acid (HCl, HNO_3, HF) digestion.

Khibina complex

All samples were prepared as homogenised powders and digested (10-50 mg of powders dried at 110°C) using 2mL HNO_3, 2mL $HClO_4$ and 4mL HF in Teflon vessels at 150°C. After evaporation to dryness the samples were re-dissolved in 1mL $HClO_4$ and evaporated again to minimise the REE co-precipitation with CaF_2. Samples were then made up in 50mL of 4%HNO_3 containing trace H_2O_2 and analysed by ICP-MS using an Agilent 7700x quadrupole mass spectrometer. Mathematical correction was applied to account for oxide and hydroxide interferences on ^{153}Eu, ^{157}Gd and ^{159}Tb from Ba, Ce, Pr and Nd.

Laser ablation ICP-MS analysis

Laser ablation ICP-MS was performed using an ESI New Wave UP193FX laser ablation accessory coupled to an Agilent Technologies 7500cs ICP-MS. Data were collected using a time resolved method. Helium was used as the sample carrier gas and mixed with Ar post laser cell. The laser spot size varied from 25 to 50 microns, dependent on grain size. Laser fluence was 3J/cm2 and repetition rate 10Hz. Data were calibrated using the National Institute of Standards and Technology (NIST) reference material NIST 612. Internal standards are: Ca for calcite, dolomite and apatite, Si for forsterite, phlogopite and tetraferriphlogopite, Mn for magnetite. Concentrations of Ca, Si and Mn were determined by microprobe analysis.

Pyrochlore and zirconolite analyses

The chemical composition of pyrochlore and zirconolite were determined by wavelength-dispersive analysis using a Cameca SX-50 microprobe. An acceleration voltage of 20 kV, beam current of 20 nA and beam diameter of 1 μm were used for analyses. Pure metals, synthetic compounds and natural minerals were used as standards.

CL

Cathodoluminesence studies were done using polished thin sections in a vacuum chamber of a cold-cathode electron gun (Technosyn Model 8200 MK II) mounted on a polarizing microscope.

Supplementary Table 1. Selected whole-rock analyses of phoscorites from Kovdor.

