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Burbankite group minerals and their alteration in rare earth carbonatites—source of elements and fluids (evidence from C–O and Sr–Nd isotopic data)

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Abstract

The 370–380 Ma Khibina and Vuoriyarvi complexes on the Kola Peninsula, Russia, which form part of the Palaeozoic Kola Alkaline Province, contain REE-rich carbonatites with burbankite $(Na,Ca)_3(Sr,Ca,REE,Ba)_3(CO_3)_5$ or calcioburbankite $(Na,Ca)_3(Ca,Sr,REE,Ba)_3(CO_3)_5$ as the principal primary REE mineral. Within each complex the C–O and Sr–Nd isotopic data are similar for burbankite group minerals and co-existing calcite or dolomite (Khibina: $\delta^{13}C$(V-PDB) = − 6.4 to − 5.8‰, $\delta^{18}O$(V-SMOW) = 7.3–7.7‰, $(^{87}Sr/^{86}Sr)_{370} = 0.70390–0.70404$ and $(^{143}Nd/^{144}Nd)_{370} = 0.51230–0.51235$; Vuoriyarvi: $\delta^{13}C = -4.2$ to -3.0‰, $\delta^{18}O = 8.1–9.4$‰, $(^{87}Sr/^{86}Sr)_{370} = 0.70313–0.70315$ and $(^{143}Nd/^{144}Nd)_{370} = 0.51243–0.51245$). This indicates that the REE mineralization and its host carbonatites in each complex are derived from the same source and are co-genetic. There is, however, a great difference between the Sr, Nd and C isotopic signatures from Khibina and Vuoriyarvi, whereas the $\delta^{18}O$ ranges are similar. This suggests that the REE carbonatites of the two complexes originate from sources with different isotopic signatures. At least three mantle components are needed to explain the variations in Sr and Nd compositions in the carbonatites from Kola. The $\delta^{13}C$ ranges of primary carbonatites with low $\delta^{18}O$ values are quite different for Khibina and Vuoriyarvi and show correlation with the radiogenic isotope compositions. The data may be best explained by subduction-related source contamination that caused $\delta^{13}C$ variations in different mantle components. During late-stage processes burbankite and calcioburbankite have been replaced by various assemblages of REE–Sr–Ba minerals. The alteration of burbankite group minerals is an open-system hydrothermal process leading to multiple element transfer. It has produced mineral assemblages which are characterized by high $\delta^{18}O$ values (Khibina: $\delta^{18}O$(V-SMOW) = 11.4–13.9‰ and Vuoriyarvi: $\delta^{18}O = 17.1–18.0$‰) compared to primary burbankite and calcioburbankite. Co-existing calcite and dolomite have retained their original C and O isotope compositions, and one calcite sample from Khibina shows strong positive $\delta^{13}C$–$\delta^{18}O$ shifts similar to those of the pseudomorph. The high $\delta^{18}O$ and sometimes high $\delta^{13}C$ values can be attributed to low-temperature isotope exchange between minerals and fluid with variable CO_2/H_2O ratio taking place during and/or after crystallization as usually observed in carbonatites. The Sr and Nd isotope compositions of pseudomorphs and associated calcite/dolomite in

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general are identical to those of burbankite/calcioburbankite and associated carbonates suggesting that the fluids which caused burbankite alteration are from the same source, i.e. carbonatitic. Small variations in the Sr and Nd isotope signatures point to interaction of the pseudomorph-forming fluid with alkali silicate wall rocks. © 2002 Published by Elsevier Science B.V.

Keywords: Burbankite; Calcioburbankite; Pseudomorph; Carbonatite; C–O–Sr–Nd isotopes; Kola Alkaline Province

1. Introduction

REE-enriched carbonatites are characteristic of many alkaline complexes, e.g., Mountain Pass (USA) (Olsen et al., 1954), Fen (Norway) (Andersen, 1986), Tundulu and Kangankunde (Malawi) (Ngwenya, 1994; Wall and Mariano, 1996), Khibina, Seblyavr, Vuoriyarvi and Sallanlatvi (Russia) (Kukharenko et al., 1965; Kapustin, 1980; Bulakh et al., 1998; Zaitsev et al., 1998; Subbotin et al., 1999) and Barra do Itapirapuã, Brazil (Andrade et al., 1999). With the exception of Mountain Pass, Kangankunde and Khibina carbonatites, they are much less common than early-stage REE-poor calcite carbonatites, forming small veins up to 1 m wide and are calcitic, dolomitic, ankeritic and rarely magnesitic or sideritic in composition. The principal rare earth minerals are Ca–fluocarbonates synchysite–(Ce) and parisite–(Ce), Ca-free fluocarbonate bastnäsite–(Ce), alkali carbonates burbankite, calcioburbankite and carbocernaite and hydrous carbonate ancylite–(Ce). The phosphate, monazite–(Ce), is a major non-carbonate REE mineral.

In many of these carbonatites, REE mineralization is believed to be a product of crystallization from carbohydrothermal fluids; in addition REE carbonatites often show secondary replacement textures (e.g., Hogarth et al., 1985; Andersen, 1986; Ngwenya, 1994; Bulakh et al., 1998, 2000; Andrade et al., 1999). However, magmatic origins have been thought possible, and indeed likely for some occurrences, e.g., Mountain Pass, which is the largest REE carbonatite known (Olsen et al., 1954; Mariano, 1989). Of particular interest are the so-called "rare earth carbonatite pegmatites" described from several occurrences, e.g., Khibina, Vuoriyarvi and Ozernyi (Russia) (Wall et al., 2001). A characteristic feature of rare earth carbonatite pegmatites is the presence of large prismatic hexagonal crystals of burbankite $(Na,Ca)_3(Sr,Ca,REE,Ba)_3(CO_3)_5$ or calcioburbankite $(Na,Ca)_3(Ca,Sr,REE,Ba)_3(CO_3)_5$. The crystals grow normal to the wall rocks and form near parallel or slightly radiating aggregates. Their textures match particularly well with shallow and intermediate granite pegmatites (Cerný, 1982) and required burbankite, which is usually regarded as a hydrothermal mineral, to crystallize from an alkaline and volatile-rich melt (Wall et al., 2001).

Typical of REE carbonatite pegmatites are distinctive hexagonal prismatic pseudomorphs up to 5 cm diameter and 15 cm in length. The pseudomorphs consist of an assemblage of various rare earth minerals, including ancylite–(Ce), synchysite–(Ce), monazite–(Ce) and other REE–Sr–Ba-bearing minerals and detailed mineralogical studies have indicated that the precursor mineral was burbankite or calcioburbankite (Zaitsev et al., 1998; Wall et al., 2001).

To learn about the nature of the source(s) that generated Khibina and Vuoriyarvi rare earth carbonatite pegmatites and fluids that caused alterations of these carbonatites we have done a C–O and Sr–Nd isotopic study of burbankite group minerals, their alteration products and host minerals calcite and dolomite.

2. General geology

Both Khibina and Vuoriyarvi complexes belong to the Palaeozoic Kola Alkaline Province that is part of the northeastern Fennoscandian Shield (Fig. 1) (e.g., Gerasimovsky et al., 1974; Kogarko, 1987; Kramm, 1993). More than 20 alkaline complexes were intruded into the Baltic Shield between 400 and 360 Ma ago (Balaganskaya et al., 2001b and references herein). The spatial distribution of alkaline complexes is controlled by rifting, particularly the NE–SW trending Kontozero graben and NW–SE trending Kandalaksha deep fracture zone (Kukharenko et al., 1971; Bulakh and Ivanikov, 1984).

Khibina is the largest (about 1327 km^2) intrusive complex of agpaitic (peralkaline) nepheline syenites and foidolites in the world (Kogarko et al., 1995). It is

