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GEOCHEMISTRY OF THE
CARGILL CARBONATITE COMPLEX
KAPUSKASING, ONTARIO

by
JOANNA SHARPE, B.Sc. (Hons.)

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Master of Science
Department of Geology
Carleton University
Ottawa, Ontario
May, 1987

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KAPUSKASING, ONTARIO"

submitted by Joanna Sharpe, B.Sc.

in partial fulfilment of the requirements for
the degree of Master of Science

Thesis Co-Supervisor

Thesis Co-Supervisor .

Chairman, Department of Geology

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May 22, 1987

ABSTRACT

Chemical, petrographic and Rb-Sr isotopic data from a suite of sovites, rauhaugites, silicocarbonatites, pyroxenites and hornblendites from the Cargill carbonatite indicate:

- 1.) an apparent magmatic trend of increasing Fe and alkalis and decreasing Ca and Mg in both silicate and carbonate magmas.
- 2.) the increasing effect on the ultramafic rocks of re-circulating fenitizing fluids with proximity to the carbonatite core.
- 3.) an age of 1891 ± 15 Ma with an initial ratio of 0.70185 ± 0.00004 , in good agreement with a U-Pb age of 1906 ± 30 Ma and a Sm-Nd age of 1903 ± 100 Ma (Kwon, 1986). Variation in initial ratios is indicated.

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CHAPTER 1 INTRODUCTION

1.1 Introduction to the Cargill Carbonatite

1.1.1 Location, Regional and Structural Setting of the Cargill Carbonatite

Canada hosts one of the largest areas of alkaline magmatism in the world. Within this 1.3 million km² area in Ontario and Quebec, emplacement of alkalic complexes appears to be controlled by large-scale structural features such as the Kapuskasing gravity and magnetic high (Kumarapeli and Saul, 1966) (Fig. 1). The Kapuskasing Structural Zone cuts across the predominantly E-W trends of the Archean Abitibi subprovince to the east and Quetico and Wawa subprovinces to the west. The Kapuskasing structure includes paragneiss, mafic gneiss, gneissic and xenolithic tonalite and anorthosite (Percival and Card, 1983).

Within 30 km of the 600 km long axis of the Kapuskasing structure, there are 11 alkalic complexes of two distinct age groups (Allen, 1972), one at approximately 1075 Ma and the other at approximately 1800 Ma (Gittins et al., 1967). These ages correspond roughly to the Grenvillian (1000 Ma) and the Hudsonian (1800 Ma) orogenies, respectively. Backlund (1932) stressed the link between alkaline igneous activity in stable areas and simultaneous orogenic activity elsewhere. The younger complexes tend to occur in the southern part of the Kapuskasing Structural Zone and are thought to be more nephelinitic in composition (Currie, 1976). The Cargill complex, a member of the older group is located 32 km SW of Kapuskasing, Ontario.

3

1.1.2. Previous Geochemical and Petrological Studies

The Cargill carbonatite has been the subject of much interest. Although many aspects of the complex have been studied, the geochemistry has not previously been examined in detail. In 1965, as part of a study of Ontario carbonatites, Powell determined an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7019 for Cargill. Bennett et al. (1967) first mapped the complex as part of an Ontario Department of Mines reconnaissance report, while in the same year, Gittins et al. determined a K/Ar age of 1840 Ma for Cargill based on the average of two biotites. Gasparrini et al. (1971) determined the chemical variations of the amphibole and phlogopite minerals within the complex.

Allen (1972) proposed a differentiation order for the rocks of the ultramafic rim after a detailed petrological study. Gittins et al. (1975) examined the phlogopitization of the pyroxenitic rocks while Bell et al. (1982, 4987b), completed some Rb/Sr and Sm/Nd isotopic analyses as part of an isotopic study of Ontario carbonatites. Twyman's (1983) study of the Cargill complex combined experimental work on rocks of the carbonatite core and some geochemical analysis. Sage (1983b) reported on the geology of the complex as part of a study of alkaline rock complexes of Ontario. Concurrent to this study, Kwon (1986), produced some Pb and Nd analyses on a number of Ontario carbonatites including Cargill.

1.1.3. Scope of the Investigation

The present study has two major objectives:

- i) To gain an understanding of the genesis of the complex through the

use of petrography, major and trace elements, mineral chemistry and isotope geochemistry.

- ii) To obtain a more accurate emplacement age, using the Rb/Sr method.

1.2 Review of Alkalic Complexes and Carbonatites

1.2.1 Association of Alkalic Complexes and Carbonatites

Carbonatites are igneous rocks which contain greater than 50 % carbonate minerals (Streckeisen, 1979). Nearly all carbonatites are closely associated with alkalic igneous complexes (Heinrich, 1966). Alkalic mafic to ultramafic complexes are commonly characterized by rock types such as nepheline syenites, pyroxenites, ijolites and carbonatites. The similarities in the trace element geochemistry and isotopic signatures suggest genetic links and/or consanguinity between carbonates and silicates. The complexes tend to be emplaced in stable cratonic areas; however, some are present in oceanic or orogenic areas (Sorensen, 1974; Bowden, 1985).

1.2.2 Origin of Carbonatites

The genesis of carbonatites and associated alkalic rocks is highly controversial. Early theories fell into four major groups: remobilization of limestone or marble; alkaline metasomatism of limestone or marble xenoliths and roof pendants; hydrothermal replacement of alkaline rocks; and magmatic (Heinrich, 1966).

The magmatic theory is now generally accepted, largely as the result of the study of the Oldoinyo Lengai carbonatite volcano.

However, there is still much controversy, for example, about the primary or derivative nature of carbonatite magmas and the nature of the source region (Le Bas, 1977).

Carbonatite Magmas: Primary or Secondary?

There is considerable support, based on experimental petrology, fluid inclusion studies and trace element data, for the derivation of secondary carbonatite magmas by liquid immiscibility from a carbonated ultramafic magma enriched in alkalis (Heinrich, 1966; Cooper et al., 1975; Mitchell and Brunfelt, 1975; Freestone and Hamilton, 1980; Moller et al., 1980; Le Bas, 1981; Alt, 1982; Sage, 1983a; Hamilton and Bedson, 1986). There is also support, based on experimental petrology, for the differentiation of carbonatite magmas from carbonated ultramafic magmas (Twyman, 1983; Wyllie and Jones, 1984). In addition, it has been experimentally determined that primary carbonatite magmas can be produced by the melting of peridotitic material in the presence of CO_2 (Koster Van Groos, 1975; Wendlandt and Mysen, 1980; Lapin, 1984; Gittins, 1986).

Source and Relationship to the Sub-Continental Upper Mantle

Carbonatites are ideal for studying the sub-continental upper mantle because: i) they have a deep-seated origin; ii) they have a rapid ascent to the surface and iii) the Sr content is so high that even if contamination were to occur they would still retain their isotopic signatures (Bell et al. 1982). There is overwhelming evidence from Nd,

Pb and Sr isotopic data that the source area for carbonatite magmas is the large ion lithophile (LIL) element-depleted upper mantle.

Isotopic data from Ontario carbonatites indicate that a time-integrated LIL-element-depleted upper mantle reservoir formed in Archean time that was complementary to the reservoir represented by the granitoid rocks of the Superior Province (Bell et al., 1982, Bell and Blenkinsop, 1987b). In addition, the depleted reservoir was closed with respect to exchange of Rb, Sr, Sm and Nd from 3000 Ma to at least 110 Ma ago. This depleted reservoir is characterized by a Rb/Sr ratio of 0.020 ± 0.002 , a Sm/Nd ratio of 0.358 ± 0.008 and present day $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.70342 ± 0.00008 ($\epsilon_{\text{Sr}}[0] = -15.3$) and 0.51292 ± 0.00003 ($\epsilon_{\text{Nd}}[0] = 5.5$) respectively. The ϵ notation of De Paolo and Wasserburg (1976) compares the initial $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{143}\text{Nd}/^{144}\text{Nd}$ ratio at time T (R_1), to the initial ratio for bulk earth or the chondritic uniform reservoir (CHUR) (R_T) at the same time i.e.

$$\epsilon_k = \left[\frac{R_1}{R_T} - 1 \right] \times 10^4$$

where $k = \text{Sr or Nd}$

In most carbonatites positive ϵ_{Nd} and negative ϵ_{Sr} values are indicative of a time-integrated depletion of the light rare earth elements (LREE) and other LIL elements in the source region while carbonatites themselves show an enrichment in LREE. There are two possible explanations for this seeming paradox. Firstly it is believed by many that this LIL element-depleted upper mantle was metasomatically enriched in rare earth elements (REE), alkalis and volatiles. The

metasomatizing fluid is thought to be derived from the undepleted lower mantle (Kay and Gast, 1973; Frey and Green, 1974; Frey and Prinz, 1978 and Wendlandt and Harrison, 1979).

Another possibility is extremely low degrees of partial melting of the source rock. The high volatile content of carbonatite magmas lowers the viscosity which is estimated to be about 0.05 poise (Treiman and Schedl, 1983). For carbonatite magmas, very low degrees (as low as 0.1 %) of partial melting of the source rock have been calculated (Gast, 1968). Doubt has been expressed as to whether such small amounts of magma could be extracted. However because of the low viscosity, these very small volumes of carbonatite melt have been shown to be able to coalesce into discrete magmas (McKenzie, 1985). This extremely low degree of partial melting could account for the high REE contents and LREE enrichment without having to invoke mantle metasomatism (Williams et al., 1986).

Postulated source materials for carbonatites include hydrous garnet peridotite (Kay and Gast, 1973), kimberlitic or alkali basaltic rocks (Heinrich, 1966) and carbonate-bearing peridotites in areas of high heat flow under continents (Gittins, 1986). A possible source of CO₂ is carbonate which is stable at mantle conditions (Eggler et al., 1976).

Rare Earth Element Behaviour in Carbonatites

Other processes that may affect carbonatite magma evolution are fractional crystallization and liquid immiscibility. The interplay of these processes and the subsequent loss of fenitizing fluids produces a diversity of carbonatite types with varying trace and rare earth element distributions.

Fractional crystallization can increase the high REE concentration in ijolites and carbonatites; however fractional crystallization alone cannot account for the high REE contents of carbonatites vs. associated silicate rocks (Mitchell and Brunfelt, 1975; Cullers and Medaris, 1977). The concentration of the REE in younger carbonatites led Barber (1974) to suggest that crystal fractionation of calcite in Kenyan carbonatites may increase the REE content in residual liquids.

When liquid immiscibility occurs, REE will be strongly fractionated into the carbonate liquid (Eby, 1975; Mitchell and Brunfelt, 1975; Cullers and Medaris, 1977). Partition coefficients for Ce, Sm and Tm favour a carbonatite melt over a silicate melt by a factor of 2 to 3 for LREE and 5 to 8 for HREE (Wendlandt and Harrison, 1979).

Fenitization, the metasomatic alteration of wall rocks, is associated with many carbonatites. This alteration is characterized by an increase in alkalis and a decrease in silica in the country rocks. From the study of fluid inclusions in apatites, the fenitizing agent is thought to be an alkali and volatile-rich fluid (Le Bas et al., 1977).

Fenitization may overprint REE distributions. During fenitization the intermediate and heavy REE appear to be more mobile because their concentrations appear to be higher in fenites (Cullers and Medaris, 1977). Volatile transport is an important process because the vapour phase is enriched in REE relative to carbonate and silicate magmas (Mysen, 1979).

