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RHOMBOHEDRAL CARBONATES FROM CARBONATITES OF THE KHIBINA MASSIF, KOLA PENINSULA, RUSSIA

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ABSTRACT

The eastern part of the Khibina alkaline massif, Kola peninsula, Russia, is made up of ijolite, foyaite, olivine melanephelinite, melanephelinite, phonolite, alkali trachyte, and rocks of the carbonatite series. The latter can be divided into (1) biotite – aegirine – apatite rocks containing less than 50% carbonate, (2) early and (3) late carbonatites and (4) carbonate–zeolite veins. These rocks are distinguished by their relative ages and by their major and accessory minerals. The rock-forming minerals include rhombohedral carbonates of Ca, Mn, Fe and Mg: calcite, manganoan calcite, dolomite, ankerite, manganoan ankerite, ferroan kutnohorite, ferroan rhodochrosite, manganoan siderite and siderite. Petrographic and cathodoluminescence observations reveal two textural types of carbonates: primary and secondary (metasomatic). The Sr content is high in primary minerals, but low in those of metasomatic origin. Values of isotope ratios $\delta^{13}C$ in the range –7.8 to –2.8‰ (PDB) and $\delta^{18}O$ in the range +5.9 to +14.3‰ (SMOW) for the rhombohedral carbonates from the Khibina carbonatites and carbonate–zeolite veins are similar to those from carbonatites elsewhere. For most samples, there is a positive correlation between $\delta^{13}C$ and $\delta^{18}O$, which can be explained by Rayleigh and temperature fractionation. However, in one type of the late carbonatites and the carbonate–zeolite veins, carbonates show wide variations in their $\delta^{13}C$ and $\delta^{18}O$ values; this has been interpreted as loss of heavy C to a gas phase. Field relations, petrographic and cathodoluminescence observations suggest that formation of the late carbonatites and carbonate–zeolite veins is more likely to have been from a carbohydrothermal (fluid) system than from a melt.

Keywords: carbonatite, calcite, dolomite, ankerite, kutnohorite, rhodochrosite, siderite, isotope composition, Khibina massif, Russia.

SOMMAIRE

La partie orientale du massif alcalin de Khibina, dans la péninsule de Kola, en Russie, contient une association d'ijolite, de foyaïte, de mélanéphélinite à olivine, de mélanéphélinite, de phonolite, de trachyte alcaline et de roches carbonatitiques. Cette dernière suite se subdivise en (1) roches à biotite + aegyrine + apatite contenant moins de 50% de carbonate, (2) carbonatite précoce, (3) carbonatite tardive, et (4) veines à carbonate + zéolites. Ces roches se distinguent par leurs âges relatifs et leurs minéraux majeurs et accessoires. Parmi les minéraux majeurs, on trouve les carbonates rhomboédriques de Ca, Mn, Fe et Mg: calcite, calcite manganifère, dolomite, ankérite, ankérite manganifère, kutnohorite ferreuse, rhodochrosite ferreuse, sidérite manganifère et sidérite. Les observations pétrographiques et par cathodoluminescence révèlent deux types de textures, indicatives de cristallisation primaire et de remplacement, respectivement. La teneur en Sr est élevée dans les minéraux primaires, mais faible dans les carbonates secondaires. Les rapports isotopiques de C ($\delta^{13}C$ entre –7.8 et –2.8‰ par rapport à l'étalon PDB) et de O ($\delta^{18}O$ entre +5.9 et +14.3‰ par rapport à l'étalon SMOW) des carbonates rhomboédriques des carbonatites de Khibina et des veines à carbonate–zéolites ressemblent aux valeurs déterminées pour les carbonatites ailleurs. Dans la plupart des échantillons, il y a une corrélation positive entre $\delta^{13}C$ et $\delta^{18}O$, qui résulterait d'un fractionnement de Rayleigh et de sa dépendance sur la température. Toutefois, dans un faciès de carbonatite tardive et dans le cas des veines à carbonate + zéolites, les carbonates varient beaucoup dans leurs rapports $\delta^{13}C$ et $\delta^{18}O$, variations qui ont été interprétées en invoquant une perte de C lourd par dégazage. D'après les relations de terrain, l'évidence pétrographique et les observations par cathodoluminescence, les carbonatites tardives et les veines à carbonates + zéolites se seraient formées à partir d'une phase fluide riche en gaz carbonique et en eau plutôt qu'à partir d'un magma.

(Traduit par la Rédaction)

Mots-clés: carbonatite, calcite, dolomite, ankérite, kutnohorite, rhodochrosite, sidérite, composition isotopique, massif de Khibina, Russie.

INTRODUCTION

The Kola alkaline province of Russia contains twenty-four alkaline complexes that range in age from 380 to 360 Ma (Kramm *et al.* 1993). The Khibina massif, 364.5 ± 4.0 Ma (Kogarko *et al.* 1981), located in the central part of the Kola peninsula (67°48′N, 33°48′E), is one of the best known and most interesting alkaline–carbonatite complexes. It is a composite pluton (Fig. 1A), elliptical in shape and concentrically zoned, consisting of various ultrabasic and alkaline silicate rocks and carbonatites. On the basis of field relationships, petrography and mineralogy, four principal groups of silicate rock-types are distinguished (Kostyleva-Labuntsova *et al.* 1978): ultramafic rocks (peridotite, pyroxenite), nepheline syenites (khibinite, foyaite, rischorrite), foidolites (urtite, ijolite, melteigite), and apatite–nepheline rocks. Numerous dykes of essexite, theralite, teschenite, olivine melanephelinite, melanephelinite, nephelinite, camptonite, phonolite and alkali trachyte cut the complex (Arzamastsev *et al.* 1988). The massif is surrounded by a metasomatic aureole of fenite and hornfels.

The carbonatites of the Khibina were discovered in 1969 during exploration drilling within the eastern part of the massif (Fig. 1A), where they are covered by alluvium 20 to 90 m thick. The carbonatites have been described by Minakov & Dudkin (1974), Minakov *et al.* (1981) and Dudkin *et al.* (1984).

In this study, I present new geological, mineralogical and C and O isotopic data concerning carbonatites and associated silicate rocks. The samples investigated were collected from drill core; the location of the drill holes is shown in Figure 1B.

GENERAL GEOLOGY

The geological relationships in the eastern part of the Khibina massif are complex (Dudkin *et al.* 1984, Zaitsev 1992). Strong tectonism has produced widespread brecciation and faulting. Reactions between silicate wallrocks and aqueous CO_2-bearing fluid have resulted in the formation of various metasomatic rocks (fenites), consisting mainly of albite, biotite and calcite. The unaltered silicate rocks are represented by ijolite, foyaite, olivine melanephelinite, melanephelinite, phonolite and alkali trachyte (from oldest to youngest).

Silicate rocks

The ijolite is a fine-grained porphyritic rock occurring as xenoliths (5 cm – 20 m) in foyaite. It consists of aegirine-augite and nepheline with trace amounts of titanite, microcline, cancrinite and apatite. The mineralogical and chemical compositions of ijolite, as well as the chemical composition of nepheline, are similar to those in other examples of ijolite at Khibina. The clinopyroxene from ijolite from the eastern part of the massif contains more Mn, and less Ti and Al than that in ijolite elsewhere in the complex (Kostyleva-Labuntsova *et al.* 1978, Zaitsev *et al.* 1990).

Foyaite is the dominant silicate rock in the area studied. It is medium grained and has a massive or trachytic texture, and consists of alkali feldspar, nepheline, arfvedsonite and aegirine, with a variable amount of biotite. Accessory minerals include titanite, apatite, ilmenite, eudialite and astrophyllite. Mineralogical and whole-rock chemical data for

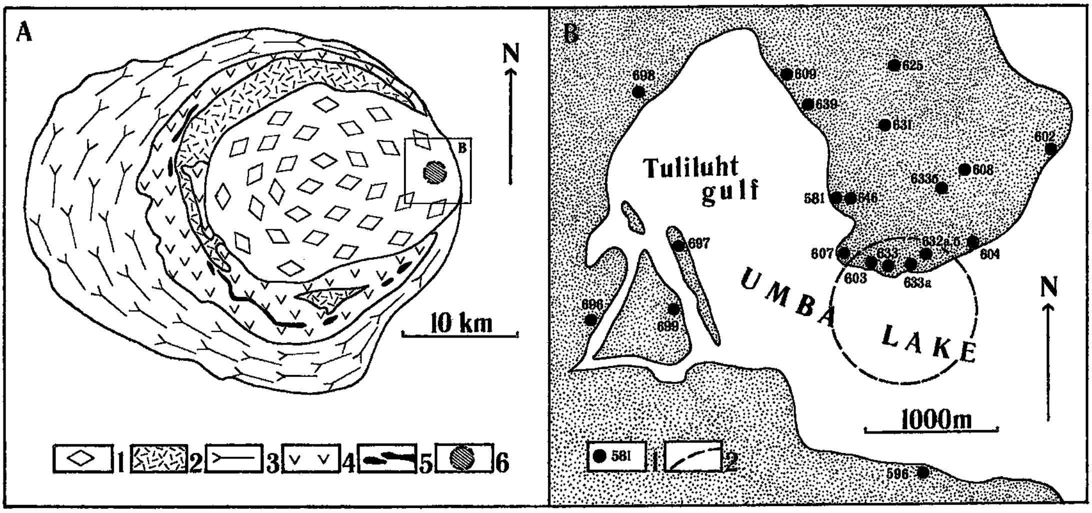

FIG. 1. Simplified geological map of the Khibina alkaline massif (A) and drill-hole localities in the area studied (B). Symbols in A: 1 foyaite, 2 nepheline syenite, 3 khibinite, 4 urtite, ijolite, melteigite and rischorrite, 5 apatite–nepheline rocks, 6 location of carbonatites; in B: 1 number and location of drill holes, 2 area of greatest development of carbonatite.

foyaite from the eastern part of the massif are similar to those for foyaite from elsewhere in the Khibina massif.