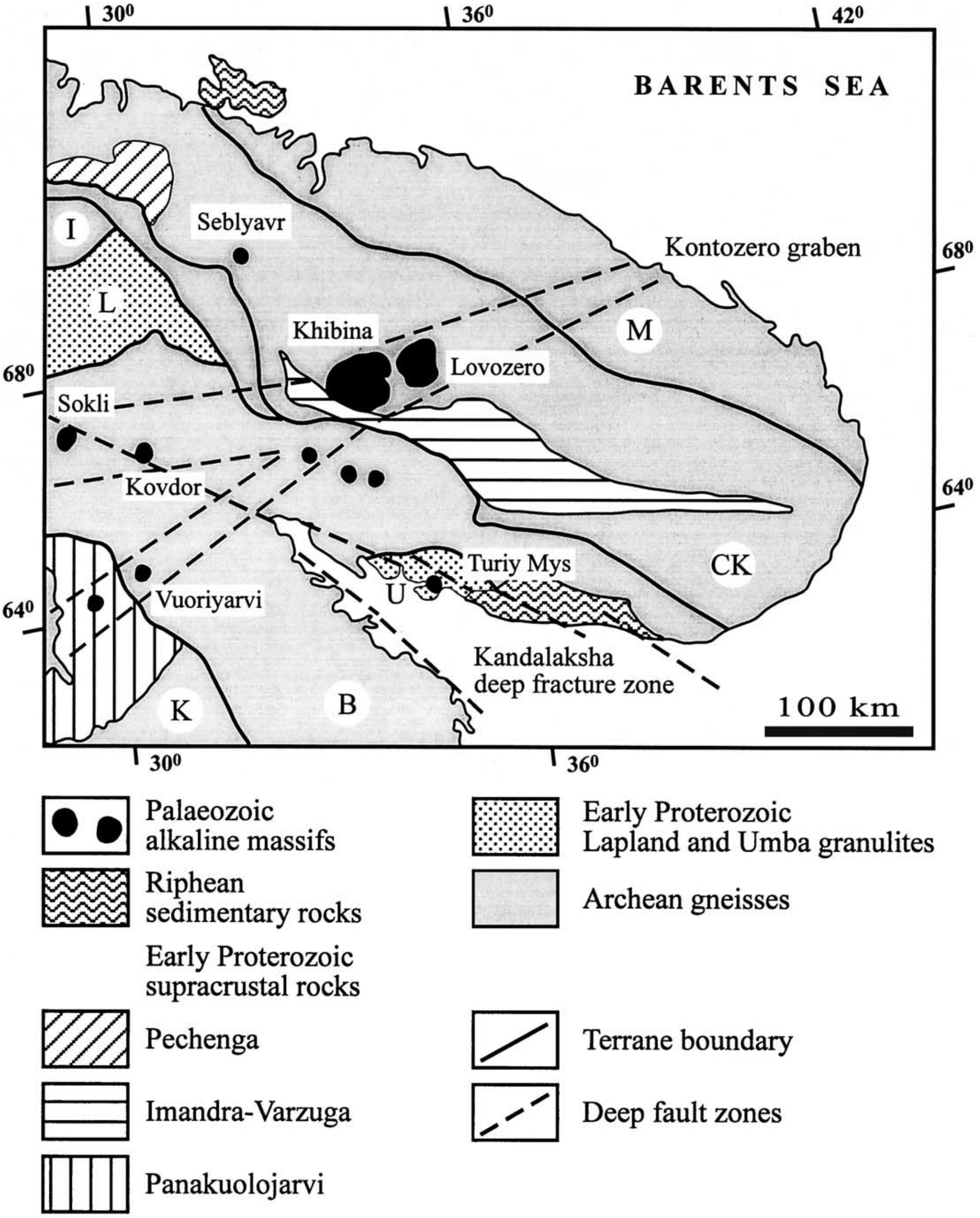

Fig. 1. Simplified geological map of the Kola peninsula showing the position of alkaline–carbonatite massifs (after Kukharenko et al., 1971; Bell et al., 1996; Balagansky et al., 1998). Dispersed terranes (fragments of a Neoarchean craton) M — Murmansk, I — Inari, CK — Central Kola, B — Belomorian and K — Karelian (Kuhmo). Accreted terranes (tectonic packages of Palaeoproterozoic island-arc suites) L — Lapland and U—Umba.

a composite pluton, elliptical in shape and concentrically zoned. The complex contains a wide variety of magmatic and metasomatic rocks including ultrabasic peridotites and pyroxenites (occurs as xenoliths), foidolites (ijolite, urtite and melteigite) and associated with them magmatic apatite–nepheline rocks and agpaitic nepheline syenites foyaite and khibinite, which are the principal rock type at Khibina (e.g., Kukharenko et al., 1971; Galakhov 1975; Kostyleva-Labuntsova et al., 1978). Carbonatites are located in the eastern part of the massif near the contact with Archean gneisses (Dudkin et al., 1984). They occur in an area of about 4 km^2, covered by alluvium 20–90 m thick and have been traced down to 1700-m depth in drill holes (Zaitsev, 1996). The carbonatitic rocks are divided into two groups represented by early REE-poor calcite carbonatites and late REE-rich calcite, ankerite and siderite–rhodochrosite carbonatites. Associated and genetically related silicate–carbonate rocks are biotite–aegirine–apatite rocks (termed phoscorites) and ankerite–siderite–natrolite rocks that are products of late-stage hydrothermal activity (Zaitsev, 1996; Zaitsev et al., 1998).

The Vuoriyarvi massif is a much smaller intrusion than Khibina, covering an area of approximately 20 km^2 (Kogarko et al., 1995). The distribution of silicate rocks in the Vuoriyarvi massif is also different from Khibina. The principal rock type is pyroxenite with blocks of olivinite and peridotite. It is surrounded by a melteigite–ijolite rim. Nepheline syenites occur as dykes but are very rare (Kukharenko et al., 1965; Kapustin, 1980). The silicate rocks are characterized by a lower degree of alkalinity compared to Khibina and many minerals that are typical accessory minerals in the Khibina rocks (e.g., eudialyte, astrophyllite) are absent or extremely rare in Vuoriyarvi. The pyroxenites in the eastern part of the massif host two distinct stockworks of phoscorites and carbonatites Neskevara (2 × 1 km) and Tukhtavara (900 × 400 m). Olivine-bearing phoscorites are similar to those from the Kovdor and Phalaborwa complexes (e.g., Russell et al., 1954; Krasnova and Kopylova, 1988), other phoscorite varieties can be enriched in tetraferriphlogopite, diopside or actinolite. The carbonatites are classified as early stage REE-poor calcite and late stage REE-rich calcite, and dolomite–ankerite types; late-stage hydrothermal quartz–carbonate rocks also occur (Kapustin, 1980; Bulakh et al., 2000).

3. Burbankite/calcioburbankite in pegmatite carbonatites

Rare earth carbonatite pegmatites containing burbankite or calcioburbankite have been described from several occurrences in Russia, Africa and America (Wall et al., 2001). In Khibina fresh burbankite is lemon yellow, it forms crystals up to 7 cm long and 4 cm diameter with a hexagonal cross-section. Sometimes the crystals grow perpendicular to the wall rock. Burbankite also occurs as 10–250 μm drop-like inclusions in host calcite or along mineral boundaries. In thin section, the mineral has a low birefrigence (grey colour) and is quite similar to apatite. Burbankite is often altered and two distinct assemblages of secondary minerals have been established (1) ancylite-(Ce) + strontianite + baryte and (2) synchysite-(Ce) + strontianite + baryte (Zaitsev et al., 1998).

Vuoriyarvi late-stage carbonatites contain both burbankite and calcioburbankite, described by Borodin and Kapustin (1962) and Subbotin et al. (1999), respectively. The minerals occur as rounded or elliptical subhedral to anhedral crystals up to 3 × 3 cm and as 10–250 μm drop-like inclusions in host dolomite or along grain boundaries of dolomite. When associated with fresh burbankite, dolomite forms white subhedral–anhedral grains. When associated with pseudomorphs, the mineral is grey and forms subhedral–anhedral grains which appear recrystallized and commonly show fan-shaped or wavy extinction under an optical microscope. Numerous (10–100 μm) veins and veinlets of later ankerite occur cutting the carbonatites. The pseudomorphs after burbankite/calcioburbankite are very complex. Carbocernaite is the first secondary mineral after burbankite/calcioburbankite, followed by ancylite–(Ce) and alstonite, olekminskite, baryte and Sr-enriched calcite in various proportions.

All stages of burbankite/calcioburbankite alteration can be seen—from thin veins of ancylite–(Ce) or carbocernaite cutting the mineral crystals to full hexagonal pseudomorphs with preserved original crystal shape indicating volume-by-volume replacement (Zaitsev et al., 1998, Fig. 3).

Replacement of burbankite/calcioburbankite and the formation of complete pseudomorphs in the Khibina and Vuoriyarvi as well as in some other carbonatites is clearly a late-stage process involving water-bearing fluids with element exchange between burbankite/calcioburbankite and fluid (Wall and Mariano, 1996; Zaitsev et al., 1998; Wall et al., 2001). The similarity of La/Nd_{cn} ratios in primary burbankite and secondary synchysite–(Ce) and ancylite–(Ce) in Khibina lead to the conclusion that the alteration of burbankite by fluids took place soon after its crystallization before the evolution of carbonatitic fluids (Zaitsev et al., 1998). Rock-forming calcite and dolomite have also been subjected to alteration, which is indicated by the development of fine veins, veinlets and irregular patches of low-Sr secondary calcite and ankerite replacing primary high-Sr calcite and dolomite.

More detailed geological and mineralogical description of these carbonatites, burbankite, calcioburbankite and their alteration is available from Borodin and Kapustin (1962), Kukharenko et al. (1965), Kapustin (1980), Zaitsev (1996), Zaitsev et al. (1998), Subbotin et al. (1999) and in Table 1 we have summarized their major mineralogical and geochemical features.

