Mineralogical Magazine, April 1998, Vol. 62(2), pp. 225–250

REE-Sr-Ba minerals from the Khibina carbonatites, Kola Peninsula, Russia: their mineralogy, paragenesis and evolution

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ABSTRACT

Carbonatites from the Khibina Alkaline Massif (360–380 Ma), Kola Peninsula, Russia, contain one of the most diverse assemblages of *REE* minerals described thus far from carbonatites and provide an excellent opportunity to track the evolution of late-stage carbonatites and their sub-solidus (secondary) changes. Twelve rare earth minerals have been analysed in detail and compared with literature analyses. These minerals include some common to carbonatites (e.g. Ca-rare-earth fluocarbonates and ancylite-(Ce)) plus burbankite and carbocernaite and some very rare Ba,*REE* fluocarbonates.

Overall the *REE* patterns change from light rare earth-enriched in the earliest carbonatites to heavy rare earth-enriched in the late carbonate-zeolite veins, an evolution which is thought to reflect the increasing 'carbohydrothermal' nature of the rock-forming fluid. Many of the carbonatites have been subject to sub-solidus metasomatic processes whose products include hexagonal prismatic pseudomorphs of ancylite-(Ce) or synchysite-(Ce), strontianite and baryte after burbankite and carbocernaite. The metasomatic processes cause little change in the rare earth patterns and it is thought that they took place soon after emplacement.

KEYWORDS: Khibina, carbonatite, *REE*, burbankite, carbocernaite, metasomatism

Introduction

RARE-EARTH-RICH carbonatites, containing wt.% levels of *REE* and discrete *RE* minerals, are common as late-stage products in carbonatite complexes. Occasionally, they form the major part of the complex and may be of economic importance, e.g. at Mountain Pass (Olsen *et al.*, 1954), Vuoriyarvi (Kukharenko *et al.*, 1965), Verkhnesayanskii and Nizhnesayanskii (Somina, 1975), and Kangankunde (Wall and Mariano, 1996) but usually their volume is small in comparison with earlier carbonatites, e.g. Fen (Andersen, 1986), and Qaqarssuk (Knudsen, 1991). Rare earth-rich carbonatites usually contain high levels of Ba and also commonly Sr. The principal *RE* minerals in carbonatites are the phosphate, monazite-(Ce); the fluocarbonates, bastnäsite-(Ce), synchysite-(Ce), and parisite-(Ce); and the hydrated carbonate, ancylite-(Ce). Other rare earth minerals such as burbankite, carbocernaite, huanghoite-(Ce), calkinsite-(Ce) and fluocerite-(Ce) have been reported from a few carbonatite localities.

Carbonatites from the Khibina alkaline massif, Kola Peninsula, Russia, (Minakov and Dudkin, 1974; Minakov *et al.*, 1981) present a good opportunity for a comprehensive study of the mineralogy and petrogenesis of *RE*-rich carbonatites. Taken from drillcore, the carbonatites are fresh, coarse-grained, and consist of a sequence of early to late carbonatites that contain high levels of *REE*, Sr and Ba.

The aims of our study are twofold: (i) to present mineralogical data on Khibina *REE*-Sr-Ba minerals because little information on many of these minerals is available in the literature and (ii) to determine the history of crystallization and subsequent alteration of the Khibina minerals.

General geology and geochemistry of the Khibina carbonatites

The Khibina alkaline massif is located in the central part of the Kola Alkaline Province which consists of 24 ultrabasic-alkaline-carbonatite complexes of Devonian age. According to Rb-Sr dating, the age of the Khibina massif ranges from 377 to 362 Ma (Kramm *et al.*, 1993; Kramm and Kogarko, 1994). The Khibina massif is a concentrically zoned pluton, consisting of ultrabasic (peridotite, pyroxenite), alkaline silicate (nepheline syenite, foidolite) and apatite-nepheline rocks and carbonatites. Its general geology, geochemistry and mineralogy have been described in numerous publications (e.g. Khomyakov, 1995; Kogarko *et al.*, 1995). Zaitsev (1996, Fig. 1) gives a general map of the Khibina massif that shows the location of carbonatite drill holes. A Sr and Nd isotope study has been made by Zaitsev and Bell (in preparation)

The carbonatites form a stockwork (Zaitsev, 1996) in which it is possible to distinguish early calcite carbonatites (C I) and later calcite, manganoan ankerite–calcite and ferroan rhodochrosite–manganoan siderite carbonatites (C II). The later carbonatites account for about 90% by volume of the Khibina carbonatite series and occur as veins 1 cm to 6 m wide. Other rocks which are not carbonatites *sensu stricto*, but are genetically connected with them, are represented by phoscorite (BAA) and carbonate-zeolite rocks (CZ III). The silicate country rocks (ijolite, foyaite, olivine melanephelinite and phonolite) hosting the carbonatites are intensively fenitized, and consist of albite, biotite and calcite.

Representative whole-rock major and trace element analyses for the carbonatites are given in Table 1. In terms of the major oxides (CaO, MgO, FeO and MnO), the Khibina carbonatites can be subdivided into calciocarbonatites and ferrocarbonatites (Fig. 1*a*) and show a progressive increase in Fe and Mn from the oldest C I to the

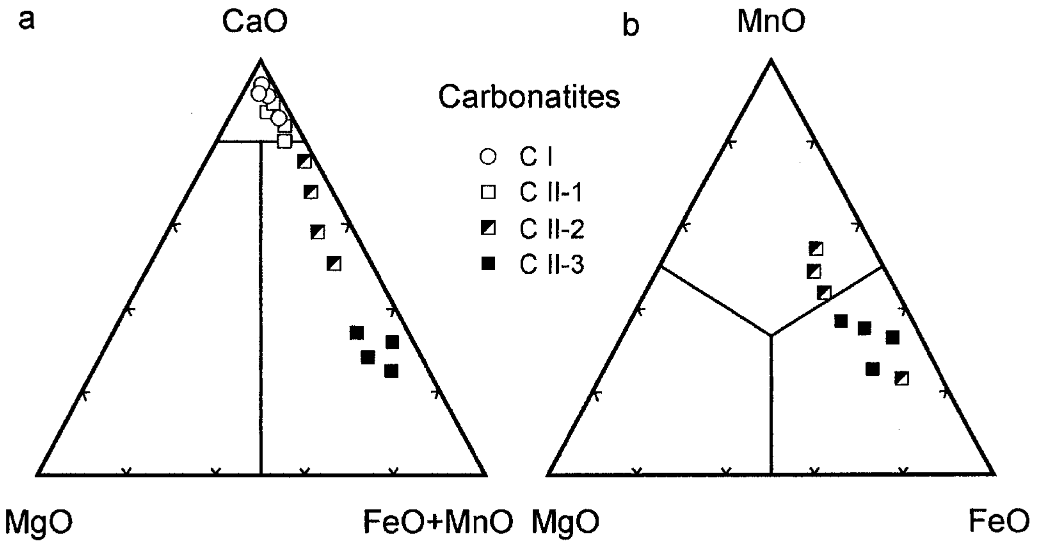

FIG. 1. Plots showing the compositional range of the Khibina carbonatites which (*a*) classify as calcio- and ferrocarbonatites according to Woolley and Kempe (1989) but (*b*) sometimes contain more Mn than Fe and may be classified as manganocarbonatites.

TABLE 1. Representative whole-rock and trace element analyses of the Khibina carbonatites

Rock Sample	C I 632B/1934	C I 632B/1960	C II-1 633/477.7	C II-1 603/165.5	C II-2 604/454	C II-2 603/225	C II-3 603/89	C II-3 604/90
SiO_2 wt %	4.81	3.68	0.64	0.19	0.44	0.87	1.88	2.09
TiO_2	0.64	0.22	0.03	0.02	0.01	0.04	0.02	0.08
Al_2O_3	0.88	0.49	0.25	0.06	0.10	0.29	0.69	0.70
FeO_T	4.99	3.02	3.79	2.29	5.64	8.09	19.14	22.97
MnO	0.37	0.39	1.56	0.85	5.86	11.39	12.78	12.60
MgO	1.20	0.97	0.41	0.35	2.05	3.72	3.97	2.35
CaO	46.50	45.95	32.52	35.12	28.70	24.59	12.13	18.40
Na_2O	0.36	0.59	3.09	1.68	0.14	0.22	0.21	0.25
K_2O	1.45	0.38	0.09	0.05	0.12	0.03	0.55	0.69
P_2O_5	1.25	1.67	0.02	0.04	0.09	0.08	0.11	0.91
S	0.32	0.20	0.73	0.53	0.74	0.41	1.59	1.12
F	0.09	0.19	0.06	0.41	0.84	1.03	0.21	0.12
Cl	0.01	0.01	0.02	0.01	0.01	0.03	0.02	0.01
$-O{=}S,F_2,Cl_2$	0.20	0.18	0.39	0.44	0.73	0.65	0.88	0.61
Total*	64.79	59.57	61.02	62.92	58.21	62.19	58.16	65.16
Rb ppm	37	25	bd	bd	bd	bd	5	9
Ba	1343	1268	13102	10205	11380	10990	28374	1280
Th	13	10	127	103	44	17	84	76
Nb	416	515	bd	10	15	28	112	86
La	437	492	28384	35565	18589	22891	2540	4064
Ce	955	1078	37990	50727	31341	37558	6823	8868
Sr	13449	12307	63819	73004	20495	16174	5533	7017
Nd	403	418	7969	10620	6395	8852	2814	3099
Zr	184	135	bd	5	bd	bd	7	20
Y	62	44	113	137	98	52	43	102
Sc	40	8	56	28	21	32	19	21
V	96	112	bd	14	25	bd	201	156
Cr	22	40	bd	15	10	bd	286	4
Co	20	18	23	14	19	bd	40	4
Cu	34	27	76	39	28	47	84	45
Ni	4	6	24	18	20	24	15	16
Zn	76	44	57	120	995	2354	1850	3073

FeO_T - total iron as FeO. * - including trace elements as oxides. bd - below detection
Whole-rock analyses were made on fusion beads for major elements and powder pellets for trace-elements by X-ray fluorescence analysis at the University of Leicester using a Philips PW1400 X-ray spectrometer. CO_2 and H_2O not analysed

youngest CII-3 carbonatites. However, some ferrocarbonatites contain more Mn than Fe and they can be classified as manganocarbonatites with CaO/(CaO + MgO + FeO + Fe_2O_3 + MnO) less than 0.8, MgO<(FeO+MnO) and MnO>FeO (Table 1 and Fig. 1*b*). The manganocarbonatites contain up to 12.8 wt.% MnO and contain Mn-bearing carbonates, such as manganoan ankerite, ferroan kutnohorite, ferroan rhodochrosite and manganoan siderite (Zaitsev, 1996). Other unusual chemical characteristics of the Khibina carbonatites include the following:

1. Some carbonatites contain burbankite or carbocernaite (C II-1) and are characterized by high Na contents (1.20–4.94 wt.% Na_2O), but contain no Na-bearing silicates such as pyroxene, amphibole or feldspar.

2. Synchysite-(Ce)-bearing carbonatites (C II-2) have high F contents (0.76–1.28 wt.%) whereas other late carbonatites (C II-1 and C II-3)

have low F contents. However, the intensive fluoritization of wall rocks around the carbonatites which now have low amounts of F suggests that the initial F content was higher.

3. The late carbonatites (C II) have high BaO (0.81–3.22 wt.%), SrO (0.61–8.65 wt.%) and light *REE* (1.25–11.35 wt.% La_2O_3 + Ce_2O_3 + Nd_2O_3) and these elements become major components of these carbonatites.

Multi-element variation diagrams for the Khibina carbonatite samples (Fig. 2), normalized to primordial mantle of Wood *et al.* (1979), show that the general chemical features of the Khibina carbonatites are similar to those described for most carbonatites (e.g. Nelson *et al.*, 1988; Clarke *et al.*, 1992). The early calcite carbonatites (C I) have comparable element variation patterns to average data for the calciocarbonatites of Woolley and Kempe (1989), although the Khibina samples show slightly higher Sr (Fig. 2*a*). The Sr is hosted by calcite which contains 1.1–1.8 wt.% SrO (Zaitsev, 1996).

