

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.% REE₂O₃ in Khibina), and dolomite (up to 77 ppm), as well as accessory pyrochlore (up to 9.1 wt.% REE₂O₃) and zirconolite (up to 17.8 wt.% REE₂O₃). Late-stage carbonatites, at some localities, are strongly enriched in REE (up to 5.2 wt.% REE₂O₃ 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, Phoscorite, Carbonatite, 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, 2012b; 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 REE₂O₃ and inferred resources are 9.5 Mt REE₂O₃ (Khramov, 2011). Mineral deposits of REE include Lovozero (nepheline syenites and foidolites: resources 7.1 Mt REE₂O₃, average ore content 1.12 wt.% REE₂O₃) and Khibina (also spelt Khibiny, apatite-nepheline rocks: resources 5.5 Mt REE₂O₃, average ore content 0.40 wt.% REE₂O₃), 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 REE₂O₃, average ore content 0.35 wt.% REE₂O₃) and Belaya Zima (carbonatites: resources 1.6 Mt REE₂O₃, average ore content 0.9 wt.% REE₂O₃). 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 REE₂O₃ was mined in 2010. Actual production of rare earth elements is even smaller, with just 1500 tons REE₂O₃ produced by the Solikamsk Magnesium Plant in 2010. Between 2001 and 2009 REE production varied between 1600 (in 2004) and 3800 (in 2001) tons REE₂O₃.

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; Seltnann et al., 2010) with demonstrated ore resources of 1.18 Mt (for Nb₂O₅ cutoff grade 3.5 wt.%), and average content 9.53 wt.% REE₂O₃, 0.595 wt.% Y₂O₃, 0.048 wt.% Sc₂O₃ and 6.71 wt.% Nb₂O₅.

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.% REE₂O₃ and 3.2 wt.% ZrO₂), (2) perovskite-bearing carbonatitic, alkaline and ultramafic rocks from Afrikanda (up to 1000 tons REE₂O₃ annually as a by-product of perovskite mining), (3) zircon-bearing alkaline rocks from Sakhariok (about 3 Mt ore resources with 0.2 wt.% REE₂O₃, yttrium and heavy REE, and 0.8 wt.% ZrO₂), and (4) phoscorites and carbonatites in alkaline-ultrabasic complexes that form the Kola Alkaline Province.

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, uncomphagrites, okaites) and diopside-nepheline rocks (melteigites, ijolites, urtites), and nepheline syenites, that range in age from ca. 385 to 360 Ma (Fig. 1) (Kukharensko et al., 1965; Gerasimovskiy et al., 1974; Bulakh and Ivanikov, 1984; Bulakh et al., 2004; Kramm and Sindern, 2004; Reguir et al., 2010; Rukhlov and Bell, 2010). 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, 2004; Bell and Rukhlov, 2004; Sindern et al., 2004; Downes et al., 2005; Lee et al., 2006; Arzamastsev and Mitrofanov, 2009; 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 (e.g., pyrochlore, zirconolite, zirkelite, lueshite, catapleiite), rare earth minerals (e.g., burbankite, carbocernaite, ancylite, cordylite, kukharenskoite, mckelveyite) (Bulakh et al., 1961, 1998a, b, 1999; Kapustin, 1980; Zaitsev et al., 1996, 1998; Chakhmouradian and Mitchell, 1998;

Subbotin et al., 1999; Chakhmouradian and Williams, 2004; Wall and Zaitsev, 2004b). Even platinum group and other 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, 1994; 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 km² 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 SiO₂, Fe₂O₃, CaO, P₂O₅, K₂O and Na₂O (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 (Kukharensko et al., 1965; Kapustin, 1980; Bulakh and Ivanikov, 1984; 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., Kukhareno et al., 1965; Lapin, 1977; 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 (Kukhareno 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.% REE₂O₃) – 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 (Kukhareno 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 REE₂O₃ 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 ($La_{CN} = La \text{ concentration in phoscorite} / La \text{ concentration in chondrite}$) 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 (\pm 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 occurring 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., Kukhareenko 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., Kukhareenko et al., 1965; Kapustin, 1980; 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.% REE₂O₃, 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.% REE₂O₃ 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 et al., 2004). Only apatite from the Khibina phoscorites and carbonatites is characterised by REE enrichments, with 0.1-1.2 wt.% REE₂O₃ in apatite from phoscorites and early-stage carbonatites, and 1.4-3.5 wt.% REE₂O₃ 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. Kukharenskiy 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. Kukharensko 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.%, Ta₂O₅ and 4.7-9.1 wt.% REE₂O₃;
- (2) REE-poor, Ta-rich uranpyrochlore in phoscorites and carbonatites containing tetraferriphlogopite (5.8-18.1 wt.% Ta₂O₅, 11.6-21.1 wt.% UO₂ and 0.5-1.3 wt.% REE₂O₃);
- (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.% REE₂O₃);
- (4) REE-bearing, Ba-rich pyrochlore in dolomite carbonatites, with 1.1-3.4 wt.% REE₂O₃.