Tectonic Emplacement

Carbonatites can occur as plutons, cone sheets, pipes, dikes, sills, breccia zones, lava flows and tephra (Heinrich 1966).

Alkalic-carbonatitic complexes are normally associated with anorogenic rifting and continental separation. Even when the complexes are not directly associated with rifting, there are usually major fractures in the vicinity (Woolley, 1986). Bailey (1964) noted that the upwarping of the crust associated with the African Shield could relieve pressure, promoting partial melting by the addition of volatiles which lower the solidus. This produces less dense minerals promoting further uplift and deformation. The resulting magma coalesces and escapes through rifts that often penetrate the mantle (Bailey, 1974).

The solidus temperature of the silica-rich phase is greater than the carbonate-rich phase thus the silicate phase will crystallize first. The carbonatite magma can then intrude and react with the solid silicate phase (Rankin, 1975; Le Bas et al., 1977). There is a considerable time interval and temperature drop between ijolite crystallization and crystallization of the main carbonatite magma (Le Bas, 1981).

Carbon dioxide plays an important role in the violent emplacement of carbonatites. At less than 80 km depth the CO_2 content in the magma dramatically decreases from about 40 weight % to 5 weight % and CO_2 is fractionated into the vapour phase. This production of gaseous CO_2 may cause the explosive volcanism and violent emplacement displayed by carbonatites (Wyllie and Huang, 1976).

1.2.3 Economic Geology of Carbonatites

Carbonatite bodies contain a diversity of mineral deposits. Dawson and Currie (1984) divide carbonatite complexes into two types; the ultramafic type which contains Cu, vermiculite, Fe, P, U and Zr concentrations and the nephelinitic type which contains Nb, REE, P, and U concentrations.

The most spectacular example of an ultramafic carbonatite is the Palabora carbonatite, South Africa. The Palabora complex has three separate open pit mines which produce phosphate, vermiculite and Cu. The by-products are sulphuric acid, magnetite, nickel sulphate, zirconium sulphate, gold, silver, platinum group elements, uranium and thorium oxides. The Palabora copper deposit is located in the carbonatite core and averages 0.69% Cu (Clarke, 1981).

The Cargill carbonatite was initially examined for Cu and Ni at various times from the 1950's to 1970's by Continental Copper Mines Ltd. and by Kennco Exploration (Canada) Ltd.. Cu and Ni contents were less than 1.10 %. Sage (1983b) determined, on the basis of two sulfide-rich samples, that the Cu ranged from 0.18-0.37% and the Ni ranged from 0.02-0.15 %. The Cargill carbonatite is similar to the Palabora Complex in that both complexes are ultramafic and are enriched in apatite and vermiculite. A residual apatite deposit of 62.5 million tonnes grading 19.6 % P_2O_5 has been outlined for the Cargill carbonatite (Sandvik and Erdosh, 1977). Above the apatite residuum is a crandallite-rich layer with a high concentration of REE. The Palabora apatite mine is located in phoscorite (apatite-magnetite rock) and pyroxenite which average 2 % P_2O_5 .

(Clarke, 1981), and not in a residual deposit such as the apatite deposit at Cargill. Sherritt Gordon Ltd. are examining the vermiculite and apatite potential of the Cargill carbonatite (Kelly, pers. comm., 1985).

CHAPTER 2 LOCAL GEOLOGY

2.1 Morphology and Structure

The Cargill carbonatite complex occupies a dumbbell-shaped area approximately 7 km long and 2 km across at its maximum width. It has a pronounced magnetic anomaly with a main NE trend. The magnetic anomaly has three peaks, termed the north, south and west sub-complexes (Fig.2). Low relief combined with moderate cover of glacial tills, sands, clays and Pleistocene lake sediments result in very little outcrop; thus most of the geology is known from drill core (Allen, 1972). Most of the 190 drill holes are located in the south sub-complex.

The north and south sub-complexes are probably the faulted halves of an originally circular body (Sage, 1983b). The right lateral displacement of these two sub-complexes is approximately 4 km (Sandvik and Erdosh, 1977). The west sub-complex is approximately 4 km west of the centre of the south sub-complex, is tear-shaped, (Sandvik and Erdosh, 1977) and trends NE. This subcomplex might be related to the south subcomplex by a cross-fault (Erdosh and Sandvik, 1976).

It is also possible that the three sub-complexes may be separate intrusions. Sandvik and Erdosh (1977) point out that there is a relatively large carbonatite unit along the fault zone which may suggest that the fault pre-dates the intrusion. However, because carbonates are less competent than the surrounding silicate rocks the carbonatite could have been deformed by a post-intrusive fault. Ragged calcite grain boundaries and alternating bands of deformed and undeformed carbonates

FIGURE 2 --- Aeromagnetic map of the Cargill complex

suggest that deformation has taken place.

2.2 Major Units

The Cargill complex is formed of an inner carbonatite core and an outer pyroxenite rim that intrudes quartz diorite gneiss country rock (Figs. 3 and 4). Between the core and rim is a narrow contact zone of hybrid rocks. An exception to this is the east side of the north subcomplex and the west side of the south subcomplex where the carbonatite core is in direct contact with the quartz diorite gneiss. The units are discussed from the outer, older rim to the inner, younger core.

2.2.1 Ultramafic Rim

Previous authors have used the term pyroxenite-amphibolite for the ultramafic silicate unit. The present author however, prefers to use the term ultramafic because these rocks are considered igneous in origin and the term amphibolite implies a metamorphic origin. Even though the amphiboles in the ultramafic rocks range from pargasite to pargasitic hornblende (confirmed by microprobe analyses) the amphibole-rich unit will be called hornblendite to simplify terminology.

The ultramafic rocks consist of hornblendites and pyroxenites which grade into each other. The ultramafic rocks vary from fresh to extensively altered. The pyroxenite-hornblendite unit is medium- to coarse-grained. It is cut by many coarse-grained, carbonatite dykes which contain up to 20 % apatite (Bennett et al., 1967). Layering on the centimetre scale, visible in some of the ultramafic rocks, reflects

Fig. 4 Cross-section of the Cargill Carbonatite from Fig. 3 (after Sandvik and Erdosh, 1977)

changes in mineral proportions (presumably pyroxene, amphibole, mica and magnetite) and grain size.

2.2.2 Contact Zone

A narrow unit of hybrid rocks occurs between the ultramafic and carbonate units. Although the width is not well known it probably varies from 20-40 m. It is made up of alternating bands of carbonatite and pyroxenite which vary in thickness from centimetres to metres. The carbonate bands become less common and narrower towards the pyroxenite (Sandvik and Erdosh, 1977).

The intrusion of the carbonatite and escape of accompanying fenitizing fluids has altered some of the pyroxene in the pyroxenite to fibrous sodic amphibole (Allen, 1972). Another effect on the pyroxenite is the development of phlogopite zones along carbonate veins (Allen, 1972; Gittins et al., 1975; Sandvik and Erdosh, 1977). The contact on both sides of this hybrid zone are almost vertical (Fig. 4).

2.2.3 Carbonatite Core

The carbonatite zone comprises three different medium-grained units. The carbonatite core of the south subcomplex has an outer calcite zone and an inner siderite zone. The contact between the outer calcite unit (sövite) and the intermediate dolomite unit (rauhaugite) is gradational (Erdosh, 1977). The calcite unit is variable in width. Between the calcite and dolomite units is a transitional unit (Sandvik and Erdosh, 1977). The siderite unit has a sharp contact with the dolomite unit (Erdosh, 1979), and is found in semi-annular, lens-shaped

bodies (Sandvik and Erdosh, 1977). Ultramafic xenoliths within the carbonatite, not observed by Allen (1972), were noted by Sandvik and Erdosh (1977) and in this study.

The upper part of the carbonate zone is leached. Because the siderite unit is found only in the weathered zone, its original character is unknown (Sandvik and Erdosh, 1977). This zone is overlain by an apatite residuum which is the result of extreme weathering of the carbonatite. The uppermost part of the residuum is a REE-rich crandallite layer.

CHAPTER 3 PETROGRAPHY

3.1 Sampling

Due to the lack of outcrop, samples were obtained from drill core. A total of 37 samples was collected from the carbonatite core and the silicate rim of the south sub-complex. A representative suite of 10 thin sections and 8 polished thin sections was petrographically examined.

The localities of the six drill holes sampled are shown in Fig. 3. Two, (C-46 and C-35), are in the ultramafic rim, with C-35 being closest to the contact with the carbonatite. Four drill holes are in the carbonatite core; two (C-6 and C-23) are in the sövite and two, (C-20 and C-7) are in the rauhaugite. Drill holes in the siderite unit were not sampled. The carbonatite contains ultramafic xenoliths and quartz veins (drill hole C-7) and the ultramafic rim contains carbonatite dykes.

The carbonatite nomenclature of Brøgger (1921) has been modified by Heinrich (1966) and further slightly modified by the present author. Pure sövite has >90% calcite. Sövite has >75% calcite and the next most abundant mineral modifies the name. Rauhaugite is the dolomitic equivalent of sövite. Silicocarbonatites have 50-75% carbonates, with a modifier indicating the next most abundant mineral. Silicosövitites predominantly contain calcite while silicorauhaugites predominantly contain dolomite. The ultramafic suite consists of pyroxenite and hornblendite.

Plate 1 Sample C-23-34, sövite. Calcite with ragged grain boundaries, plane polarized light.

Plate 2 Sample C-6-326, apatite silicosövite. Curved mica cleavage traces and pull-apart texture filled with calcite, plane polarized light. cc=calcite, ph=phlogopite.

Table 1. Petrography

Sample #	Rock Type	cc	da	ap	rl	ph	ol	di	px	ts	sp	ms	mg
C-6-13	apatite-	d		r	c								
PTS	silica-silicate												
C-6-14	apatite-	d		c									
TS	silica-silicate												
C-6-63	apatite-	d		a	l	c							
PTS	silica-silicate												
C-6-16	apatite-	d		d		c							
TS	silica-silicate												
C-2-101	apatite-	d		t									
PTS & TS	silica-silicate												
C-2-173	apatite-	d		t	c	d							
TS	silica-silicate												
C-23-31	apatite-	d		c	r	t							
TS	silica-silicate												
C-23-56	apatite-	d		t	c								
PTS	silica-silicate												
C-23-73	apatite-	d		c	c	t							
TS	silica-silicate												
C-23-352	apatite-	d		c	r	t							
PTS	silica-silicate												
C-35-63	apatite-	d											
PTS	silica-silicate												
C-35-93	apatite-	d											
PTS & TS	silica-silicate												
C-35-101	apatite-	d											
PTS	silica-silicate												
C-35-176	apatite-	d											
PTS	silica-silicate												
C-46-139	apatite-	d											
PTS	silica-silicate												
C-46-167	apatite-	d											
TS	silica-silicate												
C-46-224	apatite-	d											
PTS	silica-silicate												
C-46-236	apatite-	d											
TS	silica-silicate												

Trace <1%, rare=1-5%, common=5-15%, abundant=15-30%, >30% or dominant mineral

apatite, apatite, hornblende, calcite, dolomite, quartz, orthopyroxene,

diopside, dolomite, idiomorphic, ilmenite, magnetite, muscovite, olivine,

phlogopite, pyroxene, pyroxene, pyroxene, pyroxene, pyroxene, pyroxene,

pyroxene, pyroxene, pyroxene.

