RARE-AERTH ELEMENTS MINERALS IN CARBONITES OF THE KOLA ALKALINE PROVINCE (NORTHERN FENNOSCANDIA)

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Abstract

Various rare earth elements minerals occur in late-stage carbonatites within the Kola Alkaline Province. The carbonatites are mineralogically diverse rocks and contain calcite, dolomite, magnesite, siderite and rhodochrosite as rock-forming minerals. REE-minerals are present as accessory, minor and rock-forming minerals related to two distinct mineral assemblages: primary (magmatic or crystallized from carbohydrothermal solution – e.g. burbankite) and secondary (metasomatic – e.g. ancylite). The REE-minerals tend to be enriched in light REE, with the Y-rich mckelveyite-group minerals as rare exceptions. Stable and radiogenic isotopes indicate a deep mantle source for C, O, Sr and Nd in primary minerals and it is thought that the original formation of REE rich carbonatites was a result of multi-stage fractional crystallization of silicate-carbonate melts.

Introduction

Rare earth-rich carbonatites are here defined as carbonatites containing levels of rare earth elements (REE) as oxides of 1 wt.% and higher in which REE minerals often attain rock-forming concentrations. In a recent review of compositional and mineralogical data for Kola carbonatites (including Khibina, Kovdor, Vuoriyarvi and Turiy Mys) (Zaitsev et al., 2014) established a threshold for the content of REE at 2,000–3,000 ppm, above which REE-minerals are likely to be present. Such rocks are potential economic sources of REE and although none of the examples cited in this paper have been mined for REE, several have previously been exploration targets.

Where successive generations of carbonatite can be defined, all varieties of REE-rich carbonatites are always observed to be late-stage rocks. Many occurrences are assumed to be products of crystallization from (carbo-)hydrothermal fluids (e.g. Fen, Norway; Seblyavr, Kola Alkaline Province) and often all REE-minerals in carbonatite are grouped in this category. However, magmatic origins have been thought possible, and indeed likely for other occurrences (Mountain Pass, USA).

Kola carbonatites

The Kola Alkaline Province contains twenty two complexes (380-360 Ma) consisting of various ultrabasic and alkaline rocks, they are, in order of their formation: olivinites, clinopyroxenites, melilititic rocks (turjaites, uncompahgrites, okaites) and foidolites (melteigites, ijolites, urtites). Nepheline syenites (foyaites, khibinites, luyavrites) are principle rock types at two giant Khibina and Lovozero complexes (Fig. 1).

The carbonatites are the youngest intrusive phase in Kola ultrabasic-alkaline complexes and they form multi-stage complex intrusions containing several varieties of carbonatities. They are mineralogically diverse rocks and contain calcite, dolomite, ankerite, kutnahorite, magnesite, siderite and rhodochrosite as major rock-forming minerals. Other typical minerals are represented by forsterite, diopside, phlogopite, tetraferriphlogopite, magnesioarfvedsonite, richterite, apatite and magnetite (Wall & Zaitsev, 2004).

Calcite carbonatites are the early-stage carbonatites (in terminology of Kapustin (1980)) in Khibina, Vuoriyarvi, Seblyavr and Sallanlatvi, while late-stage carbonatites are quite different in terms of mineralogy in these localities. Dolomite, and rarely ankerite carbonatites are known from Vuoriyarvi, Seblyavr and Sallanlatvi, magnesite and siderite carbonatites are present at Sallanlatvi, and Mn-rich carbonatites (including kutnahorite and rhodochrosite varieties) occur at Khibina.

The Kola carbonatites are characterised by the diverse mineralogy of their accessory minerals, and some of these can attain major or minor minerals status in late-stage rocks. They contain assemblages of various primary and subsolidus minerals of REE (e.g. burbankite and carbocernaite in Khibina and Vuoriyarvi, cordylite and kukharenkoite in Khibina and ancylite in all carbonatites) and Nb and Zr (e.g. pyrochlore, uranpyrochlore and bariopyrochlore at Khibina; lueshite and pyrochlore at Sallanlatvi.

The REE-mineralisation in the Kola carbonatites is highly variable ranging from tens of ppm in REE-poor Turiy Mys carbonatites to several wt.% in REE-rich Khibina, Vuoriyarvi and Sallanlatvi carbonatites. All carbonatites are enriched in light REE compared with heavy REE with $(La/Lu)_{CN}$ ratio between 9.3 and 1230 (Zaitsev et al., 2014).

