THE GEOLOGY AND PETROLOGY OF THE IRON AND MANITOU ISLANDS ALKALINE CARBONATITE COMPLEXES AT NIPISSING LAKE, ONTARIO

By

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ABSTRACT

The Iron and Manitou Islands complexes are 560 m.y. old. They were associated with a magma chamber lying at moderate depth below these complexes. On a regional scale the emplacement is controlled by the Nipissing graben system, an extension of the St. Lawrence rift system, along which an alkaline igneous province, 560 m.y. old, is well developed.

A variety of rock types is developed in these complexes in spite of their small size. This is a result of extensive differentiation, interaction of late fractions with already crystallized early fractions, interaction of a "fluid phase" with country rocks, partial melting of country rocks, and finally various late hydrothermal alterations. The high degree of differentiation is probably a consequence of the high amount of volatile components in the magma which lowers its viscosity, extends its crystallization range, and consequently enhances fractional crystallization. In addition, liquid immiscibility played an important role in the differentiation.

During differentiation the pyroxenes changed in composition from Ca-rich varieties through aegirine-augite to acmite. There is no evidence of an immiscibility gap between Ca-rich and Na-rich pyroxenes as has been proposed by Aoki (1964) but criticized by later investigators. Members of the phlogopite-biotite solid solution series exhibit a compositional range from annite_{12} to annite_{63}.

The characteristic assemblage melilite; Ca-rich pyroxene, and olivine (partially or completely replaced olivine phenocrysts) occurring

in some lamprophyres indicates low silica activity, $10^{-1.6}$ to $10^{-1.2}$. However, the silica activity of the Lamprophyres is not restricted to the above range since the presence of sphene in some Lamprophyre dykes indicates silica activity above this range.

The required condition of excess sodium silicate for the crystallization of acmite in synthetic melts seems to be required in nature too.

Lamprophyres have a crystallization temperature of about 950°C. Fenitization of the country rocks takes place from relatively low temperature, probably 480°F, to about 740°C where partial melting of the rocks occur.

The development of the graben system and the alkaline igneous activity are both believed to be related to devolatilization processes in the mantle.

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CHAPTER I

INTRODUCTION

I.1. Location and Physiography

The Iron and Manitou Islands alkaline complexes belong to a group of four alkaline intrusions that form a series of islands and almost circular depressions extending westward from Callander along the long axis of Lake Nipissing.

These islands are, from east to west: a) islands of the Callander Bay complex: Darling, McPherson and Grand Trunk Islands; b) Islands of the Manitou complex: Great Manitou, Little Manitou, Calder, Newman, and Rankin Islands; and c) Islands of the Iron and Burritt complexes: Iron and Burritt Islands respectively. The above complexes are shown in fig. I.1 marked by squares. These complexes are within a western extension of the St. Lawrence rift system (Kumarapeli and Saull 1966) along the Mattawa Valley and Lake Nipissing. They constitute the Nipissing Lake Alkaline province.

The Manitou islands are about 5 miles west of the city of North Bay. Iron island is ten miles further west (fig. I.1). From North Bay the islands are easily reached by boat. A boat is also very useful during sampling and field observation work as it is the only means of access of most of the outcrops which occur along the shores of the islands.

Lake Nipissing lies within the North Bay area which is shown in fig. I.1, consequently its physiography requires consideration of the physiography of the whole North Bay area. The North Bay area is in the

NW part of the Grenville Province of the Canadian Precambrian shield and covers about 1700 square miles between Latitudes 46° 00' N and 46° 30' N, and Longitudes 79° 00' W and 80° 00' W.

Relief in the area increases from west to east (fig.I.1). There are two water partings in the eastern part. The first has a N-S direction and the second an E-W direction. The latter extends eastward from the first. West of the first water parting the area is mainly occupied by Lake Nipissing, which is a shallow lake that rarely exceeds 60 feet in depth. Lake Nipissing (average elevation 644 feet) is the lowest point in the area. Maximum relief in the whole area is 950 feet. North of Lake Nipissing prominent escarpments with elevations 800-1000 feet show a NW trend and mark either zones of faulting or strand lines related to the Nipissing and earlier stages of the Upper Great Lakes (Hough 1963). East of the first (N-S) water parting the area is dominated by an eastward trending, south-facing escarpment marking a fault zone and rising as much as 600 feet above the northern side of Trout Lake and the Mattawa River (Lumbers 1971).

Glacial drift in various forms is thickest in the eastern half of the area and is largely absent in the southwestern quarter and near Lake Nipissing.

Summarizing the physiography we could say that the physiographic features of the area were formed by various geologic processes active over a long period of time. High-grade metamorphic gneisses underlying most of the area were formed during the Middle and Late Precambrian. They were subjected to faulting during the Late Precambrian and the Early Paleozoic. They were eroded to a peneplain by the Middle Ordovician which is

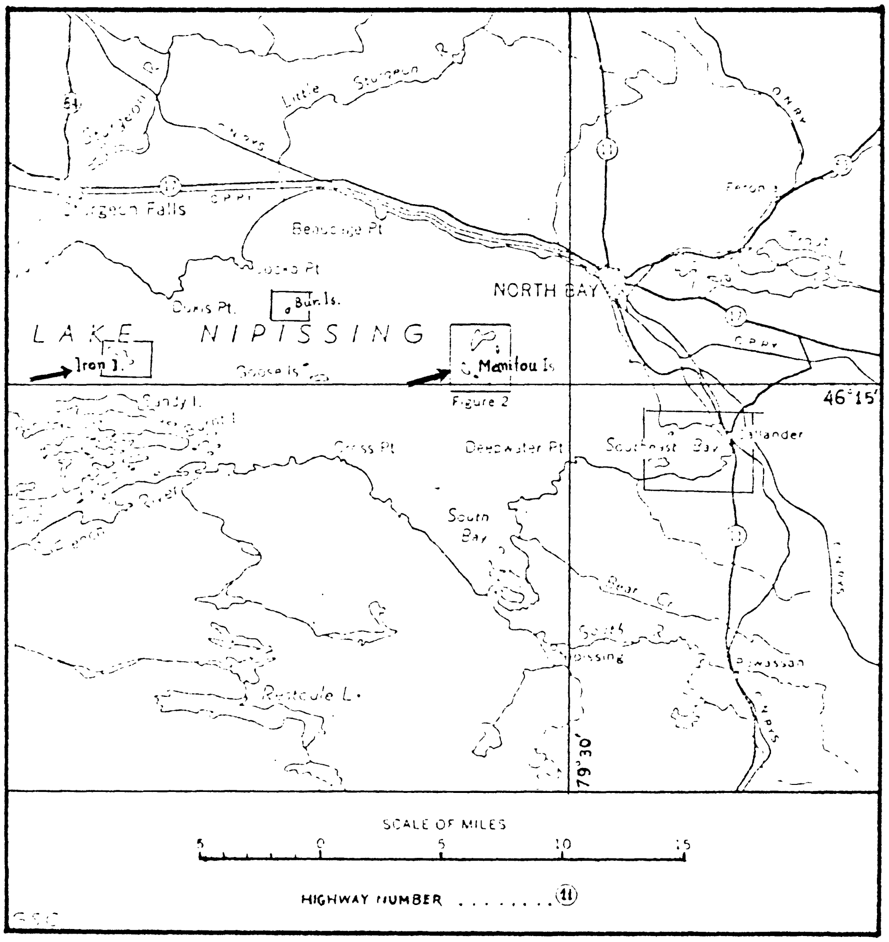


Fig. I.1. Index map, showing location of Manitou Is., Iron I., Burrit I., and Islands of the Callander Bay complex. Lake Nipissing.

represented by marine sediments of this age occurring in the area. These sediments were eroded by subsequent erosion and by Pleistocene continental glaciation.

I.2. Previous Work

Barlow (1908, pp. 215-216) noted that the Manitou Islands are underlain by Precambrian rocks consisting chiefly of altered hornblende-granite gneiss, crystalline limestone, dykes of basic rocks, and small outliers of the Birds Eye and Black River formations of Ordovician age. Barlow also described the basic dyke rocks occurring on the islands as follows: the rock doubtlessly belongs to the group which includes the alnoites, monchiquites, and fourchites but it is now so decomposed that its exact position cannot be determined. He concluded that the rocks rich in carbonates represent portions of the Grenville limestones.

The fact that certain outcrops on the Manitou Islands are radioactive was discovered by James Strohl. Mineralogical studies in the laboratories of the Geological Survey of Canada showed that a rock specimen from the Manitou Islands contained a member of the pyrochlore-microlite series. On February 17, 1953, Beaucage Mines Limited was formed to take over the Manitou Islands property.

Field studies were conducted by R. B. Rowe in 1953, 1954, and 1955. Rowe (1958) described the various major rock types and concluded that their genesis was as follows: the silicate rocks of these bands (the bands of the aureole) are believed to be fenites, rocks that have been made alkaline by the addition of material from an alkaline magma. The origin of the calcite rock is not known. It could be sedimentary or magmatic or both.

Owens (1953) studied the outcrops and diamond drill-cores, and describes the general geology as follows: the rocks exposed on the islands and observed in drill cores are mainly gneisses, crystalline limestone and various intrusives. A complex assemblage typical of the Grenville province, but with local peculiarities, notably concentrations of sodium, phosphorus, fluorine, uranium, and columbium.

Concentrations of pyrochlore present in the fenitic rocks and carbonatite were explored extensively by diamond drilling and underground workings in the 1950s. There were five uranium pyrochlore deposits found. The largest is just to the east of Newman Island fig. I.2. These were the first large pyrochlore deposits to be discovered in North America.

Considerable work has been done on the Newman deposit. Preliminary work consisted of magnetic surveys and more than 80 diamond drill holes. A vertical shaft was sunk on Newman Island and stations were established at the 275-foot and 400-foot levels. Over 12,000 feet of diamond drilling has been done from the 400-foot level and over 9000 tons of rock has been mined for extraction tests. The deposit has been traced along its easterly strike for 1100 feet and has a maximum width of about 400 feet. Its eastward extent is unknown, but calcite-biotite-apatite-uranium pyrochlore rock becomes abundant near the eastern extremity of the explored part. In 1958, Nova Beaucage Mines reported 1,893,000 tons of mineralized rock averaging 0.049 percent U_3O_8 and 0.86 percent Nb_2O_5, and 2,962,000 tons of mineralized rock averaging 0.041 percent U_3O_8 and 0.69 percent Nb_2O_5 all 200 feet below the lake bottom. At the Great Manitou deposit the mineralized rock is 27,000 tons averaging 0.38 percent Nb_2O_5, 0.10 percent U_3O_8, and 10 percent P_2O_5. At the Calder deposit 19 drill holes that intersected mineralization failed to reveal a continuous high-grade mineralized zone (Owens 1953).

Considerable work has been done on the Iron Island complex too. Exploration work has centred mainly on the iron mineralization that was noted by Barlow (1899) and Knight (1949). In 1948 Dominion Gulf Company carried out an aeromagnetic survey of the area and outlined two anomalies (2000 gammas and 400 gammas). Nipiron Mines Limited explored the complex by ground gravimetric and magnetic surveys on the ice, and 26 diamond drill holes, totalling 16,000 feet. The locations of the holes are shown in fig. I.3.

The greatest concentrations of iron oxides were found in dolomitic carbonatite which contains up to 60 percent disseminated grains and massive stringers of hematite and magnetite. Alkalic pyroxenite is reported with an average concentration of 5 to 10 percent disseminated iron-titanium oxide minerals. Disseminated sulfide minerals are in the drill logs from all the intrusive phases of the complex. Niobium and Uranium mineralization, in the form of uranian pyrochlore, is present in silicocarbonatite and ijolitic rocks. Apatite is reported forming locally as much as 20 percent of the silicocarbonatite exposed on Iron Island. Fluorite and barite are mainly confined to late veins that cut across the major rock types of the complex.

Most of the above data are from: a) Assessment work files, Resident Geologist's office, Ont. Dept. of Mines and Northern Affairs, Toronto; b) Lumbers (1971); and c) Rowe (1954, 1958). Except otherwise indicated.

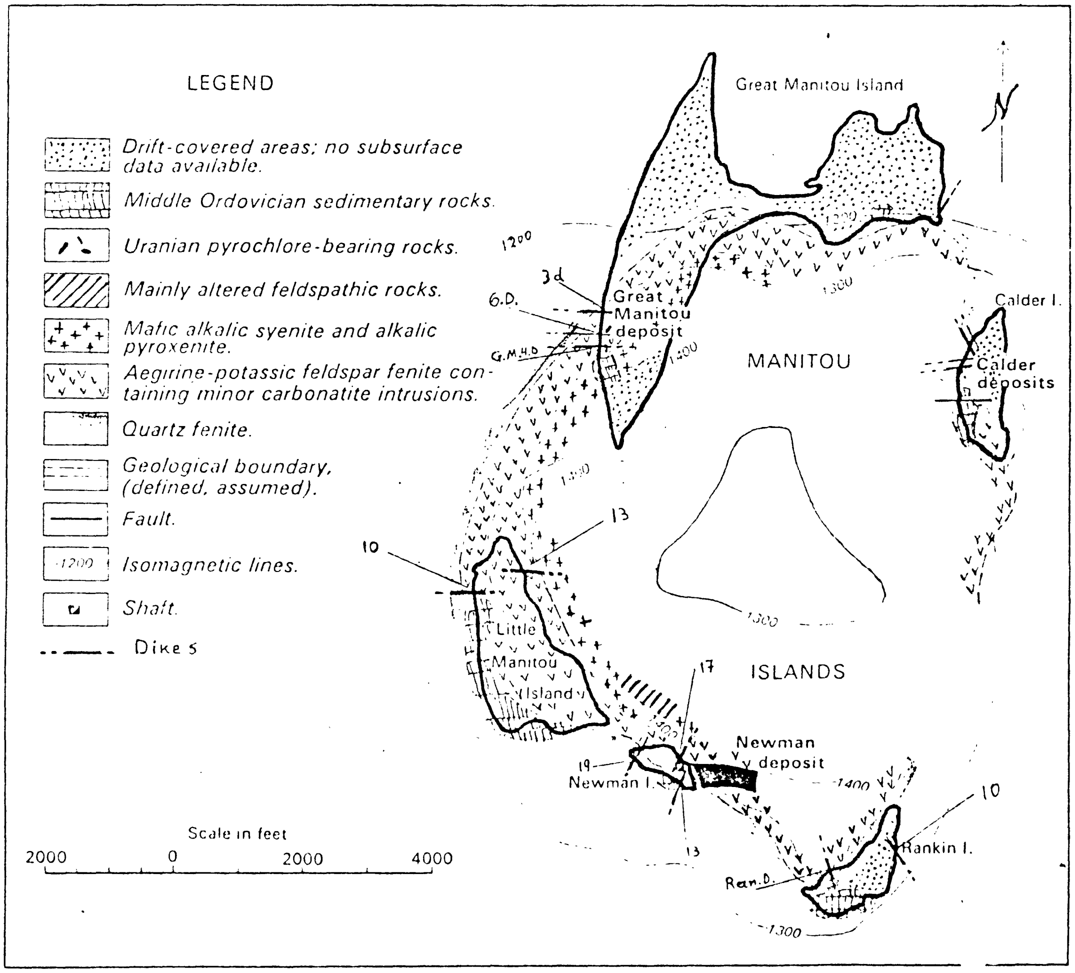


Fig. I.2. Sketch map showing the major geological features and mineral deposits of the Manitou Islands Complex (modified after Rowe 1958, Figure 14).

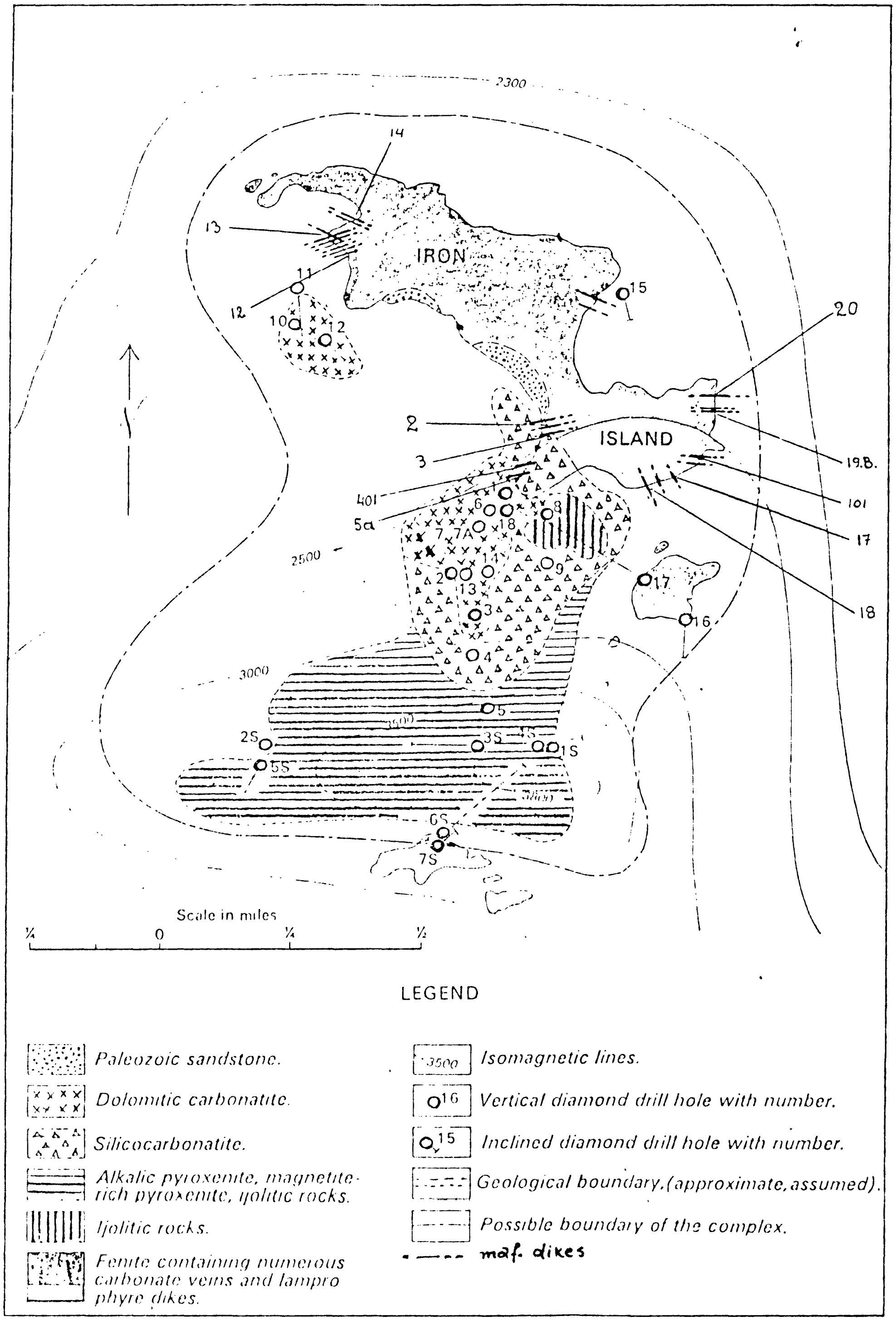


Fig. I.3. Sketch map showing the major geological features of the Iron Island Complex.

I.3. Scope and Content of Present Study

Iron and Manitou Islands complex attracted the attention of investigators early. The Manitou islands complex is well known because it contains the first large Niobium deposits discovered in North America.

Considerable work has been done on both complexes (see chapter I.1). However most of the work was done in the 1950s and was centered mainly on pyrochlore and iron mineralization.

At that time the carbonatite controversy, igneous versus sedimentary (limestone assimilation) origin, persisted in the petrological literature. The suggested petrogenesis of the rocks of these complexes, especially the suggested origin of the calcite-rich rock, by previous investigators reflects this controversy (see chapter I.1). In addition, the age of the rocks was unknown and the tectonics of the area and its possible connection to major first order structural features (continental rifting) had not been revealed.

In the last decade most of the above questions have received a partial or complete answer. The most important step was made in 1966 when E. Heinrich published his monograph devoted to carbonatites and at the same time O. F. Tuttle and J. Gittins brought together, in their book on carbonatites, a series of articles dealing with field and laboratory studies of carbonatites and associated rocks. These studies and their excellent presentation have convinced even the most stubborn geologists of the magmatic origin of these unusual rocks. However, the acceptance of a magmatic origin introduces new questions related to the origin of the CO_2 and the differentiation processes involved in the formation of these rocks. From this point of view the Iron and Manitou alkaline complexes are very interesting, apart from their economic interest. Their petrological interest is increased by textural evidence of liquid immiscibility. For these reasons a study of these rocks was felt worth while.

In the present study a detailed description and interpretation of outcrop, petrographic, mineralogical and chemical data was undertaken. The data were obtained from the occurring rock types, especially from dykes which appear to expose fundamental processes in the development of alkaline rocks arrested at various stages of development. The principal object was to establish the significant features associated with the petrogenesis of these rocks.

The field work on which this study was based was carried out during the summer of 1975. The field work was designed to sample the outcrops, to examine if the dykes conform to any characteristic pattern, and to obtain as much information on the country rocks and fenites as was necessary to understand the fenitization process. Laboratory work included petrographic examination of over 130 thin and thin-polished sections. Staining techniques for K-feldspar, calcite, ferroan calcite and ankerite were used. X-ray powder diffraction and/or microprobe analyses were used to confirm the identification, of rare or difficult minerals, in thin section.

Microprobe analyses were carried out on 28 thin-polished sections. Fifty pyroxene grains were analyzed for Na, Mg, Al, Si, Ca, Ti, Mn, K, Fe, and Cr. Thirty phlogopite grains were analyzed for the same elements. 36 grains of carbonates were analyzed for Ca, Mg, Fe, and Mn. Eleven K-feldspar grains were analyzed for Na, Al, Si, K, Ca, and Fe. Thirteen amphibole grains, three garnet grains, and seven plagioclase grains were analyzed for the ten elements mentioned above for the pyroxenes. The above grains were checked for zoning and other possible chemical changes across the grains.

CHAPTER II

TECTONIC SETTING AND AGE

II.1. General Geology

The oldest rocks exposed on the Iron and Manitou Islands are gneissic rocks. These rocks belong to the metamorphic complex that forms the basement of the Grenville structural province. The region was subjected to faulting during the Late Precambrian, and at least Early Paleozoic. During the tectonism gabbroic stocks and dykes intruded rocks of the metamorphic complex, and by the Cambrian, a westerly trending graben had formed across the central part of the area (fig. II.2) through Lake Nipissing. Within this graben, Cambrian alkalic complexes, including the ones described in this study, and lamprophyre dykes were emplaced. Middle Ordovician sedimentary rocks are exposed on Manitou Islands. They occur either as flat-lying or dipping at low angles. They overlie unconformably the Precambrian gneiss and the Cambrian intrusive and metasomatic rocks. Fossiliferous limestone and dolostone is included in these Ordovician exposures, and Colquhoun (1958) showed that these rocks are Middle Ordovician in age. The thickest and most complete section exposed, about 28 feet, is on the western shore of Little Manitou Island. Two small patches of almost flat-lying, non-fossiliferous sandstone unconformably overlie rocks of the Iron Island alkalic complex (fig. I.4). Several boulders of this sandstone are scattered along the shore of the island. This rock is composed of subrounded to rounded quartz and minor chert grains with an average grain-size of about 1-2 mm in a barite cement that forms up to 30 percent of the rock. Reddish color appears to be due to red ferric oxide stain in the barite cement. Sandstones with a barite cement are uncommon. Lumbers (1971) suggests the following: the fact that late barite dykes are associated with the underlying alkalic complex could indicate that the barite cement was derived from this complex probably by circulating ground waters or late magmatic fluids. The age of this rock is unknown. Lumbers (1971) suggests that it is paleozoic. The central part of the complexes which shows a crater-like depression is covered by water. Three of the Manitou Islands (Great Man, Calder, and Rankin) are partly covered by debris from the pleistocene glacial deposits (fig. I.2). The complexes are characterized by aeromagnetic anomalies. Published aeromagnetic data (GSC 1487 G, 1488 G) are shown in fig. II.1. The major geological features of Iron and Manitou complexes are shown in fig. I.3 and I.2 respectively.

II.2. Age

Lowdon and others (1963) dated Biotite from the Manitou Islands complex by the K-Ar method. The sample was collected by C. H. Stockwell from carbonatites of the Newman deposit (fig. I.2). He obtained an age of 560 ± 15 m.y. About the same age (570 m.y.) was determined by Gittins et.al.(1967).

The age of the Iron Island complex has not been reported. However it seems to be of the same age (560 m.y.) for it is a member of the Nipissing Alkaline province which comprises all four Alkaline complexes found in the area of Lake Nipissing (J. Ferguson and K. C. Currie, 1971). The latter authors also suggested that this alkaline igneous province was developed by a regional emplacement controlled by the Nipissing graben system and according to their personal communication with M. Shafiqullah all complexes give potassium-argon dates of about 560 million years.

Lumbers (1971) also suggested a similar genetic relationship for these complexes.

II.3. Tectonic Setting

It was mentioned earlier that the Nipissing Alkaline province comprises four alkaline complexes extending from east to west across Lake Nipissing (fig. I.1). Currie (1971) proposed Brent crater as a fifth member of the province. The Brent crater, located 50 miles E-SE of North Bay (fig. II.2), is strikingly similar in size, shape, structural setting, presence of fenitization and lamprophyres, and sedimentary infilling, to the above four complexes (Currie 1971). However, for nearly 15 years this crater has been interpreted as a typical example of a "fossil impact crater" formed by collision of the earth with a meteorite or comet. A sixth alkalic complex may be present in a low swampy area, west of Highway 64 at the northwest corner of the index map shown in figure I.1, where a local concentration of carbonatite dykes is accompanied by metasomatic alteration of the wall rock gneisses (Lumbers 1971).

All the above Alkaline complexes are situated within a western extension of the St. Lawrence rift system along the Ottawa River Valley, Mattawa valley, and Lake Nipissing valley. This western branch forms the Ottawa-Bonnechere graben system shown in fig. II.2 (Kumarapeli and Saull, 1966).

The Nipissing Alkaline Province constitutes one of four centres of Alkalic intrusive activity present along a 1200 mile segment of the rift system (Doig and Barton, 1968).

K-Ar dating by Doig and Barton (1968) has distinguished four main periods of alkaline igneous activity associated with the St. Lawrence rift system. During the first period, Precambrian, syenites, granites and

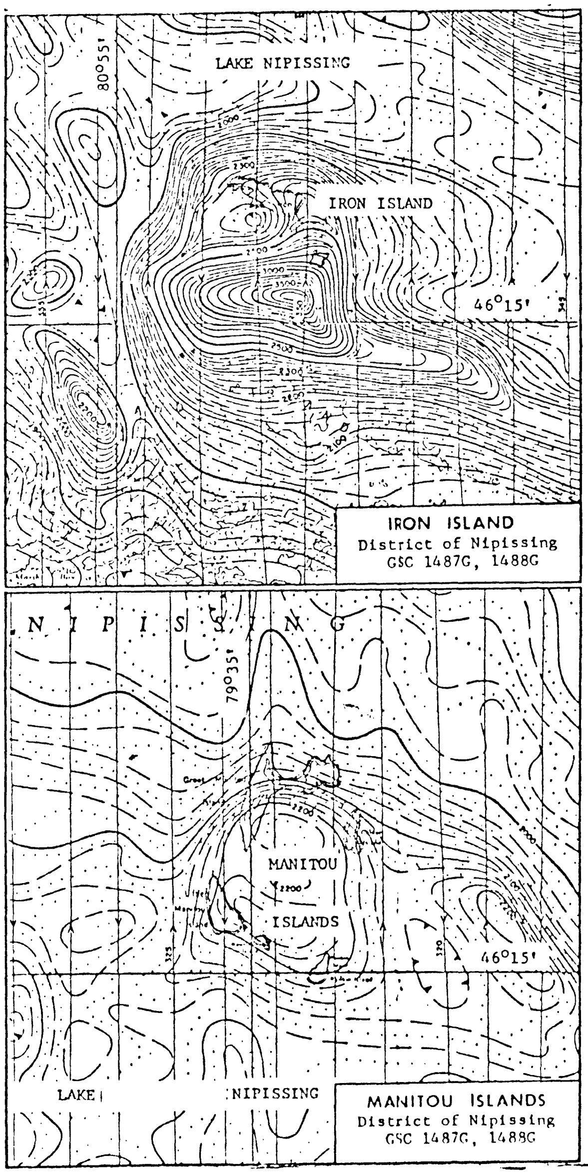


Fig. II.1. Aeromagnetic maps of the complexes. Highs are caused by either magnetite-bearing carbonatite or other alkalic rocks containing magnetite.

