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THE CARBONATITES AND FENITES OF CHIPMAN LAKE, ONTARIO

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ABSTRACT

Simple and composite dikes of dolomitic and ankeritic carbonatite, up to one meter thick, cut and fenitize Archean country rocks around Chipman Lake, Ontario. The carbonate compositions define a complete series from dolomite to ankerite, and coexist with calcite. Cathodoluminescence studies indicate an early dolomitic phase brecciated by later ankeritic carbonate. Drop-like inclusions of burbankite within the dolomite are taken as evidence for an early Na-rich fluid or immiscible liquid. Compositional data are given for burbankite and other phases in the carbonatite, including synchysite, parisite, bastnäsite, norsethite, barytocalcite (alstonite?), strontianite, apatite, strontian apatite, monazite and F-rich phlogopite. The fenites comprise Na- and K-rich feldspars, magnesio-arfvedsonite and aegirine, with phlogopite particularly concentrated along carbonatite contacts. The evolution of the carbonatite liquid from magnesian to more iron-rich compositions paralleled a decrease in the Na:K ratio, which was responsible for early fenitization of a predominantly sodic character changing later to potassium fenitization.

Keywords: carbonatites, fenites, cathodoluminescence, mineral chemistry, Chipman Lake, Ontario.

SOMMAIRE

Des filons simples et composés de carbonatites dolomitique et ankéritique, atteignant un mètre d'épaisseur, recoupent et ont causé la métasomatose alcaline d'un socle archéen autour du lac Chipman, en Ontario. La composition des carbonates définit une série complète de dolomite à ankérite, en coexistance avec la calcite. Les études par cathodoluminescence témoignent de la formation précoce de la dolomite, qui est bréchifiée par un carbonate ankéritique tardif. Des gouttelettes de burbankite dans la dolomite seraient une indication de la formation précoce d'un liquide ou d'un fluide enrichi en Na. Nous avons déterminé la composition chimique de la burbankite et des autres phases dans la carbonatite, y inclus synchysite, parisite, bastnäsite, norsethite, barytocalcite (alstonite?), strontianite, apatite, apatite strontifère, monazite et phlogopite fluorée. Les fénites contiennent feldspaths sodique et potassique, magnésio-arfvedsonite et aegyrine, avec phlogopite surtout le long des contacts avec la carbonatite. L'évolution du magma carbonatitique, d'un coeur magnésien vers une bordure enrichie en fer, a été accompagnée d'une diminution du rapport Na:K, qui a été responsable de la fénitisation précoce à caractère surtout sodique, suivie d'une fénitisation tardive à caractère potassique.

(Traduit par la Rédaction)

Mots-clés: carbonatites, fénites, cathodoluminescence, composition des minéraux, lac Chipman, Ontario.

INTRODUCTION

The Chipman Lake carbonatite occurrence (49°58′N; 86°12′W) consists of a series of dikes intruding rocks of the Archean Wabigoon Subprovince of the Superior Province some 350 km northeast of Thunder Bay, Ontario. The small dikes, generally less than 1 meter thick, and their associated marginal fenites, crop out at the southern end of Chipman Lake (Fig. 1). According to Sage (1985), the carbonatite dikes are spatially associated with a major regional fault that runs along the length of Chipman Lake. In turn, this fault is considered to be the northeastern extension of the Big Bay - Ashburton fault, which crosses the Lake Superior basin, and with which the alkaline and carbonatite intrusive complexes of Coldwell, Killala Lake and Prairie Lake seem to be associated. The specific age of the Chipman Lake dikes is unknown, but probably is similar to that of the nearby Proterozoic carbonatites and alkaline rocks of Prairie Lake, Coldwell and Killala Lake (*i.e.*, 1000 - 1200 Ma; Platt & Mitchell 1984, Bell & Blenkinsop 1980). A preliminary K–Ar age of 1022 ± 31 Ma was obtained on amphibole from fenite (Sage 1985).

Apart from preliminary studies by Biczok (1976), reviewed and expanded by Sage (1985), no previous detailed petrological or mineralogical work has been undertaken on this occurrence. The present study is based on a suite of specimens collected from glaciated outcrops around the lake, the locations of which are shown on Figure 1. Reconaissance electron-microprobe studies of the mineralogy of the carbonatites and fenites were undertaken at Lakehead University (Hitachi SEM 560, Tracor Northern Energy-Dispersion Spectrometry) and the University of Edinburgh (Cambridge Instruments Geoscan, automated Wavelength-Dispersion Spectrometry). Detailed analytical studies were made at the British

