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THE ISOTOPIC GEOCHEMISTRY OF THE
PRAIRIE LAKE CARBONATITE COMPLEX, ONTARIO

by

STEPHEN JOHN POLLOCK, B.Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Master of Science

Department of Geology

Carleton University
Ottawa, Ontario
June 1987

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Prairie Lake Carbonatite Complex, Ontario"
submitted by Stephen John Pollock, B. Sc.,
in partial fulfilment of the requirements
for the degree of Master of Science.

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August 7, 1987

Abstract

A detailed Rb-Sr and Sm-Nd isotopic study of whole rocks and minerals from the Prairie Lake carbonatite complex, Ontario, Canada, suggests an emplacement age of 1165 Ma based on an 18 point Rb-Sr isochron (1130 ± 10 Ma) and an 8 point Sm-Nd isochron (1200 ± 40 Ma).

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the Prairie Lake complex, 0.70254 ± 0.00003 and 0.51129 ± 0.00004 respectively, indicate a depleted lithospheric mantle source for the large ion lithophile (LIL) elements of the Prairie Lake complex. Variation of 0.02 % in the initial Sr isotopic composition is similar to that seen in other complexes. In combination with data from other Keweenaw-related rocks, this suggests that during the Proterozoic, alkalic-carbonatitic complexes in the Lake Superior region were derived from a heterogeneous mantle source.

A strong enrichment in the LREE for the Prairie Lake rocks and minerals contrasts with the time-integrated depletion indicated by the high initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio. Models involving scavenging by CO_2 , mantle metasomatism, or disequilibrium melting of a LREE-enriched accessory phase appear able to explain the LREE enrichment, but not the Nd isotopic composition.

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CHAPTER I: Introduction

1.1: Location

The Prairie Lake carbonatite complex is located at latitude $49^{\circ} 02' N$ and longitude $86^{\circ} 43' W$ approximately 40 km northwest of Marathon, Ontario, Canada (Figure 1). It is one of a large number of alkalic and carbonatitic complexes that were emplaced in the Superior Province approximately 1100 Ma ago (Bell and Blenkinsop, 1987). Sage (1983a) suggested that the Prairie Lake complex is located at the intersection of faults which are parallel and subsidiary to the northern extension of the Big Bay - Ashburton Bay Fault which transects the Lake Superior basin (see Figure 2).

1.2: Previous Work

To the best of the author's knowledge, the first record of work on the Prairie Lake complex is an unpublished report by Parsons (1959). He described the complex as having a central core of ijolitic rocks and an outer rim of carbonatite. The complex was first mapped in detail by Watkinson in 1969 and more recently by Sage in 1974 (Sage, 1983a). Satterly (1968) reported an aeromagnetic anomaly (approximately 1,400 nanoteslas above background) associated with the complex.

The complex was first explored, for U and Nb, by Newmont Mining Corporation of Canada Ltd. from 1968 to 1970. Ore-grade mineralization was found but of uneconomic tonnage. In 1975 and 1976 International Minerals and Chemicals Corporation explored for phosphate. Their results indicated neither a paleokarst topography nor an apatite - rich residuum, similar to those at the Cargill complex near Kapuskasing, Ontario (Erdosh, 1976). Nuinsco Resources Ltd. presently holds the mineral

Figure 1. Location map for the Prairie Lake complex.
(After Satterly (1968) and Bell and Blenkinsop (1987))

★ PL = Prairie Lake alkaline - carbonatitic complex. • = other alkaline or carbonatitic complexes. ● C = Coldwell alkaline complex, ● K = Killala Lake alkaline complex. Also shown are the Mid - Continent and Kapuskasing gravity highs (shaded), the Grenville Front and the Ottawa - Bonnechere graben.

Figure 2. Sketch map of the regional geology north of Marathon, Ontario (After Sage, 1983a).

CL = Chipman Lake carbonatite dikes, K = Killala Lake alkalic complex, PL = Prairie Lake alkalic rock - carbonatitic complex, C = Coldwell alkalic complex. □ = Archean granitic gneiss, ▨ = greenstone-belt rocks. The extension of the Big Bay - Ashburton Bay fault, and faults parallel and subsidiary to it are suggested by Sage, 1983a.

rights to the Prairie Lake complex and has worked the property intermittently from 1976 to the present. Work done by Nuinsco Ltd. includes: diamond drilling 15 holes (P16 - P30) for a total of 5154 feet of BQ core in 1977, an unpublished petrographic study by Mariano (1979a), diamond drilling 12 holes (P21A and P31 - P41) for a total of 5618 feet of BQ core in 1983, and an unpublished report by Kretschmar (1983). All samples used in the thesis, with the exception of two, are from the Nuinsco Ltd. drill core stored at Lac Dufault, Quebec.

Watkinson and Barnett (1971) have described the petrology and U - Nb mineralization. Watkinson (1973) has also documented the occurrence of pseudoleucite at Prairie Lake. Petrographic work is also included in Sage's (1983a) open file report on the geology of the Prairie Lake complex. Melnik (1984) found abundant textural evidence for a magmatic origin for the complex; however, the textural evidence for the occurrence of liquid immiscibility was inconclusive.

1.3: Purpose of thesis

The objectives of this thesis are to: 1) obtain a precise age of intrusion for the complex, 2) obtain a precise determination of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the complex, and 3) provide additional insight into the nature of the depleted lithospheric mantle.

1.4: Basic Concepts

Two commonly-used systems in isotope geochemistry are the Rb-Sr and Sm-Nd systems. ^{87}Rb and ^{147}Sm are parental nuclides that decay to ^{87}Sr and ^{143}Nd respectively. The decay schemes are summarized as:

where β^- is a beta particle and α is an alpha particle.

The growth of the radiogenic daughter products can be expressed in terms of the following equations:

$$\begin{array}{l}
 1) \left({}^{87}\text{Sr}/{}^{86}\text{Sr} \right)_p = \left({}^{87}\text{Sr}/{}^{86}\text{Sr} \right)_i + \left({}^{87}\text{Rb}/{}^{86}\text{Sr} \right)_p (e^{\lambda_1 t} - 1); \\
 2) \left({}^{143}\text{Nd}/{}^{144}\text{Nd} \right)_p = \left({}^{143}\text{Nd}/{}^{144}\text{Nd} \right)_i + \left({}^{147}\text{Sm}/{}^{144}\text{Nd} \right)_p (e^{\lambda_2 t} - 1);
 \end{array}$$

where the subscripts p and i denote the present-day value and initial value at time t ago, respectively. The decay constants for ${}^{87}\text{Rb}$ and ${}^{147}\text{Sm}$ are $\lambda_1 = 1.42 \times 10^{-11} \text{ yr}^{-1}$ and $\lambda_2 = 6.54 \times 10^{-12} \text{ yr}^{-1}$ respectively.

The above equations of a straight line of the type $y = mx + b$, where $y = \left({}^{87}\text{Sr}/{}^{86}\text{Sr} \right)_p$ or $\left({}^{143}\text{Nd}/{}^{144}\text{Nd} \right)_p$, $m = (e^{\lambda t} - 1)$, $x = \left({}^{87}\text{Rb}/{}^{86}\text{Sr} \right)_p$ or $\left({}^{147}\text{Sm}/{}^{144}\text{Nd} \right)_p$, and $b = \left({}^{87}\text{Sr}/{}^{86}\text{Sr} \right)_i$ or $\left({}^{143}\text{Nd}/{}^{144}\text{Nd} \right)_i$. The quantities y and x can be measured; thus for any geologic system with variable Rb/Sr or Sm/Nd ratios data from two or more samples can be used to calculate a line whose slope and intercept yield the age and initial isotopic composition respectively. In the isochron model the following assumptions are made: 1) the geologic system has remained chemically closed with respect to exchange of both parent and daughter elements, 2) the analysed minerals or rocks are coeval, and 3) the analysed suite of minerals or rocks are comagmatic, i.e. had the same initial isotopic composition at $t = 0$.

The isotopic composition of Sr or Nd in a mineral or rock sample is a function of 1) the Rb/Sr or Sm/Nd ratio of both the sample and the source from which it was derived, and 2) the age of the sample. Any process which changes the Rb/Sr or Sm/Nd ratios of a system will result in a variation in the time-integrated isotopic composition of Sr or Nd. The

evolution of large-scale reservoirs such as the crust or mantle with time can therefore be studied using ^{87}Sr and ^{143}Nd as tracers.

These reservoirs are often discussed in terms of the models called CHUR and bulk Earth. The assumption is made that the primitive material which gave rise to the Earth's mantle and crust has the same Sm-Nd ratio as that of chondritic meteorites (0.32); i.e., it has a present-day $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.1967 (Jacobsen and Wasserburg, 1980) and a present-day $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.51264 (O'Nions et al., 1979).

The present-day Sr isotopic composition of the primitive material is inferred from the mantle array. The latter is a negative correlation defined by the fields of mid-ocean ridge basalts (MORB), ocean island basalts (OIB), and selected continental flood basalts (CFB), all of essentially zero age, on a plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ (DePaolo and Wasserburg, 1976b; Richard et al., 1976; O'Nions et al., 1977). The mantle array is thought to reflect either different degrees of mixing of two mantle reservoirs, sampling of several mantle reservoirs each with its own geochemical signature (Allègre et al., 1979; DePaolo, 1979), or injection of crustal material into the mantle (White and Hofmann, 1982). When only MORBs are used to define the mantle array the present-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of bulk Earth is 0.7045 and the present-day $^{87}\text{Rb}/^{86}\text{Sr}$ ratio is 0.0816, on the assumption that the primordial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Earth was 0.69899 (Papanastassiou and Wasserburg, 1969) and that the age of the Earth is 4600 Ma.

DePaolo and Wasserburg (1976a) introduced the epsilon notation as a means of comparing initial isotopic $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (R_i) to values for bulk Earth or CHUR at the same time, T; i.e.,

$$\epsilon_k(T) = [(R_i / R_{\text{CHUR}}) - 1] \times 10^4$$

where $k = \text{Sr or Nd}$. A negative ϵ_{Sr} , together with a positive ϵ_{Nd} , indicate a source that has been depleted in the large-ion lithophile (LIL) elements such as Rb, K, U, Th and Nd for a considerable period of time, while a positive ϵ_{Sr} , together with a negative ϵ_{Nd} , indicate a source enriched in the LIL elements.