REE-minerals

A total of twenty-five REE-minerals are known from the Kola carbonatites (Wall & Zaitsev, 2004). Mostly, they are carbonates, including unhydrous sodium-rich burbankite and carbocernaite, hydrous ancylite, Ca- and Ba-fluocarbonates synchysite, bastnäsite and cordylite; in addition to oxides (loparite), silicates (cerite) and phosphates (monazite) (Table 1).

Burbankite is a typical early-crystallised mineral in Khibina and Vuoriyarvi late-sage carbonatites, of which the latter also contains calcioburbankite. These minerals form crystals up to 7 cm long and 4 cm diameter, eudhedral hexagonal crystals; also they occur as 10-250 μm drop-like inclusions hosted by calcite or dolomite-ankerite or mineralized along boundaries of calcite/dolomite. The minerals have low birefrigence and optical data resembling apatite. Burbankite and calcioburbankite contain up to 21.7 and 18.5 wt.% REE_2O_3 respectively in Khibina and Vuoriyarvi.

Burbankite and calcioburbankite often show variable degrees of alteration and several assemblages of secondary minerals have been established. Rather simple assemblages, ancylite+strontianite+baryte and synchysite+strontianite+baryte, are typical for the Khibina carbonatites but the pseudomorphs after burbankite-carbocernaite in Vuoriyarvi are very complex with carbocernaite, ancylite, alstonite, olekmenskite, baryte, monazite and Sr-enriched calcite (Fig. 1).

Neither burbankite nor calcioburbankite have been found in the Seblyavr and Sallanlatvi carbonatites but a few samples contain “pseudomorph-like” polycrystalline assemblages of ancylite, strontianite and baryte that suggest the possible former presence of burbankite.

Ancylite is another common REE mineral for the Kola carbonatites. Typically it forms veinlets and thin veins within burbankite-calcioburbankite, and also full pseudomorphs (with strontianite and other minerals) after these minerals. Also, ancylite forms monomineralic veins cross-cutting carbonatites and occurs as euhedral crystals in rock cavities, containing up to 46.5 wt.% REE_2O_3.

Examples of rare REE minerals are the Ba fluocarbonates (cordylite and kukharenkoite) in Khibina carbonatites and Y-rich hydrous carbonates (mckelveyite, donnayite and ewaldite) in Khibina and Vuoriyarvi carbonatites. These minerals are the latest in the crystallisation sequence of the rare earth minerals. While cordylite and kukharenkoite are well studied minerals, the mckelveyite group minerals are not well characterised, particularly their crystal structure.

Origin of REE carbonatites

Studies of Kola REE-rich carbonatites (Wall & Zaitsev, 2004) have showen that there are two groups of rare earth minerals. The first consists of primary minerals crystallised directly from a magma or carbohydrothermal solution; examples are burbankite, calcioburbankite, synchysite, bastnäsite (magmatic minerals), ancylite, mckelveyite (hydrothermal minerals). The second group consists of secondary minerals that were formed during replacement of early-formed REE minerals; ancylite and synchysite are the best examples of these.

Stable and radiogenic isotopes for REE minerals from the Khibina and Vuoriyarvi carbonatites indicate a deep mantle source for C, O, Sr and Nd in primary minerals, but show significant changes for stable isotopes and no changes for radiogenic isotopes in secondary minerals (Zaitsev et al., 2002). Formation of REE rich carbonatites was probably a result of multi-stage fractional crystallization of silicate-carbonate melts (Chakhmouradian & Zaitsev, 2012).