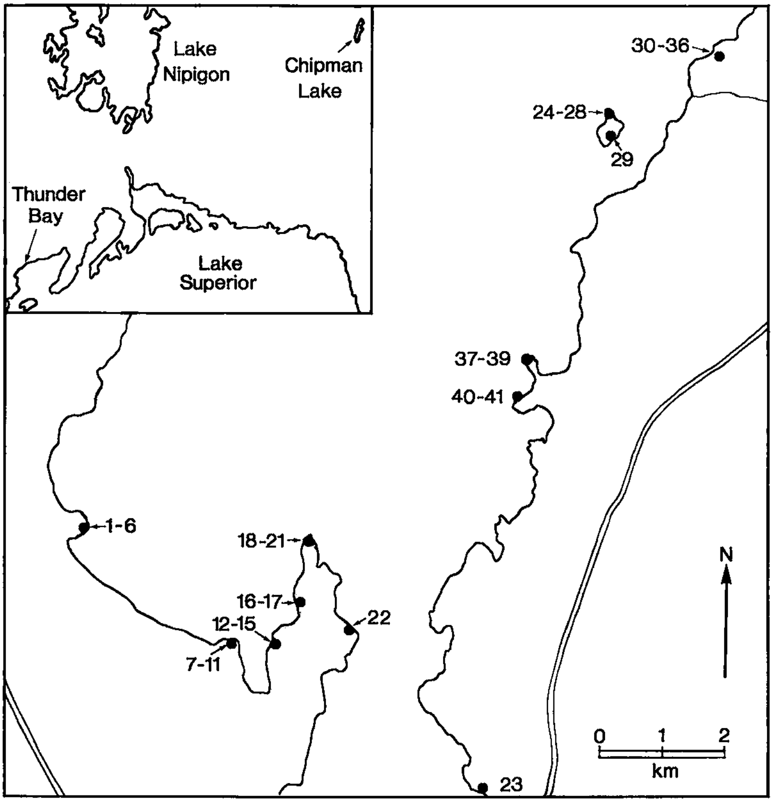

FIG. 1. Location of the Chipman Lake complex of carbonatite dikes (inset diagram) and specimen localities around the southern end of the lake.

Museum (Natural History) (Hitachi SEM 2500, Link Systems EDS; Cambridge Instruments Microscan 9, WDS) under the conditions described by Platt & Woolley (1986) and Platt *et al.* (1987). General, but not detailed, cathodoluminescence studies were made with a Nuclide luminoscope.

PETROGRAPHY OF THE CARBONATITES

The dikes are generally fine to medium grained, white to grey, and may show banding parallel to the margins caused by streaks of dark silicate minerals, principally phlogopite, and grain-size variations. Blocks and streaks of mica-rich fenite are observed in the dikes and in veinlets of carbonate that penetrate the country rock.

Cathodoluminescence studies reveal two major carbonate phases within some dikes. An earlier phase, generally red to orange, forms angular blocks of relatively coarse, sometimes drusy crystals that are penetrated and surrounded by a later, finer-grained phase showing no luminescence. This relationship is depicted in Figure 2. The inference from this texture, where seen, is that such dikes are composite. As discussed later, the carbonate of the earlier carbonatite is dolomite, whereas the carbonate of the later carbonatite is more Fe-rich and ranges in composition toward ankerite. Simple carbonatite dikes generally consist of the more Fe-rich carbonate. Numerous round, drop-like, luminescent yellow inclusions of burbankite are prominent within the earlier dolomite (Fig. 2). The potential importance of this rare carbonate is discussed later. Observations using the distribution of back-scattered electrons are invaluable in differentiating this phase for electron-microprobe studies. Such images also reveal the occurrence of narrow, irregular, late-stage veinlets of calcite, quartz, albite and synchysite, which transect the earlier carbonatites.

Apatite is common to both carbonatites, whereas phlogopite becomes an important phase in the more Fe-rich carbonatite. Accessory minerals, not all of which have been studied in detail, include magnetite, sulfides (pyrite, pyrrhotite, chalcopyrite, galena, sphalerite), pyrochlore, barite, monazite, calcite, magnesian siderite, burbankite, norsethite, barytocalcite (alstonite?), strontianite, synchysite, parisite, bastnäsite, albite, orthoclase, zircon and quartz. With the exception of burbankite, all these phases tend to be associated with the Fe-rich carbonatite and with minor late-stage cross-cutting veinlets.

CARBONATITE MINERALOGY

Ca–Mg–Fe carbonates

Data on the carbonates, plotted in the system $CaCO_3$-$MgCO_3$-$FeCO_3$ (Fig. 3), define three groups, dolomite - ankerite, calcite and magnesian siderite. The principal carbonate trend, collectively observed from both carbonatite types, ranges progressively from dolomite through ferroan dolomite to ankerite, with a maximum of approximately 50 mol.% $CaFe(CO_3)_2$. From the limited carbonate data in the literature (*cf.* the Sarfartôq carbonatite complex, southern West Greenland: Secher & Larsen 1980) and the authors' unpublished data, this evolutionary trend is consistent with that observed in other dolomitic–ankeritic carbonatites.

Although the complete carbonate trend is not seen in all dikes, in most rocks there is a range of Mg:Fe values, as is clearly shown by samples 7 and 10 (Fig. 3, subsidiary diagram). These two rocks contain turbid, irregular areas of carbonate within a matrix of a finer-grained, clearer carbonate, corresponding to the texture observed by cathodoluminescence (Fig. 2). The irregular patches of carbonate, which appear to be earlier, are dolomitic, whereas the later matrix carbonate is richer in Fe and Mn (Fig. 3). The latter carbonate represents crystallization from a more evolved iron-rich magma, which is believed to have been injected later, thereby creating composite dikes.

The early dolomite contains "blebs" of calcite that is interpreted an exsolved phase. Application of the calcite–dolomite geothermometer for the exsolved calcite "blebs", using the calcite limb of the calcite-dolomite solvus (Goldsmith & Newton 1969, Anovitz & Essene 1987), suggests temperatures of exsolution in the range of 550 to 600°C. Considering the criticism of Gittins (1979), this temperature must be treated with caution.

Calcite also occurs as discrete grains associated with quartz, synchysite and albite in irregular mm-wide late-stage veinlets that cross-cut carbonates of the dolomite–ankerite series.

Small patches of calcite and magnesian siderite, apparently in equilibrium with each other but not with the surrounding ankeritic dolomite, occur in one sample. Late in origin, this relationship, as briefly discussed by Buckley & Woolley (1990), suggests evolution of the carbonatite residual fluid into the two-phase field calcite + siderite of the carbonate ternary system (Fig. 3). The observed siderite compositions are richer in magnesium than would be expected from the experimental studies of Rosenberg (1967) and from the studies of natural carbonate pairs (Anovitz & Essene 1987) for temperatures as low as 400°C. One consequent inference is that the temperature of the residual fluid was less than 400°C. However, without a full knowledge of these fluid compositions, care must be taken in applying, without reservation, the observed relationships in the simple carbonate ternary system.