Bell and Blenkinsop (1987) found that initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of some carbonatites and related alkalic rocks intruded into the Canadian Shield define development lines on a plot of initial ratio versus age. These development lines intersect the development line for bulk Earth and CHUR at about 2900 Ma. The intersection age is interpreted in terms of a model which involves differentiation of a mantle, similar in its Rb/Sr ratio to that of bulk Earth, and of Sm/Nd to CHUR, into granitoid rocks of the Superior Province and a residual, LIL-depleted, upper mantle. Bell and Blenkinsop (1987) note that the present-day isotopic composition of the depleted lithospheric mantle reservoir plots as a point that falls very close to the mantle array.

1.5: Previous Isotopic Work

In the first isotopic study of the Prairie Lake complex (Powell, 1965) a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7028 ± 0.0006 was reported for a carbonatite. Bottriell (1975) obtained an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7018 ± 0.0004 whereas Bell et al. (1982) reported an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7025 ± 0.0003 for the complex. Bell and Blenkinsop (1987) report higher precision $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70256 and 0.70272) that agree with their previously-determined value, and initial $^{143}\text{Nd}/^{144}\text{Nd}$ values (0.51137 and 0.51142).

The Prairie Lake complex has been dated by Gittins et al. (1967) and Bottrill (1975). Gittins et al. (1967) report a K-Ar date of 1112 Ma which is the average of dates from two biotites. One is 1164 Ma, the other is 1059 Ma, a difference of about 10 % or $\pm 5\%$. Lowden et al. (1963) estimate that the uncertainty associated with a K-Ar age is $\pm 6\%$ at 1000 Ma. The age determinations made by Gittins et al. (1967) thus appear to be within analytical uncertainty of each other. Bottrill (1975) reports an age of 1030 ± 60 Ma that is determined from a whole-rock, Rb-Sr isochron based on only four points.

1.6: Significance of Carbonatites

Until about ten years ago carbonatites were studied mainly for petrologic and economic reasons. The petrologic reasons are most eloquently stated by Heinrich (1966):

"No igneous rocks have so fascinated petrologists as those of the undersaturated alkalic group - the nepheline syenites and their relatives [carbonatites]. Rare, mineralogically esoteric, texturally heterogeneous, and structurally distinctive, these rocks have commanded a detailed scrutiny completely disproportionate to their abundance."

The economic reasons include: Cu, Nb, Ta, Th, Ti, U, Zr, the rare earth elements, apatite (for phosphate), barite, calcite, fluorite and vermiculite (Deans, 1966).

Within the last decade isotope geochemists have recognized the importance of carbonatites for investigating the geochemical evolution of the Earth's mantle. Carbonatites are well suited for monitoring the subcontinental upper mantle because they: (i) are mainly restricted to continental areas, (ii) are of mantle origin, (iii) ascend rapidly so that interaction with continental crust is minimized, and (iv) have Sr and light rare-earth element concentrations so high that even if a

volumetrically significant amount of crustal material were incorporated, carbonatites should still retain their original Sr and Nd isotopic compositions (Bell et al., 1982).

CHAPTER II: Geology of the Prairie Lake Complex

2.1: Regional Geology

The Prairie Lake complex intrudes Archean granitic gneisses of the Wawa belt of the Superior structural province. Extensive glacio-lacustrine deposits cover much of the region. The regional geology is discussed in detail by Coates (1970).

Sage (1983a), on the basis of topographic maps and photographs from the Canada Centre for Remote Sensing, has suggested that the Prairie Lake complex occurs at the intersection of two linear trends. One is a north - south trend defined by the Steel River; the other is a northeast - southwest trend defined by a series of lakes between Prairie Lake and Killala Lake. The latter trend coincides with an aeromagnetic trend of about 200 nanoteslas above background (see Satterly, 1968). Sage (1983a) suggests that this magnetic trend reflects, in part, the regional geology as mapped by Coates (1970).

From aeromagnetic studies Hinze et al. (1966) identified the Big Bay - Ashburton Bay fault as a major crustal fracture which crosses the Lake Superior basin. The Collinwood and Killala Lake alkalic complexes and the Chipman Lake carbonatite dykes define a north - south trend which Sage (1983a) suggests may be a northern extension of the Big Bay - Ashburton Bay fault (see Figure 2). Sage (1983a) therefore believes that the Prairie Lake complex occurs at the intersection of fractures which are parallel - and subsidiary to the Big Bay - Ashburton Bay fault.

2.2: Local Geology

General Geology

The Prairie Lake complex is small, covering about 2.3 km² in area. It has a roughly circular outline and a somewhat concentric distribution of rock types (see Figure 3). The nomenclature used in this thesis for carbonatites and alkaline silicate rocks is presented in Appendix 1. The locations of the samples used in this thesis are shown in Figure 3. The first two digits of the sample number refer to the Nuinsco Resources Ltd. drill hole number and the last three digits refer to the drill core footage.

Maps of the Prairie Lake complex by Watkinson (pers. comm.) and Sage (1983a) are in general agreement. Apparent discrepancies over the exact lithologies present and the locations of their contacts are due to lack of exposure, limited trenching and shallow drilling, rapid lithologic variation, and different field classifications of rock types. In general, the complex consists of complexly related, vertically dipping, arcuate to curvilinear layers of carbonatite and alkaline silicate rocks. Carbonatites predominate towards the margin of the complex and alkaline silicate rocks towards the centre. This spatial distribution of rock types is the reverse to that found in many complexes.

Fenites and Country Rocks

The outer margins of the complex, based on a magnetic survey carried out by Newmont, generally correspond to the base of the hill associated with the complex. Contacts between country and intrusive rocks have not been observed although fenitized granitic, granodioritic and gneissic

Figure 3. Local geology of the Prairie Lake complex
(After Watkinson, pers. comm.)

▲ = location of samples obtained from Nuinco Resources Ltd. drill core. The first two digits of the sample number refer to the diamond drill hole number, the last three to the footage. See Appendix 1 for carbonatite and alkalic rock nomenclature.

rocks crop out near the southeast margin (Watkinson, 1976; Sage, 1983a). These rocks are characterized by pyroxene which partially replaces quartz, and alkali feldspar which partially replaces plagioclase. Collectively these features indicate only a weak degree of fenitization (Heinrich, 1966).

Carbonatites

The annulus of the complex is characterized by extreme variability, gradational contacts and an overall predominance of calcitic silicocarbonatites, although both pyroxene-rich rocks of the ijolite series and calcite carbonatites are common (Kreischmar, 1984). Lenses and layers of cumulate phoscorite are associated with carbonatites (Watkinson, 1976). Carbonatites at Prairie Lake are commonly flow-banded with foliation dipping towards the centre of the complex (Watkinson, 1974). Banding, of the order of several centimetres, is commonly defined by the relative proportions of silicate and oxide minerals to carbonate minerals (Sage, 1983a). The alignment of silicate minerals and ovoid apatite grains mark a flow texture (Mariano, 1979a).

From oldest to youngest, the normal intrusive sequence of carbonatites is calcite, dolomite and ankerite (Heinrich, 1966). At Prairie Lake dolomite and ankerite carbonatites are uncommon and their relationships with calcite carbonatites are uncertain (see Sage, 1983a). Calcite carbonatites at Prairie Lake are normally fine- to medium-grained with an interlocking mosaic texture of anhedral to subhedral calcite. Micas are the most common silicate minerals with compositions that range from biotite to phlogopite (Watkinson, 1976). Other essential to minor minerals include apatite, diopside, magnetite, olivine, pyrochlore

(Watkinson, 1974) and pyrrhotite.

Alkaline Silicate Rocks

Alkaline silicate rocks of the ijolite series (pyroxenite to urtite) predominate towards the centre of the intrusion. Pyroxenites commonly show a gradational relationship with the carbonatites. Gradational relationships also occur amongst the alkaline silicate rocks. For example rocks varying from melteigite to urtite can be found in the same outcrop (Sage, 1983a). Sage (1983a) also notes occasional occurrences of banding, four to six centimetres wide, with compositional variation ranging from melteigite to urtite.

The alkaline silicate rocks of the central area are divided into two main groups - pyroxenites and urtites (Watkinson, 1974). The urtites tend to be more centrally located than the pyroxenites (see Figure 3). Minor occurrences of juvite and malignite are also associated with the urtites.

Melteigites at Prairie Lake are generally fine- to medium- grained cumulate phases. In contrast, the urtites are commonly later stage phases, and are more variable in grain size, ranging from fine-grained to pegmatitic (Watkinson, 1976; Sage, 1983a). The pyroxene - rich rocks invariably contain nepheline or, more commonly, its altered equivalent (Watkinson, 1974). In pegmatitic urtite, nepheline is partially altered to cancrinite although in most urtite nepheline is extremely fresh and normally occurs in the anhedral groundmass (Watkinson, 1976).

Sage (1983a) recognizes two groups of alkaline silicate rocks within the core area based on the presence or absence of wollastonite. Medium- to coarse-grained ijolite with abundant interstitial wollastonite occurs

in the north and northwest parts of the complex whereas medium-grained ijolite with minor or no wollastonite occurs in the south and southeast. Detailed petrographic studies by Mariano (1979a) indicate that the wollastonite is a reaction product. Wollastonite and aegirine are found in some urtites (Watkinson, 1974). It therefore appears that Sage's subdivision may delineate areas of a particular type or relative degree of metasomatism.

Dyke rocks

Dyke rocks of widely different compositions and textures form a small percentage of the complex. The rock types include glomeroporphyritic ~~diabase~~, olivine diabase, ijolites, gabbros, and xenocrystic to xenolithic carbonate dyke rock that contains xenoliths representative of all the rocks of the complex (Sage, 1983a). Mariano (1979b) postulated that the diabase dykes may fill late tensional fractures caused by contraction of the complex after initial emplacement. There is no geologic evidence that relates any of the dyke rocks to the regional Keweenaw dyke swarm.

2.2.1: Thin Section Petrography

Eighteen samples were chosen for study in this thesis. With the exception of samples 7-5 and 7-7, collected by Dr. K. Bell, all samples are from drill core belonging to Nuinsco Resources Ltd. The suite of samples consists of 6 carbonatites, 3 silicocarbonatites, 3 'phoscorites', 3 pyroxene-rich rocks of the ijolite series, 1 mal~~igne~~ite and 2 rocks which are referred to by mineral names. Thin sections were studied to evaluate any processes which may have affected the isotopic

composition of the samples.