Olivine melanephelinite, melanephelinite, phonolite and alkali trachyte occur as dykes from 10 cm to 10 m wide. A stock-like body of phonolite, 150–200 m across, has also been documented in this area (Dudkin *et al.* 1984). The geochemistry and mineralogy of silicate dykes of the Khibina massif were discussed by Arzamastsev *et al.* (1988).

The carbonatite series

Ijolite, foyaite and all silicate dyke-rocks are cut by various carbonate-bearing rocks, which have been assigned to a carbonatite series. According to Bulakh & Ivanikov (1984), rocks of the carbonatite series include phoscorite, carbonatite, late quartz–carbonate veins and various alkali–silicate metasomatic rocks surrounding carbonatite. Rocks belonging to the carbonatite series were formed at approximately the same time, have similar mineral associations, and invariably occur in the same order of emplacement.

At least eight mineralogical types of carbonate-bearing rocks have been identified at Khibina, on the basis of relative ages and their major and accessory minerals (Zaitsev & Pavlov 1988, Zaitsev 1992). The rocks are classified into biotite – aegirine – apatite rocks containing less than 50% carbonate, various carbonatites and carbonate–zeolite veins. Relative ages of these rocks, established by cross-cutting relationships, are given in Table 1. Rocks of stage I and II are regarded as magmatic, and rocks of stage III and IV are considered of carbohydrothermal–metasomatic origin.

TABLE 1. SEQUENCE OF FORMATION OF ROCKS OF THE KHIBINA CARBONATITE SERIES*

Stage	Type of rock	Symbol
I phoscorite	biotite-aegirine-apatite	BAA
II early carbonatites	calcite-biotite-aegirine-apatite	C I
III late carbonatites	calcite with burbankite	C II-1
	manganoan ankerite-calcite with synchysite-(Ce)	C II-2
	ferroan rhodochrosite-manganoan ankerite with synchysite-(Ce)	C II-3
IV carbonate-zeolite veins	manganoan siderite-manganoan ankerite-natrolite	CZ III-1
	manganoan siderite-nordstrandite-natrolite	CZ III-2
	natrolite-manganoan siderite-dawsonite	CZ III-3

* after Zaitsev & Pavlov (1988) and Zaitsev (1992)

Both the biotite – aegirine – apatite rocks (BAA rocks) and calcite – biotite – aegirine – apatite carbonatite (C I) occur mainly at a depth of 1700 m, and they represent approximately 5% by volume of the carbonatite series. BAA rocks form veins in silicate rocks, with thicknesses from 0.5 to 2.0 m, but more often occur as relics (1 cm to 30 cm in size) in the carbonatites. The BAA rocks are fine grained and homogeneous where they contain less than 5% carbonate, and are medium to coarse grained and heterogeneous where more than 5–10% carbonate is present. Petrographic observations show the presence of at least two paragenetic mineral associations. The first association includes apatite, aegirine, pyrrhotite and pyrochlore, and seems to be primary. The second association is represented by biotite and pyrite, which replace aegirine and pyrrhotite, respectively. In comparison to the field relationships and mineralogy of other carbonatite complexes within the Kola peninsula, the BAA rocks are interpreted to be belong to the phoscorites (Zaitsev 1992), as suggested by their association with carbonatites, their relative age and mineral chemistry. In contrast to typical phoscorite (*e.g.*, from Kovdor, Vuorijarvi), the BAA rocks, like the carbonatites from Khibina, do not contain olivine or magnetite. Olivine-poor but aegirine- and biotite-rich phoscorite with minor amounts of magnetite has been described from the Seblyavr massif, Kola peninsula by Lapin (1979), and Bulakh & Ivanikov (1984) have shown that the mineral composition of phoscorite is correlated with the mineralogy of the principal silicate rocks in the ultrabasic–alkaline massif. Olivine-poor, pyroxene–amphibole- and mica-rich varieties of phoscorite occur in alkaline massifs containing mainly foidolite, and olivine-rich phoscorite occurs in alkaline massifs containing dunite.

Calcite – biotite – aegirine – apatite carbonatites (C I) occur as veins 0.1 to 4.0 m wide. They are medium to coarse grained, heterogeneous and contain minor amounts of pyrrhotite, pyrite with trace amounts of ilmenite, magnetite, pyrochlore and chalcopyrite. Banding parallel to the walls of the carbonatite veins is rarely observed. Locally, the carbonatites contain xenoliths of the wallrocks: foyaite, foyaite pegmatite, melanephelinite and alkali trachyte. These xenoliths seem unaltered, angular, and have sharp contacts with the surrounding carbonatite. Contacts between carbonatites and the silicate wallrocks are sharp. In contrast, there is a gradual transition from the BAA rocks to the C I carbonatites. This transition is expressed as increasing contents of apatite, aegirine and biotite in the carbonatites. Field relations, petrographic observations and mineral chemistry show that all non-carbonate minerals were incorporated into the carbonatites from the BAA rocks (Zaitsev 1992). Relative age, mineralogy and geochemistry of the C I carbonatites (abundances of major and trace elements) indicate that they belong to the category of “early

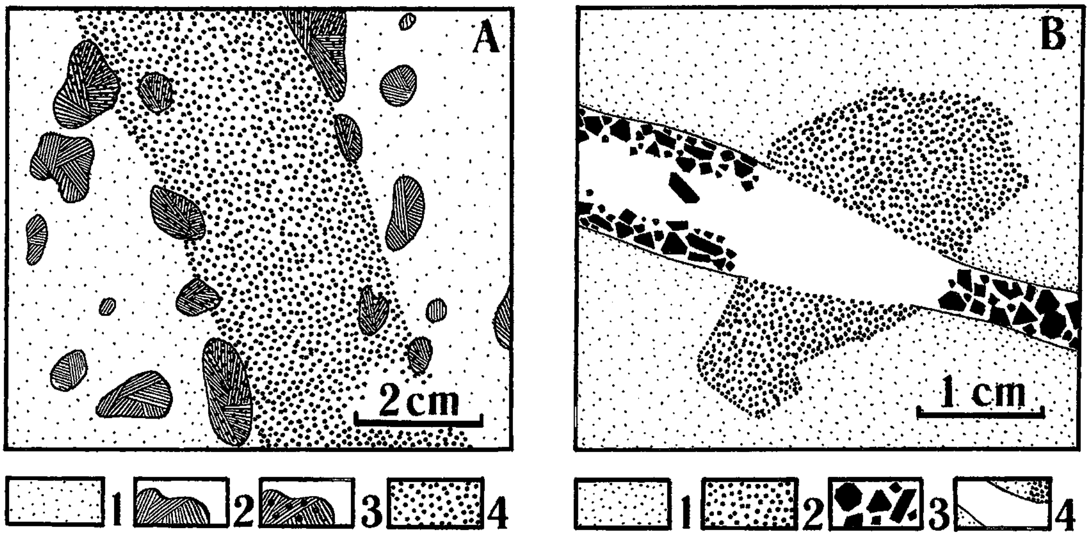

FIG. 2. Relations between the late carbonatites and the carbonate – zeolite vein. A. "Undisturbed" relics at the vein contact between late calcite and manganoan ankerite carbonatites with synchysite-(Ce); 1 calcite, 2 yellow synchysite-(Ce) + strontianite + barite + calcite, 3 red synchysite-(Ce) + strontianite + barite + manganoan ankerite + relics of calcite, 4 manganoan ankerite + relics of calcite; red color of synchysite-(Ce) is due to of small inclusions of Fe phase. B. Changes in mineral composition of the carbonate–zeolite vein cutting late carbonatite; 1 manganoan ankerite, 2 orthoclase, 3 manganoan siderite + magnetite (black), 4 natrolite + relics of orthoclase.

carbonatites" (Kapustin 1980) or to sövite (calciocarbonatite) (Woolley & Kempe 1989).