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.% Nb₂O₅ and 9.5-17.8 wt.% REE₂O₃;
- (2) low Nb and low REE zirconolite in calcite carbonatites with forsterite and phlogopite (3.7 wt.% Nb₂O₅ and <0.05 wt.% REE₂O₃);
- (3) Nb-rich zirconolite (15.8-22.2 wt.% Nb₂O₅) with moderate contents of REE₂O₃ (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 Kukharensko 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, 2013). 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.% REE₂O₃) to 44411 ppm (5.20 wt.% REE₂O₃).

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, Vuorijarvi, 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 °C (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 Vuorijarvi 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 (\pm 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 asthenospheric 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 \pm 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 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, and initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ 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., 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 $\delta^{13}\text{C}(\text{V-PDB}) = -6.4$ to -5.8 ‰, $\delta^{18}\text{O}(\text{V-SMOW}) = 7.3$ to 7.7 ‰, $(^{87}\text{Sr}/^{86}\text{Sr})_{370} = 0.70390$ – 0.70404 and $(^{143}\text{Nd}/^{144}\text{Nd})_{370} = 0.51230$ – 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 Vuoriharvi, 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, 2004). 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), Arzamastsev and Mitrofanov (2009), 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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References

- Afanasev, B.V., 2011. Mineral resources of the alkaline-ultramafic massifs of the Kola Peninsula. Roza Vetrov, St. Petersburg. 224 pp. (in Russian).
- Amelin, Yu., Zaitsev, A.N., 2002. Precise geochronology of phoscorites and carbonatites: the critical role of U-series disequilibrium in age interpretations. *Geochimica et Cosmochimica Acta* 66, 2399-2419.
- Arzamastsev, A.A., Glaznev, V.N., Raevsky, A.B., Arzamastseva, L.V., 2000. Morphology and internal structure of the Kola alkaline intrusions, NE Fennoscandian Shield; 3D density modelling and geological implications. *Journal of Asian Earth Sciences* 18, 213-228.
- Arzamastsev, A.A., Mitrofanov, F.P., 2009. Paleozoic plume–lithospheric processes in northeastern Fennoscandia: evaluation of the composition of the parental mantle melts and magma generation conditions. *Petrology* 17(3), 300-313.
- Arzamastsev, A.A., Arzamastseva, L.V. 2013. Geochemical indicators of the evolution of the ultrabasic–alkaline series of Paleozoic massifs of the Fennoscandian Shield. *Petrology* 21(3), 249-279.
- Bagdasarov, Yu.A., 1992. On the polyformation state of carbonatites and the extension of the term "carbonatite". *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva* 121(2), 110-115 (in Russian).
- Bagdasarov, Yu.A., 1997. Geochemical features of carbonatites and associated silicate rocks in the Tomtor alkaline carbonatite massif, Eastern Anabar region, Yakutia. *Geochemistry International* 35(1), 7-16.
- Balashov, Y.A., Pozharitskaya, L.K., 1968. Factors governing the behavior of rare earth elements in carbonatite process. *Geochemistry International* 5, 271-288.
- Bell, K., Rukhlov, A.S., 2004. Carbonatites from the Kola Alkaline Province: origin, evolution and source characteristics. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 433-468.
- BGS, 2011. Rare earth elements. BGS-NERC, November 2011. <http://www.bgs.ac.uk/mineralsuk/home.html>
- Birkett, T.,C.,Simandl, G.J., 1999. Carbonatite-associated deposits: magmatic, replacement and residual. In:

- (Simandl, G.J., Hora, Z.D., Lefebure, D.V. (Eds.), Selected British Columbia Mineral Deposit Profiles, Volume 3. Industrial Minerals, BC Ministry of Energy and Mines.
<http://www.empr.gov.bc.ca/Mining/Geoscience/MineralDepositProfiles/ListbyDepositGroup/Pages/NCarbonatites.aspx>
- Borodin, L.S., Lapin, A.V., Kharchenkov, A.G., 1973. Rare metal camaforites. Nauka, Moscow. 176 pp. (in Russian).
- Bühn, B., Wall F., Le Bas M.J., 2001. Rare-earth element systematics of carbonatitic fluorapatites, and their significance for carbonatite magma evolution. *Contributions to Mineralogy and Petrology* 41, 572-591.
- Bulakh, A.G., Kondrateva, V.V., Baranova, E.N., 1961. Carbocernaite, a new rare earth carbonate. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva* 90, 42-49 (in Russian).
- Bulakh, A.G., Ivanikov, V.V. 1984. The problems of mineralogy and petrology of carbonatites. Leningrad State University, Leningrad. 242 pp. (in Russian).
- Bulakh, A.G., Ivanikov, V.V., 1996. Carbonatites of the Turja peninsula, Kola: role of magmatism and metamorphism. *Canadian Mineralogist* 34, 403-409.
- Bulakh, A.G., Nesterov, A.R., Williams, C.T., Anisimov, I.S., 1998a. Zirkelite from the Sebl'yavr carbonatite complex, Kola Peninsula, Russia: an X-ray and electron microprobe study of a partially metamict mineral. *Mineralogical Magazine* 62, 837-846.
- Bulakh, A.G., Le Bas, M.J., Wall, F., Zaitsev, A.N., 1998b. Ancyelite-bearing carbonatites of the Sebyavr massif, Kola peninsula, Russia. *Neues Jahrbuch für Mineralogie Monatshefte* 1998(4), 171-192.
- Bulakh, A.G., Nesterov, A.R., Anastasenko, G.F., Anisimov, I.S., 1999. Crystal morphology and intergrowths of calzirtite $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$, zirkelite $(\text{Ti,Ca,Zr})\text{O}_{2-x}$, zirconolite $\text{CaZrTi}_2\text{O}_7$ in phoscorites and carbonatites of the Kola Peninsula (Russia). *Neues Jahrbuch für Mineralogie Monatshefte* 1999 (1), 11-20.
- Bulakh, A.G., Nesterov, A.R., Zaitsev, A.N., Pilipuk, A.N., Wall, F., Kirillov, A.S., 2000. Sulfur-containing monazite-(Ce) from late-stage mineral assemblages at the Kandaguba and Vuorijarvi carbonatite complexes, Kola Peninsula, Russia. *Neues Jahrbuch für Mineralogie Monatshefte* 2000(5), 217-233.
- Bulakh, A.G., Ivanikov, V.V., Orlova, M.P., 2004. Overview of carbonatite-phoscorite complexes of the Kola Alkaline Province in the context of a Scandinavian North Atlantic Alkaline Province. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 1-43.
- Castor, S.B., 2008. The Mountain Pass rare-earth carbonatite and associated ultrapotassic rocks, California. *Canadian Mineralogist* 46, 779-806.
- Castor, S.B., Hedrick, J.B., 2006. Rare earth elements. In: Kogel, J.E., Trivedi, N.C., Barker, J.M., Krukowski, S.T. (Eds.), *Industrial Minerals and Rocks: Commodities, Markets, and Uses*, 7th edition. SME, pp. 769-792.
- Chakhmouradian, A.R., Zaitsev, A.N., 1999. Calcite-amphibole-clinopyroxene rock from the Afrikanda complex, Kola peninsula, Russia: mineralogy and a possible link to carbonatites. I. Oxide minerals.