Detailed thin section descriptions of the samples studied in this thesis are given in Appendix 2, Table A3. The samples consist of varying proportions of biotite (or phlogopite), calcite, garnet, nepheline (or its alteration products) and pyroxene. Less common or minor minerals include: alkali feldspar, apatite, ferroan monticellite, magnetite and olivine. Minor to trace minerals include: sphene, pyrrhotite, and zircon.

The major minerals in most of the rocks that were observed share a common order of crystallization. This sequence from early to late is: 1) apatite (which appears to have continued crystallizing throughout the crystallization period) 2) olivine - magnetite, 3) pyroxene - garnet, 4) nepheline, 5) biotite, 6) alkali feldspar and 7) calcite. Sage (1983a) determined a similar order of crystallization for minerals in the Prairie Lake complex.

Diopside is commonly light green to yellow brown and many grains contain colourless cores. These features may possibly be due to weak sodic alteration; however, the optical properties closely match those of diopside. There is no correspondence between the type of rock and the colour of diopside.

A common feature of micas is the occurrence of red, reversely-pleochroic rims, possibly 'tetraferriphlogopite', on green, normally-pleochroic, biotite. The red mica has the same crystallographic orientation as the biotite but has an irregular boundary with, and occasionally transects the biotite. These features suggest that the red mica is present because of a change in magmatic conditions.

In some samples (e.g. 32029) magnetite is rimmed and partially

replaced by mica. The degree of replacement ranges from weak (e.g. 32265) to very strong (e.g. 32171) and most probably occurred before the "alteration" of biotite. The replacement of magnetite may represent an initial stage of biotitization or phlogopitization, a hydrothermal process (Heinrich, 1966) in which ijolite series rocks are converted to glimmerites. An incipient stage of biotitization is consistent with the observation that neither pyroxene nor nepheline is replaced by biotite.

Fresh nepheline occurs in two samples. In two other samples it is interpreted to have been present on the basis of cross-sections in which the angular relationship between crystal faces is consistent with that of an hexagonal cross-section of nepheline. The altered nepheline appears to be associated with the alkali feldspar. In sample 39083 totally altered 'nepheline' occurs as core-like inclusions which have straight, sharp contacts with the surrounding alkali feldspar. A similar rock between the north ends of Anomaly and Centre Lakes has been described by Mariano (1979a). Further study is needed to determine the cause of the relationship between altered nepheline and alkali feldspar.

In most samples olivine is a minor mineral that is skeletal in habit and ranges from fresh to totally altered (magnetite and chlorite?). Ferroan monticellite was identified as the major mineral in sample 32265. These euhedral crystals are fresh with slight alteration along cleavage traces, and they define a cumulate texture. Microprobe data in Appendix 7, Table A6, show that the ferroan monticellite has a normal zonal composition with respect to the development of minerals in magmatic rocks, i.e. it has a magnesium-rich core and iron-rich rim.

Thin section studies show diopside, biotite, nepheline and olivine are

quite fresh. Any alteration can be attributed to either chemical changes within the magma or incipient deuteric alteration. This agrees with Watkinson's suggestion that magmatic processes dominated during the formation of rocks of the Prairie Lake complex with metasomatic or hydrothermal processes being of only very minor importance (Watkinson, 1974). There is insufficient petrographic data to evaluate the timing of fenitization with respect to carbonatite formation.

Three other minerals studied are apatite, calcite and garnet. Prairie Lake garnets have Ti contents intermediate between that of melanite and schorlomite varieties of andradite, and significant Zr contents (Watkinson, 1976). The garnet, however, is tentatively identified as hydrogrossular, based on X-ray diffraction work and solubility of the garnet in HCl. It has been noted that most varieties of garnet are soluble with difficulty in HF whereas hydrogrossular is soluble in HCl or HNO_3 (Deer et al., 1966).

In both carbonatite and silicate rocks studied in this thesis some of the calcite grains are biaxial with an optic axial angle of up to 20° . Biaxial calcite is also found at other complexes, e.g. Kaiserstuhl (Heinrich, 1966) and Oka (Pouloit, 1970). Pouloit (1970) cites three previously proposed causes for a biaxial character in calcite: inversion from aragonite, molecular rearrangements following crystallization at high temperature, and post-consolidational deformation. Pouloit also proposes that a high Sr content makes only a minor contribution to the biaxial character of carbonatitic calcite. Further study is required to determine the significance of biaxial calcite in the Prairie Lake complex.

Either liquid immiscibility or differentiation can account for the

occurrence of calcite and apatite as clots interstitial to cumulate pyroxene, or as inclusions in pyroxene, in the silicate rocks. Either magmatic process can also account for the occurrence of nepheline and alkali feldspar intergrowths which are interpreted by Watkinson (1973) to be pseudoleucite. Watkinson (1973) notes that the carbonatite - pyroxenite and pyroxenite - urtite gradational sequences may be explained by either liquid immiscibility or differentiation of "two pulses of ijolitic magma, one rich and the other poor in H_2O and CO_2 ". Further work is needed to determine the specific magmatic processes which occurred during emplacement of the Prairie Lake complex.

In summary petrographic studies indicate that the samples from the Prairie Lake complex are generally fresh. Their isotopic compositions are therefore not likely to have been affected by contamination or weathering.

CHAPTER III: Analytical Results

3.1: General Statement

Nine whole rocks and fifteen mineral separates were analysed for Rb and Sr concentrations and isotopic compositions. The whole rock and mineral data are given in Tables 1 and 2 respectively. Seven whole rocks and ten mineral separates were analysed for Sm and Nd concentrations and isotopic compositions. Sm and Nd data for the whole rocks are given in Table 3; Table 4 gives the data for the mineral separates. Most of the samples used for Rb and Sr analyses were also used for Sm and Nd analyses. Also given in Tables 1 and 3 are $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ values for the International NBS 987 and La Jolla standards respectively.

Present-day $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were determined using unspiked aliquots of the sample solution. Concentrations of Rb, Sr, Sm and Nd were determined by isotope dilution using ^{87}Rb -, ^{84}Sr -, ^{149}Sm - and ^{145}Nd -enriched spikes. The estimated uncertainties, quoted at the 2 sigma level as a percentage of the measured value, are as follows: 1.0 % and 0.5 % for Rb and Sr concentrations respectively, 0.3 % for both Sm and Nd concentrations, 1.5 % for Rb/Sr ratios and 0.4 % for Sm/Nd ratios (both by weight), 1.5 % and 0.003 % for $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios respectively, and 0.4 % and 0.004 % for $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios respectively (Blenkinsop, pers. comm., 1987). The details regarding sample collection, preparation and analytical procedure are given in Appendices II, IV and V.

3.2: Age of the Prairie Lake Complex

Whole Rock Rb - Sr Isochron

The data from nine whole rocks are shown in Table 1. Full petrographic descriptions are given in Appendix II, Table A3. Using the least-squares-fit method of York (1969) a six point isochron was calculated excluding three samples, 7-7, 27208 and 39083, which are discussed latter. The isochron gives an age of 1165 ± 30 Ma and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70254 ± 0.00003 . The uncertainties quoted are at the 2 sigma level. Given the very limited range of the whole rock data, the low uncertainty attributable to the age indicates that the whole rock data are of very high precision.

The mean squares of weighted deviates (MSWD) is an indication of the 'goodness - of - fit' to a straight line (Brooks et al., 1972). In the ideal case the MSWD approaches a value of 1 if the line fits the data points within their experimental uncertainty. In practice an isochron is considered acceptable if the MSWD is ≤ 2.5 . (It should be noted that the value of the MSWD is also dependent on the estimated analytical uncertainty and the number of points used to calculate the isochron.) Although inclusion of the data for samples 7-7 and 27208 does not significantly change the age, the MSWD rises significantly from 1.3 to > 8 . The inclusion of the data for sample 39083 produces an age in excess of 1200 Ma and an MSWD > 28 .

Sample 7-7 contains about 1 % chlorite possibly due to weathering. This may explain why the data from 7-7 do not fall on the isochron. Although samples 32029 and 39083 are petrographically similar only the data from sample 39083 do not lie on the isochron. Sample 39083 does

Table 1 Whole Rock Data (Rb-Sr)

Sample Number	Rock Type	Rb (ppm)	Sr (ppm)	Rb/Sr (weight)	$^{87}\text{Rb}/^{86}\text{Sr}$ (atomic)	$^{87}\text{Sr}/^{86}\text{Sr}$ (atomic)
NBS 987 (standard)						0.71023
BCR-1 (standard)		47.6	334			
27208	melteigite	37.9	1500	0.025	0.073	0.70360
22064	pyroxene phoscorite	85.5	3420	0.025	0.079	0.70388
32029	alkali feldspar - bearing melteigite	101	3610	0.028	0.08	0.70393
32265	phoscorite	1.26	2750	0.0046	0.0013	0.70258
34431	calcite - biotite nepheline rock	207	4550	0.0455	0.132	0.70470
38220	apatite carbonatite	15.2	9930	0.0015	0.0044	0.70259
39083	melanocratic malinite	134	3500	0.038	0.110	0.70475
39218	calcite - garnet pyroxenite	18	2690	0.0068	0.0197	0.70287
7 - 7	calcite carbonatite	4.07	5130	0.00079	0.00230	0.70273
7 - 5	calcite carbonatite					0.70257

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios are normalized to a $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194

however, have high Cr, Na, Nb and Ti contents relative to the other samples (see Appendix 6, Table A6) and may well have been altered. Sample 27208 shows neither petrographic nor chemical signs of weathering or contamination. Its Sr isotopic composition may reflect real variations in the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Prairie Lake complex.

Biotite Rb - Sr Isochron

The data from five biotite mineral separates from different rock types are given in Table 2. Figure 4 shows a well-defined isochron which gives an age of 1135 ± 15 Ma and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7011 ± 0.0010 , and an MSWD of 1.2. The low uncertainty associated with the age is related to the large spread in Rb/Sr values. At the 2 sigma level the biotite age overlaps the whole rock age and is therefore indistinguishable from it. The uncertainty in the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio determined from the biotite isochron does not quite overlap that of the whole rock isochron.