Table 1 cont'd

Sample	cl	pl	others	texture	notes
C-6-145 TS			cl	f.g., inequigranular sub-an.	curved mica cleavage traces and plan, lower pleochroic curved mica cleavage traces
C-6-146 TS				m.g., inequigranular sub.	
C-6-143 PTS			pl	c.g., inequigranular sub-an.	note to saturated color grain if resolved in m.
C-6-144 TS			pl	f.m.g. sub-an.	curved mica cleavage traces
C-2-179 PTS & TS				f.g., an.	appears recrystallized
C-2-173 TS			pr	f.g., inequigranular an-sub.	trace of an. in pyrochlore
C-2-174 TS				f.g., inequigranular an.	appears recrystallized weak foliation, capillary elongation evidence of alteration
C-2-175 PTS			se	c.g., inequigranular an.	
C-2-177 TS			pr	f.g., inequigranular sub-an.	
C-2-178 PTS				f.g., an.	
C-3-61 PTS				f.m.g., inequigranular an.	if resolved in m.
C-3-91 PTS & TS				v.c.g., inequigranular	appears recrystallized
C-3-101 PTS				f.m.g. an. bl. (cl)	deuteric alteration of bl. to po. if resolved in m.
C-3-176 PTS				c.g., inequigranular sub-an.	if resolved in m.
C-46-139 PTS			id, bo sr	c.g., inequigranular an-sub.	
C-46-167 TS				m.g., inequigranular	highly altered (last specimen filled with pore space)
C-46-224 PTS			id, bo sr	c.g., inequigranular an-sub.	
C-46-226 TS			id, bo sr	c.g., inequigranular an-sub.	reaction rim (logically) to sub. d.

PTS=polished thin section, TS=thin section. All samples in thin sections are polished against 100.

f.g.=fine-grained, m.g.=medium-grained, c.g.=coarse-grained

an.=anhedral, sub.=subhedral, an.=anhedral

to serrate grain boundaries (Plate 1).

Smooth grain boundaries tend to occur between calcite and other minerals. Calcite grain boundaries are commonly serrate. The degree of serration can be very pronounced. The ragged grain boundaries are associated with bent twin lamellae, fragmented crystals and pull-apart textures (Plates 2 and 3). Twyman (1983) attributes these features to brecciation caused by faulting. Sage (1983b) notes that core samples collected from the same general area display varying degrees of deformation.

Twyman (1983) observed rare dolomite lamellae within the calcite crystals. Microprobe analyses indicate that some sovite samples contain dolomite crystals (Table II). However carbonate staining and cathodoluminescence indicate that dolomite is present only as tiny inclusions within calcite crystals.

Apatite, magnetite and phlogopite are ubiquitous. Apatite, occurring as fine-grained, euhedral, six-sided stubby or elongate crystals, ranges from 1-30% of the rock and is usually concentrated in bands. Fluid inclusion trains and solid inclusions are common. Some isolated inclusions appear to be primary.

Magnetite is fine-, to medium-grained and can occur as a cumulus or intercumulus mineral or as an alteration product resulting from serpentinization of olivine. It contains exsolved ilmenite and hercynite. The crystals usually occur as anhedral which commonly poikilitically enclose other minerals. Discrete subhedral crystals are less common. Magnetite is also commonly present as inclusions in other minerals.

Phlogopite (Table III) occurs as an interlocking mosaic of fine-

Plate 1 Sample C-23-34, sövite. Calcite with ragged grain boundaries, plane polarized light.

Plate 2 Sample C-6-326, apatite silicosövite. Curved mica cleavage traces and pull-apart texture filled with calcite, plane polarized light. cc=calcite, ph=phlogopite.

hornblende units. On the basis of mineralogy, textures and chemistry he divided the ultramafic rocks into 7 units. They are, in order of increasing differentiation (in Allen's terminology): Unit 1, olivine clinopyroxenite; Unit 2, olivine-rim magnetite clinopyroxenite; Unit 3, magnetite hornblende clinopyroxenite; Unit 4, hornblendite; Unit 5, hornblende oligoclase clinopyroxenite; Unit 6, soda-pyroxene hornblendite; and Unit 7, late stage veins and segregations.

The main pyroxene in rocks lacking soda-enrichment is diopside, however, some augite is present. Diopside (Table IV) occurs as fine- to medium-grained crystals and makes up 50 to 80% of the rock. It is anhedral to subhedral and displays zoning and twinning. Many crystals contain opaque reddish inclusions, identified by Allen (1972) as titanomagnetite, oriented along cleavage traces. Diopside exhibits minor to extensive deuteric alteration to pargasite along grain boundaries and cleavage traces.

Pargasite (Table IV) is also present in veinlets. Within the ragged pargasite crystals are small inclusions of optically continuous phlogopite with normal pleochroism. There is coarser phlogopite within and around pyroxene. In places the phlogopite is partially altered to green hydroblotite.

Olivine (Table III) is very common in the ultramafic rim and makes up 0-40% of the rock. It occurs as clusters of interlocking fine- to coarse-grained anhedral crystals. Olivine can be fresh to almost completely altered. Alteration products include "iddingsite", serpentine and magnetite along fractures, and "bowlingite" along grain boundaries.

Table II Microprobe Analyses of Carbonates

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SrO	0.5	0.5	0.5	0.5	0.8	0.2	0.3	0.2	0.3	0.2	0.8	0.8	0.8	0.8
FeO(T)	4.0	3.6	4.0	4.0	3.8	3.8	3.3	4.1	3.5	0.2	0.1	0.1	0.1	0.2
MnO	0.4	0.4	0.4	0.4	0.4	0.2	0.2	0.3	0.2	0.1	0.1	0.2	0.1	0.1
MgO	19	19	19	19	19	19	19	17	19	1.0	1.0	1.1	1.1	1.4
CaO	29	30	29	29	29	29	29	30	31	55	54	55	54	54
Tot.	54	54	54	54	54	52	52	53	54	57	56	57	56	56

Ions Per Formula Unit

Sr	0.01	0.01	0.01	0.01	0.2	0.01	0.01	0	0.01	0.01	0.02	0.01	0.02	0.02
Fe(T)	0.10	0.10	0.10	0.10	0.11	0.10	0.11	0.10	0.01	0	0	0	0.01	0
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0	0	0.01	0	0
Mg	0.89	0.89	0.90	0.91	0.90	0.94	0.94	0.91	0.91	0.05	0.05	0.05	0.05	0.07
Ca	0.99	0.99	0.98	0.97	0.98	1.0	1.0	1.1	1.1	1.9	1.9	1.9	1.9	1.9

- 1). C-20-100, coarse dolomite rim
 4). C-20-100, coarse dolomite
 7). C-23-342, dolomite core
 10). C-6-436, calcite rim
 13). C-6-436, calcite core
- 2). C-20-100, coarse dolomite core
 5). C-20-100, fine dolomite
 8). C-23-342, dolomite rim
 11). C-6-436, calcite core
 14). C-6-436, turbid calcite,
- 3). C-20-100, fine dolomite
 6). C-23-342, dolomite rim
 9). C-23-342, dolomite core
 12). C-6-436, calcite rim

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
SrO	0.8	0.8	0.8	0.8	0.78	0.8	0.8	0.9	0.8	0.8	0.8	0.9	0.8	0.9
FeO(T)	0.2	0.4	0.5	0.5	0.4	0.1	0.4	0.4	0.4	0.5	0.3	0.4	0.3	0.3
MnO	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.2	0.1	0.1	0.04	0.2	0.1
MgO	1.1	0.8	0.8	0.8	0.7	1.1	1.1	1.2	1.1	1.1	0.8	0.9	1.4	0.9
CaO	53	54	52	51	52	55	54	53	54	54	54	54	53	54
Tot.	55	56	54	54	54	57	56	56	56	56	56	56	56	56

Ions Per Formula Unit

Sr	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Fe(T)	0	0.01	0.02	0.01	0.01	0	0.01	0.01	0.01	0.01	0	0.01	0.01	0.01
Mn	0	0.01	0.01	0.01	0.01	0	0	0.01	0.01	0	0	0	0	0
Mg	0.06	0.04	0.04	0.04	0.04	0.06	0.06	0.06	0.05	0.06	0.04	0.05	0.07	0.04
Ca	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9

- 15). C-6-436, calcite core
 18). C-23-342, calcite rim
 21). C-35-93, coarse calcite rim
 24). C-35-93, coarse calcite core
 27). C-35-93, coarse calcite
- 16). C-23-342, calcite rim
 19). C-23-342, calcite core
 22). C-35-93, coarse calcite core
 25). C-35-93, fine calcite
 28). C-35-93, fine calcite
- 17). C-23-342, calcite core
 20). C-6-436, calcite core
 23). C-35-93, coarse calcite rim
 26). C-35-93, fine calcite

Cation Abundances Based on 6 Oxygen. All cation abundances total either 2.0 or 2.1
 Oxides in weight percent

Table III Microprobe Analyses of Micas, Vesuvianite and Olivine

	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	37	36	38	40	40	37	43	39	43	39	39	39
TiO ₂	0.2	2.9	0.2	0.4	0.3	0.3	0	0	0	0	0	0
Al ₂ O ₃	14	15	14	8.9	8.7	19	40	0.1	0	0	0	0
Fe(T)	17	15	17	13	14	5.2	0.3	19	17	18	17	3.7
MnO	0.4	0.3	0.4	0	0	0.2	0.3	0.4	0.5	0.6	0.7	0.1
MgO	16	15	16	23	22	1.2	0.1	41	23	43	44	41
CaO	0	0	0.1	0.1	0.1	35	0	0.1	0.2	0.1	0.1	0
K ₂ O	10	9.6	10	9.6	10	0.1	12	0	0	0	0	0
Na ₂ O	0.2	0.7	0.2	0.2	0.1	0.8	0.1	0	0	0	0	0
Total	95	94	96	95	96	99	94	100	84	100	100	84
Si	5.9	5.7	5.9	6.2	6.2	5.6	6.0	1.5	1.9	0.99	0.99	1.1
Ti	0.02	0.35	0.02	0.04	0.04	0.04	0	0	0	0	0	0
Al	2.6	2.7	2.6	1.6	1.6	3.4	6.5	0	0	0	0	0
Fe(T)	2.2	2.0	2.2	1.7	1.8	0.65	0.03	0.62	0.62	0.37	0.36	0.09
Mn	0.05	0.04	0.05	0	0	0.02	0.04	0.01	0.02	0.01	0.01	0
Mg	3.9	3.7	3.8	5.3	5.2	0.26	0.03	2.4	1.5	1.6	1.6	1.7
Ca	0	0	0.02	0.01	0.02	5.7	0	0	0.01	0.02	0	0
K	2.1	2.0	2.1	1.9	2.1	0.01	2.2	0	0	0	0	0

- 1). C-23-56, pale phlogopite (Ca,Na,K)2.2 (Mg,Fe,Ti,Al,Mn)6.7 (Si,Al)8.0
- 2). C-23-56, red phlogopite " 2.2 " 6.5 " 8.0
- 3). C-23-56, pale rim (red phlog.) " 2.2 " 6.6 " 8.0
- 4). C-23-342, phlogopite " 2.0 " 7.0 " 7.9
- 5). C-23-342, phlogopite " 2.1 " 7.0 " 7.9
- 6). C-23-56, vesuvianite* (Ca,Na,K,Mn)5.9 " 4.3 " 5.6
- 7). C-23-56, sericite (Ca,Na,K)2.2 " 4.6 " 8.0
- 8). C-46-139, olivine (Mg,Fe,Mn)3.0 (Si,Al)1.5
- 9). C-46-139, alt. of olivine " 2.2 " 1.9
- 10). C-6-436, olivine " 2.0 " 1.0
- 11). C-6-436, olivine " 2.0 " 1.0
- 12). C-6-436, alt. of olivine " 1.8 " 1.1

Cationic abundances based on 22.0 for micas, and 4.0 for olivines.