Carbonatites containing Ba–Sr–*REE*-bearing minerals (C II) make up about 90% by volume of the carbonatite series in the Khibina massif. Three different types of the C II carbonatites were selected for study on the basis of cross-cutting relations and mineralogy (Table 1). They occur as veins 1 cm to 6 m wide, and are medium to coarse grained and heterogeneous. The contacts between C II carbonatite and wallrocks may be gradational or sharp. Where gradational, the transition to the wallrocks is characterized by a high content of extremely altered (metasomatized) relics of ijolite, foyaite, melanephelinite and alkali trachyte, into which carbonate has been introduced along fractures and grain boundaries. The carbonatite veins that have sharp contacts with the wallrocks are characterized by crustification (vein-filling) and contain druses. In the case of wallrocks surrounding the carbonatites with Ba–Sr–*REE* mineralization, a high content of carbonate, albite, biotite and fluorite is typical. Field and microscope observations in some instances show "undisturbed" relics at the vein contacts between late carbonatites. Figure 2A shows manganoan ankerite carbonatite that cuts calcite carbonatite. Petrographic observations reveal that calcite is replaced by manganoan ankerite, and synchysite-(Ce) – strontianite – barite intergrowths from calcite carbonatite are preserved near the contact within manganoan ankerite carbonatite. This feature gives evidence of the metasomatic character of the latter (Krasnova 1988).

The field relations and mineralogy of the carbonatites containing Ba–Sr–*REE* minerals (C II) are interpreted to suggest that they are "late carbonatites" (Kapustin 1980) or *REE* carbonatites (Pecora 1956). According to the chemical classification of carbonatites proposed by Woolley & Kempe (1989), the carbonatites of this group can be subdivided into calciocarbonatite and ferrocarbonatite (A.N. Zaitsev & M.J. Le Bas, unpubl. data). Some samples of ferrocarbonatite, however, contain more Mn than Fe (*e.g.*, 11.37 wt.% MnO *versus* 8.09 wt.% FeO_{total} and 3.72 wt.% MgO, 24.59 wt.% CaO), and they can be classified as manganocarbonatite with CaO/(CaO + MgO + FeO + Fe_2O_3 + MnO) less than 0.8, MgO < (FeO + Fe_2O_3 + MnO) and MnO > (FeO + Fe_2O_3).

Carbonate–zeolite veins (CZ III), the youngest carbonate rocks in the Khibina massif (Zaitsev & Pavlov 1988), are rarely more than 20 cm across, and are medium to coarse grained and heterogeneous. Three types of carbonate–zeolite veins were distinguished according to their cross-cutting relations and mineralogy (Table 1). The veins are discordant to silicate wallrocks and are characterized by crustification (vein-filling) and commonly contain numerous druses. Where the carbonate–zeolite veins cut carbonatite, they may show significant changes in their mineral composition, so as to reflect the surrounding carbonatite (Fig. 2B). This feature indicates metasomatic formation of such carbonate–zeolite veins (Krasnova 1988).

MINERALOGY OF RHOMBOHEDRAL CARBONATES

Analytical methods

Identification of the carbonates was based on staining, optical examination, infrared spectroscopy (UR–20 Carl Zeiss spectrophotometer), X-ray diffraction (RKU camera, 57.3 mm in diameter and Fe$K\alpha_1$ radiation, and 114.6 mm in diameter and Cr$K\alpha_1$ radiation), scanning electron microscopy investigations (SEM, Hitachi S–430), cathodoluminescence (Technosyn cold cathode Luminescence, model 8200 Mark II), and electron-microprobe analysis. Both energy- and wavelength-dispersion analyses of carbonates were made using a JEOL JXA–8600S electron microprobe (Leicester University), a Cambridge Microscan (MK 5) electron microprobe (Carleton University), and a Cameca MS–46 electron microprobe (Geological Institute, Apatity, Russia). Acceleration voltages of 15 or 20 kV and beam currents of 20 or 25 nA were used for analyses. The following standards were used: natural dolomite (Ca, Mg), diopside (Ca), wollastonite (Ca), pyrope (Mg), siderite (Fe), ilmenite (Fe), rhodochrosite (Mn), celestite (Sr) and synthetic phases MgO (Mg), Fe (Fe), SrF_2 (Sr), LaF_3 (La) and CeF_3 (Ce). CO_2 was calculated by stoichiometry based on one atom of C for calcite, siderite and rhodochrosite, and two atoms of C for dolomite, ankerite and kutnohorite per formula unit.

Calcite

Calcite, the dominant carbonate in the early carbonatites (C I) and two types of late carbonatite (C II–1 and C II–2), occurs as white subhedral or anhedral grains, 0.5 mm to 12 mm in size. Calcite crystals are usually twinned, and they have nearly straight crystal boundaries and almost 120° triple junctions. Calcite shows an orange-red cathodoluminescence (CL) activated by Mn^{2+} (Marshall 1988). Rarely, in early carbonatites (C I) and late carbonatites with burbankite (C II–1), internal zones of calcite can be observed (Fig. 3). This zoning is similar to that observed in calcite phenocrysts from the Kerimasi and Kaiserstuhl carbonatites (Mariano & Roeder 1983, Keller 1989).

Electron-microprobe analyses show that the calcite of the Khibina carbonatites is characterized by wide variations in its trace-element content. Selected compositions are given in Table 2, and results are plotted on Figures 4 and 5. Calcite in the C I and C II carbonatites has a low Mg content. The difference in its chemical composition in various types of carbonatite is mainly in the content of Mn, Fe and Sr. Early calcite in the C I carbonatites has a low Mn and Fe content, but it is rich in Sr. Late calcite in the C II carbonatites is characterized by similar content of Fe and much more Mn than the early calcite. Sr is enriched in the

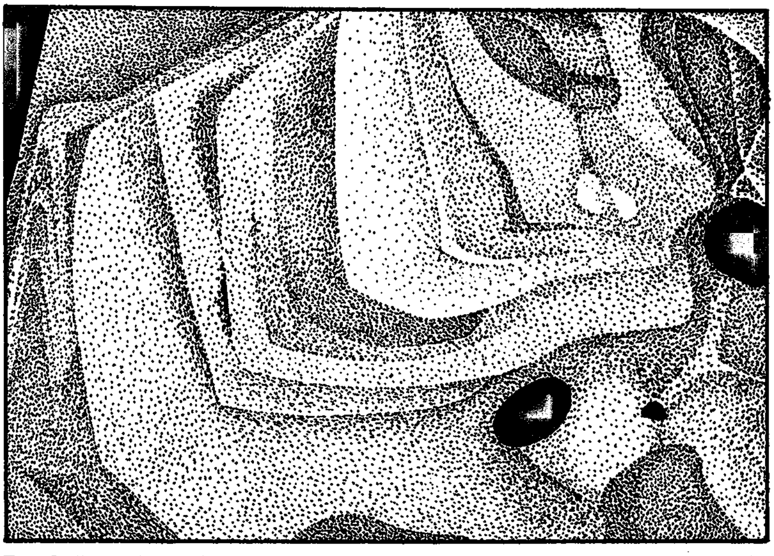

FIG. 3. Internal zonation of calcite crystal under cathodoluminescence. Late calcite carbonatite with burbankite (black), C II–1. Width of image is 2 mm. Drawn from color slide.

TABLE 2. RESULTS OF SELECTED ANALYSES OF CALCITE AND MANGANOAN CALCITE

Rock symbol	C I	C I	C I	C II-1	C II-1	C II-1	C II-2	C II-2	C II-2
Sample #	632B	632B	632B	608	646	607	603	603	633A
	1984.0	1963.0	1847.0	97.0	451.0	281.5	36.3	165.5	253.0
CaO wt.%	52.74	53.29	51.57	52.42	51.54	47.64	53.34	54.90	53.70
MgO	0.35	0.48	0.25	0.21	0.21	0.25	0.06	0.04	bd
MnO	0.45	0.38	0.67	1.94	3.37	5.69	2.99	1.31	1.58
FeO*	1.12	0.60	0.96	0.64	1.07	1.75	0.55	0.19	0.40
SrO	1.49	1.51	1.71	1.56	1.11	0.92	0.13	0.47	bd
La_2O_3	nd	0.06	nd	nd	0.15	nd	0.06	nd	nd
Ce_2O_3	nd	0.12	nd	nd	0.07	nd	bd	nd	nd
CO_2	43.39	43.68	42.81	43.63	44.01	42.66	44.20	44.27	43.37
Total	99.54	100.12	98.41	100.40	101.53	98.91	101.33	101.18	99.05

FeO* - total Fe calculated as FeO; nd - not determined; bd - below detection

late calcite from carbonatite type C II–1; the range of Sr contents overlaps with data for the early calcite, but the level of Sr is very low in carbonatite type C II–1.