In the early calcite, which coexists with dolomite, SrO averages 0.91 wt.%, which is close to the average of 0.86 wt.% for calciocarbonatites (Woolley & Kempe 1989). In contrast, Sr is below detection in the later calcite, which coexists with magnesian siderite, indicating depletion of this element in the most evolved fluid. The tenor of Mn, in contrast, increases during crystallization, averaging 0.96 wt.% MnO in the dolomite–ankerite series and reaching 1.55 wt.% in the magnesian siderite. Again, this closely matches averages of 0.96 and 1.65 wt.% in ferro- and magnesiocarbonatites, respectively (Woolley & Kempe 1989).

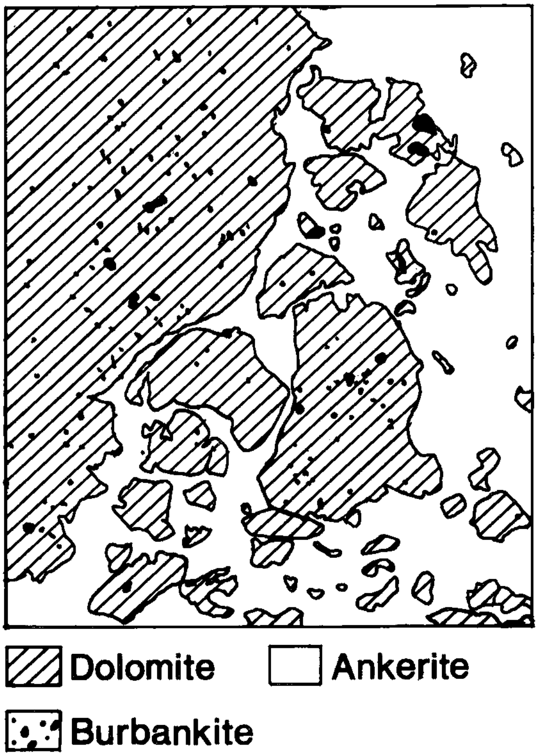

FIG. 2. Diagram, based on cathodoluminescence photograph, showing early dolomite, containing numerous blebs of burbankite, brecciated by a later ankeritic carbonate. Scale 1 cm = 0.4 cm.

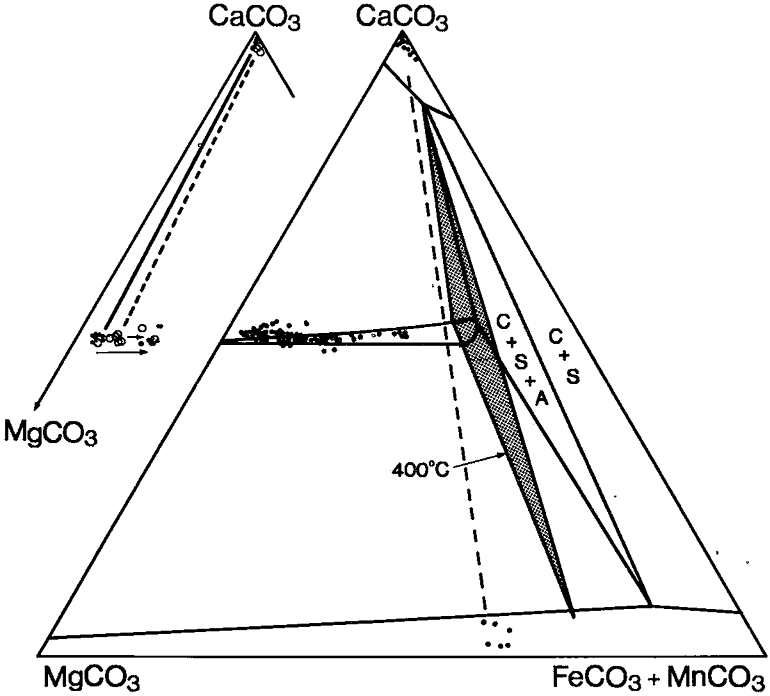

FIG. 3. Plots of mol.% carbonate compositions in the system $CaCO_3$–$MgCO_3$–$FeCO_3$. The boundaries of the fields pertain to 450°C (Rosenberg 1967), with the three-phase field at 400°C shaded. The dashed tie-line is for one rock containing a small amount of magnesian siderite coexisting with calcite, which suggests that at temperatures below 400°C the two-phase field calcite + siderite may extend even further toward the magnesian component. The subsidiary diagram to the left is for two rocks containing coexisting calcite + ferroan dolomite in which zoning indicates evolution toward more iron-rich compositions (as indicated by arrows). C, calcite; S, siderite; A, ankerite.

Burbankite

The comparatively rare carbonate burbankite occurs principally as drop-like inclusions within the early dolomite (Fig. 2). Locally it is present as inclusions within early apatite, but it has not been seen in association with the later ankeritic carbonates. Burbankite is difficult to discern by optical microscopy, but appears orange-yellow under cathodoluminescence and exhibits strong matrix effects on the back-scattered electrons.

Representative compositions of burbankite are given in Table 1; CO_2-free structural formulae, calculated on the basis of 5 oxygen atoms, correspond reasonably well with the general formula $A_3B_3(CO_3)_5$, where A represents Na and Ca, and B, Ca, Sr, Ba and the *REE*. However, cation deficiencies in the A site are evident in all cases, a phenomenon noticed in burbankite analyzed by electron microprobe from Mont St. Hilaire, Quebec (Chen & Chao 1974). Whether this deficiency truly involves the A site or results from elemental loss on analysis cannot be answered definitively. However, beam damage to all analyzed samples and A-site Na contents of between 27 and 55%, considerably below the 65 to 90% range quoted by Tikhonenkova *et al.* (1978), strongly suggest Na loss on analysis.