4. Analytical techniques

For C, O, Sr and Nd isotope analyses, mineral separates (calcite, dolomite, burbankite, and calcio-

Table 1
Summary of mineralogy of the burbankite/calcioburbankite and pseudomorphs

Massif	Khibina		Vuoriyarvi	
Primary mineral	Burbankite		Calcioburbankite	
Occurrence	Fresh mineral is lemon yellow. It forms crystals up to 7 cm long and 4 cm diameter with a hexagonal cross section and also occurs as 10–250 μm drop-like inclusions in host calcite or along grain boundaries of calcite.		Fresh mineral is lemon yellow to brownish. It occurs as small prismatic crystals up to 2 cm long, rounded/elliptical euhedral to anhedral crystals up to 3 × 3 cm and as 10–250 μm drop-like inclusions in host calcite or dolomite or along boundaries of the minerals	
Chemistry (all oxides numbers are wt.%)	$Na_2O = 10.5-12.7$ $CaO = 8.9-13.3$ $SrO = 16.4-25.2$ $BaO = 0.8-7.3$ $REE_2O_3 = 13.2-21.8$		$Na_2O = 12.9-14.2$ $CaO = 10.0-12.9$ $SrO = 8.8-17.7$ $BaO = 5.1-14.0$ $REE_2O_3 = 14.6-19.1$	
Alteration	All stages of alteration can be seen — from thin veins of ancylite–(Ce) or carbocernaite cutting burbankite/calcioburbankite to full hexagonal pseudomorphs			
Secondary minerals	Ancylite–(Ce) + strontianite + baryte; Synchysite–(Ce) + strontianite + baryte		Carbocernaite + ancylite–(Ce) + baryte + alstonite + barytocalcite + olekminskite + calcite	
Chemistry (all oxides numbers are wt.%)	Ancylite–(Ce) $SrO = 19.0-25.2$ $CaO = 0.9-2.6$ $BaO = 0.5-1.1$ $REE_2O_3 = 43.0-47.6$ $F = 1.0-2.5$	Strontianite $SrO = 61.8-68.8$ $CaO = 1.2-6.1$ $BaO = 0.4-2.6$ $REE_2O_3 = 0.2-1.6$	Carbocernaite $Na_2O = 4.0-4.7$ $CaO = 12.6-15.5$ $SrO = 15.5-20.7$ $BaO = 5.0-6.4$ $REE_2O_3 = 26.4-34.1$	Ancylite–(Ce) $SrO = 13.7-20.9$ $CaO = 1.9-3.7$ $BaO = 0.7-2.0$ $REE_2O_3 = 46.54-55.9$
	Synchysite–(Ce) $CaO = 15.2-16.9$ $SrO = 0.2-1.5$ $BaO = < 0.2$ $REE_2O_3 = 50.9-53.6$ $F = 5.4-6.0$	Baryte $BaO = 65.9-66.5$ $CaO = < 0.1$ $SrO = 0.1-1.8$	Baryte $BaO = 60.0-66.2$ $CaO = < 0.1$ $SrO = 0.5-5.8$	Barytocalcite $BaO = 50.5-54.2$ $CaO = 16.7-18.9$ $SrO = 0.1-0.3$
			Alstonite $BaO = 44.1-48.7$ $CaO = 16.0-17.7$ $SrO = 4.1-8.8$	Olekminskite $BaO = 29.1-41.3$ $CaO = 14.4-17.2$ $SrO = 12.1-24.9$

burbankite) and bulk pseudomorph samples were used. Before mineral separations all samples were studied using an Hitachi S2500 scanning electron microscope equipped with a Link AN10/55S energy-dispersive analysis system and the minerals were analyzed using a Cameca SX 50 wavelength-dispersive electron microprobe at The Natural History Museum (London, UK). The minerals were separated by hand-picking under binocular microscope and washed in ethanol. Burbankite and calcioburbankite were separated from large (> 1 cm) crystals manually crushed in agate mortar.

Carbon and oxygen isotope compositions of carbonates were determined using the conventional H_3PO_4 digestion method (McCrea, 1950). In the absence of known carbonate-acid fractionation factors for REE- and Sr-carbonates, the fractionation factor for calcite was used. This treatment is validated by the observation that these carbonates reacted quickly like calcite. $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios were determined on CO_2 using a Finnigan MAT delta S mass spectrometer at the Laboratory for Geochemical Research (Budapest, Hungary). The results are expressed in the δ-notation (δ=$(R_1/R_2-1)\times 1000$ where R_1 and R_2

Table 2
C–O and Sr–Nd isotopic data for burbankite and pseudomorphs

Massif	Sample		$\delta^{13}C$ ‰ VPDB	$\delta^{18}O$ ‰ VSMOW	Rb (ppm)	Sr (ppm)	$^{87}Sr/^{86}Sr$ measured	ε_{Sr} (370)	Sm (ppm)	Nd (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$ measured	$^{143}Nd/^{144}Nd$ 370 Ma	ε_{Nd} (370)
Khibina	633/477.7	calc[a]	− 5.8	7.5	–	12470	0.70390 (1.2)	− 2.33	33.6	262	0.0775	0.51254 (1)	0.51235	3.68
		burb[a]	− 5.8	7.6	0.15	193630	0.70391 (1.4)	− 2.19	1130	15850	0.0130	0.51238 (1)	0.51235	3.68
	581/115	calc	− 6.4	7.7	0.3	10174	0.70390 (0.9)	− 2.33	24	152	0.0949	0.512544 (15)	0.51231	2.98
		burb	− 6.3	7.3	–	61871	0.70404 (1.2)	− 0.35	206	4756	0.0262	0.512368 (15)	0.51230	2.79
	607/242.2	calc	− 6.0	7.6	–	7993	0.70394 (1.2)	− 1.77	21	126	0.1005	0.512572 (15)	0.51233	3.26
		pseud	− 5.4	13.9	–	73544	0.70390 (1.0)	− 2.33	500	9330	0.0324	0.512417 (15)	0.51234	3.46
	603/26.5	calc	− 3.3	11.6	–	6143	0.70395 (1.6)	− 1.62	13	164	0.0473	0.512442 (15)	0.51233	3.24
		pseud	− 3.3	11.4	–	193428	0.70400 (2.1)	− 0.91	801	13993	0.0346	0.512424 (15)	0.51234	3.49
Vuoriyarvi	477/309	dol	− 3.0	8.3	–	7606	0.70315 (1.1)	− 12.99	13	131	0.0590	0.512588 (15)	0.51245	5.54
		caburb	− 4.0	8.1	–	64176	0.70313 (1.1)	− 13.27	425	7454	0.0344	0.512517 (15)	0.51243	5.31
	404/160	dol	− 3.7	9.4	–	–	–		–	–	–	–		
		caburb	− 4.2	8.1	–	–	–		–	–	–	–		
	V-5	dol	− 3.9	9.2	–	–	–		–	–	–	–		
		pseud	− 4.0	18.0	–	–	–		–	–	–	–		
	364/82	dol	− 2.8	9.1	–	2911	0.70312 (1.0)	− 13.41	9	62	0.0918	0.512579 (15)	0.51236	3.81
		pseud1	− 2.8	17.1	–	74152	0.70317 (1.1)	− 12.90	373	7586	0.0297	0.512499 (15)	0.51243	5.19
		pseud2	− 2.7	17.1	–	82193	0.70314 (0.9)	− 13.13	642	9514	0.0408	0.512488 (15)	0.51239	4.45

calc — calcite, dol — dolomite, burb — burbankite, caburb — calcioburbankite, pseud — pseudomorph. Numbers in parenthesis are 2σ errors of individual analyses.

[a] Sr and Nd data are from Zaitsev et al. (1997), (–) = not analyzed.

are the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios in the sample and the standard, respectively, in parts per thousand (‰) relative to V-PDB (for C) and V-SMOW (for O). Reproducibility is better than ± 0.15‰.

For Sr and Nd isotopic analysis, powdered samples were spiked with $^{87}Rb-^{84}Sr$ and $^{149}Sm-^{150}Nd$ mixed spikes and completely dissolved in hot HCl. Rb-, Sr- and bulk-REE fractions were produced using DOWEX AG-50 W * 8 resin (200–400 mesh) and 2.5 and 6 M HCl as eluants. Sm and Nd were effectively separated with KEL-F powder coated with di-(2-ethylhexyl)-orthophosphoric acid (HDEHP) and 0.17 and 0.4 M HCl as eluants as described by Richard et al. (1976). Sr was loaded with Ta-fluoride on W-filaments, Sm and Nd were loaded as chlorides on Re filaments. All three elements were analysed in a VG sector 54 mass spectrometer at the laboratory of the Institut für Mineralogie (Münster, Germany). For Sr and Nd, the mass fractionation corrections were based on $^{86}Sr/^{88}Sr = 0.1194$ and $^{146}Nd/^{144}Nd = 0.7219$. Re- peated analyses of the $^{87}Sr/^{86}Sr$ ratio of the NBS 987 Sr standard ($n = 29$) and the $^{143}Nd/^{144}Nd$ ratio of the LaJolla Nd standard ($n = 19$) yielded 0.710278 ± 0.000030 and 0.511862 ± 0.000010, res-pectively (errors are 2σ for all analyses). Total blanks are $Sr < 400$ pg, $Sm < 100$ pg and $Nd < 100$ pg.