The element variation patterns for the late carbonatites C II (Fig. 2*b*) suggest that these carbonatites have undergone fractional crystallization similar to that shown by Clarke *et al.* (1992). The plot shows a depletion in La, Ce, Nd and Sr normalized values from the relatively early-formed calcite carbonatites with burbankite or carbocernaite (C II-1) to the late manganoan ankerite-calcite carbonatites with synchysite-(Ce) (C II-2), and to the latest ferroan rhodochrosite–manganoan siderite carbonatites with synchysite-(Ce) or cordylite-(Ce) (C II-3).

Although the normalized Ba values are similar in the C II-1 and C II-2 carbonatite types, they show wide variation in C II-3 carbonatites. Some of the C II-3 carbonatites are depleted in Ba compared to C II-1 and C II-2 types and they contain synchysite-(Ce) as a minor or accessory mineral. However, most of C II-3 carbonatites are enriched in Ba and contain cordylite-(Ce) as a major mineral.

Analytical methods

The identification and description of *REE*-Sr-Ba minerals is often difficult due to their complex chemical compositions, with a wide variety of solid solutions and some polymorphs. As a result, they have variable physical properties, infra-red and X-ray diffraction patterns. Other difficulties arise from the limitations of electron microprobe analysis including the inability to determine H_2O

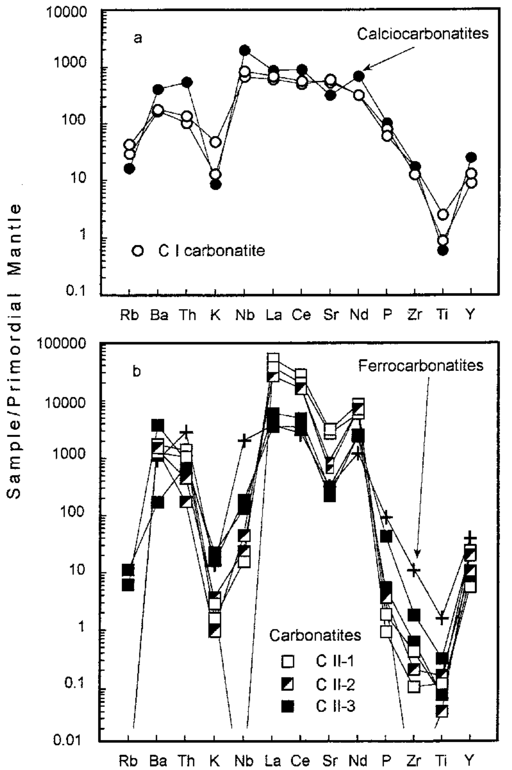

FIG. 2. Multi-element variation diagrams for (*a*) early and (*b*) late Khibina carbonatites, normalized to primordial mantle of Wood *et al.* (1979). Calcio- and ferrocarbonatites are average values from Woolley and Kempe (1989).

and CO_2, loss of Na and F under the electron beam, and the high interference corrections for Ba and the *REE*. In addition, *RE* mineral data available from the literature are commonly incomplete and sometimes inconsistent. These facts prompted us to use as many different techniques as possible for the mineralogical investigation of the *REE*-Sr-Ba minerals from the Khibina carbonatites.

Identification of minerals was based on optical examination, IR-spectroscopy (UR-20 Carl Zeiss spectrophotometer) and X-ray diffraction (RKU camera - 57.3 mm diameter and Fe-$K\alpha$ radiation, 114.6 mm diameter and Cr-$K\alpha$ radiation). Electron microprobe analyses were made using a Cameca SX 50 wavelength-dispersive electron microprobe at The Natural History Museum, London, after preliminary work had been carried out on a Hitachi S2500 scanning electron microscope equipped with a Link AN10/55S energy-dispersive analysis system. The Cameca was operated at 15 kV and 10–20 nA, with spot sizes, as large as possible, up to 30 μm in order to minimize beam damage. Individual *REE* calcium aluminium silicate glasses obtained from the University of Edinburgh were used as standards for the *REE*; jadeite was used for Na, wollastonite and apatite for Ca, celestine for Sr and barium fluoride for Ba and F. Detailed information about conditions of microprobe analyses is available from Williams (1996).

Mineralogy and mineral chemistry

At least 17 minerals containing *REE*, Sr and/or Ba as major elements have been identified in the late carbonatites (C II) and the carbonate-zeolite rocks (CZ III) (Table 2). The mineralogy and paragenesis of these, and the associated minerals, is summarized in Table 3. This table also shows the sequence of formation of phoscorites, carbonatites and carbonate-zeolite rocks in the Khibina massif.

TABLE 2. Minerals containing *REE*, Sr and/or Ba as major elements identified in Khibina late carbonatites (C II) and carbonate-zeolite rocks (CZ III)

Mineral	Formula
burbankite	$(Na,Ca)_3(Sr,Ba,Ce)_3(CO_3)_5$
carbocernaite	$(Na,Ca)(Sr,Ce,Ba)(CO_3)_2$
ancylite-(Ce)	$SrCe(CO_3)_2(OH)\cdot H_2O$
synchysite-(Ce)	$Ca(Ce,La)(CO_3)_2F$
parisite-(Ce)	$Ca(Ce,La)_2(CO_3)_3F_2$
bastnäsite-(Ce)	$(Ce,La)(CO_3)F$
cordylite-(Ce)	$Ba(Ce,La)_2(CO_3)_3F_2$
cebaite-(Ce)	$Ba_3(Ce,La)_2(CO_3)_5F_2$
kukharenkoite-(Ce)	$Ba_2Ce(CO_3)_3F$
mckelveyite-(Y)	$Ba_3Na(Ca,U)Y(CO_3)_6\cdot 3H_2O$
ewaldite	$Ba(Ca,Y,Na,K)(CO_3)_2$
donnayite-(Y)	$Sr_3NaCaY(CO_3)_6\cdot 3H_2O$
edingtonite	$BaAl_2Si_3O_{10}\cdot 4H_2O$
harmotome	$(Ba,K)_{1-2}(Si,Al)_8O_{16}\cdot 6H_2O$
strontianite	$SrCO_3$
baryte	$BaSO_4$
barytocalcite	$BaCa(CO_3)_2$

Alkaline Sr-Ca-REE-Ba carbonates: burbankite and carbocernaite

The alkaline Sr-Ca-*REE*-Ba carbonates, burbankite and carbocernaite, are rock-forming minerals in the calcite carbonatites (C II-1) (Table 3). Field relationships show that the carbonatites with burbankite and carbocernaite are the earliest of the C II group of carbonatites (Zaitsev, 1996).

Burbankite, a rare mineral known from several carbonatite complexes, always occurs in late-stage carbonatites. It has been described from the Bearpaw Mountains (Pecora and Kerr, 1953), Vuoriyarvi (Kukharenko *et al.*, 1965; Kapustin, 1980), Ozernyi (Zdorik, 1966), Arbarastakh (Zhabin *et al.*, 1971), Nizhnesayanskii (Somina, 1975), Chipman Lake (Platt and Woolley, 1990) and Qaqarssuk (Knudsen, 1991).

Burbankite is a double carbonate with the general formula $A_3B_3(CO_3)_5$, where the *A*-site is occupied by Na and Ca and the *B*-site contains Sr, *REE*, Ba and Ca (Effenberger *et al.*, 1985). There are only seven wet chemical analyses of burbankite from carbonatites, made more than 25 years ago (Pecora and Kerr, 1953; Kukharenko *et al.*, 1965; Zdorik, 1966; Zhabin *et al.*, 1971; Kapustin, 1980) and twelve electron microprobe analyses published recently (Effenberger *et al.*, 1985; Platt and Woolley, 1990; Knudsen, 1991).

These data show a large variation in major oxides: Na_2O (4.04–13.89 wt.%), SrO (6.17–32.60 wt.%), CaO (9.81–21.09 wt.%), ΣREE_2O_3 (2.50–23.00 wt.%) and BaO (1.85–14.60 wt.%). Wet chemical analyses of burbankite can show high contents of Si, Al and S but these are probably the result of admixtures. Published microprobe analyses have high cation deficiencies in the *A*-site (up to 0.65 per formula unit), attributed to the loss of Na under the electron beam (Platt and Woolley, 1990), or have high totals with calculated CO_2 (108.26–113.49 wt.%) (Knudsen, 1991) which also indicate possible analytical problems.

Average chemical compositions of the Khibina burbankite determined by wet chemical analysis of 2 g of pure hand-picked burbankite and approximately 40 electron microprobe analyses are given in Table 4. The wet chemical and microprobe results are in good agreement and indicate that the burbankite is relatively low in Ba compared with other carbonatites. The one

TABLE 3. Mineralogy and paragenesis of Khibina *REE*-Sr-Ba minerals

BAA phoscorite-biotite-aegirine-apatite No primary rare earth minerals		
CI early calcite carbonatite No primary rare earth minerals		
C II-1 late calcite carbonatite with burbankite or carbocernaite		
Primary phases		
Burbankite 10–50% volume, yellow-brown in freshly broken hand specimens. Usually large, hexagonal prismatic crystals (5–50 mm long × 1–25 mm diameter). Sometimes grow in from, and about perpendicular to, the contact of the veins. Distribution is heterogeneous. Also as drop-like inclusions (30–200 μm) in calcite associated with euhedral zoned apatite (Fig. 3*a*).		*Carbocernaite* 10-50% volume N.B. does not occur with burbankite. Lemon yellow in hand specimen. Isometric grains 1–5 mm diameter in distinct clusters
Alteration		
Either of two alteration assemblages can completely pseudomorph burbankite, preserving its prismatic, hexagonal crystal form (Fig. 3*b*). 1) Replacement assemblage of *ancylite-(Ce),* strontianite, and less often, baryte and rarely harmotome and edingtonite. All stages of alteration seen: from single fine veins (5–20 μm) of ancylite-(Ce) in burbankite (Fig. 3*d*) to porous aggregates of ancylite-(Ce) and strontianite completely replacing burbankite. Ancylite-(Ce) usually as pink to red anhedral crystals up to 4 mm but also some euhedral crystals and zoned strontianite in cavities. 2) Porous aggregates of *synchysite-(Ce),* strontianite and baryte. Burbankite relics seen in strontianite crystals and also in synchysite-(Ce) and baryte. Fig. 3*c*.	Carbocernaite is often partly replaced by porous aggregates of strontianite, *cordylite-(Ce), synchysite-(Ce)* and baryte. Carbocernaite usually preserved in central parts of the former crystals.	*Strontianite* usually colourless anhedral crystals but also as prismatic zoned crystals up to 2 mm *Baryte,* usually colourless, anhedral, 0.1–1 mm grains. *Edingtonite* and *harmotome,* spherulitic aggregates on ancylite-(Ce) or strontianite.

TABLE 3 (*contd*)

C II-2 late manganoan ankerite-calcite carbonatite with synchysite-(Ce)

Primary phases

Syntaxial intergrowths (Donnay and Donnay, 1953) of synchysite-(Ce), parisite, and bastnäsite-(Ce) (Fig. 4*a*) Intergrowths are very fine – 1–20 µm wide and 50–500 µm long. Associated with strontianite.

Synchysite-(Ce) which is not intergrown is a major rock-forming mineral. White, yellow (usually with calcite) or red (usually with ferroan kutnohorite) tabular crystals, 0.1–3 µm diameter. Often irregular to radiating agregates.

Kukharenkoite-(Ce), as late-stage 0.01–1 mm prismatic crystals in tiny cavities. Often as stellate, dendritic or irregular intergrowths up to 3 mm diameter. Rarely as anhedral, 0.05–0.2 mm grains or platy 0.1–2 mm crystals. Associated with cordylite-(Ce), strontianite, and rarely mckelveyite-(Y).