*approximate formula for vesuvianite based on 38 O.

Oxides in weight percent.

grained anhedral but is also present as coarse discrete booklets. The crystals display deep orange-red reverse pleochroism typical of "tétriferri-phlogopite" (Rimskaya-Korsakova and Sokolova, 1964). Farmer and Boettcher (1981) report that within reversely pleochroic phlogopites, the amount of Si + Al + Ti is insufficient to fill the silica tetrahedra, enabling tetrahedral Fe^{3+} (IVFe^{3+}) substitutions. This indicates an environment which is undersaturated in Al, Ti and Si similar to the kimberlitic phlogopites studied by Farmer and Boettcher (1981). They interpreted reversely pleochroic phlogopites as grains which crystallized in situ in mantle peridotites. With recent evidence (Waychunas, 1987) it appears that tetrahedral Ti^{4+} only occurs at very small concentrations even when Si^{4+} and Al^{3+} concentrations are below that required to fill the tetrahedral sites. Thus it is unlikely that "tetraferri-phlogopite" will provide any information regarding Ti content in the source region.

The micas at Cargill also display a pronounced zoning and commonly contain solid inclusions. Zoned micas display much stronger reverse pleochroism on the rims indicating that IVFe^{3+} increased and IVAl^{3+} decreased during crystallization. This conclusion agrees with mineral chemistry of Table III if FeO(T) is recalculated as ferric and ferrous iron and is also suggested by the microprobe data of Gasparini et al. (1971). Some micas display curved cleavage traces and pull-apart textures filled with later calcite (Plate 2).

Other minerals include olivine, richterite, magnesioarfvedsonite, pyrrhotite, clinohumite and vesuvianite. Olivine, averaging Fe_{80} , is fine- to medium-grained, euhedral to subhedral and varies from very fresh to almost completely altered. Alteration products are serpentine,

iddingsite and bowlingite. Clinohumite, observed in only one thin section, occurs as fine corroded grains. It was identified on the basis of optical properties and energy dispersive microprobe data. In addition Sage (1983b) identified clinohumite from Cargill on the basis of X-ray diffraction. Twyman (1983), on the basis of textural evidence, interpreted this mineral to be a primary magmatic phase and suggested that clinohumite could replace olivine in a peritectic reaction.

Amphiboles are identified as magnesio-arfvedsonite (Leake, 1979) on the basis of optical and chemical data (Table IV) and richterite on the basis of optical properties. Amphibole needles occur as aggregates of pale green, fine-grained, acicular and prismatic crystals. Some amphiboles are corroded and partially replaced by calcite. Fine-grained pyrrhotite is present in minor amounts. Vesuvianite (alternatively, grossular), is indicated by optical properties, X-ray diffraction and microprobe data (Table III). However vesuvianite is an unusual mineral for carbonatites.

Rauhaugites and Silicorauhaugites

The rauhaugites and silicorauhaugites contain much less silicate, oxide and phosphate minerals than the calcite-rich rocks. Phlogopite can have either normal or reverse pleochroism in these layers. These rocks are fine-grained and inequigranular and the crystals are subhedral to anhedral.

The degree of recrystallization is greater in the rauhaugites than in the sövites. The grain boundaries are serrate. Dolomite displays a

bimodal grain size distribution with larger grains (ave. 0.75 mm) set in a finer-grained (ave. 0.20 mm) matrix. Within the larger grains, there are some fine-grained patches. Twin lamellae are discontinuous, terminating at the fine-grained patches, but can be traced into the coarse-grained patches. This suggests that the fine-grained material is due to recrystallization strain. Chemical analyses of fine and coarse grains are given in Table II.

The amphibole is identified as magnesio-arfvedsonite on the basis of optical properties. It occurs as fine acicular and prismatic crystals concentrated in layers throughout the drill core. The layers, sub-parallel to the core axis, are wavy and range from 0.5 to 1.5 mm wide. Phlogopite (Table III) with normal pleochroism occurs in these layers. These crystals form fine-grained, interlocking anhedral mosaics and contain inclusions of calcite and magnesio-arfvedsonite.

Apatite and magnetite are less common than the silicate minerals. Apatite occurs as fine isolated crystals or in veinlets while magnetite is found as scattered anhedral grains or along cleavage traces in the mica.

3.2.2 The Ultramafic Rim

The rocks of the ultramafic rim can be divided into two major types, pyroxenite and hornblendite. The pyroxenites can be sub-divided into two groups; those with soda-enrichment (containing aegirine-augite) and those without soda-enrichment (containing diopside).

Allen (1972), in a study of the rocks of the ultramafic rim suggested that fractional crystallization produced the Na-pyroxene

hornblende units. On the basis of mineralogy, textures and chemistry he divided the ultramafic rocks into 7 units. They are, in order of increasing differentiation (in Allen's terminology): Unit 1, olivine clinopyroxenite; Unit 2, olivine-rim magnetite clinopyroxenite; Unit 3, magnetite hornblende clinopyroxenite; Unit 4, hornblendite; Unit 5, hornblende oligoclase clinopyroxenite; Unit 6, soda-pyroxene hornblendite; and Unit 7, late stage veins and segregations.

The main pyroxene in rocks lacking soda-enrichment is diopside, however, some augite is present. Diopside (Table IV) occurs as fine- to medium-grained crystals and makes up 50 to 80% of the rock. It is anhedral to subhedral and displays zoning and twinning. Many crystals contain opaque reddish inclusions, identified by Allen (1972) as titanomagnetite, oriented along cleavage traces. Diopside exhibits minor to extensive deuteric alteration to pargasite along grain boundaries and cleavage traces.

Pargasite (Table IV) is also present in veinlets. Within the ragged pargasite crystals are small inclusions of optically continuous phlogopite with normal pleochroism. There is coarser phlogopite within and around pyroxene. In places the phlogopite is partially altered to green hydrobiotite.

Olivine (Table III) is very common in the ultramafic rim and makes up 0-40% of the rock. It occurs as clusters of interlocking fine- to coarse-grained anhedral crystals. Olivine can be fresh to almost completely altered. Alteration products include "iddingsite", serpentine and magnetite along fractures, and "bowlingite" along grain boundaries.

Table 12. Microprobe Analyses of Amphiboles and Pyroxenes.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
SiO ₂	56	56	53	51	50	50	51	51	53	53	50	51	53	56
FeO	0.1	0.2	3.6	3.1	2.5	2.7	2.8	1.1	0.8	0.5	1.7	1.3	0.6	0.7
Al ₂ O ₃	0.1	0.2	11	11	11	13	13	2.5	1.9	0.7	3.6	3.2	2.6	2.1
FeO(T)	0.1	7.2	11	15	15	2.8	7.99	8.1	0.3	0.3	5.1	4.9	3.0	11
MnO	0	0	0.2	0.3	0.4	0.3	0	0.3	0.1	0.1	0.1	0.1	0.3	0.2
MgO	19	20	16	12	12	17	17	12	17	17	15	15	17	11
CaO	0.0	0.0	1.2	1.1	1.1	1.3	1.3	0	0	0	2.5	2.6	0	0
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.12	2.8	1.2	0.3	0.5	0.6	0.7	0.3	0.4
K ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	0	0
Total	96	97	97	99	98	97	99	99	100	99	101	100	100	101

Ions Per Formula Unit

Si	3.1	3.0	2.4	2.1	2.1	2.0	2.0	1.9	2.0	2.0	2.1	2.0	2.1	2.0
Al	0.01	0.02	0.4	0.4	0.3	0.3	0.3	0.03	0.2	0.1	0.9	0.8	0.02	0.02
Al	0.02	0.03	1.5	1.5	1.5	2.2	2.2	0.1	0.08	0.03	0.16	0.14	0.09	0.08
Fe(T)	1.1	0.89	1.3	1.9	2.0	0.97	0.96	0.25	0.20	0.13	0.16	0.13	0.11	0.33
Mn	0	0	0.02	0.04	0.05	0.04	0	0.01	0	0	0	0	0.01	0.01
Mg	4.1	4.3	3.2	2.7	2.7	3.7	3.6	0.73	0.86	0.92	0.82	0.84	0.86	0.62
Ca	0.32	0.57	1.8	1.7	1.8	2.1	2.0	0.88	0.94	0.89	0.98	0.95	0.89	0.81
Na	2.3	2.0	0.84	0.98	1.1	0.96	0.78	0.09	0.05	0.03	0.06	0.05	0.17	0.12
K	0.06	0.04	0.16	0.28	0.26	0.30	0.29	0	0	0	0	0	0.04	0

1). C-23-342, magnesioarfvedsonite (Ca,Mg,R)Al₂(Si,Fe,Ti,Al,Mn)O₂ (Si,Al)O₄

2). C-23-342, magnesioarfvedsonite

3). C-46-139, pargasitic hornblende

4). C-35-176, pargasite

5). C-23-56, pargasite

6). C-35-101, pargasite

7). C-35-101, pargasite

8). C-35-176, actinolite

9). C-46-139, actinolite

10). C-46-139, diopside

11). C-35-101, diopside

12). C-35-101, diopside

13). C-23-56, actinolite

14). C-23-56, actinolite

Cationic abundances for pyroxenes based on 6 oxygens and for amphiboles on 23 oxygens, oxides in weight percent.

An olivine rim can occur between magnetite and clinopyroxene crystals.

The olivine appears to have reacted with the magma to produce magnetite and pyroxene.

Magnetite occurs as anhedral and as fine grains along olivine fractures. The anhedral can poikilitically enclose other minerals and commonly subhedral magnetite is poikilitically enclosed by pyroxene. Hercynite and ilmenite are exsolved in magnetite. The diopsidic unit also contains minor chalcopyrite and pyrrhotite and secondary sphene and calcite associated with fractures and void spaces. Sphene and olivine do not occur together.

In the pyroxenites and hornblendites pargasite and pargasitic hornblende (Table IV) occur as coarse anhedral or as alteration products along cleavage traces or grain boundaries of the aegirine-augite (Plate 5). Some amphibole poikilitically encloses optically continuous phlogopite with discontinuous rims of chloritized or reduced phlogopite. This material also fills cleavage traces in the amphibole. Amphibole can poikilitically enclose the soda-pyroxene.

The green pyroxene is identified as aegirine-augite (Deere et al. 1978) on the basis of optical properties and microprobe data (Table IV). It is medium-grained and contains many calcite crystals, interpreted as fracture fillings. Phlogopite appears as a replacement mineral. Aegirine-augite is altered to an unidentified yellowish material along fractures.