Manganoan calcite

Manganoan calcite, with more than 4.0 wt.% MnO, occurs in carbonatite as pink subhedral or anhedral grains that range in size from 0.2 to 3.0 mm. Two distinct textural types of the mineral were distinguished. The first is found only in the late C II–1 carbonatite. Here, manganoan calcite occurs as subhedral crystals, 1–3 mm wide. Cathodoluminescence observations reveal internal zonation of the crystals, which are similar to those of calcite. The second textural type forms vein-like, fine-grained aggregates that occur along fractures and calcite boundaries in the early C I carbonatites and late C II–1 and C II–2 carbonatites. Here, calcite and manganoan calcite are easily distinguished one from another by cathodoluminescence color (orange-red for calcite and deep red for manganoan calcite). CL observations show that calcite is replaced by manganoan calcite. This feature is evidence for the late secondary origin of the second type of manganoan calcite.

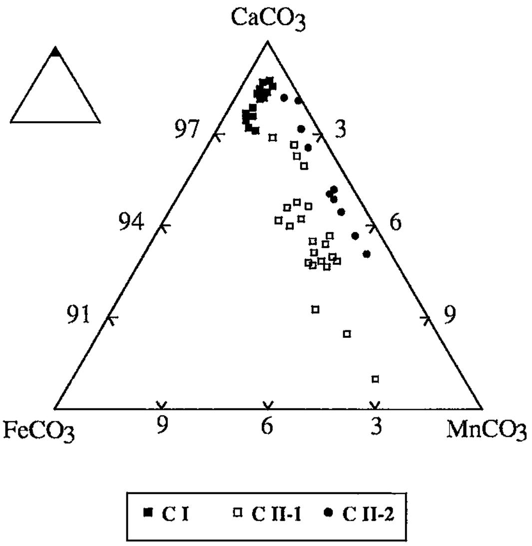

FIG. 4. Composition (mol.%) of calcite and manganoan calcite in the system $CaCO_3$ – $FeCO_3$ – $MnCO_3$. Symbols: C I early carbonatite, C II–1 late calcite carbonatite with burbankite, C II–2 late manganoan ankerite – calcite carbonatite with synchysite-(Ce).

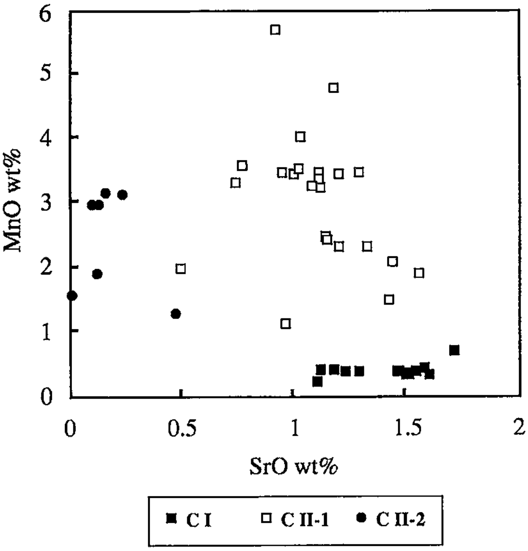

FIG. 5. Composition of the calcite and manganoan calcite in terms of SrO *versus* MnO. Symbols: see Fig. 4.

Manganoan calcites of the first and second textural types are also distinguished by their Sr content. High Sr is typical of the first type of manganoan calcite (range 0.86–1.19 wt.% SrO), whereas low Sr content was determined for the second textural type (range 0.35–0.49 wt.% SrO). Selected compositions of the first type are given in Table 2 and shown on Figures 4 and 5.

Dolomite

Dolomite was found in only one vein of late C II–3 carbonatite. This vein contains ferroan kutnohorite, manganoan ankerite and ferroan rhodochrosite as major carbonate phases. Dolomite occurs as xenoliths

TABLE 3. RESULTS OF SELECTED ANALYSES OF DOLOMITE, ANKERITE, MANGANOAN ANKERITE AND FERROAN KUTNOHORITE

Rock symbol		C II-3	C II-3	BAA	C II-1	C II-2	C II-2	C II-3	C II-3	C II-3
Sample #		604	604	632B	604	603	603	608	604	604
		413.0	413.0	1953.0	113.2	225.2	36.3	213.2	413.5	413.0
		C	R							
CaO	wt.%	27.34	27.88	28.41	28.74	28.05	27.65	26.51	24.60	27.01
MgO		20.66	20.55	11.89	5.87	4.19	4.39	2.58	2.68	0.97
MnO		1.17	0.82	1.85	8.41	8.10	13.10	17.47	20.10	21.52
FeO*		0.39	0.39	11.99	12.99	17.86	11.69	11.38	10.28	8.11
SrO		3.88	2.32	0.52	0.41	0.06	0.24	nd	0.09	0.12
La_2O_3		bd	0.15	bd	nd	nd	bd	nd	0.14	0.10
Ce_2O_3		bd	bd	bd	nd	nd	0.12	nd	bd	bd
CO_2		46.63	46.12	44.00	42.27	42.67	41.84	41.44	41.10	40.66
Total		99.93	98.19	98.66	98.69	101.11	98.85	99.38	98.99	98.49

FeO*-total Fe calculated as FeO; nd-not determined; bd-below detection; C-core, R-rim

(or relics?) that range in diameter from 5 to 15 mm, and consist of white subhedral grains (0.5–2.0 mm).

Electron-microprobe analyses reveal that the dolomite is zoned, with Sr content decreasing, from core to rim, from 3.88 wt.% to 2.32 wt.% SrO. These values are unusually high. Buckley & Woolley (1990) reported Sr concentrations in dolomite–ankerite from Lueshe, Newania, Kangankunde and Chipman Lake complexes ranging from 0.38 wt.% to 0.80 wt.% SrO; dolomite from the Meech Lake carbonatites, Quebec contains 0.9 to 1.1 wt.% SrO (D. Hogarth, pers. comm., 1993). Compositions of dolomite are given in Table 3, and the results are plotted in terms of $CaMg(CO_3)_2 - CaFe(CO_3)_2 - CaMn(CO_3)_2$ in Figure 6.

Ankerite

Ankerite was found only in a thin (5 mm) vein cutting the BAA rock. It occurs as white or grey subhedral grains, 0.5–1.5 mm in diameter. A composition is given in Table 3, and the results are presented in Figure 6. The $CaFe(CO_3)_2$ component ranges from 31 to 46 mol.%, with only small amounts of Mn (1.03–2.05 wt.% MnO). The Sr content is 0.42–0.82 wt.% SrO.

Manganoan ankerite

Manganoan ankerite occurs variously in major, accessory or trace amounts in all types of the late carbonatites (C II) and carbonate–zeolite veins (CZ III), and forms white or grey, subhedral or

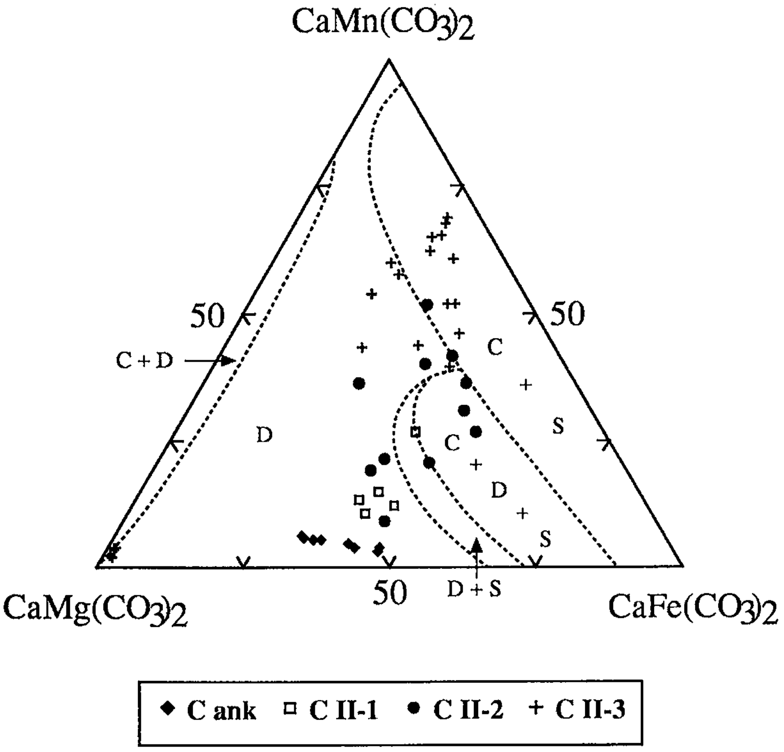

FIG. 6. Composition (mol.%) of dolomite – ankerite – manganoan ankerite – ferroan kutnohorite in the system $CaMn(CO_3)_2 - CaMg(CO_3)_2 - CaFe(CO_3)_2$. Symbols: C ank ankerite carbonatite, C II–1 calcite carbonatite with burbankite, C II–2 manganoan ankerite – calcite carbonatite with synchysite-(Ce), C II–3 ferroan rhodochrosite – manganoan ankerite carbonatite with synchysite-(Ce). Symbols of the fields: D: dolomite solid-solution, C: Ca-rich solid-solution, S: Ca-poor solid-solution. T = 450°C, P_{total} in the range 2.1–2.6 kbars (Rosenberg 1968).