5. Results

5.1. C and O isotope compositions

The C and O isotope compositions of the studied samples are listed in Table 2 and plotted in Fig. 2.

The samples from Khibina and Vuoriyarvi have quite different isotope signatures, but within each complex the C–O isotopic data are similar for co-existing calcite and/or dolomite and burbankite group minerals. The calcite–burbankite pairs from Khibina carbonatites show a small $\delta^{13}C-\delta^{18}O$ scatter with $\delta^{13}C = -6.4$‰ to -5.8‰ and $\delta^{18}O = 7.3-7.6$‰ and within each mineral pair the C and O isotopic compositions are nearly identical.

A similar relationship between dolomite and calcioburbankite is found in the Vuoriyarvi carbonatites, however the ranges in $\delta^{13}C$ and $\delta^{18}O$ values are wider

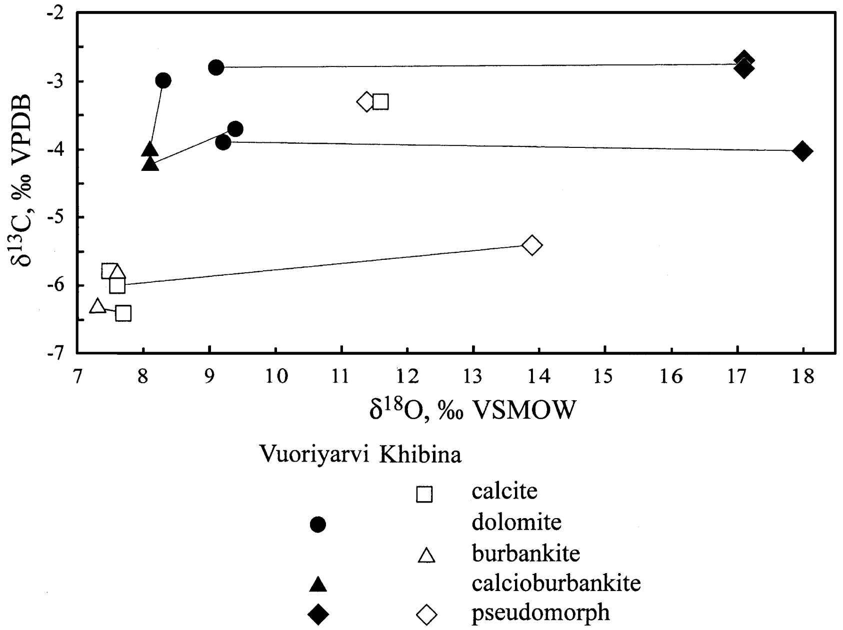

Fig. 2. Carbon $\delta^{13}C$(V-PDB, ‰) and oxygen $\delta^{18}O$(V-SMOW, ‰) isotopic composition of calcite, dolomite, burbankite, calcioburbankite and pseudomorphs from Khibina and Vuoriyarvi carbonatites. Tie-lines join calcite–burbankite, dolomite–calcioburbankite, calcite pseudomorph and dolomite pseudomorph from identical samples.

with $\delta^{13}C = -4.2$ to -3.0‰ and $\delta^{18}O = 8.1-9.4$‰. The two calcioburbankite samples have the lowest values and identical $\delta^{13}C$ and $\delta^{18}O$ isotopic signatures, whereas the co-existing dolomite has higher $\delta^{13}C$ and $\delta^{18}O$ values by 0.5–1.0‰ and 0.2–1.3‰, respectively.

Pseudomorphs (mixtures of ancylite–(Ce), strontianite and baryte; synchysite–(Ce), strontianite and baryte; carbocernaite, ancylite–(Ce), alstonite, barytocalcite, olekminskite, calcite and baryte) are characterized by high $\delta^{18}O$ values compared with precursor burbankite or calcioburbankite. In Khibina the $\delta^{18}O$ values are between 11.4‰ and 13.9‰ and in Vuoriyarvi they are higher and range from 17.1‰ to 18.0‰. In three of the four studied samples, the co-existing calcite or dolomite are characterized by low $\delta^{18}O$ values (-7.6‰ in Khibina and 9.1–9.2‰ in Vuoriyarvi) similar to the $\delta^{18}O$ values of the minerals associated with unaltered burbankite/calcioburbankite. This is also true for the C isotopic composition. In Vuoriyarvi, co-existing dolomite and pseudomorphs have overlapping compositions of C ($\delta^{13}C$ values of -2.8‰ to -2.7‰ and -4.0‰ to -3.9‰, respectively) and in Khibina sample 607/242.2 calcite and pseudomorph have similar $\delta^{13}C$ values (-6.0‰ and -5.4‰, respectively). It is noteworthy that these values are similar to data from unaltered burbankite/calcioburbankite and calcite/dolomite.

Sample 603/26.5 (Khibina) is characterized by different C and O isotope compositions. The calcite and associated pseudomorph show a strong positive shift in C and O isotopic composition (calcite $\delta^{13}C = -3.3$‰ and $\delta^{18}O = 11.6$‰ and pseudomorph $\delta^{13}C = -3.3$‰ and $\delta^{18}O = 11.4$‰) compared to the calcite–burbankite pairs.

5.2. Sr/Nd isotope ratios

Table 2 shows the results of Sr- and Nd-isotope analyses. All studied samples are characterized by high Sr contents, 2931–12,470 ppm in calcite and dolomite and 61,871–193,630 ppm in burbankite group minerals and pseudomorphs after them. Sm and Nd concentrations are low in calcite and dolomite (Sm = 9–34 ppm and Nd = 62–262 ppm) and they are high in burbankite, calcioburbankite and related pseudomorphs with 206–1130 ppm of Sm and 4756–15 850 ppm of Nd.

The $^{143}Nd/^{144}Nd$ signatures have been recalculated to an age of 370 Ma, which is considered to be an

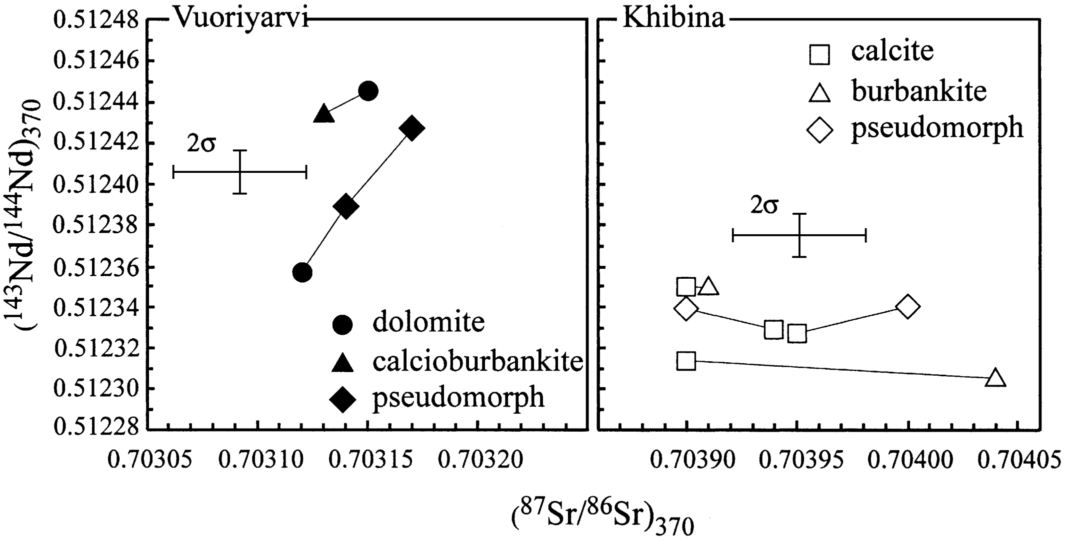

Fig. 3. Strontium $(^{87}Sr/^{86}Sr)_{370}$ and neodymium $(^{143}Nd/^{144}Nd)_{370}$ isotopic composition of calcite, dolomite, burbankite, calcioburbankite and pseudomorphs from Khibina and Vuoriyarvi carbonatites. Tie-lines join calcite–burbankite, dolomite–calcioburbankite, calcite pseudomorph and dolomite pseudomorph from identical samples. 2σ is the uncertainty given by repeated standard analyses.

average age for the Khibina complex (Kramm and Kogarko, 1994) and is similar to recent Rb–Sr dating of Vuoriyarvi carbonatites of 375 ± 7 Ma (Gogol and Delenitsin, 1999). The $^{87}Sr/^{86}Sr$ ratios are constant since the Rb concentrations in carbonate minerals are negligible (Table 2) and $^{87}Rb/^{86}Sr$ ratios are very low (< 0.00008).