Rock	AF	FM	AFM	CFM	CFM	CFM_{tfph}	CFM_{tfph}	DFM
Sample	A3 20	99/03	99/12	99/06	99/07	A3 23	99/13	720/78
SiO_2	32.38	7.01	5.85	6.07	12.69	7.27	13.67	4.28
TiO_2	0.09	0.56	0.27	0.37	0.27	1.95	2.41	0.31
Al_2O_3	0.22	2.37	1.32	1.98	3.16	0.72	1.61	2.42
Fe_2O_3	9.30	72.50	36.02	54.17	45.97	62.34	45.57	64.55
MnO	0.27	0.39	0.24	0.31	0.37	0.37	0.38	0.41
MgO	41.84	12.76	10.40	12.52	18.08	10.29	15.10	12.29
CaO	9.68	3.08	26.07	14.62	10.44	10.37	9.93	6.02
Na_2O	0.08	0.16	0.14	0.13	0.12	0.07	0.11	0.16
K_2O	0.12	0.54	0.11	0.09	1.29	0.76	1.88	0.51
P_2O_5	7.04	2.07	19.02	3.00	0.09	5.65	6.01	0.18
LOI	1.00		0.34	7.71	9.08	1.27	1.97	6.99
Total	102.01	101.45	99.77	100.96	101.56	101.05	98.63	98.13
Sc	9.61	60.4	42.5	51.8	90.2	73.1	67.1	58.5
V	44.1	594	322	424	434	1138	532	401
Cr	81.6	0.10	3.46	0.66	0.50	11.3	1.26	0.53
Co	53.6	124	63.3	105	72.9	0.44	110	176
Cu	25.1	41.7	28.5	130	32.4	1358	1182	116
Zn	80.6	350	149	227	273	276	288	332
Rb	3.23	23.1	3.74	3.96	57.1	42.4	101	13.8
Sr	361	154	1007	891	1226	1224	1211	502
Y	7.02	1.75	14.3	5.18	4.78	9.68	13.5	1.41
Zr	409	3335	744	934	1583	545	1551	930
Nb	19.1	90.2	36.3	49.3	128	367	885	59.8
Ba	78.5	283	65.6	92.3	1331	178	182	383
Hf	13.6	112	25.5	28.1	52.7	7.96	43.5	30.4
Ta	1.57	18.0	6.09	6.87	24.3	58.2	182	13.1
Th	2.89	2.75	6.11	2.57	2.98	30.1	149	3.18
U	0.23	0.54	0.58	0.16	0.55	106	151	0.40
La	37.2	8.94	54.5	23.9	31.2	88.8	98.8	6.44
Ce	72.5	18.3	115	45.0	56.3	194	234	13.0
Pr	8.72	2.26	14.5	5.23	6.20	23.5	30.0	1.41
Nd	30.4	8.06	52.8	18.0	20.5	82.3	114	5.06
Sm	4.76	1.22	8.59	2.71	2.96	11.4	17.4	0.73
Eu	1.27	0.34	2.30	0.73	0.87	2.88	3.84	0.22
Gd	3.91	1.02	7.17	2.26	2.55	8.48	12.6	0.71
Tb	0.43	0.11	0.81	0.26	0.27	0.82	1.30	
Dy	1.79	0.48	3.47	1.12	1.17	2.96	5.91	0.44
Ho	0.28	0.07	0.55	0.19	0.19	0.42	0.69	
Er	0.64	0.17	1.21	0.46	0.47	0.86	1.55	0.19
Tm	0.07	0.02	0.13	0.05	0.05	0.08	0.13	
Yb	0.38		0.72	0.40	0.48	0.44	0.84	0.20
Lu	0.05		0.09	0.04	0.05	0.16	0.05	

Supplementary Table 1. Selected whole-rock analyses of phoscorites from Turiy Mys.

Rock	DiM	AFM	AFM	ACFM	FCA$_{tfph}$	CFM$_{tfph}$	FM$_{tfph}$
Sample	99/23	97/46	97/41	99/31	99/07	97/33	99/13
SiO_2	17.65	5.11	8.55	20.11	8.55	6.94	7.46
TiO_2	3.41	0.34	1.83	0.64	0.45	0.04	4.51
Al_2O_3	0.57	0.07	2.06	5.31	0.51	1.78	1.24
Fe_2O_3	54.72	30.51	26.67	10.80	11.52	51.38	65.51
MnO	0.54	0.14	0.13	0.14	0.09	0.06	0.62
MgO	7.86	7.29	5.43	10.56	4.43	0.26	6.06
CaO	11.54	33.18	31.87	27.01	44.00	9.18	7.76
Na_2O	0.47	0.11	0.59	0.64	0.93	0.60	0.65
K_2O	0.58	0.24	1.82	0.43	0.15	0.86	0.43
P_2O_5	0.20	21.48	21.48	3.58	18.28	5.99	1.41
LOI	1.41	4.94	1.94	16.89	13.39	20.83	1.78
Total	98.92	103.41	102.38	96.11	102.29	97.91	97.42
Sc	45.1	20.3	7.94	4.89	20.5		24.2
V	992	359	639	139	219	84.7	979
Cr	1.20	2.80	28.7	1.05	2.45	1.81	2.31
Co	124	71.0	46.1	64.0	31.9		134
Cu	283	43.4	64.7	373	47.6	6284	16.7
Zn	309	133	78.1	103	50.6	133	388
Rb	9.06	5.46	62.9	52.7	21.6	26.5	17.9
Sr	322	1176	3494	3362	3342	1395	576
Y	1.89	15.7	66.9	16.9	28.9	11.7	3.79
Zr	566	2540	107	73.9	668	66.8	397
Nb	37.8	35.3	242	352	797	13.9	64.6
Ba	154	91.2	508	422	215	86.0	303
Hf	16.9	83.0	3.10	1.74	19.4		14.0
Ta	1.92	27.3	68.7		514		18.8
Th	0.40	3.97	8.08	12.4	24.0	5.03	3.81
U	0.27	1.12	54.3	1.06	609	1.58	7.90
La	4.77	37.6	151	193	205	97	16.4
Ce	11.8	84.1	328	373	451	159	38.3
Pr	1.31	11.8	40.7	40.4	54.3	16.2	4.40
Nd	5.13	49.0	152	133	191	49.8	16.2
Sm	0.95	9.18	24.3	16.1	27.9	5.90	2.57
Eu	0.30	2.24	6.69	3.46	6.66	0.93	0.70
Gd	0.93	8.41	22.6	12.7	21.5	5.63	2.18
Tb		1.01	2.30	1.13	2.31	0.55	0.16
Dy	0.66	5.08	17.4	5.44	10.3	3.06	1.22
Ho		0.70	2.85	0.69	1.37	0.43	0.14
Er	0.28	1.67	7.56	1.70	3.20	1.15	0.47
Tm		0.17	0.74	0.16	0.30	0.11	0.04
Yb	0.23	1.18	5.11	0.84	1.59	0.55	0.30
Lu		0.08	0.59	0.10	0.17	0.05	