- Canadian Mineralogist 37, 177-198.
- Chakhmouradian, A.R., Mitchell, R.H., 1998. Lueshite, pyrochlore and monazite-(Ce) from apatite-dolomite carbonatite, Lesnaya Varaka complex, Kola Peninsula, Russia. *Mineralogical Magazine* 62, 769-782.
- Chakhmouradian, A.R., Williams, C.T., 2004. Mineralogy of high-field-strength elements (Ti, Nb, Zr, Ta, Hf) in phoscoritic and carbonatitic rocks of the Kola Peninsula, Russia. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 293-340.
- Chakhmouradian, A.R., Zaitsev, A.N. 2004. Afrikanda: an association of ultramafic, alkaline and alkali-silica-rich carbonatitic rocks from mantle-derived melts. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 247-291.
- Chakhmouradian, A.R., Wall, F., 2012. Rare earth elements: minerals, mines, magnets (and more). *Elements* 8, 333-340.
- Chakhmouradian, A.R., Zaitsev, A.N., 2012. Rare earth mineralization in igneous rocks: sources and processes. *Elements* 8, 347-353.
- Cordeiro, P.F.O., Brod, J.A., Dantas, E.L., Barbosa, E.S.R., 2010. Mineral chemistry, isotope geochemistry and petrogenesis of niobium-rich rocks from the Catalão I carbonatite-phoscorite complex, Central Brazil. *Lithos* 118, 223-237.
- Demény, A., Sitnikova, M.A., Karchevsly, P.I., 2004. Stable C and O isotope compositions of carbonatite complexes of the Kola Alkaline Province: phoscorite-carbonatite relationships and source compositions. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 407-431.
- Downes, H., Balaganskaya, E., Beard, A., Liferovich, R., Demaiffe, D., 2005. Petrogenetic processes in the ultramafic, alkaline and carbonatitic magmatism in the Kola Alkaline Province: a review. *Lithos* 85, 48-75.
- Dunworth, E.A., Bell, K., 2001. The Turiy massif, Kola Peninsula, Russia: isotopic and geochemical evidence for multi-source evolution. *Journal of Petrology* 42, 377-405.
- Eby, G.N., 1975. Abundance and distribution of the rare earth elements and yttrium in the rocks and minerals of the Oka carbonatite complex, Quebec. *Geochemica et Cosmochimica Acta* 39, 597-620.
- Egorov, L.S., 1991. Ijolite-carbonatite plutonism. Nedra, Leningrad. 260 pp. (in Russian).
- Evans, A.M., 1993. *Ore geology and industrial minerals - an introduction*. Third Edition, Blackwell Scientific Publications. 389 pp.
- Frolov, A.A., Tolstov, A.V., Belov, S.V., 2003. *Carbonatites deposits of Russia*. NIA-Priroda, Moscow. 494 pp. (in Russian).
- Gerasimovsky, V.I., Volkov, V.P., Kogarko, L.N., 1974. The Kola Peninsula. In: Sørensen, H. (Ed.), *The Alkaline Rocks*. John Wiley and Sons, London. pp. 206-220.
- Hatch, G.P., 2012. Dynamics in the global market for rare earths. *Elements* 8, 341-346.

- Henderson, P., 1996. The rare earth elements: introduction and review. In: Jones, A.P., Wall, F., Williams, C.T. (Eds.), *Rare Earth Minerals: Chemistry, Origin and Ore Deposits*. Mineralogical Society Series, 7. Chapman & Hall, London, pp. 1-19.
- Hogarth, D.D., 1989. Pyrochlore, apatite and amphibole: distinctive minerals in carbonatite. In: Bell, K. (Ed.), *Carbonatites: Genesis and Evolution*. Unwin Hyman, London. pp. 105-148.
- Hornig-Kjarsgaard, I., 1998. Rare earth elements in sövitic carbonatites and their mineral phases. *Journal of Petrology* 39, 2105-2121.
- Hughes, J.M., Cameron, M., Mariano, A.N., 1991. Rare-earth-element ordering and structural variations in natural rare-earth-bearing apatites. *American Mineralogist* 76, 1165-1173.
- Ionov, D., Harmer, R.E., 2002. Trace element distribution in calcite–dolomite carbonatites from Spitskop: inferences for differentiation of carbonatite magmas and the origin of carbonates in mantle xenoliths. *Earth and Planetary Science Letters* 198, 495-510.
- Ivanikov, V.V., Rukhlov, A.S., Bell, K., 1998. Magmatic evolution of the melilitite-carbonatite-nephelinite dyke series of the Turiy Peninsula, Kandalaksha Gulf, White Sea region, Russia. *Journal of Petrology* 39, 2043-2059.
- Kapustin, Yu.L., 1980. *Mineralogy of carbonatites*. Amerind Publishing, New Dehli. 259 pp.
- Karchevsky, P.I., Moutte, J., 2004. The phoscorite-carbonatite complex of Vuorijarvi, northern Karelia. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 163-199.
- Khomyakov, A.P., Semenov, E.I., 1971. *Hydrothermal deposits of rare earth fluorocarbonates*. Nauka, Moscow. 135 pp. (in Russian).
- Khramov, D.G., (Ed.), 2011. State report “Status and use of raw-mineral resources of the Russian Federation in 2010”. Mineral, Moscow. 418 pp. (in Russian).
<http://www.mnr.gov.ru/regulatory/list.php?part=1257>
- Klemme, S., 2010. Experimental constrains on the evolution of iron and phosphorus-rich melts: experiments in the system CaO-MgO-Fe₂O₃-P₂O₅-SiO₂-H₂O-CO₂. *Journal of Mineralogical and Petrological Sciences* 105, 1-8.
- Kogarko, L.N., Suddaby, P., Watkins, P., 1997. Geochemical evolution of carbonatite melts in Polar Siberia. *Geochemistry International* 35(2), 113-118.
- EuroChem, 2012. Annual Report and Accounts 2012. <http://www.eurochem.ru/reports/annual-reports/#annual-report-2012-2>
- Kramm, U., Kogarko, L.N., 1994. Nd and Sr isotope signatures of the Khibina and Lovozero agpaitic centres, Kola Alkaline Province, Russia. *Lithos* 32, 225-242.
- Kramm, U., Kogarko, L.N., Kononova, V.A., Vartiainen, H., 1993. The Kola alkaline province of the CIS and Finland: Precise Rb-Sr ages define 380-360 Ma ages for all magmatism. *Lithos* 30, 33-44.
- Kramm, U., Sindern, S., 2004. Timing of Kola ultrabasic, alkaline and phoscorites-carbonatite magmatism. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key*