Combined Whole Rock - Mineral Separate Rb - Sr Isochron

All the whole rock and mineral separate data were used to calculate an isochron. An 18 point isochron with an age of 1130 ± 10 Ma, an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70255 ± 0.00002 and an MSWD of 2.0 is obtained when whole rocks 39083, 7-7, 27208, and minerals 27208 garnet, 32455 apatite, and 39218 calcite are excluded. This isochron is shown in Figure 5. Whole rocks, calcites, and apatites dominate the determination of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio while biotites determine the age.

Table 2 Mineral Data (Rb - Sr)

Sample Number	Mineral	Rock Type	Rb (ppm)	Sr (ppm)	Rb/Sr (weight)	$^{87}\text{Rb}/^{86}\text{Sr}$ (atomic)	$^{87}\text{Sr}/^{86}\text{Sr}$ (atomic)
32029	apatite	alkali feldspar - bearing melteigite	0.30	6,500	0.00005	0.00013	0.70254
32455	apatite	apatite carbonatite	0.23	6,320	0.000036	0.00011	0.70247
38220	apatite	apatite carbonatite	0.09	5,450	0.000016	0.000047	0.70251
27208	garnet	melteigite	6.9	226	0.0305	0.088	0.70422
32265	garnet	phoscorite	0.20	329	0.00061	0.00176	0.70259
39218	garnet	calcite - garnet	2.44	79.5	0.0307	0.089	0.70396
22064	calcite	pyroxenite	0.032	14,500	0.0000022	0.0000063	0.70257
27208	calcite	pyroxene phoscorite	0.024	18,000	0.0000013	0.0000039	0.70251
38220	calcite	melteigite	0.059	11,000	0.0000054	0.000015	0.70254
39218	calcite	apatite carbonatite	0.094	16,300	0.0000058	0.000017	0.70262
22064	biotite	calcite - garnet	433	45.5	9.50	28.7	1.1731
32171	biotite	pyroxene phoscorite	384	154.2	2.49	7.28	0.81790
33428	biotite	calcite - diopside - biotite rock	412	157.2	2.62	7.67	0.82582
34431	biotite	calcite carbonatite	597	37.3	16.0	49.9	1.5064
38220	biotite	calcite - biotite - nepheline rock	485	459	1.06	3.07	0.75116

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios are normalized to a $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194

Figure 4. Biotite Rb - Sr isochron.

The data are listed in Table 2. R_1 = initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, MSWD = mean squares of weighted deviates. The size of the solid symbols corresponds to the range in analytical uncertainty as listed in section 3.1. Samples with small symbol size are shown within open circles only for the sake of visibility. The range of Figure 5 corresponds to the thickness of the left boundary line at the intercept.

Figure 5. Whole rock - mineral Rb - Sr isochron

The data are listed in Tables 1 and 2. The biotite data are included in the calculation of the age, initial ratio (R_i) and mean squares of weighted deviates (MSWD) but are not shown in this figure because of the extreme values. The size of the solid symbols corresponds to the range in analytical uncertainty as listed in section 3.1. The open circles denote samples not included in calculations (see Chapter 3 for discussion).

Sm - Nd Isochron

Table 3 gives the data from seven whole rocks. The data from nine mineral separates are given in Table 4. The $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for both whole rocks and mineral separates are plotted in Figure 6. The well-defined isochron shown in this figure yields an age of 1200 ± 40 Ma and an initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.51129 ± 0.00004 (MSWD = 0.7). The whole rock data are not considered separately because the range of values is so small that a precise age cannot be obtained. The Sm-Nd isochron is only the third Sm-Nd isochron obtained from an alkalic rock - carbonatite complex. The other isochrons yield ages of 2094 ± 105 Ma (Basu and Puustinen, 1982) and 1900 ± 100 Ma (Kwon, 1986) for the Siilinjärvi complex, Finland and the Cargill complex, Ontario, respectively.

The Sm-Nd age of 1200 ± 40 Ma overlaps the Rb-Sr whole rock age of 1165 ± 30 Ma with the 2 sigma error estimate, but does not quite overlap the biotite age of 1135 ± 15 Ma. The age from the biotite data may be due to a later thermal disturbance such as intrusion of the Coldwell complex. The biotite age, however, is not significantly different from the Rb-Sr whole rock age. Thus the preferred estimate for the age of the Prairie Lake complex is the Rb/Sr whole rock age of 1165 ± 30 Ma because it overlaps both the biotite age and the Sm-Nd age.

3.3: He Isotope Analyses

Two whole rocks (32265 and 39218) and their corresponding apatite and calcite separates were sent to M. Ozima at the University of Tokyo for isotopic analyses of the rare gases He, Ar, Kr and Xe. Because the content of radiogenic ^4He is so much greater than that of ^3He the $^3\text{He}/^4\text{He}$

Table 3 Whole Rock Data (Sm-Nd)

Sample Number	Rock Type	Sm (ppm)	Nd (ppm)	Sm/Nd (weight)	$^{147}\text{Sm}/^{144}\text{Nd}$ (atomic)	$^{143}\text{Nd}/^{144}\text{Nd}$ (atomic)
La Jolla (standard)						
BCR-1 (standard)		6.60	29.2	0.226	0.1367	0.51185
22064	pyroxene phosphorite	83.0	466	0.178	0.1077	0.51213
32029	alkali feldspar - bearing melteigite	81.8	483	0.169	0.1022	0.51209
32265	phosphorite	185.7	1037	0.179	0.1083	0.51215
34431	calcite - biotite - nepheline rock	76.8	331	0.232	0.1402	0.51239
38220	apatite carbonatite	60.9	386	0.158	0.0955	n.d.
39083	melanocratic melteigite	n.d.	125	n.d.	n.d.	0.51209
39218	calcite - garnet pyroxenite	125.2	590	0.212	0.1283	0.51228

$^{143}\text{Nd}/^{144}\text{Nd}$ ratios are normalized to a $^{146}\text{Nd}/^{144}\text{Nd}$ value of 0.7219
 n.d. = not determined

Table 4 Mineral Data (Sm-Nd)

Sample Number	Mineral	Rock Type	Sm (ppm)	Nd (ppm)	Sm/Nd (weight)	$^{147}\text{Sm}/^{144}\text{Nd}$ (atomic)	$^{143}\text{Nd}/^{144}\text{Nd}$ (atomic)
32029	apatite	alkali feldspar - bearing melteigite	440	2664	0.165	0.0999	0.51205
32455	apatite	apatite carbonatite	396	n.d.	n.d.	n.d.	0.51206
38220	apatite	apatite carbonatite - melteigite	426	2662	0.160	0.0967	0.51206
27208	calcite	calcite	19.72	156.9	0.126	0.076	n.d.
38220	calcite	apatite carbonatite	11.25	63.2	0.178	0.1076	n.d.
39218	calcite	calcite - garnet pyroxenite	25.50	188.2	0.135	0.0819	n.d.
27208	garnet	melteigite	n.d.	510	n.d.	n.d.	0.51322
32265	garnet	phoscorite	563	1394	0.404	0.244	n.d.
39218	garnet	calcite - garnet pyroxenite	262	668	0.392	0.237	0.51315

$^{143}\text{Nd}/^{144}\text{Nd}$ ratios are normalized to a $^{146}\text{Nd}/^{144}\text{Nd}$ value of 0.7219

n.d. = not determined

Figure 6 Sm - Nd isochron

The data are listed in Tables 3 and 4. R_i = initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, MSWD = mean squares of weighted deviates. Number of samples given in parentheses.

ratios of the Prairie Lake samples do not show a mantle signature (Ozima, pers. comm. to Bell, 1986).

CHAPTER IV: Discussion

4.1: Sr - Nd Relationship

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio determined for the Prairie Lake complex of 0.70254 ± 0.00003 agrees well with the values determined by Powell (1965), (0.7024 ± 0.0006) and Bell and Blenkinsop (1987), (0.70256 ± 0.00003) . The initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.51129 ± 0.00003 is consistent with that of Bell and Blenkinsop (1987) when their data are corrected for radiogenic ^{143}Nd using an age of 1165 Ma.

In order to assess the extent of possible variation in the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Prairie Lake complex only those samples with a $^{87}\text{Rb}/^{86}\text{Sr}$ ratio ≤ 0.005 were considered. The value of 0.005 was chosen to minimize any error due to the correction for radiogenic Sr. The maximum correction for these samples was 0.00007 which is approximately equal to the range of analytical uncertainty. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these samples are plotted in a histogram in Figure 7. The distribution of initial ratios appears to be fairly uniform. The range in ratios of 0.00015 (0.70247 to 0.70262) is about twice the range encompassed by analytical uncertainty. A similar total spread of values (0.00014) was found at Oka (Wen, 1985) and Roden et al. (1984) cite other examples. It therefore appears that a small but significant variation ($\sim 0.02\%$) in the initial Sr isotopic composition of carbonatite complexes is common. Although a slight variation in the initial isotopic composition of Nd may exist at Prairie Lake, it is difficult to assess this because mineral phases with Sm/Nd ratios near zero do not exist. Some variation in the initial $^{206}\text{Pb}/^{204}\text{Pb}$ ratio of the Prairie Lake complex has also been shown (Kwon, 1986).

Figure 7.

Initial Sr Isotopic Compositions of the
Prairie Lake Complex

Data used are selected from Tables 1 and 2 (see section 4.1 for discussion). Estimated analytical uncertainty = ± 0.00003 .

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ values for the Prairie Lake complex plot close to the respective Sr and Nd development lines (Bell and Blenkinsop, 1987) for a depleted lithospheric mantle at $t = 1165 \text{ Ma}$ (see Figures 8a and 8b) indicating a depleted lithospheric source for the LIL elements of the Prairie Lake complex. This is supported by the Pb initial ratios from Kwon (1986) which, on a plot of $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, fall well below the crustal evolution curve of Stacey and Kramers (1975) indicating a U - depleted source.

Insight into the nature of the upper mantle can be gained by careful consideration of the model of Bell and Blenkinsop (1987) and the relationship of the Prairie Lake data points determined in this thesis to their model. Bell and Blenkinsop (1987) note that the approximation of their data to a straight line implies, on a gross scale, that Sr and Nd in carbonatites must have been derived from a source with a relatively uniform Rb/Sr and Sm/Nd ratio that existed from 2700 Ma until at least 110 Ma ago. Depletion of this source region in the LIL elements is indicated by Rb/Sr and Sm/Nd ratios which are respectively lower (0.020 vs. 0.03) and higher (0.358 vs. 0.32) than those of a primitive mantle similar to bulk Earth. Such depletion can occur as a result of preferential removal of Rb relative to Sr, and Nd relative to Sm, during processes of differentiation and fractionation. They also note that because the Sr development line for bulk Earth is derived from present-day Nd data for mantle-derived rocks, the similarity of the intersection ages indicates that both the Sm-Nd and Rb-Sr systematics were established at the same time, about 2900 Ma ago. The significance of intersection ages is that they represent mean ages for reservoir formation (Jacobsen and Wasserburg, 1979; Allègre, 1982, 1985). This intersection age is

Figure 8a. Development of Sr isotopic composition.
(After Bell and Blenkinsop, 1987)

Figure 8b. Development of Nd isotopic composition.