Isotopically, the two suites of samples from the two massifs have quite different characteristics (Fig. 3). Vuoriyarvi samples have higher $(^{143}Nd/^{144}Nd)_{370}$ (0.51236–0.51245) and lower $^{87}Sr/^{86}Sr$ ratios (0.70312 –0.70317) than those from Khibina (0.51230–0.51235 and 0.70390–0.70404, respectively). Also within each data set there are significant differences. All the samples from Vuoriyarvi overlap in their $^{87}Sr/^{86}Sr$ signatures within the limits of uncertainty given by repeated standard analyses but there are larger variations in Nd. The dolomite and calcioburbankite fractions of sample 477/309 also have identical $(^{143}Nd/^{144}Nd)_{370}$ ratios within the limits of uncertainty, the $(^{143}Nd/^{144}Nd)_{370}$ ratios of the two pseudomorphs and the dolomite fractions of sample 364/82 differ within a range of 0.51236–0.51243.

In contrast, the Khibina samples show less variation in their $(^{143}Nd/^{144}Nd)_{370}$ isotopic ratios and each of the four calcite–burbankite/pseudomorph pairs analysed have identical $(^{143}Nd/^{144}Nd)_{370}$ ratios. $^{87}Sr/^{86}Sr$ signatures are more variables compared to Vuoriyarvi, but in most cases they do not exceed the limits of uncertainty, the largest difference is between the calcite and burbankite from sample 581/115, where there is a difference of 0.00014 between the $^{87}Sr/^{86}Sr$ isotope ratios.

6. Discussion

6.1. Calcite/dolomite–burbankite/calcioburbankite association

The C–O and Sr–Nd isotopic data from calcite/dolomite and burbankite/calcioburbankite samples show that the minerals in Khibina and Vuoriyarvi are characterized by different isotopic signatures of C, Sr and Nd but broadly similar O isotopic compositions (Figs. 2 and 3).

Co-existing calcite and burbankite in the Khibina carbonatites have identical C and O isotopic compositions, and similar relationships between dolomite and calcioburbankite are also found in Vuoriyarvi. However, in Vuoriyarvi calcioburbankite is slightly depleted in ^{13}C and ^{18}O compared to dolomite with a difference of less than 1.3 ‰. This observation is consistent with the theoretical dolomite–calcite isotope fractionation, with the dolomite being enriched in the heavy isotopes (e.g., Schwartz, 1966). Owing to late-stage carbonate-fluid isotope exchange reactions, which are especially important in fluid-rich carbonatite complexes, the oxygen isotope fractionation among carbonate minerals would correspond to a closure temperature and is not expected to yield primary information on crystallization conditions (Demény, unpublished data), thus thermometric implications are not taken into consideration.

The Khibina burbankite and associated calcite have significantly lower $\delta^{13}C$ values (− 6.4 ‰ to − 5.8 ‰) compared to the minerals from Vuoriyarvi ($\delta^{13}C$ value ranges from − 4.2 ‰ to − 3.0 ‰) and on the $\delta^{13}C$–$\delta^{18}O$ diagram they plot just in the middle of so-called “carbonatite box” (Taylor et al., 1967; Hoefs, 1987) and are close to the field of Oldoinyo Lengai natrocarbonatites that are believed to represent pristine mantle compositions (Keller and Hoefs, 1995) (Fig. 4). The $\delta^{18}O$ values of burbankite group minerals and associated calcite/dolomite from Khibina and Vuoriyarvi are not as varied as the $\delta^{13}C$ values although a slight difference appears with $\delta^{18}O$ values 7.3–7.7 ‰ for Khibina samples and 8.1–9.4 ‰ for Vuoriyarvi. It is therefore most unlikely that the original formation of burbankite, calcioburbankite and co-existing carbonates was related to late-stage low-temperature hydrothermal activity.

Like the C isotopic compositions, Sr and Nd isotope ratios in the carbonates from Khibina and Vuoriyarvi carbonatites are quite different (Fig. 3) but co-existing minerals within each complex show similar radiogenic isotope compositions. In two studied samples (477/309 from Vuoriyarvi and 633/477.7 from Khibina) co-existing dolomite/calcite and burbankite group minerals have identical Sr and Nd isotope compositions. However, in sample 581/115 (Khibina) burbankite has a slightly more radiogenic Sr ($^{87}Sr/^{86}Sr = 0.70404$) signature compared to calcite ($^{87}Sr/^{86}Sr = 0.70390$), whereas the Nd isotope compositions of both minerals are identical within analytical uncertainty. Either these burbankite or calcite are derived from sources with different $(^{87}Sr/^{86}Sr)_{370}$

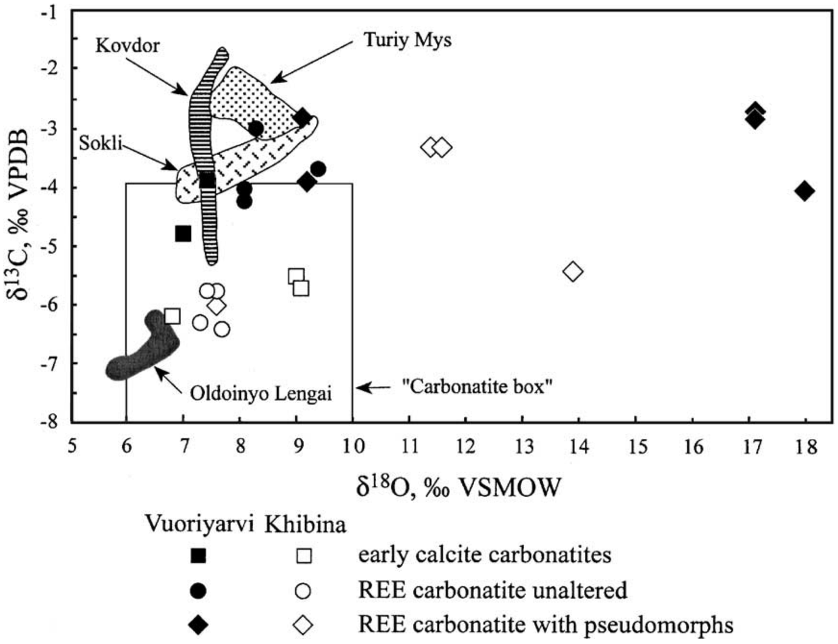

Fig. 4. Plot of δ^{13}C(V-PDB, ‰) vs. δ^{18}O(V-SMOW, ‰) for Kola carbonatites: Khibina, this work and Zaitsev (1996); Vuoriyarvi, this work; Kovdor, Zaitsev and Bell (1995); Turiy Mys, Dunworth and Bell (2001); Sokli (A. Demény, unpublished data). “Carbonatite box” is from Taylor et al. (1967) and Hoefs (1987); Oldoinyo Lengai data are from Keller and Hoefs (1995).

ratios or their isotope ratios were changed by a process subsequent to mineral formation.

The general similarity in isotopic signatures of burbankite, calcioburbankite, calcite and dolomite as well as low δ^{18}O values indicate a primary origin for the minerals. A primary origin—i.e., the derivation of the burbankite-bearing pegmatitic carbonatites directly from the carbonatitic magma (alkali volatile-rich melt as suggested by Wall et al., 2001)—is also indicated by a comparison of the C–O and Sr–Nd values from these REE-rich carbonatites (late-stage varieties) and early stage REE-poor calcite carbonatites.

C–O data are available for early-stage calcite carbonatites at both complexes. They are $\delta^{13}\mathrm{C} = -6.2$ ‰ to -5.5 ‰ and $\delta^{18}\mathrm{O} = 6.8$–$9.1$ ‰ ($2\sigma = \pm 0.3$ ‰) for the Khibina carbonatites (Zaitsev, 1996) and $\delta^{13}\mathrm{C} = -4.8$ ‰ to -3.9 and $\delta^{18}\mathrm{O} = 7.0$–$7.4$ ‰ for the Vuoriyarvi carbonatites (this work) (Fig. 4). Sr and Nd isotope characteristics of early stage calcite carbonatites are also available from both complexes (Zaitsev et al., 1997; Balaganskaya et al., 2001a) and have ranges similar to those for the burbankite/calcioburbankite carbonatites (Fig. 5).