Supplementary Table 1. Selected whole-rock analyses of phoscorites from Vuoriyarvi.

Rock	CFM	CFM	CFM	ACFM	CAFM	CAM$_{tfph}$	CAM$_{tfph}$	CAM$_{tfph}$
Sample	125/39.8	125/42	125/51	117/99.1	109/171.5	393/257	393/298.7	364/84
SiO_2	23.21	23.26	14.76	12.36	11.74	8.60	14.11	5.17
TiO_2	1.67	1.47	2.53	1.19	0.67	2.33	3.21	1.84
Al_2O_3	0.09	0.41	0.43	0.10	0.20	0.61	3.33	0.94
Fe_2O_3	30.39	23.52	53.43	23.89	24.49	21.18	31.61	44.93
MnO	0.69	0.68	0.73	0.57	0.44	0.40	0.37	0.41
MgO	30.12	27.43	15.79	15.60	14.70	4.73	9.88	6.38
CaO	6.40	7.68	2.32	25.88	27.64	37.03	19.66	19.63
Na_2O	0.07	0.11	0.07	0.12	0.11	0.79	0.30	0.33
K_2O	0.22	1.01	0.42	0.19	0.26	0.58	3.02	0.87
P_2O_5	0.35	0.41	0.29	5.03	13.77	5.64	9.50	6.77
LOI	7.90	12.21	6.59	17.04	7.57	20.36	5.93	8.68
Total	101.10	98.17	97.36	101.96	101.59	102.27	100.92	95.94
Sc	42.3	68.3	49.4	57.8	37.5	19.3	6.83	41.1
V	362	263	740	295	235	457	811	585
Cr	15.7	13.2	8.16	1.36	2.33	16.5	47.6	1.29
Co	76.7	47.8	165	37.7	52.4	26.2	32.2	25.4
Cu	420	839	2451	72.2	210	89.5	41.4	289
Zn	293	264	456	187	167	233	340	462
Rb	9.64	41.3	16.1	6.39	7.88	15.2	81.1	52.2
Sr	703	940	243	2286	1754	4029	2272	2410
Y	10.5	29.6	5.07	48.0	44.9	129	63.8	30.62
Zr	1883	8561	2560	998	796	4210	3605	349
Nb	307	833	139	365	69.3	1408	1540	12179
Ba	167	372	228	223	146	336	741	1116
Hf	57.9	373	63.2	30.3	21.9	122	108	15.9
Ta	19.9	154	0.00	36.4	3.91	155	194	435
Th	21.8	24.1	7.96	152	28.5	327	163	274
U	7.91		5.82	10.2	1.39	150	150	20.9
La	27.1	48.0	11.9	176	170	284	251	199
Ce	77.7	178	28.7	447	423	740	657	707
Pr	11.3		3.77	62.9	57.9	106	89.6	80.0
Nd	48.8	127	15.2	260	243	457	350	296
Sm	9.06		2.83	47.5	41.6	91.5	60.0	45.0
Eu	2.58	8.23	0.84	12.3	10.5	25.9	15.2	11.7
Gd	6.68		2.39	35.1	32.1	69.5	44.4	30.5
Tb	0.77		0.23	3.11	2.77	8.41	4.27	2.29
Dy	3.94		1.66	17.3	15.4	45.7	22.8	13.0
Ho	0.50		0.21	2.26	1.99	6.68	2.98	1.45
Er	1.23		0.69	5.13	4.40	15.2	7.11	3.27
Tm	0.12		0.08	0.30	0.41	1.43	0.75	0.28
Yb	0.85	4.15		2.29	2.19	8.23	3.82	1.47
Lu	0.05		0.05		0.25	0.73	0.44	0.14