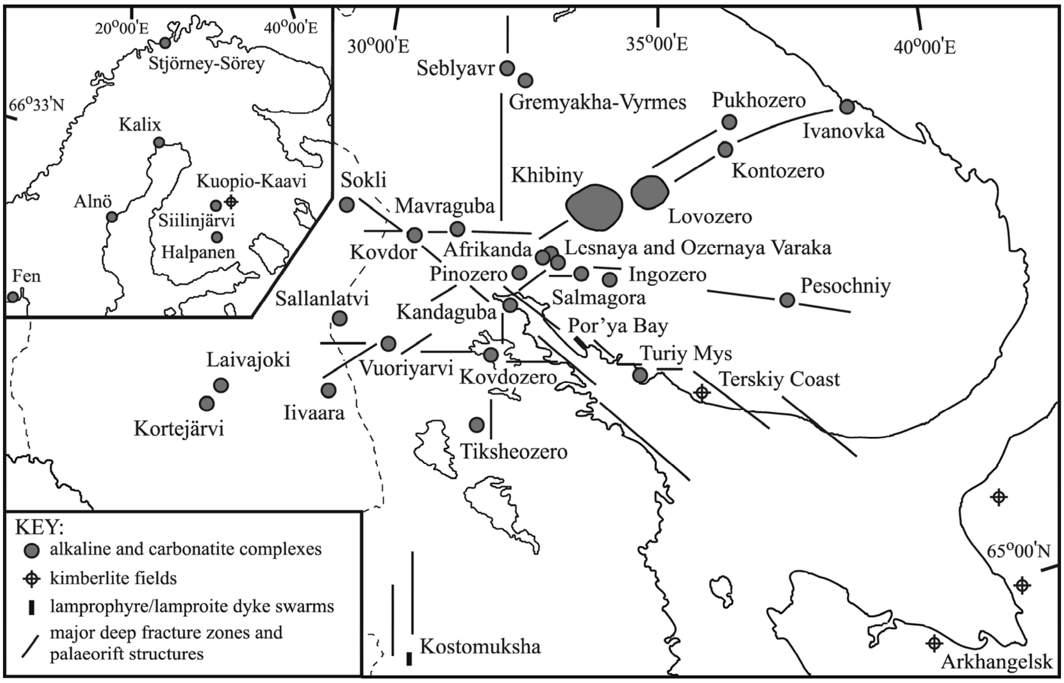

Figure 1: Simplified map of the Kola province showing the distribution of ultrabasic-alkaline-carbonatite complexes, kimberlites, lamproites and lamprophyres (after Bell & Rukhlov, 2004 in Wall & Zaitsev, 2004).

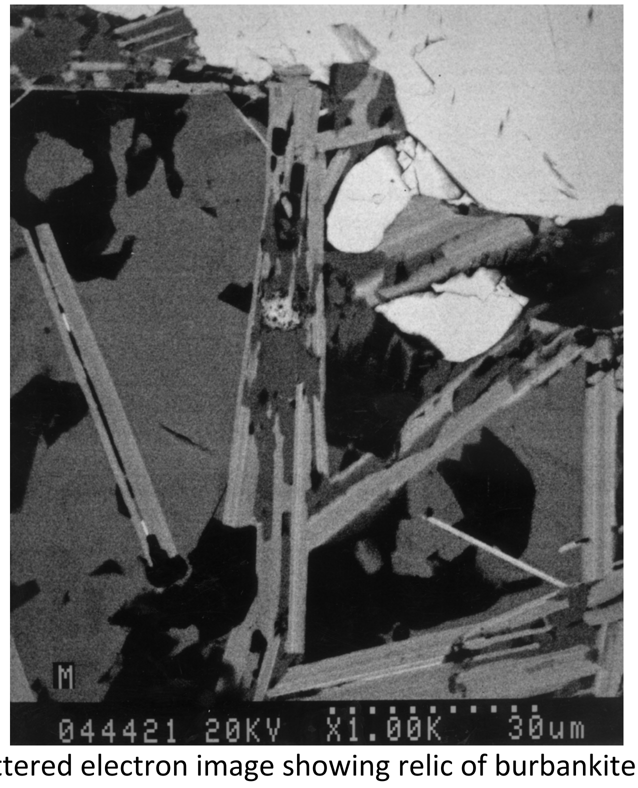

Figure 2: Backscattered electron image showing relic of burbankite in platy crystal of synchysite (centre of image), strontianite (gray) and baryte (white).

Table 1: REE minerals in Kola carbonatites

Mineral	Formula
Burbankite	$(Na,Ca)_3(Sr,Ba,REE)_3(CO_3)_5$
Calcioburbankite	$(Na,Ca)_3(Ca,Sr,Ba,REE)_3(CO_3)_5$
Carbocernaite	$(Na,Ca)(Sr,REE,Ba)(CO_3)_2$
Ancylite	$SrREE(CO_3)_2(OH)xH_2O$
Synchysite	$CaREE(CO_3)_2F$
Bastnäsite	$REE(CO_3)F$
Cordylite	$(Na,Ca)Ba(REE,Sr)_2(CO_3)_4F$
Kukharenkoite	$Ba_2REE(CO_3)_3F$
Mckelveyite	$Ba_3NaCaY(CO_3)_6x3H_2O$
Monazite	$REE(PO_4)$
Loparite	$(REE,Na,Ca)(Ti,Nb)O_3$
Cerite	$(REE,Ca)_9(Fe,Al)(SiO_4)_6(SiO_3OH)(OH)$

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