- Example of the Kola Alkaline Province. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 75-97.
- Krasnova, N.I., Kopylova, L.N., 1988. The geological basis for mineral-technological mapping at the Kovdor ore deposit. *International Geology Review* 30, 307-319.
- Krasnova, N.I., Petrov, T.G., Balaganskaya, E.G., Garcia, D., Moutte, J., Zaitsev, A.N., Wall, F., 2004a. Introduction to phoscorites: occurrence, composition, nomenclature and petrogenesis. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 45-74.
- Krasnova, N.I., Balaganskaya, E.G., Garcia, D., 2004b. Kovdor – classic phoscorites and carbonatites. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 99-132.
- Kravchenko, S.M., Bagdasarov, Yu.A., 1987. Geochemistry, mineralogy and genesis of apatite-bearing massifs (Maymeicha-Kotui carbonatite province). Nauka, Moscow. 128 pp. (in Russian).
- Kukhareno, A.A., Orlova, M.P., Bulakh, A.G., Bagdasarov, E.A., Rimskaya-Korsakova, O.M., Nefedov, E.I., Ilinskiy, G.A., Sergeev, A.S., Abakumova, N.B., 1965. The Caledonian complex of ultramafic, alkaline rocks and carbonatites of the Kola Peninsula and Northern Karelia. Nedra, Leningrad. 772 pp. (in Russian).
- Kynicky, J., Smith, M.P., Xu, C., 2012. Diversity of rare earth deposits: the key example of China. *Elements* 8, 361-367.
- Lapin, A.V., 1979. Mineral parageneses of apatite ores and carbonatites of the Sebyavr massif. *International Geology Review* 21, 1043-1052.
- Le Bas, M.J., 1977. Carbonatite-nephelinite volcanism. John Wiley & Sons, London. 347 pp.
- Lee, M.J., Garcia, D., Moutte, J., Williams, C.T., Wall, F., 2004. Carbonatites and phoscorites from the Sokli Complex, Finland. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 133-162.
- Lee, M.J., Lee, J.I., Hur, S.D., Kim, Y., Moutte, J., Balaganskaya, E., 2006. Sr–Nd–Pb isotopic compositions of the Kovdor phoscorite–carbonatite complex, Kola Peninsula, NW Russia. *Lithos* 91, 250-261.
- von Maravic, H., Morteani, G., 1980. Petrology and geochemistry of the carbonatite and syenite complex of Lueshe (N.E. Zaire). *Lithos* 13, 159-170.
- Mariano, A.N., Mariano, A., Jr., 2012. Rare earth mining and exploration in North America. *Elements* 8, 369-376.
- Mitchell, R.H., 2005. Carbonatites and carbonatites and carbonatites. *Canadian Mineralogist* 43, 2049-2068.
- Möller, P., 1986. Rare earth mineral deposits and their industrial importance. In: Möller, P., Cerný, P., Saupé, F. (Eds.), *Lanthanides, tantalum and niobium. Mineralogy, Geochemistry, Characteristics of Primary Ore Deposits, Prospecting, Processing and Applications*. Special Publication No. 7 of the Society for Geology Applied to Mineral Deposits. Springer-Verlag, Berlin, pp. 171-188.