(After Bell and Blenkinsop, 1987)

CHUR = chondritic uniform reservoir, ● = the initial Nd isotopic composition for the Prairie Lake complex as determined in this thesis. Solid data points are for other alkalic and carbonatite complexes; data are given in Bell and Blenkinsop (1987).

also within the 2500 - 3000 Ma range reported for most granitoid rocks of the Superior Province. Bell et al. (1982) therefore interpreted the intersection age as the mean time of differentiation of a primitive mantle (similar to bulk Earth) into the granitoid rocks of the Superior Province and a residual, LIL - depleted, lithospheric upper mantle which was later the source for the Sr and Nd in the Ontario carbonatites. The data obtained in this thesis support the model of Bell and Blenkinsop (1987) and may also provide some fine detail for their model.

Bell and Blenkinsop (1987) note that some of the scatter shown by their data may be due to uncertainty in the ages of the different complexes, and to variation in initial Sr and Nd isotopic compositions within the complexes. Given these constraints they feel that a linear approximation best suits their data. The two extreme data points of Bell and Blenkinsop (1987) at 2700 Ma and 110 Ma are well determined. The Prairie Lake complex provides a third, well constrained, point with an intermediate age. Although the position of the Prairie Lake point (see Figure 8a) might indicate that a second degree polynomial may ultimately fit their Sr data, the linear approximation of Bell and Blenkinsop (1987) is preferred. The position of the Prairie Lake Sr point shown in Figure 8a may be due to 1) a later age of differentiation for that part of the mantle from which the Prairie Lake magma was derived, or 2) minor heterogeneity in the Rb/Sr ratio of the depleted lithospheric mantle. The latter suggestion is supported by the variation seen in the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Prairie Lake complex. In contrast to Sr, the Nd initial ratio for the Prairie Lake complex plots on the depleted lithospheric mantle reservoir development line (see Figure 8b).

The isotopic signature of a source reservoir can be compared to those of bulk Earth (b.E.) and chondritic uniform reservoir (CHUR) respectively, at the same time (T), using the epsilon notation of DePaolo and Wasserburg (1976a). At $T = 1165$ Ma the Prairie Lake source has $\epsilon_{Sr} = -8.0$ and $\epsilon_{Nd} = 2.7$; the depleted lithospheric mantle has $\epsilon_{Sr} = -9.1$ and $\epsilon_{Nd} = 2.5$. From Figure 9, a plot of $\epsilon_{Nd}(T)$ versus $\epsilon_{Sr}(T)$, it can be seen that the uncertainties ($\pm 0.5\epsilon$) associated with ϵ_{Sr} for the Prairie Lake and depleted lithospheric mantle data points almost overlap.

Figure 9 also shows the mantle array defined by the fields of mid-ocean ridge basalts (MORB), ocean island basalts (OIB) and selected continental flood basalts (CFB), all of essentially zero age ($T = 0$) (DePaolo and Wasserburg, 1976b; Richard et al., 1976; O'Nions et al., 1977). It has been argued that the slope of the mantle array is invariant with time (Allègre et al., 1979; DePaolo, 1979). For rocks derived from the same reservoir, the distance along the mantle array from the origin is proportional to a) the amount of time between separation of the source reservoir from the primordial mantle and b) the extent of fractionation of the Sm/Nd and Rb/Sr ratios with respect to the primordial mantle values. Rocks of similar age that plot in distinctly different positions must therefore be at least partially derived from different reservoirs. Figure 9 clearly shows that the Coldwell complex, 40 km southwest of Prairie Lake, has a near chondritic source, in contrast to the depleted source for the Prairie Lake complex. Pb isotopic data however indicate a U-depleted source for the Coldwell alkaline complex (Kwon, 1986). Different isotopic signatures may indicate that the Prairie Lake and Coldwell complexes were derived from a heterogeneous mantle.

Figure 9. $\epsilon_{Nd}(T)$ versus $\epsilon_{Sr}(T)$

PL = Prairie Lake, C = Coldwell, dlmr = depleted lithospheric mantle reservoir, MORB = Mid-Ocean Ridge Basalt, OIB = Ocean Island Basalt, CFB = Continental Flood Basalt. Data for MORB, OIB and CFB are from DePaolo and Wasserburg (1976b), Richard et al. (1976) and O'Nions et al. (1977). ϵ notation of DePaolo and Wasserburg (1976a) is defined in section 1.4. Calculated mantle array is from DePaolo (1979); shaded area represents uncertainty.

4.2: Tectonic Significance

The relationship of carbonatites to deep-seated faults is well known (see Heinrich, 1966). Kumarapeli and Sauli (1966) suggested an easterly migration of carbonatite magmatism in eastern Canada along a rift - related fracture system extending from the Lake Superior region through Lake Nipissing to the vicinity of Montreal. Gittins et al. (1967) considered such a migration unlikely in light of the age data they presented for a larger number of complexes. They noted that carbonatites of 1000 - 1200 Ma age occur throughout a large part of the Superior Province. Gittins et al. (1967) do acknowledge the possibility that the extensive fracture system proposed by Kumarapeli and Sauli (1966) may be a major factor in the emplacement of carbonatite complexes in eastern Canada, but note that a widespread system of subsidiary faults is needed for the model to be acceptable.

Gittins et al. (1967) found four distinct ages of carbonatite emplacement in Ontario and Quebec. From more recent data summarized in Wen (1985) and Bell and Blenkinsop (1987) these groups are more precisely defined at 110 - 125 Ma, 550 - 600 Ma, 1000 - 1200 Ma and 1700 - 1900 Ma. The most striking features of these groups is the close correspondence in age of the 1000 - 1200 Ma and 1700 - 1900 Ma groups to the Grenville and Hudsonian orogenies respectively (Gittins et al., 1967). Gittins et al. (1967) suggested that "the possibility exists that the carbonatites were intruded in the stable forelands outside the orogenic belts corresponding to the Grenville and Hudsonian orogenies".

The age of the Coldwell complex is the subject of much debate (see Turek et al., 1985). Turek et al. (1985) cite ages ranging from 1010 Ma to 1280 Ma with most being between 1050 and 1080 Ma. The preferred age

of the Coldwell is considered to be 1130 Ma (Thorpe, 1986). The Killala Lake complex is of similar age. Bell and Blenkinsop (1980) obtained a Rb - Sr whole rock age of 1098 ± 48 Ma for the Killala Lake complex; Doig (1967, pers. comm. cited in Coates, 1970) obtained a K-Ar age of 1185 ± 90 Ma. The Chipman Lake carbonatite dykes have a minimum age of 1025 ± 31 Ma (unpublished data cited in Sage, 1983c) based on K-Ar analyses of amphibole in adjacent fenites. Considering their isotopic ages and spatial relationship (section 2.1) it seems that the Prairie Lake, Coldwell, Killala Lake complexes and, the Chipman Lake carbonatite dykes are related.

The Basaltic Volcanism Study Project (1981) and Gordon and Hempton (1986) review the K-Ar, Rb-Sr and U-Pb isotopic studies on Keweenawan volcanic and intrusive rocks. These studies suggest that Keweenawan, rift - related igneous activity occurred between 1180 - 1100 Ma ago with the highest quality dates supporting the interval of 1120 - 1100 Ma (Silver and Green, 1972) for the bulk of Keweenawan magmatism. Temporal relations therefore suggest that the alkaline and carbonatite rocks of the Prairie Lake area are the products of igneous activity associated with regional Keweenawan magmatism.

The possibility that Keweenawan rifting formed as a result of the synchronous Grenville Orogeny was first proposed by Donaldson and Irving (1972) and has since been accepted by Van Schmus and Hinze (1985) and Gordon and Hempton (1986). The best U-Pb and Rb-Sr dates indicate that the Grenville Orogeny could have occurred in as narrow a range of time as 1150 - 1100 Ma ago but almost certainly occurred between 1250 and 1100 Ma ago (Gordon and Hempton, 1986). Gordon and Hempton (1986) have proposed a model in which rifts, such as the Keweenawan and Red Sea/ Gulf of Aden,

are formed as a result of strike-slip faulting in either the foreland or the hinterland of orogenic zones. In summary, it is conceivable that the Prairie Lake complex and nearby alkaline and carbonatitic rocks were the products of rift-related igneous activity related to the Grenville orogeny.

4.3: Light Rare Earth Element (LREE) Enrichment

Faure (1986) lists the average Sm and Nd contents of carbonatite as about 39 and 179 ppm respectively based on 47 samples, and Bell and Blenkinsop (1987) give best estimates of about 37 and 248 ppm respectively, based on 13 samples. The Prairie Lake rocks thus appear to have Sm and Nd contents similar to those of average carbonatite.

Prairie Lake whole rocks and mineral separates, with the exception of garnet, have low Sm/ Nd ratios ranging from 0.126 to 0.226. This indicates that the magma from which they crystallized was strongly enriched in LREE relative to HREE. The initial Nd isotopic composition, however, indicates that the mantle source had a time - integrated LREE depletion rather than enrichment relative to bulk Earth. These findings are in full agreement with those of Bell and Blenkinsop (1987) who suggested that LREE enrichment occurs slightly before or at the same time as carbonatite magma generation. The question therefore remains as to the source of the Nd in these rocks.

Wen (1985) proposed that CO₂ behaves as a carrier and scavenges incompatible elements from the sub-continental lithosphere. Experimental work by Wendlandt and Harrison (1979) has shown that the REE partition preferentially into CO₂ vapor/ carbonate melt with respect to silicate melts or solids, under mantle pressure - temperature conditions. A

problem with a "CO₂ scavenger model" is the source of the CO₂.