Supplementary Table 1. Whole-rock analyses of phoscorites from Phalaborwa.

Rock	Calcite-apatite-forsterite-magnetite		
Sample	Pb 1	Pb 2	Pb 3
SiO_2	17.57	14.15	10.94
TiO_2	0.76	0.97	0.89
Al_2O_3	0.19	0.28	0.21
Fe_2O_3	25.07	27.82	26.88
MnO	0.14	0.14	0.15
MgO	21.56	17.81	14.43
CaO	18.52	22.23	25.56
Na_2O	0.05	0.05	0.06
K_2O	0.10	0.15	0.12
P_2O_5	12.06	14.73	16.22
LOI	5.04	3.75	5.70
Total	101.04	102.07	101.15
Sc	14.3	13.6	13.5
V	206	241	244
Cr	3.43	4.66	4.29
Ni	184	169	134
Cu	6254	308	4990
Zn	122	95.7	129
Rb	5.20	9.69	6.67
Sr	1204	1313	1641
Y	57.6	54.6	74.7
Zr	1314	2055	1646
Nb	10.5	10.6	10.8
Ba	96.2	120	247
Hf		58.7	17.8
Ta	3.35	4.01	30.6
Pb	21.8	9.13	14.0
Th	12.9	6.37	28.7
U		14.7	7.72
La	199	207	251
Ce	529	517	607
Nd	365	380	454
Eu	15.3	15.6	20.2
Yb	2.42	2.58	2.93

Supplementary Table 2. Selected whole-rock analyses of carbonatites from Kovdor.