6.2. Calcite/dolomite–pseudomorph association

The general trend related to alteration is an increase in the δ^{18}O values of the pseudomorph minerals compared to the burbankite group minerals. The pseudomorphs from Vuoriyarvi have the highest δ^{18}O values of 17.1–18.0 ‰, whereas the pseudomorphs from Khibina have δ^{18}O values from 11.4 ‰ to 13.9 ‰. In three studied samples, this strong positive shift of δ^{18}O in pseudomorphs is not accompanied by any changes in the C isotopic ratios of the pseudomorphs; the primary C and O isotope compositions have also been preserved in co-existing calcite or dolomite. The δ^{13}C values of the pseudomorphs and δ^{13}C and δ^{18}O values of the calcite/dolomite are identical to those of primary unaltered calcite, dolomite, burbankite and calcioburbankite. In Khibina sample 603/26.5 however the behaviour of C and O isotopes is different. Both calcite and pseudomorph minerals show increased and identical δ^{13}C and δ^{18}O values. Of note is the pseudomorph mineralogy in this sample—the newly formed secondary minerals are the Ca–fluocarbonate synchysite–(Ce), strontianite and

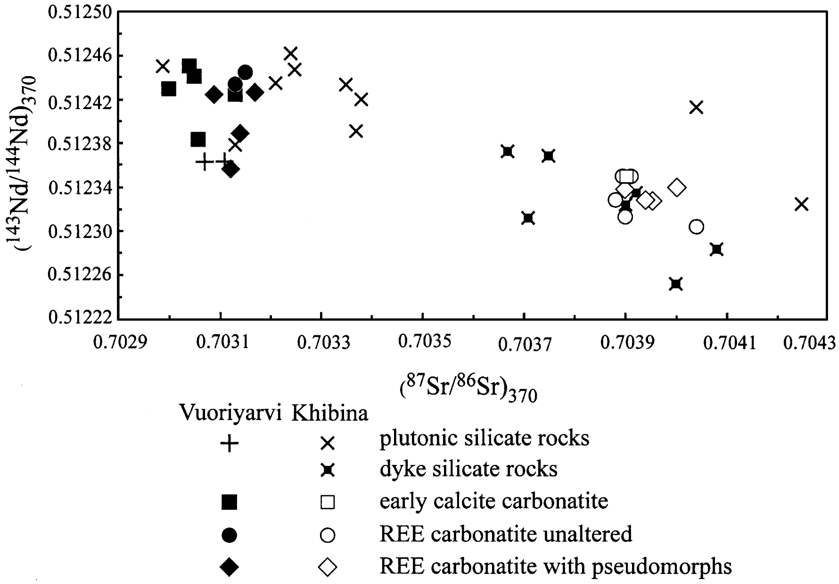

Fig. 5. Plot of $(^{87}Sr/^{86}Sr)_{370}$ vs. $(^{143}Nd/^{144}Nd)_{370}$ for the Khibina and Vuoriyarvi rocks: Khibina, this work, Kramm and Kogarko (1994), Zaitsev et al. (1997), Zaitsev and Sindern (unpublished data); Vuoriyarvi, this work, Balaganskaya et al. (2001a).

baryte. In other samples, the pseudomorphs do not have synchysite–(Ce), but contain the hydrous carbonate, ancylite–(Ce), ± carbocernaite, strontianite and baryte in various proportions. This suggests alteration of sample 603/26.5 under different fluid composition and/or different conditions (temperature?) compared to the other samples.

The Sr–Nd isotopic patterns of the pseudomorphs containing secondary mineral assemblages in Vuoriyarvi and Khibina carbonatites are different from each other.

In Vuoriyarvi, dolomite and two associated pseudomorphs (pseudomorph 1 and 2, Table 2) show more significant variation in their Nd isotope composition compared with Sr isotope composition. Dolomite has the lowest Sr and Nd isotope values ($^{87}Sr/^{86}Sr = 0.70312$ and $(^{143}Nd/^{144}Nd)_{370} = 0.51236$), pseudomorph 1 has the highest Sr–Nd values ($^{87}Sr/^{86}Sr = 0.70317$ and $(^{143}Nd/^{144}Nd)_{370} = 0.51243$) and pseudomorph 2 has intermediate Sr–Nd isotope values. The isotopic difference between pseudomorph 1 and pseudomorph 2 correlates with their mineralogical composition. Pseudomorph 1 contains water-free carbocernaite $(Ca,Na)(Sr,REE,Ba)(CO_3)_2$ as a major secondary mineral, with traces of ancylite–(Ce) and baryte, whereas pseudomorph 2 contains water-bearing ancylite–(Ce) $(Sr,REE)_2(CO_3)_2(OH)xH_2O$ with traces of carbocernaite. These mineral assemblages indicate different degrees of alteration. Carbocernaite has been described as mineral formed first during alteration of burbankite in a previous study of the Vuoriyarvi carbonatite (Kapustin, 1980) and in the Ozernyi carbonatite, Siberia (Zdorik, 1966), with subsequent alteration to ancylite–(Ce) and baryte.

The calcite and pseudomorph samples from Khibina show no significant changes in their $(^{143}Nd/^{144}Nd)_{370}$ ratios, but have variable $^{87}Sr/^{86}Sr$ signatures (Fig. 3). However, there is no systematic variation in Sr isotopic ratios.

6.3. Cause of burbankite/calcioburbankite alteration

An important question arising from the observed C–O and Sr–Nd isotope variations is the source of fluids that caused alteration of burbankite and calcioburbankite. It is well known that fluid-induced alteration of carbonatites may be associated with varying degrees of $\delta^{13}C$ and $\delta^{18}O$ changes (e.g., Andersen, 1987; Deines, 1989; Santos and Clayton, 1995; Simonetti and Bell, 1994; Andrade et al., 1999; Ray and Ramesh, 1999). The most frequent feature is the elevation of $\delta^{18}O$ values that may occur due to (i) retrograde isotope exchange with magmatic H_2O at decreasing temperature, or (ii) isotope exchange with or secondary precipitation from infiltrating external water (formation water, meteoric water, or magmatic water emanating from subsequent intrusions). The $\delta^{18}O$ increase may be associated with $\delta^{13}C$ change depending on the alteration process and fluid composition.

Alteration of burbankite group minerals in both Khibina and Vuoriyarvi carbonatites by high-temperature (>250 °C) meteoric groundwater can be excluded because this process leads to decreasing $\delta^{18}O$ values coupled with negative $\delta^{18}O-^{87}Sr/^{86}Sr$ and positive $\delta^{13}C-^{87}Sr/^{86}Sr$ correlation (e.g., Andersen, 1984, 1987; Simonetti and Bell, 1994).

The strong $\delta^{18}O$ change at constant $\delta^{13}C$ observed for the pseudomorphs in the Vuoriyarvi carbonatites may be interpreted as a result of postmagmatic isotope exchange with water-rich carbonatitic fluid or interaction with meteoritic groundwater at low temperature (e.g., Deines, 1989; Santos and Clayton, 1995; Horstmann and Verwoerd, 1997; Ray and Ramesh, 1999).

Alteration of burbankite was suggested to be an open-system hydrothermal process (Wall and Mariano, 1996) and this was confirmed by reactions calculated for burbankite alteration in Khibina (Zaitsev et al., 1998). The replacement reactions (elements mass balance) have been calculated taking into account that the volumes of primary burbankite and secondary minerals are the same (full hexagonal pseudomorphs are strong evidence for this); proportions of secondary minerals were calculated from BSE images and actual average mineral compositions were used (Zaitsev et al., 1998; Wall et al., 2001). They show that a sufficient amount of H_2O and Sr, together with Ba, REE, S and F must be introduced to form secondary ancylite–(Ce), synchysite–(Ce), strontianite and baryte. In contrast, Na, Ca and CO_2 are removed from the system.

It is unlikely that meteoric groundwater derived from continental crust can carry a large amount of Sr, Ba, REE, S and F. Commonly these elements are present in small amounts in a range of x–x00 μg/l (e.g., Land and Öhlander, 1997; De Caritat et al., 1998; Verplanck et al., 2001).

A more plausible explanation is that burbankite/calcioburbankite alteration is caused by a carbonatite-derived fluid phase. A recent detailed study of fluid inclusions in the Kalkfeld carbonatite complex has shown a high capability of carbonatitic fluids to transport Sr (up to 3.3 wt.%), REE (up to 3 wt.%), F (up to 1.2 wt.%) and Ba (up to 8000 ppm) (Bühn and Rankin, 1999). This fluid is assumed to be expelled from "a highly evolved, alkali carbonatitic fluid after dominant mineral fractionation" (Bühn and Rankin, 1999). Alteration of burbankite by carbonatitic fluids soon after its crystallization was also suggested for the Khibina samples on the basis of similarity of La/Nd_{cn} ratios in primary burbankite and secondary synchysite–(Ce) and ancylite–(Ce) (Zaitsev et al., 1998).

The C–O and Sr–Nd isotopic study on Kangankunde carbonatitic rocks also led to the conclusion that the pseudomorphs were formed by carbonatite-derived fluids, with little ground water contribution (Wall et al., 1994).

The stable isotope variations are more complex in the Khibina carbonatites compared to Vuoriyarvi rocks. Pseudomorph samples from Khibina are characterized by less ^{18}O enrichment. The degree of $\delta^{18}O$ shift is 4–6.5‰ in Khibina carbonatites compared to 8–9‰ in Vuoriyarvi. From the carbonate-fluid exchange model discussed by Deines (1989) and later developed by Santos and Clayton (1995) and Ray and Ramesh (1999) one would expect that burbankite alteration at Khibina has occurred at higher temperature than the alteration of the Vuoriyarvi carbonatites. Also, the constant $\delta^{13}C$ values in Vuoriyarvi pseudomorphs that are similar to co-existing dolomite and unaltered dolomite and calcioburbankite will indicate a low CO_2/H_2O ratio in a fluid (Santos and Clayton, 1995; Ray and Ramesh, 1999).