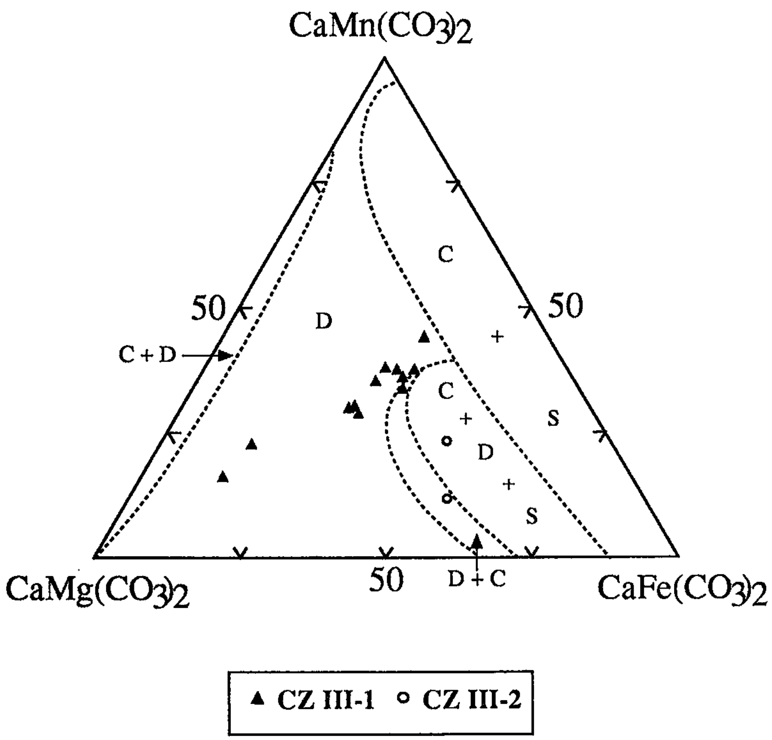

FIG. 7. Composition (mol.%) of manganoan ankerite in the system $CaMn(CO_3)_2$ – $CaMg(CO_3)_2$ – $CaFe(CO_3)_2$. Symbols: CZ III–1 manganoan siderite – manganoan ankerite – natrolite veins, CZ III–2 manganoan siderite – nordstrandite – natrolite veins. Symbols of the fields are defined in Fig. 6.

anhedral grains, 0.05–5.0 mm in diameter. Petrographic observations reveal two distinct textural types. In the first, the mineral forms subhedral crystals (1–5 mm) coexisting variously with either calcite or ferroan rhodochrosite or manganoan siderite; this textural type was found in the late carbonatites (C II) and carbonate–zeolite veins (CZ III–1). Contacts between the manganoan ankerite and associated carbonates are sharp, with no evidence of replacement, and the manganoan ankerite seems to be a primary phase. In the second textural type, which was found in the late carbonatites (C II–2 and C II–3) and carbonate-zeolite veins (CZ III–1 and CZ III–2), manganoan ankerite is represented by vein-like aggregates of anhedral grains, 0.05–1 mm in diameter, developed along grain boundaries of calcite, ferroan rhodochrosite or manganoan siderite, and cleavage cracks within these minerals. The typical feature of the manganoan ankerite of the second textural type is a fan-shaped or wavy extinction. These observations show that the manganoan ankerite of the second textural type is a late-stage secondary mineral.

Selected compositions of manganoan ankerite from both late C II carbonatite and CZ III carbonate–zeolite veins are given in Table 3 and shown on Figures 6 and 7. The mineral from the late carbonatites defines a continuous series from low-manganese ankerite (calcite carbonatite with burbankite), through manganoan ankerite [manganoan ankerite – calcite carbonatite with synchysite-(Ce)] to ferroan kutnohorite, which occurs in some veins of manganoan ankerite – ferroan rhodochrosite carbonatite with synchysite-(Ce) (Fig. 6). The chemical composition of the manganoan ankerite from the CZ III–1 and CZ III–2 carbonate–zeolite veins is similar to that of the manganoan ankerite from the late C II–2 carbonatite. Sr is abundant in the manganoan ankerite of the first textural type from both the late carbonatite and carbonate–zeolite veins (average 0.37 wt.% SrO, range 0.18–0.41 wt.%), but Sr is low in the second textural type (average 0.07 wt.% SrO, range "below detection" –0.12 wt.%). Manganoan ankerite of the second textural type also has a high content of $CaFe(CO_3)_2$ relative to that of the first textural type.

Ferroan kutnohorite

Ferroan kutnohorite is the major carbonate phase in some veins of late C II–3 manganoan ankerite – ferroan rhodochrosite carbonatite with synchysite-(Ce). It forms white or grey aggregates of fine needles or, less commonly, banded aggregates with fan-shaped or wavy extinction. Petrographic observations show that ferroan kutnohorite replaces both manganoan ankerite and ferroan rhodochrosite, and is secondary.

Selected electron-microprobe data are given in Table 3, and the results are plotted in Figure 6. The maximum content of $CaMn(CO_3)_2$ component is 69 mol.%. The average amount of Sr in ferroan kutnohorite is 0.10 wt.% SrO.

Ferroan rhodochrosite and manganoan siderite

Ferroan rhodochrosite and manganoan siderite are the dominant carbonates in one late carbonatite (C II–3) and in all carbonate–zeolite veins (CZ III), respectively. These carbonates take the form of brown or grey anhedral or subhedral grains ranging in size from 0.1 to 10 mm. Two distinct textural types may be distinguished. In the first, ferroan rhodochrosite (in the C II–3 carbonatites) and manganoan siderite (in the CZ III–1 carbonate–zeolite veins) form subhedral crystals (up to 10 mm in size) and have sharp contacts with manganoan ankerite, without evidence of replacement between the two. In the second textural type, manganoan siderite occurs as anhedral, small grains (0.1–2.0 mm) with wavy extinction.

The analytical data (Table 4) show that there is a large compositional range of rhodochrosite – siderite solid solution. The $FeCO_3$ content gradually increases from 37.5 mol.% in late carbonatite to 68 mol.% in carbonate–zeolite veins (Fig. 8). The ferroan rhodochrosite and manganoan siderite of the first textural type (primary) contain more Sr (average 0.19 wt.% SrO, range 0.12–0.29 wt.%) than those of the second textural type (secondary) (average 0.05 wt.% SrO, range "below detection" –0.07 wt.%).

TABLE 4. RESULTS OF SELECTED ANALYSES OF FERROAN RHODOCHROSITE-MANGANOAN SIDERITE AND SIDERITE

Rock index		C II-3	C II-3	C II-3	CZ III-1	CZ III-3
Sample		604	604	603	607	608
		413.0	417.0	238.0	75.0	253.0
CaO	wt.%	1.39	1.08	0.24	1.47	0.44
MgO		1.74	1.83	3.58	2.64	0.15
MnO		34.00	32.07	28.01	18.41	1.29
FeO*		23.07	24.69	28.80	37.59	60.21
SrO		0.06	0.22	nd	0.06	0.02
La_2O_3		0.10	nd	nd	bd	nd
Ce_2O_3		bd	nd	nd	bd	nd
CO_2		38.27	37.95	39.12	38.50	38.22
Total		98.63	97.84	99.75	98.68	100.33

FeO* - total Fe calculated as FeO; nd - not determined; bd - below detection

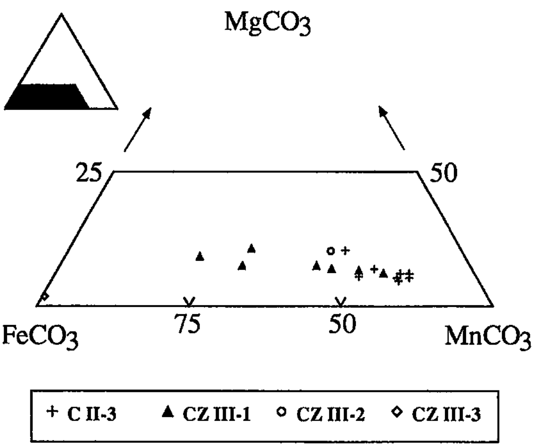

FIG. 8. Composition (mol.%) of ferroan rhodochrosite – manganoan siderite – siderite in the system $MgCO_3$ – $FeCO_3$ – $MnCO_3$. Symbols: C II–3 ferroan rhodochrosite – manganoan ankerite carbonatite with synchysite-(Ce), CZ III–1 manganoan siderite – manganoan ankerite – natrolite veins, CZ III–2 manganoan siderite – nordstrandite – natrolite veins, CZ III–3 natrolite – manganoan siderite – dawsonite veins.