The B-site cations are dominated by Sr (50 to 71% of the position, with one exception) followed in general order of abundance by Ca, Ba and *REE* (Table 1). Absolute concentrations of the rare-earth elements vary widely both within and between specimens, ranging between 1% and 17%. La and Ce predominate in this group.

Synchysite, parisite and bastnäsite

Of these late-stage *REE* carbonates, synchysite is the most common, the other two occurring rarely. Associated with calcite, quartz and albite, synchysite is fibrous to acicular and forms irregular to radiating patches. Less commonly, distinct tabular prisms of densely packed fibers also are present.

The synchysite (anal. 1–3, Table 2) conforms well to the generally accepted formula of $(Ce,La)Ca(CO_3)_2F$, although F was not sought. Densely packed regions of synchysite may, however, contain substantial Fe (*e.g.*, anal. 4, Table 2). The structural incompatiblity of Fe^{2+} and Fe^{3+} in Ca–*REE* carbonates suggests that Fe is present as an admixture of an oxide, hydroxide and carbonate. This is generally confirmed by the compositional trend observed in synchysite toward the FeO apex in Figure 4. Elsewhere, synchysite has been observed intergrown with hematite (Klemic *et al.* 1959, Heinrich *et al.* 1962).

Parisite (anal. 5, Table 2) is extremely rare at Chipman Lake. It occurs as very small irregular patches within the late-stage veinlets of calcite, quartz, albite and synchysite. Bastnäsite (anal. 6, Table 2) is observed occasionally as a replacement of synchysite in the same veinlets.

Norsethite, barytocalcite (alstonite?) and strontianite

These uncommon carbonates form very small grains associated with the later Fe-rich carbonates. They were only identified for analysis by backscattered electron imagery. Compositions of these phases are given in Table 3. Norsethite compositions conform well to the accepted formula of $BaMg(CO_3)_2$, with minor replacement by Sr, Ca and Fe. Similar compositions are reported by Kapustin (1980, Table 21). Barytocalcite $[CaBa(CO_3)_2]$ or the chemically equivalent carbonate, alstonite, occurs as a rare phase in late-stage calcite or ankeritic carbonatite veins (Kapustin 1980). Chemically, the Ca–Ba carbonate conforms to the accepted formula (Table 3) and is similar to compositions reported by Kapustin. It is not possible to say, however, if this phase is barytocalcite or alstonite. Strontianite shows minor replacement of Sr by Ca and Ba (Table 3). Barker (1989) lists this phase among those typically present as accessory components of Kapustin's (1980) stage-3 and stage-4 carbonatites. This would conform well to its paragenesis in the Chipman Lake carbonatites.

TABLE 1. CHEMICAL COMPOSITIONS OF BURBANKITE

Sample #	1B/5	1B/9	7A/3	10A/4	10A/5	22A/4	19A/5
Analysis #	1	2	3	4	5	6	7
CaO wt.%	21.09	18.35	15.01	19.91	18.97	14.60	13.53
FeO*	0.25	0.37	0.53	0.13	0.08	0.00	0.13
MnO	0.15	0.06	0.13	0.00	0.00	0.00	0.00
MgO	0.04	0.24	2.88	0.12	0.16	0.10	0.00
BaO	4.06	6.31	1.85	3.44	6.14	10.36	3.37
SrO	29.12	32.60	30.44	29.84	28.51	31.26	28.63
Na_2O	7.38	4.04	7.20	6.21	5.30	5.98	6.70
La_2O_3	0.76	0.65	0.54	0.58	1.80	0.19	4.34
Ce_2O_3	1.20	1.41	0.77	1.60	3.32	1.55	5.80
Pr_2O_3	0.18	0.08	0.15	0.25	0.46	0.19	0.60
Nd_2O_3	0.21	0.34	0.26	0.82	0.97	0.86	1.64
Sm_2O_3	0.15	0.15	0.07	0.29	0.19	0.51	0.00
Y_2O_3	0.47	0.30	0.71	0.47	0.27	0.41	0.45
Total	65.06	64.90	60.54	63.66	66.17	66.01	65.19
Structural Formulae based on 5 atoms of Oxygen (CO_2-free)							
Na	1.421	0.827	1.459	1.239	1.057	1.263	1.407
Ca	1.232	1.527	1.217	1.302	1.338	1.292	1.039
Σ_A	2.653	2.354	2.676	2.541	2.395	2.555	2.446
Ca	1.011	0.549	0.464	0.894	0.752	0.413	0.531
Fe*	0.021	0.033	0.046	0.011	0.007	0.000	0.012
Mn	0.013	0.005	0.012	0.000	0.000	0.000	0.000
Mg	0.006	0.038	0.449	0.018	0.025	0.016	0.000
Ba	0.158	0.261	0.076	0.139	0.248	0.442	0.143
Sr	1.675	1.996	1.844	1.781	1.700	1.974	1.797
La	0.028	0.025	0.021	0.022	0.068	0.008	0.173
Ce	0.044	0.054	0.029	0.060	0.125	0.062	0.230
Pr	0.007	0.003	0.006	0.009	0.017	0.008	0.024
Nd	0.007	0.013	0.010	0.030	0.036	0.034	0.064
Sm	0.005	0.006	0.003	0.010	0.007	0.019	0.000
Y	0.025	0.017	0.040	0.026	0.015	0.024	0.026
Σ_B	3.000	3.000	3.000	3.000	3.000	3.000	3.000