Pollack (1986) suggests that continental lithospheric roots are stabilized by the loss of volatiles. Meen (in press) has shown that water- and carbon dioxide-bearing magmas rising from depths in excess of 70 km may react with peridotite wall-rock to produce a carbonated mantle. Subsequent melting of this metasomatized mantle can produce carbonated hyper-alkaline magmas with LREE enrichment. If the CO₂ (or carbonate) involved in mantle metasomatism, as proposed by Meen, is from a reservoir which is physically distinct from the subcontinental lithosphere, then it is reasonable to assume the CO₂ will bring with it Nd of quite different isotopic composition from that of lithospheric Nd. A model in which CO₂ carries or scavenges the incompatible elements from their source therefore appears untenable.

An alternative model to mantle metasomatism or scavenging by volatiles to account for the LREE enrichment of carbonatites is partial melting of a mantle assemblage involving disequilibrium participation of a LREE-rich accessory phase. Campbell and Gorton (1980) propose disequilibrium melting of a LREE-rich accessory phase such as loparite, a member of the perovskite group of minerals, or a REE carbonate such as sahamalite (Ce₂Mg(CO₃)₄), in a simple chondritic mantle to account for two well known petrographic features. The first is the similar La/Sm ratios of the alkali basalt - kimberlite suite over a range of total REE concentrations. The second is the strong LREE enrichment of nodules in otherwise depleted ultramafics. Based on thermodynamic considerations Campbell and Gorton argue that a LREE-rich phase will be among the first to melt and thus dominate the REE patterns of early formed liquids, even when subsequent partial re-equilibration is allowed for.

Two problems arise, however. The first is whether such a phase is still preserved after differentiation of a primitive mantle into the granitoid rocks of the Superior Province and a residual, depleted, subcontinental upper mantle. The second is that a LREE enriched phase would have a low Sm/Nd ratio. If such a mineral phase were present for a significant length of time before formation of the carbonatite magma, both the mineral and the derived carbonatite magma would have a low $^{143}\text{Nd}/^{144}\text{Nd}$ ratio relative to CHUR. In other words one would expect the carbonatite to have an enriched Nd isotopic signature rather than the observed, depleted signature. In summary, a model in which a LREE - rich accessory phase is stable in the depleted subcontinental upper mantle may have some merit in helping to explain the REE characteristics of carbonatites. However, such a model is unable to explain the depleted isotopic signature of carbonatites.

CHAPTER V: Summary and Conclusions

The most significant findings of this thesis are:

1. An 18 point Rb-Sr isochron, defined by whole rock and mineral data, yields an age of 1130 ± 10 Ma for the Prairie Lake complex. The whole rock and biotite data, calculated separately, yield ages of 1165 ± 30 Ma and 1135 ± 15 Ma respectively. At the two-sigma level the uncertainties associated with the ages overlap, indicating that the Rb-Sr mineral system has probably remained closed since the time of intrusion.
2. An 8 point Sm-Nd isochron, defined by whole rock and mineral data, yields an age of 1200 ± 40 Ma. This is one of the first, and the most precise of the Sm-Nd isochrons obtained from a carbonatite complex.
3. The Rb-Sr whole rock age (1165 ± 30 Ma) is considered to be the best estimate of the emplacement age because it overlaps both the biotite (1135 ± 15 Ma) and Sm-Nd (1200 ± 40 Ma) ages.
4. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ten samples (whole rocks and mineral separates) with very low $^{87}\text{Rb}/^{86}\text{Sr}$ ratios (< 0.005) are fairly uniform and range from 0.70247 to 0.70262. This total range of $\sim 0.02\%$ is similar to that seen in other complexes (e.g. Wen, 1985). This slight but distinct variation in initial Sr isotopic composition is attributed to slight heterogeneity in the Rb/Sr ratio of the source.
5. The initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of the Prairie Lake complex is 0.51129 ± 0.00004 . Because this ratio is obtained by extrapolation of the Sm-Nd isochron rather than direct measurement, it is not possible to determine if there is variation in the initial Nd isotopic composition of the Prairie Lake complex.
6. In plots of initial ratio versus age, the Sr and Nd isotopic compositions of the Prairie Lake complex plot near the respective develop-

ment lines for a depleted lithospheric mantle determined by Bell and Blenkinsop (1987). This indicates a depleted lithospheric source for the LIL elements of the Prairie Lake complex and supports the model of Bell and Blenkinsop (1987) of an ancient, depleted lithospheric mantle.

7. In an $\epsilon_{Nd}(T)$ versus $\epsilon_{Sr}(T)$ plot, the data from the Prairie Lake carbonatite complex plot in the depleted quadrant and fall on the mantle array. In contrast, data from the nearby Coldwell alkalic complex plot near bulk Earth/ CHUR. This may indicate that the Proterozoic mantle in the Lake Superior region was somewhat heterogeneous.

8. The 1165 Ma old Prairie Lake carbonatite complex is similar in age to the nearby Coldwell and Killala Lake alkalic complexes both of which are approximately 1100 Ma old. These ages are also similar to those accepted for the bulk of the regional Keweenaw magmatism (~1120 - 1140 Ma), and the Grenville orogeny (1250 - 1100 Ma). These similarities suggest that the Prairie Lake carbonatite complex and nearby alkalic complexes are the products of rift-related magmatism related to the Grenville orogeny.

9. All analyzed rocks and minerals (except garnet) show a strong enrichment in the LREE relative to the HREE. The initial $^{143}Nd/^{144}Nd$ ratio of 0.51129 however, indicates that the mantle source had a long, time-integrated depletion rather than enrichment. Scavenging of the LREE by CO_2 , mantle metasomatism, and partial melting of a mantle assemblage involving disequilibrium melting of a LREE enriched accessory phase are three ways of producing a melt with the LREE enrichment of carbonatites. However, none of these processes can account for the high $^{143}Nd/^{144}Nd$ ratios that characterize carbonatites.

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APPENDIX I

Nomenclature

Carbonatites

Carbonatites are igneous rocks that contain more than 50 % by volume of carbonate minerals. The descriptive nomenclature used in this thesis is given in Tables A1 and A2.

Alkaline - Silicate Rocks

The classification scheme used for the alkaline silicate rocks is after that of Sarantsina and Shinkarev (1967, in Sorensen, 1974) and is illustrated in Figure 10. Most alkaline rocks in the Prairie Lake complex are of the continuous series pyroxenite - melteigite - ijolite - urtite, which are respectively defined by decreasing ratios of their two principle constituents, pyroxene and nepheline. Rocks of this series are collectively referred to as ijolite series rocks or ijolitic rocks.

Several rocks of the thesis suite cannot be reasonably classified using either of Tables A1 or A2, or Figure 10. At Palabora Hanekom et al. (1965) loosely used the name phoscorite for the apatite ore rocks consisting of apatite, magnetite and olivine (or its alteration product serpentine) $\pm$ vermiculite. They noted that the average composition of the phoscorite ore was 25 % apatite, 35 % magnetite, 18 % carbonate and 22 % serpentine, vermiculite plus other minerals but emphasized that the relative proportions and grain size of the minerals vary considerably. Therefore the name phoscorite is applied to any rock consisting largely of apatite, magnetite and olivine $\pm$ carbonate and mica (biotite or phlogopite). The modifier pyroxene is used when the main mafic mineral

is pyroxene rather than olivine. Where no previously defined rock name could be found a mineral list rock name is used.

Table A1 Hybrid Carbonate - Silicate Rocks, (after Heinrich, 1966)

Modal Composition	100 - 90 % Carbonate(s)	50 % Carbonates > silicates	50 % Silicates > carbonates	90 - 100 % Silicates
General Name	Carbonatite	Silicocarbonatite	e.g. Carbonatitic (or calcitic) ijolite	e.g. ijolite see Table 1 - 4

Table A2 Carbonatites containing mixtures of carbonate minerals (after Streckiesen, 1979)

Modal Composition	100 - 90 % Calcite	50 % Calcite > dolomite	50 % Dolomite > calcite	90 - 100 % Dolomite
Name	Calcite Carbonatite	Dolomite - calcite Carbonatite	Calcite - dolomite Carbonatite	Dolomite Carbonatite

* Characteristic contents of minerals are indicated by prefixes, e.g. apatite silicocarbonatite. When the presence of a minor constituent (< 10 %) must be emphasized, a qualification is used, e.g. calcite - bearing ijolite.

Figure 10 An alkaline rock classification scheme
(After Sarantisina and Shinkarev, 1967 in Sorensen, 1974)

Ne = nepheline, Px = pyroxene, A = alkali feldspar. The shaded areas denote the most common alkaline silicate rock types in the Prairie Lake complex.

APPENDIX II

Table A3 Thin Section Descriptions

Sample Number	Rock Type	Mineral	Modal %	Size mm (ave)	Form	Texture of Occurrence	Inclusions	Alteration	Other Features
20106	silico-carbonatite	calcite	60	1 - 2 {1.5}	A	blocky, tabular	K-feldspar		
		potassium feldspar	40	0.1 - 0.3	A	rounded		mod - str., ragged	embayed, separate gral optically continuous
21A064	pyroxene-phoscorite	diopside	45	0.1 - 0.4 {0.8}	S, E		ap, mt, bio		colourless, very fresh
		magnetite	20	0.1 - 0.3 (1)	A, S		diop, embold ap	ragged, bio	
		apatite	15	0.1 - 0.3 {0.4}	S, E	mosaic, clots commonly bent			gr/br films on boundaries/ fractures
		biotite	10	0.1 - 0.3 (0.5)	A			nm gr core rev rd rim	
22064	pyroxene-phoscorite	diopside	30	1 - 4 {1.5}	S, E		ap, bio, mt	weak, gr color	
		apatite	25	0.1 - 0.5 {0.2}	S	int clots 1 - 3 mm			gr/br films on boundaries/ fractures
		magnetite	20	0.1 - 0.3 (1)	A, E		ap		
		biotite	15	1 - 6 (3)	A, S	often bent, broken			
		calcite	5	1 - 3	A	int to bio, diop, pyrr		nm gr core rev rd rim	
		pyrrhotite	5	???					
		silicon	trace						
27208	melteigite	diopside	65	0.5 - 4 (1)	A	blocky	ap	weak	some grains show oscillatory zoning
		nepheline - cancrinite	10	0.5 - 1.5 {0.8}	A	blocky	ap	weak,	partial bio rims
		garnet	10	1 - 3 (2)	S, E		ap (<0.1), cal, mt, neph		darker cores
		apatite	7	0.1 - 0.9 {0.4}	A, E	int to gnt, diop, mosaic clots			rims of higher interference color
		calcite	5	0.5 - 2 (0.8)	A	int			
		magnetite	3						
		pyrrhotite	1						
		biotite	trace						
32024	silico-feldspar-bearing melteigite	diopside	68	0.1 - 4 (1)	S, E	cm		varying weak, sodic	colorless - 1 gr, br
		biotite	10	???	A	slight bending			
		nepheline - cancrinite	6	???	A, E	int to diop		totally altered	often rimmed by bio
		apatite	6	(0.3)	S, E	int to diop as mosaic clots + cal less common on cal grain boundaries			
		orthoclase	4	0.3 - 3 {0.5}	A			cloudy, cal corrodes	sharp contacts with 'nepheline'
		calcite	3	0.1 - 1 {0.5}	A, S	int to diop, bio, ortho			
		magnetite	2	???				corroded by rimming bio	
		pyrrhotite	1						
		silicon	trace						
		aphane	trace						
32171	calcite - diopside - biotite rock	biotite	40	2 groups 1 - 5 0.1 - 0.5	A	all ragged; tabular, bent, subequant.		all grains nm gr core rev rd rim	
		diopside	30	0.1 - 0.5 (0.5)	S, E	subequant	embold cal (0.2 - 0.5), bio (rd/gr), mt, ap (prism, emb)		
		calcite	30	0.1 - 1.5 (1)	A	int to bio, diop, mosaic clots; bio, ap, diop (all <0.5) on grain boundaries			
		magnetite	trace		A	ragged		bio corrodes	
		pyrrhotite	trace						