Siderite

Siderite was found in the natrolite – manganoan siderite – dawsonite veins (CZ III–3) only and is present in minor to accessory amounts. It forms either as white or grey subhedral grains (0.5–2.0 mm) or as rhombohedral crystals in vein cavities. The composition (Table 4, Fig. 8) shows limited substitution of Mn for Fe.

CARBON AND OXYGEN ISOTOPE COMPOSITION

Isotopic analyses of C and O were made at the Institute of Geochemistry and Geophysics, Minsk. Measurements were performed on a MI–1201 B mass spectrometer with sample "100–K" (Kiev) as the laboratory standard. The "100–K" standard was calibrated to the PDB and SMOW scales ($\delta^{13}C$ = –0.9‰ PDB and $\delta^{18}O$ = +20.3‰ SMOW). The uncertainty is considered to be ±0.2–0.3‰. The carbon and oxygen isotope data are shown in Figure 9 and Table 5.

In general, the isotope ratios of C ($\delta^{13}C$ in the range –7.8 to –2.8‰ PDB) and O ($\delta^{18}O$ in the range +5.9 to +14.3‰ SMOW) for the rhombohedral carbonates from the Khibina carbonatites and carbonate–zeolite

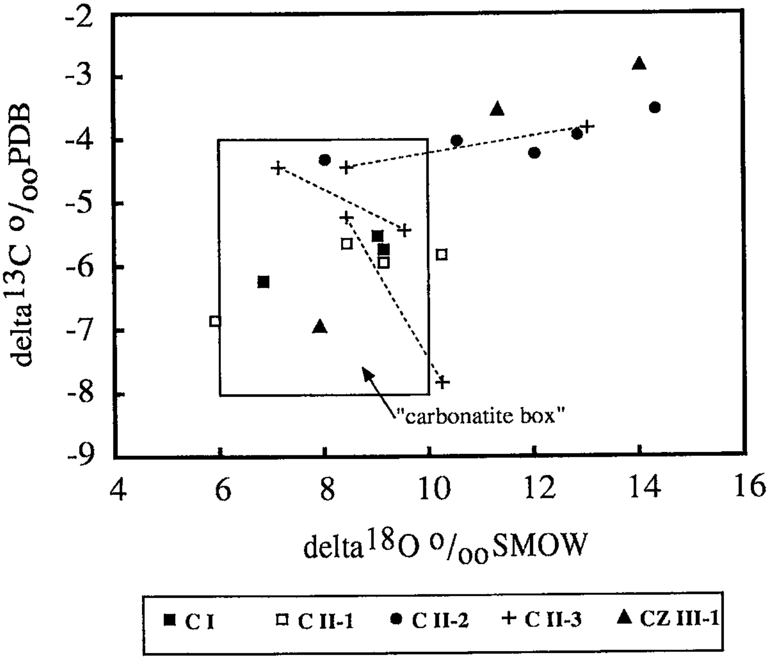

FIG. 9. Carbon and oxygen isotopic composition of the carbonates in the Khibina carbonatites. Symbols: C I early calcite carbonatite, C II–1 late calcite carbonatite with burbankite, C II–2 late manganoan ankerite – calcite carbonatite with synchysite-(Ce), C II–3 late ferroan rhodochrosite – manganoan ankerite carbonatite with synchysite-(Ce), CZ III–1 manganoan siderite – manganoan ankerite – natrolite veins. Field of "carbonatite box" is after Taylor *et al.* (1967), Sheppard & Dawson (1973) and Hoefs (1987). Dotted lines join coexisting carbonates.

veins are similar to carbonatites from many other localities (Deines 1989). Data for fifteen carbonate samples ($\delta^{13}C$ in the range –7.8 to –4.0‰ PDB and $\delta^{18}O$ in the range +5.9 to +10.2‰ SMOW) plot within or near the "carbonatite box" of primary, high-temperature carbonatite according to Taylor *et al.* (1967), Sheppard & Dawson (1973) and Hoefs (1987). Data for five carbonate samples show slight enrichment in ^{13}C ($\delta^{13}C$ in the range –4.2 to –2.8‰ PDB) and ^{18}O ($\delta^{18}O$ in the range +12.0 to +14.3‰ SMOW), as shown in Figure 9.

On the basis of isotope ratios of C and O in various carbonates, the early C I carbonatites, late C II carbonatites and CZ III carbonate–zeolite veins are divided into three groups. Group 1 includes early C I carbonatites and late C II–1 carbonatites with burbankite. Calcite from these types of carbonatites has similar carbon ($\delta^{13}C$ in the range –6.8 to –5.5‰ PDB) and oxygen ($\delta^{18}O$ in the range +5.9 to +10.2‰ SMOW) isotopic composition. This indicates a common source for carbon and oxygen in each case.

Group 2 is represented by manganoan ankerite – calcite carbonatite with synchysite-(Ce) (C II–2), where carbonates have higher $^{13}C/^{12}C$ and $^{18}O/^{16}O$ values than the calcite from the carbonatites of group 1. Manganoan ankerite and calcite have similar carbon isotopic compositions ($\delta^{13}C$ in the range –3.9 to –4.5‰ PDB), but show a very wide range in $\delta^{18}O$ (+8.0 to +14.3‰ SMOW). There is a positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values for the calcite, manganoan calcite and manganoan ankerite from carbonatite of groups 1 and 2.

Group 3 includes the ferroan rhodochrosite – manganoan ankerite carbonatites with synchysite-(Ce) (C II–3) and manganoan siderite – manganoan ankerite – natrolite veins (CZ III–1), and these carbonates exhibit a wide variation in isotopic composition of C ($\delta^{13}C$ in the range –7.8 to –2.8‰ PDB) and O ($\delta^{18}O$ in the range +7.9 to +14.0‰ SMOW). In this group, the isotopic composition of carbon ($\delta^{13}C$) in manganoan ankerite, ferroan rhodochrosite and manganoan siderite correlates with depth of sample location in the drill hole. In the upper part of a drill hole, carbonates have a lower $\delta^{13}C$ values than those obtained from the deeper parts of the drill hole (Fig. 10). It is important to note, however, that the carbon and oxygen data from

TABLE 5. $\delta^{13}C$- AND $\delta^{18}O$-VALUES FOR CARBONATES IN THE KHIBINA CARBONATITES

#	Hole	Depth (m)	Mineral	$\delta^{13}C$ ‰ PDB	$\delta^{18}O$ ‰ SMOW
Early calcite carbonatites C I					
1	632B	1934.0	calcite	-6.2	+6.8
2	632B	1960.0	calcite	-5.5	+9.0
3	632	1984.0	calcite	-5.7	+9.1
Late calcite carbonatites with burbankite C II-1					
4	603	158.0	calcite	-5.6	+8.4
5	603	191.9	calcite	-5.8	+10.2
6	607	281.5	manganoan calcite	-5.9	+9.1
7	633	477.7	calcite	-6.8	+5.9
Late manganoan ankerite-calcite carbonatites with synchysite-(Ce) C II-2					
8	603	122.1	calcite	-4.0	+10.5
9	603	165.5	calcite	-3.5	+14.3
10	603	225.2	manganoan ankerite	-4.2	+12.0
11	633A	414.1	manganoan ankerite	-3.9	+12.8
12	604	454.0	manganoan ankerite	-4.3	+8.0
Late ferroan rhodochrosite-manganoan ankerite carbonatites with synchysite-(Ce) C II-2					
13	603	34.5	manganoan ankerite	-7.8	+10.2
14	603	34.5	ferroan rhodochrosite	-5.2	+8.4
15	603	89.0	manganoan ankerite	-4.4	+7.1
16	603	89.0	ferroan rhodochrosite	-5.4	+9.5
17	603	238.0	manganoan ankerite	-3.8	+13.0
18	603	238.0	ferroan rhodochrosite	-4.4	+8.4
Manganoan siderite-manganoan ankerite-natrolite veins CZ III-1					
19	603	49.8	manganoan siderite	-6.9	+7.9
20	603	184.0	manganoan siderite	-3.5	+11.3
21	608	235.0	manganoan siderite	-2.8	+14.0

manganoan ankerite, ferroan rhodochrosite and manganoan siderite from deeper parts of drill hole are in agreement with carbon–oxygen relations in the carbonates of groups 1 and 2. These data plot in the $\delta^{13}C$- and $\delta^{18}O$-enriched field on the diagram.