* Total iron calculated as FeO

TABLE 2. CHEMICAL COMPOSITION OF SYNCHYSITE, PARISITE AND BASTNÄSITE

Sample #	10A	38B	36A	37A	10A	22A
Analysis #	1	2	3	4	5	6
CaO wt.%	18.66	15.23	16.71	16.80	5.31	1.11
FeO*	0.62	0.98	1.57	7.19	0.00	0.45
La_2O_3	15.46	16.04	11.49	9.81	19.31	22.17
Ce_2O_3	23.83	26.12	19.95	19.63	30.65	31.82
Pr_2O_3	1.90	2.48	2.28	2.00	2.24	2.32
Nd_2O_3	5.57	6.85	7.82	6.82	6.76	6.19
Sm_2O_3	0.06	0.49	0.81	0.54	0.00	0.00
Y_2O_3	0.00	0.00	0.00	0.00	0.00	0.00
Total	66.10	68.19	60.63	62.79	64.27	64.06

Samples 1 - 4 synchysite; 5 parisite; 6 bastnäsite
* Total iron calculated as FeO

Phosphates

Apatite is the dominant phosphate; it occurs both as single grains and irregular patches in association with the earlier dolomitic and later ankeritic carbonatites. It generally exhibits blue to lavender cathodoluminescence in response to *REE* activators (Marshall 1988). Chemically, three distinct forms of apatite are observed; the earliest crystallizes with turbid dolomite and contains small amounts of Sr and trace amounts of *REE* (anal. 1, 2c and 3c, Table 4). A second generation, richer in Sr and *REE* (anal. 2r and 3r, Table 4) and associated with the ankeritic carbonate, forms individual grains, rims on earlier apatite cores, and anastomosing veins through earlier apatite. Lower analytical totals of this apatite and the apparent absence of Cl suggest enhanced F contents. The third and least common form of apatite is enriched in Sr and seemingly devoid of *REE* (anal. 4 and 5, Table 4); it occurs as individual grains within the ankeritic carbonatite.

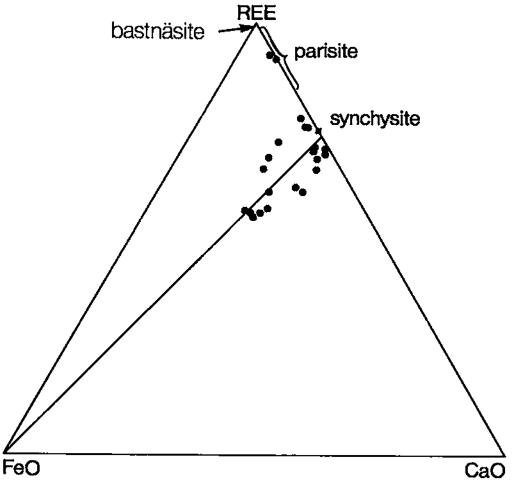

FIG. 4. Plot of synchysite compositions in terms of total rare-earth elements (*REE*), CaO and FeO (wt.%), to illustrate the probable admixture of iron oxide, hydroxide and carbonate in the synchysite.

TABLE 3. CHEMICAL COMPOSITIONS OF ACCESSORY CARBONATES

Sample #	22A	22A	1B	10A	1B
Analysis #	1	2	3	4	5
CaO wt.%	0.31	0.62	19.23	3.37	6.27
FeO*	1.04	0.82	0.28	0.40	0.27
MnO	0.34	0.03	0.03	0.06	0.04
MgO	14.90	15.47	0.10	0.01	0.48
BaO	53.23	53.24	48.82	2.59	1.47
SrO	0.09	0.09	0.59	61.55	56.41
Na_2O	0.00	0.18	0.49	0.02	0.14
La_2O_3	nd	nd	0.00	0.72	0.12
Ce_2O_3	nd	nd	0.00	0.59	0.13
Pr_2O_3	nd	nd	0.00	0.14	0.00
Nd_2O_3	nd	nd	0.00	0.09	0.00
Total	69.91	70.95	69.54	69.54	65.33
Structural Formulae based on 2 atoms of Oxygen (CO_2-free)					
Ca	0.015	0.029	1.006	0.174	0.326
Fe*	0.039	0.030	0.011	0.016	0.011
Mn	0.013	0.001	0.001	0.002	0.002
Mg	0.996	1.013	0.007	0.001	0.035
Ba	0.935	0.917	0.934	0.049	0.028
Sr	0.002	0.002	0.017	1.717	1.586
Na	0.000	0.015	0.046	0.002	0.013
La	nd	nd	0.000	0.013	0.002
Ce	nd	nd	0.000	0.010	0.002
Pr	nd	nd	0.000	0.003	0.000
Nd	nd	nd	0.000	0.002	0.000

Samples 1 and 2 norsethite; 3 barytocalcite (alstonite?); 4 and 5 strontianite
* Total iron calculated as FeO; nd = not determined

TABLE 4. CHEMICAL COMPOSITION OF PHOSPHATES

Sample #	22A	20A	20A	20A	20A	22A	22A	22A	22A
Analysis #	1	2c	2r	3c	3r	4	5	6	7
Type	A	A	A	A	A	SA	SA	M	M
CaO wt.%	55.15	55.16	51.92	55.65	52.67	49.10	49.18	0.15	0.21
FeO*	0.46	0.19	0.00	0.11	0.18	0.77	0.56	0.68	0.10
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.00	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.33	0.12	0.30	0.09
SrO	0.67	0.53	0.64	0.43	0.61	7.95	8.20	1.10	1.67
La_2O_3	0.11	0.26	0.27	0.00	0.29	0.00	0.00	22.37	14.50
Ce_2O_3	0.40	0.22	1.20	0.14	0.70	0.00	0.00	36.19	32.01
Pr_2O_3	0.06	0.00	0.48	0.12	0.00	0.00	0.00	3.31	3.71
Nd_2O_3	0.26	0.00	0.97	0.11	0.80	0.00	0.00	6.96	14.69
Sm_2O_3	0.17	0.12	0.24	0.20	0.56	0.00	0.00	0.00	1.52
Y_2O_3	0.10	0.24	0.74	0.00	0.32	0.00	0.00	0.00	0.00
P_2O_5	43.23	42.53	41.59	42.98	41.71	41.34	41.18	30.89	31.31
Total	100.61	99.25	98.05	99.74	97.84	99.49	99.50	101.95	99.81

A apatite; SA strontian apatite; M monazite
* Total iron calculated as FeO
c = core; r = rim

Monazite (anal. 6 and 7, Table 4) is comparatively rare and forms small individual grains within the ankeritic carbonatite.