- Möller, P., Morteani, G., Schley, F., 1980. Discussion of REE distribution patterns of carbonatites and alkalic rocks. *Lithos* 13, 171-179.
- Orris, G.J., Grauch, R.I., 2002. Rare earth element mines, deposits and occurrences. U.S. Geological Survey Open File Report 02-189, 174 pp.
- Petrov, S.V., 2004. Economic deposits associated with the alkaline and ultrabasic complexes of the Kola Peninsula. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 469-490.
- Pozharitskaya, L.K., Samoilov, V.S., 1972. Petrology, mineralogy and geochemistry of carbonatites from East Siberia. Nauka, Moscow, 265 pp. (in Russian).
- Pyatenko, I.K., Saprykina, L.G., 1976. Carbonatite lavas and pyroclastics in the Palaeozoic sedimentary volcanic sequence of the Kontozero District, Kola Peninsula. *Doklady Akademii Nauk SSSR* 229, 185-187 (in Russian).
- Pyatenko, I.K., Osokin, Ye.D., 1988. Geochemical features of the carbonatite palaeovolcano at Kontozero, Kola Peninsula. *Geokhimiya* 5, 723-737 (in Russian).
- Reguir, E.P., Chakhmouradian, A.R., Halden, N.M., Yang, P., Zaitsev, A.N., 2008. Early magmatic and reaction-induced trends in magnetite from the carbonatites of Kerimasi, Tanzania. *Canadian Mineralogist* 46, 879–900.
- Reguir, E.P., Chakhmouradian, A.R., Halden, N.M., Malkovets, V.G., Yang, P., 2009. Major- and trace-element compositional variation of phlogopite from kimberlites and carbonatites as a petrogenetic indicator. *Lithos* 112(S1), 372–384.
- Reguir, E.P., Camacho, A., Yang, P., Chakhmouradian, A.R., Kamenetsky, V.S., Halden, N.M., 2010. Trace-element study and uranium-lead dating of perovskite from the Afrikanda plutonic complex, Kola Peninsula (Russia) using LA-ICP-MS. *Mineralogy and Petrology* 100, 95-103.
- Reguir, E.P., Chakhmouradian, A.R., Pisiak, L., Halden, N.M., Yang, P., Xu, C., Kynický, J., Couëslan, C.G., 2012. Trace-element composition and zoning in clinopyroxene- and amphibole-group minerals: Implications for element partitioning and evolution of carbonatites. *Lithos* 128-131. 27-45.
- Ribeiro, C.C., Brod, J.A., Junqueira-Brod, T.C., Gaspar, J.C., Petrinovic, I.A., 2005. Mineralogical and field aspects of magma fragmentation deposits in a carbonate–phosphate magma chamber: evidence from the Catalão I complex, Brazil. *Journal of South American Earth Sciences* 18, 355-369.
- Ripp, G.S., Kobylkina, O.V., Doroshkevich A.G., Sharakshynov, A.O., 2000. Late Mesozoic carbonatites of Western Transbaikalia. Buryat Science Centre SB RAS, Ulan-Ude. 230 pp. (in Russian).
- Rudashevsky, N.S., Kretser, Yu.L., Rudashevsky, V.N., Sukharzhevskaya, E.S. 2004. A review and comparison of PGE, noble-metal and sulphide mineralization in phoscorites and carbonatites from Kovdor and Phalaborwa. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 375-405.
- Rukhlov, A.S., Bell, K., 2010. Geochronology of carbonatites from the Canadian and Baltic Shields, and the