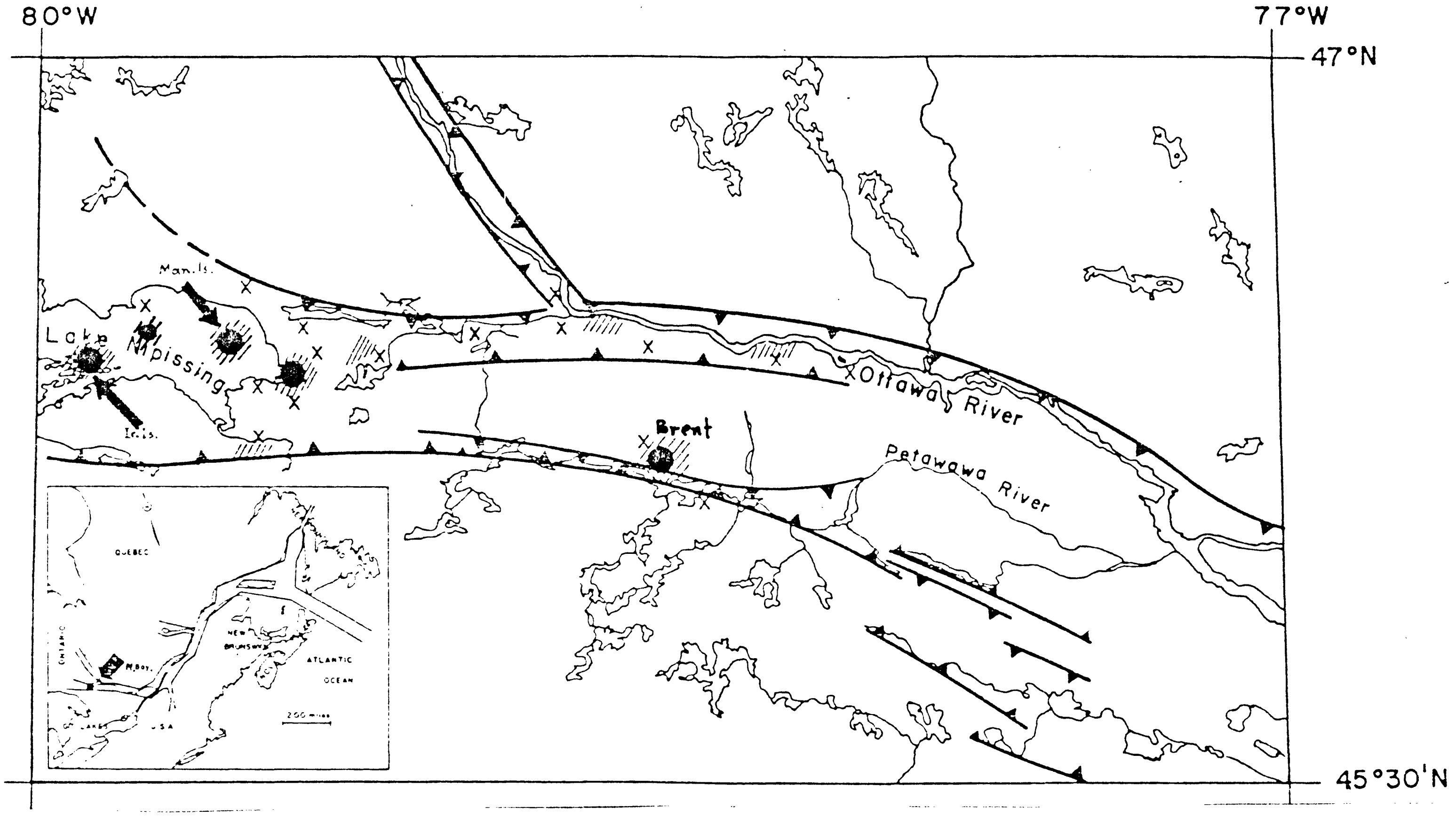


Fig. II.2. The Ottawa - Bonnechere graben system. The teeth along each fault are on the down-thrown side. Solid circles are alkaline complexes, hachured areas display fenitization. Lamprophyre dykes are concentrated at localities marked by an x. The inset map shows the relation of the Ottawa - Bonnechere graben system to the St. Lawrence rift system defined by Kumarapeli and Saull carbonatites were emplaced to the north and west of the Monteregian province. The second period 565 ± 15 m.y., involved the emplacement of alkaline carbonatite complexes, lamprophyres and syenites along the northern edge of the St. Lawrence valley and along the Ottawa-Bonnechere graben, Nipissing Province. During the third period of activity 450 ± 20 m.y. two alkaline syenite-granite complexes were emplaced in the Chatham - Grenville area and at Rigaud. These lie on the north and South sides respectively of the Ottawa graben at the western end of the main Monteregian province, approximately 60 Km west of Mount Royal. The fourth and most recent period of intrusion associated with the St. Lawrence and Ottawa grabens was the Monteregian activity at 110 ± 20 m.y.

Some writers have suggested possible extensions of the St. Lawrence rift system. Kumarapeli and Saull (1966) have pointed out that current seismic activity along a straight zone running through Lakes Ontario and Erie into the Mississippi embayment may indicate an extension of the St. Lawrence system. The structural evidence is fragmentary and weak in itself, but there is supporting evidence from the spatial distribution of alkaline intrusives, kimberlites, and carbonatites. They also discussed another possible extension west of Lake Nipissing through Lake Superior into Wisconsin and Minnesota. Doig (1970) proposed a similar extension of the St. Lawrence rift through Lake Superior on the evidence of an intrusion in Colorado. Some writers have proposed relations of this system with the alkaline complexes of Lake Superior. However, some of the complexes in the area northeast of Lake Superior have been dated radiometrically and have been found much older, indicating that the

Lake Superior trough may be a much older feature than the rift valleys of the St. Lawrence system. D. W. Herdman and B. J. Burley (1974) have suggested that the Kapuskasing high is an ancient spreading center and all the alkaline intrusions northeast of Lake Superior along this lineament are related by age and origin. They also suggested two episodes of activity, 1700 m.y. and 1100 m.y.

It seems that there is no relationship between the St. Lawrence rift system and the alkaline complexes of Lake Superior which belong to a different tectonic system. Consequently any extension of the St. Lawrence system through Lake Superior does not seem justified.

Extension of the northeast edge of the system has been proposed too. Doig (1970) proposed such an extension from Canada to eastern Sweden. He presented a reconstruction map of the North Atlantic region on which had been superposed the various graben structures, the fractures or lineaments away from which the continents separated, and the lower Cambrian alkaline rocks. He concluded that there is continuity in the fracture system and that the 565 m.y. carbonatites are associated with remarkably synchronous movements along this fracture system.

However, the mechanism that causes rifting and spreading is a controversial topic. Some writers have suggested that magma plumes may be the driving force for rifting and movement of the plates.

The Geodynamics Project which is devoted to unravelling the problems of the dynamics and dynamic history of the earth is in its second stage of development which is a period of active research that ends in 1979. One research group is working on the "History and Interaction of Tectonic, Magmatic and Metamorphic Processes. This group is expected to present a model explaining among others the relationship between continental rifting and endogenous processes, magmatism. Unfortunately in a report (Ch. L. Drake 1976) which was sent by this group to the President of I.C.G. (inter-union commission on Geodynamics) V. Beloussov explains that they have somewhat advanced in their study but a rather large part of the work remains to be performed. However from reports of other working groups it seems that mantle plumes are generally accepted as playing an important role in continental updoming and rifting. This explains the association of updoming, which is caused by upwelling material, and location of alkaline igneous occurences in such updomed or arched structures as for example in the Siberian alkaline province (Butakova E. L. in Sorensen 1974) and the Nigeria-Niger province, West Africa (Black and Girod, 1970).

Furthermore, it has been suggested that alkaline intrusions may represent fossilized plumes. Indeed, many of them which are well exposed are circular, steep-sided in shape, and suggest long narrow bodies rising from depths. They are often related to tectonically active zones. A good example is the Port Coldwell alkaline intrusion (D. W. Herdman and B. J. Burley 1974) which is the largest single alkaline intrusion in Ontario and one of the largest in the world. Outcropping over an area of 400 square miles. The Lovozero Massif (650 Km^2) is another well exposed complex. It occurs within the Kola tectonic region (V. I. Gerasimovsky et. al. in Sorensen 1974).

In our case the examined complexes are relatively small high-level exposures of elliptical ring structures of fenites, alkalic rocks, and carbonatites. The similar rock facies occurring in these complexes plus their characteristic geochemistry and mineralization combined with their spatial association suggest an underlying source tapped by deep faults. This source should be extended to comprise the suggested magma source at moderate depth below the Callander Bay alkaline complex (Currie 1972). In this sense the observed complexes represent minor apophysis of this major magma chamber intruded along zones of weakness (fault intersections). Considering the volatile rich character of most of the facies and the presence of fluids which caused the fenitization of the country rocks and late hydrothermal alterations we could suggest that these chimney-shaped complexes were also used as devolatilization channels of the suggested magma chamber which, in itself, is a result of devolatilization processes occurring in the upper mantle.

On a local scale their distribution along the graben seems to be controlled by the existing faults and mainly intersection of faults (Lumbers 1971). The suggested magma chamber explains the fact that lamprophyre dykes are concentrated, but, by no means confined around the alkaline complexes. The floor of the graben system is intruded by such ultramafic dykes (Currie 1971, Lumbers 1971).

Modern examples of continental rifting and alkaline magmatism occur in Africa.

CHAPTER III

PETROLOGY AND MINERALOGY

A. PETROGRAPHY AND FINE STRUCTURE

III.A.1. Introduction

An effort is made in this chapter to present the petrography of the sampled rocks. The most characteristic feature of these rocks is their heterogenity which reaches a maximum at the carbonatites and the palingenic rocks. There are gradational or sharp differences in texture, grain size, and mineralogy. This phenomenon is observed on various scales, that of an outcrop or even of a hand specimen which sometimes may appear relatively uniform macroscopically, but microscopically it shows heterogenity. Another problem is the classification of these rare rocks when an appropriate name is sought for each of them. A serious problem is caused by the multiplicity of equivalent or overlapping rock names introduced by different authors for identical rocks. Unfortunately the application of the recommended classification system and nomenclature by the I.U.G.S. Subcommission on the Systematics of igneous rocks (1973) is not easy to apply. The main difficulties arise from rocks under the general name silicocarbonatites which show a gradational increase of $CaCO_3$ covering the range from silicate rocks to carbonatites.

In spite of the difficulties the silicate rocks were classified following as close as possible to the above mentioned classification system. The names and modal analyses representative of all the major rock types are displayed in Table III 13, 14 and 15. The petrography of these various rock types is briefly as follows.

III.A.2. Alakli Pyroxenite

Macroscopically the alkali pyroxenites have a dark green to green-gray color, they are holocrystalline and very fine grained. They occur in radial dykes cutting the inner fenite zone of the Manitou Island complex, their contacts with adjacent rocks are commonly sharp. Dykes range in width from 10 cm to about 1 m. Similar rocks have been described from drill core specimens obtained during an underground exploration, of the pyrochlore deposits of the complexes, by Beaucage Mines Ltd. and Nipiron Mines Ltd. in the 1950s (Owens 1953). The above rocks, under the name alkalic pyroxenites, are shown on the geological maps of the complexes in Lumber's (1971), Ont. Dept. of Mines, geological report 94 pp. 80 and 82. The above maps with the addition of the dykes which are relatively well exposed on the islands have been included in this work (fig. I.2. and I.3).

The term alkali is used to indicate the alkalic character of the pyroxenes and amphiboles occurring in these rocks. The scarcity of feldspars and the absence of orthopyroxenes, combined with the presence of distinctive minor constituents do not permit any possible confusion with the pyroxenites produced as differentiates of normal basalts.

Two varieties of pyroxenites are present, in the first one (microph. III.1.A and C) the dominant mafic is a pyroxene with pleochroic schemes X-bright green; Y-yellowish green; Z-yellow green. The above pyroxene is aegirine augite. Chemical analyses are displayed in table III.1 (G. M. 4D, CAL. 11.B, NEWM. 15). The pyroxene crystals are subhedral to anhedral with an average size of 0.2 mm X 0.3 mm. However, elongated rather anhedral crystals up to 2.5 mm long were found in a few samples. Many of the elongated crystals show twinning. Calcite and sometimes K-feldspar occur as interstitial phases. Biotite, apatite and opaques are common accessory phases. The carbonate in the rock was stained applying a technique proposed by Dickson (1965) to determine whether dolomite was present: none was observed. The same technique applied to the second pyroxenite variety gave positive results: Ferroan dolomite was detected. This is one of the main differences between the two varieties, another one is the presence of an amphibole as a second major mafic phase (microph. III.1.B) in the second type of pyroxenite. The amphibole shows pleochroism as follows: X-light bluish green; Y-light brown-yellow; Z-light yellowish green. The addition of the amphibole in the mode requires an additional characteristic adjectival term at the name of this rock: <<Alkali amphibole pyroxenite>>. The high sodium of the amphibole plus the ratio of Na:Ca ($Na \gg Ca$) places it in the alkali amphibole field. Taking into account the total Fe:Mg ratio, its low Al content, and its physical properties, the amphibole was classified as a magnesioriebeckite-magnesioarfvedsonite solid solution. The relatively high Mn content is noteworthy, $\sim$2.3% MnO in wt%, (see table III.1. - specimen Lit.10.M.D. - amphibole). The Mn content is high enough to characterize the mineral as a <u>manganous</u> Mg-arfvedsonite -- Mg-riebeckite one. (Mangamous: $MnO > 2.0\%$ wt. according to the proposed nomenclature by Miyashiro 1957, page 57). The amphibole crystals are subhedral, cross sections are relatively well bounded by their own crystal faces, while long sections show a more or less irregular outline.

The average cross sections are 0.1 X 0.2 mm and the long ones are 0.2 mm long with some of them reaching 0.4 mm. The coexisting pyroxene crystals are anhedral and very fine, less than 0.05 mm, however some prismatic crystals 0.1 mm to 0.2 mm long occur too. In a few cases these two mafic minerals were found closely associated. There are amphibole crystals with pyroxene along cleavage traces, amphiboles with pyroxene rims and crystals showing an intergrowth of pyroxene with amphibole. The difference in grain size and form between the amphiboles and pyroxenes is expressed by the microporphyritic texture of the rock. These two minerals seem compatible. However the late crystallization of the pyroxene is quite evident. The chemical compositions of these two coexisting phases are given in table III.1 (specimen Lit.10 M.D - PYROX. and -AMPHIB.). There is a remarkable difference in MgO, FeO^{total} and Na_2O content. The pyroxene is one of the most fractioned ones (rich in FeO^{total} and Na_2O, and poor in MgO) found in the whole complex, it is an aegirine. The coexisting amphibole is richer in MgO and poorer in FeO^{total} and Na_2O. Similar coexisting Na-amphiboles and Na pyroxenes have been reported by McKie (1966) from the Oldonyo Dili alkaline rocks (from quartz-free aegirine-magnesioarfvedsonite-fenites). McKie's data (McKie 1966, page 279, table X, anal. Am-6 and Px-6) and data from this study are displayed below for comparison.

	Na_2O	CaO	MgO	FeO^{tot}	K_2O
McKie's px	11.17	3.75	1.57	28.10	0.40
this study px	11.25	4.85	1.95	26.55	-
McKie's Amph.	8.35	2.22	11.20	16.90	1.97
this study Amph.	6.46	4.20	10.60	18.00	1.74

Chemical analyses of the pyroxenes from the first pyroxenite variety are shown in table III.1. (specimen G.M.4D, CAL.11.B, NEWM. 15). These pyroxenes contain less Na_2O and FeO^{total}, and more MgO and CaO than

TABLE III.1.

Composition of pyroxenes and Amphibole from pyroxenites (wt%)

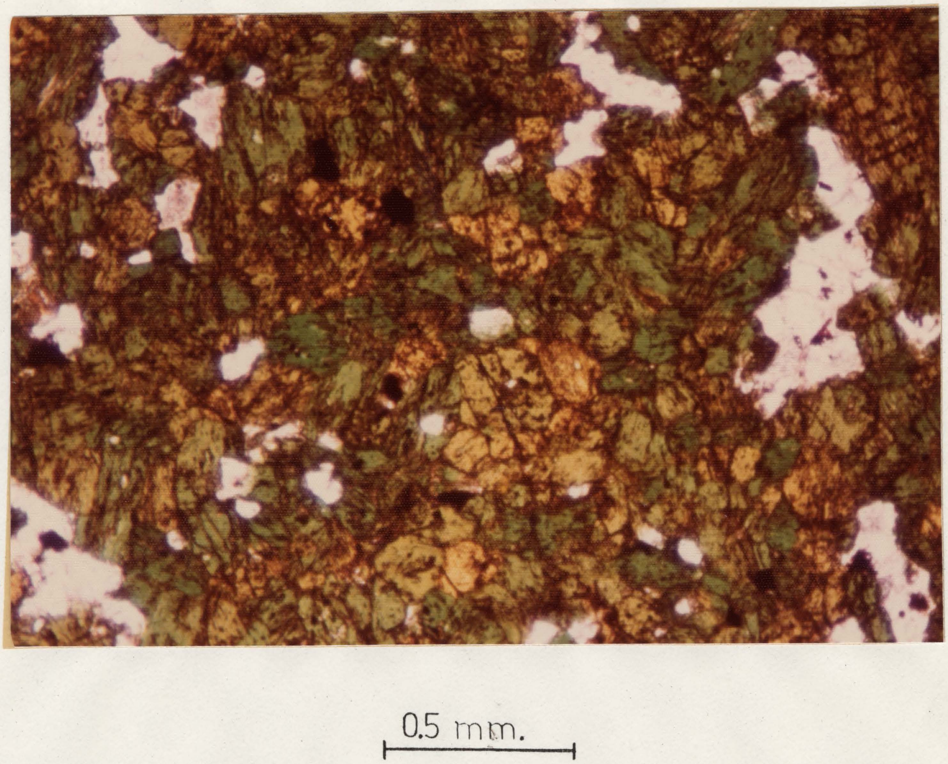
Specimen	Mineral	Na_2O	CaO	MgO	FeO*	Al_2O_3	SiO_2	TiO_2	MnO	K_2O	Total
LIT.10.M.D.	PYROX.	11.25	4.85	1.95	26.55	0.95	53.05	0.70	0.90	-	100.20
LIT.10.M.D.	AMPHIB.	6.46	4.21	10.59	18.00	1.65	52.36	0.70	2.40	1.74	100.16
G.M.4.D.	PYROX.	4.95	15.40	4.60	21.30	0.65	51.85	0.25	1.60	-	100.60
CAL.11.B.	PYROX.	2.35	20.25	9.10	14.40	0.70	51.75	0.10	1.05	-	99.70
NEWM.15	PYROX.	7.30	11.10	3.60	23.50	0.80	52.00	0.50	1.30	-	100.10

FeO* = total iron expressed as FeO.

TABLE III.2.

Composition of plagioclase and pyroxene from diabase dikes (wt%)

Specimen	Mineral	Na_2O	CaO	MgO	FeO*	Al_2O_3	SiO_2	TiO_2	MnO	K_2O	Total
Ran.13.A	PYROX.	0.45	16.08	18.75	9.65	1.80	53.21	0.25	-	-	100.18
RAN.13.A	PLAG.-6	3.65	13.90	-	0.80	29.70	51.30	-	-	-	99.35



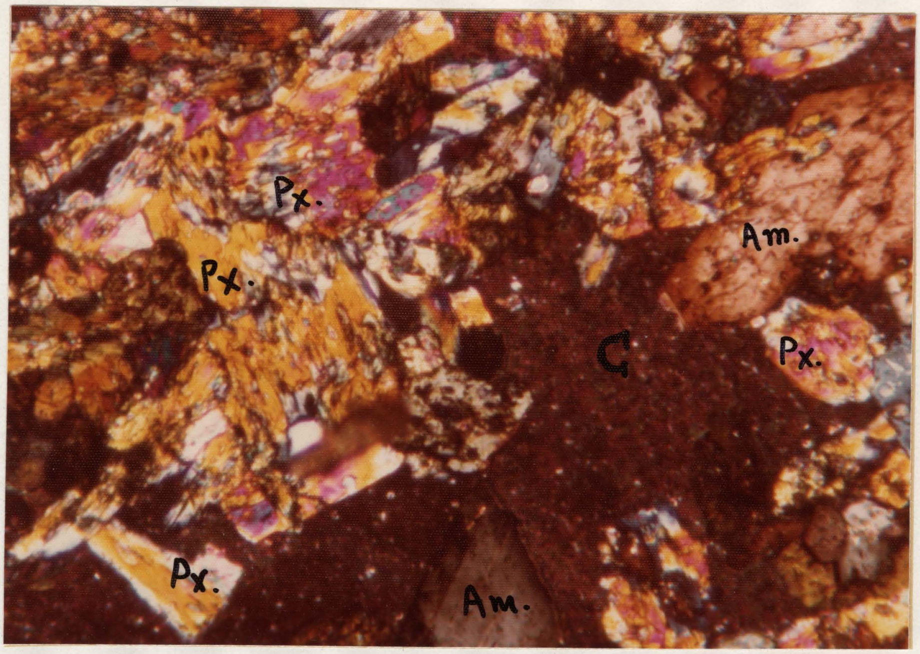
Microphotograph III.1.A.

Microphotographs III.1.A, B, and C: Pyroxenites.

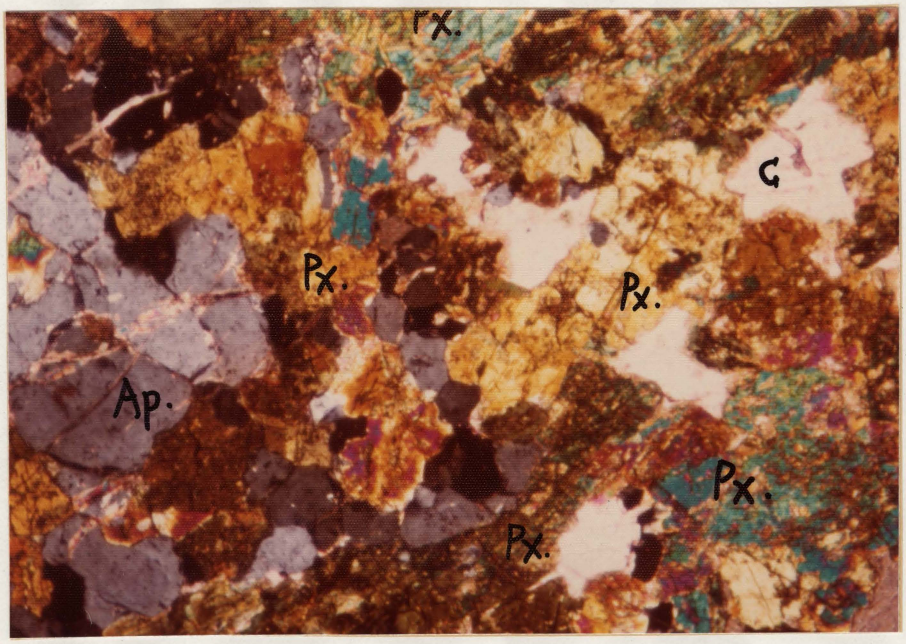
A. Alkali pyroxenite. The colored crystals, showing pleochroic colors from green to yellow green, belong to Aegirine Augite. The colorless (white) areas are occupied by calcite, K-feldspar, and apatite. Parallel nicols. Sample: G.M.4.D

B. Alkali Amphibole Pyroxenite. Crossed nicols. Sample: LITT.10.M.D., Am = Amphibole, Px = Pyroxene, C = Ferroan Dolomite.

C. Alkali Pyroxenite. Crossed nicols. Sample: CALL.11.B. Ap = Apatite, Px = pyroxene, C = calcite.



Microphot. III.1.B.



Microphot. III.1.C.

the pyroxenes of the second pyroxenite variety. They are aegirine augites to aegirines.

III.A.3. Diabase Dykes

These dykes occur rather rarely. They have a basaltic composition, consisting essentially of plagioclase (labradorite to bytownite) and pyroxene (Augite). The chemical compositions of the above phases are shown in table III.2. The mode of the rock is shown in table III.15. (code number 7).

This intermediate to mafic rock is fine to medium grained with dark grey colour. In thin section, randomly oriented laths of plagioclase are enclosed by larger, irregularly bounded crystals of Augite constituting an ophitic texture (microphot. III.2).

According to I. Carmichael, F. Turner and J. Verhoogen (1974 page 24) the development of ophitic texture in diabase dykes is a result of an intermediate cooling rate. In their discussion they invoke the different melting entropies of Diopside and anorthite, and the fact that the nucleation and growth rates can be shown to be proportional and inversely proportional respectively to the entropy of melting.

III.A.4. Lamprophyre Dykes

These dyke rocks are concentrated within the fenite aureoles of the two complexes (fig. I.3.I.4) although they are by no means confined to them. Concentrations of dykes are found in the adjacent area within a radius of 15 km. Very similar dykes occur sporadically over the floor of the paleozoic rift system with which these complexes are associated

Microphotograph III.2 Diabase. Laths of plagioclase are enclosed by larger augite crystals. Crossed nicols. Sample RAN.13.A.

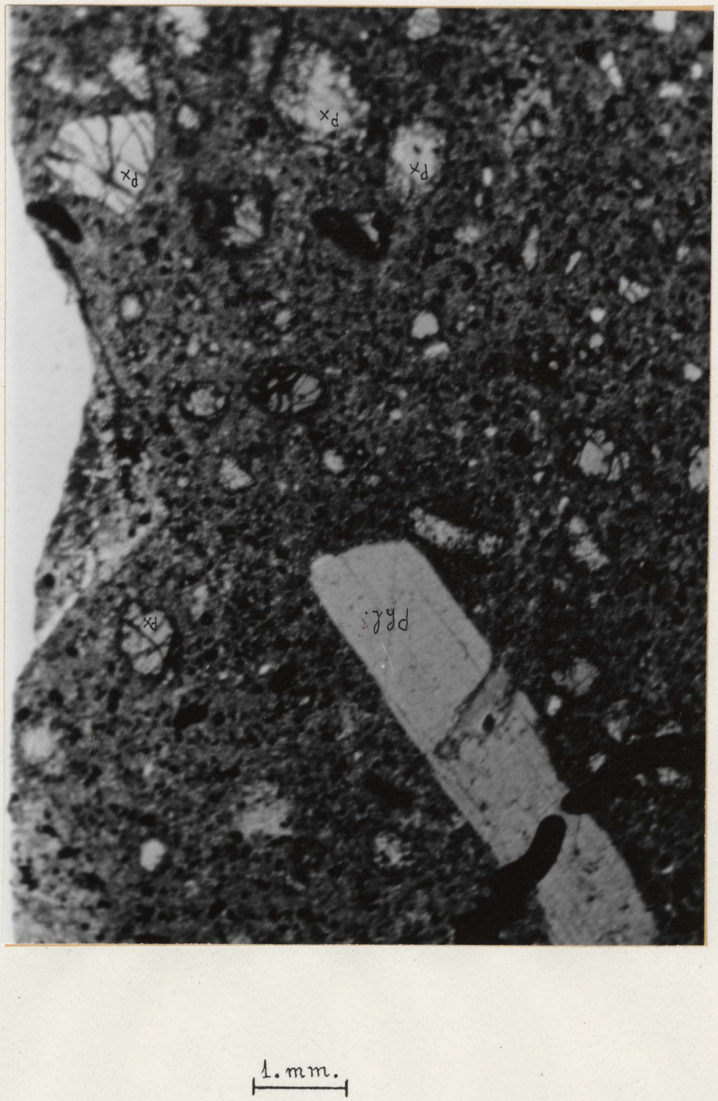
(fig. II.2). Their width ranges from 15 cm to 3 m (10 feet), with a large majority between 40 and 90 cm.

This group of mafic dykes have traditionally been grouped together under this traditional name, in spite of considerable mineralogical variety, on the basis of their distinctive porphyritic texture with mafic silicates occuring in crystals of two generations (microphot. III. 3, III.4, and III.5). All are fine grained with phenocrysts ranging from 0.7 to 15 mm with a large majority between 1 and 2 mm. Chemically they are ultrabasic ($SiO_2 < 45\%$ wt). Their SiO_2 content is approximately 35%, however in many cases the SiO_2 content is much lower because of the high calcite content of the numerous ocelli occuring in some dykes.

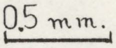
All the specimens contain phlogopite. Some, however, have mica in two generations. These are the micaceous or mica lamprophyres. Calcite is largely a primary phase that crystallized directly from the magma. Other varieties include wollastonite bearing Lamprophyres, lamprophyres with clinopyroxene and altered olivine, and finally lamprophyres with melanite-melilite and/or clinopyroxene. Chemical compositions of most of the major phases were determined by microprobe. These compositions are shown in table III.3 and III.4. Some of the modes of these rocks are shown in table III.15 (code numbers: 11, 12, 13, 18,21).

Ocelli. In most of the lamprophyres there are ubiquitous spherical to ellipsoidal or sometimes irregular, sharply bounded, leucocratic masses which range from 0.4 mm to 25 mm in diameter, averaging 1-2 mm. They constitute 5 - 15% of the rock volume, (microphotograph III.3, III.4, III.6.A).

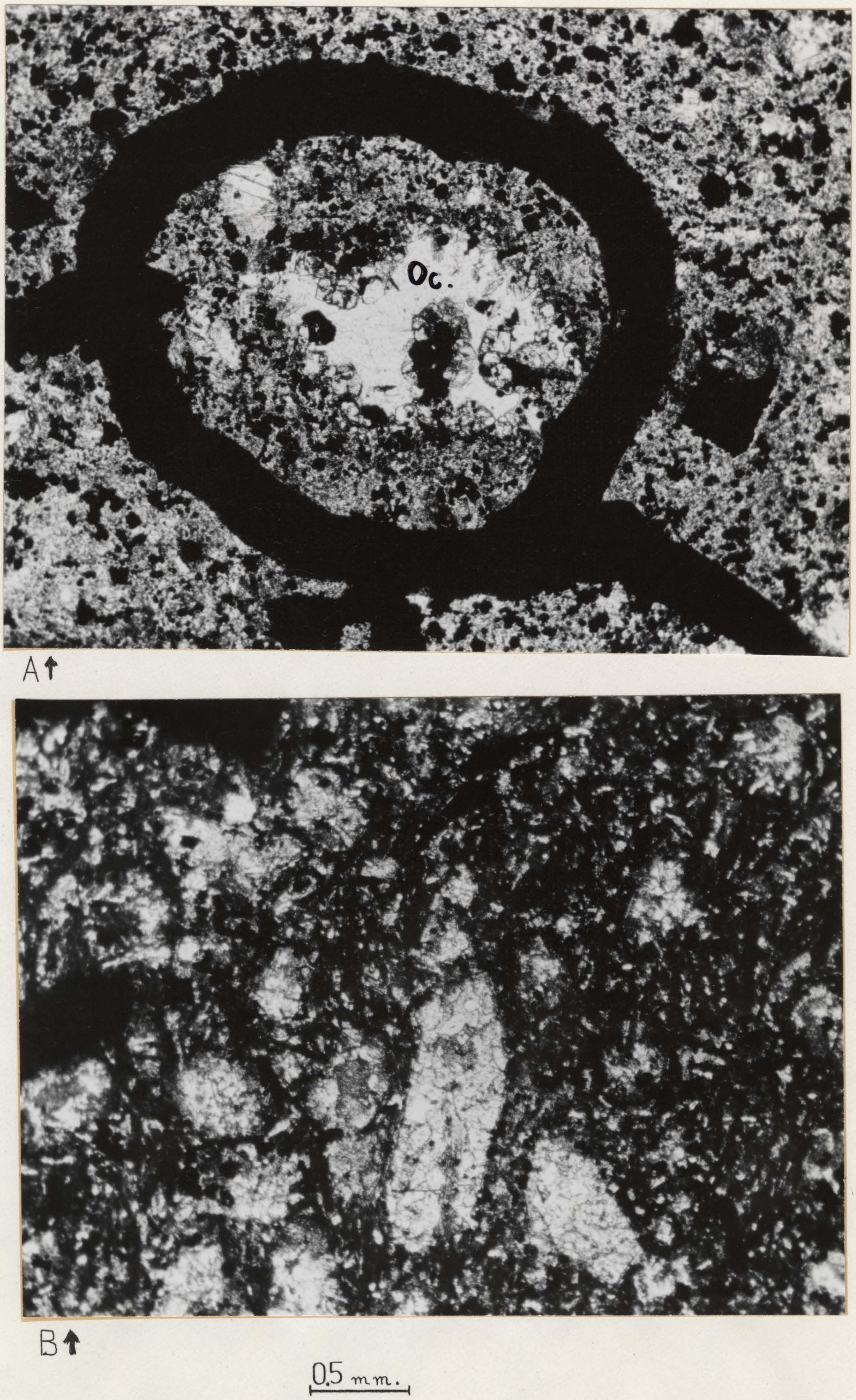
Microphotograph III.3. Lamprophyre dyke containing Ti-salite phenocrysts and ocelli (oc = ocelli, Px = pyroxene). Note the opaques along the cleavage traces of the pyroxene phenocryst. Phlogopite phenocrysts occurring in this lamphrophyre are not shown in this photograph. Parallel nicols. Sample IR.19.B.