Strontianite usually occurs as colourless, subhedral crystals up to 2 mm diameter.

C II-3 late carbonatites-ferroan rhodochrosite-manganoan ankerite with synchysite-(Ce) or cordylite-(Ce)

Primary phases

Synchysite-(Ce) sometimes present in fine syntaxial intergrowths with parisite-(Ce).

Cordylite-(Ce), is a typical mineral. White or yellow tabular crystals, 0.1–1 mm and sometimes up to 5 mm, either single or in aggregates.

Mckelveyite-(Y), ewaldite, and *donnayite-(Y)* in cavities. Yellow or white crystals, various habits from tabular, columnar to barrel-shaped. Some crystals are hemimorphic.

Strontianite, primary, usually colourless, subhedral crystals up to 2 mm.

Kukharenkoite-(Ce) (See above)

Edingtonite and *harmotome* are common accessory minerals. Usually, euhedral crystals, up to 2 mm, in cavities.

Alteration

Vein-like aggregates of *synchysite-(Ce), strontianite, baryte* and *bastnäsite-(Ce)* replace the syntaxial intergrowth in some rocks.

Strontianite, usually colourless anhedral crystals.

Baryte, usually colourless, anhedral, 0.1–1 mm grains.

TABLE 3. (*contd*)

CZ III-1 carbonate-zeolite veins-manganoan siderite-manganoan ankerite-natrolite				
Synchysite-(Ce) sometimes present	*Cordylite-(Ce)* is a typical mineral. White or yellow tabular crystals, 0.1–1 mm and sometimes up to 5 mm, either single or in aggregates. 2 varieties (Fig. 4*b*).	*Cebaite-(Ce),* found in cavities as yellow, white or colourless crystals up to 0.2 mm. Dendritic, stellate or irregular intergrowths. Commonly associated with mckelveyite-(Ce), cordylite and strontianite.	*Mckelveyite-(Y), ewaldite* and *donnayite-(Y)* see above.	*Edingtonite* and *harmotome* common accessory minerals. Usually, euhedral crystals, up to 2 mm, in cavities.
Kukharenkoite-(Ce) (See above)	*Strontianite* with cordylite-(Ce), primary	*Baryte,* often short, prismatic crystals in cavities		
CZ III-2 carbonate-zeolite veins-manganoan siderite-nordstrandite-natrolite				
Cordylite-(Ce) is a 'typical' mineral. White or yellow tabular crystals, 0.1–1 mm and sometimes up to 5 mm, either single or in aggregates.	*Mckelveyite-(Y), ewaldite* and *donnayite-(Y)*	*Barytocalcite,* euhedral or subhedral, 1–2 mm white crystals in cavities. Identification based on XRD and IR spectra.	*Strontianite* with cordylite-(Ce), primary	*Baryte,* often short, prismatic crystals in cavities.
CZ III-3 carbonate-zeolite veins-natrolite-manganoan siderite-dawsonite				
Mckelveyite-(Y), ewaldite and *donnayite-(Y)*	*Strontianite* with cordylite-(Ce), primary	*Baryte,* often short, prismatic crystals in cavities.		

TABLE 4. Chemical composition of burbankite at Khibina

Rock				C II-1					
Sample	607/277	633/477.7		633/477.7		581/013		633B/79.5	
		large crystal		drop-like inclusion		large crystal		large crystal	
		mean (9)	sd	mean (4)	sd	mean (10)	sd	mean (9)	sd
Na_2O	12.45	11.93	0.13	11.80	0.27	12.60	0.44	12.03	0.85
CaO	12.60	11.94	0.53	12.57	0.54	10.20	0.49	10.08	1.22
SrO	19.60	24.74	0.31	24.57	0.38	18.38	0.61	17.71	0.92
BaO	0.78	1.76	0.12	1.86	0.04	2.52	0.49	6.65	0.47
La_2O_3	5.20	5.65	0.14	5.11	0.25	7.05	0.30	4.77	0.26
Ce_2O_3	9.91	7.15	0.16	6.97	0.28	11.06	0.41	9.26	0.43
Pr_2O_3	0.64	0.47	0.04	0.47	0.05	0.80	0.10	0.88	0.07
Nd_2O_3	1.53	1.24	0.10	1.33	0.03	2.53	0.28	3.11	0.31
Sm_2O_3	0.05	b.d.		b.d.		0.31	0.11	0.39	0.12
Gd_2O_3	b.d.	b.d.		b.d.		b.d.		0.20	0.07
ThO_2	n.d.	b.d.		b.d.		b.d.		0.16	0.10
CO_2	35.40	34.68		34.79		34.21		33.38	
Total	99.76*	99.56		99.47		99.66		98.62	
Calculated to 5 $(CO_3)^{2-}$ groups									
Na	2.508	2.442		2.408		2.615		2.558	
Ca	0.338	0.498		0.529		0.267		0.345	
A site total	2.846	2.941		2.937		2.882		2.903	
Sr	1.181	1.514		1.499		1.141		1.126	
Ca	1.065	0.852		0.889		0.903		0.840	
La	0.199	0.220		0.198		0.278		0.193	
Ce	0.377	0.276		0.268		0.433		0.372	
Pr	0.024	0.018		0.018		0.031		0.035	
Nd	0.056	0.047		0.050		0.097		0.122	
Sm	0.003					0.011		0.015	
Gd								0.007	
Ba	0.032	0.073		0.077		0.106		0.286	
Th								0.004	
B site total	3.000**	3.000		3.000		3.000		3.000	
C	5.021								

Sample 607/277 - wet chemical analysis; other samples - electron microprobe analyses.
sd - standard deviation.
* - including MgO 0.02, K_2O 0.02, MnO 0.07, FeO 0.42, SiO_2 0.20, F 0.04 and H_2O 0.85, all wt.%.
** - including Mn 0.006, Fe 0.037 and Si 0.021.
b.d. - below detection limits. Mg, Mn, Fe, Y and F are below detection limits in the microprobe analyses. CO_2 in microprobe analyses calculated by stoichiometry. n.d. – not determined.

exception (sample 633B/79.5) has 6.65 wt.% BaO. There is no zoning in Khibina burbankite crystals and the compositions are also uniform within each rock sample.

There are two morphological types of burbankite, large prismatic crystals and small drop-like inclusions within calcite crystals and along their boundaries (Fig. 3*a*, Table 3). Although their compositions are the same (Table 4), the difference in morphology suggests they may have formed by different processes. Large euhedral prismatic crystals could have crystallized at an early stage of carbonatite formation, and sometimes large burbankite crystals are observed near the contact of veins that are characterized by a crustification texture (vein-filling). The drop-like burbankite inclusions in calcite probably did not form by exsolution of

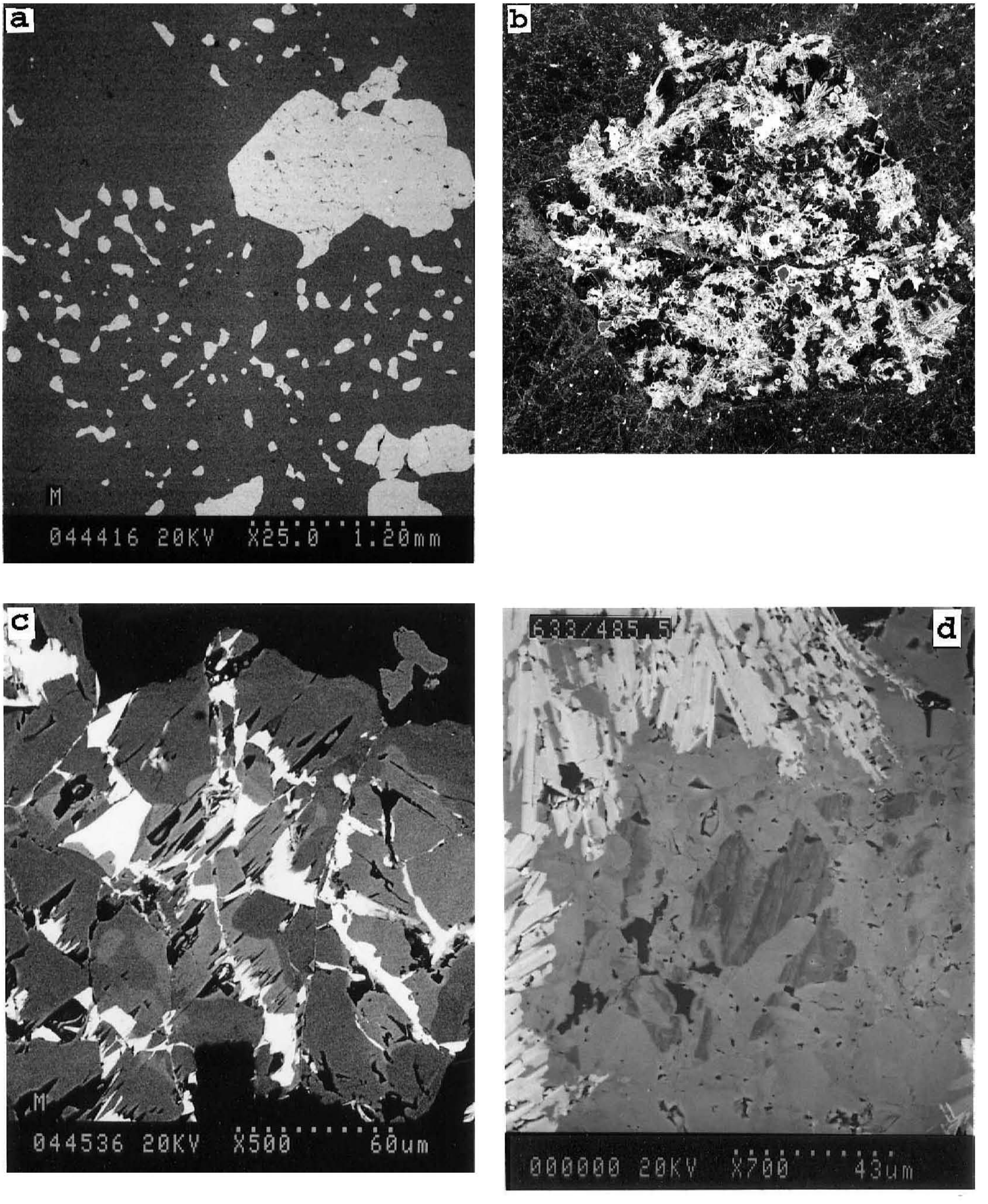

FIG. 3. Backscattered electron images (BEI) of (*a*) large crystals and drop-like inclusions of burbankite (white) in calcite (black); (*b*) a contact print of a thin section containing a pseudomorph of synchysite-(Ce), strontianite and baryte after burbankite,. The width of the burbankite pseudomorph is 9 mm. C II-1 calcite carbonatite, sample 603/26.5; (*c*) zoned altered burbankite (grey and dark-grey) with ancylite-(Ce) veins (white), C II-1 calcite carbonatite, sample 633B/79.5 (*d*) relics of burbankite (dark grey) in strontianite (grey) and synchysite-(Ce) (white).

burbankite from calcite rich in Na, Sr and *REE* as might be thought at first from Fig. 3*a*, and as proposed for a similar occurrence by Knudsen (1991), because the burbankite crystals are associated with euhedral zoned apatites. They are more likely to be the result of 'cotectic' crystallization of burbankite and calcite after the precipitation of the apatite.

Carbocernaite has been found in many Khibina carbonatite samples (Table 3). It was described originally as a primary mineral crystallized at a late stage of carbonatite formation at Vuorijarvi, Kola Peninsula (Bulakh *et al.*, 1961). Zdorik (1966) and Kapustin (1980) found that carbocernaite in carbonatites from the Ozernyi and Vuoriyarvi massifs occurs as a secondary mineral after burbankite. The most unusual occurrence of carbocernaite is the exsolution lamellae and cotectic textures for carbocernaite and calcite in Sarnu-Dandali carbonatite described by Wall *et al.* (1993). Carbocernaite is also reported from carbonatite in the Si Pan Range, Vietnam (Bulakh and Izokh, 1966).