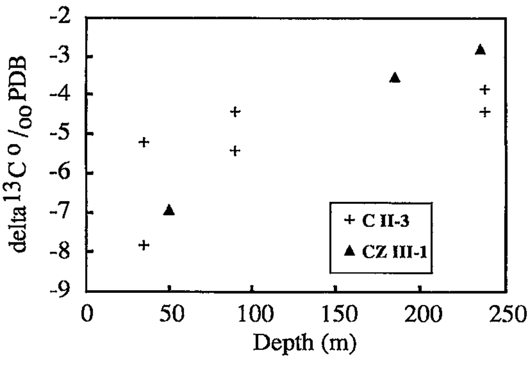

FIG. 10. Variations in $\delta^{13}C$ in the carbonates in a vertical section of the drill hole. Symbols: see Fig. 9.

DISCUSSION AND CONCLUSIONS

The compositions of carbonates from most carbonatite complexes are well represented in the system $CaCO_3 - MgCO_3 - FeCO_3$. Carbonates from early varieties of carbonatite usually plot within the subsystem $CaCO_3 - CaMg(CO_3)_2 - CaFe(CO_3)_2$, and those from late varieties of carbonatites are well described in the subsystem $CaMg(CO_3)_2 - CaFe(CO_3)_2 - FeCO_3 - MgCO_3$. The evolution of carbonates in carbonatites has been discussed in detail by Samoylov (1984), Sokolov (1985) and Buckley & Woolley (1990). According to their data, one common scheme for the mineralogical evolution of carbonatites, based on age relationships and chemical composition, can be described by the following succession (from early to late): calcite → calcite + dolomite → calcite + dolomite + ferroan dolomite → ferroan dolomite + ankerite → ankerite + siderite + magnesite.

Some of the carbonates described above are unusual for carbonatite complexes. For example, at Kovdor, Vuorijarvi, Sallanlatva and other carbonatitic massifs, only Ca–Mg–Fe phases (calcite, dolomite–ankerite, magnesite–siderite) have been observed as major minerals (Kapustin 1980). However, carbonates with a high Mn content are not unique to the carbonatites from Khibina. Other carbonatite complexes contain manganoan calcite (Bolshetaginskii), kutnohorite(?) (Bolshetaginskii), rhodochrosite (Kovdor, Vuorijarvi, Sallanlatva, Mbeya, Amba Dongar), and manganoan–magnesian siderite (Kangankunde), but in all of these complexes, these carbonates occur as accessory minerals, and few descriptions are available in the literature.

The field relations of carbonatites and carbonate–zeolite veins and mineral chemical data show that there is a mineralogical evolution of carbonates in the Khibina carbonatites. The earliest carbonate phase to crystallize was calcite in the C I carbonatites. In the late C II carbonatites, calcite evolved to manganoan calcite, which was followed by an association of calcite and manganoan ankerite or manganoan ankerite only. The late carbonate phases to crystallize in the C II carbonatites are represented by the association of manganoan ankerite and ferroan rhodochrosite, and the formation of ferroan kutnohorite was followed by the same coexisting carbonates. In CZ III carbonate–zeolite veins, the sequence manganoan ankerite + manganoan siderite (or manganoan ankerite alone) followed by manganoan siderite and siderite is observed.

This sequence of carbonate evolution is supported by data from mineral chemistry. The rhombohedral carbonates show gradational changes in their content of major and trace elements from early to late carbonatites. High-Sr, low-Mn calcite in the early C I carbonatites changed to high-Sr, high-Mn calcite in the late C II–1 carbonatites, and to low-Sr, high-Mn calcite in the C II–2 carbonatites (Fig. 5). Such a distribution of Sr and Mn in early- and late-stage calcite (high-Sr – low-Mn early calcite and low-Sr – high-Mn late calcite) has also been documented from other carbonatites (Pouliot 1970, Hogarth *et al.* 1985, Sokolov 1985, Platt & Woolley 1990, Clarke *et al.* 1992) and seems to characterize most early- and late-stage calcite. Compositional evolution is also observed for ankerite–kutnohorite and rhodochrosite–siderite solid solutions. The $CaMn(CO_3)_2$ component increases from low-Mn ankerite (C II–1 carbonatites) to ferroan kutnohorite (C II–3 carbonatites) (Fig. 6), and ferroan rhodochrosite in the C II–3 carbonatites is followed by manganoan siderite (CZ III carbonate–zeolite veins), with pure siderite being found in the latest CZ III–3 veins (Fig. 8).

There are no clear criteria to indicate the relative position of dolomite and "pure" ankerite in this scheme, but the high Sr content in these minerals may indicate formation in the early stages, possibly after calcite and before manganoan ankerite.

Petrographic and cathodoluminesence observations reveal two different textural types of carbonate minerals. In the first type, carbonates occur as subhedral crystals, in cases with internal zonation, which show an equilibrium relation to coexisting minerals and seem to be primary phases. In the second textural type, carbonates occur as vein-like fine-grained aggregates containing anhedral grains, which are developed along grain boundaries and cleavage cracks of crystals and envelop grains of other minerals. Carbonates showing such textural relations are interpreted to be secondary and metasomatic in origin. These petrographic observations are also supported by data on Sr distribution between minerals from different textural types. The Sr content is relatively high in minerals of the first type, but is relatively low in the same minerals of the second textural type.

The rhombohedral carbonates of the Khibina carbonatites can be described in terms of the $CaCO_3$ – $MgCO_3$ – $FeCO_3$ – $MnCO_3$ tetrahedron. Coexisting calcite and low-Mn ankerite from the late C II–1 and C II–2 carbonatites belong to the $CaCO_3$ – $MgCO_3$ – $FeCO_3$ system. Subsolidus relationships in this system were determined by Goldsmith, Rosenberg and other investigators (Goldsmith 1983). The calcite–dolomite geothermometer of Talantsev (1981), which includes a correction for Mn, suggests equilibration temperatures of 260–330°C for carbonates from the late C II–1 and C II–2 carbonatites. Coexisting pairs of calcite – manganoan ankerite yield equilibration temperatures of 260°, 270° and 300°C (all ±15°C) for calcite carbonatite with burbankite (C II–1) and 285° and 330°C (all ±15°C) for manganoan ankerite – calcite carbonatite with synchysite-(Ce) (C II–2) (A.S. Talantsev, pers. comm., 1989, Zaitsev 1992). The lack of subsolidus alteration, *e.g.*, exsolution or recrystallization, shows that temperatures of carbonate equilibrium are probably close to their temperature of formation.

Minerals of the dolomite group from the late C II carbonatites and CZ III carbonate–zeolite veins are well represented in the system $CaMg(CO_3)_2$ – $CaFe(CO_3)_2$ – $CaMn(CO_3)_2$. This dolomite compositional space is not as well studied experimentally as other carbonate systems. The subsolidus relationships in this system are indicated on Figures 6 and 7 (Rosenberg 1968). At a T of 450°C and a P_{total} of 2.1–2.6 kbars, the dolomite compositional space contains one single-phase, one three-phase and three two-phase areas. The three-phase field of coexisting dolomite solid-solution and Ca-rich and Ca-poor solid-solutions indicates a limited solubility of the $CaFe(CO_3)_2$ component in dolomite, up to approximately 74 mol.%, and this field extends from the join $CaMg(CO_3)_2$ – $CaFe(CO_3)_2$ to approximately 40 mol.% of $CaMn(CO_3)_2$. The experimental data of Rosenberg (1968), as well as data from the mineral chemistry of natural samples (Essene 1983), show that there is complete solid-solution between dolomite–ankerite and kutnohorite, and there is no solid solution between kutnohorite and the $CaFe(CO_3)_2$ component.

The results of carbonate analyses from the Khibina carbonatites and carbonate–zeolite veins plot in four fields: 1) one-phase dolomite solid-solution field, 2) two-phase dolomite solid-solution + Ca-poor solid-solution (magnesite – siderite – rhodochrosite solid-solutions) field, 3) two-phase Ca-poor solid-solution + Ca-rich solid-solution (calcite) field, and 4) three-phase dolomite solid-solution + Ca-poor solid-solution + Ca-rich solid-solution field (Figs. 6, 7). Equilibrium assemblages of carbonates in the Khibina carbonatites are calcite + manganoan ankerite, manganoan ankerite + ferroan rhodochrosite and manganoan ankerite + manganoan siderite, and the presence of these mineral pairs is generally consistent with experimental data.