Microphotograph III.4 Lamprophyre dyke, with phlogopite and Ti-salite phenocrysts. The groundmass contains a high percentage of Phlogopite. (Phl. = phlogopite, Px = pyroxene, Oc = ocelli). Parallel nicols. Sample IR.19.B.



Microphotograph III.5. Lamprophyre dyke with pyroxenes of two generations. Dashed line marks the outline of the occurring pyroxene phenocrysts. Parallel nicols. Sample LIT.M.13.M.D.



Microphotograph III.6. A. Ocelli containing calcite phlogopite and opaque. Parallel nicols. Sample IR.19.B. B. Pseudomorphs of calcite after olivine and clinopyroxene showing euhedral to subhedral outlines. They contain more than ninety percent calcite. Parallel nicols. Sample CAL.12.

There seems to be a relation between the grain size of the specimen and the size of the ocelli, that is, a decrease of their size with decreasing grain size. Microscopically the two portions of the rock, the matrix and the ocelli, are composed of the same minerals, with the exception of altered olivine and melilite, which are not found in the ocelli. Also the calcite content of the ocelli is very high.

In most of the lamprophyres, except the mentioned ocelli, occur pseudomorphs of calcite after olivine and/or clinopyroxene (microph. III. 6.B.). The euhedral to subhedral outlines of the pseudomorphs clearly distinguish them from the near spherical to globular or sometimes irregular ocelli. Opaques are dominant in some pseudomorphs whereas they are almost absent from the ocelli. Some crystals were found to straddle the boundary of the ocelli and consequently they were not wholly contained within the ocelli. However their optical properties and chemical composition do not change throughout the whole crystal.

Some of the lamprophyre dykes contain hedenbergites inverted from ferro-wollastonite solid solution. They also contain melanite garnet as a product of the break-down of melilite. These phenomena may be explained as follows.

Melilite→Melanite.

The formation of melanite garnet is attributed to a later event at a much lower temperature than the solidification temperature of the original lamprophyre dyke. This is evident from both, macroscopical and microscopical (textural) observations. The above mentioned later event is the intrusion of a carbonatitic magmatic fraction which raised the temperature of the lamprophyre. The carbonatite intruded along the

TABLE III.3. Electron microprobe analyses of Phlogopites and Pyroxenes from Lamprophyre dykes (wt %)

Specimen	Mineral	Na_2O	K_2O	CaO	MgO	FeO*	Al_2O_3	SiO_2	TiO_2	MnO	H_2O	Total
IR.401	CPX	0.85	---	24.55	16.30	2.70	0.35	54.00	0.35	0.30	---	
IR.12	Phlog.C.	0.55	10.07	0.44	18.95	10.12	13.85	37.12	4.28	0.58	4.08	100.15
IR.12	Phl.r.	0.48	10.32	0.31	21.40	8.77	13.52	39.53	2.33	0.27	4.17	101.10
IR.8A	Phlog.	1.33	8.97	0.12	23.59	6.14	14.41	39.32	1.98	---	4.21	100.10
IR.401	Phlog.	1.50	9.00	---	23.80	6.10	12.30	39.65	1.60	---	4.20	98.15
RAN.DIKE	Phlog.	1.00	9.45	0.30	17.82	8.24	14.59	37.72	6.41	---	4.20	99.73
IR.17.B.	»	1.28	9.90	0.20	17.29	15.03	11.57	38.11	1.50	0.80	4.00	99.70
IR.5.B.	»	0.60	10.10	---	22.90	6.50	13.10	39.00	1.45	0.60	4.10	98.35
IR.9.C.	»	0.60	10.10	---	22.75	5.90	14.35	38.05	2.50	0.20	4.10	98.60

* Total iron expressed as FeO, C = core, r = rim

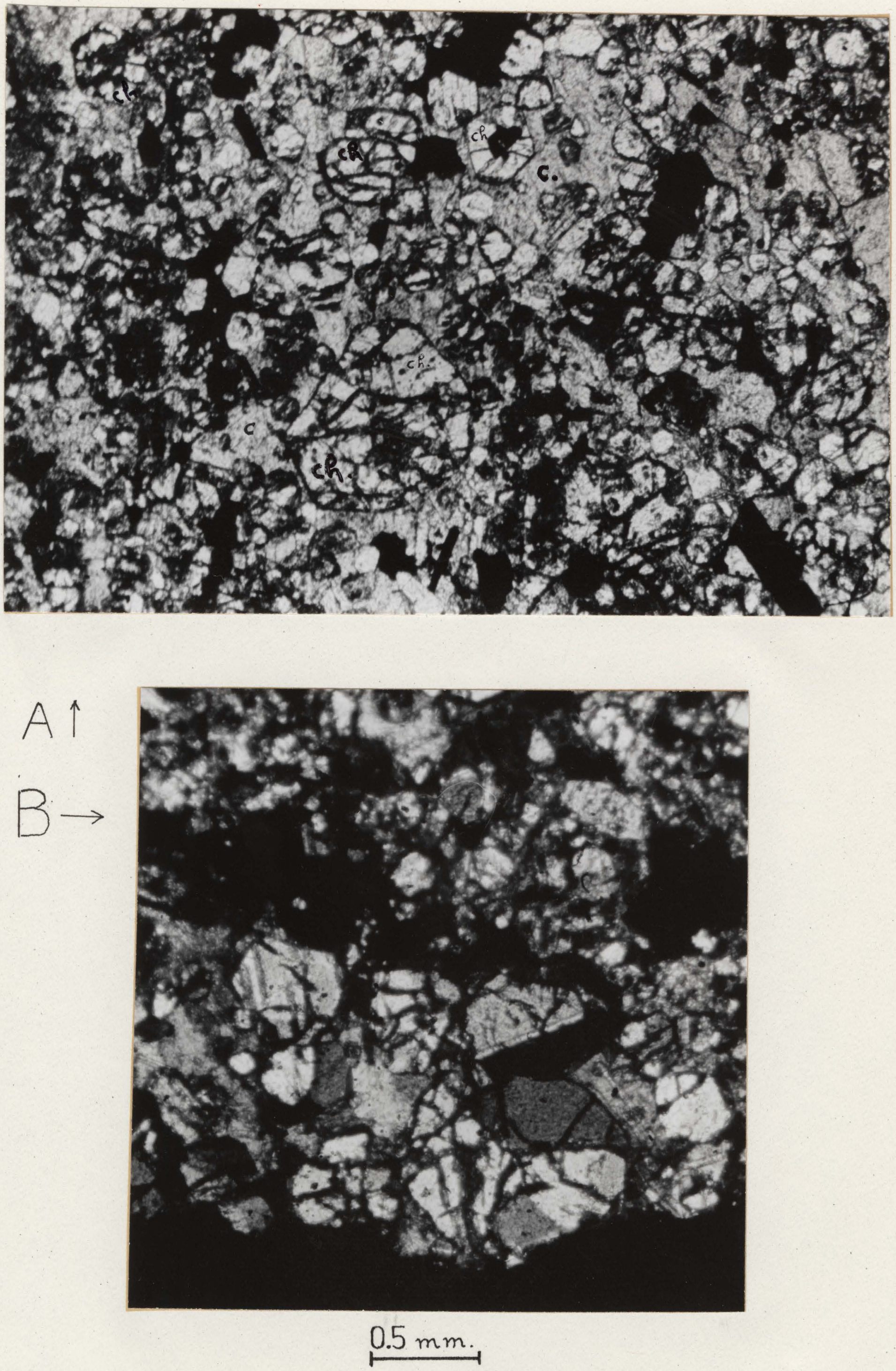
TABLE III.4. Compositions of carbonates from lamprophyre dykes (moles %)

Specimen	Mineral	$CaCO_3$	$MgCO_3$	$FeCO_3$	$MnCO_3$	Total
IR.12	Calcite	98.48	0.77	0.22	0.52	100
IR.8A	»	99.06	0.72	0.21	----	100
IR.17.B	»	99.71	----	0.06	0.23	100

contacts of the lamprophyre with the wall rocks, this is shown in a drawing in fig. III.1. which shows distorted blocks of lamprophyre surrounded by carbonatite. A two inch thick skin has been formed around these blocks which has protected their interior from metasomatism.

Carbonates from the carbonatite and from the interior of the blocks were found to be different, dolomite and calcite respectively. However, there are much smaller fragments of lamprophyre; average size 2 to 4 inches, which show extreme metasomatism. Chondrodite is a characteristic mineral formed in these metasomatized fragments and the crust of the bigger blocks. At this point a parenthesis will be opened for a brief description of this rare mineral: Chondrodite occurs in subhedral crystals (microph. III.7A) which show a pleochroism from pale yellow to neutral. Some samples containing chondrodite show a micro-layering, phlogopite rich bands alternate with chondrodite rich ones. Simple and multiple lamelar twinning on 001 is common (microph. III.7.B). Some sectorial twins were found too. Some larger crystals contain inclusions of apatite and opaques. Chondrodite is associated with phlogopite, apatite, calcite, magnetite and pyrite. Modes of these metasomatic rocks are shown in table III.15. (code numbers 19,20).

Chondrodite and similar minerals of the humite group have been reported from various metasomatic environments. Huang (1957) has described clinohumite in quartzo-feldspathic veins and pegmatites from a contact zone between gabbro and granophyre, as well as in the associated rocks of intermediate composition and hybrid character from Wichita Mountains, Oklahoma. Geijer (1939) described minerals of the humite group



Microphotograph III.7. A. Chondrodite crystals (ch) in a metasomatic rock. Parallel nicols. Sample IR.9.B.

B. Twinned chondrodite crystals. Crossed nicols. Sample IR.9.B.

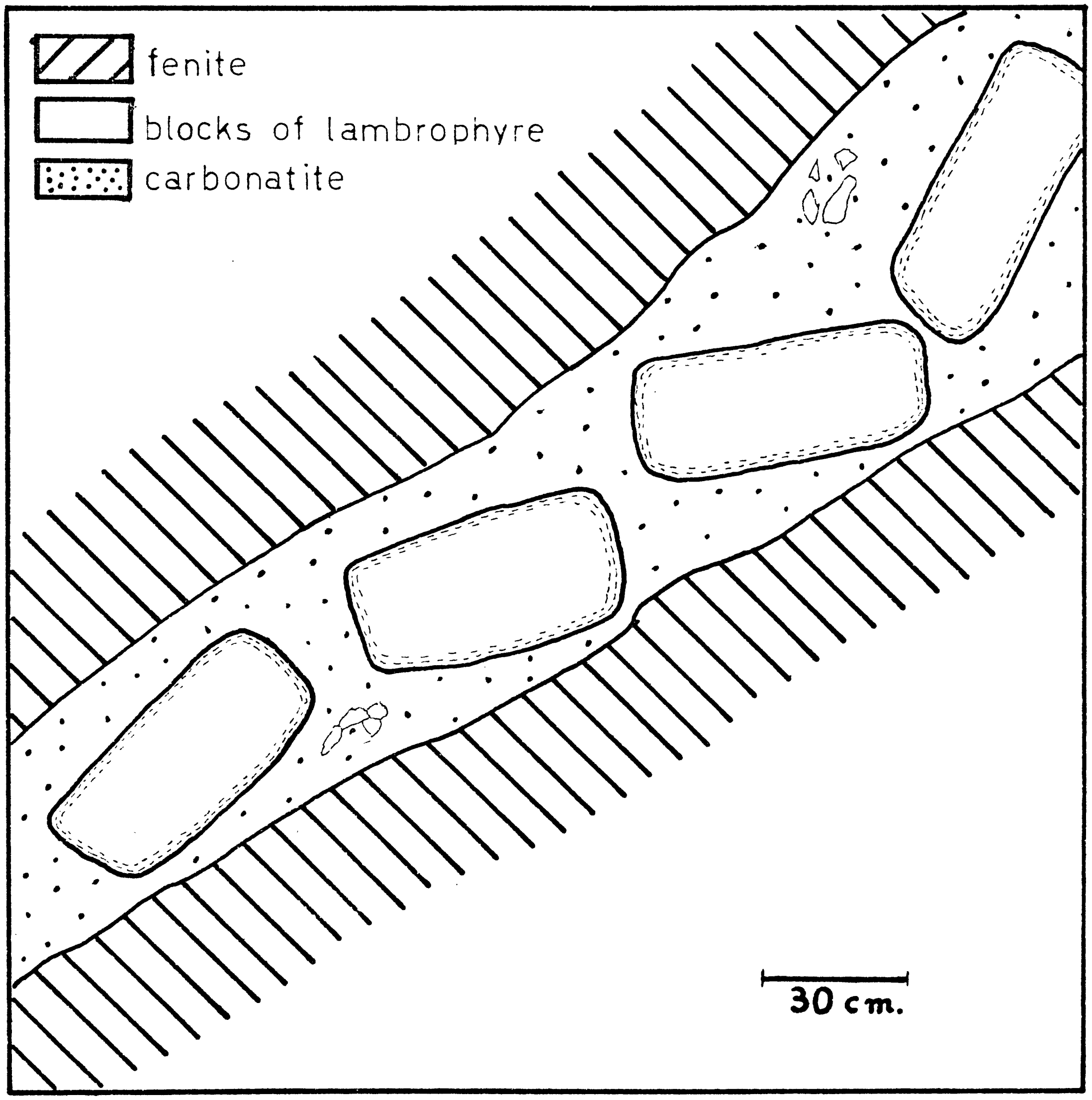
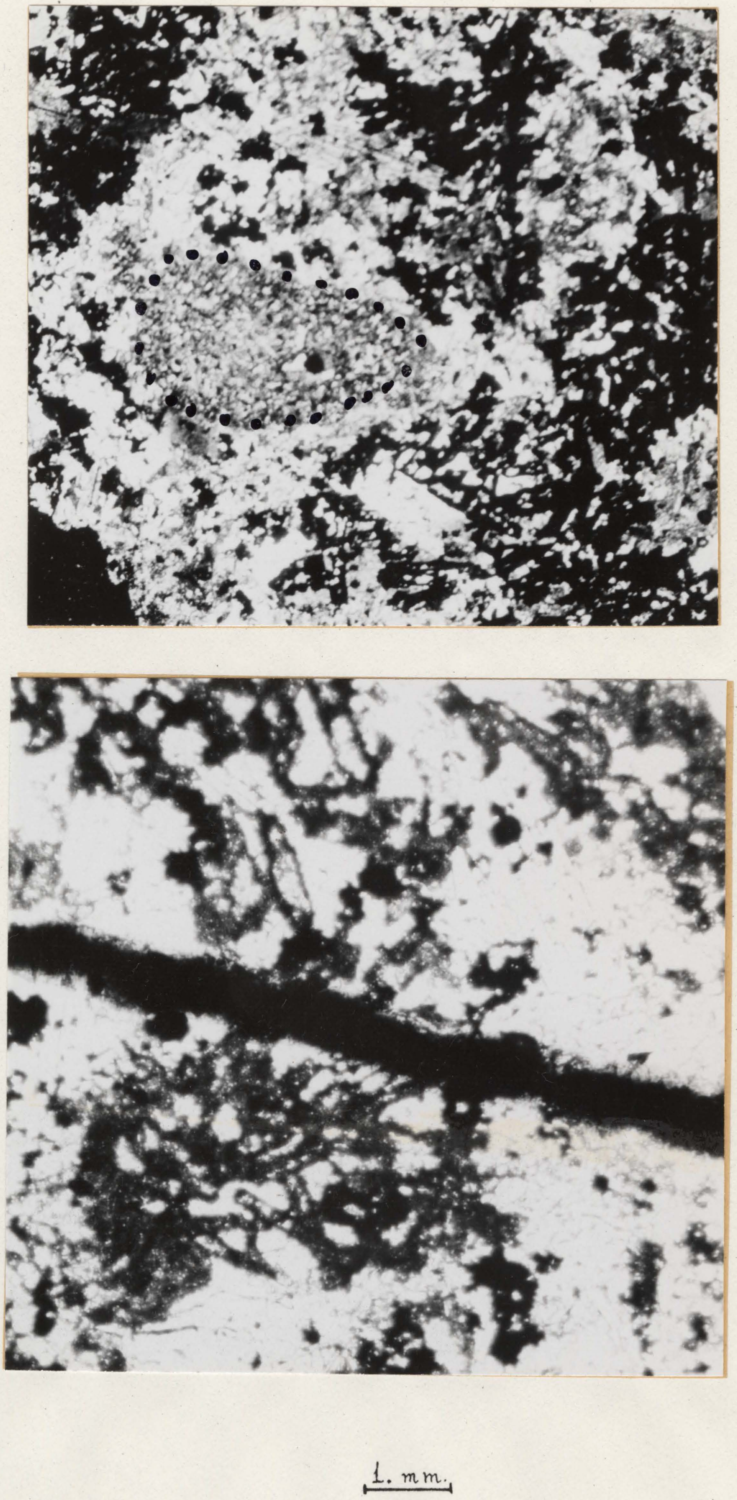


Fig.III.1. Shows a lamprophyre dyke broken up by the enclosing carbonatite in Swedish iron ores. Tilley (1951) reported these phases occurring in skarns of the Broadford area.

Chondrodite is also reported from a similar carbonatitic complex, in Eastern Transvaal, by Russell et al. (1955). H. Winkler (1974), in his discussion of the sequence of assemblages formed in siliceous dolomites, with increasing temperature, says that at high temperature of metamorphism (600-700°C) and at probably rather low pressures, clinohumite and chondrodite may occur together with clinochlore and forsterite. Unfortunately there is little data about chondrodite and the melilite-melanite discussion is continued. The macroscopic observations give us a quite clear picture of the mentioned later thermic event.

The results of this event are observable in microscopic scale too. In thin sections of this sample there are abundant pseudomorphs of melanite after melilite (microphotograph III.8.B). The probable occurrence of melilite will be discussed later. In the majority of the pseudomorphs melanite is the only replacement mineral, however there are pseudomorphs where replacement minerals include melanite plus various mixtures of very fine grained nonidentified phases, probably calcite and amphibole. In these later pseudomorphs melanite forms the rim and the other phases the core of the pseudomorph (microph. III.8.B). The chemical composition of the melanite has been determined by microprobe, the obtained analysis is shown in table III.5. The chemical composition of the melilite is not known. A melilite with composition similar to that of melanite is the iron akermanite. The ideal akermanite formula is $Ca_2MgSi_2O_7$,however, according to W. A. Deer et al. (1962-63) natural samples may contain a considerable proportion of the iron akermanite component. The replacement



Microphotograph III.8. A. Wollastonite partially decomposed. Crossed Nicols. Sample IR.8A. (outlined by dots)
B. Pseudomorphs of Melanite after Melilite. Crossed nicols. Sample IR.8A.

Table III.5. Electron microprobe analyses of melanite garnet from a lamprophyre dyke, oxides in wt % and cation ratios based on 24 oxygen atoms.

oxides	MgO	Al_2O_3	SiO_2	CaO	TiO_2	FeO*
oxides wt %	2.45	1.05	33.80	30.90	6.30	23.70
cations (O=24)	0.640	0.220	5.980	5.840	0.825	3.500

* Total iron calculated as FeO.

process is not a simple one even in the simplest types of reactions. For example, the replacement of kyanite by sillimanite (same composition) involves simultaneous diffusion of constituents away from the growing sillimanite since the phases do not have the same density and unit volume. In our case there must be even more complicated relationships, involving migration of ions both toward and away from the growing melanites, since the chemical compositions are not exactly the same. These ionic migrations will not be discussed because there are not enough data. Similar replacements have been reported from the following localities.

D. Watkinson (1970) has described the melilite → melanite replacement in carbonatites at Oka Quebec. At Oka there are melilite carbonatites and garnet monticellite carbonatites, and in some cases, rocks which show the formation of garnets from melilite (partly replaced crystals). D. Watkinson (1965) found that in the Join $NaAlSiO_4$-$Ca(OH)_2$-$CaCO_3$-H_2O melilite was unstable below 625°C at 1 kbar. Melilite breaks down in the presence of liquid and vapour to form gehlenite hydrate or hydrogarnet. In other investigations of the experimental breakdown of various melilite compositions garnets, wollastonite, monticellite, vesuvianite, cancrinite and other phases have been produced, Christie (1962), Edgar (1965). According to D. Watkinson (1970) in nature, garnet may take the place of hydrogarnet or gehlenite hydrate. Therefore, it seems that melilite may undergo a reaction analogous to that encountered in the experiments. Von Eckerman (1948) described rocks with melanite associated with aegirine, (Melanite-melteigite-porphyrite) from the Alnö island alkalic complex in Sweden. In his discussion of the fenitization of the country rocks he states that with rising temperature and pressure the fenites pass through a stage where release of the leucocratic components of the fenite leaving a pyroxenitic "rest-fenite" rich in melanite formed by the break-up of the aegirine molecule can be observed. Larsen (1942) described the complex alterations of the Iron Hill, Colorado, uncompahgrite. He found the melilite replaced by diopside, garnet, vesuvianite, and calcite. From the above it is evident that the formation of melanite from melilite has been reported from other similar complexes. There are also relevant experimental studies which support this idea. However different parent minerals have been reported in some cases. In our case there is also textural evidence that favors melilite. The form of the pseudomorphs is that of euhedral crystals of tabular habit which show rectangular sections similar to the usual forms of melilite. Finally Lumbers (1971) reports melilite occuring in drill core samples from this complex.

Fe-wollastonite-Hedenbergite

The Fe-wollastonite hedenbergite inversion has been observed in some wollastonite bearing lamprophyres. All of the wollastonite crystals occurring in this rock have undergone complete or partial inversion. In the best cases the volume occupied by the old mineral (wollastonite) is now occupied by the new mineral (Hedenb.) or rather by a number of hedenbergite crystals showing a mosiac texture. However there are cases where the area of the old mineral is occupied by very fine hedenbergite plus a mixture of nonidentified minerals containing a high proportion of opaques (magnetite). The same picture is observed in cases of partial inversion (microph. III.8.A) with the only difference that a part of the area is occupied by the old mineral (woll). The above inversion has been described at Skaergaard by Wager and Deer (1939) where some hedenbergites show an unusual mosaic texture which has been attributed to the inversion of iron-wollastonite solid solution. Synthetic hedenbergite inverts at 965°C to an iron wollastonite (Bowen et al 1933).

D. H. Lindsley and I. D. Muir (1969) determined experimentally the Hd_{ss}-Wo_{ss} inversion in several analyzed Mg-poor clinopyroxenes from the late stages of crystallization of the Skaergaard intrusion where inverted wollastonites were found. It was found that the inversion temperature increases with increasing pressure and Mg content. Finally the inversion temperature of the Hedenbergites which were wollastonite inversion products was determined at pressures from 0 to 5 Kbr. The obtained values start at 930°C for zero pressure (vacuum) and reach, approximately, up to 1100°C at 5 Kbr pressure. One point which must be emphasized is that the inversion temperature is at least 930°C. This is an indication of the high solidification temperature of this rock and the crystallization of this phase (Fe-wollastonite) on the liquidus.

Wollastonite has been found in other rocks of the complex (palingenic rocks) where it represents a metasomatic phase formed at much lower temperature. The metasomatic wollastonite which is an iron-poor one (FeO = 0.50) will be discussed later.

III.A.5. Carbonatites

The notion that carbonatites must always be replacement or hydrothermal deposits, in a previously established alkaline complex, is untenable. At the examined complexes, carbonatites show an evolution that implies a relatively wide temperature range. They occur as dykes and irregular intrusive bodies in the inner fenite zone. Similar dykes are reported in drill logs (Rowe R. B., 1954, 1958) to cut across all the major rock types. However, a large mass in the middle of the Iron Island complex resembles a plug (fig. I.3).

The dykes range from a few inches to approximately seven feet in width. The irregular bodies reach widths of thrity feet. The narrow dykes show sharp contacts, in contrast, the wider dykes and irregular bodies usually show gradual or reaction contacts.

Carbonatites range in mineralogical composition from esentially monomineralic types consisting nearly entirely of calcite or dolomite to varieties in which carbonates are accompanied by numerous light and dark silicates and by phosphates: Apatite, sulfates:Barite, iron oxide minerals, sulfides:pyrite, and Nb-minerals:pyrochlore.

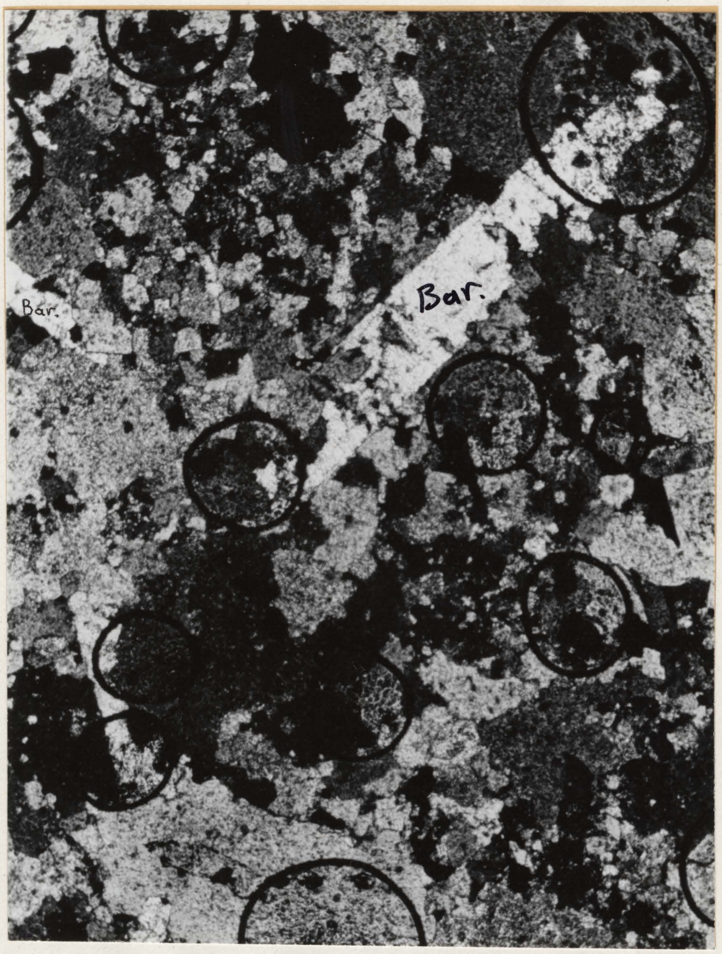
Apatite and magnetite are the most ubiquitous of the nonsilicate minerals. Apatite appears with such carbonatite types as Aegirine and phlogopite carbonatites which represent higher temperature types and barite bearing carbonatites which represent late low temperature carbonatites. Apatite also occurs in most of the intermediate temperature types.

Dominant among the major mineralogical constituents are the rhombohedral carbonates calcite, dolomite, and ankerite. Chemical analyses of the above carbonates are shown in table III.11. (code numbers: 9, 10, 11, 12, 18, 19, 20, 22, 23). Most calcites also contain significant amounts of Sr. A semiquantitative analysis for Sr gave values from 0.2 to 0.8 per cent (in wt.).

Barite is restricted in late carbonatites (microph. III.9). It forms long prismatic crystals (max. length 5.0 mm). The host carbonatite is a dolomitic (ferroan dolomite) carbonatite with a pink color. This color is a result of the finely disseminated hematite.

Among the iron oxide minerals magnetite is the most widespread. Magnetite occurs in widely varied amounts, from accessory constituent to major constituent in some of them. Hematite occurs in the late, low temperature, carbonatites. Two of the most representative hematite carrying samples are IR-2 and IR-3. They contain 2 and 12 per cent hematite, respectively. Hematite occurs as a finely disseminated phase in both of them. They also contain abundant fluid inclusions. The second sample, which contains much more hematite, has abundant very fine veinlets of hematite and secondary small vugs associated with silicification in these vugs hematite occurs at the interface of adjacent quartz grains. It is evident that this rock has undergone change by late hydrothermal fluids or circulating meteoric waters. These carbonatites contain the previously mentioned barite. It should be mentioned that sulfur occurs in its highest oxidation state in this phase.