In the Khibina carbonatites, the pseudomorphs show $\delta^{18}O$ shifts at both constant and elevated $\delta^{13}C$ values. The former case may be interpreted similarly to the Vuoriyarvi samples, whereas the change to more positive $\delta^{13}C$ ratios needs further explanation.

Deines (1989) established a model of coupled C–O isotope fractionation in the crystallized silicate–carbonate–fluid system that explains the observed positive $\delta^{13}C-\delta^{18}O$ correlation. This Rayleigh fractionation model produces $\delta^{13}C-\delta^{18}O$ correlation with a slope of 0.4. However, the degree of $\delta^{13}C$ shift at Khibina (almost +3‰) is higher than that expected in Deines (1989) model, thus an external source of heavy carbon isotopes needs to be considered.

The positive $\delta^{13}C-\delta^{18}O$ shift can be explained by CO_2-H_2O–carbonate isotope exchange reactions at decreasing temperatures and varying CO_2/H_2O ratios in the fluid; increasing $\delta^{13}C$ values will indicate a relatively high proportion of CO_2 in fluid (Santos and Clayton, 1995; Ray and Ramesh, 1999). It was already mentioned above that the Khibina pseudomorph sample with high $\delta^{13}C$ and $\delta^{18}O$ values is quite different in terms of its mineralogical composition compared with the other Khibina and Vuoriyarvi samples because it contains synchysite–(Ce) as the major secondary mineral instead of ancylite–(Ce). There are no data on the relative temperature stability fields of ancylite–(Ce) and synchysite–(Ce); but ancylite–(Ce) as a water-bearing mineral containing both H_2O and OH^- groups appears to be stable at lower temperatures than anhydrous synchysite–(Ce). This leads to the conclusion that synchysite–(Ce)-bearing pseudomorphs after burbankite could be formed first at higher temperatures, followed by those containing ancylite–(Ce).

6.4. Carbonatites–silicate rocks radiogenic isotopic relations

The variable and non-systematic changes in the Sr–Nd isotopic signatures developed during late-stage hydrothermal alteration in both complexes can be explained with the help of the general isotopic patterns. Fig. 5 shows the $(^{143}Nd/^{144}Nd)_{370}$ and $(^{87}Sr/^{86}Sr)_{370}$ ratios of early and late stage carbonatites, as well as those of associated alkali silicate rocks. It can be seen that the field of the carbonatite signatures in both complexes is partly enclosed in the field of the alkali silicate rock signatures.

The Sr–Nd isotopic characteristics of the Khibina carbonatites are quite different from the isotopic ratios of the main Khibina plutonic silicate rocks (nepheline syenites, ijolite–urtites) but they overlap with the isotopic compositions of spatially associated silicate dyke rocks, monchiquites, nephelinites and phonolites. The carbonatites also show similarities with the Sr and Nd isotopic compositions of xenoliths of pyroxenite (rare) and ijolite (common) that occur in nepheline syenites, and are also spatially associated with the carbonatites (Fig. 5).

In Vuoriyarvi most of the early stage calcite carbonatite and unaltered calcioburbankite carbonatites are different from silicate rocks (pyroxenite and ijolite) in terms of their $(^{143}Nd/^{144}Nd)_{370}$ ratios but have similar $(^{87}Sr/^{86}Sr)_{370}$ ratios. The pseudomorph-bearing carbonatites, particularly the major rock-forming mineral dolomite fractions, are isotopically similar to the silicate rocks (Fig. 5).

Despite the overlap of Sr–Nd isotope signatures of carbonates and silicate rocks in both complexes the larger spread of isotopic signatures in the latter points to the fact that the alkali silicate rocks—at least in part—must have evolved in a different way than the carbonate forming fluids. Thus, a simple orthomagmatic genetic relationship between carbonatitic fluids and silicate melts, e.g. by fractional crystallization or unmixing, can be excluded. The isotope characteristics of the silicate dyke rocks (monchiquite, phonolite) from Khibina will be discussed in a separate paper. For the purpose of the present study the observation is underlined that carbonatites occur in dykes cross-cutting the alkali silicate rocks and must therefore be later. The carbonatites and fluids emanating from them thus represent reaction partners of the silicate rocks rather than genetic partners.

If the carbonatite-derived fluids responsible for the late stage pseudomorph formation had migrated through the isotopically heterogeneous alkali silicate rocks as well as the carbonatites, they could have interacted with these rocks and caused element exchange of Nd and/or Sr. The fluid/rock ratio necessary for the transport of Sr and Nd depends on the transport capacity of the fluid and on reaching exchange equilibrium between fluid and rock. Taking the high transport capacity of carbonatitic fluids for both elements indicated by the work of Bühn and Rankin (1999) into consideration, as well as the large amount of fluid associated with the occurrence of carbonatite and the larger volume of the alkali silicate rocks relative to the carbonates, such fluid–rock exchange seems highly plausible.

6.5. Sources of Kola carbonatites

As has been shown above, although the relationships between carbonatite types are similar in the Khibina and Vuoriyarvi complexes, the absolute $\delta^{13}C$ ranges are quite different. Taking the ranges of other Kola carbonatite complexes—Kovdor (Zaitsev and Bell, 1995), Turiy Mys (Dunworth and Bell, 2001) and Sokli (Demény, unpublished data) (Fig. 4), into consideration, it appears that there are two "end members", one with a $\delta^{13}C$ range around -3 ‰ to -2 ‰ (Turiy Mys) and another around -5.5 ‰ to -6.5 ‰ (Khibina). The Kovdor carbonatite complex forms a transition between these end members. This $\delta^{13}C$ variation is not associated with significant $\delta^{18}O$ changes. This is most apparent in the Kovdor phoscorite and carbonatites in which a $\delta^{18}O$ variation of 0.5 ‰ is observed at a $\delta^{13}C$ variation of 3.4 ‰.

Direct assimilation of sedimentary carbonate would result in a coupled $\delta^{13}C$–$\delta^{18}O$ shift that is not observed in the complexes studied. Changes in $\delta^{13}C$ at constant $\delta^{18}O$ may be produced by sedimentary carbonate contamination if an O-buffering silicate melt is present beside the carbonate melt (Demény et al., 1998). The contamination process may occur within the crust during the emplacement process or in the mantle by subduction-related source contamination. Since sedimentary carbonates are not frequent in the Kola Alkaline Province, the latter process provides a more plausible explanation. The subducted crustal material may have contaminated the pristine mantle either by direct assimilation of contaminated lithosphere or by a metasomatic influence of subduction-related CO_2 (Ray and Ramesh, 1999).

Apart from the Palaeozoic Caledonides, active continental margins existed in the Svecofennian and Sveconorvegian–Grenvillian blocks in Proterozoic times. Furthermore, an active continental margin was also developed between the Belomorian and Kola Province on one side and the Karelian Province on the other side during the Lopian orogeny (2.9–2.6 Ga; Gàal and Gorbatschev, 1987; Gorbatschev and Bogdanova, 1993).

Geological and geochemical data from the Lapland Granulite Belt, which includes Lapland and Umba terranes (Fig. 1), suggest that it commenced about 2.0 Ga during the change of the Tanaelv palaeorift into a basin with oceanic crust with subsequent subduction and collision (Balagansky et al., 1998). REE patterns and whole-rock geochemistry of igneous rocks from this belt suggest that these rocks belong to an island-arc formation. Subduction related material could have been incorporated into the mantle beneath the Kola during such collisional processes.

A further possibility is oxidation of mantle diamond (or graphite) followed by subsequent carbonate melt formation (Dunworth and Bell, 2001). From an isotopic fractionation point of view this process is theoretically viable, however, the existence of such a large amount of diamond required to produce the carbonatite melt is questionable. Interaction with ^{13}C-enriched seawater can also be excluded on the basis of primitive Sr isotope ratios.

The radiogenic isotope ratios provide further insight into the origin of mantle heterogeneity. Khibina and Vuoriyarvi again form end members (Fig. 6) falling on or close to the Kola Carbonatite Line [KCL "old"—Kramm, 1993 and KCL "new"—Dunworth and Bell, 2001], whereas Kovdor is a transitional complex. At least two mantle components are necessary to produce an array such as the KCL, an "EMI-like" component at the lower right end and a depleted, primitive "MORB-OIB-like" mantle component. On the basis of trace element and ^{3}He-data, the latter has been attributed to plume activity (Dunworth and Bell, 2001). The distribution shown in Fig. 6 indicates that the Khibina carbonatites and one Kovdor carbonatite are slightly displaced from the KCL toward the enriched "EMII-like" (Hofmann, 1997) component of Siilinjarvi carbonatites (Belyatsky et al., 2001), Amba Dongar (Simonetti et al., 1995) and Jacupiranga (Roden et al., 1985). This would represent a third mantle component needed in order to explain the $(^{143}Nd/^{144}Nd)_{370}$–$(^{87}Sr/^{86}Sr)_{370}$ data from Khibina and Vuoriyarvi.