Mica

Although mica is the principal silicate mineral of the ankeritic carbonatite, it rarely exceeds a few volume percent, and may be absent in some rocks. In general, it occurs as thinly banded zones of pale yellow, weakly pleochroic grains without evident zoning. The mica is phlogopitic, with significant fluorine and Na contents (Table 5). Calculations of structural formulae indicate the need for some ferric iron to satisfy the tetrahedral site requirements of 8 cations. However, reverse pleochroism, characteristic of micas with such tetrahedral ferric iron, *i.e.*, tetraferriphlogopite, is uncommon. Where observed, this mica irregularly replaces the common phlogopite.

Locally, phlogopite has a remnant irregular reddish brown core of Ti- and Ba-rich phlogopite (Table 6). In addition to a decrease in Ba and Ti from core to rim, it is general for Al and Fe to decrease and for Si, Mg, K and F to increase. Sodium is variable in its behavior.

PETROGRAPHY OF THE FENITE

The carbonatite dikes fenitize the surrounding Archean granites, metavolcanic greenstones, and the syenites and monzodiorites of the Chipman Lake stock. The fenites are particularly well developed in the granites, but in all instances, the zone of fenitization is narrow, although wider than the associated dikes. The fenitized rocks generally are reddened.

The initial effect of fenitization on the country rocks, as observed in thin section, is manifest as turbidity of the feldspars along grain boundaries and partings. As fenitization becomes more pronounced nearer the dikes, blue alkali amphibole develops as stellate clusters and as fibrous grains in veinlets.

Alkali pyroxene also forms clusters of acicular crystals that may be intergrown with the amphibole, albeit in lesser abundance. The mafic minerals of the country rocks are generally replaced by amphibole and phlogopite, and carbonate becomes a significant phase. In the immediate vicinity of the dikes, the turbidity in the feldspars clears, or remains only in the crystal cores, and a new, clear alkali feldspar develops. Quartz, where originally present, disappears. This results in a rock consisting of alkali feldspar, alkali amphibole, phlogopite and carbonate. Alkali pyroxene may or may not develop. Narrow phlogopite-rich zones, which may pass outward into zones of phlogopite and alkali amphibole, develop at the dike–fenite contacts. Similar mica-rich zones are observed also around thin ankeritic carbonatite veinlets that extend from the dike margins into the country rock.

MINERALOGY OF THE FENITE

Mica

The mica in the fenites is phlogopite (Table 7). Of variable grain-size, the yellow to brown, weakly pleochroic, unzoned grains are similar chemically to those of the carbonatite, with the exception of higher fluorine contents (>4 and as high as 8 wt.%). These exceptionally high values suggest a paucity of water in the structure.

Amphibole

Analyses (Table 7) indicate that the amphibole is magnesio-arfvedsonite closely similar to that described from other fenite occurrences [*e.g.*, Sökli: Vartiainen & Woolley 1976; Fen: Kresten & Morogan 1986; Alnö: Morogan & Woolley 1988]. Of particular interest is the high value for F, which generally exceeds >2 wt.% and may reach 3%. This presumably, as for the micas, reflects a high tenor of F in the fenitizing medium.

Pyroxene

No zonation was detected in the pyroxene grains, and all, with the exception of those in one rock, proved to be essentially pure aegirine. In the atypical pyroxene, the combined molecular percentages of diopside and hedenbergite reach 18%. However, there is no evidence for systematic variation in pyroxene compositions across the fenite aureoles.

Feldspar

Albite and twinned microcline, both close to their respective end-member compositions, are typical of the inner zones of the fenite aureoles. No intermediate compositions were detected, and both phases are present in most fenites.