Abbreviations Used in Table A3

Form:	A anhydral S subhedral E euhedral	Texture of Occurrence:	cm cumulate int interstitial prism prismatic amsh ameboid	Mineral Names:	ap apatite bio biotite cal calcite chl chlorite diop diopside fs feldspar gnt garnet mt magnetite neph nepheline ortho orthoclase pyrr pyrrhotite
Colour:	br brown gr green or orange rd red ye yellow l light	'Alteration':	nm normal rev reverse pleo pleochroism		

Table A3 continued

Sample Number	Rock Type	Mineral	Modal %	Size mm (ave)	Form	Texture of Occurrence	Inclusions	Alteration	Other Features
32265	phoscorite	ferroan monticellite	55	1 - 8 (3)	E	cm	ap, ovoid cal		embayed by cal, ap
		calcite	25	0.5 - 3	A, S	mosaic, int to Fe mont			
		magnetite	10	0.2 - 3 (0.7)	S, E	cm		thin rim of corroding bio	
		apatite	10	0.1 - 0.5 (0.2)	A, E	ovoid - prism in mosaic clots within or near ap clots	round cal (< 0.05) ap (< 0.05)		br film on fractures
		garnet	trace	(0.5)	E				
		biotite	trace	(0.8)	A				1 gr, ye - br haloes around ap, gnt
		pyrrhotite perovskite	trace	1.0	E				black cubes in magnetic mineral separate
32455	apatite - calcite carbonatite	calcite	83	0.5 - 1.5 (0.8)	S	granular			
		apatite	8	0.1 - 1 (0.3)	A, E	ovoid - prism, even distrib along cal grain boundaries	round cal (< 0.05 mm)		br film on fractures
		olivine	4	0.2 - 1.5 (0.5)	A	rounded to anhedral - ragged	cal, ap	weak (st) - total (chlor 74 norm gr core rev rd rim	
		biotite	2	0.1 - 1.5 (1)	A		cal, ap		
		magnetite	2						
		pyrrhotite							
33035	apatite - silico-carbonatite	calcite	70	0.4 - 6 (1.5)	S	tabular, orientated			
		diopside	15	0.5 - 1 (1.5)	A, E	small anhedral	intergrown ap		some larger E grains coned, twinned
		apatite	12	0.1 - 1 (0.3)	E	stringers, clots along cal grain boundaries	rounded cal (< 0.1)		br film on fractures, faint zoning
		pyrrhotite	2	1.5 - 1.5 (1)	A				
		magnetite	trace	0.5 - 3 (1)					
33428	calcite carbonatite	calcite	94	1 - 6 (3)	S	blocky, mosaic			
		apatite	2	0.1 - 0.7 (0.3)	S	single grains on cal boundaries in patches			gr/br film on fractures
		biotite	2	0.3 (0.5)	A				ye br - gr br, darker br when contacting ap;
		chlorite ?	2	0.3 - 2 (0.5)	A	patches, core of olivine ?			
34431	nepheline - biotite - calcite rock	calcite	35	0.3 - 3 (0.5)	S	mosaic patches			smaller Beph, gnt, ap along grain boundaries
		biotite	35	0.3 - 4 (3)	A	patchy grains some bending blocky	small gnt, ap, neph, cal, blo	very fresh	pleochroic haloes around gnt, ap
		nepheline	18	0.3 - 1 (0.5)	E				small gnt occurs along grain boundaries
		garnet	10	2 groups (0.02 - 0.05) (0.003) 0.1 - 0.5 (0.3)	E				
		apatite	2	0.01 - 0.1 (0.3)	S		ap intergrown		dark cores
38220	apatite - calcite carbonatite	calcite	85	0.8 - 4 (1.5)	S	mosaic			
		apatite	10	1.1 - 1.1 (0.3)	S, E	separate grains on cal boundaries less commonly along cal clots; defines banding	cal: oval cal: oval on cal boundaries less commonly anhedral or stringy		gr/br film on fractures
		biotite	3	1 - 3	A	tabular	minor ap, cal		br haloes around ap
		pyrrhotite magnetite diopside	2 trace trace	1 - 3 0.3 - 3	A A A	irregular anhedral	cal, ap		embayed by cal

Abbreviations Used in Table A3

Form:	A	anhedral	Texture of Occurrence:	cm	cumulate	Mineral Names:	ap	apatite
	S	subhedral		int	interstitial		blo	biotite
	E	euhedral		prism	prismatic		cal	calcite
				anh	anhedral		chl	chlorite
							diop	diopside
							Fe	ferroan monticellite
Colour:	br	brown	'Alteration':	norm	normal		gnt	garnet
	gr	green		rev	reverted		MC	magnetite
	or	orange		pleo	pleochroism		neph	nepheline
	rd	red					orth	orthoclase
	ye	yellow					pyrr	pyrrhotite
	l	light						

Table A3 continued

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Abbreviations Used in Table A3

Form:	A S Z .	anhedral subhedral anhedral	Texture of Occurrence:	ca int prism emb	cusate interstitial prismatic amibold	Mineral Names:	ap blo cal chl diop	apstite biotite calcite chlorite diopside
Colour:	br gr or rd ya l	brown green orange red yellow light	'Alteration':	norm rev pleo	normal reverse pleochroism	Fe mont gnt mt neph ortho pyrrh	ferrous monticellite garnet magnetite nepheline orthoclase pyrrhotite	

APPENDIX III

Sample Selection and Preparation

Drill core samples were chosen on the basis of unaltered appearance, sample homogeneity, medium grain size where possible (to facilitate mineral separation), and significant content of calcite, apatite, biotite or phlogopite, and garnet.

Samples were split with a rock saw, washed in de-ionized water, and then acetone. Two pieces were chosen from each sample, one for whole rock work, the other for mineral separation. The outer 1 - 2 mm of the core were removed using a tungsten carbide drill. Fifty to two hundred grams of coarsely-crushed core were pulverized to < 200 mesh in a stainless steel Bleuler mill. The mill was cleaned between samples first with de-ionized water, then with acetone. Pure quartz was then pulverized and the mill was cleaned again.

Mineral separates were prepared from up to 1 kg of core. The coarsely-crushed sample was washed in de-ionized water, then dried on filter paper under a heat lamp. Magnetite and pyrrhotite were removed using a strong hand magnet wrapped in tissue. Samples were sieved using polyethylene screens to avoid cross-contamination. The -60 +80 mesh fraction was passed through a magnetic separator to obtain a non-magnetic fraction that consisted mainly of calcite and apatite, and a magnetic fraction consisting of biotite and pyroxene + garnet and olivine.

Calcite (S.G. = 2.7) and apatite (S.G. = 3.1) were separated using bromoform (S.G. = 2.87). Further purification was obtained by further magnetic separation. Finally each mineral separate was immersed in

ethanol and hand-picked under a binocular microscope at 30 X magnification. Garnet was hand picked from the -60 +80 mesh magnetic fraction. Because of apatite inclusions garnet was further crushed in a Spex mill to between -120 and +200 mesh. The Spex mill was cleaned as was the Bleuler mill. Methylene Iodide (S.G. = 3.2) was used to separate garnet (S.G. = 3.5) from apatite (S.G. = 3.1). Final purification was done by hand picking under a binocular microscope using a fine (000), wet brush.

Biotite mineral separates were obtained from the -60 +80 mesh fraction by adding de-ionized water to the sample and decanting the suspended biotite into a funnel. The biotite was dried, crushed in a Spex mill, wet sieved for the -80 +120 mesh fraction, dried again, then hand-picked under a binocular microscope using a wet brush.

All samples were finally rinsed clean with acetone and stored in glass vials. The minimum purity of all mineral separates is estimated to be 99.9 %.

APPENDIX IV

Chemical PreparationSample Dissolution

Fifty to one hundred mg of sample was weighed, placed in a clean Teflon evaporating dish and wetted with Nanopure (NP) H₂O. Blanks for the water contained < 1 pg/ ml of Sm, Nd and Rb, and about 2 pg/ ml for Sr (Blenkinsop, pers. comm. 1987). The sample was digested using 15 ml of ultra pure HF, several drops of Suprapur HClO₄ and 15 ml of 2.5 N HCl, then taken to dryness at a temperature of 100 - 200° C.

Carbonates were taken into solution using only HCl. The residue was taken into solution using several ml of 2.5 N HCl, transferred to a clean Teflon bottle and diluted with 30 - 60 ml of 2.5 N HCl. About one-third of the sample solution was used for unspiked Sr - Nd analyses. The remaining solution was spiked for Rb, Sr, Sm, Nd.

Sample Spiking

⁸⁷Rb-, ⁸⁴Sr-, ¹⁴⁹Sm- and ¹⁴⁵Nd- enriched spikes were added to the sample solution aliquot. The concentrations and isotopic compositions of the spikes, as well as the normal isotopic compositions are given in Table A2.