Rock	Cc	Cc	Cc_{tfph}	Cc_{tfph}	Cc_{tfph}	Dc	Dc	Dc
Sample	57/249	99/04	99/08	A3 25	A3 26	99/10	99/11	99/13
SiO_2	1.38	1.08	0.66	1.23	0.77	2.43	<0.01	0.04
TiO_2	0.03	0.10	0.12	0.12	0.07	0.09	<0.01	<0.01
Al_2O_3	0.52	0.21	0.09	0.18	0.08	1.35	<0.01	0.02
Fe_2O_3	8.56	4.24	3.02	4.80	1.91	23.16	1.90	2.04
MnO	0.16	0.08	0.11	0.15	0.12	0.23	0.32	0.27
MgO	5.07	1.92	2.53	3.87	2.95	17.42	20.81	19.46
CaO	45.68	52.16	50.05	49.60	51.10	22.09	30.47	32.43
Na_2O	0.09	0.10	0.09	0.11	0.07	0.11	0.12	0.13
K_2O	0.28	0.21	0.17	0.28	0.12	0.65	0.04	0.04
P_2O_5	0.16	4.36	2.27	2.04	2.41	0.05	0.64	2.61
LOI	37.09	35.42	39.42	38.53	39.78	32.99	45.98	43.62
Total	99.02	99.86	98.53	100.90	99.37	100.58	100.27	100.66
Sc	24.8	6.21	12.7	14.9	19.2	23.7	7.45	2.68
V	48.8	52.6	40.6	54.8	20.7	138	3.14	5.31
Cr	1.90	2.18	1.35	5.07	5.24	1.17	2.29	1.76
Co	39.5	23.6	8.06	18.5	5.58	28.1	2.51	5.04
Cu	28.9	25.3	178	236	117	17.1	8.88	11.1
Zn	30.9	14.3	18.7	38.4	34.3	80.5	8.76	14.1
Rb	4.64	4.69	3.75	5.23	2.12	15.8		
Sr	2729	2364	8479	6180	7987	1406	3426	4338
Y	15.1	20.5	26.6	23.8	23.3	1.63	3.98	10.6
Zr	637	134	373	252	398	414	136	172
Nb	7.75	3.51	279	449	153	27.8	6.39	53.8
Ba	141	375	238	270	147	440	73.4	72.8
Hf	19.7	3.46	9.55	5.76	10.8	12.0	4.69	4.32
Ta	1.46		24.7	32.3	23.8	5.60		4.94
Th	0.17	4.79	25.0	31.2	11.9	2.98	2.54	1.53
U	0.03	0.19	29.1	16.9	34.5	0.14	0.17	15.6
La	43.0	77.2	197	135	157	11.2	18.5	57.0
Ce	81.9	150	364	254	300	18.9	33.6	111
Pr	9.22	18.0	41.0	29.0	35.3	1.98	3.57	13.1
Nd	33.5	62.3	135	94.0	117	6.09	11.3	44.4
Sm	5.17	9.66	18.8	12.9	16.7	0.82	1.70	6.70
Eu	1.55	2.67	4.59	3.42	4.49	0.26	0.47	1.72
Gd	4.48	7.65	14.9	10.2	13.3	0.74	1.40	5.21
Tb	0.54	0.96	1.58	1.09	1.56	0.08	0.18	0.55
Dy	3.17	4.06	7.60	4.61	6.02	0.34	0.84	2.34
Ho	0.52	0.74	1.04	0.75	1.05	0.06	0.14	0.39
Er	1.45	1.67	2.54	1.77	2.26	0.13	0.32	0.94
Tm	0.18	0.25	0.26	0.21	0.36	0.02	0.04	0.12
Yb	1.12	1.09	1.45	1.17	1.36	0.15	0.19	0.74
Lu	0.15	0.21	0.18	0.17	0.19	0.02	0.03	0.11

Supplementary Table 2. Selected whole-rock analyses of carbonatites from Turiy Mys.