TABLE 5. MICA COMPOSITIONS IN CARBONATITE

Sample #	19A	19A	19A	19A	24C	24C	24C	24C
Analysis #	1	2	3	4	5	6	7	8
SiO_2	42.55	40.86	42.54	41.50	41.06	40.42	40.38	39.82
TiO_2	0.07	0.94	0.07	0.17	0.61	1.17	1.58	1.18
Al_2O_3	9.87	10.90	10.01	10.54	11.46	11.30	10.48	11.57
FeO*	6.75	8.20	6.28	6.19	10.57	10.46	10.45	10.80
MnO	0.08	0.11	0.05	0.05	0.00	0.10	0.02	0.13
MgO	23.61	22.31	23.90	23.42	20.77	19.54	19.49	19.56
CaO	0.01	0.01	0.01	0.09	0.07	0.00	0.07	0.00
BaO	0.03	0.09	0.09	0.01	0.54	0.29	0.00	0.12
Na_2O	0.54	0.25	0.77	0.32	0.31	0.36	0.45	0.33
K_2O	10.46	10.32	10.39	10.59	10.02	10.28	10.10	10.07
ZrO_2	nd	nd	nd	nd	0.00	0.15	0.00	0.00
F	1.36	1.00	1.59	1.19	nd	nd	nd	nd
Total	95.33	94.59	95.70	94.07	95.41	94.07	93.02	93.58
O = F	0.57	0.42	0.67	0.50				
Structural Formulae based on 22 atoms of Oxygen (F-free)								
Si	6.209	6.014	6.189	6.120	6.019	6.021	6.067	5.961
Ti	0.008	0.104	0.008	0.019	0.067	0.131	0.179	0.133
Al	1.698	1.891	1.717	1.832	1.980	1.984	1.856	2.042
Fe*	0.824	1.009	0.764	0.763	1.296	1.303	1.313	1.352
Mn	0.010	0.014	0.006	0.006	0.000	0.013	0.003	0.017
Mg	5.134	4.894	5.182	5.147	4.538	4.338	4.364	4.364
Ca	0.002	0.002	0.002	0.014	0.011	0.000	0.011	0.000
Ba	0.002	0.005	0.005	0.001	0.031	0.017	0.000	0.007
Na	0.153	0.071	0.217	0.092	0.088	0.104	0.131	0.096
K	1.947	1.938	1.929	1.993	1.874	1.954	1.936	1.923
Zr	nd	nd	nd	nd	0.000	0.011	0.000	0.000
Fe#	0.14	0.17	0.13	0.13	0.22	0.23	0.23	0.24

*Total iron calculated as FeO; nd = not determined.
Fe# = (Fe + Mn) / (Fe + Mn + Mg)

TABLE 6. CORE - RIM RELATIONSHIPS IN CARBONATITE MICAS

Sample #	10A/7	10A/8	10A/14	10A/15	33	33	33	33
Analysis #	1c	1r	2c	2r	3c	3r	4c	4
SiO_2 wt.%	39.17	41.88	37.59	42.33	37.25	44.10	37.10	43.05
TiO_2	2.32	0.13	2.39	0.34	4.94	0.82	3.94	0.27
Al_2O_3	14.57	8.03	13.96	11.19	15.29	10.32	14.10	9.92
FeO*	7.05	9.93	7.37	5.51	6.97	5.18	10.01	5.30
MnO	0.10	0.07	0.08	0.07	0.05	0.00	0.00	0.03
MgO	22.95	24.76	21.90	25.37	19.61	22.85	17.97	22.21
CaO	0.00	0.03	0.02	0.03	0.00	0.03	0.02	0.10
BaO	0.48	0.00	0.43	0.02	0.82	0.09	0.80	0.10
Na_2O	0.66	0.27	0.59	0.32	0.52	0.89	0.15	0.91
K_2O	9.41	10.25	9.31	10.38	9.44	10.51	10.01	10.70
ZrO_2	nd	nd	nd	nd	nd	nd	0.06	0.11
F	2.17	2.85	1.96	2.92	0.56	2.53	nd	nd
Total	98.88	98.50	95.60	98.48	95.45	97.32	94.16	92.70
O = F	0.91	1.20	0.83	1.23	0.24	1.07		
Structural Formulae based on 22 Atoms of Oxygen (F free)								
Si	5.574	6.132	5.549	6.031	5.431	6.312	5.547	6.332
Ti	0.248	0.014	0.265	0.036	0.542	0.088	0.443	0.030
Al	2.444	1.386	2.429	1.879	2.627	1.741	2.485	1.720
Fe*	0.839	1.216	0.910	0.657	0.850	0.620	1.252	0.652
Mn	0.012	0.009	0.010	0.008	0.006	0.000	0.000	0.004
Mg	4.867	5.403	4.818	5.387	4.261	4.874	4.004	4.869
Ca	0.000	0.005	0.003	0.005	0.000	0.005	0.003	0.016
Ba	0.027	0.000	0.025	0.001	0.047	0.005	0.047	0.006
Na	0.182	0.077	0.167	0.088	0.147	0.247	0.044	0.260
K	1.708	1.915	1.754	1.887	1.756	1.919	1.910	2.008
Zr	nd	nd	nd	nd	nd	nd	0.004	0.008
Fe#	0.15	0.18	0.16	0.11	0.17	0.11	0.24	0.12

* Total iron calculated as FeO; nd = not determined
Fe# = (Fe + Mn) / (Fe + Mn + Mg)
c = core; r = rim

DISCUSSION

Textural evidence obtained from cathodoluminescence studies indicates that some of the dikes at Chip-