Quartz is uncommon as a primary phase of the calcitic and dolomitic carbonatites, but relatively abundant quartz occurs in some of the hydrothermal replacement zones of these rocks. Late stage silification seems to be an important process that has strongly modified a major part of the carbonatitic plug which is located in the central part of the iron



Microphotograph III.9. Barite bearing carbonatite. Bar = Barite, C = calcite. Crossed nicols. Sample IR.2.

island complex. A representative sample of this unit has been described above (IR-3) with the iron oxides. This silicified carbonatite consisting chiefly of ferroan dolomite, barite, hematite, and quartz, forms relatively resistant outcrops.

Pyrite is the only common sulfide occurring in the carbonatites. It occurs in minor amounts. The highest pyrite content was found in SAFT-1 sample (6% in wt.). This sample is from an ore* carbonatite consisting mainly of magnetite, ferroan calcite, apatite, aegirine and Na-amphibole.

Pyrochlore is the chief host for Nb in the examined carbonatites. It is, isometric and some six-sided crystals were found. However the majority of its crystals are octahedral. The crystals are well preserved and most of them are euhedral to subhedral (microphotograph III.11). Pyrochlore is chocolate-brown and generally resinous to submetallic in lustre. Under the microscope it is found that the crystals may be composed of light and dark-coloured varieties of pyrochlore or entirely of the light variety (microph. III.11.A and B). The light variety ranges from almost colourless to brown, whereas the dark variety is dark brown to opaque and submetallic in lustre. However, the two varieties were examined by Rowe (1954) and were found to produce identical X-ray diffraction powder patterns. An X-ray fluorescence analysis, made in the laboratories of the Radioactive Resources Division of the Geological

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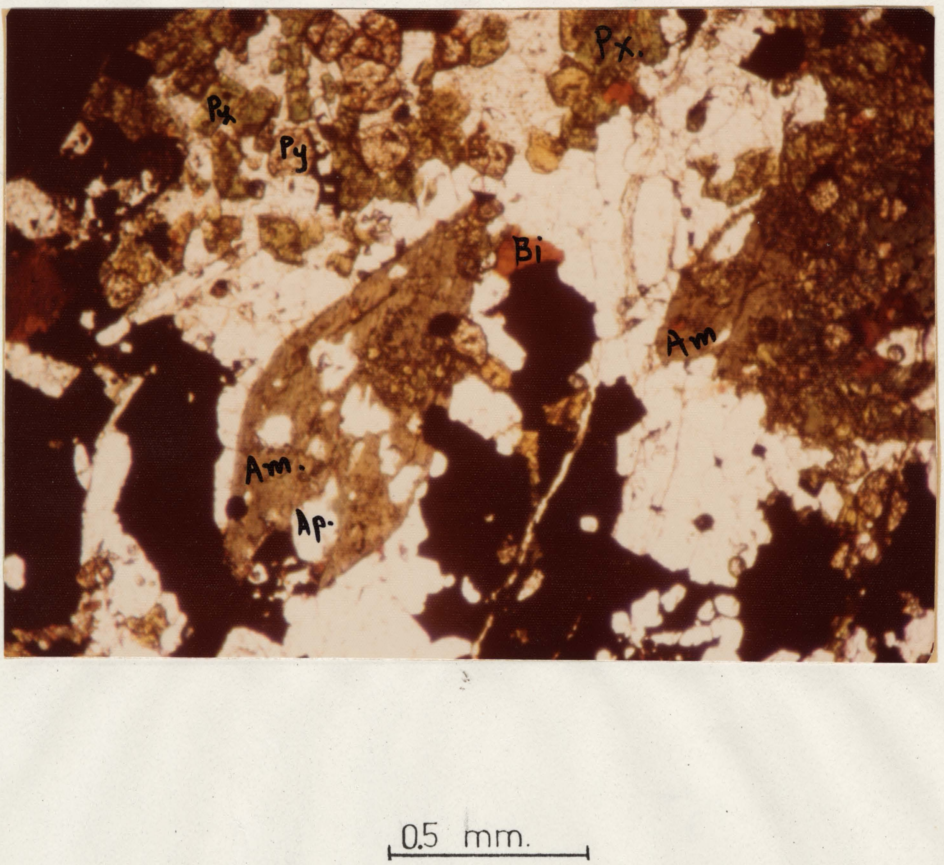
*Ores are usually regarded as being composed of two categories of material. Ore minerals, from which the metals are extracted, and gangue minerals, which form the useless matrix. When one looks upon ores as rocks this distinction has no meaning since both groups of minerals are rock-forming constituents.

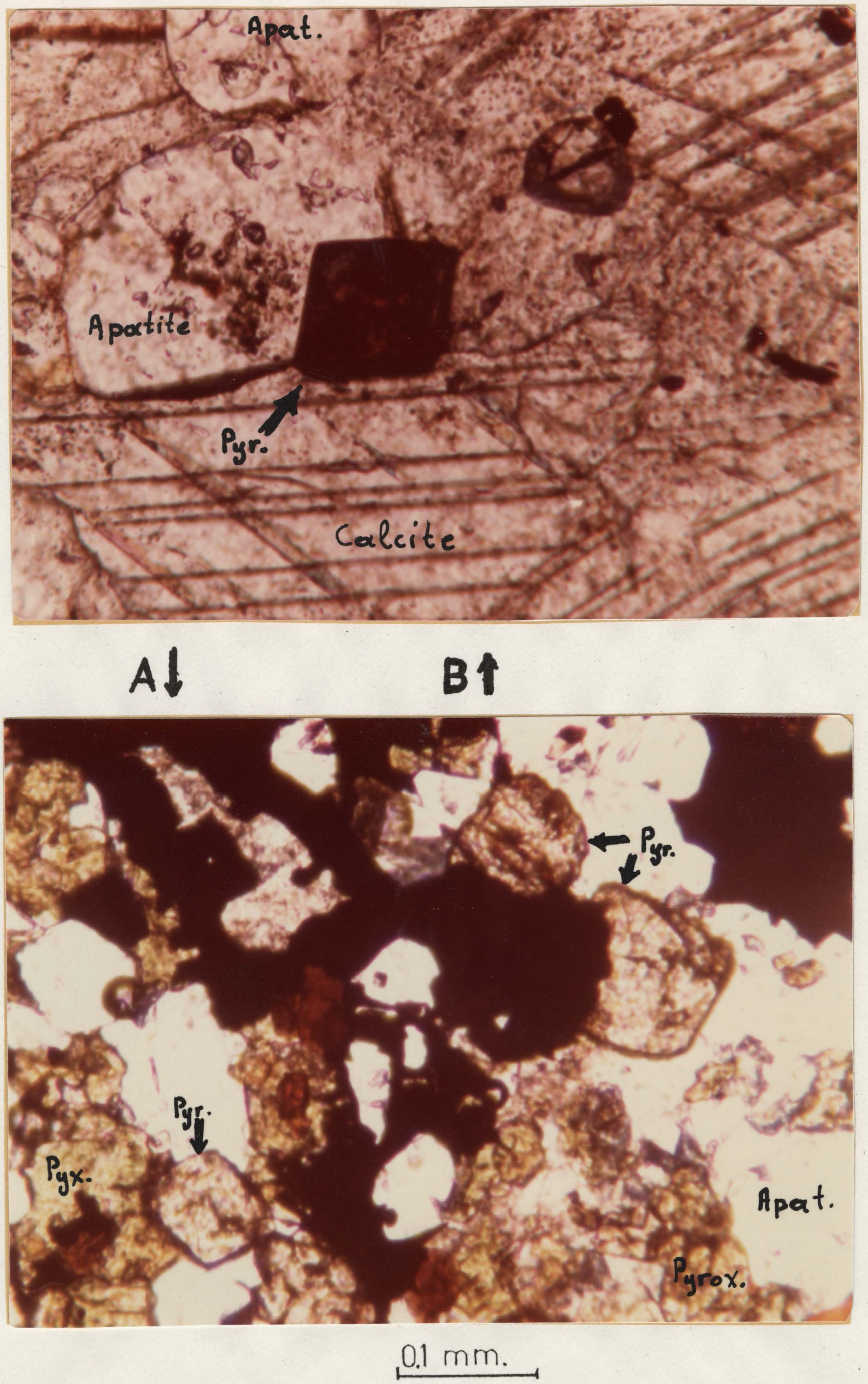
Survey, of pyrochlore from Newman deposit gave 7.3 percent U_3O_8. Consequently it is a uranian pyrochlore. Microscopic evidence indicates that pyrochlore crystallized relatively early. It occurs as inclusions in larger poikilitic crystals of amphiboles and biotites which are abundant in some samples. This carbonatite has a pegmatitic appearance and contains abundant poikilitic biotites and Na-amphiboles (microph. III.10). It is a member of the high temperature carbonatites (samples:RAN-15, and SAFT-1). Three deposits carrying niobium and uranium (mainly in pyrochlore) have been discovered on or near islands of these complexes, and are known as the Newman, Calder, and Great Manitou deposits (fig. I.2).

The Fe-Mg-silicates from carbonatites are characterized by low Niggli's mg values. Pyroxenes are represented by one of the most differentiated Na-pyroxenes, aegirine. It occurs as scattered subhedra to unhedra (microph. III.10) or in lenticles. Na-amphibole occurring in carbonatites is an arfvedsonitic variety. It occurs as euhedra to subhedra and sometimes as poikilitic phenocrysts with inclusions of apatite, calcite, megnetite, and pyrochlore (microph. III.10). Biotite is the common variety of the brown micas found in carbonatites. Both primary and secondary biotite was found. It replaces pyroxene or amphibole or forms independent phenocrysts, sometimes poikilitic. Chemical analyses of the above silicates are displayed in table III.7.A (No. 13), III.10. (RAN-15 and SAFT-1), and III.9.A. (No. 28, 30, 32, 23) respectively.

The above described phases participate in the various assemblages found in carbonatites. According to the prevailing or characteristic phases the carbonatites can be classified in the following types: Barite bearing carbonatite (Microph. III.9.) with barite $< 9\%$ (in the mode) and



Microphotograph III.10. Carbonatite from Newman deposit with pyrochlore (Py), magnetite (black), poikilitic amphibole (Am), Pyroxene (Px), Biotite (Bi), calcite, and apatite (Ap). The white area is occupied by calcite and apatite. Parallel nicols. Sample SAFT.1.



Microphotograph III.11. Light (A) and dark-coloured (B) varieties of pyrochlore. A: parallel nicols, sample RAN.15
B: parallel nicols, sample SAFT-1.
Pyr = pyrochlore, Pyrox. = pyroxene

carbonates $>$ 70% (sample: IR-2, IR-3, and IR-18B.C.). Ore carbonatite Microph. III.10), with extremely high magnetite content $\sim$30% (in the mode) and $\sim$6% pyrite accompanied by Fe-Mg-silicates and apatite (SAFT-1). Biotite carbonatites, with biotite $>$10% and apatite, Na-amphibole, Na-pyroxene $<$10% (RAN-15, IR_5.B.).

Their texture shows wide variation. There were found: pegmatitic carbonatites carrying pyrochlore, coarse grained calcite and poicilitic biotite and Na-amphibole. Fine grained carbonatites. Carbonatites showing well-defined primary foliation. The primary foliation results from the parallel orientation of crystals of biotite, aegirine, apatite, and other species or from thin layers or bands rich in aegirine, magnetite and other species.

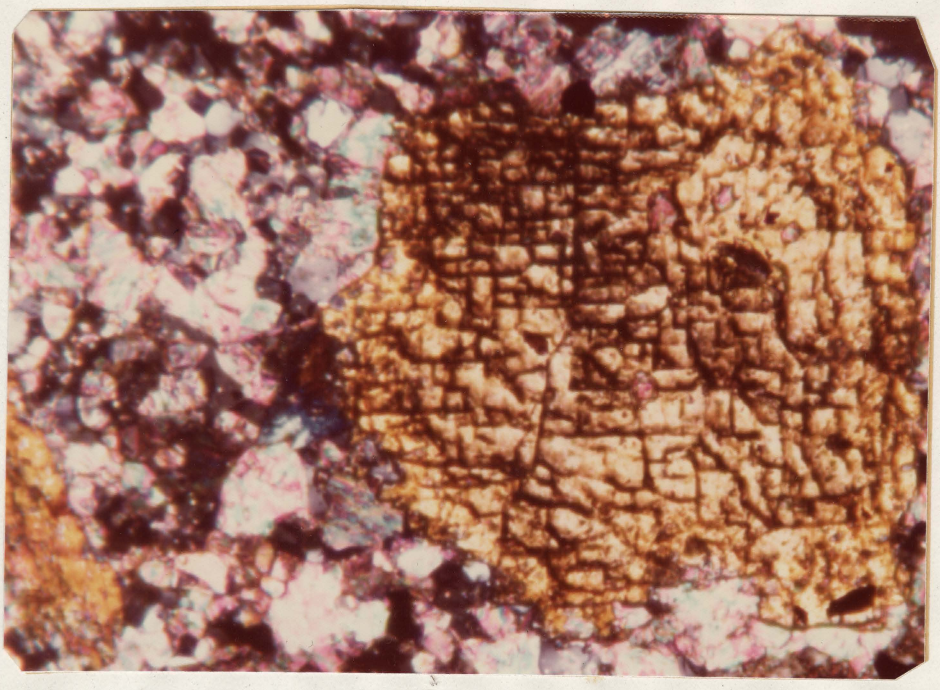
Summarizing the above descriptions we should point out that much evidence points to the early formation of many silicate species in carbonatites and that many difficulties are related to the heterogeneity, composite nature, and interaction of later carbonatites with earlier or with wall rocks.

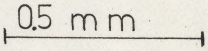
III.A.6. Palingenic (hybrid) Rocks

Wollastonite occurs in two distinct assemblages. In the first assemblage it represents a metasomatic mineral connected with palingenic (hybrid) rocks found at the contact of intrusive carbonatitic bodies with the inner fenite zone. In the second assemblage wollastonite is a constituent of some (ultrabasic) lamprophyre dykes where it seems to be a phase crystallized on the liquidus.

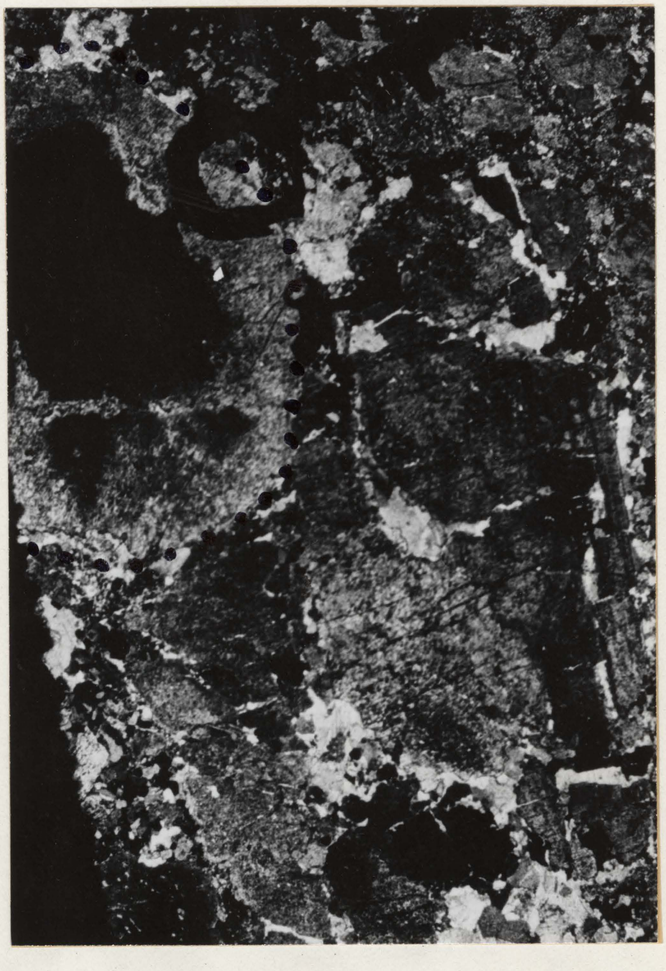
The rocks carrying the first type of wollastonite have been characterized as "palingenic". This term is used to emphasize their formation by the partial melting and mobilization of the wall rocks with heat from the intrusive bodies, and addition of material (melt) from the intrusive bodies as well. The stage of partial melting facilitates their mobilization and intrusion along fractures, they are usually found intruding fenites. The partial melting and their reomorphism constitute the main criteria used for their distinction from fenites. Fenites are characterized by in situ metasomatism (Heinrich 1966, page 49). The palingenic character of these rocks is evident from, firstly, their textual heterogeneity and irregularity of mineralogical composition in one and the same specimen due to uneven distribution of wollastonite, apatite, k-feldspar, and Na-pyroxene. Pyroxene is usually allotriomorphic and medium to coarse grained (Microph. III.12), whereas wollastonite occurs in two grain sizes. It usually occurs as medium to coarse grained, however very fine grained wollastonite coexisting with apatite calcite and larger pyroxene crystals occurs too. Such an assemblage is shown in microphotograph III.12. Their texture is generally hypidiomorphic-granular. In this case anhedral to subhedral, medium grained cyrstals of Na-pyroxene, K-feldspar, and wollastonite constitute the major mineralogical constituents.

Some pyroxenes show overgrowth rims (Microph. III.13) which are pleochroic. The pleochroic colors of the rims are lighter than the pleochroic colors of the cores. Chemical analyses of both the rim and the core of the pyroxenes are shown in table III.7.A (code number 8 and 5). These two areas of different composition are separated by a relatively abrupt transition zone. The rim is richer in Na_2O, FeO and poorer in MgO, CaO than the core. Smaller pyroxene crystals with chemical composition





Microphotograph III.12. Allotriomorphic pyroxene from palyngenic rock. Very fine grained wollastonite, calcite, and apatite constitute the major species of the matrix. Crossed nicols. Sample CAL.14.



1. m.m

Microphotograph III.13. Pyroxene with overgrowth rim from palyngenic rock. The core (dark) is in the position of extinction. Dots mark the outline of the crystal. Crossed nicols. Sample CAL.15.

similar to the composition of the overgrowth rim of the larger crystals were found. These rocks become even more complicated with the discovery that some of the smaller pyroxenes are chemically and optically inhomogeneous. It seems that they have probably undergone an almost complete substitution of their Mg and Ca by Na and (Ti, Fe). In some crystals the above substitution is restricted to the rims in other cases it extends to cover most of their volume and in some cases the whole crystal. This may be observed in thin sections because the Titaniferous Aegirine is much darker green, and it is also evident from microprobe analysis. In the above pyroxenes the Na_2O sontent goes from 6.3% (which is the original Na_2O content) up to 13.6% in substituted pyroxenes and TiO from 0.3% to 7.6% and $FeO^{tot.}$ from 19.5% to 22.4% whereas MgO drops from 5.6% to 0.9% and CaO from 13.3% to 0.2% (all in wt %). Chemical analyses of the above pyroxenes are displayed in table III.7.A. (key number 7, 14). From the atomic ratios of the pyroxenes (table III.7.B) and electronegativity requirements it seems that Ti and Fe occur in their +3 oxidation state, mainly. The substitution is of the type:

$$Na^{+1} + (Ti^{+3}, Fe^{+3}) \rightleftharpoons Ca^{+2} + Mg^{+2}$$

Hand specimens of these rocks show an irregular network of veinlets where wollastonite $[CaSiO_3]$ has been altered to pectolite $[NaCa_2Si_3O_8(OH)]$. The latter mineral is much like wollastonite in some of its properties. However it may be distinguished by its higher birefringence observed under the polarizing microscope, and the presence of Na_2O in its chemical composition revealed by microprobe analysis which shows an atomic ratio: Na:Ca:Si = 1:2:3. Presumably this network has been formed at a later stage by injected supercritical fluids rich in sodium. The

Table III.6. Oxides in wt % of analyzed k-feldspars from different facies of the complex.

Key No.	1	2	3	4	5
Sample	G.M.8.b	NEW.17	CAL.15	G.M.4.D	NEW.15
Na_2O	0.55	0.80	0.50	0.60	0.90
Al_2O_3	17.90	18.30	18.00	17.40	18.10
SiO_2	65.60	65.60	66.10	64.80	64.25
K_2O	16.40	16.10	16.30	15.90	15.40
CaO	---	---	---	0.10	---
FeO	0.40	0.20	---	1.00	0.60
Total	100.65	101.00	100.90	99.80	99.25

CATION RATIO (0 = 24)

Na	0.15	0.22	0.12	0.19	0.22
Al	2.90	2.96	2.90	2.85	2.95
Si	9.02	8.99	9.06	9.00	8.97
K	2.87	2.81	2.85	2.82	2.76
Ca	----	----	----	0.01	----
Aver. of	3	1	2	7	6

alteration of wollastonite, which in terms of cation concentration change is a substitution of Ca by Na, combined with the substitution of Ca and Mg by Na and (Ti,Fe) in pyroxene suggests that probably the fluid was the same in both cases and that consequently it was charged with Na, Ti and Fe. Summarizing the above it is suggested that the Ti poor pyroxenes crystallized from the melt and the titaniferous aegirine and pectolite are later fluid attack alteration products.

III.A.7. Altered Pegmatitic Alkali Syenite

Dykes of altered alkali syenite were found on the west shore of Great Manitou Island and on Newman Island. Rowe (1958) reports that this rock has been intersected by many diamond drill-holes, and that it bounds the inner west margin of the fenite aureole.

This rock is very coarse grained, massive, and granitoid. It is composed mainly of white to grey or sometimes pink potash feldspar and prismatic grains of green soda pyroxene which is usually altered. Feldspar crystals up to 5 cm were found in samples from Great Manitou Island. On Newman Island a dike 30 cm wide was found with prismatic crystals of soda pyroxene that range up to about 5 cm. These crystals show an interesting arrangement. Their long axis is perpendicular to the walls of the dyke. The coarser crystals are concentrated at the margins of the dyke and they give the impression that they have grown from the walls of the dyke inwards.

In thin section the potash feldspar is generally cloudy and shows partial alteration. Fine-grained potash feldspar and some minor plagioclase occurs interstitially to the larger potash feldspar grains and laths. The soda pyroxene grains are pleochroic from green to yellow-green and many of them are altered to a mixture of very fine-grained carbonate, white mica, and chlorite, or have a fibrous appearance. Very small amounts of apatite, biotite, and fluorite are present.

III.A.8. Fenites and Country Rocks

Von Eckermann (1948) defines a fenite as a country rock altered "in situ" by alkaline metasomatism. Alkaline carbonatite complexes are commonly surrounded by an aureole of fenites. Fenite aureoles of this type exist around the alkaline carbonatite complexes at Manitou and Iron Islands, Nipissing Lake.

The fenitic aureole around the Manitou Islands complex is relatively well defined since fenitic rocks are exposed on the five islands of the Manitou group. Also aeromagnetic and diamond drill log data are very helpful particularly for those parts of the aureole which are covered by Lake Nipissing. The aureole is narrow at the east side of the complex with an average width of 500 feet. At the west side of the complex it becomes much wider, it reaches widths of 2,200 feet. A complete cross section of the aureole is exposed along the west shore of Great Manitou Island. We can divide the aureole in two concentric bands. Potash feldspar - soda pyroxene - quartz fenite (quartz syenite) forms the first or outer band, and the second band consists of k-feldspar, soda pyroxene fenite (Alkali syenite), sometimes accompanied by significant amounts of calcite. The aureole contains carbonatite intrusions, lamprophyre, diabase, and alkali pyroxenite dykes. The fenitic aureole is shown in figure I.2.

The fenitic aureole of the Iron Island complex is mainly covered by Lake Nipissing, but from available exposures on Iron Island and on nearby islands to the south, together with available aeromagnetic and diamond drill log data, the shape of the aureole appears to be as shown in Fig. I.3. Its width is variable. The aureole is only a few hundred feet wide where defined along the southern part of the complex and appears to widen along the eastern part and becomes perhaps as much as a few thousand feet wide along the northern part. Shattered and locally breciated quartz fenite predominates along the northern and northeastern shores of Iron Island, but aegirine-potassic feldspar fenite is present locally and increases in abundance towards the central part of the complex and predominates elsewhere on the island. On the other islands, fenitic rocks are mainly shattered, slightly fenitized monzonitic to granitic rocks and minor quartz fenite. These fenites also, contain abundant carbonate veins, hematite-rich stringers, and lamprophyre dykes.

Rocks outside the fenite zones of the two alkaline complexes are similar. Outcrops of these rocks occur on the Manitou group islands, the north shore of Iron Island, and on nearby islands. These precambrian country rocks are mainly adamellite (quartz monzonite) gneiss, and related migmatitic rocks, of the metamorphic complex that forms the basement of the Grenville province (Lumbers, 1971). Megascopically, this gneiss can be distinguished by its gneissosity (and local lineation). It displays a near massive fabric of feldspar, in which the mafic minerals occur either as single anhedral grains, or usually as lenticular or rod-like aggregates 0.4-1.0 centimetres in diameter which define a foliation and in some cases a lineation. Sporadic garnet concentrations and quartz lenses enhance the foliation locally. Segregation banding is rarely present. Gneissic adamellite is a homogenous medium grained rock which is usually pink coloured. Lumbers (1971) reports this rock as a widespread type of the North Bay area. Microscopically, the adamellite consists principally of k-feldspar anhedra with lesser amounts of plagioclase and quartz and small amounts of mafic minerals. The majority of plagioclase anhedra show polysynthetic twinning according to the albite law. Their anorthitic content places them in the range of oligoclase. The potash feldspars dominantly orthoclase micro- to cryptoperthites, however some microcline crystals with gridiron structure are present. Hornblende, usually altered, forms an interpenetrative structure with subordinate biotite and occurs as an interstitial phase. Sericite and carbonate are occasionally present as alteration products of hornblende.

Field and microscopic observation has revealed that the lithology of the fenites of these two complexes is similar. The lithology of the fenites and various mineralogical changes occurring with increasing fenitization are briefly as follows:

The fenitic aureoles have been divided into two concentric zones for ease of description. The division, although it appears natural, is to some extent arbitrary, since lenses and patches of low grade fenites (see below) occur in higher grade rocks. Conversely, outcrops of middle grade fenites up to 80 m. long and 25 - 30 m thick occur in outer zone fenites (low grade fenites), related either to intense shatter jointing, or intense hematization. The transition from the outer to the inner fenite zone is gradational. Fenitization first appears in the form of hematized fractures, usually forming 0.5 to 3.0 m.m. thick veinlets of hematite, rarely accompanied by breccia zones up to 3.0 cm wide in which mafic chloritized minerals are found. Hematite staining may extend a few millimetres into the rock from these veinlets. Sometimes a little Na-pyroxene is present in these veinlets accompanied by small amounts of carbonate. Within this zone the texture and structure of the original rock are essentially maintained. However minor fractures are common and movement has taken place along some of these. The above described rocks are the low grade fenites. With increasing fenitization we gradually reach the middle grade fenites which commonly show exaggerated foliation due to development of sodic pyroxenes and amphiboles. The colour of the rock becomes darker. The number and size of the veinlets increases. Quartz diminishes whereas Na-pyroxene becomes more abundant. The veinlets usually contain Na-pyroxene and small amounts of calcite. Plagioclase anhedra with their characteristic polysynthetic twinning disappear while the number of k-feldspar anhedra increases. k-feldspar is cloudy with dust that is greyish white in reflected light.

Higher grade zones appear to be related to more extensive shattering. In the higher grade fenites quartz disappears and sodic pyroxene, (aegirine), becomes the second major phase. In this stage of fenitization aegirine is no longer largely confined to veins, but forms an essential constituent of the texture of the rocks. Some samples are abnormal in that they contain patches of calcite. They have apparently been affected either during or after fenitization by solutions capable of precipitating calcite, solutions that should probably be regarded as distinct from the fenitizing solutions, which do not normally deposit significant amounts of carbonates. This distinction is also suggested by the presence of apatite in such patches. Ford (1972) in order to explain the low calcite content of the normal fenites suggests that a reaction such as:

$$2Na_2CO_3 + CaMgSi_2O_6 \rightleftharpoons 2(Ca,Mg)CO_3 + 2Na_2SiO_3$$

produces a fluid phase rich in Na_2SiO_3. According to Ford such a fluid would have the necessary incompatibility relationships with quartz and feldspars without the need for carbonate precipitation in fenite zones. Presumably Ford emphasizes the peralkaline character of the fluid which upon reaction with granitic rocks will lead to the formation of feldspathoids. If iron is present then under appropriate PO_2 conditions another peralkaline phase (acmite) may be formed.

A Na-amphibole occurs in many samples from the inner fenite zone. This amphibole is a riebeckite-arfvedsonite s.s. with the pleochroic scheme: X, very pale lavender; Y, pale lavender; Z, pale greenish blue. Its birefringence is weak, the interference colors are gray and white first order but are masked by the color of the mineral. The coexisting pyroxene is aegirine with pleochroic colours: X, green; Y, pale green; Z, yellowish-green. Aegirine has a higher birefringence than the coexisting Na-amphibole but its darker colors mask much the interference colors. The Na-pyroxenes of the inner fenite zone are sodic types with a compositional range from aegirine to aegirine augite. Chemical analyses of aegirine augite from the inner fenite zone are displayed in table III. 7.A. key numbers 6 and 10. K-feldspars from the inner fenite zone were also analyzed, their chemical analysis are shown in table III.6. key number 1 and 2. In terms of end member mol. fractions the feldspars are $Or_{95.0}Ab_{5.0}$ and $Or_{92.8}Ab_{7.2}$ respectively. According to their optical properties they are orthoclase. Their composition is potash rich and consequently soda poor although their environment is rich in both sodium and potassium. However there is experimental evidence which justifies their low sodium content. Ford (1972) reports that feldspar compositions in the system Acmite-Orthoclase-$Na_2O.4H_2O$-H_2O remain K-rich (less than Ab_{10})

even in extremely soda rich compositions and contain very small amounts of iron orthoclase molecule even at fO_2 values defined by the wustite magnetite buffer (fig. III.8). Some characterisitc accessory minerals appear or some other phases become more abundant in this zone than the outer fenite zone. These include sphene, apatite, calcite, pyrite, and pyrochlore. Rocks of the inner fenite zone are characterized by recrystallization which has destroyed all the features of the original texture. Modes of the described fenites are shown in table III.13.