Carbocernaite, like burbankite, is a double carbonate with a general formula $AB(CO_3)_2$ with Na and Ca in the *A*-site and Sr, *REE* and Ba in the *B*-site. There are few studies of the chemical composition of carbocernaite. Before the detailed investigation of Wall *et al.* (1993) only a few wet chemical analyses were published (Bulakh *et al.*, 1961; Bulakh and Izokh, 1966; Zdorik, 1966; Kapustin, 1980). Although available data for carbocernaite show some variation in the content of major elements, there is less variation than in burbankite. The Na_2O values range from 2.43 to 6.12 wt.%, the BaO from 0.95 to 5.96, the SrO from 5.58 to 23.98, the CaO from 15.93 to 19.27 and the ΣREE_2O_3 from 17.06 to 26.31, all wt.%. In general the compositional variations in burbankite and carbocernaite are similar, but carbocernaite contains less Na_2O (commonly about 4–5 wt.%) compared with burbankite (commonly about 10–12 wt.%). This difference in sodium content makes it possible to identify carbocernaite and burbankite on the basis of electron microprobe analyses.

Selected average compositions of carbocernaite from Khibina are given in Table 5. These data show that carbocernaite from the Khibina carbonatites is a low Ba variety. Khibina carbocernaite, like burbankite, is not zoned.

Harris (1972) reported high F (3.86 wt.%) in carbocernaite from Sturgeon Narrows, Canada, and proposed that F together with OH could be additional anion group $(F,OH)_2$ in the mineral formula. Our data show that the F content of Khibina carbocernaite is near the electron microprobe detection limit of about 0.1 wt.% and IR investigations show an absence of any absorption band related to OH^- group or H_2O. It is possible that the mineral described from the Sturgeon Narrows is a different mineral species. The lack of Na in Sturgeon Narrows carbocernaite also supports our conclusion.

In the Khibina carbonatite samples burbankite and carbocernaite do not occur together so it has not been possible to establish their relative ages. However, both burbankite and carbocernaite-containing carbonatites are cut by later C II-2 and C II-3 carbonatites.

TABLE 5. Chemical composition of carbocernaite at Khibina

Rock	C II-1			
Sample	603/165		603/287	
	mean (12)	sd	mean (10)	sd
Na_2O	4.98	0.18	4.33	0.42
CaO	11.94	0.42	13.60	0.33
SrO	22.33	0.76	20.20	0.27
BaO	0.37	0.13	0.56	0.07
La_2O_3	9.27	0.61	10.53	0.33
Ce_2O_3	13.19	0.51	14.19	0.30
Pr_2O_3	0.97	0.09	0.94	0.08
Nd_2O_3	2.34	0.25	2.56	0.19
Sm_2O_3	0.14	0.05	0.32	0.04
F	0.10	0.10	0.14	0.03
CO_2	32.79		33.79	
$-O{=}F_2$	0.04		0.06	
Total	98.36		101.10	
Calculated to 2 $(CO_3)^{2-}$ groups				
Na	0.431		0.364	
Ca	0.571		0.632	
A site total	1.003		0.996	
Sr	0.578		0.508	
La	0.153		0.168	
Ce	0.216		0.225	
Pr	0.016		0.015	
Nd	0.037		0.040	
Sm	0.002		0.005	
Ba	0.007		0.010	
B site total	1.008		0.971	
F	0.014		0.019	

Mg, Mn, Fe, Gd, Y, Th and U are below detection limits. CO_2 calculated by stoichiometry

Alteration of burbankite and carbocernaite

Burbankite in carbonatites is commonly replaced by ancylite-(Ce), strontianite and baryte (Somina, 1975; Kapustin 1980) and rarely by ancylite-(Ce), calkinsite, lanthanite and baryte (Pecora and Kerr, 1953). Multi-stage alteration of burbankite from the Ozernyi carbonatites has been documented by Zdorik (1966) where carbocernaite, strontianite, bastnäsite-(Ce), calcite, baryte, allanite-(Ce), monazite-(Ce) and epidote have been identified as alteration products of burbankite.

In the Khibina carbonatites, burbankite and carbocernaite are commonly replaced by various combinations of ancylite-(Ce), strontianite, synchysite-(Ce), baryte; less commonly by cordylite-(Ce) and rarely by harmotome and edingtonite (Table 3). Even when burbankite is completely replaced, evidence of its existence is preserved in the form of hexagonal prismatic pseudomorphs (Fig. 3*b*) and islands of relict burbankite (Fig. 3*c* and *d*). Pseudomorphs of a similar form have been mentioned from some other rare earth-rich carbonatites, e.g. Gem Park, Wigu Hill, Kangankunde (Wall and Mariano, 1996) but in these cases there is no evidence of the precursor mineral. The presence of primary and replaced burbankite at Khibina is good evidence that the pseudomorphs reported from these other carbonatites may well have originally been burbankite.

Ancylite

Ancylite-(Ce) is a hydrous carbonate containing *REE* and Sr as major cations. On the basis of a structural study of material from the Mont Saint-Hilaire massif, its formula has been proposed as $REE_x(Sr,Ca)_{2-x}(CO_3)_2(OH)_x{\cdot}(2-x)H_2O$ with a cation-anion substitution of $Sr^{2+} + H_2O \rightleftharpoons REE^{3+} + OH^-$ (Dal Negro *et al.*, 1975). Although ancylite-(Ce) is a relatively common mineral in carbonatites there are only a few analyses available (Kukharenko *et al.*, 1965; Kapustin, 1980; Knudsen, 1991), and this is the first detailed investigation of its chemical composition. Selected average chemical compositions are given in Table 6. The composition of ancylite-(Ce) from Khibina is relatively uniform with Ca, Ba and Th present only as traces. The atomic proportion of Sr and *REE* in the formula is near 1:1 with a small excess of *REE*. An important finding is the presence of fluorine in ancylite-(Ce). The Khibina ancylite-(Ce) contains between 0.75 and 2.50 wt.% of fluorine corresponding to 0.148–0.488 F per formula unit. Since *REE* and Sr are present in equal abundances it is suggested that F^- substitutes for OH^-. Thus, the mineral from the Khibina carbonatites can be classified as F-bearing ancylite-(Ce). Fluorine was also detected in two ancylite-(Ce) samples from Qaqarssuk carbonatites at 0.37 and 0.58 wt.% respectively (Knudsen, 1991).

Ca-REE fluocarbonates

Synchysite-(Ce) is common at Khibina, bastnäsite-(Ce) and parisite-(Ce) are also found but are rare (Table 3). The textures vary, as described in Table 3, and include syntaxial intergrowths (Fig. 4*a*). Ca-*REE* fluocarbonates are present in numerous carbonatites, e.g. Mountain Pass (Olsen *et al.*, 1954), Gatineau (Hogarth *et al.*, 1985), Kizilçaören (Hatzl, 1992), Tundulu (Ngwenya, 1994) and are the most well-studied of the carbonatite *REE*-minerals (e.g. Kapustin, 1980; Hogarth *et al.*, 1985; Andersen, 1986; Wall and Mariano, 1996). Selected average microprobe analyses of Khibina synchysite-(Ce) made on minerals from different mineral assemblages are presented in Table 7. Synchysite-(Ce) is characterized by having little substitution of other elements for Ca and *REE*. Primary synchysite-(Ce) from syntaxial intergrowths, secondary synchysite-(Ce) from the alteration products of burbankite, carbocernaite and syntaxial intergrowths of synchysite-(Ce) with parisite-(Ce) all have similar chemical compositions. Sr, Ba and Th are typical minor constituents in all the synchysite-(Ce) and Fe is present in the red variety associated with manganoan ankerite or ferroan kutnohorite.

Parisite-(Ce) and bastnäsite-(Ce) (Table 8) are near their theoretical compositions with only minor amounts of Sr and Ba substituting for Ca and Th substituting for *REE*.

Syntaxial intergrowths of Ca-*REE* fluocarbonates are considered to be evidence for their primary origin, the intergrowth being related to changes in the chemical composition of the host fluid (Ni *et al*, 1993).

Ba-REE fluocarbonates

Ba-*REE* fluocarbonates are extremely rare in carbonatites. Huanghoite-(Ce) is the only member of the group previously described, from an unnamed Siberian carbonatite (Kapustin, 1973) and from Qaqarssuk carbonatites (Knudsen, 1991). However cordylite-(Ce), kukharenkoite-

TABLE 6. Chemical composition of ancylite-(Ce) at Khibina

Rock	C II-1					
Sample	633B/79.5		646/001		646/451	
	mean (8)	sd	mean (21)	sd	mean (24)	sd
SrO	23.97	1.25	21.70	1.19	20.65	1.63
CaO	1.35	0.40	2.09	0.51	1.93	0.59
BaO	0.59	0.09	0.85	0.24	0.85	0.25
FeO	0.19	0.35	b.d.		0.20	0.30
La_2O_3	13.08	1.18	15.56	0.83	16.53	1.17
Ce_2O_3	23.40	1.04	23.46	1.09	23.59	0.89
Pr_2O_3	1.94	0.11	1.74	0.14	1.69	0.12
Nd_2O_3	5.35	0.52	4.42	0.38	4.34	0.33
Sm_2O_3	0.29	0.06	0.28	0.05	0.23	0.04
Gd_2O_3	0.14	0.13	0.17	0.09	b.d.	
ThO_2	0.53	0.20	b.d.		b.d.	
F	2.15	0.30	1.83	0.34	1.19	0.17
CO_2	23.44		23.32		23.07	
$-O{=}F_2$	0.90		0.77		0.50	
Total	95.51		94.66		93.77	
Calculated to 2 $(CO_3)^{2-}$ groups						
La	0.300		0.357		0.381	
Ce	0.532		0.534		0.539	
Pr	0.044		0.040		0.039	
Nd	0.119		0.098		0.097	
Sm	0.006		0.006		0.005	
Gd	0.003		0.004			
Th	0.008					
Total	1.012		1.038		1.061	
Sr	0.864		0.783		0.748	
Ca	0.090		0.139		0.129	
Ba	0.014		0.021		0.021	
Fe	0.010				0.010	
Total	0.979		0.943		0.909	
F	0.422		0.360		0.235	

Na, Mg, Mn, Y and U are below detection limits
CO_2 calculated by stoichiometry

(Ce) and cebaite-(Ce) have all been identified at Khibina (Table 3).

Cordylite-(Ce) is known only from Greenland (Flink, 1901), Mont Saint-Hilaire, Canada (Chen and Chao, 1975) and Bayan Obo, China (Zhang and Tao, 1986). Its occurrence at Khibina is the first documented occurrence which is certainly from carbonatites. Kukharenkoite-(Ce) is a new Ba-*REE* fluocarbonate mineral which has been found in the Khibina carbonatites, and from Vuoriyavri, Kola Peninsula, Mont Saint-Hilaire and the Saint-Amable sill, Quebec, Canada (Zaitsev *et al.*, 1996). The occurrence of cebaite-(Ce) at Khibina is only the second documented occurrence. The first was from Bayan Obo (Zhang and Tao, 1986).