Rock	Cc	Cc	Cc	Cc_{tfph}	Cc_{tfph}	Dc
Sample	177	99/59	97/68	99/46	99/08	97/90
SiO_2	2.30	3.45	2.34	4.29	0.72	0.24
TiO_2	0.06	0.12	0.09	0.06	0.01	0.01
Al_2O_3	0.29	0.41	0.12	0.10	<0.01	0.05
Fe_2O_3	1.96	2.80	1.68	1.73	3.05	1.09
MnO	0.10	0.13	0.13	0.11	0.10	0.27
MgO	0.86	3.37	1.46	2.57	1.14	19.28
CaO	53.95	50.98	53.64	52.32	50.55	33.88
Na_2O	0.32	0.33	0.04	0.54	0.10	0.08
K_2O	0.22	0.45	0.11	0.23	0.57	0.07
P_2O_5	0.20	4.52	1.46	5.65	2.69	0.53
LOI	39.59	33.96	38.56	33.27	35.93	42.29
Total	99.84	100.54	99.62	100.86	94.87	97.77
Sc	4.34	7.38	0.38	14.3	2.87	10.2
V	19.6	19.4	24.6	28.7	4.74	3.42
Cr	0.86	1.79	1.48	4.41	1.07	1.48
Co			7.12		94.1	3.31
Cu	141	177	19.6	153	423	17.7
Zn		16.2	22.6	12.8	6.85	10.2
Rb		6.54	7.53	1.74	1.51	1.00
Sr	6345	4107	4206	4804	5161	2392
Y	21.9	20.1	23.6	25.8	14.2	3.50
Zr		386	348	157	88.4	37.0
Nb		74.5	154	53.5	72.5	2.63
Ba	222	373	209	287	273	74.0
Hf		11.1	9.95	5.60	2.49	1.91
Ta		27.0	7.65	11.2	31.7	
Th		3.96	6.43	5.31	1.35	0.08
U	22.4		11.8	14.8	58.9	0.10
La	127	63.8	179	127	115	8.30
Ce	260	150	372	270	223	14.7
Pr			44.2		24.3	2.03
Nd	96.4	75.4	158	123	85.7	7.51
Sm			21.8		12.1	1.33
Eu	3.23	3.19	5.23	4.66	2.80	0.39
Gd			16.7		9.25	1.24
Tb			1.98		1.03	0.16
Dy			9.85		5.14	0.95
Ho			1.49		0.74	0.13
Er			3.84		1.89	0.47
Tm			0.44		0.20	0.05
Yb	1.34	1.22	2.35	1.46	1.09	0.31
Lu			0.32		0.14	0.03

Supplementary Table 2. Selected whole-rock analyses of carbonatites from Vuoriyarvi.

Rock	Cc	Cc	Cc$_{tfph}$	Cc$_{tfph}$	Cc$_{tfph}$	Dc
Sample	419/182	419/269	393/201	419/16	393/214	393/356
SiO_2	1.06	0.23	8.31	1.75	2.03	0.85
TiO_2	0.07		0.35	0.65	0.13	0.05
Al_2O_3	0.33	0.08	0.67	0.23	0.04	0.22
Fe_2O_3	6.56	0.41	3.71	12.60	11.82	4.29
MnO	0.14	0.11	0.17	0.23	0.43	0.89
MgO	1.95	0.83	4.13	2.84	4.24	16.29
CaO	50.89	54.12	47.20	46.23	44.83	31.40
Na_2O	0.11	0.13	0.99	0.23	0.20	
K_2O	0.20	0.06	0.81	0.24	0.16	0.04
P_2O_5	3.39	0.95	5.26	1.89	0.18	3.80
LOI	36.27	41.87	30.67	34.17	29.63	38.73
Total	100.96	98.78	102.26	101.06	93.68	96.56
Sc	16.0	6.05	23.7	14.3	11.4	
V	106	2.71	111	308	75.8	11.2
Cr	1.09	0.76	1.67	14.4	4.11	
Co	3.55	1.49	3.57	6.14	29.0	3.67
Cu	4.05	77.6	25.7	46.7	317	48.8
Zn	43.1	9.32	46.8	113		155
Rb	4.41		13.6	4.57	5.31	
Sr	3769	5857	4799	4928	7521	10513
Y	28.9	45.5	74.9	43.0	59.5	70.4
Zr	192	196	423	240		156
Nb	14.4	3.00	111	680	195	924
Ba	217	232	312	252		556
Hf	6.10	5.52	11.4	6.91		14.2
Ta	3.19		11.7	36.7		1.62
Th	4.68	1.73	26.7	125	3.68	34.6
U					0.38	
La	96.3	198	300	161	290	604
Ce	193	397	596	345	588	1136
Pr					69.4	131
Nd	105	171	295	159	248	500
Sm					35.7	83
Eu	5.05	7.35	14.4	8.03	9.11	17.2
Gd					28.9	50.0
Tb					3.44	7.1
Dy					16.5	29.1
Ho					2.41	5.48
Er					5.92	11.3
Tm					0.68	1.33
Yb	2.05	2.13	4.03	3.49	3.79	5.02
Lu					0.52	0.61

Supplementary Table 3. List of phoscorite and carbonatite samples for LA ICP-MS analysis.