The temperature during fenitization could be estimated from experimental data of some relevant reaction. The following reaction may be pertinent.

$$Na^{+} + Fe^{+3} + 3\ SiO_2 = NaFe\ Si_2O_6 + Si^{+4}$$

This reaction has been studied by Sieber and Tiemann (1968) in connection with silica leaching by Na(OH) from taconite iron ores. From Sieber's (1968) data on equilibrium temperature of 480°F is obtained (at about 50 bars fluid pressure). The above reaction has been suggested by Ferguson and Currie (1972) as a particularly characteristic reaction for the estimation of the temperature during fenitization at Callander Bay. It should be mentioned that at Callander Bay country rocks similar to the country rocks at Manitou and Iron Island complex have undergone fenitization. In our case, in the fenitic aureole, aegirine pyroxene rare or absent in the outermost part, is found filling veinlets in the transition (middle) zone, and throughout the rock in the inner zone fenites. Similar distribution of aegirine at Callander Bay has been interpreted by Ferguson and Currie (1972) as follows. In the outer zone the temperatures were below 480°F* (equilibrium temperature of the above reaction), in the transition zone the temperature of the solutions was above 480°F* but only a part of the wall-rocks was heated to this temperature or slightly above this temperature, finally in the inner zone the whole rock was above this temperature. Applying the above reasoning to the fenites of our case, we could suggest the above mentioned temperatures for the outer, middle, and inner fenite zone. Ferguson and Currie made an independent estimate of temperature in the outer part of the fenite aureole applying the Barth feldspar thermometer. They obtained a temperature of 490°C. According to the above authors the agreement for the temperature of the lowest grade fenites is very satisfactory, and they concluded that fenitization takes place essentially at temperatures above 450°C. However, there is something which makes the above agreement of temperatures (the temperature inferred for the outer fenite zone from Sieber's data and the temperature obtained from the application of the feldspar thermometer) doubtful. Ferguson and Currie (1972) used Sieber's data which show that the equilibrium temperature of the reaction is near 485°F, but, in their discussion they report degrees Celcius (485°C) which is a much higher temperature. If we accept Sieber's 485°F, then this temperature disagrees with the feldspar thermometer temperature. Because of the above disagreement of the temperatures and the fact that Sieber's reaction has not been reversed we cannot suggest that Sieber's reaction can be used as an indicator of fenitization temperatures. This reaction would become useful after better study. The disagreement may be caused by the nonredistribution of sodium between the feldspars during

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* Ferguson and Currie (1972) report degrees Celcius in their discussion. This difference will be discussed later.

fenitization. This could lead to a temperature determination that does not represent the fenitization temperature. However the latter does not mean that the temperatures based on Sieber's data are correct or incorrect.

The maximum temperature at which fenitization can take place is limited by the melting temperature of the rocks. In the Manitou Islands complex it seems clear that fenitization and anatexis (rheomorphism) form a continuous spectrum. Consequently fenitization took place up to melting temperatures. According to pertinent experimental data the melting temperature is probably 720-780°C (see chapter III.C.3).

The chemistry of the fenitization shows that the fenitizing agent was charged with sodium and iron, mainly, and that significant amount of the above constituents was introduced during the fenitization process into the country rocks. This is in agreement with experimental data invoked for the discussion of the petrogenesis of the Manitou and Iron Island complex (Chapter III.C.2). The fact that we do not have introduction of significant amounts of potassium during fenitization indicates that the Na:k ratio of the solutions (fenitizing agent) must have been much higher than the ratio of the country rocks (Burnham, 1967).

III.B. MINERALOGY

III.B.1. Introduction

Field observations and petrographic examination of the sampled rocks revealed the heterogeneity of many of them particularly emphasized by the presence of ocelli. The bulk rock composition is strongly influenced by these two features and by secondary alteration which is evident in some cases, therefore the use of the bulk rock compositional changes for differentiation inferences for example is not satisfactorily applicable. However these compositional changes are reflected also by the mineralogical changes. The most instructive phases to study in this case are the pyroxenes, minerals of the phlogopite-biotite solid solution series, and the carbonates, which are present in nearly all of the various rock types, and portray the main chemical trends. The above phases were examined by electron microprobe for homogeneity. They were found homogeneous in the majority of samples. In addition some minor coexisting phases were analyzed. From the chemical analysis data various parameters were calculated and then plotted on variation diagrams in order to obtain information regarding their evolution and consequently the evolution of the whole complex. In the following paragraphs some of these phases will be discussed.

III.B.2. Pyroxenes

The pyroxenes in six rock types were analyzed and the results are presented in table III.7.A. The analyses given in table III.7.A, represent the averages of 2 to 8 spot determinations in each of 2 to 9 grains per thin section. The physical properties of most of them have been described earlier in this chapter with their host rock petrographic description. Little was achieved, concerning their compositional variation, by measuring their optical properties. The two main reasons are: a) many elements in these pyroxenes exceed the values assigned to the pyroxene standards on which such diagrams are based and b) there is the problem of differing effects on optical properties, depending on the position of a particular ion in the pyroxene structure. Consequently, analytical data provide the only reliable means of determining compositional variation.

Evolution of the pyroxenes:

The pyroxenes are rarely colorless. Colorless pyroxenes were found only in rocks which are believed to rperesent facies of relatively high temperature, for example RAN.13.A and IR.401. These colorless pyroxenes are members of the diopside-hedenbergite series more specifically salites or Ca-rich augites. In most cases pyroxenes show a slightly purplish brown (titanian) or greenish (acmititic) tint. The latter, from pale green at the intermediate members of the evolutionary series (aegirine augites), becomes green at the end members (aegirines) of the series (microphotograph III.1.A and III.10). Their chemical composition shows the following trend. With decreasing Mg/Mg + Fe* + Mn (Niggli's mg in the pyroxenes) from 0.9065 to 0.1135, they become poorer in MgO, CaO, Al_2O_3, TiO_2 and richer in Na_2O, $FeO^{tot.}$, MnO. Plots of the above constituents versus Niggli's mg x 100 of analyzed pyroxenes from different facies of the intrusion are shown in fig. III.2 and III.3, Niggli's mg values are given in table III.8. Aluminum shows an inverse relationship to silicon: when Si is low, Al is compensatingly high (fig. III.2). This relationship combined with the Al, Si contents suggests that Al occurs in tetrahedral coordination. This is expected in our case which is a relatively low pressure environment. A generally sympathetic relationship exists between Al_{iv} and Ti contents (fig. III.2). Generally, Al and Ti contents are very low ($<$1% in wt.), except in some of the early members in which they reach values of 5.15 and 2.35 percent respectively.

Chemical definition of titanaugite or titansalite is purely

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* The ionic proportions in this case have been calculated on the basis that all the iron is present as Fe^{+2}.

arbitrary. Huckenholz (see Deer, Howie and Zussman 1962-63) chooses a lower limit of 3% TiO_2 for titanaugites or titansalites, and calls those with 2 to 3 % TiO_2 titaniferous augites or titaniferous salites. Yagi and Onuma (1967) have placed the lower limit of titania in titanaugites at 2% TiO_2.

Because of the sympathetic relationship of Al_{iv} and Ti Yagi and Onuma (1967) have suggested that these ions are mainly present as the hypothetical titanpyroxene molecule $CaTiAl_2O_6$. The maximum solubility of $CaTiAl_2O_6$ in Diopside at atmospheric pressure is about 11% (Yagi and Onuma, 1967), corresponding to 4% TiO_2. At high pressures (10-25 kb), the solubility of $CaTiAl_2O_6$ in Diopside decreases markedly, suggesting that, despite high Al contents, most titanaugites are comparatively low pressure phases, a conclusion consistent with the subvolcanic environment of the present complex.

Verhoogen (1962, p. 216) suggested that incorporation of Ti is favoured by low silica activity and high temperatures, conditions that were realized during the early stages of evolution of the complex. Furthermore Verhoogen suggested that at early stages of crystallization the magma is enriched in both Al and Ti and the incorporation of Al in tetrahedral sites of the silicate structure facilitates the entry of Ti (Verhoogen 1962, p. 217). This latter suggestion is analogous to Yagi's (1967) hypothetical titanpyroxene molecule. Summarizing the above we conclude that titanaugite, or titansalites indicate a low pressure, and low silica activity environment.

The clearest and most impressive variation of the chemical composition of the pyroxenes is the decrease of CaO + MgO and the increase of Na_2O + FeO content with a parallel increase of the Fe^{+3}:Fe^{+2} ratio. The early members are Ca, Mg-rich and Na, Fe-poor ones. The last members of the series are Ca, Mg-poor and Na, Fe-rich. They range from CaO + MgO = 40.85% and Na_2O + $FeO^{tot.}$ = 3.55% to CaO + MgO = 4.0% and Na_2O + $FeO^{tot.}$ = 40.10%, all in wt. %. This variation in chemical composition is shown in fig. III.3 and III.4.

Fig. III.3 shows a diagram of CaO, MgO, $FeO^{tot.}$, and Na_2O wt. % versus Niggli's mg. Fig. III.4 shows a diagram of CaO + MgO versus Na_2O + FeO^{tot}. From fig. III.4 we can see that the present pyroxenes suite is a complete one covering the whole range from Ca-rich pyroxenes to alkali pyroxenes. From the same diagram and the chemical data of table III.7.A it is evident that a coupled substitution ($Ca^{+2} + Mg^{+2} \leftrightarrows Fe^{+3} + Na^{+1}$) has taken place. However if we consider the diagrams of fig. III.5 which show plots of the pyroxenes in the triangles Mg, Fe^{+2}, Na and Mg, $Fe^{tot.}$ + Mn, Na + K (the chemical analysis are expressed in atoms %) then it is evident that the substitution is somewhat more complicated. At the beginning we have a substitution of Mg by Fe^{+2} with a change of the chemical composition parallel to the Join Diopside Hedenbergite, at approximately $Di_{70}Hd_{30}$ the above mentioned coupled substitution starts taking place, very soon predominates and becomes the major substitution taking place. This substitution leads the pyroxenes very close to the aegirine end member.

The pyroxene trend for later differentiates requires consideration of the Di-Ac solid solution (Yagi, 1962), (Nolan & Edgar 1963), and the question of either complete solid solution or an operative solvus in the system Di-Ac-Hed.

Aoki (1964) made a detailed genetic investigation of clinopyroxenes from the alkalic rocks of Japan. He suggested that actual pyroxene compositions of the Morotu magma lie within either aegirine-rich pyroxene field or within the diopside-hedenbergite (Ca-rich px) field, although he suggested the average pyroxene composition precipitated from the Morotu magma changes continuously from augite to aegirine. Based on the above conclusion he suggested the presence under igneous conditions of a wide region of immiscibility, separating Na-rich clinopyroxenes from Ca-rich ones. Yagi (1966) criticized Aoki's proposal. He suggested that Aoki came to this conclusion as a consequence of plotting the different suites of volcanic (low fo_2) and pegmatitic pyroxenes (high fo_2) in one diagram. Reinvestigation of the pyroxenes from the Morotu alkalic rocks by Yagi (1966) showed that aegirine-augites whose composition lies within the immiscibility region of the Ac-Hed-Di system proposed by Aoki do exist under some igneous conditions. Aoki's proposal has received little support in the light of increasing data on natural and synthetic pyroxenes belonging to the Di-Hd-Ac system. Experimental studies in the system Di-Ac-Hed. indicate a complete series of solid solutions in the subsolids region (Yagi 1966 and 1962, Nolan and Edgar 1963, Nolan 1969). The same conclusion is indicated by the available data on natural pyroxenes (Nash and Wilkinson 1970, Tyler and King, 1967, Yagi 1966). Our chemical data slso indicate that there is no immiscibility gap between Ca-rich and Na-rich pyroxenes under the conditions of crystallization of the Manitou and Iron Island complex (fig. III.6). In fig. III.6.A. we can see that some of the pyroxenes are plotted in the central part of Aoki's immiscibility region.

One more point which should be considered is the role of oxygen fugacity in the crystallization of Na-rich pyroxenes. Yagi (1966) plotted the analyses of pyroxenes of this series (Ca-rich to Na-rich) available at that time in the Na-Fe^{+2}-Mg diagram. He distinguished four groups of pyroxenes according to their host rock, that is volcanic rocks, plutonic rocks, crystalline schists and pegmatites. Using this diagram he showed that pyroxenes of different kinds of rocks have their own fields. He also showed the existence of a rather regular shift of the compositional fields of alkali pyroxenes according to their parentage beginning from those of volcanic rocks (low in aegirine), through plutonic rocks (intermediate in aegirine content), to pegmatites where pyroxenes are Na-rich, and sometimes nearly pure aegirine is found. He combined this shift of the compositional fields with the observation that oxygen fugacity is usually low in the volcanic magmas as compared with the pegmatitic liquids, which are rich in volatiles (water, etc.). He also invoked experimental evidence indicating that the stability field of acmite is increased with increasing fo_2 and that higher fo_2 favors the crystallization of pyroxenes high in acmite. From the above he suggested that the very high content of acmite in pyroxenes from some pegmatites may be ascribed to the high oxygen fugacity and the low content of acmite in the volcanic pyroxenes to the low fo_2, even when the original liquid is sufficiently high in Na. Finally he prescribed a model in which Diopside (fo_2 insensitive) is stable throughout the whole range of variation of fo_2, and plays such a role in the pyroxene solid solution as a "solvent" in which either Hed or Ac (both fo_2 sensitive) molecule is present as solute and being controlled by the prevailing fo_2. Aoki (1964) also concluded that high or increasing oxygen fugacities favored the crystallization of highly sodic pyroxenes. However according to Nash and Wilkinson (1970) both Aoki (1964) and Yagi (1966) failed to speculate upon the role that oxygen fugacity plays in the crystallization of Na-rich pyroxenes. Nash and Wilkinson (1970) invoked experimental cases where acmite could crystallize at relatively low oxygen fugacity. For example, Bailey (1969) found that acmite could crystallize from a hydrous synthetic melt under oxygen fugacity conditions at least as reduced as those defined by the fayalite-magnetite-quartz oxygen buffer, and Gilbert (1969) synthesized acmite at high pressures under anhydrous conditions at very low oxygen fugacities, i.e., in equilibrium with iron.

This is justified since at a given temperature and partial pressure of oxygen the state of oxidation of an element depends on the lattice site in which it is present. However it has been observed that although acmite and fayalite have been found to co-exist in synthetic systems, they are not usually found in rocks. This observation indicates that the conditions under which these two mutually exclusive assemblages crystallize in nature are not the same. Nash and Wilkinson (1970) in their study of the Shonkin sag intrusion showed that Acmitic pyroxene does crystallize with falling oxygen fugacities and, moreover, does not require high oxygen fugacities in nature. However, Na-rich pyroxenes do require oxygen fugacities greater than those for which the assemblage olivine plus magnetite is stable for that particular magma type in which the pyroxenes occur. A similar fo_2 trend has been inferred from the petrological study of peralkaline liquids by Nicholls, J. and Carmichael, I. S. E. (1969), that is, a decrease of oxygen fugacity but with values always slightly higher than the analogous values of the buffer MQF.

Two characteristic assemblages were noted which give some information about the oxygen fugacity of these rocks. The first is the pair magnetite-olivine. At the high temperature facies abundant replaced olivine crystals were found (microph. III.14) and in some cases as for example in chilled margins partially replaced olivine was found (microph. III.15). In the above rocks magnetite is the most abundant opaque mineral. The oxygen buffer reaction in which the above phases participate is the following: $2\ Fe_3O_4 + SiO_2 = 3\ Fe_2SiO_4 + O_2$. In order to determine the oxygen fugacity from the above equation we need the activities of magnetite, fayalite and quartz. Unfortunately both magnetite and fayalite are not pure end members. A usual assumption in such cases is that the olivine and ulvospinel-magnetite solid solution series are ideal (Nash and Wilkinson 1970, Carmichael et al. 1970), then mole fractions may be substituted for activities. It is apparent that for fixed mole fractions of Fe_3O_4 and Fe_2SiO_2, log fo_2 is a function of the activity of silica in the melt. With the available data we cannot estimate the exact silica activity. However some characteristic phases as for example melilite and sphene which occur in the lamprophyres indicate that silica activity was very low. Sphene occurs in lamprophyres in which biotite of two generations has been found. The biotite phenocrysts coexist with pyroxene phenocrysts and/or sphene microphenocrysts. Judging from the kind of phenocrysts (olivine, wollastonite, pyroxene, sphene, phlogopite) of the lamprophyres and the relative abundances of the phenocrysts we could characterize these lamprophyres (the lamprophyres with sphene) as those with the higher degree of silica saturation. This is in agreement with the fact that melilite occurs in lamprophyres with wollastonite and pyroxene phenocrysts and pseudomorphs of various phases after olivine whereas sphene occurs in micaceous lamprophyres. The above observations could suggest that in the less silica saturated lamprophyres (with melilite and phenocrysts of olivine* and pyroxene) the silica activity was buffered, for the cooling interval in which the above phases and the liquid were in equilibrium, by

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*Olivine phenocrysts have undergone partial or complete replacement.

the buffer Forsterite and melilite + SiO_2 = Diopside. Silica activity values for the temperature range 600°-1200°C, have been calculated from the above reaction by Carmichael et al. (1970). Pure end members have been used in all calculations. The calculated melilite reactions (for each end member, gehlenite, akermanite) fall in the feldspar-free region of the silica activity - T diagram. They fall below the $CaTiO_3$ (perovskite) + SiO_2 = $CaTiSiO_5$ (sphene) reaction which is a silica buffer too. The appearance of sphene in later lamprophyres (micaceous) can be attributed to the increase of the silica activity. It should be pointed out that perovskite, which could help in the determination of the silica activity in the sphene-bearing lamprophyres, has not been detected in these rocks. This may be explained in the following way. The very fine grained nature of these rocks and the high concentration of opaques make difficult the identification of some phases particularly if one phase is fine grained and occurs in small amount. Perovskite may be such a nonidentified constituent of the above rocks. Another explanation is that the silica activity was higher than the activity defined by the reaction "perovsk. + SiO_2 = sphen". In this case perovskite has been consumed for the formation of sphene. According to the above it is suggested that the silica activity in the lamprophyres increased from values as low as those defined by the melilite reactions up to values defined by the "perovskite + SiO_2 = sphene" reaction or slightly higher. In order to get an idea of these values it was assumed that the involved phases have compositions close to their written formulas, but as for example the analyses of sphene shows a small amount of iron is present (2.35% in wt.), the same is probably the case with the other phases. With the above mentioned assumption the following silica activity values were obtained from the a_{SiO_2} - T diagram of Carmichael et al. (1970): $a_{SiO_2} = 10^{-1.4}$ and $a_{SiO_2} = 10^{-0.9}$. The first value has been determined from the reaction of melilite (akermanite) at 950°C. The second value has been determined from the reaction "perovskite + SiO_2 = sphene" at 950°C. In the case of melilite the a_{SiO_2} has been obtained from the akermanite end member reaction which gives lower silica activity values. The silica activities have been determined at 950°C. This is the inferred solidification temperature of the lamprophyres. Substituting the above values of silica activity and the mole fractions of fayalite (0.2) and Magnetite (0.8) in the following equation

$$\log fo_2 = \frac{-25.7}{T} + 9 + 2 \log X_{mt} - 3 \log X_{fa} + 3 \log a_{SiO_2}$$

(Nash and Wilkinson 1970) the following P_{O_2} values were obtained: $P_{O_2} = 10^{-15}$ for $a_{SiO_2} = 10^{-1.4}$ and $P_{O_2} = 10^{-13}$ for $a_{SiO_2} = 10^{-0.9}$.

It is evident that many assumptions are involved in the above estimations. Some of them seem reasonable but on the other hand some assumptions may be questioned. However, such assumptions help in taking an idea of the range of magnitude of some interesting variables as the above.

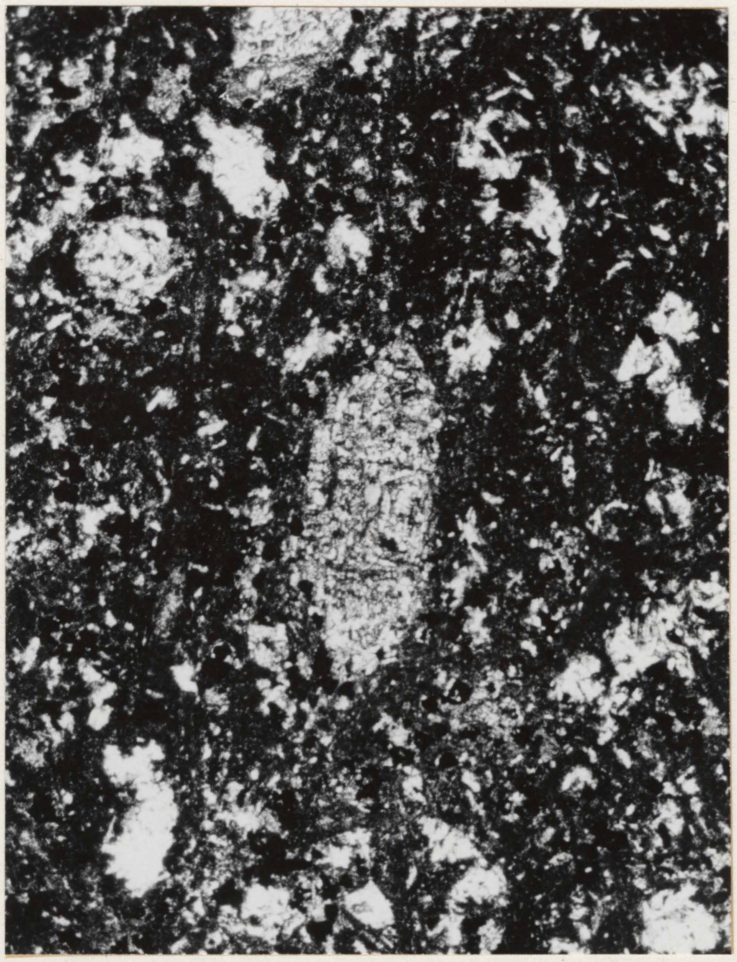
Another interesting assemblage which could give information about the oxygen fugacity is the mineral pair aegirine, magnesioarfvedsonite-magnesioriebeckite which is oxygen fugacity sensitive (Ernst 1962, Bailey 1969). The latter phases could give an idea of the P_{O_2} in the more evolved facies (e.g. carbonatites). Unfortunately from the above experimental data, which will be discussed later, the P_{O_2} in the above carbonatites cannot be inferred.

The oxygen fugacity values mentioned above (10^{-13} and 10^{-15}) fall within the stability field of magnetite which is a common phase of the lamprophyres. Consequently there is agreement between the obtained values of oxygen fugacity and petrographic observation.

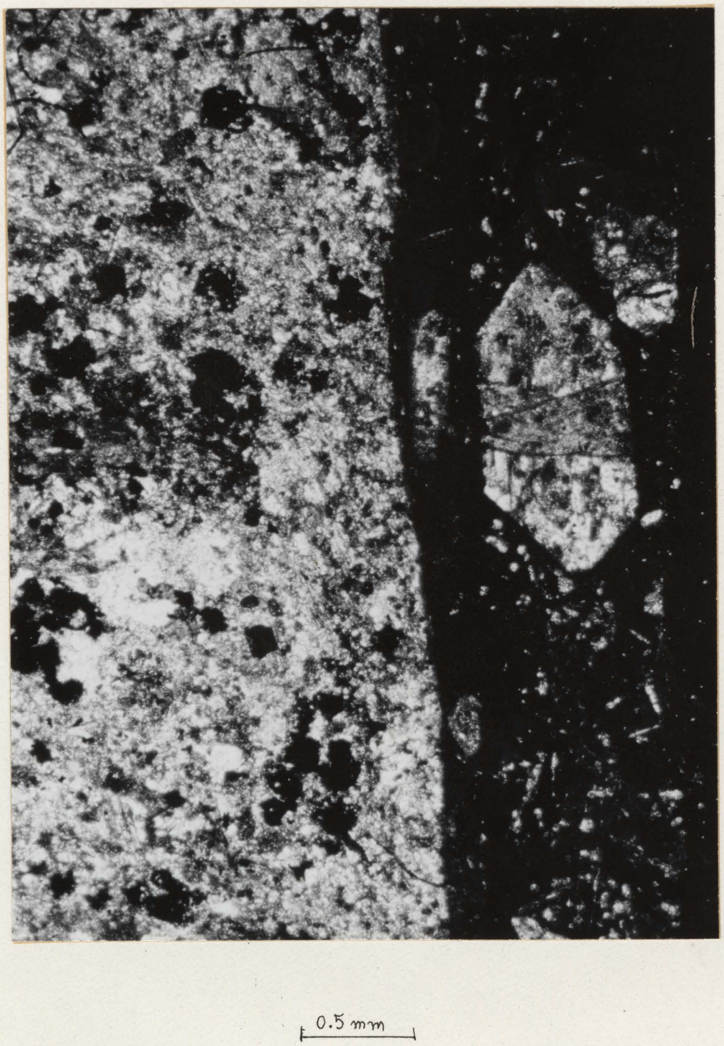
Comparison with pyroxenes from other alkalic intrusions.

Clinopyroxene crystallization trends in differentiated alkaline intrusives and alkali volcanic lineages are now comparatively well defined. In differentiated intrusions, such as the Black Jack teschenite sill, Gunnedah, New South Wales (Wilkinson 1957), and the Square Top theralite-tinguaite intrusion, Nundle, New South Wales (Wilkinson 1966) and alkaline sequences such as those at Morotu, Sakhalim (Yagi 1953) and Shonkin Sag, Montana (Nash and Wilkinson 1970), the clinopyroxenes belonging to the Di-Hed series show a compositional change parallel to the Di-Hed Join of the pyroxene quadrilateral. Substitution of Mg by Fe^{+2} is usually limited, compositions more Fe-rich than Fe_{30} being rare. However, microprobe data on individual grains of Ca-rich pyroxenes in the more evolved Shonkin Sag soda syenites have been reported with substantial substitution of Mg by Fe^{+2} (Nash and Wilkinson, 1970).

With more advanced differentiation the clinopyroxenes become enriched in aegirine and trend away from the Ca-Mg-Fe plane towards aegirine $NaFe^{+3}Si_2O_6$. This trend is very well illustrated by pyroxenes from the alkali dolerite-monzonite-syenite differentiation sequence at Morotu (Yagi 1966) and the Shonkinite-syenite series at Shonkin Sag (Nash and Wilkinson, 1970). The pyroxenes of the Shonkin Sag laccolith are remarkable since they exhibit a complete and progressive variation in composition from Ca-rich phases through aegirine-augite to acmite within the one intrusion.



Microphotograph III.14. Olivine phenocryst breaking down. Lamprophyre dyke. Crossed nicols. Sample CAL.12.



Microphotograph III.15. Partially replaced olivine in chilled margin of a lamprophyre dyke. Crossed nicols. Sample I.101.b.

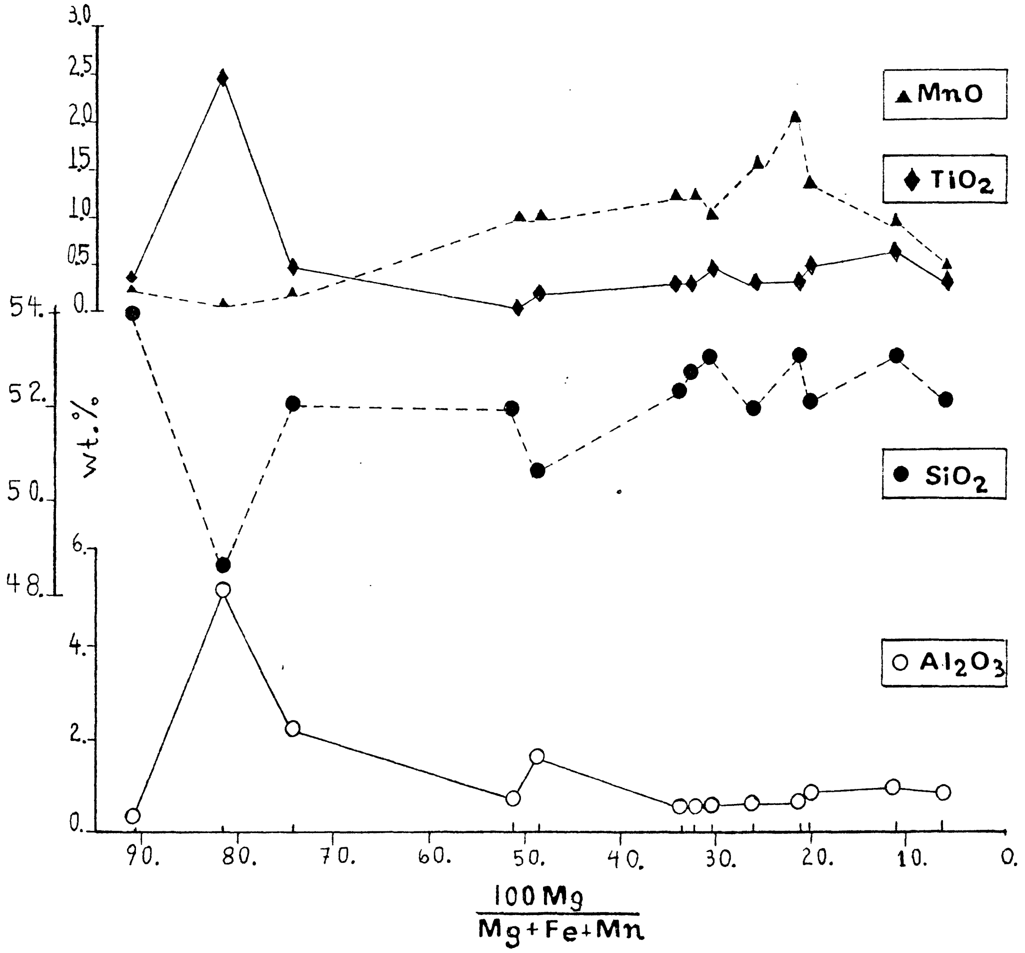


Fig. III.2. Plot of weight percent Al_2O_3, SiO_2, TiO_2 and MnO versus Niggli's mg of chemically analyzed pyroxenes from different facies of the intrusion.