- Canadian Cordillera: clues to mantle evolution. *Mineralogy and Petrology* 98, 11-54.
- Russell, H.D., Hiemstra, S.A., Groeneveld, D., 1954. The mineralogy and petrology of the carbonatite at Loolekop, Eastern Transvaal. *Transactions of the Geological Society of South Africa* 57, 197-208.
- Samoilov, V.S., 1984. *Geochemistry of carbonatites*. Nauka, Moscow. 189 pp. (in Russian).
- Seltmann, R., Soloviev, S., Shatov, V., Pirajno, F., Naumov, E., Cherkasov, S., 2012. Metallogeny of Siberia: tectonic, geologic and metallogenic settings of selected significant deposits. *Australian Journal of Earth Sciences* 57(6), 655-706.
- Sindern, S., Zaitsev, A.N., Dem'ny, A., Bell, K., Chakmouradian, A.R., Kramm, U., Moutte, J., Rukhlov, A.S., 2004. Mineralogy and geochemistry of silicate dyke rocks associated with carbonatites from the Khibina complex (Kola, Russia) – isotope constraints on genesis and small-scale mantle sources. *Mineralogy and Petrology* 80, 215-239.
- Shramenko, I.F., Stadnik, V.A., Osadchii, V.K., 1992. *Geochemistry of carbonatites in the Ukrainian Shield*. Naukova Dumka, Kiev. 210 pp. (in Russian).
- Strelnikova, L.A., Polezhaeva, L.I., 1981. Accessory minerals of the pyrochlore group from carbonatites of some alkali-ultramafic massifs. In: *Composition of Alkaline Intrusive Complexes of the Kola Peninsula*. Kola Branch of the USSR Academy of Sciences, Apatity. pp. 81-88 (in Russian).
- Subbotin, V.V., Voloshin, A.V., Pakhomovsky, Ya.A., Bakhchisaraitsev, A.Yu., 1999. Calcioburbankite and burbankite from carbonatites of Vuoriyarvi massif (new data). *Zapiski Vserossiskogo Mineralogicheskogo Obschestva* 128(1), 78-87 (in Russian).
- Subbotin, V.V., Subbotina, G.F., 2000. Minerals of the pyrochlore group in phoscorites and carbonatites of the Kola Peninsula. *Proceedings of the Murmansk State Technical University* 3(2), 273-284 (in Russian).
- Tolstov, A.V., Gunin, A.P., 2001. Comprehensive assessment of the Tomtor deposit. *Vestnik Voronzhskogo Universiteta* 11, 144-160 (in Russian).
- Tuttle, O.F., Gittins, J., (Eds.), 1966. *Carbonatites*. Wiley, New York. 591 pp.
- Vartiainen, H., 1980. The petrography, mineralogy and petrochemistry of the Sokli carbonatite massif, northern Finland. *Geological Survey of Finland, Bulletin* 313, 126 pp.
- Veksler, I.V., Nielsen, T.F.D., Sokolov, S.V., 1998. Mineralogy of crystallized melt inclusions from Gardiner and Kovdor ultramafic alkaline complexes: implications for carbonatite genesis. *Journal of Petrology* 39, 2015-2031.
- Veksler, I.V., Dorfman, A.M., Dulski, P., Kamenetsky, V.S., Danyushevsky, L.V., Jeffries, T., Dingwell, D.B., 2012. Partitioning of elements between silicate melt and immiscible fluoride, chloride, carbonate, phosphate and sulfate melts, with implications to the origin of natrocarbonatite. *Geochimica et Cosmochimica Acta* 79, 20-40.
- Verhulst, A., Balaganskaya, E., Kirnarsky, Yu., Demaiffe, D., 2000. Petrological and geochemical (trace elements and Sr-Nd isotopes) characteristics of the Palaeozoic Kovdor ultramafic, alkaline and carbonatite intrusion (Kola Peninsula, NW Russia). *Lithos* 51, 1-25.
- Viladkar, S.G., Pawaskar, P.B. 1989. Rare earth element abundances in carbonatites and fenites of the