For spiked sample analyses about one-third of the spiked sample solution was evaporated to dryness in a beaker, transferred to a test tube using about 1.0 ml of 2.5 N HCl including wash, and centrifuged for 10 minutes. Unspiked samples were similarly transferred and centrifuged.

Table A4 Spike Concentrations and Isotopic Composition

Concentration (μ moles/g)		Isotopic Composition (atomic ratio)		
Spike		Spike		Normal ^s
⁸⁷ Rb	0.0765	⁸⁵ Rb/ ⁸⁷ Rb	0.00803	2.591
⁸⁴ Sr	0.01353	⁸⁴ Sr/ ⁸⁶ Sr	21.1999	0.05646
¹⁴⁹ Sm	0.011903	¹⁴⁷ Sm/ ¹⁴⁹ Sm	0.00376	1.08507
¹⁴⁵ Nd	0.09942	¹⁴⁵ Nd/ ¹⁴⁴ Nd	0.348417	0.348417

^s from Faure (1986)

First Column Separation of Rb, Sr and REE

Rb, Sr and the REE were separated using ion exchange chromatography. The column is illustrated in Figure 11 and the procedure is summarized in Table A5. Typical calibration curves are given in Figure 12.

Sample aliquots were collected in disposable plastic beakers and dried at moderate temperature (< 135° C). Rb and Sr solutions were evaporated to dryness prior to mass spectrometric analysis.

Second Column Separation of Sm and Nd

Sm and Nd are separated from each other and from the other rare earth elements using reverse phase chromatography (Richard et al., 1976). The procedure is summarized in Table A6. Details regarding column construction and calibration are given in Wen (1985). The column is illustrated in Figure 13 and the results of a typical Sm-Nd column calibration are shown in Figure 14.

Table A5 First Column Procedure

Add 0.5 ml of sample solution
 (sample dissolved in 2.5 N HCl)
 Add 5 ml of 2.5 N HCl
 Add 30 ml of 2.5 N HCl
 Add 20 ml of 2.5 N HCl (collect Rb - spiked only)
 Add 25 ml of 2.5 N HCl

- When running
 for unspiked Sr
 these steps can
 be combined.

Add 20 ml of 2.5 N HCl (collect Sr)
 Add 20 ml of 6 N HCl
 Add 20 ml of 6 N HCl (collect REE)

Add 65 ml of 6 N HCl (cleaning)
 Add 65 ml of 2.5 N HCl (cleaning)

Table A6 Second Column Procedure

Add 0.2 mls of sample solution (dissolve sample in 0.25 N HCl)
 Add 0.2 ml of 0.25 N HCl
 Add 10 ml of 0.1 N HCl

Add 5 ml of 0.25 N HCl
 Add 3 ml of 0.25 N HCl (collect Nd)
 Add 7 ml of 0.25 N HCl

Add 2 ml of 0.5 N HCl
 Add 3 ml of 0.5 N HCl (collect Sm - spiked only)

Add 100 ml of 6 N HCl (cleaning)
 Add 100 ml of 0.25 N HCl (cleaning)

Figure 11. Sketch diagram of the first (Rb-Sr) column.

Figure 12. Schematic calibration curves for the first (Rb-Sr) column.

The dashed lines represent possible concentration curves for the eluted elements.

Figure 13. Sketch diagram of the second (Sm-Nd) column.

Figure 14. Schematic calibration curves for the second (Sm-Nd) column.

The dashed lines represent possible concentration curves for the eluted rare earth elements.

APPENDIX V

Mass SpectrometrySample Loading

Re double filaments were used for Rb analysis and Ta single filaments for Sr. For Rb analyses about 2 to 3 μ l of NP H₂O is placed on top of the sample but is not stirred, i.e. the entire sample is not dissolved, and 1 μ l of solution is loaded onto the evaporating filament. The evaporating filament is then heated to about 0.9 A in air until the sample is dried, then taken up to 1.5 A for a short period of time to ensure dryness.

For Sr analyses one μ l of 1 M ultrapure phosphoric acid is first loaded onto the filament which is then set to warm at about 0.7 A. The sample is completely dissolved in about 2 μ l of NP H₂O and then 1 μ l of solution is carefully loaded on top of the phosphoric acid. By gradually increasing the current the sample slowly dries and the phosphoric acid is driven off. The current is immediately turned to zero when the filament turns a dull red.

Re double filaments were used for Sm and Nd analyses. The sample is dissolved in 1 μ l of NP H₂O all of which is then loaded directly onto the evaporating filament. The filament is heated at 1.2 A in air until the sample is dried then quickly returned to zero to prevent sample oxidation which may adversely affect analysis on the mass spectrometer.

Analyses

Isotopic analyses were performed using a Finnigan-MAT 261, multi-collector, solid-source mass spectrometer at Carleton University. The

machine is a 90° deflection, magnetic sector instrument with a 23 cm radius of curvature, but the extended geometry results in an effective radius of curvature of 46 cm. The mass spectrometer's nine collectors are positioned such that several isotopes of an element can be measured simultaneously. A Hewlett - Packard 9845 computer controls the operation of the machine (Blenkinsop, 1983).

A standard was run once for every twelve samples. The NBS 987 and the La Jolla standards give a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71023 ± 0.00003 and a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.51185 ± 0.00002 respectively. The estimated uncertainties are 2 standard deviations of a measured value. These values agree well with the accepted values of 0.71014 ± 0.00010 and 0.51185 ± 0.00003 for the NBS 987 and La Jolla standards respectively.

Rb analyses were run at an ionizing filament current of about 1.8 - 2.1 A, corresponding to a temperature of about $1100 - 1400^\circ\text{C}$. Each run consisted of two blocks of data; each block was made up of five scans.

All Sr analyses were performed in the multi - collector mode. Most Sr runs consisted of eight blocks of five scans. The filament current ranged from about 2.2 - 2.5 A corresponding to temperatures of about $1400 - 1500^\circ\text{C}$. $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$ ratios were measured for the spiked samples.

For each Sm run six blocks were obtained with each block consisting of ten scans. $^{152}\text{Sm}/^{149}\text{Sm}$ and $^{147}\text{Sm}/^{149}\text{Sm}$ ratios were measured using a single collector. The current for the ionizing filament ranged from 3.7 - 4.3 A with most samples running at about 4.0 - 4.2 A. The corresponding filament temperatures were $1600 - 1750^\circ\text{C}$. The current for the sample (evaporating) filament usually ranged between 0.9 - 1.5 A but the minimum and maximum values for successful runs were 0.3 and 1.5 A

respectively.

Nd samples were run at an ionizing filament current of between 3.1 - 4.5 A. As with Sm samples, the usual range was 4.0 - 4.2 A. The corresponding temperatures were between 1400 - 1750°C. For both unspiked and spiked samples the evaporating filament current usually ranged between 1.0 - 1.1 A; extreme values were 0.0 A and 1.5 A.

The double collector mode was used for unspiked Nd analyses and multiple collector mode for spiked Nd analyses. For unspiked samples the ratios $^{145}\text{Nd}/^{146}\text{Nd}$, $^{145}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ were measured. Eight blocks of eight scans were obtained. For spiked samples only six blocks were obtained. All samples were monitored for isobaric interference from ^{144}Sm by measuring the $^{147}\text{Sm}/^{145}\text{Nd}$ ratio. Only two spiked samples had significant Sm contamination - so much so that simple correction was not possible. For these two samples the ratios $^{142}\text{Nd}/^{145}\text{Nd}$ and $^{146}\text{Nd}/^{145}\text{Nd}$ were measured. $^{142}\text{Nd}/^{145}\text{Nd}$ was normalized to 3.27719 (Wasserburg et al., 1981) which is compatible with $^{146}\text{Nd}/^{144}\text{Nd}$ of 0.7219.

APPENDIX VI

Major and Trace Element Geochemistry

All samples of Table A3 (thin section petrography) were analysed for the major elements Si, Al, Fe, Mg, Ca, Na, K, Ti, P, Mn, and S as well as the trace elements Ba, Cr, Zr, Sr, Rb, Y, Nb, Zr, and V on a Philips 1410 automated X - ray fluorescence unit at University of Ottawa. The determinations were made on fused disks ($\text{Li}_2\text{B}_4\text{O}_7$, LiCO_3 , and sample) using a Rh tube. Sample 39083 has anomalous Na_2O , TiO_2 , Nb and Cr contents relative to the other samples as shown in Table A7.

Table A7 Comparison of Na, Ti, Nb and Cr contents of sample 39083 relative to the other samples

oxide/ element	<u>sample 39083</u>	<u>all other samples</u>
Na_2O (wt. %)	1.23	n.d. - 0.76
TiO_2 (wt. %)	7.19	n.d. - 2.43
Nb (ppm)	3590	n.d. - 2247
Cr (ppm)	60	n.d.

n.d. = not detected

APPENDIX VII

Microprobe Data

A polished thin section was prepared for microprobe analysis of olivine in sample 32265. The data for the outer (rim) and inner (core) locations for two different grains are given in Table A8.

The analyses were performed using the wavelength dispersion method in a Cambridge Microscan 5 electron probe. Analytical conditions were 15 KV accelerating voltage beam diameter of 1-2 μ m, and a specimen current of 50 nanoamperes referenced to pure iron. Raw X-ray data were reduced using the computer program (EMPADR VII) of Rucklidge and Gasparrini (1969).

Table A8 Microprobe Data for 'Olivine' in Sample 32265

Oxide	Weight Percent			
	Rim	Core	Rim	Core
FeO	18.44	16.70	18.26	17.22
MgO	11.59	12.70	11.49	12.41
MnO	3.09	2.80	3.19	2.80
Na ₂ O	0.03	0.04	0.03	0.03
CaO	32.42	32.73	32.37	32.99
TiO ₂	0.06	0.08	0.07	0.05
Al ₂ O ₃	0.02	0.02	0.02	0.01
SiO ₂	34.95	34.95	34.75	34.88
Total	100.59	100.13	100.16	100.42
Molecular % end-members [§]				
Mont.	48.9	53.7	48.8	52.5
Kir.	43.7	39.6	43.5	40.8
Glauc.	7.4	6.7	7.7	6.7

[§] Ideal compositions of end-members:

Monticellite CaMgSiO_4

Kirschsteinite CaFeSiO_4

Glaucocroite CaMnSiO_4

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