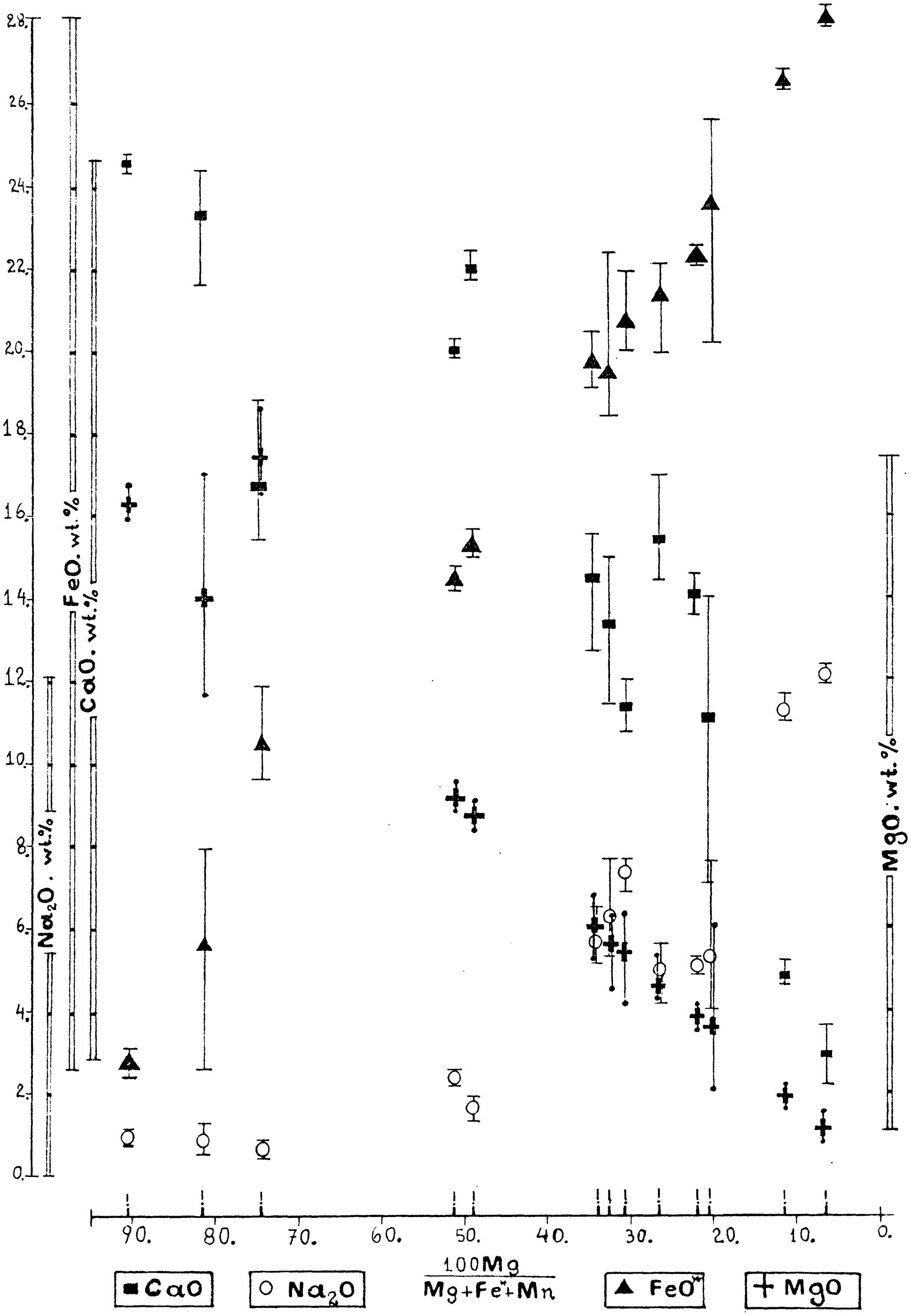


Fig. III.3. Plot of weight percent CaO, Na_2O, FeO and MgO versus Niggli's mg.(100 Mg./Mg + Fe + Mn) of chemically analyzed pyroxenes from different facies of the intrusion.

* total iron calculated as FeO.

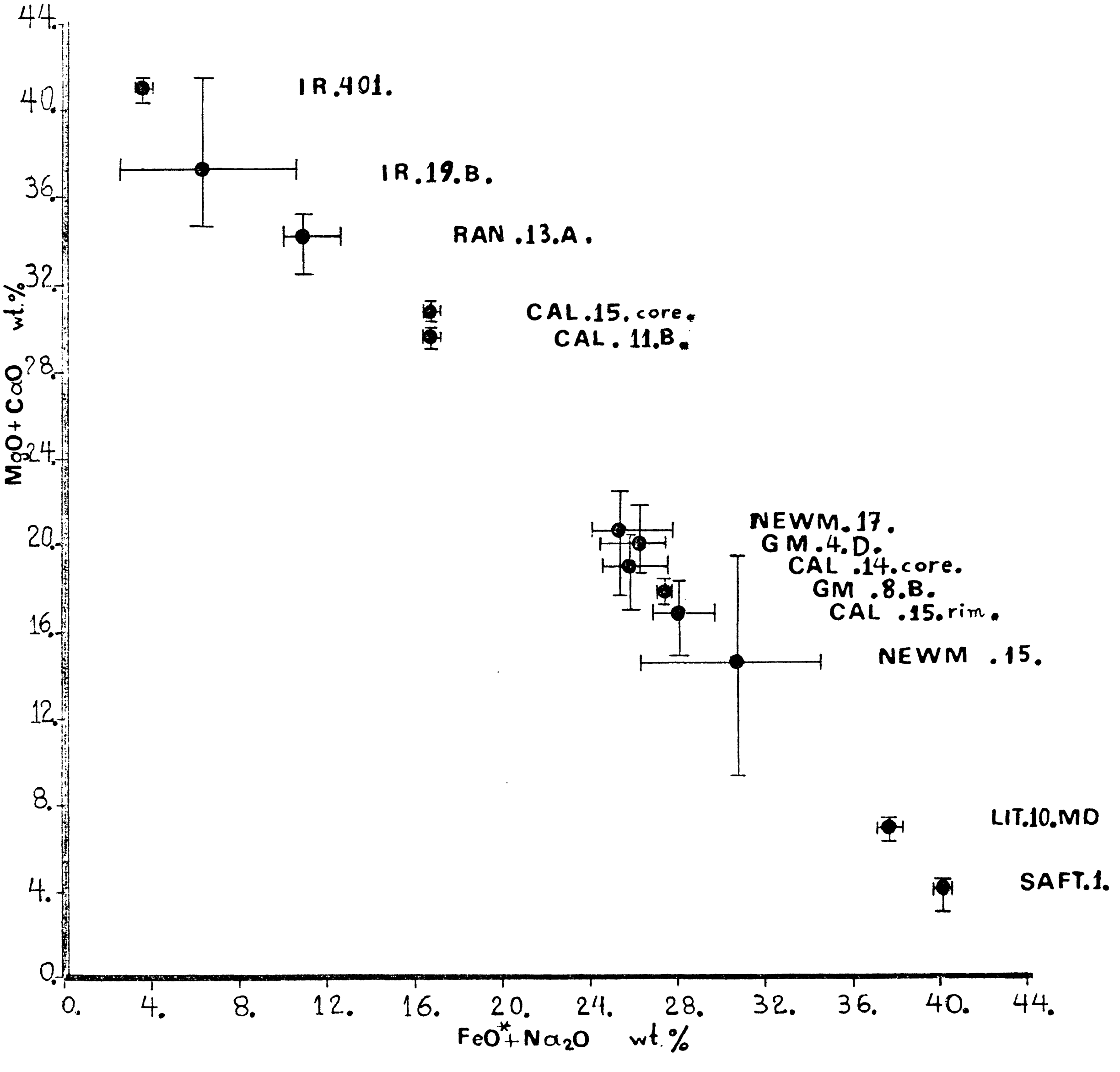


Fig. III.4. Graphical expression of the main variation in the chemical composition of the pyroxenes as a result of the replacement Na,$Fe^{+3} \rightleftarrows$ Ca, Mg.

*total iron calculated as FeO.

Fig. III.5. A. Microprobe analyses of pyroxenes from different facies of the intrusion expressed in terms of atom percent Mg, Fe^{+2}, and Na. Total iron is determined as FeO, and Fe_2O_3 is calculated by allotting equivalent molecular proportions of Fe_2O_3 to Na_2O. Aoki's immiscibility region is indicated by two curves. Arrow indicates pyroxene trend from alkalic rocks of Morotu district Japan. For key to analyses and pyroxens nomenclature according to their aegirine content see the following table. Salite, Augite ($Na < 0.1$) - soda Augite ($Na = 0.1-0.2$) - Aegirine Augite ($Na = 0.2-0.7$)- Aegirine ($Na > 0.7$). Na = the sodium in the pyroxene formula on the basis of $0 = 6$.

Key No.	1	2	3	4	5	6	7
Sample	IR.401	IR.19.B.	RAN.13.A	CAL.11.B.	CAL.15c.	NEW.17	CAL.14.c
Px name	Salite	Tisalite	Augite	Soda Aug.	Soda Aug.	Aeg.Aug.	Aeg.Aug.

Key No.	8	9	10	11	12	13
Sample	CAL.15c	G.M.4.D.	G.M.8.B.	NEW.15	LIT.10.M.D.	SAFT-1
Px name	Aeg.Aug.	Aeg.Aug.	Aeg.Aug.	Aeg.Aug.	Aegirine	Aegirine

Fig. III.5. B. Microprobe analyses of pyroxenes from Manitou and Iron islands in terms of atom percent Mg, Na + K, $Fe^{tot.}$ + Mn. For pyroxene analyses see table III.7. Numbers and px names are shown in the table, above.

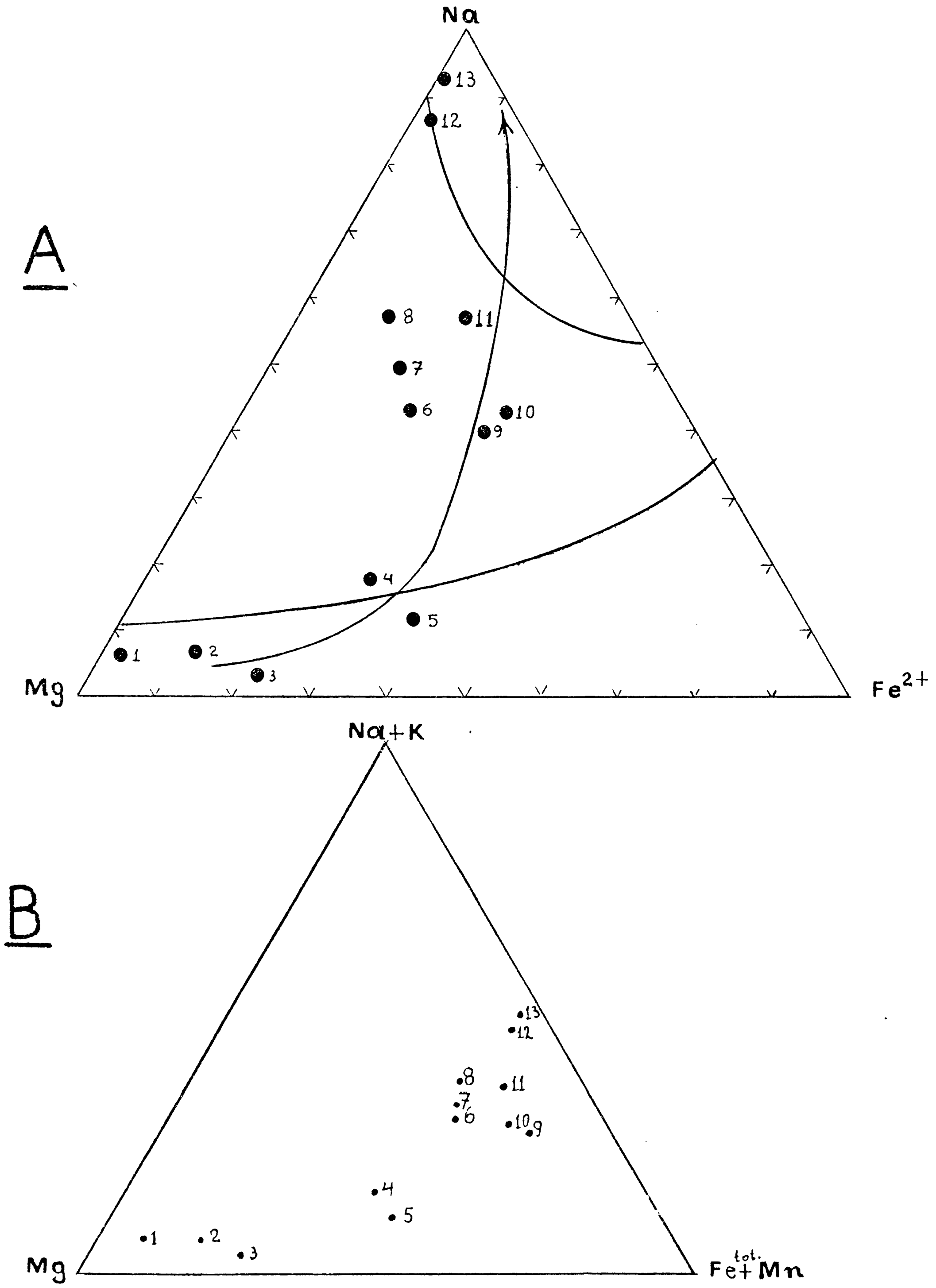

A
Na
13
12
8
11
7
6
10
9
4
5
1
2
3
Mg
Fe2+
B
Na+K
13
12
8
11
7
6
10
9
4
5
1
2
3
Mg
Fe tot. + Mn

Fig. III.5.

Table III.7.A. Oxides in wt. % of chemically analyzed pyroxenes from different facies of the intrusion.

Key No.	12	9	2	3	5	6	4
Sample	LIT.10.M.D.	G.M.4.D	IR.19.B	RAN.13.A	CAL.15.c	NEW.17	CAL.11.B
Na_2O	11.25	4.95	0.80	0.60	1.55	5.60	2.35
MgO	1.95	4.60	14.00	17.40	8.70	6.00	9.10
Al_2O_3	0.95	0.65	5.15	2.20	1.60	0.50	0.70
SiO_2	53.05	51.85	48.60	52.10	50.60	52.30	51.75
K_2O	---	---	---	---	---	---	---
CaO	4.85	15.40	13.25	16.75	22.00	14.45	20.25
TiO_2	0.70	0.25	2.35	0.45	0.25	0.35	0.10
Cr_2O_3	0.15	---	---	0.10	0.20	---	---
MnO	0.90	1.60	0.10	0.20	0.95	1.15	1.05
FeO	26.55	21.30	5.60	10.40	15.25	19.70	14.40
Total	100.35	100.60	99.85	100.20	101.10	100.05	99.70

Table III.7.B CATIONS (O = 24)

Na	3.463	1.507	0.233	0.172	0.465	1.703	0.709
Mg	0.466	1.076	3.097	3.830	1.993	1.401	2.097
Al	0.180	0.116	0.906	0.381	0.285	0.099	0.126
Si	8.434	8.161	7.227	7.705	7.773	8.171	7.989
Ca	0.824	2.595	3.709	2.653	3.622	2.420	3.346
Ti	0.081	0.028	0.263	0.051	0.028	0.041	0.012
Mn	0.120	0.211	0.014	0.027	0.125	0.154	0.140
$Fe^{tot.}$	3.527	2.803	0.695	1.289	1.957	2.575	1.858
Fe^{+2}	0.064	1.296	0.462	1.117	1.492	0.872	1.149
Analyses	3 x 2	14 x 2	10 x 2	3 x 2	4 x 2	3 x 2	3 x 2

Table III.7.A. (continued)

Key No.	1	7	10	8	11	13	14
Sample	IR.401	CAL.14.	G.M.8.B.	CAL.15.r	NEW.15	SAFT.1	CAL.14.T
Na_2O	0.85	6.25	5.05	7.40	7.30	12.15	13.60
MgO	16.30	5.60	3.75	5.40	3.60	1.15	0.90
Al_2O_3	0.35	0.50	0.60	0.60	0.80	0.80	0.25
SiO_2	54.00	52.60	52.95	53.00	52.00	52.15	52.70
K_2O	---	---	---	---	---	---	---
CaO	24.55	13.30	14.10	11.40	11.10	2.85	0.20
TiO_2	0.35	0.30	0.30	0.45	0.50	0.35	7.60
Cr_2O_3	---	---	---	---	---	---	---
MnO	0.30	1.20	2.10	1.00	1.30	0.40	0.25
FeO	2.70	19.45	22.30	20.70	23.50	27.95	22.40
Total	99.40	99.20	101.15	99.95	100.10	97.80	

B. CATIONS (O = 24)

Na	0.243	1.912	1.593	2.241	2.238	3.860	4.150
Mg	3.577	1.312	0.869	1.253	0.847	0.274	0.200
Al	0.057	0.096	0.108	0.111	0.149	0.159	0.050
Si	7.939	8.256	8.281	8.291	8.246	8.536	8.367
Ca	3.869	2.251	2.348	1.912	1.885	0.502	0.035
Ti	0.037	0.037	0.035	0.052	0.060	0.044	0.900
Mn	0.036	0.160	0.275	0.132	0.176	0.054	0.035
$Fe^{tot.}$	0.334	2.563	2.900	2.703	3.119	3.827	2.975
Fe^{+2}	0.091	0.651	1.307	0.462	0.881		---
analyses	3 x 2	5 x 2	2 x 2	6 x 2	6 x 2	4 x 2	2 x 2

The clinopyroxene crystallization trends of these two intrusions (Morotu, Shonkin Sag) are similar to the trend followed by the clinopyroxenes of the present study. This trend has been described earlier and is shown in fig. III.5.A, B and III.4.

Table III.8. Niggli's mg x 100 in each pyroxene. $\left(\frac{100\ mg}{Mg + Fe^{tot.} + Mn}\right)$

Key No.	12	9	2	3	5	6	4
Sample	LIT.10.M.D	G.M.4.D	IR.19.B	RAN.13.A	CAL.15.c	NEW.17	CAL.11.B
Nig.mg x 100	11.35	26.30	81.35	74.45	48.90	33.90	51.20

Key No.	1	7	10	8	11	13
Sample	IR.401	CAL14c.	G.M.8.B	CAL.15.r	NEW.15	SAFT.1
Nig.mg x 100	90.65	32.50	21.50	30.65	20.45	6.60

3.Phlogopite-Biotite s.s.

Biotite-phlogopite is common and widespread, it becomes more abundant than pyroxene in the majority of lamprophyres. Both primary and secondary phlog.-Biot. was found. In the latter case Biotite replaces pyroxene or Amphibole. Phlogopite was found occurring in two generations in the mica lamprophyres, it was found as single generation in some carbonatites and finally poikilitic biotite was found in aegirine apatite carbonatites and ore carbonatites accompanying pyroxene, opaques and apatite inclusions. The crystals were examined for homogeneity. They were found homogeneous, except some of the largest phenocrysts which show a chemical but not optical zoning. However even in these large phenocrysts the elemental variation is small. Rutile needles commonly occur on (001) planes of the first generation phlogopite (phlog. phenocrysts) occurring in lamprophyres. In some specimens bent biotite flakes are common.

Chemical analyses of brown mica from different facies of the intrusion are set down in table III.9.A. If we plot these micas on the square defined by the end members Annite-Phlogopite-siderophyllite-Eastonite (Deer, Howie and Zussman, 1966, p. 212), and adopt the ratio Mg:Fe = 2:1 for distinction of biotite and phlogopite, then, most of the micas fall within the phlogopite field and close to the phlogopite end member. Micas from three samples only (IR.18.B.C., CAL.11.B, SAFT.1.), fall within the biotite field. They fall close to the boundary line (Mg:Fe = 2:1). In contrast to the pyroxenes, the micas exhibit a less extensive variation in Niggli's mg. Over the entire differentiation sequence the range in composition is from Annite_{12} to Annite_{63}. Niggli's mg varies from 90.5 to 35.9 (see table III.9.B.). Variation of the principal oxides is shown in fig. III.7. Aluminum shows an inverse relationship to silicon. A similar relationship exists between sodium and potassium, that is, when potassium is low, sodium is compensatingly high. Fig. III.6.A. shows the iron-magnesium variation under approximately constant K + Na content. The trend defines a line parallel to the base of the triangle.

III.B.4. Amphiboles

Amphiboles are not a common phase in these rocks. From a genetic point of view we can distinguish two amphibole categories, primary and secondary. Both categories were found, but in different facies. Primary amphiboles are alkalic. They occur in the most evolved facies coexisting with aegirine. Secondary amphiboles occur in lamprophyres where they replace olivine (microph. III.14) and/or Ca-rich pyroxene in pseudomorphs. This latter amphibole is a member of the tremolite-actinolite solid solution series, close to tremolite composition.

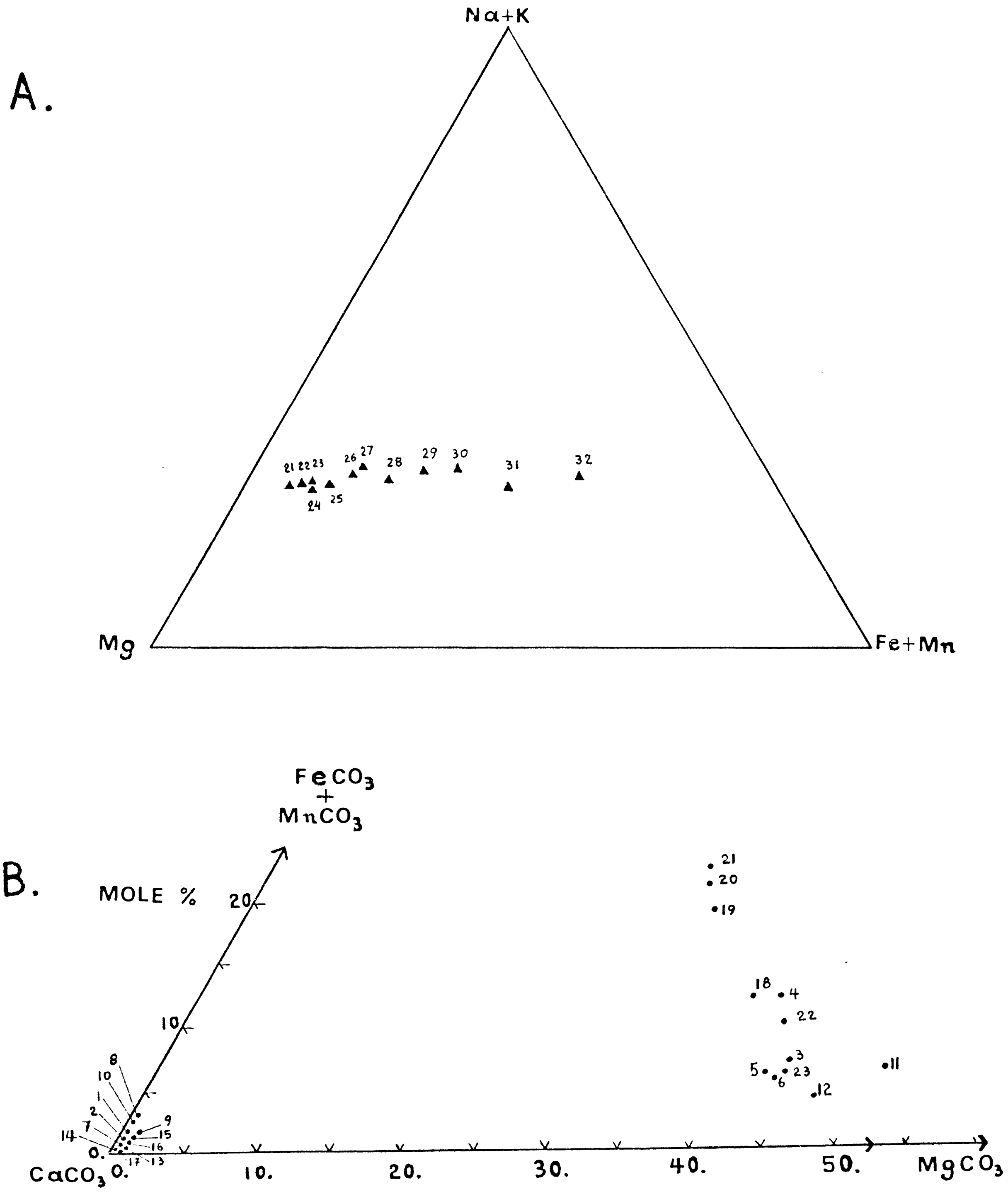


Fig. III.6. A. Biot.-phlog. Na + K, Mg, $Fe^{tot.}$ + Mn cations.
The used key numbers are from table III.9.
B. Carbonates Moles %.
The used key numbers are from table III.11.

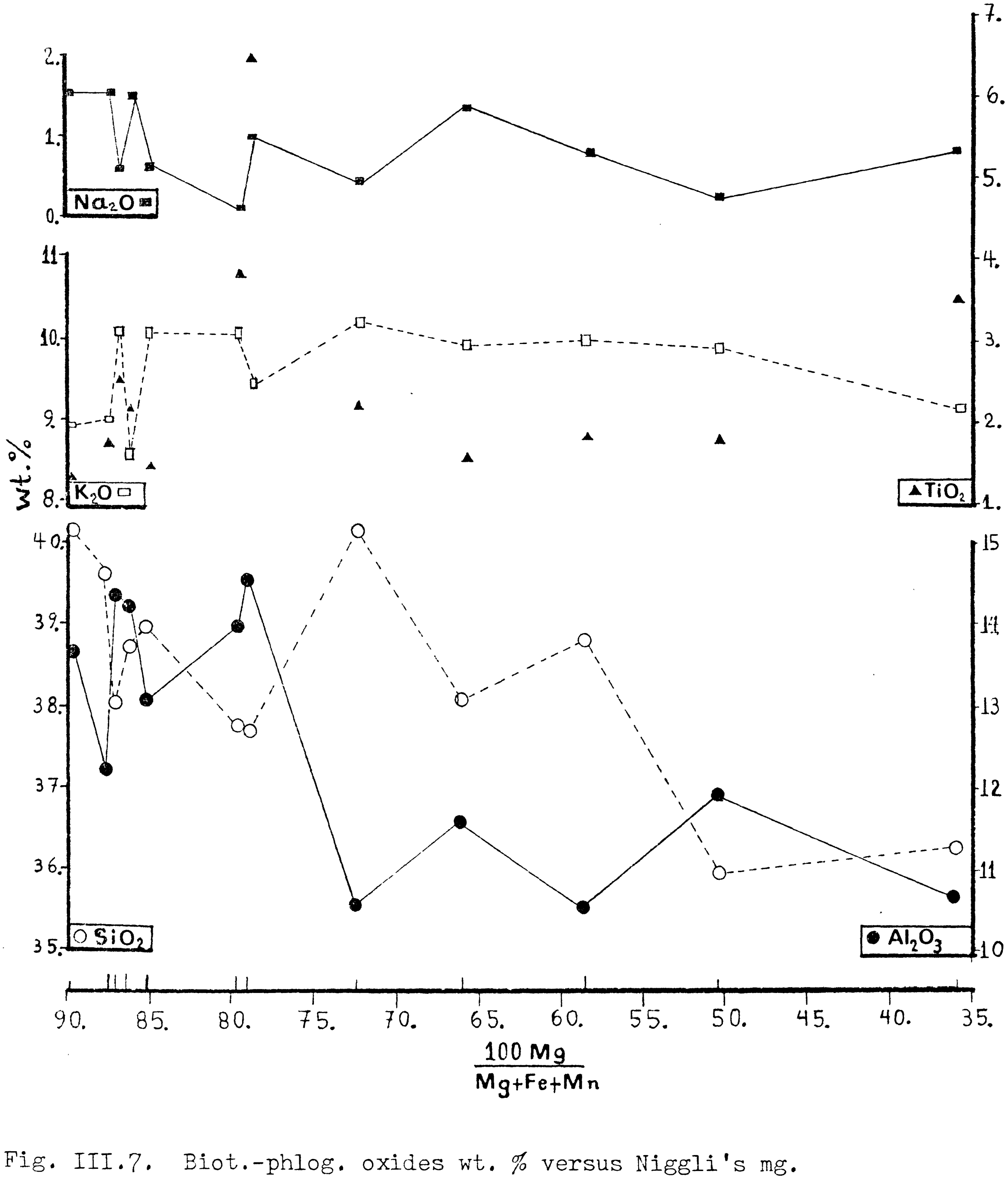


Fig. III.7. Biot.-phlog. oxides wt. % versus Niggli's mg.

Table III.9.A. Oxides in wt. % of chemically analyzed minerals of the Biotite-phlogopite s.s. series from different facies of the intrusion.