There are no data on the chemical composition of cordylite-(Ce) from carbonatites and our report is the first for this mineral (Table 9). There are three distinct chemical compositions of cordylite-(Ce) from Khibina. Cordylite-(Ce) with low Ca and Sr (Table 9) occurs in manganoan siderite-manganoan ankerite-natrolite veins (CZ III-1), where it forms tabular crystals which are associated with strontianite and sometimes kukharenkoite-(Ce). High Ca and Sr cordylite-

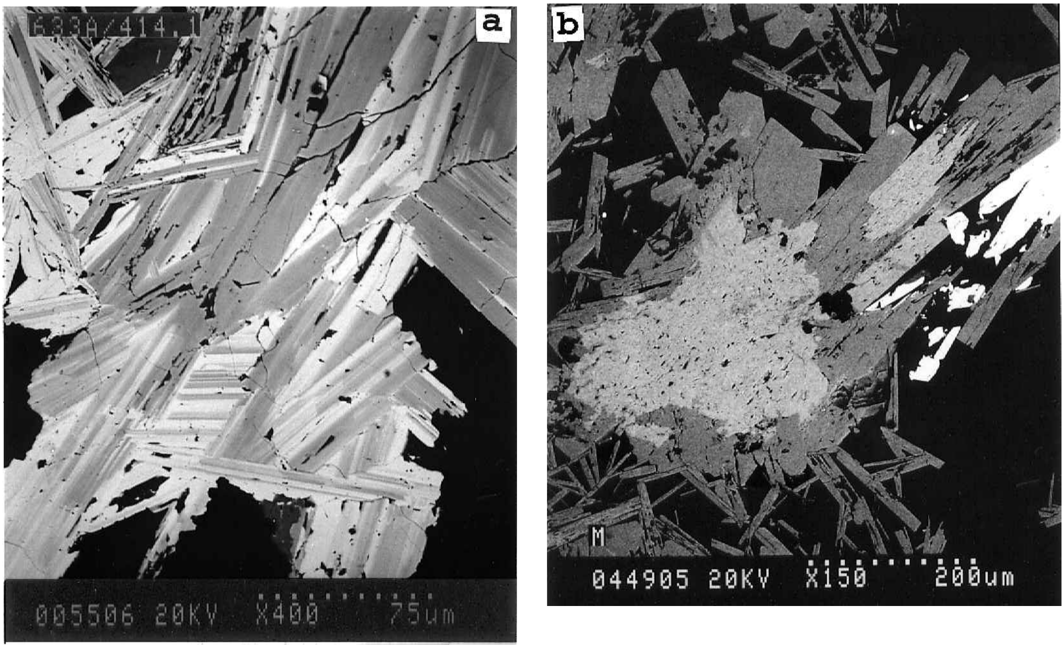

FIG. 4 (*a*) BEI of syntaxial intergrowths of synchysite-(Ce) (grey), parisite-(Ce) (grey) and bastnäsite-(Ce) (white), C II-2 manganoan ankerite-calcite carbonatite, sample 633A/414. 1 (*b*) BEI of large crystals of low Ca and Sr cordylite-(Ce) pale grey in centre) associated with laths of high Ca and Sr cordylite-(Ce) (dark grey) and kukharenkoite-(Ce) (white), CZ III-1 manganoan siderite-manganoan ankerite – natrolite vein, sample 607/75.

(Ce) (Table 9) is observed in the same samples as mantles on crystals of low Ca and Sr cordylite-(Ce) and as abundant laths in the surrounding natrolite and manganoan ankerite (Fig. 4*b*). It has also formed as a secondary mineral during carbocernaite alteration. Cordylite-(Ce) with moderate Ca and Sr (Table 9) occurs in ferroan rhodochrosite-manganoan ankerite carbonatites (C II-3) and is associated with strontianite.

The atomic proportions of Na-Ca and *REE*-Sr pairs show a negative correlation with a slope near –1 and a plot of Na+*REE* *vs.* Ca+Sr (Fig. 5) shows a trend in composition from Sr-Ca-poor to Sr-Ca-rich cordylite-(Ce). The slope of this correlation suggests a 1:1 exchange of Na and *REE* for Ca and Sr with a substitution scheme of $Na^{+} + REE^{3+}$ $Ca^{2+} + Sr^{2+}$. On the basis of these observations a general formula for cordylite-(Ce) can be expressed as $(Na,Ca)Ba(REE,Sr)_2(CO_3)_4F$. Our X-ray and IR data are identical for each compositional variety and also identical to those of 'baiyuneboite-(Ce)' (Fu and Su, 1988), which is now recognized to be cordylite-(Ce) (J. Zemann, personal communication, 1996).

Kukharenkoite-(Ce) occurs in Khibina C II-2 and C II-3 carbonatites and in carbonate-zeolite veins (Table 3). It was described as a new mineral by Zaitsev *et al.* (1996). The composition of the kukharenkoite-(Ce) (Zaitsev *et al.*, 1996), deter-

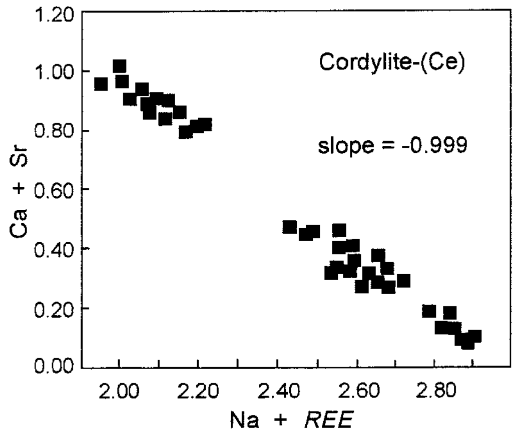

FIG. 5. Atomic proportions of Na+*REE* *vs.* Ca+Sr for cordylite-(Ce).

TABLE 7. Chemical composition of synchysite-(Ce) at Khibina

Rock	C II-2		C II-3		C II-1		C II-1		C II-1	
Sample	633A/414.1		604/413		633/485.5		603/26.5		603/165	
	syntaxial intergrowths				secondary after burbankite				secondary after carbocernaite	
	mean (8)	sd	mean (6)	sd	mean (9)	sd	mean (15)	sd	mean (4)	sd
CaO	17.47	0.38	16.89	0.62	16.18	0.70	16.08	0.88	17.23	0.33
FeO	b.d.		0.35	0.49	b.d.		b.d.		b.d.	
SrO	0.24	0.12	0.43	0.18	0.87	0.66	0.59	0.28	0.56	0.21
BaO	0.09	0.05	0.15	0.04	0.12	0.07	0.06	0.05	0.11	0.06
La_2O_3	16.54	0.42	13.06	0.58	17.98	0.87	20.34	0.86	13.63	0.73
Ce_2O_3	26.19	0.85	27.21	0.79	25.91	0.65	25.77	0.50	25.26	0.85
Pr_2O_3	2.15	0.12	2.53	0.07	1.94	0.11	1.78	0.08	2.58	0.10
Nd_2O_3	6.14	0.44	7.90	0.22	5.54	0.27	4.53	0.41	9.69	0.86
Sm_2O_3	0.38	0.06	0.62	0.10	0.38	0.04	0.31	0.07	0.68	0.38
Y_2O_3	b.d.		b.d.		b.d.		b.d.		0.11	0.09
ThO_2	b.d.		0.38	0.21	0.15	0.09	b.d.		0.17	0.14
F	5.49	0.18	5.69	0.21	5.83	0.23	5.61	0.23	5.78	0.11
CO_2	28.12		27.81		27.18		27.59		28.11	
$-O{=}F_2$	2.31		2.40		2.46		2.36		2.43	
Total	100.49		100.62		99.61		100.30		101.46	
Calculated to 2 $(CO_3)^{2-}$ groups										
Ca	0.975		0.953		0.934		0.915		0.962	
Sr	0.007		0.013		0.027		0.018		0.017	
Ba	0.002		0.003		0.002		0.001		0.002	
Fe			0.015							
Total	0.984		0.985		0.964		0.934		0.981	
La	0.318		0.254		0.357		0.398		0.262	
Ce	0.499		0.524		0.511		0.501		0.481	
Pr	0.041		0.049		0.038		0.034		0.049	
Nd	0.114		0.149		0.107		0.086		0.180	
Sm	0.007		0.011		0.007		0.006		0.012	
Y									0.003	
Th			0.005		0.002				0.002	
Total	0.979		0.991		1.022		1.025		0.990	
F	0.904		0.948		0.994		0.943		0.953	

Na, Mg, Mn and U are below detection limits
CO_2 calculated by stoichiometry

mined from electron microprobe analysis is BaO 48.93, SrO 0.42, MnO 0.26, Na_2O 0.08, CaO 0.05, La_2O_3 6.16, Ce_2O_3 15.12, Pr_2O_3 1.49, Nd_2O_3 4.08, ThO_2 0.10 and F 3.20, wt.%. The atomic ratios of Ba, *REE* and F are near 2:1:1, requiring 3 $(CO_3)^{2-}$ groups per formula unit (calculated CO_2 21.73 wt.%) and the ideal formula for kukharenkoite-(Ce) is $Ba_2REE(CO_3)_3F$.

The chemical composition of cebaite-(Ce) from Khibina was determined by 18 electron microprobe analyses (Table 10). Although, analysis totals are less then 100 %, calculated atomic ratios for Ba, *REE* and F are near 3:2:2 and closely correspond to an ideal formula of $Ba_3REE_2(CO_3)_5F_2$. Cebaite-(Ce) contains minor SrO (1.01–2.61 wt.%), CaO (0.33–1.18 wt.%) and ThO_2 (0.49–1.26 wt.%), in addition relatively high MnO (up to 0.83 wt.%) and FeO (up to 0.61 wt.%) were observed in some analyses. All cebaite-(Ce) crystals are unzoned. See Table 3 for mineralogical details.

TABLE 8. Chemical composition of parisite-(Ce) and bastnäsite-(Ce) at Khibina

Rock	C II-2	C II-3		C II-2	
Sample	633A/414.1	604/413		633A/414.1	
Mineral	parisite-(Ce)			bastnäsite-(Ce)	
	mean (2)	mean (5)	sd	mean (6)	sd
CaO	9.72	9.29	1.03	0.84	0.29
SrO	0.56	0.79	0.18	0.85	0.34
BaO	0.07	0.30	0.29	0.08	0.05
FeO	0.05	0.38	0.28		
La_2O_3	19.63	15.96	0.72	26.35	0.99
Ce_2O_3	31.72	32.28	0.45	37.41	0.54
Pr_2O_3	2.30	2.87	0.14	2.50	0.13
Nd_2O_3	6.83	8.74	0.22	6.60	0.48
Sm_2O_3	0.45	0.60	0.02	0.36	0.07
Y_2O_3	0.10	0.22	0.12	b.d.	
ThO_2	b.d.	0.24	0.10	b.d.	
F	7.02	6.79	0.17	8.11	0.22
CO_2	24.33	24.54		20.67	
$-O{=}F_2$	2.95	2.86		3.42	
Total	99.82	100.13			100.35
	Calculated to 3 $(CO_3)^{2-}$ groups			Calculated to 1 $(CO_3)^{2-}$ group	
Ca	0.941	0.892		0.033	
Sr	0.029	0.041		0.018	
Ba	0.002	0.011		0.001	
Fe	0.004	0.029			
Total	0.976	0.972			
La	0.654	0.527		0.357	
Ce	1.048	1.057		0.503	
Pr	0.076	0.094		0.033	
Nd	0.220	0.280		0.087	
Sm	0.014	0.018		0.005	
Y	0.005	0.010			
Th		0.005			
Total	2.017	1.992		1.037	
F	2.004	1.923		0.942	

Na, Mg, Mn and U are below detection limits
CO_2 calculated by stoichiometry

Y-rich carbonates mckelveyite-(Y), ewaldite and donnayite-(Y)

A detailed description of these minerals from Khibina, Vuoriyarvi and Sallanlatvi, is given by Voloshin *et al.* (1990, 1992). This was the first time that they had been documented in carbonatites. Mckelveyite-(Y) is the best-studied of the group at Khibina (Table 3).

Chemical compositions of mckelveyite-(Y) and ewaldite from Kola carbonatites are represented by three electron microprobe analyses of mckelveyite-(Y) from Vuoriyarvi carbonatites, one from the Sallanlatvi carbonatite and two analyses of ewaldite from Vuoriyarvi (Voloshin *et al.*, 1990, 1992). However, even these limited data show compositional variation and three groups have been identified: Na-free mckelveyite-(Y), Y-free L*REE*-enriched mckelveyite and Y-free ewaldite.