A similar three-mantle component model for Kola carbonatites and alkaline rocks has been also developed by Rukhlov et al. (2001) in their study of Turiy Mys and Kandaguba carbonatites. Mixing of two isotopically distinct end members, depleted and enriched with a low $^{143}Nd/^{144}Nd$ ratio and a moderate $^{87}Sr/^{86}Sr$ ratio (ca. 0.705), has been used for an explanation of Sr–Nd data from the carbonatites. The third end member with a near chondritic or moderate $^{143}Nd/^{144}Nd$ ratio and a very high $^{87}Sr/^{86}Sr$ ratio (ca. 0.709) has been suggested on the basis of Sr–Nd data from Kandalaksha lamprophyres and melilitites of the Terskii Coast (Beard et al., 1996, 1998).

A fourth component characterised by low $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ ratios mentioned by Dunworth and Bell (2001) which is attributed to metasomatized lithospheric mantle beneath the Kola peninsula (Mahotkin et al., 2000) cannot be proven on the basis of our data.

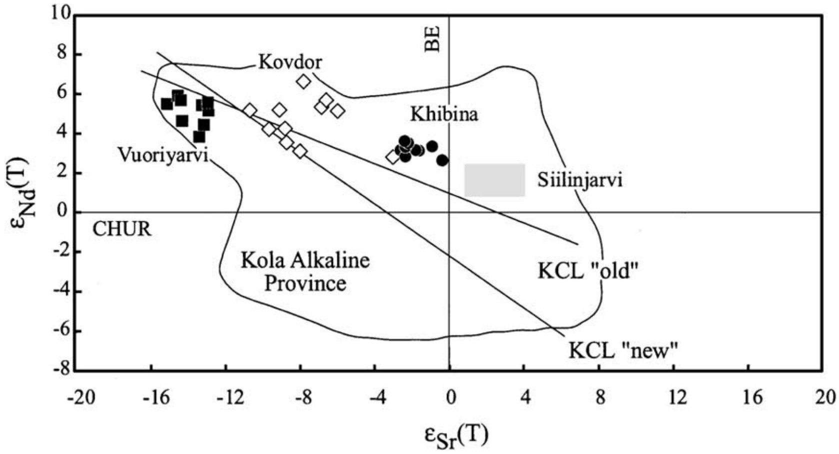

Fig. 6. Plot of εNd(T) vs. εSr(T) for the Kola alkaline–carbonatite complexes: Khibina carbonatites, this work, Zaitsev et al. (1997); Vuoriyarvi carbonatites, this work, Balaganskaya et al. (2001a); Kovdor phoscorites and carbonatites, Zaitsev and Bell (1995). Data for Kola Alkaline Province (silicate rocks, phoscorites and carbonatites) are from Kramm (1993), Kramm and Kogarko (1994), Verhulst et al. (2000), Balaganskaya et al. (2001b), Dunworth and Bell (2001). Kola Carbonatite Line (KCL) "old" is as defined by Kramm (1993) and KCL "new" is from Dunworth and Bell (2001). Siilinjarvi box is from Belyatsky et al. (2001). The parameters used for Nd are CHUR values, and those for Bulk Earth (BE) are: present day $^{87}Sr/^{86}Sr = 0.7045$, initial $^{87}Sr/^{86}Sr = 0.69898$, $^{87}Rb/^{86}Sr = 0.0827$, and the age of the Earth = 4.55 Ga.

Since the heterogeneity is also pronounced in the carbon isotope compositions, the Sr isotope ratios are plotted vs. $\delta^{13}C$ data in Fig. 7. The most striking feature is that the Khibina carbonatites with mantle-like $\delta^{13}C$ values have higher Sr isotope ratios than the Vuoriyarvi carbonatites that we have speculated contain crustal C. There are two possible explanations: (i) the enriched "EMII-like" component contains no crustal C and thus its addition to the mantle source has no effect on the carbon isotopic composition or (ii) the enriched "EMII-like" component contains organic-derived C that shifts the $\delta^{13}C$ range toward strongly negative values. We cannot make a distinction between the two models, however, the proximity of the primary compositions of the Khibina carbonatites and the presumed pristine mantle compositions of Keller and Hoefs (1995) would rather support the first model.

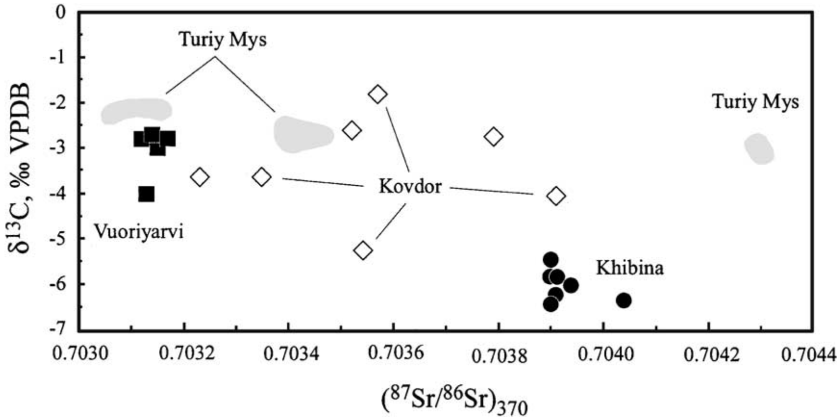

Fig. 7. Plot of $\delta^{13}C$(V-PDB) vs. $(^{87}Sr/^{86}Sr)_{370}$ for Kola phoscorites and carbonatites: Khibina, this work, Zaitsev (1996), Zaitsev et al. (1997); Vuoriyarvi, this work; Kovdor, Zaitsev and Bell (1995) and Turiy Mys, Dunworth and Bell (2001).

On the other hand, the Vuoriyarvi carbonatites have low Sr isotope ratios close to the depleted "MORB-OIB-like" component and high $\delta^{13}C$ ranges. The distribution may be explained by the CO_2 metasomatic process proposed for Deccan province carbonatites by Ray and Ramesh (1999). In this model high-$\delta^{13}C$ crustal material would be subducted to the mantle. The crustal carbon may be transported in the form of sedimentary carbonate or altered oceanic crust (Alt and Teagle, 1999). Sedimentary carbonate and dissolved carbon in seawater are thought to be characterized by close to present-day carbon isotope compositions in the last 3.5 Ga (Schidlowski, 2001), thus, subduction would have brought high-$\delta^{13}C$ material into the mantle well before the formation of Kola carbonatites. The carbonate material may survive metamorphic devolatilization during subduction (Kerrick and Connolly, 2001), and thus preserve the original carbon isotope signature (Rumble et al., 2000). CO_2 mobilization in the mantle has been modelled by Matsumoto et al. (2000), whose model also explains the decoupling of carbon from other trace elements that may carry a crustal signature. Thus, subducted and re-mobilized crustal carbon may have metasomatized mantle domains without causing changes in the trace element composition or radiogenic isotope ratios.

7. Conclusions

The observed C–O and Sr–Nd relationships in co-existing calcite/dolomite, burbankite/calcioburbankite and pseudomorphs from Khibina and Vuoriyarvi complexes lead to the following conclusions.

(1) Low and similar $\delta^{18}O$ values indicate the lack of late-stage, low-temperature hydrothermal processes in burbankite and calcioburbankite carbonatites at Khibina and Vuoriyarvi. The data are consistent with a pegmatitic origin for these types of carbonatites as has been suggested by Wall et al. (2001).

(2) The similarity in both C–O and Sr–Nd isotope compositions of co-existing calcite/dolomite and burbankite/calcioburbankite shows that REE mineralization and their host carbonatites in each complex are derived from the same source.

(3) The formation of pseudomorphs after burbankite/calcioburbankite is the result of interaction of these minerals with carbonatitic fluids, which had variable CO_2/H_2O ratios and probably also variable temperatures.

(4) The pseudomorph-forming fluid might well be derived from the same source as the original carbonatite, and represent the last hydro-carbothermal stage of the magmatic evolution. This is indicated by the rough similarity between the Sr–Nd isotopic signatures of the early REE-poor carbonatites and burbankite/calcioburbankite on one hand and pseudomorphs on the other hand. However, the slight variability of the pseudomorphs' Sr–Nd isotopic signatures is also indicative of fluid–rock exchange between the pseudomorph-forming fluid and alkali silicate rocks associated with the carbonatites.

(5) The substantial differences in C, Sr and Nd mineral isotopic compositions between Khibina and Vuoriyarvi REE-rich carbonatites indicate an origin from different mantle sources. Highly variable $\delta^{13}C$ values in Kola carbonatites coupled with low (within mantle range) and relatively constant $\delta^{18}O$ values may indicate the presence of a crustal component related to subduction source contamination. At least three, four in Dunworth and Bell (2001), mantle components are needed to produce the Sr–Nd isotopic variations observed in Kola carbonatites. $\delta^{13}C-{}^{87}Sr/{}^{86}Sr$ relationships indicate that the enriched "EMII-like" component responsible for radiogenic Sr isotope ratios did not contain crustal carbon, whereas the depleted "MORB-OIB-like" mantle component had a C isotope composition modified by crustal-derived CO_2 metasomatism. A third component needs to be "EMI-like".

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