Key No.	21	22	23	24	25	26
Sample	IR.19.B	IR.401	IR.9.c	IR.8.A	IR.5.B	IR.12
Na_2O	1.50	1.50	0.60	1.45	0.60	0.10
Al_2O_3	13.70	12.30	14.35	14.20	13.10	13.95
SiO_2	40.15	39.65	38.05	38.75	39.00	37.75
K_2O	8.90	9.00	10.10	8.60	10.05	10.00
TiO_2	1.20	1.65	2.50	2.15	1.40	3.75
MgO	24.75	23.85	22.75	23.50	22.90	20.20
FeO	4.50	6.00	5.90	6.35	6.45	8.85
CaO	---	---	---	---	---	0.30
MnO	0.10	0.05	0.20	---	0.60	0.40
H_2O	4.10	4.10	4.10	4.15	4.10	4.10
Total	98.90	98.10	98.55	99.15	98.20	99.40
analyses	4	3	2	6	4	4

Table III.9.B. CATIONS (O = 24)

Na	0.413	0.423	0.162	0.395	0.173	0.156
Al	2.288	2.103	2.461	2.405	2.257	2.400
Si	5.700	5.756	5.530	5.517	5.703	5.503
K	1.614	1.666	1.871	1.600	1.878	1.858
Ti	0.124	0.182	0.271	0.237	0.154	0.411
Mg	5.236	5.160	4.932	5.000	4.987	4.380
$Fe^{t.}$	0.535	0.730	0.718	0.759	0.792	1.081
Ca	---	---	---	---	---	0.040
Mn	0.014	0.006	0.022	0.014	0.069	0.048
Niggli's mg	90.51	87.50	86.95	86.60	85.28	79.50

Table III.9.A. (continued)

Key No.	27	28	29	30	31	32
Sample	RAN.DYKE	RAN.15	IR.17.B.	IR.18.B.C	CAL.11.B	SAFT.1
Na_2O	1.05	0.45	1.30	0.80	0.25	0.80
Al_2O_3	14.60	10.55	11.60	10.50	11.90	10.65
SiO_2	37.70	40.15	38.10	38.80	35.95	36.25
K_2O	9.45	10.20	9.90	9.95	9.85	9.15
TiO_2	6.40	2.15	1.50	1.80	1.75	3.50
MgO	17.80	18.95	17.30	14.75	12.90	8.80
FeO	8.25	12.70	15.05	17.50	21.40	26.85
CaO	0.30	0.30	0.20	0.50	---	0.20
MnO	---	0.20	0.80	0.75	1.20	1.10
H_2O	4.15	4.05	3.95	3.90	3.80	3.80
Total	99.70	99.70	99.70	99.25	99.00	101.10
analyses	2	4	2	2	2	6

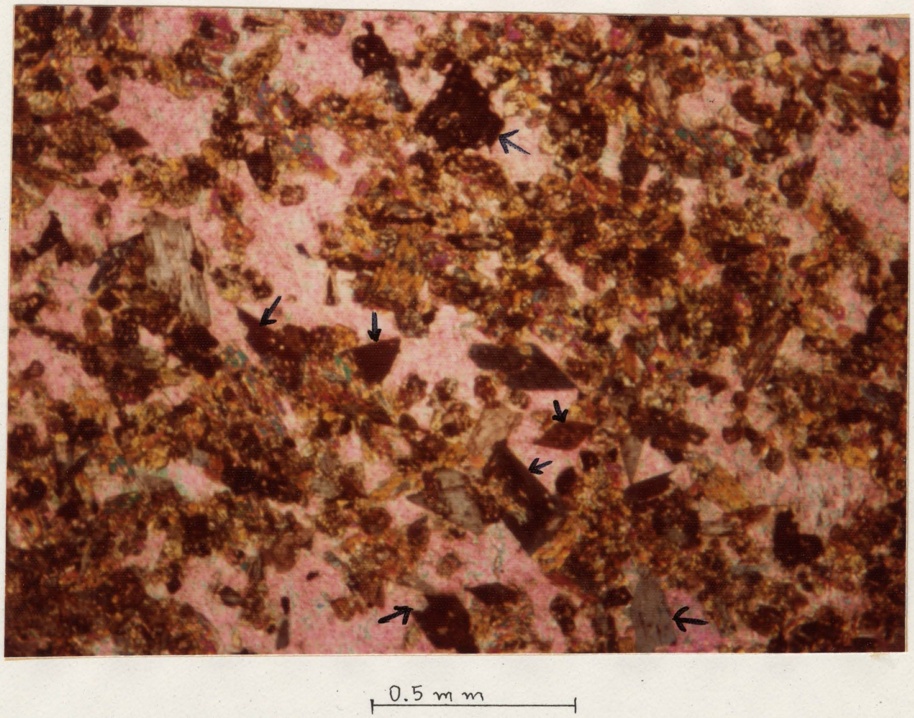
Table III.9.B. (continued)

Na	0.290	0.125	0.374	0.233	0.069	0.240
Al	2.488	1.840	2.056	1.896	2.199	1.975
Si	5.456	5.948	5.749	5.929	5.635	5.700
K	1.744	1.925	1.904	1.940	1.969	1.832
Ti	0.697	0.240	0.170	0.207	0.208	0.410
Mg	3.841	4.177	3.886	3.360	3.017	2.059
$Fe^{t.}$	0.996	1.575	1.896	2.238	2.805	3.531
Ca	0.047	0.050	0.034	0.082	---	0.030
Mn	---	0.023	0.102	0.098	0.159	0.148
Niggli's mg	79.40	72.30	66.05	58.60	50.45	35.90

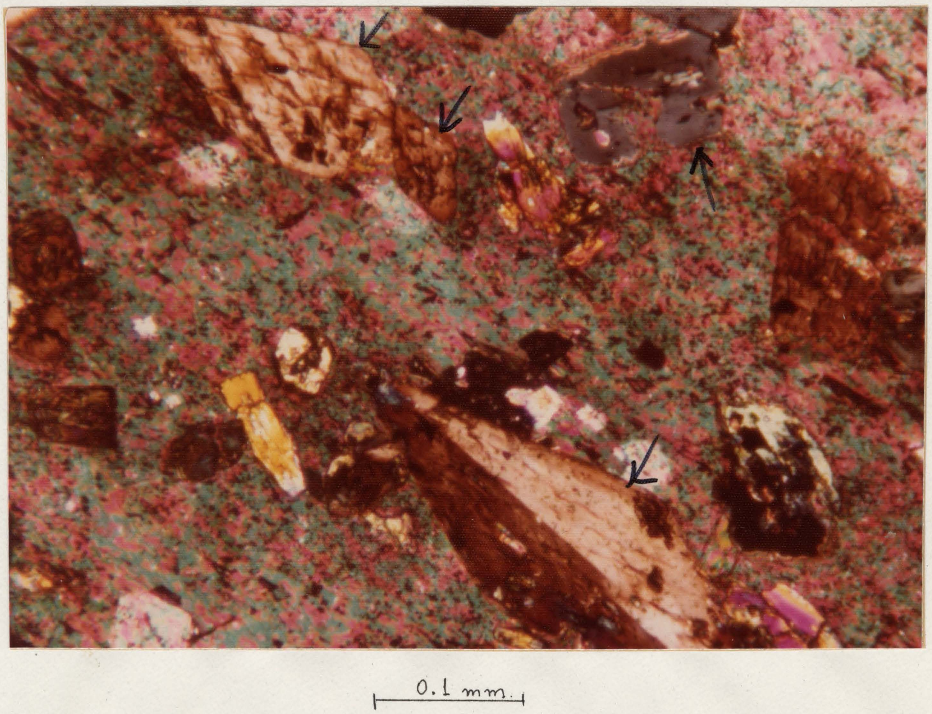
The sodic amphiboles were analyzed and their chemical analyses are displayed in table III.10. Their cations based on 24 (O, OH) are displayed too. They contain appreciable magnesium, 2.1 to 3.5 atoms of Mg in their half-unit cell based on 24 (O, OH). Sodium plus Potassium range from 2.3 to 3.0 atoms per half-unit cell. This high alkali content indicates coordinated alkali metal ions in the A site, consequently they are arfvedsonitic. Their aluminum and titanium content is low. Manganese is up to 0.3 atoms per formula or 2.3 MnO (in wt. %) in the amphiboles from LIT.10.M.D. which is enough to characterize them as a manganous variety. Calcium is low, it ranges from 0.60 to 2.50 percent CaO in wt. % or 0.01 - 0.67 calcium atoms per half unit (O, OH = 24). Miyashiro (1957) has pointed out that chemical analyses of natural alkali amphiboles of this series (riebeckite-arfvedsonite) show essential amounts of lime, which is not present in synthetic analogues because they are synthesized from calcium free oxides, and he suggests the formula for arfvedsonite be written $Na_2Ca_{0.5}Fe^{+2}_{3.5}Fe^{+3}_{1.5}Si_{7.5}Al_{0.5}O_{22}(OH)_2$. However, in our case Ti, Al, Ca, and even Mn content is low. Na, Fe, Mg, and Si are the major, elements. The only variation of their optical properties is that their color becomes darker with increasing iron content. According to the above elemental contents (see also table III.10), and their physical properties, the sodic amphiboles were characterized as members of the magnesioriebeckite $Na_2(Mg,Fe)_3Fe^{+3}_2\ Si_8O_{22}(OH)_2$-magnesioarfvedsonite $Na_3(Mg,Fe)_4Fe^{+3}\ Si_8O_{22}(OH)_2$ solid solution series.

It has been mentioned that alkali amphiboles are not common. The amphiboles and the coexisting minerals, especially the pyroxenes and iron oxides are very interesting since they are P_{O_2} sensitive. Ernst (1962) in his study of the stability of riebeckite and riebeck.-arfveds. s.s. found that at lower oxygen fugacity (close to that defined by the FMQ buffer, fig. III.8) the crystallized amphibole was not riebeckite. It was riebeckite-arfvedsonite s.s. This arfvedsonitic amphibole is stable at higher temperatures and coexists with melt at 712°C and 2 kbr fluid. In contrast, riebeckite is stable at lower temperatures and higher P_{O_2}, it never reaches the solidus. In our case the partial substitution of iron by magnesium (the amphibole is a magnesioriebeck.-magnesioarfveds. s.s.) extends the stability field of these amphiboles to even higher temperatures and makes their coexistence with melt even more realizable. There is a relevant experimental study by Ernst (1960) for the results of the substitution of iron by magnesium. It was found that at appropriate oxidation states the high temperature stability limit of riebeckite is more than 400°C lower than that of magnesioriebeckite end member. Ernst (1962) also found that the melting temperature of the arfvedsonitic amphibole is relatively insensitive to total pressure, especially in the range 1 to 2 kbr. It appears to be insensitive to bulk chemical composition, too, in the range arfvedsonite-acmite. Bailey (1969) studied the stability of acmite. He showed that acmite is relatively insensitive to total pressure in the range 2 to 5 kbr, as the oxygen fugacity is reduced it becomes even less dependent on total pressure until, under FMQ condition $dt/dP = 0^{\circ}C/kbr$. However it was found that the acmite melting temperature is sensitive to oxygen fugacity. At lower oxygen fugacity (wustite-magnetite, fig. III.8) acmite is unstable in the pressure of excess H_2O at least between 1 and 4 kbr. The estimated pressure for the present complex falls at the lower part of this range, consequently the presence of acmite places a lower limit for the oxygen fugacity. This limit is very close to the FMQ curve (fig. III.8). Under hematite-magnetite conditions, acmite melts incongruently to hematite + magnetite + liquid at 880°C and 1 kbr total pressure. At the same pressure, under quartz-fayalite-magnetite conditions (which is very close to the lower PO_2 stability limit of acmite), acmite melts at 810°C to magnetite + liquid. From the above it is evident that because of the PO_2 sensitive character of the Na-pyroxene we cannot define an upper stability temperature. However the above temperature range can be used as a higher crystallization temperature limit of this phase. There is textural evidence that Na-pyroxene is one of the late crystallized phases in rocks in which it occurs. Consequently the above higher crystallization temperature limit of the Na-pyroxene can be used as an upper limit of the crystallization temperature of the Na-pyroxene-carrying rocks (higher temperature carbonatites).

It was mentioned earlier that both phases, acmite and magnesioriebeck.-magnesioarfv. have been found to coexist with melt in relevant experimental studies. Our observations show that the above phases crystallized from the magma (they are liquidus phases) and that acmite crystallized after Na-amphibole in some samples. This is evident from textural observations (microphotograph III.10, III.1.B.,III.16, and III.17). A possible explanation for the order of crystallization of the double and single chain silicates seems to be the following. One remarkable result of Bailey's (1969) experimental studies is that acmite crystallizes only from a liquid containing excess sodium silicate. The same has been found by Bailey and Schairer (1966) in the system Na_2O-Al_2O_3-Fe_2O_3-SiO_2, and by Ford (1972) in the system Acmite-orthoclase-$Na_2O.4SiO_2$-H_2O. It was mentioned that in some of the examined assemblages aegirine appears as a very late



Microphotograph III.16. Amphibole is well formed and larger than the coexisting pyroxene. Crossed nicols. Sample LIT.10.M.D. Amphiboles are shown by vectors. **Pink is stained carbonate.**



Microphotograph III.17. Euhedral amphiboles showing characteristic rhombic cross sections, cleavage in two directions, and twinning with (100) as twin-plain. The coexisting pyroxene distinguished by its higher in interference colors is much smaller and anhedral. Crossed nicols. Sample LIT.10.M.D. **Pink is stained carbonate.**

Table III.10. Oxides in wt. % of chemically analyzed amphiboles.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	FeO	H_2O	Total	Aver. of
LIT.10.M.D.	6.70	10.90	1.60	52.00	1.90	2.50	0.70	2.30	18.20	2.00	98.80	12
RAN.15	8.95	16.25	0.70	55.40	2.70	0.60	0.25	----	12.85	2.05	99.95	6
SAFT.1.	8.15	9.50	1.80	51.20	1.60	2.20	0.60	1.30	21.60	2.00	99.95	10

IONS on the base of O = 24.

Sample	Na	Mg	Al	Si	K	Ca	Ti	Mn	Fe	OH	Niggli's mg
LIT.10.M.D.	1.95	2.43	0.28	7.80	0.37	0.67	0.08	0.29	2.28	2.00	0.49
RAN.15	2.52	3.51	0.12	8.03	0.49	0.01	0.03	0.01	1.56	2.00	0.69
SAFT.1.	2.40	2.17	0.32	7.79	0.28	0.36	0.07	0.17	2.75	2.00	0.43

crystallizing phase. This indicates that if excess sodium silicate in the melt is necessary under all conditions, it has been achieved by the continuous crystallization of other phases from a melt that had already achieved peralkalinity, but not excess sodium silicate. These phases seem to be the alkali amphibole and magnetite in sample SAFT-1 and LIT.10.M.D. In sample RAN 15 there is Na-amphibole present but there is no Na-pyroxene. Consequently we may attribute the absence of the pyroxene to the fact that the magma in this case failed to achieve the required excess sodium silicate state.

III.B.5. Carbonates

Three carbonate types were found throughout the various facies of the complexes. Their chemical analyses expressed in moles percent are displayed in table III.11. These chemical analyses are plotted on a ternary diagram (fig. III.7.B) using the following parameters: $CaCO_3$-$MgCO_3$-$FeCO_3$+$MnCO_3$, moles. This comparison, of chemical compositions, shows that we can distinguish three groups of carbonates. Chemical analyses of the first group are plotted very close to calcite. They contain minor amounts ($<$ 1% in wt.) of FeO, MgO, MnO and SrO. The second group is concentrated around dolomite. Members of this group range from dolomite to ferroan dolomite with maximum FeO content, 4.5% in wt. Iron is usually accompanied by minor amounts of Mn, $<$ 1%. The third group contains ankerites. These ankerites are from a kimberlitic dyke (RAN.DYKE) and from ankeritic carbonatites which show hydrothermal alteration. It seems that the iron enrichment of this group is secondary.

Carbonates are the most widespread phases. However, they occur in significant amounts only in carbonatites and lamprophyres, especially those

Table III.11. Moles % of chemically analyzed carbonates from different facies of the intrusion. ($CaCO_3 + MgCO_3 + FeCO_3 + MnCO_3 = 100$)

Code number	1	2	3	4	5	6	7	8	9	10	11
Sample	G.M.8.B calc.6	G.M.4.D	LIT.10.M.D sp.1	LIT.10.M.D sp.2	LIT.10.M.D sp 3	LIT.10.M.D sp.3 Av.	CAL.11.B Sp.3	NEW.15	RAN.15	IR.18.B.C.	IR.3.
$MgCO_3$	0.30	0.50	43.80	40.70	42.70	43.10	0.50	0.85	1.30	0.65	50.50
$CaCO_3$	98.40	98.75	49.60	47.50	51.70	51.20	99.10	96.70	97.60	97.55	43.15
$MnCO_3$	0.60	0.40	0.95	2.75	1.00	0.90	0.20	1.40	0.50	1.10	0.80
$FeCO_3$	0.66	0.35	5.60	9.00	4.60	4.75	0.20	1.00	0.60	0.70	5.55
Aver. of	2	4	2	2		3	2	4	4	2	3

Key number	12	13	14	15	16	17	18	19	20	21	22	23
Sample	IR.2.	IR.19.B	CAL.14	IR.12	IR.8.A	IR.17.B	IR.6 N.3	IR.6 Dol.2	IR.6 Dol.1	RAN.DIKE Carb.4.	IR.5.B Cal.3	IR.9.C Dol.1
$MgCO_3$	46.90	0.72	----	0.77	0.72	----	38.43	32.75	31.11	30.47	41.97	43.31
$CaCO_3$	49.35	99.07	99.78	98.48	99.06	99.71	49.55	48.63	48.04	47.56	48.52	50.52
$MnCO_3$	0.70	0.17	0.10	0.52	----	0.23	0.65	0.85	0.56	3.61	0.98	1.70
$FeCO_3$	3.06	0.04	0.10	0.22	0.21	0.06	11.37	17.75	20.29	18.36	0.53	4.48
Aver. of	3	2	3	6	4	2	2	2	2	2	2	3

Table III.12. List of identified minerals

Ankerite	
Apatite	
Barite	
Biotite	
Calcite	
Chondrodite	
Chlorite	
Clinoamphibole	Magnesioriebeckite-Magnesioarfvedsonite s.s. (manganous) hornblende Tremolite-Actinolite s.s.
Clinopyroxene	Aegirine-Augite Aegirine and Titaniferous Aegirine Augite Salite Hedenbergite
Dolomite, ferroan dolomite	
Garnet	Melanite Andradite
K-Feldspars	Orthoclase Microcline
Plagioclase	Oligoclase Labradorite to Bytownite
Pectolite	
Phlogopite	
Pyrochlore	
Quartz	
Sphene	
Wollastonite	
Opaque(s)	Magnetite Hematite Pyrite Rutile Leucoxene

Table III.13. Modal composition of country rocks and fenites.

Specimen number	country rocks				Fenites - increasing fenitization						
	G.M.10	RAN.11	RAN.12	NEW.10	G.M.10.A	NEW.1	NEW.16	G.M.5.C	NEW.18	NEW.17	G.M.8.B.
Quartz	19.0	18.5	18.0	19.5	17.0	10.0	----	9.0	----	----	----
Plagioclase	33.0	33.0	38.0	30.5	32.0	20.0	4.0	2.0	----	----	----
K-felds. + perthite	38.0	40.0	36.0	38.0	35.0	48.0	72.0	70.0	70.0	49.0	46.0
Biot. + alter.	3.0	3.0	2.0	3.0	2.0	----	----	1.5	----	----	----
Hornbl. + alter.	3.0	3.5	4.0	7.0	2.0	7.0	----	----	----	----	----
Aegirine + alter.	----	----	----	----	6.0	8.0	18.0	10.0	15.0	38.0	37.0
Na-Amphibole	----	----	----	----	----	----	----	1.0	10.0	1.5	1.0
Calcite	1.0	1.0	1.0	1.0	1.0	3.0	2.0	4.0	1.0	1.5	11.5
Apatite	0.5	----	----	----	1.0	2.5	3.0	2.5	3.0	4.0	3.0
Sphene	----	----	----	----	----	----	----	----	----	2.0	----
Opaques.	2.0	1.0	1.0	1.0	3.0	1.0	1.0	0.5	0.5	4.0	1.5

Modes based on count of 1000 or more points spaced 0.3 mm apart on lines 1.0 mm apart

Table III.14. Code numbers and sample names for use in table III.15.

1 = LITT.MAN.10.M.D.
2 = CAL.11.B.
3 = G.M. 4.D. Alkali Pyroxenite
4 = NEWM. 15

5 = RAN. 15
6 = SAFT.1
8 = IR.2.
9 = IR.3 Carbonatites
10 = IR.18.B.C
14 = IR.9.C
15 = IR.5.B

7 = RAN.13.A. Diabase

16 = CAL.15
17 = CAL.14 palingenic, hybrid rocks
19 = IR.9.B.
20 = IR.8.B.

11 = IR.12
12 = IR.8.A.
13 = IR.401 Lamprophyres
18 = LIT.M.13.M.D.
21 = IR.19.B

Table III.15. Modes of intrusive and hybrid rocks.

Code Number	1	2	3	4	5	6	7	8	9
Ankerite									73
Apatite		3	3	2	6	9		tr.	
Barite								9	2
Biot.-Phlog.		1		<1	13	5			
Calcite		27	10	1	72	22			
Chlorite									
Clinoamphibole	32				5	12			
Clinopyroxene	34	68	77	86		10	45		
Dolomite	33							87	
Garnet									
K-feldspar			6	9					
Plagioclase							51		
Pectolite									
Pyrochlore					1	2			
Quartz	tr.					1		tr.	11
Sphen									
Wollastonite									
Magnetite	<1	<1	tr	<1		33	2		
Hematite	<1		4	<1				2	12
Pyrite		<1	tr	<1	3	6	2	tr	<1
Rutile									

Table III.15. (continued)

Code Number	10	11	12	13	14	15	16	17	18
Ankerite									
Apatite			6	3	3	4	6		tr.
Barite	3								
Biot. Phlog.	1	42	32	39	43	25			10
Calcite	94	14	21	21	43		17	10	14
Chlorite									
Clinoamphibole		23							
Clinopyroxene			3	27			46	20	32
Dolomite						60			
Garnet			21						
K-feldspar							30	30	
Plagioclase									
Pectolite								24	
Pyrochlore									
Quartz	tr.								
Sphen		9		2					
Wollastonite			4					15	
Magnetite		7	9	6	8		<1		5
Hematite	<1							<1	
Pyrite					3	2			2
Rutile									
Leucoxene		5	4	2					
extra fine matrix									38

Table III.15 (continued)

Code Number	19	20	21
Apatite	8	15	1
Biot.-phlog.	24	10	4
Calcite	31	35	7
Chondrodite	21	30	
Clinoamphib.			
Clinopyrox.			7
Dolomite			
Garnet			
K-feldspar			
Plagioclase			
Pectolite			
Quartz			
Sphen			
Wollaston.			
Magnetite	7	5	17
Hematite			
Pyrite	5	5	1
Rutile			
groundmass*			64

*mainly phlogopite and calcite.

with abundant ocelli. In these rocks calcite is a primary and early phase. In pyroxenites calcite is an interstitial but primary phase as well. Calcite is sparingly present in the country rocks but in some cases accompanies fenitized rocks. In the less altered zones it appears as veinlets, but in many middle zone rocks it forms discrete pegmatoid patches, either separately or intergrown with aegirine and K-feldspar. In some fenites it was found finely dispersed throughout the rock.

From the chemical analyses and the observed paragenesis it is evident that calcite occurs at a higher temperature paragenesis, in lamprophyres, pyroxenites, and higher temperature carbonatites, whereas dolomite and ferroan dolomite are restricted at lower temperature facies. However, dolomite was found in lamprophyres but it was secondary dolomite replacing olivine or pyroxene phenocrysts. It seems that the local chemistry favored the formation of dolomite in this latter case. Concerning the distribution of the primary carbonates, it seems that at higher temperatures the P_{CO_2} was not high enough to stabilize dolomite. Consequently dolomite appears much later, at loser temperatures, where it is stable at lower P_{CO_2}.

III.C. PETROGENESIS

III.C.1. Introduction

It is suggested that the rocks of the Manitou Is. complex are cogenetic. A similar relationship is suggested for the rocks of the Iron Is. complex. This suggestion is based on a number of factors. Firstly, the examined rock types belong to the well established association "Igneous alkaline rocks - metasomatic alkaline rocks (fenites) - carbonatites". The above trinity has been established from similar alkaline-carbonatite ring complexes occurring in many localities throughout the world with similar tectonic-settings. The various rock types show the characteristic field relationships. The igneous rocks occur in the form of ring and radial dykes and the fenites form an aureole of variable width. The carbonatites may occur in the form of a central plug too. Such a plug occurs in the Iron I. complex.

Secondly, age determinations on different facies (carbonatites, lamprophyres) give the same value, 560 ± 15 m.y.

Thirdly, there are mineralogical trends (Chapter III.B) explicable by rational processes. These trends are similar to well established trends from other alkaline complexes.

Fourthly, the dykes appear to expose fundamental processes in the development of the alkaline rocks and the associated carbonatites arrested at various stages of development.

Developing liquid compositions and crystallizing phases within a magma chamber below a volcano may be revealed by periodic eruptions and are usually fossilized in the form of successive lava flows.

An analogous reasoning applied to our case, which has been developed in a hypabyssal (subvolcanic) environment, could suggest the following model: Periodic paroxysms of the magmatic activity fractured the surrounding rocks and magma from the upper part of the magma chamber was injected into these fissures forming the present dykes. In this sense the fissures played the role of a natural sampler which sampled the magma chamber at different times and various depths (restricted to the upper part of the chamber) during its evolution. Consequently, the dykes represent the magmatic samples.

Examination of these dykes shows that olivine, pyroxene, and probably phlogopite phenocrysts, which are ubiquitous, were probably involved in a magmatic differentiation process, namely, fractional crystallization. However, there is textural evidence that an additional differentiation process was involved, namely liquid immiscibility. The existence of liquid immiscibility is also supported by the chemistry of the crystallized phases from these two immiscible liquids, plus experimental evidence of liquid immiscibility from melting experiments on these rocks and from studied synthetic systems of relevant composition. It seems that the latter differentiation process played a major role in the magmatic differentiation of the present complex and consequently in the formation of the present rocks.

III.C.2. Magmatic Differentiation -Liquid Immiscibility

Liquid immiscibility has been considered a geologically unlikely, process since Bowen (1928) showed that the evidence adduced in its support at that time was more readily explicable by other processes.

Liquid immiscibility in complex silicate-oxide systems (i.e. containing O^{-2} as the only simple anion) was demonstrated experimentally by Greig (1927). However, Greig has shown that two liquids may be in equilibrium in these systems only in a rather narrow compositional range, characterized by extremely high concentrations of silica, and low alkalis and alumina concentrations. According to Greig (1927) even the most acid of the natural igneous rocks are located outside the immiscibility gap. The compositions of alkaline rocks rich in alkalis and alumina are situated still farther from the two-liquid region.

More recent studies have shown that the chemical composition of the melt, especially, high concentrations of K, Na, Fe, and volatiles play an important role in liquid immiscibility phenomena. This is evident from the the following discussion.

It was mentioned earlier that O^{-2} is the only simple anion in the systems studied by Grieg (1927). Kogarko (1974), and Kogarko et al. (1974) discussed the role of volatile components in magmatic crystallization and differentiation. According to the above authors the addition of volatile components (F, Cl, S. P. etc.) leads to the expansion of the two-liquid regions in silicate systems. From a brief survey of experimental data for silicate systems displaying immiscibility in the molten state Kogarko et al. (1974) concluded that the substitution of the O^{-2} of the silicate melt by such acid anions as F^-, Cl^-, PO_4^{-3}, CO_3^{-2}, SO_4^{-2}, etc. may lead to the formation of immiscible liquids.

These authors suggested that this is related to the fact that the above substitution leads to the appearance of exchange equilibria of the type $2\ Na_2O + Sicl_4 \longrightarrow 4\ Nacl + SiO_2$. The equilibria are shifted in such a way that salt-forming anions are bound with basic cations Na, K, Ca, Mg, etc., while silicon is surrounded by the polarizable oxygen. This leads to a microheterogeneity of the silicate melt, and in the case of strong displacement of equilibria (large values of $\triangle G$ of these reactions) it causes a heterogeneity in a megascopic scale i.e. two separate melts are formed. One rich in salt components (ionic) and the other rich in silicates (polymerized).

Alkaline rocks are characterized by maximum abundances of volatiles (this is shown, in our case, by the presence of phlogopite, carbonates, amphiboles, sulfides, sulfates, etc.). According to Kogarko et al. (1974) the concentrations of volatiles are not usually sufficient for the separation of liquid phases prior to crystallization. However, they suggested that during the crystallization of the magma the concentrations of volatile components are continuously increasing and the conditions of the separation of immiscible liquid may be realized. Actually, the above suggestion seems to be applicable to our case where mafic minerals (phenocrysts) were crystallizing when immiscibility (ocelli) appeared. The coexistence of two immiscible liquids (matrix and ocelli) with phenocrysts of mafic minerals, which is observed in lamprophyre hand specimens, has been verified experimentally by Ferguson and Currie (1971). They carried out melting experiments on specimens of similar ocellar lamprophyre dykes from a nearby complex, Callander Bay complex. The olivine lamprophyres with carbonate-rich ocelli began to melt at about 940°C. Two different glasses were detected in the quenched samples up to 1100°C where the only remaining crystalline phases were olivine and clinopyroxene.

Fractional crystallization is not the only mechanism that can increase the concentrations of the volatile constituents of the liquid phase. Many authors have suggested various processes which have been grouped by Kogarko et al. (1974) under the main heading, "pneumatolytic differentiation". B. G. J. Upton (1967) suggested that thermodiffusive processes are important in the genesis of alkaline rocks, strong compositional gradients may be set up in a magma chamber in response to the thermal gradients. Saether (1948) and Kennedy (1955) emphasized the role of diffusion along pressure and temperature gradients resulting in a concentration of volatiles in the upper parts of magma chambers, characterized by the lower temperatures and pressures, in order to maintain the physiochemical equilibrium in the magma. Alkalis accompany the volatiles towards the apical parts. Thermodiffusion (soret effect) is thus not the only cause of differentiation but pressure gradients also provoke diffusion.

Some investigators have invoked such "pneumatolytic differentiation" to explain the petrology of some region (provinces) as for example the Roman volcanic province (Locardi,E. and Mittempergher, M. 1969). Some very interesting examples of fossilized compositional gradients are offered by differentiated, well exposed, sills and other small intrusions. A famous example is the Shonkin Sag laccolith (Nash and Wilkinson, 1970) in which the upward increase in the content of volatiles is seen in increasing grain size and zeolite content, and in the change of mafic minerals from olivine-augite to sodic pyroxenes and amphiboles. Another interesting case is a basic dyke studied by Wells et al. (1974) in which a gradational increase in concentration of CO_2 towards the margins of the dyke is seen in increasing content of carbonates (particularly siderite). According to Wells et al. the dyke provides a unique glimpse of influences on a basic magma exerted by what S. J. Shand has aptly termed the "fugitive constituents", the transient effects of which are rarely preserved in the rocks.