The oxides consist of medium-, to coarse-grained magnetite anhedral with exsolved ilmenite blebs and lamellae. The sulfide assemblage consists of fine-, to medium-grained pyrrhotite containing blebs of chalcopyrite and in some cases pentlandite. Chalcopyrite also occurs as

Plate 5 Sample C-23-56, aegirine-augite hornblendite xenolith.
Alteration of pyroxene to amphibole along grain boundaries,
plane polarized light. aeg=aegirine-augite, ps=pargasite.

discrete grains.

Sphene rims magnetite grains but is more common as porous networks and discrete crystals which appear to invade and replace the pyroxene/hornblende assemblage. It is embayed by calcite.

Phlogopite varies from fine-, to coarse-grained, has bent cleavage traces and normal pleochroism. The mica formed as a result of the fenitizing fluid (Gittins et al., 1975). It is present in fractures within the pyroxene and in some samples it appears to replace amphibole. It also contains calcite and amphibole inclusions.

Irregular patches of sericite occupy many interstices as a replacement phenomenon. Sericite is intermixed with calcite, corroded pargasite and reddish-brown needles of an unidentified mineral. When sericite patches and pargasite are in contact there is often a bluish-green rim on the pargasite which may be a replacement amphibole.

Calcite occurs interstitially or as fracture fills within grains. It appears to be the last mineral to crystallize. It can also replace sericite.

CHAPTER 4 GEOCHEMISTRY: RESULTS AND DISCUSSION

4.1 Introduction

The data obtained include major element, trace and rare earth element abundances, and Rb-Sr isotope measurements. Thirty-six powdered samples from Cargill were analyzed by X-ray fluorescence for major and trace elements. Fifteen samples were selected for Instrumental Neutron Activation Analysis (INAA) of trace and rare earth elements. Twelve whole rock samples and 4 mineral separates from Cargill were analyzed for Rb and Sr contents and Sr isotopic composition. In addition, microprobe data from pyroxenes was used to try to establish magmatic trends.

4.2 Major and Trace Elements by X-Ray Fluorescence

Major and trace elements were analysed at the Department of Geology, University of Ottawa. Analytical details are given in Appendix II. The results from 36 samples are given in Table V. Results from rocks within the carbonatite core are first compared internally and then compared to those from other carbonatites.

The major element variations among sovites, silicocarbonatites and rauhaugites are shown in Table V. SiO_2 , Al_2O_3 , Na_2O , K_2O , TiO_2 and P_2O_5 increase from rauhaugites to sovites to silicocarbonatites, a relationship related to changes in proportions of mica, apatite, amphibole and ilmenite. The SiO_2 content is higher in sovites than in rauhaugites reflecting the petrographic observation that the dolomitic types contain less silicate minerals. Variations in MgO and CaO

Table V Major and Trace Elements by XRF and Loss On Ignition

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ T	MgO	CaO	Na
C-6-83	4.1	0.6	2.9	4.0	46	
C-6-93	18	3.7	12.4	12	25	0.8
C-6-135	22	2.3	7.7	15	25	1.0
C-6-198	14	2.1	15	7.8	31	0.0
C-6-285	0.4	0.1	2.9	2.4	50	0
C-6-326	3.8	1.1	12	3.7	41	0
C-6-407	0.6	0.1	2.2	1.9	51	0
C-6-436	2.8	0.2	6.5	3.8	47	0
C-6-514	2.7	0.2	10	3.3	47	0
C-6-547	3.7	0.4	7.1	4.7	45	0
C-7-66	81	0.1	7.3	0.1	4.0	0
C-7-69	63	0	6.7	0	2.1	0
C-20-100	5.3	0	10	18	26	0.0
C-20-159	0.6	0	4.7	19	30	0
C-20-173	0.5	0	4.6	19	30	0
C-20-238	0.8	0	4.7	19	30	0.0
C-20-267(1)*	0.1	0	4.8	19	30	0
C-20-267(2)*	0.1	0	4.8	19	30	0
C-23-34	0.3	0	1.0	2.2	51	0
C-23-56	33	10	17	12	10	1.0
C-23-58	1.2	0.1	1.4	2.7	50	0
C-23-73	1.9	0	1.5	3.0	49	0
C-23-154	11	2.2	17	8.1	30	0.0
C-23-184	8.1	0.5	7.9	6.3	39	0.0
C-23-278	4.6	0.1	2.3	4.1	46	0.0
C-23-342	1.6	0.1	3.0	2.6	49	0
C-35-68	36	3.4	23	7.7	17	1.0
C-35-93	0.1	0	0.5	1.0	53	0.0
C-35-101	37	3.3	22	12	18	0.0
C-35-154	28	9.3	18	13	12	0.0
C-35-201	9.0	1.9	5.4	5.6	40	0
C-46-139	50	1.5	8.5	17	20	0.0
C-46-160	36	6.2	21	15	9.7	2.0
C-46-167	35	6.5	16	14	14	2.0
C-46-192	42	3.9	19	14	16	0.0
C-46-224	38	3.7	23	16	14	0.0
C-46-226	39	3.5	22	17	14	0.0

C-6-83= sövite, C-6-93= phlogopite silicosövite, C-6-135= phlogopite
C-6-326= apatite sövite, C-6-407, sövite, C-6-436, apatite sövite,
sövite, C-7-66= quartz vein, C-7-69= quartz, NG-1= nearby gabbroic
C-20-173= phlogopite silicorauhaugite, C-20-238= rauhaugite, C-20-
C-23-58= sövite, C-23-73= apatite silicosövite, C-23-154= phlogopite
C-23-278= richterite silicosövite, C-23-342= apatite sövite, C-35-
C-35-154= diopsidic pyroxenite, C-35-201= silicosövite dyke, C-46-
C-46-167= hornblende pyroxenite, C-46-192= diopsidic pyroxenite, C-

	K ₂ O	TiO ₂	P ₂ O ₅	MnO	S	LOI	Total
0.1	0.5	0.3	2.2	0.2	0	37	98
3	2.9	1.9	2.2	0.2	0.2	18	98
0	1.9	1.1	1.0	0.2	0.1	22	100
7	1.9	1.5	4.6	0.2	0.1	21	100
	0	0.2	0	0.1	0	42	98
	0.9	1.0	3.3	0.1	0.3	30	98
	0.1	0.1	0.8	0.1	0.1	41	98
	0.1	0.4	6.8	0.1	0.2	32	100
	0.1	0.8	24	0.1	0.1	18	107
	0.3	0.5	5.5	0.1	0.1	32	99
	0	0.1	3.9	0.2	0.3	4.0	101
	0	0.0	2.2	0	0.1	4.2	79
1	1.1	0	0.9	0.4	0.2	45	107
	0	0	0	0.4	0	46	100
	0	0	0	0.4	0	39	94
1	0.1	0	0	0.4	0	45	100
	0	0	0	0.4	0	45	100
	0	0	0	0.4	0	45	99
	0.3	0	0	0.2	0	43	99
2	6.1	4.0	0	0.2	0	6.0	100
	0.1	0	0.1	0.2	0	42	98
	0.1	0	0.9	0.2	0	40	102
1	2.7	1.1	0	0.2	0.2	29	102
4	0.7	0.2	5.1	0.2	0.5	25	94
2	0.3	0	3.3	0.2	0.2	36	98
	0.2	0	3.6	0.1	0.1	36	97
4	0.5	8.1	0	0.3	0.3	1.3	99
1	0	0	0	0.1	0	43	99
5	0.1	4.5	0	0.2	0.1	0.3	98
8	6.2	3.2	0.4	0.2	0	8.5	99
	1.6	1.4	6.2	0.1	0	26	98
5	0	0.8	0	0.1	0.1	1.4	100
0	0.9	2.2	1.3	0.2	0.4	5.6	100
6	0.7	2.0	0.5	0.2	0.1	8.5	100
8	0.1	2.5	0	0.2	0.3	0.7	100
6	0.1	3.0	0	0.2	0.1	1.2	100
5	0	2.8	0	0.2	0.2	0.9	100

te silicosövite, C-6-198= phlogopite silicosövite, C-6-285= sövite,
C-6-514, apatite sövite, C-6-547= phlogopite
pyroxenitic body, C-20-100= rauhaugite, C-20-159= rauhaugite, C-
267= rauhaugite, C-23-34= sövite, C-23-56= hornblendite xenolith,
te silicosövite, C-23-184= richterite silicosövite,
63= hornblende pyroxenite, C-35-93= sövite dyke, C-35-101= diopsidic pyroxenite,
139= olivine pyroxenite, C-46-160= phlogopite pyroxenite,
46-224= olivine pyroxenite, C-46-226= olivine pyroxenite, * sample run in duplicate

Table V Continued (ppm)

Sample	Be	Cr	Zr	Sr	Rb	Y	Nb
C-6-83	275	<10	200	4000	10	100	20
C-6-93	275	20	175	2000	90	60	100
C-6-135	200	20	1600	2000	55	60	100
C-6-198	275	350	500	2400	50	65	50
C-6-285	275	<10	110	4500	<10	90	<10
C-6-326	275	10	90	3400	20	65	20
C-6-407	275	<10	100	4000	<10	100	<10
C-6-436	200	<10	150	3500	<10	100	<10
C-6-514	150	<10	100	3200	<10	120	<10
C-6-547	225	<10	2000	3500	10	100	<10
C-7-66	40	200	250	250	<10	130	<10
C-7-69	45	160	350	140	<10	70	<10
C-20-100	110	<10	90	4000	100	20	700
C-20-159	65	<10	80	3500	<10	20	<10
C-20-173	50	<10	80	4000	<10	20	<10
C-20-238	55	<10	90	4000	<10	20	<10
C-20-267(1)*	50	<10	90	4000	<10	20	<10
C-20-267(2)*	55	<10	90	4000	<10	10	<10
C-23-34	450	<10	100	4500	<10	90	<10
C-23-56	900	20	500	700	200	20	170
C-23-58	350	<10	120	5000	<10	90	<10
C-23-73	325	<10	125	5000	<10	90	40
C-23-154	225	20	70	2800	80	40	70
C-23-184	225	<10	90	3400	20	80	20
C-23-278	400	<10	800	4000	10	100	<10
C-23-342	250	<10	100	4000	<10	90	<10
C-35-63	<10	40	800	325	10	55	450
C-35-93	300	<10	130	6000	<10	90	<10
C-35-101	<10	450	140	225	<10	20	35
C-35-154	2000	20	400	1200	180	20	140
C-35-201	275	<10	275	3600	50	80	110
C-46-139	45	2200	20	120	<10	20	<10
C-46-160	120	350	600	175	30	20	120
C-46-167	130	300	400	300	20	30	90
C-46-192	<10	900	55	170	<10	20	<10
C-46-224	<10	550	45	110	<10	20	<10
C-46-226	<10	600	40	90	<10	20	<10

Zn	Ni	K/Rb	Rb/Sr	Ba/Sr
10	<10	294	0.0	0.07
90	45	285	0.04	0.13
45	<10	286	0.03	0.10
110	20	324	0.02	0.12
<10	<10	412	0	0.06
70	<10	300	0.01	0.08
20	4	984	0	0.06
35	<10	178	0	0.05
50	<10	263	0	0.05
50	0	251	0	0.06
<10	20	—	0	0.16
10	10	—	0	0.33
45	<10	94	0.03	0.03
10	<10	18	0	0.02
20	<10	50	0	0.01
10	<10	79	0	0.01
10	10	0	0	0.01
<10	<10	0	0	0.01
<10	<10	0	0	0.10
200	10	265	0.27	1.19
<10	<10	163	0	0.07
<10	<10	181	0	0.07
120	<10	283	0.03	0.08
30	<10	376	0.	0.07
<10	<10	245	0	0.09
<10	<10	202	0	0.06
140	<10	347	0.04	0
<10	<10	0	0	0.05
80	130	1390	0	0
160	60	292	0.15	1.59
<10	10	266	0.01	0.08
20	450	0	0	0.33
130	400	271	0.14	0.64
100	400	287	0.07	0.46
90	500	0	0	0
110	400	—	0	0.07
100	400	—	0	0

correspond to the type of carbonate mineral present. The total Fe increases from sövites to rauhaugites to silicocarbonatite reflecting the increasing amounts of magnetite.