Five separate crystals of mckelveyite-(Y) were analysed from Khibina (Table 11) and are uniform in chemical composition. The formula

TABLE 9. Chemical composition of cordylite-(Ce) at Khibina

Rock	CZ III-1		C II-3		CZ III-1		CZ III-1		C II-1	
Sample	607/75		603/264.6		603/251.5		607/75		603/165.0	
Variety	low Ca and Sr		moderate Ca and Sr				high Ca and Sr			
	mean (15)	sd	mean (17)	sd	mean (15)	sd	mean (10)	sd	mean (17)	sd
Na_2O	4.12	0.12	3.66	0.24	3.67	0.12	2.60	0.15	2.56	0.16
CaO	0.73	0.18	1.54	0.31	1.50	0.08	3.82	0.18	4.10	0.26
SrO	0.58	0.23	2.48	0.57	2.09	0.31	6.03	0.43	5.90	0.50
BaO	22.28	0.33	22.29	0.51	22.32	0.32	23.02	0.25	23.11	0.36
La_2O_3	9.94	0.36	10.46	0.38	11.82	0.53	7.58	0.30	11.49	0.51
Ce_2O_3	24.46	0.43	23.82	0.68	22.18	0.28	20.26	0.38	17.90	0.67
Pr_2O_3	2.41	0.18	1.85	0.24	1.69	0.25	2.19	0.27	1.45	0.30
Nd_2O_3	7.47	0.49	5.88	0.31	5.70	0.41	6.97	0.49	5.36	0.54
ThO_2	0.11	0.17	0.13	0.14	0.12	0.16	0.13	0.12	0.13	0.16
F	2.62	0.10	2.97	0.28	2.95	0.33	2.60	0.08	2.85	0.31
CO_2	24.92		25.16		24.78		25.77		25.75	
$-O{=}F_2$	1.10		1.25		1.24		1.10		1.20	
Total	98.55		98.98		97.57		99.88		99.40	
Calculated for 4 $(CO_3)^{2-}$ groups										
Na	0.945		0.821		0.837		0.579		0.567	
Ca	0.093		0.191		0.189		0.470		0.501	
Total	1.038		1.012		1.026		1.049		1.068	
Ba	1.032		1.011		1.028		1.036		1.033	
La	0.434		0.446		0.513		0.321		0.483	
Ce	1.058		1.008		0.954		0.851		0.747	
Pr	0.104		0.078		0.072		0.092		0.060	
Nd	0.315		0.243		0.239		0.286		0.218	
Sr	0.040		0.167		0.142		0.402		0.390	
Th	0.003		0.003		0.003		0.003		0.003	
Total	1.954		1.945		1.923		1.955		1.901	
F	0.981		1.088		1.096		0.946		1.029	

Fe, Mn and Sm are below detection limits
CO_2 calculated by stoichiometry

of mckelveyite-(Y) is still the subject of debate. In the original description Milton *et al.* (1965) gave the formula as $Na_{1.9}Ba_{4.0}Ca_{1.1}Sr_{0.2}REE_{1.5}U_{0.3}(CO_3)_9{\cdot}5H_2O$. Later, Chao *et al.* (1978) suggested an isomorphous relationship between mckelveyite-(Y) and donnayite-(Y) and gave the formula of $NaCaBa_3Y(CO_3)_6{\cdot}3H_2O$. In a recent study of mckelveyite-(Y) and ewaldite Voloshin *et al.* (1990, 1992) showed a similarity between these two minerals and suggested that they are probably polymorphs. The formula of ewaldite was determined as $(Ca,Na,REE)(Ba,Sr)(CO_3)_2{\cdot}nH_2O$ where part of the H_2O is zeolitic.

Chemical data from the Khibina mckelveyite-(Y) were calculated on the basis of the IMA accepted formula $NaCaBa_3Y(CO_3)_6{\cdot}3H_2O$ (Table 11). Our data and those of Voloshin *et al.* (1990) show significant substitutions, the main one being Ba^{2+} Sr^{2+} which is related to the mckelveyite-(Y)-donnayite-(Y) pair where these minerals are Ba and Sr end-members respectively. The assignation of *REE* to two different sites in the mckelveyite-(Y) formula is problematic. It is based on formula balance and the *REE* chondrite-normalized distribution which is discussed below in the section on 'Rare earth patterns'.

Strontianite, baryte, barytocalcite, edingtonite and harmotome

Minerals rich in Ba and Sr but with no *REE* are represented in the Khibina carbonatites by

TABLE 10. Chemical composition of cebaite-(Ce) at Khibina

Rock				CZ III-1				
Sample				603/143.5				
Analysis	14	24	25	29	30	33	Mean (18)	Sd
Na_2O	0.09	0.10	0.08	0.11	0.13	0.10	0.10	0.03
CaO	0.40	1.18	0.47	0.61	0.52	0.70	0.61	0.21
MnO	0.07	0.47	0.12	0.73	0.83	0.13	0.16	0.24
FeO	0.45	0.13	b.d.	0.14	0.61	b.d.	0.16	0.19
SrO	1.40	1.27	1.45	1.25	1.28	1.31	1.43	0.36
BaO	43.93	40.51	42.19	42.09	42.59	42.93	42.77	1.84
La_2O_3	5.30	7.28	6.71	5.58	5.48	5.72	5.67	0.52
Ce_2O_3	13.59	14.33	14.52	14.66	13.66	14.91	14.45	1.16
Pr_2O_3	1.54	1.69	1.83	1.78	1.51	1.81	1.63	0.19
Nd_2O_3	6.15	5.69	5.99	6.32	5.70	5.34	5.54	0.48
Sm_2O_3	0.60	0.61	0.50	0.38	0.42	0.34	0.48	0.11
Eu_2O_3	0.17	0.18	b.d.	0.24	b.d.	b.d.	0.07	0.11
Gd_2O_3	0.59	0.66	0.53	0.49	0.40	0.37	0.50	0.13
ThO_2	0.99	0.51	0.49	0.92	1.07	0.99	0.92	0.22
F	4.24	4.10	4.15	3.78	3.99	3.61	3.76	0.21
CO_2	21.57	21.79	21.41	21.79	21.65	21.41	21.42	
$-O=F_2$	1.78	1.73	1.75	1.59	1.68	1.52	1.58	
Total	99.31	98.77	98.78	99.29	98.15	98.15	98.10	
Calculated for 5 $(CO_3)^{2-}$ groups								
Na	0.031	0.032	0.025	0.038	0.042	0.034	0.032	
Ca	0.073	0.212	0.085	0.111	0.095	0.130	0.114	
Mn	0.010	0.066	0.018	0.105	0.119	0.018	0.023	
Fe	0.064	0.018	0.020	0.087		0.023		
Sr	0.137	0.124	0.143	0.123	0.127	0.132	0.144	
Ba	2.915	2.659	2.802	2.805	2.855	2.926	2.900	
Total	3.230	3.111	3.072	3.201	3.325	3.240	3.236	
La	0.331	0.450	0.419	0.350	0.346	0.367	0.362	
Ce	0.841	0.878	0.900	0.911	0.854	0.948	0.914	
Pr	0.095	0.103	0.113	0.110	0.094	0.115	0.102	
Nd	0.372	0.340	0.362	0.384	0.348	0.332	0.342	
Sm	0.035	0.035	0.029	0.022	0.024	0.021	0.029	
Eu	0.010	0.011	0.014		0.004			
Gd	0.033	0.036	0.030	0.028	0.023	0.021	0.029	
Th	0.038	0.019	0.019	0.036	0.042	0.039	0.036	
Total	1.755	1.872	1.873	1.855	1.730	1.843	1.819	
F	2.268	2.174	2.221	2.033	2.159	1.986	2.057	

Y, Dy, Er, Yb and Lu are below detection limits
CO_2 calculated by stoichiometry

strontianite, baryte, barytocalcite, edingtonite and harmotome (Table 3). The first two minerals are common in late-stage carbonatites, e.g. Mountain Pass (Olsen *et al.*, 1954), Vuoriyarvi, Seblyavr, Sallanlatvi (Kapustin, 1980), Sarnu-Dandali (Wall *et al.*, 1993) and Kangankunde (Wall and Mariano, 1996).

Barytocalcite is extremely rare in carbonatites and has been described only from Vuoriyarvi and an unnamed Siberian carbonatite (Kapustin, 1980) and possibly Chipman Lake (Platt and Woolley, 1990).

Edingtonite and harmotome are barium zeolites. Their occurrence at Khibina is the first

TABLE 11. Chemical position of mckelveyite-(Y) at Khibina

Rock				CZ III				
Sample				603/143.5				
Point	1	2	4	5	9	10	Mean (12)	sd
Na_2O	3.12	3.05	3.21	3.10	3.33	3.14	3.19	0.10
CaO	4.56	4.34	4.32	4.34	4.20	4.72	4.43	0.38
MnO	0.06	b.d	b.d	b.d	b.d	0.06		
FeO	b.d	b.d	0.64	b.d	0.07	0.11	0.18	0.26
BaO	29.43	29.89	28.47	28.73	29.69	27.13	28.97	0.98
SrO	9.16	9.56	9.29	10.41	8.25	12.42	9.56	1.26
Y_2O_3	6.39	6.33	5.32	7.02	5.84	8.42	6.44	0.93
La_2O_3	1.22	1.22	1.60	0.85	1.84	0.96	1.34	0.34
Ce_2O_3	1.93	1.79	2.43	1.17	2.96	1.77	2.18	0.65
Pr_2O_3	0.22	0.22	0.15	0.30	0.24	0.15	0.22	0.06
Nd_2O_3	0.69	0.77	0.91	1.11	0.71	0.37	0.84	0.24
Sm_2O_3	0.81	0.87	0.81	0.89	0.85	0.20	0.78	0.23
Eu_2O_3	0.49	0.64	0.50	0.36	0.60	0.34	0.47	0.10
Gd_2O_3	2.15	1.94	2.18	2.05	2.32	1.05	2.02	0.38
Dy_2O_3	2.39	2.40	2.97	2.29	2.83	2.00	2.48	0.29
Er_2O_3	1.03	1.09	1.28	0.87	0.68	1.03	0.94	0.19
Yb_2O3	0.44	0.44	0.56	0.59	0.25	0.61	0.47	0.12
ThO_2	b.d	0.17	b.d	b.d	b.d	b.d		
F	0.18	0.15	b.d	b.d	0.17	0.16	0.14	0.09
CO_2	25.71	25.70	25.86	25.81	25.71	26.72	25.93	
H_2O	10.52	10.51	10.58	10.56	10.52	10.93	10.61	
$-O{=}F_2$	0.07	0.06			0.07	0.07	0.06	
Total	100.43	101.01	101.07	100.44	100.98	102.24	101.13	
Calculated to 6 $(CO_3)^{2-}$ and $3H_2O$ groups								
Na	1.000	0.984	1.000	1.000	1.000	0.978	1.000	
Ca	0.735	0.757	0.561	0.778	0.565	0.785	0.676	
Na	0.009		0.040	0.006	0.075		0.023	
La	0.075	0.075	0.099	0.052	0.113	0.057	0.082	
Ce	0.118	0.109	0.148	0.071	0.181	0.104	0.132	
Pr	0.013	0.013	0.009	0.018	0.014	0.009	0.013	
Nd	0.041	0.046	0.054	0.067	0.042	0.021	0.050	
Mn	0.009					0.008	0.000	
Fe			0.089		0.010	0.015	0.025	
Total	1.000	1.000	1.000	0.992	1.000	1.000	1.000	
Ba	1.923	1.950	1.865	1.884	1.941	1.707	1.880	
Sr	0.885	0.922	0.900	1.009	0.798	1.156	0.917	
Ca	0.080	0.017	0.212		0.185	0.026	0.110	
Total	2.888	2.890	2.977	2.893	2.924	2.889	2.907	
Y	0.567	0.561	0.473	0.625	0.518	0.719	0.567	
Sm	0.047	0.050	0.047	0.051	0.049	0.011	0.045	
Eu	0.028	0.036	0.029	0.021	0.034	0.018	0.026	
Gd	0.119	0.107	0.121	0.114	0.128	0.056	0.111	
Dy	0.128	0.129	0.160	0.123	0.152	0.104	0.132	
Er	0.054	0.057	0.067	0.045	0.036	0.052	0.049	
Yb	0.023	0.022	0.028	0.030	0.013	0.030	0.024	
Th		0.007						
Total	0.965	0.969	0.925	1.009	0.930	0.990	0.954	
F	0.092	0.081			0.088	0.082	0.071	