Data from some samples of the manganoan ankerite [with high content of $CaFe(CO_3)_2$] and ferroan kutnohorite plot outside their stability fields, and can probably be related to the difference in the P–T conditions of experiments and those of carbonatite formation. Limited experimental data in the $CaMg(CO_3)_2$ – $CaFe(CO_3)_2$ and $CaFe(CO_3)_2$ – $CaMn(CO_3)_2$ systems show displacement of phase boundaries with changing of temperature. However, with a fall in temperature, the stability fields of ankerite and kutnohorite shrink, and this explanation is regarded as less likely.

An alternative explanation of this phenomenon may lie in the metastable compositions of manganoan ankerite [with high content of $CaFe(CO_3)_2$] and ferroan kutnohorite. The tendency for compositional metastability at low temperature of high-Fe carbonates from the dolomite group has been noted by Goldsmith

(1983). As was described above, high-Fe manganoan ankerite and ferroan kutnohorite from the Khibina carbonatites show evidence of a metasomatic origin, and their temperature of formation can be 260°C and below.

Carbonates belonging to the siderite–rhodochrosite solid solution from the late C II–3 carbonatites and CZ III carbonate–zeolite veins lie close to the $FeCO_3$–$MnCO_3$ join (Fig. 8). The carbonate compositions are consistent with experimental data of Rosenberg (1963) and with data on the mineral chemistry of natural samples (Essene 1983), which show complete solid-solution between $FeCO_3$ and $MnCO_3$ and limited incorporation of $MgCO_3$ (up to 30 mol.%) in this system.

The evolution of carbonatites, as well as of carbonates in carbonatites, is also revealed by their C and O isotope compositions. Relations between carbon and oxygen isotope compositions usually show a trend of enrichment in $\delta^{13}C$ and $\delta^{18}O$ during carbonatite evolution (Deines 1989). Interpretation of a positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values in carbonatites includes: 1) a Rayleigh fractionation model and 2) a temperature-controlled fractionation model.

Rayleigh fractionation of C and O isotopes has been demonstrated by Pineau *et al.* (1973) and Deines (1989). According to Pineau *et al.* (1973), the C and O isotopic composition of carbonatites depends on the molar ratio H_2O/CO_2 in the CO_2–H_2O fluid phase that accompanies carbonatite magma. The temperature-controlled fractionation model was presented by Plyusnin *et al.* (1980), Samoylov & Plyusnin (1982) and Samoylov (1984). According to this model, carbonate phases precipitating in the system $CaCO_3 - CO_2 - CO_3^{2-} - H_2O$ will be characterized by an increase in $\delta^{13}C$ and $\delta^{18}O$ values as the temperature decreases, and this is in accord with the observed field relations, which show low $\delta^{13}C$ and $\delta^{18}O$ values in high-temperature, early-stage carbonatites, and high $\delta^{13}C$ and $\delta^{18}O$ values in low-temperature, late-stage carbonatites (Samoylov & Plyusnin 1982, Samoylov 1984).

Isotope data describing the Khibina carbonates are consistent with both models; it is possible that both Rayleigh and temperature-induced fractionation took place during formation of the Khibina carbonatites. However, these models cannot explain the wide variation in carbon and oxygen compositions of the carbonates from C II–3 carbonatites and CZ III–1 carbonate–zeolite veins (group 3). The tendency for changing $\delta^{13}C$ in carbonates from this group with depth of sample location has already been noted. An other important observation is the difference in isotopic composition between coexisting manganoan ankerite and ferroan rhodochrosite. Values of $\Delta^{13}C_{\text{manganoan ankerite – ferroan rhodochrosite}}$ and $\Delta^{18}O_{\text{manganoan ankerite – ferroan rhodochrosite}}$ are –2,6; +1.0; +0.6 and +1.8; –2.4; +4.6, respectively. These features show that the coexisting carbonates were not in isotopic equilibrium during their formation (Deines 1989). Petrographic and CL observations do not reveal any evidence of alteration or other secondary processes in these samples of the carbonatites or the carbonate–zeolite veins.

The depletion in heavy carbon in carbonates from the upper part of drill holes may be explained as partitioning of heavy C into CO_2 gas phase, which escaped during carbonatite emplacement. The possibility of such a mechanism has been proposed by Suwa *et al.* (1975) and Knudsen & Buchardt (1991) to explain low $\delta^{13}C$ values in carbonatites of the Oldoinyo Lengai and Qaqarssuk, and by Clarke *et al.* (1992) for carbonatite tuffs at Kruidfontein.

Field relations, petrographic and CL observations suggest that the late C II carbonatites and CZ III carbonate–zeolite veins are more likely to have formed from a fluid phase rather than from a melt. The evidence for this hypothesis includes: field relations of carbonatites and wallrocks (gradational contacts, presence of extremely metasomatized relics of silicate wallrocks in carbonatite, intensive fluoritization of wallrocks), relationships between various types of carbonatites and carbonate–zeolite veins (metasomatic character of contacts between carbonatites, changing of mineral composition of carbonate–zeolite veins in conjunction with those of surrounding carbonatite), textural and structural features of carbonatites [two distinct textural types of carbonates, primary and secondary, crustification (vein-filling), druses]. The best explanation of these observations is precipitation of carbonatites from gas-rich fluid phase.

The geochemistry of late carbonatites also supports this suggestion; these rocks are extremely enriched in rare-earth elements, with La + Ce + Nd contents in the range between 12200 and 74350 ppm (A.N. Zaitsev & M.J. Le Bas, unpubl. data). Experimental data show that enrichment in *REE* in CO_2-rich gas phase relative to carbonatite melt increases with decreasing T and P (Wendlandt & Harrison 1979).

Experimental data suggest that the primary carbonatitic fluid necessary for the formation of late carbonatites and carbonate–zeolite veins must have been an alkaline (Na, K) carbohydrothermal system containing a $Ca(CO_3)_n(OH)_m^{p-}$ or $HCO_3^- - CO_3^{2-} - CO_2 - OH^-$ aqueous solution and CO_2–H_2O vapor (Malinin & Dernov-Pegarev 1974, Dernov-Pegarev & Malinin 1976). Thermodynamic calculations for a range of temperatures (350–600°C) and P = 1 kbar show the existence of such fluids with $X(CO_2)$ in the range 0.4–0.6. This fluid is homogeneous at temperatures higher than 250–270°C, and heterogeneous (H_2O-rich solution and CO_2-rich vapor) at temperatures less than 250–270°C. The process of fluid transformation from homogeneous to heterogeneous can be accompanied by explosive events (Bulakh & Ivanikov 1984). More detailed information about thermophysical properties of CO_2–H_2O mixtures, namely P–V–T–*X* measurements, equations of state and experimentally determined phase-equilibria is available from the work of Mäder (1991).

Temperatures of equilibration of 260–330°C for coexisting calcite – manganoan ankerite in the C II–1 and C II–2 carbonatites, which are probably similar to their temperatures of formation, suggest the formation of C II–2 and C II–3 carbonatites and CZ III carbonate–zeolite veins at a temperature of 260°C or less. At such temperatures, a late-stage carbonatitic system will be heterogeneous (solution + vapor), and volatiles can be lost through explosive events accompanying transformation of the fluid. Loss of a vapor phase from carbonatite is also supported by data on He, Ne and Ar isotopic compositions of gases in the Khibina carbonatites. The isotopic composition of inert gases shows that the carbonatites were intruded close to the surface with intensive degassing (Tolstihin *et al.* 1985). There is no sign of oxidation accompanying the degassing.

This study shows that the carbonate-bearing rocks from the Khibina massif belong to the rocks of carbonatite series and that they define a crystallization sequence from biotite – aegirine – apatite rocks through various carbonatites to carbonate–zeolite veins. The study of the rhombohedral carbonates, calcite, manganoan calcite, dolomite, ankerite, manganoan ankerite, ferroan kutnohorite, ferroan rhodochrosite, manganoan siderite and siderite, reveals a mineralogical and chemical evolution of these minerals during carbonatite emplacement. That most carbonatites are of magmatic origin has been accepted in the Western scientific literature for many years (*e.g.*, Bailey 1993). At the same time, Russian investigators proposed a hydrothermal–metasomatic origin for some carbonatites (Kukharenko *et al.* 1965, Bulakh & Iskoz-Dolinina 1978, Kapustin 1980). This study shows that the Khibina carbonatites are polygenetic in origin. Early C I carbonatites are magmatic, late C II carbonatites are interpreted as precipitated from volatile-rich fluid (carbohydrothermal system), derived from early-crystallizing magmatic carbonatite, and CZ III carbonate–zeolite veins are hydrothermal veins. The mineral assemblages, mineral chemistry, and C and O isotopic data suggest that the evolution of the Khibina carbonatites may be interpreted as produced by crystallization-induced fractionation.

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