Minor elements except for Zr and Sr do not vary significantly between rock types. Increasing amounts of zircons cause Zr to increase from rauhaugites to sövites to silicocarbonatites. Sr increases from silicocarbonatite to rauhaugite to sövite in accord with the amount of calcite present. These variations among rock types suggest that the carbonate magma was becoming enriched in Fe and Mg and depleted in Si, Al, Na, K, Ti and P with differentiation. These trends could be caused by fractionation of apatite, calcite and mica.

The data of ~~Table~~ V were used to construct variation diagrams. Forty-seven variation diagrams were produced by computer reduction of the data. The abscissae were SiO_2 , Al_2O_3 , Sr, Ba, Fe_2O_3 and CaO. The ordinates were Na_2O , K_2O , TiO_2 , P_2O_5 , Zr, Ba, Nb and Ba/Sr. All abscissae were plotted against all ordinates. Fair linear trends were observed in several variation diagrams, in particular Na_2O vs SiO_2 and K_2O vs SiO_2 . Many of the variation diagrams show an approximate linear trend from the pyroxenite to silicocarbonatite to sövite to rauhaugite data, suggesting a genetic link among these rock types.

Several attempts have been made to establish the average and range of carbonatite compositions. The main problem is the extreme variability of carbonatites and of carbonatite nomenclature. The typical carbonatite values of Gold (1966), which are used widely in the literature as a comparison, include analyses of both sövites and silicocarbonatites from 55 carbonatites.

The data from Cargill are compared with Gold's typical values (Table VI). It is apparent that the concentration of P_2O_5 is nearly double and the MnO , Al_2O_3 and Na_2O contents are slightly less than the typical carbonatite. The other major elements are similar to the typical values of Gold (1966). All of the trace elements in the Cargill carbonatite are present in about half the amount found in the typical carbonatite except for Ba which is an order of magnitude lower than the value cited by Gold (1966). The low trace element contents suggest that the original magma was impoverished in the trace elements to some degree. This could be related to either a lower degree of metasomatism of the source area or a higher degree of partial melting of the source rock.

4.3 Trace and Rare Earth Elements (REE) by Instrumental Neutron Activation Analysis

Fifteen Cargill whole rock samples were analyzed by Nuclear Activation Services, McMaster University, for trace and rare earth elements. Analytical details are given in Appendix III. There is good agreement between XRF and INAA for all elements except Fe. Since the agreement is better for samples with low Fe contents, a probable explanation is that both methods are calibrated for Fe at trace element levels.

In general, carbonatites have the highest REE concentrations of any rock type known. Total rare earth element contents for carbonatites range from 72-15,515 ppm and La/Lu ratios range from 7.1-1240 (Henderson, 1984). Rocks from Cargill have total REE contents that range from 570 ppm in the rauhaugites, 640 ppm in the ultramafics, 1960 ppm in the

Table VI A Comparison of Cargill With A Typical Carbonatite

	1	2	3	4	5	6
SiO ₂ (wt %)	1.44	2.62	12.67	42.62	4.88	5.67
Al ₂ O ₃	0.02	0.35	1.81	4.35	0.65	1.77
Fe ₂ O ₃ T	5.81	3.78	11.70	17.36	6.19	7.59
MgO	18.56	3.20	8.69	11.4	7.80	6.10
CaO	28.98	47.52	32.75	12.82	39.93	37.06
Na ₂ O	0.03	0.04	0.49	0.98	0.15	1.09
K ₂ O	0.24	0.38	1.71	1.15	0.66	0.87
TiO ₂	0.01	0.3	1.1	2.82	0.44	0.5
P ₂ O ₅	0.17	2.52	6.19	0.65	2.94	1.73
MnO	0.42	0.15	0.17	0.2	0.21	0.78
S	0.03	0.09	0.20	0.16	0.10	---
Ba (ppm)	65.6	297	230	243	231.7	4031
Cr	3	1.85	72.2	459	19.7	102
Zr	85.4	325	413	284	296.7	641
Sr	3885	4257	2625	306	3771	7256
Rb	23.8	10.8	47.8	32.9	22.8	52
Y	19.2	91.3	71.8	34.2	71.3	---
Nb	140.4	16.5	56.2	79.5	52.4	---
Zn	19.6	15.1	76.3	96.2	31.3	---
Ni	2.4	1.23	12.5	228	4.3	32
LOI	44.1	36.7	21.0	3.32	---	---

- 1) average of Cargill rauhaugites (5 analyses)
- 2) average of Cargill sövites (13 analyses)
- 3) average of Cargill silicocarbonatites (6 analyses)
- 4) average of ultramafics (11 analyses)
- 5) average Cargill carbonatite
- 6) "typical" carbonatite; Gold (1966).

silicocarbonatites and 2240 ppm in the sövites. Chondrite-normalized La/Lu ratios range from 18 in the ultramafics, 31 in the sövites, 34 in the silicocarbonatites and 77 in the rauhaugites (Tables VII and VIII). The LREE enrichment is more pronounced in the carbonate rocks, particularly the rauhaugites. In ijolites, tinguates and sövites from the Fen alkaline complex, the La/Yb ratios range from 40-60 (Mitchell and Brunfelt, 1975) whereas the carbonate and ultramafic rocks of Cargill have La/Yb ratios which range from 15-69. Therefore, the total REE contents and LREE/HREE ratios of the Cargill complex are not exceptionally high for carbonatites.

In general sövites and rauhaugites have similar REE contents and trends on chondrite-normalized diagrams (Henderson, 1984). Within Cargill, rauhaugites and sövites have similar patterns but rauhaugites have much lower REE contents than sövites (Fig. 5). This has also been documented at Alno, Sweden and Fen, Norway (Moller et al., 1980). The opposite situation exists in some Kenyan carbonatites (Barber, 1974).

Alkalic rocks associated with carbonatites normally have lower REE contents (Henderson, 1984) but at Cargill the REE contents of the associated ultramafic rocks are intermediate between those of the rauhaugites and sövites. The unusually low REE contents in rauhaugite may reflect the low abundance of apatite in these rocks. The ultramafic rocks also display negative La, Ce and Nd anomalies. This may occur because heavy and intermediate REE are more mobile in fenitizing fluids (Cullers and Medaris, 1977) and will be enriched to a greater extent in fenitized rocks, making the LREE appear relatively depleted. This is supported by the mineralogical evidence that many of the ultramafics were fenitized

Table VII Trace and Rare Earth Element Data

Element (ppm)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sr	Rb
C-1-135	1.1	3.2	2900	17	650	71	60	31	110	170	1	1	1	1	1.5	3.7
C-2-135	1.1	0.5	510	4.7	7.7	2.2	11	50	30	30	1	1	1	1	1.3	4.0
C-3-135	1.1	0.3	670	19	4.1	3.5	10	50	63	63	1	1	1	1	0.5	5.0
C-4-135	0.6	0.7	430	14	7.9	3.4	8.6	50	50	48	1	1	1	1	1.2	1.1
C-5-135	0.8	0.3	950	25	4.0	3.7	7.9	80	80	80	1	1	1	1	0.1	0.2
C-6-135	0.6	0.2	460	8.1	7.8	0.72	1.9	50	50	30	1	1	1	1	0.3	1.1
C-7-135	1.2	4.0	9400	26	13	11	57	50	50	30	1	1	1	1	0.2	4.7
C-8-135	1.4	2.4	5900	23	9.4	6.2	6.3	90	90	80	1	1	1	1	1.0	4.30
C-9-135	0.8	1.0	1200	7	9.1	2.4	14	60	60	40	1	1	1	1	0.2	0.4
C-10-135	0.4	0.4	620	1.9	6.5	0.40	0.3	60	60	20	1	1	1	1	0.2	0.7
C-11-135	0.1	0.1	1200	1.2	90	31	150	180	40	40	1	1	1	1	0.2	0.2
C-12-135	1.7	4.6	3100	9.0	20	4.1	25	50	60	60	1	1	1	1	0.1	1.1
C-13-135	0.7	0.2	430	60	380	6.2	55	50	50	190	1	1	1	1	1.1	0.1
C-14-135	36	12	3.7	1	1	271	133	133	22	6.9	2.7	2.7	2.7	2.7	0.30	80
C-15-135	10	10	0.5	1	1	446	200	200	33	12	4.1	4.1	4.1	4.1	0.52	2.30
C-16-135	21	21	0.5	1	1	453	200	200	35	10	3.9	3.9	3.9	3.9	0.84	3.30
C-17-135	10	10	0.5	1	1	131	59	59	48.9	2.7	0.8	0.8	0.8	0.8	0.1	0.40
C-18-135	71	0.2	0.25	1	1	1.6	70	70	8.5	2.4	0.6	0.6	0.6	0.6	0.09	1.30
C-19-135	74	0.2	1.0	1	1	1.9	100	100	8.5	2.4	0.6	0.6	0.6	0.6	0.09	1.30
C-20-135	212	0.2	0.5	2	2	428	202	202	35	11	3.7	3.7	3.7	3.7	0.08	4.20
C-21-135	48	14	18	3	3	113	58	58	12	3.7	0.7	0.7	0.7	0.7	0.05	0.40
C-22-135	235	0.2	3.2	4	4	52	260	260	43	11	4.1	4.1	4.1	4.1	0.08	1.30
C-23-135	235	0.2	0.5	4	4	523	276	276	46	11	4.1	4.1	4.1	4.1	0.08	1.30
C-24-135	103	30	79	12	12	136	214	214	42	11	4.1	4.1	4.1	4.1	0.08	1.30
C-25-135	306	0.2	0.5	4	4	641	280	280	47	11	4.1	4.1	4.1	4.1	0.08	1.30
C-26-135	12	12	6.7	13	13	90	56	56	12	3.7	0.9	0.9	0.9	0.9	0.27	3.30
C-27-135	25	6.3	13	5	5	375	278	278	47	19	3.9	3.9	3.9	3.9	0.65	4.40
C-28-135	7.3	1.5	0.5	54	7	33	12	12	2.6	0.83	0.4	0.4	0.4	0.4	0.1	3.30

C-1-135= phlogopite sillimanite; C-2-135= phlogopite sillimanite; C-3-135= phlogopite sillimanite; C-4-135= phlogopite sillimanite; C-5-135= phlogopite sillimanite; C-6-135= phlogopite sillimanite; C-7-135= phlogopite sillimanite; C-8-135= phlogopite sillimanite; C-9-135= phlogopite sillimanite; C-10-135= phlogopite sillimanite; C-11-135= phlogopite sillimanite; C-12-135= phlogopite sillimanite; C-13-135= phlogopite sillimanite; C-14-135= phlogopite sillimanite; C-15-135= phlogopite sillimanite; C-16-135= phlogopite sillimanite; C-17-135= phlogopite sillimanite; C-18-135= phlogopite sillimanite; C-19-135= phlogopite sillimanite; C-20-135= phlogopite sillimanite; C-21-135= phlogopite sillimanite; C-22-135= phlogopite sillimanite; C-23-135= phlogopite sillimanite; C-24-135= phlogopite sillimanite; C-25-135= phlogopite sillimanite; C-26-135= phlogopite sillimanite; C-27-135= phlogopite sillimanite; C-28-135= phlogopite sillimanite.