Lu is below detection limit, CO_2 and H_2O calculated by stoichiometry

TABLE 12. Chemical composition of strontianite at Khibina

Rock	C II-2		C II-3		CZ III-1	C II-1		C II-1		C II-1					
Sample	633A/414.1		604/413.0		603/251.5	646/451.0		603/36.3		646/001					
	primary strontianite associated with					secondary strontianite (after burbankite) associated with									
	synchysite-(Ce), parisite-(Ce) and bastnäsite-(Ce)		synchysite-(Ce) and parisite-(Ce)		cordylite-(Ce)	ancylite-(Ce) and baryte		synchysite-(Ce) and baryte		ancylite-(Ce) and baryte					
	mean (10)	sd	mean (6)	sd	mean (3)	mean (25)	sd	mean (4)	sd	mean (6) core	sd	mean (4) mantle	sd	mean (8) rim	sd
Na_2O	b.d.		b.d.		b.d.	0.14	0.05	b.d.		0.21	0.05	0.10	0.04	b.d.	
CaO	3.25	0.56	3.23	0.44	3.07	3.46	1.00	3.37	0.33	1.58	0.37	3.72	0.32	5.97	0.20
SrO	66.21	0.68	66.80	0.51	66.62	63.57	1.26	64.34	0.51	68.20	0.60	63.95	1.00	62.58	0.78
BaO	0.19	0.17	0.16	0.07	0.22	1.61	0.47	1.63	0.15	0.72	0.29	0.83	0.09	2.00	0.57
La_2O_3	b.d.		b.d.		0.16	0.48	0.20	b.d.		0.62	0.12	0.33	0.06	0.15	0.04
Ce_2O_3	0.18	0.12	0.11	0.11	0.57	0.61	0.24	0.19	0.08	0.76	0.16	0.42	0.05	0.25	0.05
CO_2	30.79		30.99		31.05	30.71		30.51		31.11		30.69		31.99	
Total	100.63		101.29		101.69	100.58		100.04		103.20		100.04		102.94	
Calculated to 1 $(CO_3)^{2-}$ group															
Na						0.006				0.010		0.005			
Ca	0.083		0.082		0.077	0.088		0.087		0.040		0.095		0.146	
Sr	0.913		0.915		0.911	0.879		0.895		0.931		0.885		0.831	
Ba	0.002		0.001		0.002	0.015		0.015		0.007		0.008		0.018	
La					0.001	0.004				0.005		0.003		0.001	
Ce	0.002		0.001		0.005	0.005		0.002		0.007		0.004		0.002	
Total	0.999		1.000		0.997	0.998		0.999		0.999		0.999		0.998	

Mg, Mn, Fe, Pr, Nd, Sm, Y, Th and U are below detection limits
CO_2 calculated by stoichiometry

documented occurrence in carbonatites (Zaitsev *et al*, 1992).

The chemical composition of strontianite from carbonatites is generally close to the end-member, containing a few percent of CaO (e.g. Kapustin, 1980; Wall and Mariano, 1996). Average microprobe results from Khibina are presented in Table 12. Primary strontianite is characterized by minor replacement of Sr by Ca which is common for carbonatitic strontianite but low contents of other elements such as Ba (0.05–0.63 wt.% of BaO), La, Ce and Nd (REE_2O_3 = 0.15–0.71 wt.%). Compared with this primary strontianite, secondary strontianite at Khibina contains more BaO (0.44–3.34 wt.%) and REE_2O_3 (0.35–2.47 wt.%), some secondary strontianite also shows core-mantle-rim zoning (Table 12).

Microprobe analyses of baryte from Khibina are in good agreement with available data for other late-stage carbonatites (Kapustin, 1980; Wall and Mariano, 1996) and show only a small replacement of Ba by Sr (0.09–1.75 wt.% of SrO, Ca (0.05–0.13 wt.% of CaO) and Na (0.08–0.22 wt.% of Na_2O).

Barytocalcite from Khibina (CaO 18.96, BaO 51.82, SrO 0.28, Na_2O 0.06, $CO_{2\ calc.}$ 29.90, total 101.02, wt.%) has less SrO than that reported previously from other carbonatites (Kapustin, 1980).

Rare earth patterns

Burbankite and carbocernaite from C II-1 carbonatites, which are early, primary *RE*-rich minerals, show almost identical *REE* distribution patterns with La/Nd_{cn} (cn = chondrite-normalized) ratios between 5.2 and 8.5 for burbankite and between 7.4 and 7.7 for carbocernaite. An exception is Ba-enriched burbankite which has a relative enrichment in Nd (La/Nd_{cn} ratio 2.9) (Fig. 6*a*).

REE distribution patterns in Ca-*REE* fluocarbonates from syntaxic intergrowths in C II-1 carbonatites are similar to those in burbankite and carbocernaite (Fig. 6*b*) with La/Nd_{cn} ratios 5.1–6.0, 5.4–6.3 and 7.1–7.5 for synchysite-(Ce), parisite-(Ce) and bastnäsite-(Ce) respectively. Average values from C II-2 carbonatites are more light-*REE*-enriched than those from the C II-3 carbonatites and the minerals from C II-3 type have relatively low La/Nd_{cn} ratios of 3.0–3.3 and 3.2–3.8 for synchysite-(Ce) and parisite-(Ce) respectively (Fig. 6*c*).

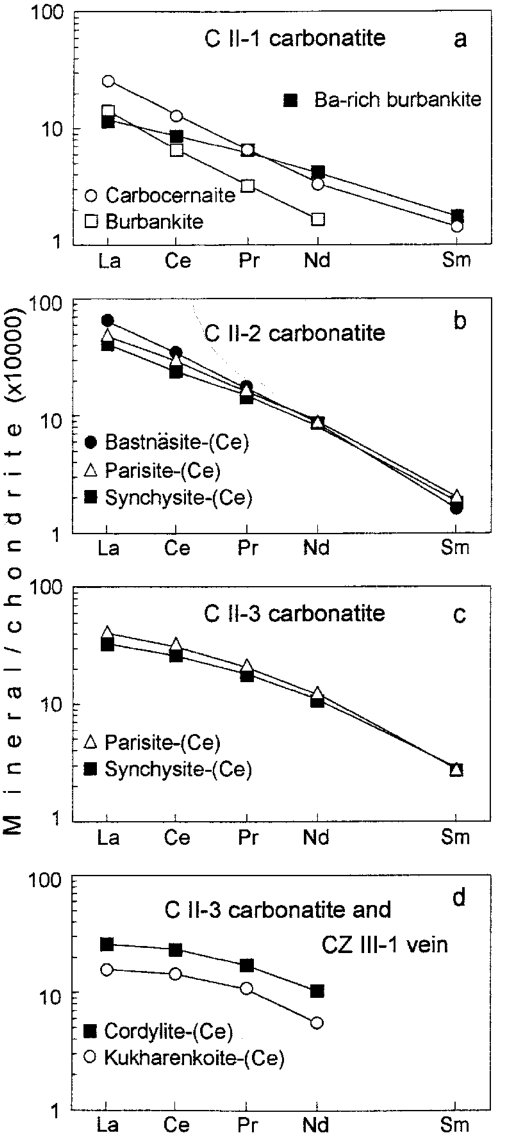

FIG. 6. Chondrite-normalized plots of (*a*) burbankite and carbocernaite from C I carbonatites; (*b*) bastnäsite-(Ce), parisite-(Ce) and synchysite-(Ce) from syntaxial intergrowths, C II-2 carbonatites; (*c*) parisite-(Ce) and synchysite-(Ce) from syntaxial intergrowths, C II-3 carbonatites; (*d*) cordylite-(Ce) and kukharenkoite-(Ce) from C II-3 carbonatites and CZ III-1 carbonate-zeolite veins. Chondrite values from Wakita *et al.* (1971).

The Ba-*REE* fluocarbonates, cordylite-(Ce), kukharenkoite-(Ce) and cebaite-(Ce), from C II-

3 carbonatites and CZ III carbonate-zeolite veins were the final light *REE* minerals to crystallize and are characterized by *REE* chondrite-normalized plots similar to those for synchysite-(Ce) and parisite-(Ce) from syntaxial intergrowths from C II-3 carbonatites (Fig. 6*d*). The La/Nd_{cn} ratios are 2.5–3.9, 2.8–3.5 and 1.6–2.4 for cordylite-(Ce), kukharenkoite-(Ce) and cebaite-(Ce) respectively.

The distribution of *REE* in primary carbonates from Khibina shows an evolutionary trend from early carbonatites (C I) through late carbonatites (C II) to carbonate-zeolite veins (CZ III). This trend is marked by changes in the La/Nd_{cn} ratio of the *REE*-minerals which gradually decreases from early burbankite and carbocernaite (La/Nd_{cn}=5.2–8.6) to later Ca-*REE* fluocarbonates (La/Nd_{cn}=5.1–7.5 for C II-2 carbonatite type and 3.0–3.8 for C II-3 carbonatite) and finally to Ba-*REE* fluocarbonates with La/Nd_{cn} between 1.6–3.9.

The extreme of this trend may be represented by the suite of Y and Sm-Er-enriched minerals (mckelveyite-(Y), donnayite-(Y) and ewaldite) which are always late. The average *REE* chondrite-normalized distribution for Khibina mckelveyite-(Y) is shown in Fig. 7. There is a bimodal distribution of *REE*, probably related to the presence of more than one site for the *REE*. Although, the crystal structure of mckelveyite-(Y) has not been solved, Chao *et al.* (1978) provided evidence that it is similar to weloganite $Na_2(Sr)_3Zr(CO_3)_6 \cdot 3H_2O$ which has co-ordination numbers of 6 for the Na site, 9 for the Zr and 10 for the Sr site. If the Ca in mckelveyite-(Y) occupies the equivalent of the 6 co-ordinated Na site (ion size of 10.0 Å) it could be substituted by La (ion size 10.32 Å), Ce (10.1 Å), Pr (9.9 Å) and Nd (9.83 Å). If the Y in the mckelveyite-(Y) structure corresponded to the Zr position in weloganite then Y would have a co-ordination number of 9 (ion size 10.75 Å) and could be substituted by heavy *REE* such as Sm-Yb where ion sizes range from 11.32 Å for Sm to 10.42 Å for Yb; all ion sizes are from Shannon (1976). Calculated formulae of mckelveyite-(Y) based on *REE* in two different sites (Table 11) produce totals close to an ideal formula.

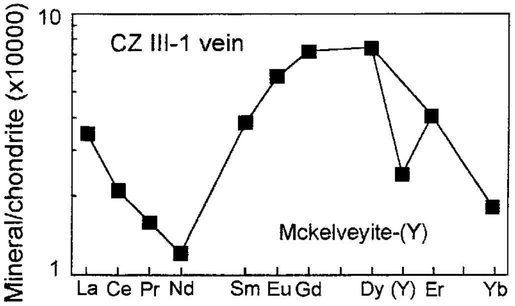

FIG. 7. Chondrite-normalized plot of mckelveyite-(Y) from CZ III-1 carbonate–zeolite vein

REE distribution during alteration

The widespread alteration of *REE* minerals at Khibina allows us to monitor the *REE* distribution during the alteration process. The main primary-secondary mineral pairs at Khibina are following:

(a) burbankite → ancylite-(Ce),
(b) burbankite → synchysite-(Ce),
(c) carbocernaite → cordylite-(Ce)+synchysite-(Ce),
(d) cordylite-(Ce) (low Ca-Sr) → cordylite-(Ce) (high Ca-Sr).