TABLE 7. MICA AND AMPHIBOLE COMPOSITIONS IN FENITE

Sample #	1B	1D	10A	1D	1B	1D	10A	1D
Analysis #	1	2	3	4	5	6	7	8
SiO_2 wt.%	41.25	41.54	42.22	41.64	55.61	56.48	56.54	55.14
TiO_2	0.29	0.28	0.47	0.41	0.29	0.14	0.03	0.23
Al_2O_3	11.09	11.19	11.73	11.16	1.16	0.55	0.38	0.96
Fe_2O_3	nd	nd	nd	nd	8.61	8.72	8.94	8.26
FeO*	7.64	6.02	6.44	6.75	2.94	2.58	1.51	4.30
MnO	0.14	0.05	0.10	0.11	0.12	0.02	0.10	0.13
MgO	23.52	24.43	24.43	23.59	17.48	17.68	18.48	16.58
CaO	0.01	0.00	0.02	0.00	1.14	0.12	1.20	0.84
BaO	0.09	0.02	0.05	0.04	nd	nd	nd	nd
Na_2O	0.32	0.26	0.51	0.34	9.40	9.70	9.51	9.60
K_2O	10.58	10.73	9.96	10.63	1.43	2.03	0.94	1.37
F	6.09	6.02	1.82	5.25	2.55	3.05	2.48	2.86
Total	101.02	100.54	97.75	99.92	100.73	100.97	100.11	100.27
O = F	2.56	2.53	0.77	2.21	1.07	1.28	1.04	1.20
Mica Structural Formulae based on 22 atoms of Oxygen								
Amphibole Structural Formulae based on 13 Cations and 23 atoms of Oxygen								
Si	6.002	6.017	6.006	6.041	7.833	7.953	7.935	7.869
Ti	0.032	0.031	0.050	0.045	0.031	0.015	0.003	0.025
Al	1.902	1.911	1.967	1.908	0.193	0.091	0.063	0.161
Fe^{3+}	nd	nd	nd	nd	0.912	0.924	0.944	0.888
Fe^{2+}	0.930	0.729	0.766	0.819	0.347	0.303	0.177	0.514
Mn	0.017	0.006	0.012	0.014	0.014	0.002	0.012	0.016
Mg	5.100	5.274	5.179	5.100	3.670	3.712	3.866	3.527
Ca	0.002	0.000	0.003	0.000	0.172	0.018	0.180	0.128
Ba	0.005	0.001	0.003	0.002	nd	nd	nd	nd
Na	0.090	0.073	0.141	0.096	2.567	2.648	2.588	2.656
K	1.964	1.983	1.808	1.968	0.257	0.365	0.168	0.249
Fe#	0.16	0.12	0.13	0.14				

Samples 1 - 4 mica; 5 - 8 amphibole
* For micas, total iron calculated as FeO; nd – not determined
Fe# – (Fe + Mn) / (Fe + Mn + Mg)

man Lake consist of two carbonatite phases emplaced sequentially (Fig. 2). These composite dikes show evidence of an earlier dolomitic carbonatite that is brecciated and intruded by a later, more Fe-rich carbonatite. However, in the suite as a whole, there is a general continuum of carbonate compositions (Fig. 3), which suggests that the change from dolomite toward more iron-rich compositions is the product of magmatic differentiation. It is probable that the melt in many large dolomitic carbonatite complexes evolves in a similar way (authors' unpublished data). At Chipman Lake, this differentiation is assumed to have occurred within a magma chamber below the present level of erosion, the periodic tapping of which gave rise to the dikes.

The mineralogy of the fenites at Chipman Lake shows that the addition of Na was a major factor in their genesis, but the mica-rich margins along the dikes and veinlets indicate that the final phase of metasomatism principally involved the addition of K and Mg. The problem of the sequential generation of Na- and K-rich fenites in aureoles around carbonatites, as seen at Chipman Lake, has been discussed by Woolley (1969) with respect to the Chilwa Province, Malawi. There, it was shown that the K-rich fenites are always adjacent to the carbonatite and cut the surrounding Na-rich fenites. It was suggested by Woolley that the two-stage fenitization involved emplacement of either (1) successive Na-rich and K-rich carbonatites, or (2) a silicate magma (phonolite or nephelinite?) that caused the Na-fenitization, followed by a K-metasomatizing carbonatite, or yet again (3) a carbonatite rich in both alkalis, similar in composition to that erupted from the Oldoinyo Lengai natrocarbonatite volcano (Dawson 1966, 1989), from which Na was released sequentially before K.

The evidence from Chipman Lake suggests a variant of mechanism 3, whereby Na and K are released sequentially from a carbonatite melt, albeit from a melt in which the total alkalis are considerably less than the 30 wt.% found in the Oldoinyo Lengai lavas. As described earlier, the Ca–Sr–Ba–Na–*REE* carbonate *burbankite* only occurs as small, rounded inclusions within dolomite and apatite precipitated from the least-evolved dolomitic magma. This observation suggests three possible parageneses for burbankite: (1) early precipitation as a primary phase from the dolomitic magma, (2) precipitation from an associated immiscible liquid rich in the components of burbankite, and (3) precipitation from a similarly enriched associated fluid phase trapped by the growing dolomite and apatite crystals.

The lack of crystal form and the concentration of incompatible elements in the early crystallizing burbankite would make it an unlikely early liquidus phase (Option 1). The evidence of the burbankite inclusions strongly suggests, therefore, that an Na-rich fluid or an immiscible liquid was associated with the earlier dolomitic phase of the carbonatite. This partitioning of Na, along with other elements, into a separate phase, particularly if it was a fluid phase, early in the evolution of the dolomitic magma, suggests a mechanism for the Na metasomatism. The later, more iron-rich carbonatite magma, from which phlogopite precipitates, appears to have been enriched in potassium, the ultimate release of which was responsible for the K metasomatism.

A further variant of mechanism 3 envisages the simultaneous release of Na and K into the wallrocks. Differential fixing of the alkalis, essentially a wallrock chromatographic effect, permits Na to migrate further from the contact compared to K. Although not dismissing this effect completely, the evidence presented above supports the sequential development of Na- and K-rich fenitizing fluids (*i.e.*, the early development of burbankite, the later development of phlogopite, and the disposition of the phlogopite-rich fenite zones adjacent to the carbonatites).

The debate between sequential release of Na and K, and wallrock chromatography, to explain the development of Na- and K-fenites around certain carbonatites has a long history, originating perhaps with the work of Woolley (1969). However, from this study, it would seem that the decrease in the Mg/Fe value of the Chipman Lake carbonatite magma with differentiation was linked to a corresponding decrease in Na/K, thus affording an explanation for the spectrum of fenites, in terms of Na and K, assuming that alkalis were lost continually from the evolving carbonatite magmas. Although the scale of the fenitization at Chipman Lake is small, this model, involving a decrease in Na/K in the carbonatites with time, also readily explains the broad potassium-rich fenite aureoles cutting earlier sodium-rich ones around large carbonatite intrusions, such as those of the Chilwa Province, Malawi (Woolley 1969).

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