Table VIII Chondrite-Normalized Rare Earth Elements

C-6-135 C-6-198 C-6-285 C-20-10 C-20-159 C-20-238 C-27-34 C-23-56 C-23-184 C-23-342 C-35-63

La	385	624	685	198	214	217	624	140	688	753	303
Ce	298	490	498	155	160	164	470	124	552	575	336
Nd	208	313	323	92	94	102	310	91	406	428	330
Sm	113	193	177	45	44	43	177	59	223	235	215
Eu	80	160	138	37	33	33	151	5.0	178	205	175
Tb	57	87	83	17	13	11	83	26	87	102	89
Dy	26	38	46	6.3	6.3	5.3	44	12	45	54	42
Yb	18	22	31	3.3	2.9	2.9	30	7.6	24	29	19
Lu	15	18	25	2.9	2.7	2.40	24	7.40	19	22	14

C-35-93 C-35-176 C-35-201 C-46-139

Ave. Sovites Rauhaugites Silicoxanthites Ultraphies

La	894	95	756	21	739	210	613	140
Ce	714	99	631	59	562	160	493	155
Nd	438	88	434	19	376	96	340	132
Sm	239	59	243	13	207	44	193	87
Eu	79	51	205	11	168	34	156	61
Tb	96	19	83	8.5	91	13	79	30
Dy	43	12	49	4.3	47	6.0	40	18
Yb	29	6.9	26	3.4	30	3.1	23	9.2
Lu	23	6.5	19	2.9	24	2.7	18	7.7
Total					2244	569	1953	643
La/Lu					31	77	34	14
La/Yb					25	39	27	15

Fig. 5 Chondrite-normalized REE of sövites, rauhaugites, silicocarbonatites, and ultramafics. Chondrite values from Wakita and Zellmer (unpublished) quoted in Wakita et al., (1971)

and also by major element chemistry (Table V) which indicates higher CaO , K_2O and Na_2O in ultramafic samples which appear to be more fenitized.

The trace and rare earth element contents of Cargill samples are normalized with respect to the estimated mantle compositions of Wood (1979) (Figs. 6,7,8,9). Within the rauhaugites, sövites and silicocarbonatites the trace and rare earth element patterns are relatively consistent for each group of rocks. In contrast the ultramafic rocks have trace and rare earth element patterns which are quite variable. Samples C-23-56, C-35-63 and C-35-176 consist mainly of hornblende and aegirine-augite while C-46-139 consists mainly of diopside. Within the three similar rock types, while the normalized Ta, La, Ce, Sr, Nd, Hf and Eu abundances are different the patterns are similar. However the distribution patterns of Cs, Rb, Ba, U and Th appear disturbed (Fig. 6). This may be related to fenitization.

There is an extreme negative Hf anomaly in some of the carbonatites because Hf is always strongly enriched in the silicate liquid. Hf has a positive correlation with Zr. The Th anomaly in some sövites can also be correlated with zirconium because zircons are host minerals for Th (Ansell, 1985).

Ta content is quite variable within both silicate and carbonate rocks and can be positively correlated with the proportions of phlogopite and amphibole. This was also noted in mantle xenoliths from the Eifel region of West Germany (Stosch and Lugmair, 1986).

Fig. 6 Spidergram of the ultramafic rocks from Carrill. Estimated primordial mantle compositions from Wood (1979). The peak value which plots out of the diagram is 1840.

Fig. 7 Spidergram of the rhyolites from Cargill. Estimated primordial mantle compositions from Wood (1979).

Fig. 8 Spidergram of the silicocarbonatites from Cargill. Estimated mantle compositions from Wood (1979).

Fig. 9 Spidergram of the rauhaugites from Cargill. Estimated mantle compositions from Wood (1979).

4.4 Mineral Chemical Trends

Allen (1972) devised a differentiation scheme for the silicate rocks, based on major element and mineral chemistry from olivine clinopyroxenite to soda-pyroxene hornblendite. Twyman (1983) determined from variation diagrams of amphiboles and micas from the carbonatite core that Fe and alkalis increased during differentiation of the Cargill carbonatite magma while Ca and Mg decreased. In the present study pyroxenes from the ultramafic rim exhibit the same trend noted by Allen (1972) and Twyman (1983) (Fig. 10). If the pyroxenes from Fig. 10 are compared with the spidergrams of their whole rock hosts (Fig. 5) the least "differentiated" sample, C-46-139, has the least disturbed pattern whereas the most "differentiated" samples, C-35-176 and C-23-56, display the most disturbed patterns. Drill hole 46 is furthest from the carbonatite core, drill hole 35 is close to the contact between carbonatite core and ultramafic rim and drill hole 23 is in the carbonatite core. This spatial distribution suggests that the increase in Fe and alkalis and the decrease in Ca and Mg in the silicate rocks may in part be caused by interaction with fenitizing fluids.

4.5 Isotope Data

Rb-Sr isotopic measurements are useful in geochronology and petrogenetic studies, Rb, an alkali metal, is highly incompatible, therefore the crust is characterized by a much higher average Rb/Sr ratio of 0.25 while the mantle is characterized by a lower average Rb/Sr ratio of 0.03 (Faure, 1986). Over time this means the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the

Fig. 10 Variation diagram for pyroxenes.

mantle material has been much lower than that of the crust. The $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios of carbonatites range from 0.702--0.707 and average 0.7034 (Faure, 1986).

^{87}Sr is produced by the radioactive decay of ^{87}Rb , according to the following decay scheme:

The systematics of the Rb-Sr system are expressed in the following equation:

$$(^{87}\text{Sr}/^{86}\text{Sr})_p = (^{87}\text{Sr}/^{86}\text{Sr})_i + (^{87}\text{Rb}/^{86}\text{Sr})_p (e^{\lambda t} - 1)$$

where p = present day value, i = initial value at time = t ago, and $\lambda = 1.42 \times 10^{-11} \text{ yr}^{-1}$. This equation is the equation of a straight line, $y = mx + b$, where $y = (^{87}\text{Sr}/^{86}\text{Sr})_p$, $x = (^{87}\text{Rb}/^{86}\text{Sr})_p$, $m = e^{\lambda t} - 1$ and $b = (^{87}\text{Sr}/^{86}\text{Sr})_i$

With data from 2 or more samples the slope and intercept of the line can be calculated. This equation is based on the following assumptions: a) the system has remained chemically closed over time t with respect to parent and daughter elements b) the analysed rocks and minerals are comagmatic and c) the samples had the same initial isotopic ratio at the time of formation.

Rb/Sr isotope analyses were completed at Carleton University according to the analytical procedure in Appendix IV. Samples were selected on the basis of fresh appearance and mineralogy which would give a reasonable variation in Rb/Sr ratios. A total of 12 whole rock and 4 mineral separates were analyzed for Rb and Sr (Table IX).

The combination whole rock and mineral isochron is based on 9 points (Fig. 11). The $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio is 0.70185 ± 0.00004 and the calculated age is $1891 \pm 15 \text{ Ma}$. The mean square of weighted deviates

Table IX Isotopic Analyses

Sample	Rb(ppm)	Sr(ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Rb}/^{86}\text{Sr}$
*C-6-285	0	3415	0.70186	0
*C-20-159	0	3463	0.70185	0
*C-20-238	0	3975	0.70182	0
*C-20-267	0	3991	0.70182	0
*C-23-34	0	4609	0.70187	0
C-23-56	184	664	0.70924	0.810
C-23-342	0	3466	0.70196	0
C-35-63	17	310	0.70420	0.156
*C-35-93	0	5730	0.70180	0
C-35-176	14	269	0.70315	0.147
C-35-201	35	2938	0.70249	0.0347
C-46-139	0	130	0.70283	0.0697
*C-6-198-ri	1.2	334	0.70221	0.0101
*C-23-154-ph	327	73	1.0646	13.4
*C-35-154-ph	366	104	0.98657	10.5
C-35-176-ps	15	509	0.70410	0.0883

* used in calculation of the isochron

ri = richierite

ph = phlogopite

ps = pargasite

C-6-285, sövite

C-20-159, rauhaugite

C-20-238, rauhaugite

C-20-267, rauhaugite

C-23-34, sövite

C-23-56, aegirine-augite hornblende xenolith within the carbonatite

C-23-342, apatite sövite

C-35-63, hornblende pyroxenite

C-35-93, sövite dyke within the ultramafic unit

C-35-176, aegirine-augite hornblende

C-35-201, sövite dyke within the ultramafic unit

C-46-139, olivine pyroxenite

C-6-198, phlogopite silicosövite

C-23-154, phlogopite silicosövite

C-35-154, diopsidic pyroxenite

C-35-176, aegirine-augite hornblende

Fig. 11. - Rb/Sr isochron based on 9 points.

(MSWD) is 2.3. This value is an estimate of the fit of points to a line and indicates that the points probably fit a line within experimental uncertainty. The value for $\epsilon_{\text{Sr}}(\text{T}) = -5.5$ and suggests derivation of Sr from a source region with a Rb/Sr ratio less than that of the "bulk Earth" reservoir.

Bell and Blenkinsop (1987b), in a Sm-Nd and Rb-Sr isotopic study of selected Ontario carbonatites, obtained initial ratios for the Cargill carbonatite of 0.51026 and 0.70198 for $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ respectively. Values for $\epsilon_{\text{Nd}}(\text{T})$ and $\epsilon_{\text{Sr}}(\text{T})$ were 1.6 and -6.3 respectively.

U-Pb data from a zircon from the Cargill carbonatite gave an upper intercept age of 1906 ± 30 Ma and a lower intercept age of 260 ± 160 Ma on a concordia plot (Kwon, 1986). The U, Th, and Pb of the carbonates and sulfides at Cargill did not behave as closed systems and these minerals define an errorchron on a $^{206}\text{Pb}/^{204}\text{Pb} - ^{207}\text{Pb}/^{204}\text{Pb}$ plot of 1890 ± 100 Ma (MSWD of 3.5). In addition Kwon (1986) calculated a 4 point Sm-Nd calcite-dolomite isochron age of 1903 ± 100 Ma (MSWD 0.2).

Only 9 data points (6 whole rock and 3 mineral separates) were used on the isochron. From Fig. 11 it seems that Cargill has some isotopic heterogeneities which may reflect heterogeneity within the source, contamination of magma during intrusion or later open system behaviour.

The points which deviate most from the isochron are from the ultramafic rocks (Fig. 11). Furthermore the ultramafic samples which were located closest to the carbonatite show the greatest degree of deviation. The one exception to this is sample C-35-154, a diopsidic pyroxenite which shows no evidence of the effects recirculating fenitizing fluids.

This isotopic behaviour of ultramafic rocks close to the core parallels the disturbed trace element behaviour.