Chondrite-normalized plots of *REE* for these pairs show two distinct types of *REE* pattern. The first type (Fig. 8*a*) is represented by mineral pairs with similar La/Nd_{cn} ratios for primary-secondary

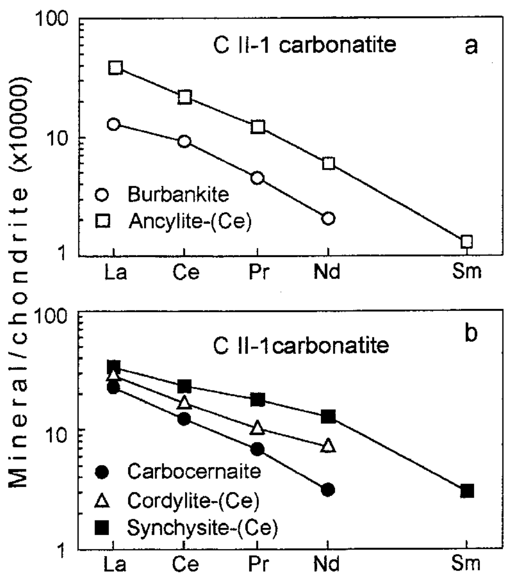

FIG. 8. Chondrite-normalized plots of primary-secondary mineral pairs for (*a*) burbankite–ancylite-(Ce) and (*b*) carbocernaite–synchysite-(Ce)+high Ca-Sr cordylite-(Ce), C II-1 carbonatites

minerals pairs. This type is the most common and includes burbankite-ancylite-(Ce), burbankite-synchysite-(Ce) and low Ca-Sr cordylite-(Ce)-high Ca-Sr cordylite-(Ce). The second type (Fig. 8*b*), seen only in an assemblage of carbocernaite, cordylite-(Ce) and synchysite-(Ce), shows a change in La/Nd_{cn} ratio from primary to secondary minerals.

Discussion and conclusions

The geological, geochemical and mineralogical data presented in this paper show that the Khibina carbonatites are unusual compared with other carbonatites. This is mainly due to the strong differentiation of the carbonatitic rocks giving the sequence phoscorite, early carbonatite, at least three types of late carbonatites, and finally three types of carbonate-zeolite veins (Table 3).

Detailed mineralogical investigations have revealed two distinct types of *REE*-Sr-Ba mineralization at Khibina: (1) primary minerals crystallized directly from a magma or other fluid and (2) minerals produced by secondary metasomatic processes (Table 3). A general sequence for the *REE*-Sr-Ba-rich mineralization in the late carbonatites and carbonate-zeolite veins can be expressed as follows:

Sr-*REE*-Ca-Na-rich carbonates (burbankite, carbocernaite) → Ca-*REE* fluocarbonates (bastnäsite group) → Ba-*REE* fluocarbonates (cordylite group) → Y-rich carbonates (mckelveyite group).

Similar age relationships for the Sr-*REE*-Ca-Na-rich carbonates burbankite and carbocernaite and the Ca-*REE* fluocarbonates have been established in carbonatites from other complexes (Zdorik, 1966; Somina, 1975; Kapustin, 1980; Platt and Woolley, 1990) and probably this sequence is universal for late-stage carbonatites.

The primary *RE* minerals in Khibina carbonatites such as burbankite, carbocernaite, cordylite-(Ce) and mckelveyite-(Y) contain essential Na (ranging from a minimum of 2.22 wt.% Na_2O in cordylite-(Ce) to 12.12 wt.% of Na_2O in burbankite) and the whole rock Na_2O content of the CII-1 carbonatites ranges up to 4.95 wt.%. These data show that carbonatite formation in the Khibina massif was characterized by a high content of alkaline elements (particularly Na) at all stages. The high content of alkaline elements (both Na and K) during the early stages is also marked by abundant aegirine and biotite in the phoscorites.

The La/Nd ratio in minerals has been shown to be a useful indicator of the paragenetic type of occurrence and geological environment by Fleischer (1965, 1978) and Fleischer and Altschuler (1969). Their results cannot be directly applied to the Khibina data because they used the La/Nd ratio from the atomic percent of total *REE* normalized to 100% but comparison of the relative changes in the La/Nd ratio can be useful. Fleischer (1978) calculated La/Nd ratios (from atomic percent of total *REE*) for bastnäsite-(Ce), synchysite-(Ce) and parisite-(Ce) from various rocks. These data show a decreasing La/Nd ratio in the sequence from carbonatites to hydrothermal rocks with average La/Nd ratios in bastnäsite-(Ce) 2.7 and 1.8 respectively and average La/Nd values for parisite-(Ce) are 2.8 (carbonatites) and 1.3 (hydrothermal rocks).

The Khibina carbonatites are interpreted as polygenetic in origin (Zaitsev, 1996). Phoscorites and early carbonatites (C I) are probably magmatic; formation of the late carbonatites (C II) is likely to be from volatile-rich fluid (carbohydrothermal) and carbonate-zeolite veins from hydrothermal fluids. The decreasing La/Nd_{cn} ratios in Khibina carbonatites probably reflect increase of 'carbohydrothermal' fraction in carbonatite-forming system.

The alteration of burbankite or carbocernaite to assemblages of ancylite-(Ce) + strontianite ± baryte, synchysite-(Ce) + strontianite+baryte or stronianite + cordylite-(Ce) + synchysite-(Ce) + baryte is probably an open-system hydrothermal process (Wall and Mariano, 1996). This conclusion is confirmed by reactions calculated for two different paths of burbankite alteration at Khibina. Calculation of the equations was based on the following: 1. volumes of primary burbankite and secondary ancylite-(Ce), synchysite-(Ce), strontianite and baryte are the same (full hexagonal prismatic pseudomorphs are strong evidence for this); 2. proportions of the secondary minerals were calculated from the backscattered electron images as ancylite-(Ce) 30 vol.%, strontianite 50 vol.%, baryte 5 vol.%, porous 15 vol.% for reaction (1) and synchysite-(Ce) 20 vol.%, strontianite 50 vol.%, baryte 10 vol.% and porous 20 vol.% for reaction (2); 3. actual mineral compositions were used; 4. coefficients in the reactions are numbers of mineral moles in a 'single' volume, which was assumed as 1000 volume units (cm^3); 5. the number of mineral moles were calculated by using mineral density and unit cell parameters. Thus, replacement of

Equation 1

$$5.55(Na_{2.42}\,Ca_{0.50})_{\Sigma 2.92}(Sr_{1.50}\,Ca_{0.86}REE_{0.55}\,Ba_{0.09})_{\Sigma 3.00}(CO_3)_5 + 6.00Sr^{2+} + 0.52Ba^{2+} + 0.25REE^{3+} + 5.20H_2O + 1.14F^- + 0.97SO_4^{2-} = 3.17REE_{1.04}(Sr_{0.78}Ca_{0.14}Ba_{0.02})_{\Sigma 0.94}(CO_3)_2(OH_{0.64}F_{0.36})\cdot H_2O + 12.86(Sr_{0.92}Ca_{0.08})_{\Sigma 1.00}CO_3 + 0.97(Ba_{0.99}Sr_{0.01})_{\Sigma 1.00}SO_4 + 13.42Na^+ + 6.07Ca^{2+} + 8.52CO_3^{2-} + 2.03H^+ \quad (1)$$

Equation 2

$$5.48(Na_{2.64}Ca_{0.30})_{\Sigma 2.94}(Sr_{1.22}Ca_{0.90}REE_{0.79}Ba_{0.09})_{\Sigma 3.00}(CO_3)_5 + 3.87Sr^{2+} + 1.43Ba^{2+} + 3.00F^- + 1.94SO_4^{2-} = 3.03(Ca_{0.93}Sr_{0.03})_{\Sigma 0.96}REE_{1.02}(CO_3)_2F_{0.99} + 11.57(Sr_{0.90}Ca_{0.09}Ba_{0.01})_{\Sigma 1.00}CO_3 + 1.94(Ba_{0.99}Sr_{0.01})_{\Sigma 1.00}SO_4 + 14.46Na^+ + 2.71Ca^{2+} + 1.24REE^{3+} + 9.76CO_3^{2-} \quad (2)$$

burbankite by an assemblage of ancylite-(Ce) + strontianite + baryte may be represented by equation (1) above.

Replacement of burbankite by the assemblage of synchysite-(Ce) + strontianite + baryte could be described by equation (2) above.

Both reactions show that H_2O (equation 1), F, S and Sr with traces of Ba and *REE* (in equation 1) must be introduced to form ancylite-(Ce), synchysite-(Ce), strontianite, and baryte. These secondary minerals do not contain Na and this element together with Ca, *REE* (in equation 2) and CO_2(aq) are removed from the carbonatite. Calculation of similar equations for the alteration of carbocernaite produces similar results to equation (2).

Residual solutions enriched in Na, Ca and CO_2(aq) may be described as alkaline carbohydrothermal fluids ('hot brines') and may be an additional cause of wall rock fenitization or may be involved in the formaion of the carbonate-zeolite veins.

The two different geochemical paths of burbankite and carbocernaite alteration (ancylite-(Ce) *versus* synchysite-(Ce) and cordylite-(Ce)) seems to imply action on these minerals by fluids of different composition. One of these fluids was characterized by a high activity of F^- and $(SO_4)^{2-}$ and low $(OH)^-$ resulting in the formation of synchysite-(Ce), cordylite-(Ce) and baryte. In contrast, the second type of fluid was characterized by a high activity of $(OH)^-$, $(SO_4)^{2-}$ and low F^- which resulted in the formation of ancylite-(Ce) and baryte. Although, there are no data on the temperature stability fields of ancylite(Ce) or synchysite-(Ce), ancylite-(Ce) as a water-bearing mineral containing both $(OH)^-$ and H_2O groups appears to be stable at lower temperatures than anhydrous synchysite-(Ce).

The nature of these fluids is unclear but there is no change in the Sr and Nd isotope ratios during the evolution (Zaitsev and Bell, in preparation) and all appear to be directly related to the carbonatite complex. The ratio of La/Nd_{cn} in primary-secondary mineral pairs can also be used to give some information about the fluids. Similar La/Nd_{cn} ratios for the pairs burbankite-ancylite-(Ce) and burbankite-synchysite-(Ce) indicate that alteration took place soon after the initial formation of burbankite, before the evolution of carbonatitic fluids. Different La/Nd_{cn} values for minerals in the system carbocernaite-synchysite-(Ce)+cordylite-(Ce) and particularly low La/Nd_{cn} ratios for synchysite-(Ce) and cordylite-(Ce) probably indicate involvement not only of fluids related to carbonatites, but also fluids responsible for the formation of the carbonate-zeolite veins. Finally, low, but similar La/Nd_{cn} ratios for the pair low-Ca-Sr cordylite-(Ce)-high-Ca-Sr cordylite-(Ce) indicate a fluid source related only to the formation of carbonate-zeolite veins.

Acknowledgements

A. Zaitsev received a Royal Society grant for two visits to the UK. Terry Williams and John Spratt are thanked for assistance and advice with the electron microprobe analyses. This work was carried out as a portion of a comprehensive study of the Kola alkaline massifs carried out at St-Petersburg University, University of Leicester and The Natural History Museum. The authors thanks A.G. Bulakh for discussion on mineralogy of *REE*-rich carbonatites and A.M. McDonald for discussion on chemistry of mckelveyite-(Y). K. Bell and an anonymous reviewer made helpful comments on the manuscript. A.N. Zaitsev would like to thank all staff of the Department of Geology, Leicester University, and Department of Mineralogy, The Natural History Museum, for hospitality. Special thanks go to Helen, Olga and

Polina Zaitseva for their support. This work was funded by the Royal Society (project 638072.P699) and partly by Russian Foundation for Fundamental Sciences (grant 96-05-66151).

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[*Manuscript received 25 February 1997: revised 4 August 1997*]