Phoscorites	Carbonatites
Apatite-forsterite (Ph 1) **sample AZ2000-20**	
Apatite-forsterite-magnetite (Ph 2) **sample AZ2000-22**	
Calcite-forsterite-magnetite (Ph 3) **sample 7307/3**	Calcite with forsterite, phlogopite, magnetite and apatite (C 1) **sample 57/249**
Calcite-forsterite-magnetite with tetraferriphlogopite (Ph 3) **sample 4046**	Calcite with tetraferriphlogopite, magnetite and apatite (C 2) ***sample A32000-26***
Dolomite-forsterite-magnetite (Ph 5) **sample 720/78**	Dolomite with forsterite and phlogopite (C 3a) **sample 3/99**
	Dolomite with Sr-apatite, strontianite and ancylite (C 3b) **sample 6/99**

Supplementary Table 4. LA ICP-MS data (ppm) for REE in silicate minerals from Kovdor phoscorites and carbonatites.

Rock	AF	AFM	CFM	Cc	CFMtfph	Cctfph	DFM	DC
	Ph 1	Ph 2	Ph 3	C 1	Ph 4	C 2	Ph 5	C 3a
Sample	AZ2000-20	AZ2000-22	7307/3	57/249	4046	AZ2000-26	720/78	3/99
				forsterite				
La	<0.08	<0.03	<0.11	<0.06	<0.02	<0.10	<0.02	
Ce	<0.07	<0.02	<0.05	<0.04	<0.02	<0.12	<0.02	
Pr	<0.05	<0.03	<0.04	<0.05	<0.01	<0.53	<0.01	
Nd	<0.23	<0.20	<0.30	<0.27	<0.08	<0.39	<0.24	
Sm	<0.15	<0.16	<0.16	<0.15	<0.06	<0.36	<0.05	
Eu	<0.07	<0.04	<0.07	<0.07	<0.02	<0.15	<0.03	
Gd	<0.10	<0.13	<0.13	<0.18	<0.05	<0.28	<0.09	
Tb	<0.04	<0.02	<0.04	<0.07	<0.08	<0.10	<0.02	
Dy	<0.06	<0.03	<0.06	<0.17	<0.03	<0.26	<0.04	
Ho	<0.05	<0.02	<0.06	<0.03	<0.01	<0.11	<0.02	
Er	<0.08	<0.10	<0.08	<0.16	<0.05	<0.22	<0.06	
Tm	<0.02	<0.02	<0.06	<0.04	<0.02	<0.09	<0.01	
Yb	<0.10	<0.14	<0.10	<0.12	<0.13	<0.28	<0.07	
Lu	<0.05	<0.05	<0.06	<0.08	<0.02	<0.12	<0.02	
			phlogopite		tetraferriphlogopite			phlogopite
La			<0.02	<0.02	<0.01	<0.01		<0.02
Ce			<0.01	<0.02	<0.01	<0.01		<0.01
Pr			<0.01	<0.01	<0.01	<0.01		<0.01
Nd			<0.10	<0.11	<0.04	<0.08		<0.10
Sm			<0.06	<0.05	<0.02	<0.02		<0.03
Eu			<0.05	<0.04	<0.03	<0.01		<0.03
Gd			<0.10	<0.09	<0.09	<0.04		<0.07
Tb			<0.01	<0.01	<0.01	<0.01		<0.01
Dy			<0.01	<0.03	<0.01	<0.01		<0.03
Ho			<0.01	<0.01	<0.01	<0.01		<0.01
Er			<0.02	<0.03	<0.01	<0.01		<0.02
Tm			<0.01	<0.01	<0.01	<0.01		<0.01
Yb			<0.03	<0.05	<0.02	<0.02		<0.04
Lu			<0.01	<0.01	<0.01	<0.01		<0.01

Supplementary Table 4. LA ICP-MS data (ppm) for REE in magnetite from Kovdor phoscorites and carbonatites.