- Newania complex, Rajasthan, India. *Bulletin of the Geological Society of Finland* 61, 113-122.
- Voloshin, A.V., Subbotin, V.V., Yakovenchuk, V.N. Pakhomovsky, Ya.A., Menshikov, Yu.P., Zaitsev, A.N., 1990. Mckelveyite from carbonatites and hydrothermalites of alkaline rocks, the Kola Peninsula (the first findings in the USSR). *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva* 119(6), 76-86 (in Russian).
- Voloshin, A.V., Subbotin, V.V., Yakovenchuk, V.N. Pakhomovsky, Ya.A., Menshikov, Yu.P., Pustcharovsky, D.Yu., 1992. New data on the ewaldite. *Zapiski Vserossiskogo Mineralogicheskogo Obshchestva* 121(1), 56-67 (in Russian).
- Wall, F., Le Bas, M.J., Srivastava, R.K., 1993. Calcite and carbocernaite exsolution and cotectic textures in a Sr,REE-rich carbonatite dyke from Rajasthan, India. *Mineralogical Magazine* 57, 495-513.
- Wall, F., Zaitsev, A.N., 2004a. Phoscorites and carbonatites from mantle to mine: the key example of the Kola Alkaline Province. *Mineralogical Society Series*, 10. Mineralogical Society, London, 498 pp.
- Wall, F., Zaitsev, A.N., 2004b. Rare earth minerals in Kola carbonatites. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. *Mineralogical Society Series*, 10. Mineralogical Society, London, pp. 341-373.
- Wall, F., Niku-Paavola, V.N., Storey, C., Müller, A., Jeffries, T., 2008. Xenotime-(Y) from carbonatite dykes at Lofdal, Namibia: unusually low LREE:HREE ratio in carbonatite, and the first dating of xenotime overgrowths on zircon. *Canadian Mineralogist* 46, 861-877.
- Williams, C.T., 1996. The occurrence of niobian zirconolite, pyrochlore and baddeleyite in the Kovdor carbonatite complex, Kola Peninsula, Russia. *Mineralogical Magazine* 60, 639-646.
- Woolley, A.R., 2003. Igneous silicate rocks associated with carbonatites: their diversity, relative abundances and implications for carbonatite genesis. *Periodico di Mineralogia* 72, 9-17.
- Woolley, A.R., Kjarsgaard, B.A., 2008a. Paragenetic types of carbonatite as indicated by the diversity and relative abundances of associated silicate rocks: evidence from a global database. *Canadian Mineralogist* 46, 741-752.
- Woolley, A.R., Kjarsgaard, B.A., 2008b. Carbonatite occurrences of the World: map and database. Geological Survey of Canada. Open File 5796.
- Yegorov, L.S., 1984. Rare-earth element and fluorine contents of apatite as reflecting formation conditions, alteration, and potential mineralization for rocks of the phoscorite-carbonatite group in ijolite-carbonatite complexes. *International Geology Review* 26, 93-107.
- Yegorov, L.S., 1993. Phoscorites of the Maymecha-Kotuy ijolite-carbonatite association. *International Geology Review* 35, 346-358.
- Zaitsev, A., Bell, K., 1995. Sr and Nd isotope data of apatite, calcite and dolomite as indicators of source, and the relationships of phoscorites and carbonatites from the Kovdor massif, Kola Peninsula, Russia. *Contributions to Mineralogy and Petrology* 121, 324-335.
- Zaitsev, A.N., 1996. Rhombohedral carbonates from carbonatites of the Khibina massif, Kola peninsula, Russia. *Canadian Mineralogist* 34, 453-468.
- Zaitsev, A.N., Yakovenchuk, V.N., Chao, G.Y., Gault, R.A., Subbotin, V.V., Pakhomovsky, Ya.A.,

- Bogdanova, A.N., 1996 Kukharenkoite-(Ce), $Ba_2Ce(CO_3)_3F$, a new mineral from Kola peninsula, Russia, and Quebec, Canada. *European Journal of Mineralogy* 8, 1327-1336.
- Zaitsev, A.N., Bell, K., Wall, F., Le Bas, M.J., 1997. Alkaline rare-earth element carbonates from carbonatites of the Khibiny Massif: mineralogy and genesis. *Doklady Akademii Nauk* 355(2), 241-245.
- Zaitsev, A.N., Wall, F., Le Bas, M.J., 1998. REE-Sr-Ba minerals from the Khibina carbonatites, Kola Peninsula, Russia: their mineralogy, paragenesis and evolution. *Mineralogical Magazine* 62, 225-250.
- Zaitsev, A.N., Demény, A., Sindern, S., Wall, F., 2002. Burbankite group minerals and their alteration in rare earth carbonatites - source of elements and fluids (evidence from C-O and Sr-Nd isotopic data). *Lithos* 62, 15-33.
- Zaitsev, A.N., Sitnikova, M.A., Subbotin, V.V., Fernández-Suárez, J., Jeffries, T.E., 2004. Sallanlatvi complex – a rare example of magnesite and siderite carbonatites. In: Wall, F., Zaitsev, A.N. (Eds.), *Phoscorites and Carbonatites from Mantle to Mine: the Key Example of the Kola Alkaline Province*. Mineralogical Society Series, 10. Mineralogical Society, London, pp. 201-245.
- Zaitsev, A.N., Williams, C.T., Wall, F., Zolotarev, A.A., 2012. Evolution of chemical composition of pyrochlore group minerals from phoscorites and carbonatites of the Khibina alkaline massif. *Geology of Ore Deposits* 54(7), 503-515.