It has already been demonstrated that the ultramafic rocks have disturbed trace element patterns which are likely caused by fenitizing fluids. Heinrich (1966) discusses geochemical recycling in which the fenitizing fluid circulates through country rock, leaches silica and returns to precipitate quartz veins. The returning fluids should have Sr isotopic ratios much different from those in the complex and thus disturb the ratios at this time.

Because the carbonatites have a much higher Sr content than the ultramafic rocks they would be much less susceptible to disturbance. The consistent trace element patterns in the carbonate rocks suggest that they were less affected by recirculating fenitizing fluids. This can be explained in terms of fracturing of the ultramafic rocks by the explosive carbonatite intrusion, thus providing conduits for returning fenitizing fluids. It is reasonable to assume that earlier carbonate phases would still be hot and ductile during later carbonate pulses therefore the carbonatite unit as a whole is less likely to contain these open fractures. A quartz vein in the rauhaugite unit (drill hole 7) suggests that the carbonatite core is not totally immune to the recirculating fluids. Only the ultramafic samples which appear to be fenitized display very disturbed trace elements and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. It seems quite likely that the disturbed Rb-Sr systematics can be ascribed to the effects of the recirculating fenitizing fluids.

However even when the 7 pure carbonate samples and one from Bell

and Blenkinsop (1987b) are examined the variation in initial ratios is greater than can be accounted for by analytical uncertainties. These samples do not appear to have been affected by the fenitizing fluids. Similar variation in initial ratios was noted by Wen (1985) at the Oka carbonatite and by Pollock (pers. comm., 1987) at the Prairie Lake, Ontario carbonatite. The suggestion is that this variation in initial ratios reflects heterogeneities in the source region. This idea is quite reasonable considering the large source area tapped by carbonatites and the short emplacement timescale which may preclude complete isotopic homogenization of the carbonatite magma.

Another possible cause of the isotopic variations shown by the ultramafic samples is subsequent open system behaviour (for example, during a later thermal event). Kwon (1986) suggests that the lower intercept age of 206 ± 160 Ma on a zircon concordia plot may indicate a thermal disturbance. He tentatively concludes that the intrusion of the Hecla-Kilmer carbonatite (approximately 100 km NE of the Cargill complex), which gives a Rb/Sr errorchron age of about 450 Ma (Bell and Blenkinsop, 1980), could have caused this disturbance. The present author disagrees with this conclusion. Firstly, apart from an possible occurrence of vesuvianite (which can indicate contact metamorphism of limestones) and some recrystallization, there is little evidence of a thermal disturbance. The mafics, which would tend to lose their radiogenic Sr in the event of a thermal disturbance, have remained isotopically closed since the time of the intrusion. Secondly, the age of the Hecla-Kilmer carbonatite is poorly constrained.

At the Borden carbonatite complex, approximately 160 km south of

the Cargill complex there is some evidence of subsequent resetting of the Rb-Sr system (Bell et al., 1987). A $^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$ age of 1872 $\pm$ 13 Ma and a Rb-Sr age of 1807 $\pm$ 13 Ma were determined. The authors suggest that the common lead age dates the intrusion of the complex while the Rb/Sr isochron indicates resetting. This is in contrast to Cargill where Sr, Nd and Pb isotope systems all give approximately the same age.

CHAPTER 5 SUMMARY

The following findings result from the study of the Cargill carbonatite:

- i) A Rb-Sr whole rock/mineral isochron indicates an age of 1891 ± 15 Ma with an initial ratio of 0.70185 ± 0.00004 . This age agrees well with a U-Pb age of 1900 ± 30 Ma and a Sm-Nd age of 1903 ± 100 Ma (Kwon, 1986). This age makes the Cargill carbonatite one of the oldest carbonatites in Canada. The age and initial ratio support the idea of the LIL element-depleted source region for Ontario carbonatites proposed by Bell et al. (1982).
- ii) The variation in initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios exceeds the analytical uncertainty. This variation is probably related to heterogeneity in the source region.
- iii) The mineral chemistry and petrography suggest that there are differentiation trends among rock types. These trends indicate a progressive enrichment of the magma in Fe and alkalis, accompanied by a progressive depletion in Ca and Mg. This trend is enhanced in the silicate rocks by the action of fenitizing fluids.
- iv) The trace element contents in the Cargill carbonatite are much lower than those of the typical carbonatite of Gold (1966). This finding is thought to be related to a higher degree of partial melting in the source region.
- v) Mineralogy, mineral chemistry, major element distributions, trace element patterns and Rb/Sr isotopic systematics all indicate that

recirculating fenitizing fluids have increasingly affected the ultramafic rocks with proximity to the carbonatite core.

APPENDIX I MICROPROBE ANALYSES

The microprobe analyses were done at Carleton University by Peter Jones using a Cambridge Instruments Microscan 5 Electron Microprobe. The wavelength-dispersive system was used to determine mineral chemistry. The energy dispersive system with an Ortec Si (Li) X-Ray detector, coupled with an Ino-tech Ultima/2 multichannel analyser and Data General computer, was used to identify unknown minerals. Major elements are estimated to have a relative accuracy of 2%. Minor elements have 5-10 % accuracy. For elements reported close to the detection limits, relative errors can range from 50-100%. The detection limits are as shown in the following table.

Table A1 Detection Limits for Microprobe Analyses (%)

SrO	0.03
MnO	0.03
K	0.02

Analytical conditions were a 15 kv accelerating potential, a beam diameter of 1-2 μm , and a specimen current of 50 nanoamperes referenced to pure iron. For carbonate analyses a defocussed beam of approximately 50 μm diameter was used. The X-ray counting data were reduced to oxide weight percents and element concentrations in ppm using the computer program (EMPADR VII) of Rucklidge and Gasparinni (1969).

APPENDIX II X-RAY FLUORESCENCE

Samples were analyzed for major and some trace elements at the University of Ottawa. Thirty seven samples were powdered to -200 mesh in a stainless steel Bleuler mill. Samples were fused into glass disks. The disks were analyzed on a Phillips PW 1410 semi-automated spectrometer, which has an Rh tube and 3 crystals (LiF, PET and TLAP). Elemental compositions were then calculated on the main frame computer at the University of Ottawa. Loss on ignition was determined by Bondar-Clegg Ltd., Ottawa.

One sample (C-20-267) was run twice. The major oxides were within 0.30% at >10% levels and 0.01% at < 10% levels. The trace elements were within 4 ppm at levels less than 100 ppm and were within 40 ppm at > 4000 ppm. The percent error is shown in the following table:

Table A2. Precision For XRF Data, % Error (Ron Hartree, pers. comm., 1985)

Concentration Range					
Oxide(wt%)	0.1-1.0	0.1-2.0	1.0-3.0	2.0-5.0	1.0-20.0 50-100
SiO ₂					1.0
Al ₂ O ₃	10		1.5	1.5	1.5
Fe ₂ O ₃	5				2
MgO	25				3
CaO	5				2
Na ₂ O		15		3	
K ₂ O	5				1
TiO ₂	2		1		
P ₂ O ₅	10		1		
MnO	10				
Trace Elements(ppm)					
	Concentration Range				
	<10	10-30	>30		
Precision (%)	<10	50	10		

APPENDIX III TRACE AND RARE EARTH ELEMENTS

Fifteen samples were analyzed for 32 trace and rare-earth elements by induced neutron activation analysis (INAA). Samples were from both the pyroxenite and the carbonatite. Included are sövites, silicocarbonatites, rauhaugites and carbonate dykes within the ultramafics and ultramafic xenoliths within the carbonatite core.

The samples were analyzed by Nuclear Activation Services at McMaster University, Hamilton, Ontario. The detection limits (ppm unless otherwise stated) are as follows:

TABLE A3 Detection Limits Of INAA Analyses (ppm unless otherwise stated)

Element		Element		Element	
As	1	Na	30	Sc	0.01
Au	5	Ni	50	La	0.1
Ba	20	Rb	5	Ce	1
Br	0.5	Sb	0.1	Nd	3
Co	0.1	Se	0.5	Sm	0.01
Cr	0.5	Sr	100	Eu	0.05
Cs	0.2	Ta	0.5	Tb	0.1
Fe(%)	.005	W	1	Dy	0.5
Hf	0.2	Zn	5	Yb	0.05
Mo	2	U	0.1	Lu	0.01
Th	0.2				

APPENDIX IV RUBIDIUM-STRONTIUM ANALYSESSample Preparation

Twelve whole rocks representing all major rock types at Cargill, and 4 mineral separates were analyzed for Rb and Sr. The outer rind of drill core samples was removed with a tungsten carbide drill. The samples were crushed in a jaw crusher and then powdered in a tungsten carbide Bleuler mill. Both the jaw crusher and Bleuler mill were cleaned between samples with double distilled water(DDW) and acetone. Minerals were separated by magnetic separation and hand-picking.

Chemistry

Approximately 50 mg samples of mineral separates and 200 mg samples of whole rocks were taken into solution with 15 ml 40 % HF and 2-3 drops HClO_4 in a Teflon dish. The solution was then evaporated to dryness on a hotplate. Ten ml of 2.5 N HCl were added to check that the entire sample was in solution, then the sample was taken to dryness. After adding 1-2 ml of 2.5 N HCl the solution was centrifuged and retained. The mineral separates were mixed with ^{87}Rb and ^{84}Sr -enriched spikes after being taken into solution and then were treated the same as the whole-rock samples. Spike data are given in Table A4. An ion exchange column was set up using a 20 cm teflon tube with a 1.1 cm diameter. The tube was filled with 15 mls of Bio-rad AG 50W-X8 cation exchange resin (200-400 mesh, hydrogen form) slurried in 2.5 N HCl.

A 0.5-1 ml portion of the centrifuged liquid was loaded onto the top of the column and followed by 5, 1 ml portions of 2.5 N HCl. Then 65

mls 2.5 N HCl is added and allowed to pass. Twenty mls of 2.5 N HCl was added and the resultant effluent is collected as a Sr sample. This sample is dried and then transferred to a small Teflon dish.

Table A4 Spike Data

Spikes	Concentration of Spike (umoles/g)	Isotopic Composition of Spike	Isotopic Composition in Nature
^{87}Rb	0.0765	$^{85}\text{Rb}/^{87}\text{Rb} = 0.00803$	2.593
^{84}Sr	0.00498	$^{84}\text{Sr}/^{86}\text{Sr} = 21.1999$	0.05646

Mass Spectrometry

Rhenium double filaments were used for Rb analysis. The sample is dissolved in one ul of DDW and loaded onto the filament. The filament is heated to 1.5 A until the sample is dried.

Tantalum single filaments were used for Sr. One ul of 1 M phosphoric acid is loaded onto the filament. The sample is dissolved in 1 ul DDW and loaded on top of the phosphoric acid. The filament is heated to 1.2 A until the sample dries, then to 1.9 A to dry the phosphoric acid and finally heated to a dull red. Standards were run regularly. The NBS 987 Sr standard gave a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71023 ± 0.00003 .

Samples were analysed on a Finnigan-MAT 261 multi-collector machine controlled by a Hewlett-Packard 9845 computer. Rb analyses for spiked samples were run using an ionizing filament current of 1.8-2.0 A, corresponding to a brightness temperature of 1000-1100°C. Sr analyses were run using an ionizing filament current of about 2.3-2.6 A, corresponding to a temperature of 1250-1350°C. Spiked samples were

measured for $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$ ratios. Unspiked Sr samples were measured for $^{88}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$. Very few runs had to be corrected for the isobaric interference of ^{87}Rb .

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