Rock	AF	AFM	CFM	Cc	CFMtfph	Cctfph	DFM	Dc
	Ph 1	Ph 2	Ph 3	C 1	Ph 4	C 2	Ph 5	C 3a
Sample	AZ2000-20	AZ2000-22	7307/3	57/249	4046	AZ2000-26	720/78	3/99
La	<0.01	<0.02	<0.02	<0.02	<0.01	<0.04	<0.01	<0.07
Ce	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.04
Pr	<0.01	<0.02	<0.01	<0.01	<0.01	<0.03	<0.01	<0.03
Nd	<0.06	<0.16	<0.11	<0.11	0.05	<0.25	<0.06	<0.45
Sm	<0.02	<0.08	<0.08	<0.05	<0.04	<0.12	<0.03	<0.17
Eu	<0.01	<0.03	<0.03	<0.01	<0.01	<0.05	<0.01	<0.06
Gd	<0.02	<0.08	<0.07	<0.05	<0.03	<0.11	<0.03	<0.27
Tb	<0.01	<0.01	<0.01	<0.01	<0.00	<0.03	<0.01	<0.03
Dy	<0.01	<0.02	<0.03	<0.03	<0.02	<0.04	<0.01	<0.12
Ho	<0.01	<0.01	<0.01	<0.01	<0.00	<0.01	<0.01	<0.03
Er	<0.02	<0.01	<0.02	<0.03	<0.02	<0.01	<0.01	<0.15
Tm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Yb	<0.03	<0.05	<0.06	<0.04	<0.02	<0.06	<0.01	<0.22
Lu	<0.01	<0.03	<0.01	<0.01	<0.01	<0.02	<0.01	<0.02

Supplementary Table 5. Composition of apatite (wt.%) from Khibina carbonatites.

Rock	Early carbonatites				Late carbonatite			
Sample	604/113.2		603/68.5		603/225.2		603/313.9	
Analysis	core	rim	core	rim				
P_2O_5	40.27	41.12	41.10	43.50	40.70	41.98	41.42	41.13
CaO	53.25	53.21	53.95	54.99	50.94	53.42	51.84	51.60
SrO	2.40	2.44	2.03	1.67	0.86	0.80	1.53	1.20
La_2O_3	0.14	0.12	0.15	<0.03	0.44	0.22	0.94	0.74
Ce_2O_3	0.58	0.39	0.28	0.05	1.31	0.74	1.29	0.94
Pr_2O_3	0.07	0.11	<0.03	<0.03	0.16	<0.03	0.08	0.25
Nd_2O_3	0.16	0.20	0.11	0.05	0.70	0.45	0.70	0.77
Sm_2O_3	0.03	<0.03	<0.03	<0.03	0.05	<0.03	0.09	0.07
F	3.27		3.71		3.77		3.75	
-O=F	1.38	1.38	1.56	1.56	1.59	1.59	1.58	1.58
Total	98.79	99.48	99.77	102.41	97.34	99.79	100.06	98.87

Microprobe analyses, F content was determined by wet chemistry on bulk samples (data are from Zaitsev et al. 1990).

Zaitsev, A.N., Pavlov, V.P. & Polezhaeva, L.I. (1990): Apatite mineralization associated with carbonatite complex of the Khibina alkaline massif. In Alkaline Magmatism of North-East Part of the Baltic Shield (Ivanova, T.N., ed.). Kola Science Centre of the USSR Academy of Sciences, Apatity, 97-105 (in Russian).