From the above discussion we can see that local concentrations of volatiles and alkalis occur in some cases, especially when we are dealing with volatile-rich alkaline magmas which have low viscosity.

In our case we have no reason to reject the participation of the first mechanism (fractional crystallization) or the second one (diffusion along pressure and temperature gradients) in the volatile enrichment of the lamprophyre magma. However, if we combine the volatile-rich character of this magma, its its high FeO + Fe_2O_3 content (15% wt), and the MgO rich phenocrysts, we can suggest that the first mechanism explains much better the parallel enrichment in iron and volatiles by the crystallization of Mg-rich silicates. This means that if the second mechanism was involved, it played a secondary role.

From the previously reported examples of volatile enrichment it comes out that high concentrations of volatile components do not lead necessarily to the formation of immiscible liquids. This may be related to the position of the two-liquid field in the system Albite-Anorthite-Na_2CO_3-H_2O (Koster Van Groos and Wyllie, 1973) as the two liquid field is restricted to the alkaline side of the triangle Albite-Anorthite-Na_2CO_3. The found miscibility gap between carbonate and silicate liquids in the join $NaAlSi_3O_8$-$CaAl_2Si_2O_8$-Na_2CO_3-H_2O has been suggested by Koster Van Groos and Wyllie as a mechanism explaining the origin of the various rocks in carbonatite complexes. The results of the study of this join are very interesting, the miscibility gap was found to separate an alkalic carbonate liquid, which was strongly enriched with CaO, from an undersaturated silicate liquid of peralkaline character. The liquid immiscibility problem becomes complex if we realize that many major components of the lamprophyre dykes such as FeO, Fe_2O_3, MgO and K_2O are absent from the studied join. This makes extrapolation, of the studied immiscibility, to the natural rocks of our case speculative. Koster Van Groos (1975) continued his studies on liquid immiscibility and he included the above mentioned components. The results establish that the miscibility gap between silicate and carbonate liquids present in the join $NaAlSi_3O_8$-$CaAl_2Si_2O_8$-Na_2CO_3-H_2O extends into systems containing in addition MgO, K_2O, and Fe_2O_3.

In the past decade experimental and observational evidence of immiscibility has accumulated indicating that immiscibility is a significant factor in the evolution of certain rare types of rocks including basic to ultrabasic alkaline rocks (Ferguson and Currie, 1971; Roedder and Weiblen, 1971; Philpotts and Hodgson 1968; Koster Van Groos and Wyllie, 1973, 1975). Immiscibility occurs in the form of spheroidal masses of different composition from that of the matrix. It was mentioned earlier that liquid immiscibility in such ocellar rocks has been confirmed experimentally. Such textural evidence requires quenching at a moment when both fractions of the rock are liquid but gravitational separation of the liquids has not occurred. Such features are fragile and ephemeral, and unlikely to persist in plutonic rocks where long periods are commonly available for differentiation. Even in hypabyssal rocks incipient aggregation and separation of the immiscible phase is commonly seen (Philpotts and Hodgson, 1968; Ferguson and Currie, 1971). According to the above every lamprophyre dyke represents the two chilled immiscible liquids. Since the studied complexes contain dykes of carbonatite it is reasonable to see this volatile-rich content of the ocelli as the source of these carbonatites. The plausibility of this hypothesis is also supported by the similarity of the composition of the ocelli and carbonatites.

It was mentioned earlier that the chemistry of the crystallized phases from the two immiscible liquids is in agreement with the existence of liquid immiscibility. Phenocrysts are a good indication of possible immiscibility. If two liquids coexist in equilibrium, then the minerals in equilibrium with each liquid must be in equilibrium with each other. Hence a mineral growing at the same time in both liquids must have the same composition in both, and if the composition changes with time, the zoning of the mineral in both liquids must be the same. Phlogopite and calcite were analyzed for this purpose. The chemical analysis of the above phases, occurring within the ocelli and the matrix, were found identical. Ferguson and Currie (1971) carried out similar analysis of minerals occurring within the ocelli and within the matrix and found similar results. They also examined zoned crystals and they found the same zoning of the mineral in both liquids (ocelli and matrix).

Except the lamprophyres and the carbonatites other significant facies are the fenites, the altered pegmatitic alkali syenite, and the pyroxenites.

From the description of the fenites (III.A.8), mainly from textural observations and mineralogical changes occurring during the fenitization process, it was concluded that they represent metasomatized country rocks. A supercritical fluid rich in Sodium and iron was inferred as the fenitizing agent. Now, we should look for a possible source of this agent. Koster Van Groos and Wyllie (1973) found a third fluid phase present with the two liquids (silicate and carbonatitic) which were mentioned earlier. This third phase is an aqueous "vapor" phase enriched with sodium silicate and CO_2. They suggested that this phase is responsible for the fenitization phenomena associated with carbonatite-alkalic rock complexes. It seems that such an explanation fits well in our case since we have already accepted the existence of liquid immiscibility and the two immiscible liquids consequently the above mentioned fenitizing agent represents the third phase found by Koster Van Groos and Wyllie to coexist with the other two liquid phases. In addition the above mentioned peralkaline character of this phase agrees with the chemistry of fenitization.

The pegmatitic syenites which have been described in Chap. III.A.7 have some similarities with the palingenic (hybrid) rocks which were found at the contact of intrusive carbonatitic bodies with the inner fenite zone (see Ch. III.A.6). Na-pyroxene is a major phase in both rocks. Its sodic character is evident from its optical properties. Pyroxenes from the palingenic rocks have been analyzed and were found to be aegirine augite to aegirine. The pyroxenes of the pegmatitic syenites have not been analyzed because of their high degree of alteration. However small relatively less altered pieces of the latter pyroxenes show optical properties similar to those of the pyroxenes from the palingenic rocks. K-feldspar is also a major phase in both rocks. A major difference is the presence of wollastonite as a major phase in some of the palingenic rocks whereas it is absent from the pegmatitic syenites. Another difference is the higher proportion of apatite and calcite found in the palingenic rocks. The above mentioned similarities which characterized these rocks as syenites and the inferred high crystallization temperatures, as for example for the lamprophyres ($>940^\circ C$), could cause partial melting of the country rocks, as in the case of the palingenic rocks. These observations could suggest an anatectic origin for the pegmatitic syenites. Sutherland (1965) proposed an anatectic origin for trachytic flow remnants surrounding a carbonatite complex. However rocks of similar mineralogical composition (Potassium trachytes) which have been found in the Callander Bay complex have been interpreted by Ferguson and Currie (1972) as liquid immiscibility products. The above authors carried out similar melting experiments (with those mentioned earlier) on Kaersutite-bearing lamprophyre dykes with carbonate-poor ocelli (syenite ocelli). These lamprophyres were found to melt at lower temperatures than the olivine-lamprophyres with carbonate-rich ocelli. From the examination of the quenched samples the above authors suggested the existence of liquid immiscibility. According to the above authors a primitive lamprophyric magma could be the source of both carbonatites and potassium trachyte dykes by means of a process of successive immiscibility. Such an origin of the pegmatitic syenites is not plausible in our case, although it could explain the mentioned differences between pegmatitic syenites and palingenic rocks, since Kaersutite-bearing lamprophyre dykes with syenitic ocelli have not been found in the studied complexes. However one could suggest that there were not found because of the poor exposure of the complexes. From the above it seems that with the available data we cannot decide about the first or the second of the discussed origins of the syenite.

Finally we should discuss the origin of the pyroxenites. The texture of these rocks suggests an accumulative origin. A remarkable feature of these rocks is the small size of the accumulate crystals (pyroxenes and amphiboles). However this is expected since many experimental petrologists have remarked how easily the above phases settle at the bottom of the vessel in which volatile rich systems (crystallizing these phases) are studied. Presumably in order to explain the presence of the pyroxenites in the form of dykes we should imagine first the accumulation, of the above crystals and after that the injection of this mash into fissures of the wall rock to form the present dykes.

III.C.3. Temperature-Pressure Environment

It was mentioned in Chapter III.A.4 that the lowest inversion temperature of Fe-wollastonite to Hedenbergite is 930°C. Assuming total pressure equal to 1 kbr (this assumption will be discussed later) we obtained from the wollastonite inversion diagram of Lindsley and Muir (1969) a temperature of 970°C. This temperature is in agreement with the melting experiment results of Ferguson and Currie (1971). The latter authors found that the lamprophyres with carbonate rich ocelli began to melt at about 940°C.

Concerning the fenitization temperatures, a lower limit of about 450°F (which is based on data presented by Sieber and Tiemann, 1968) is doubtful. The reaction of acmite formation studied by the above authors and suggested by Ferguson and Currie (1972) as an indicator of fenitization temperatures has been discussed earlier (see Chapt. III.A.8).

It was mentioned in Chapter III.A.8 that the maximum temperature at which fenitization can take place is limited by the melting temperature of the rocks. The melting process itself is a complex phenomenon since it is not the result of a simple increase of temperature. It is an extreme case of metasomatism which leads to partial melting of the rock. Ford (1972) suggested that Mobilization of the melt in various stages in this process could produce alkali-granite- alkali-syenite, nepheline syenite, and ijolite magmas. In our case we have formation of alkali-syenite. According to Ford (1972) the system $NaFeSi_2O_6$-$KAlSi_3O_8$-Na_2O $4SiO_2$-H_2O is applicable to the alkali-granites and syenites formed by such processes. Judging from the high and approximately equal proportions of acmite and K-feldspar found in these rocks we could suggest that the Join acmite-orthoclase-H_2O shown in fig. III.10 (from Ford 1972) can help on melting or solidification temperature speculations. A remarkable feature of this diagram is its solidus which from approximately $Ac_{30}Or_{70}$ to $Ac_{100}Or_0$ becomes almost parallel to the axis of compositions. At the above compositional range and at temperatures close to the solidus, acmite, magnetite, and K-feldspar are the solid phases coexisting with liquid and vapour. According to Ford this part of the solidus (acmite-rich) is strongly dependent on oxygen fugacity as is the case with acmite-itself. The solidus falls from 780°C at PO_2 buffered by the hematite-magnetite buffer ($PO_2=10^{-9}$) to 715°C at PO_2 buffered by the Ni-NiO buffer ($PO_2 = 10^{-16}$, see fig. III.10). There is evidence that the PO_2 of these rocks falls within the range defined by the above mentioned values of PO_2. The evidence is the fact that magnetite is a common accessory phase of these rocks and sometimes coexists with hematite. Ford also reports that at lower PO_2, close to the $FeO-Fe_3O_4$ buffer (fig. III.8), acmite is not a stable phase in the subsolidus. It is substituted by arfvedsonite. The latter phase has not been found in these rocks. According to the above we cannot define exactly the crystallization temperature but it seems that we can restrict it within the range 715°C - 780°C. Accepting the above temperature range we are in agreement with temperatures required for the formation of wollastonite which has been found in samples of these rocks. According to Winkler's diagram fig. III.9. (taken from Winkler, 1974, page 127) at $P_{total} = P_{fluid} = P_{CO_2} = 1$ kbr wollastonite is formed at temperatures $\gtrapprox 685°C$. Even if we accept a dilution of the CO_2 liberated by the wollastonite reaction by water (up to $X_{CO_2} = 0.75$ and $X_{H_2O} = 0.25$) we still need temperatures higher than 650°C (see fig. III.9).

It was mentioned earlier that a total pressure of 1 kbr could be a reasonable approximation. Such a pressure could be suggested by the subvolcanic character of the complexes, the formation of chondrodite which according to Winkler (1974) is formed at rather low pressure, and the formation of Wollastonite which at higher pressures (assuming $P_{total} = P_{CO_2}$) needs higher temperatures for example at 3 kbr needs 800°C at least. These temperatures are higher than those inferred for the wollastonite carrying rocks. Another indication of low depth (low pressure) could be the presence of the fossiliferous sedimentary rocks. Beginning in latest Cambrian or earliest Ordovician time, the troughs became a site of sedimentary deposition now recorded in scattered outliers (Colqhoun 1958, Lumbers 1971). This means that the present erosion level is similar to the late Cambrian one. Considering the age of the intrusive rocks (Cambrian) we could suggest that the overlying rocks which have been removed by erosion should represent a maximum pile of 3-5 km. This corresponds to a pressure of $\sim$1 kbr (for an average granitic rock density). A similar pressure has been suggested by Ferguson and Currie (1972) for the Callander Bay complex. They based their suggestion on the above sedimentary rocks of the Manitou and Iron Island complexes.

III.C.4. Parent Magma

There are some indications which suggest that the lamprophyric magma is slightly modified primary magma. The indications are the following: The silica activity in the lamprophyre dykes is very low (see Chapter III.B.2). The estimated silica activity values fall in the field of the alkali olivine-basalts and Nephelinites which are shown in the diagram of silica activity versus temperature presented by Carmichael et al. (1974) page 52. The crystallizing phases before the injection of the lamprophyric magma, that is the phenocrysts, are similar to phases which occur in alkali olivine-basalts and nephelinites (melilite basalts) as major phases. The inferred solidification temperature of the lamprophyres (970°C) is in the range of the solidification temperature of alkali olivine-basalts and similar undersaturated magmas. The CaO- and MgO-rich character of the lamprophyres is probably an inherent characteristic. According to the above it is suggested that the probable parent magma is an ultrabasic alkalic basalt. Probably a melilite or nephelinite basalt. According to Currie (1970) such magmas may arise by desilication of alkali basaltic magma, a generally accepted primitive magma, by flux of water through it. The above author suggested a nephelinite as a parent magma at

Callander Bay. Bailey (1974) discussed the formation of alkaline rocks by partial melting of the crust. He made clear from the very beginning of his discussion that it is safe to assume that alkali basalts, basanites, and nephelinites are primarily of mantle origin, and hence his discussion is restricted on trachyte, phonolites, pantellerites and comendites. The deep origin of the ultrabasic alkaline magmas has been accepted by the majority of the investigators working on alkaline rocks. This is based on the results of experimental work in the melting behaviour and fusion products of mafic and ultramafic meterial of mantle compostion. P. G. Harris (1972) discussed the relationship between basaltic magma type and its geological environment. He propsoed a scheme in which the major and trace element compositions of the magma types-tholeiite, alkali basalt, nephelenite, kimberlite - can be explained in terms of depth of magma-mantle equilibration and geothermal environment. According to this scheme Nephelinites have a magma-mantle equilibration depth of 90-120 km.

According to Mysen (1975) the solubility of CO_2 in silicate melts increases with increasing percentage of basic oxides (Na_2O, K_2O, CaO, MgO). Mysen examined the solubility of CO_2 in melts of the following composition: albite, Jadeite, nepheline, and a natural olivine melilite nephelinite composition. Mysen found that the solubility of CO_2, was much higher in the last melt (ol. mel. nephelinite). This capability of the ultrabasic magmas is very significant since they can provide the required CO_2 for the formation of the associated carbonatites in the alkaline complexes.

Recent phase equilibrium studies relating to the origin of magmas in the upper mantle in the presence of volatiles (CO_2, H_2O) have shown that carbon dioxide affects phase relations in model mantle systems at high pressure. According to Mysen et al. (1975) liquids formed by anatexis of mantle peridotite are andesitic under conditions of $X^{V}_{H_2O} \geqq 0.6$ at least 25 kbr total pressure and to more than 200°C above the peridotite solidus. In contrast, partial melts are olivine normative with $X^{V}_{H_2O} \leqq 0.5$, and initial liquids contain normative ol. and ne. at $X^{V}_{H_2O} \leqq 0.4$. The alkalinity of these liquids increases with decreasing $X^{V}_{H_2O}$ below values of 0.5. The (ol. + opx)-normative liquids resemble oceanic basalts whereas (ol + ne)-normative liquids resemble olivine nephelinite and melilite basalts. From the above we can conclude that low a_{H_2O} and high a_{CO_2} conditions may be those under which ultrabasic alkaline magmas are formed. The latter model does not require the flux of water through alkali basalt suggested by Currie (1970). Currie's model does not consider the role of CO_2 which should be an important component of systems representing ultrabasic alkaline basalts.

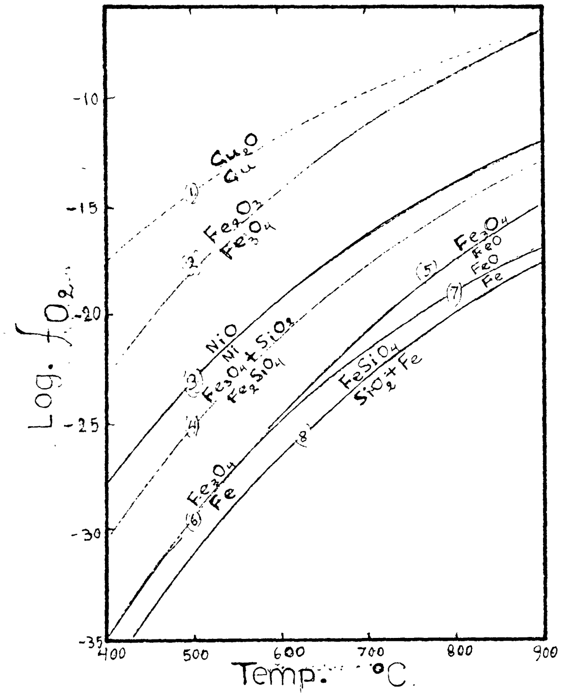


Fig. III.8. f_{O_2}-T plot of univariant oxygen buffer reactions. Influence of total pressure on fugacity of oxygen is negligible.

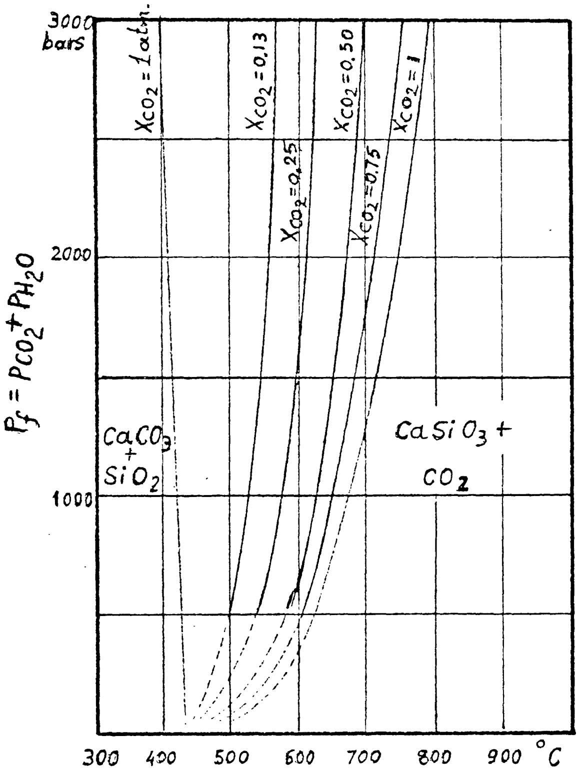


Fig. III.9. Formation of wollastonite. Dependence of equilibrium temperature on the fluid pressure P for various constant compositions of the fluid phase (const. X_{CO_2}).

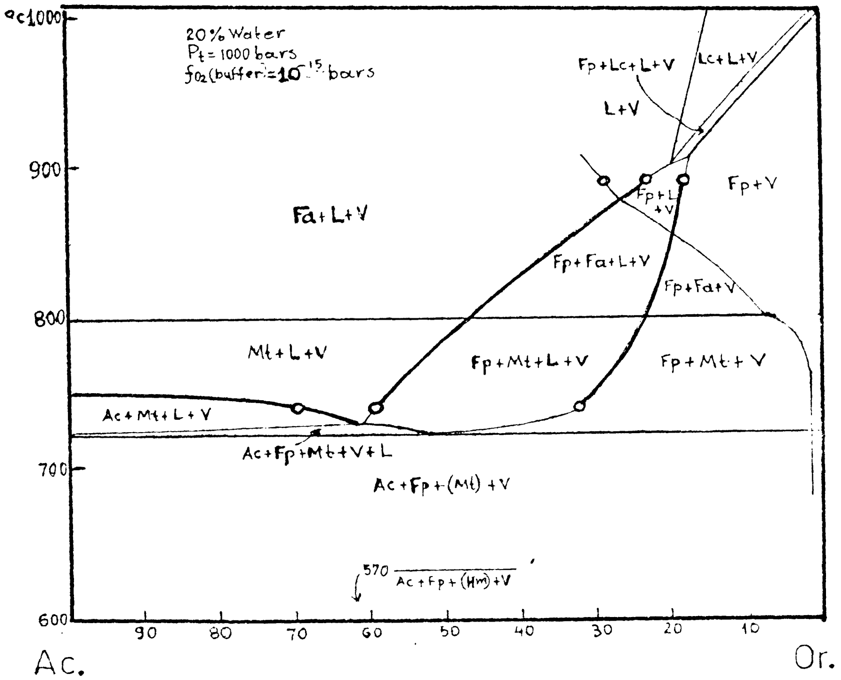


Fig. III.10. The join acmite-orthoclase.

CHAPTER IV

SUMMARY AND CONCLUSIONS

1. The Manitou and Iron Island complexes are high level exposures of two alkaline-carbonatite ring complexes with an average diameter of 1.8 miles. The exposed rock types belong to the characteristic trinity "igneous alkaline rocks - metasomatic alkaline rocks (fenites) - carbonatites".

The complexes are associated with the Ottawa-Bonnechere graben system which is a western extension of the St. Lawrence rift system (Kumarapeli and Saull, 1966).

The associated lamprophyre dykes which are concentrated within the above alkaline complexes but occur sporadically over the floor of the Ottawa-Bonnechere rift system, together with the other rocks of the complexes, are related by age and origin, and there is evidence that there has been one episode of activity, 560 ± 15 m.y.

2. The petrography of the low grade fenites, mainly the restriction of fenitization along channels such as Joints and veinlets, suggests that the fenitizing fluids flowed along definite channels, rather than diffusing through a passive medium.

The petrography of the high grade fenites suggests that the two chief fenitic species (aegirine, K-feldspar) have been formed by a re-arrangement of the components of the original rock (in plag., K-felds, biot., hornbl., and quartz) plus metasomatically introduced components (mainly Na_2O, FeO and Fe_2O_3). Extensive fenitization leads to partial melting which was inferred to occur at 720-780°C.

3. There are indications that the lamprophyres represent slightly modified primary magma (by enrichment in volatile and iron content).

The proposal that an alkaline magma can immiscibly segregate a carbonate fraction is an explanation of phenomena exhibited by the lamprophyres. The above differentiation mechanism (liquid immiscibility) is suggested for the generation of the carbonatitic magma which formed the carbonatites.

4. The mineralogical peculiarities of the later (lower temperature) intrusive facies are determined by the molecular excess of alkalis over alumina (peralkalinity) or by the molecu;ar excess of alkalis over alumina and iron (excess alkali silicate).

There is evidence that Na-pyroxene crystallized after Na-amphibole in rocks in which they have been found coexisting.

It is suggested that a possible explanation of the order of crystallization of the double and single chain silicates is the requirement of excess sodium silicate conditions for the crystallization of acmite. This necessary condition has been established from experimental studies (Bailey 1969, Bailey and Schairer 1966, Ford 1972). Excess sodium silicate can be achieved by the crystallization of other phases less alkaline.

There is a particularly interesting change in the composition of crystallizing pyroxenes. The pyroxenes change from Ca-rich phases (members of the Di-Hed. s.s. series) through aegirine augite to acmite. Their trend is similar to pyroxene trends from other alkaline complexes, Shonkin Sag (Nash and Wilkinson 1970) and Morotu-Japan (Yagi 1966).

There is evidence of complete solid solution between Ca-rich and Na-rich pyroxenes under the conditions of crystallization of the Manitou and Iron Island complexes.

Minerals of the phlogopite-biotite solid solution series changed in composition from Annite_{12} to Annite_{63}.

5. The magma parental to the Manitou and Iron Island complexes came from the mantle. The magma-mantle equilibration depth is probably 90-120 km. Both CO_2 and H_2O played an important role. During the magma-mantle equilibration $X^{v}_{H_2O} \leq 0.4$ and $X^{v}_{CO_2} \geq 0.6$.

The magma rose in the crust and was emplaced at a moderate depth below the Manitou and Iron Is. complexes where immiscibility transformed the upper part of the magma chamber to a fluidized system with extremely penetrative capabilities which formed the lamprophyre dykes. After the formation of the lamprophyres, a period of quiescence permitted the complete separation of the carbonatites.

The temperatures deduced for the lamprophyres suggest that substantial amounts of syenite may be generated by anatexis around ultrabasic alkaline magmas in the crust. There is evidence of partial melting in the Manitou Island alkaline complex.

The altered alkali syenite dykes were probably formed from an anatectic magma.

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APPENDIX

A. Analytical Procedure

All minerals were analyzed using an ARL-AMX electron microprobe with a take-off angle of 52.5°.

The elements Si, Al, Ti, Fe, Mn, Mg, Ca, Na, and K were determined by energy dispersive techniques, using standards whose energy spectra had been previously stored on magnetic tape. The apparatus includes a lithium-drifted silicon solid-state detector, NS-880 multichannel analyzing system, and PDP-11 computer. Resolution of the MnKa peak was 160 eV(FWHH). Operating conditions were: accelerating voltage 15 KV, beam current about 0.38×10^{-7} amps, and counting time 120 seconds. During the course of the analyses, standards were measured at frequent intervals to test the stability of the instrument.

Ten elements were measured in the following silicates: Pyroxene, Phlogopite, Amphibole, Plagioclase, and Melanite. Six elements were measured in K-feldspar (Na, Al, Si, K, Ca, Fe), and four elements were measured in carbonates (Mg, Ca, Mn, Fe). The used standards are the following:

Elements	Standards
Na	NaCl
Al	Al_2O_3
Mg	MgO
Si	SiO_2
K	Or-1

Elements	Standards
Ca	Anorthite
Ti	TiO_2
Cr	Cr, metal
Mn	Mn, metal
Fe	Fayalite

Spectra collected from minerals being analyzed were compared to standard spectra by means of a multiple least-squares routine, and the resulting apparent concentrations were corrected for matrix effects by the method of Bence and Albee(1968)* as well as for drift, using a Fortran computer program written by P. L. Roeder. This program was modified to consider the matrix effects of H_2O in hydrous minerals and CO_2 in carbonates. Alpha factors used in the iterative correction procedure were taken from Albee and Ray (1970).**

Analyses of a few grains are based on a single 120 second counting period, for which P. L. Roeder has estimated the following uncertainties using the energy dispersive technique at Queen's University.

Concentration	Standard deviation of amount present
$> 20\%$	2%
10-20%	3%
5-10%	5%
3-5%	8%
0.5-2%	20%
$< 0.5\%$	unreliable

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* Bence, A. E. and A. L. Albee: Jour. Geol. V.76, pp.382-403 (1968)

** Albee, A. L. and L. Ray, Anal. Chem. V. 42, pp. 1408-1414 (1970)

However for most minerals the analyses are averages of between two and eight or simetimes more separate analyses, each with a counting time of 120 seconds. With such long counting times (240 to 960 seconds) the uncertainties, especially in minor element concentrations, will be less than those stated above for a counting time of only 120 seconds.

Some factors involved in quantitative analyses are:

1. Mounting and Polishing of specimens.
2. Surface Coating.

1. The probe slides available were prepared commercially, thin-polish section laboratory, Ecole Polytechnic, Montreal. Sweatman and Long (1969) noted that for probes with a 20° take off angle, pits 0.5 microns deep will reduce the intensity of light elements as much as 10% (eg. for Mg). Thus Na and Mg intensities may show up to 10% variation in the samples unless a very fine abrasive (0.25 microns) is used. The used microprobe has a much higher take off angle (52.5°) and a very fine abrasive was used for better results.

2. The specimens were coated with a thin carbon film by the writer. The coating is necessary in order to conduct the high current in the electron beam away from the spot being analyzed, because of the poor conductive nature of silicates. This coating also absorbs the intensities of the elements being analyzed and it is important to have a uniform thickness of carbon on all samples and standards. Because of the numbers of samples used, the most obvious method, that of coating them all at the same time and under the same conditions was not possible. Therefore alternate methods were employed. Two methods are available, one is qualitative and entails comparing colour changes induced by carbon coating on the sample with a standard slide previously coated. The other method

is more quantitative and employs the use of a metre which measures the resistance of the sample, which is a function of the surface coating. The first technique was employed. In addition the operating conditions of the used coating apparatus were the same for all slides. The time of exposure to carbon precipitation was also constant.

However both methods have their limitations and differences in carbon thickness will affect count rates and thus the total concentrations of oxides. That is, samples with more carbon than the standards will give totals less than 100%, and those with less give totals more than 100%.

Specimen Alignment

The specimens and standards were held flush to a metal stage by copper clips. This is to minimize differences in the angles of the planes of the sample and standards. However this is crucial in low take off angle probes (less than 20°) as a difference of 5° may cause up to 10% error in intensity measurements. This effect is greatly reduced by using a higher take off angle. For example, in a 75° take off angle probe the same difference, 5°, causes less than 1% error.

There are also some other instrumental errors involved in the performed analyses. The instrumental errors affect precision and accuracy of electron probe analysis (see Smith and Rucklidge, 1973). The precision is affected by certain technical instrumental factors. The accuracy is affected by instrumental effects, by experimental parameters, and by matrix effects.

Common factors resulting in instrumental errors are:

Changes in Instrumental Behaviour: Ideally, the microprobe should be perfectly stable for maximum precision at a particular count rate. Unfortunately, no instrument is ideal and several possible errors from changes in instrumental characteristics must be considered.

Operating Voltage Measurements: As the size of matrix effects, depends strongly on the energy of the incident electrons, an error in the value assumed for the operating voltage will produce inaccuracies in the final results.

Line Interference: When the first-order reflection of different lines (eg. K_α and K_β) of the two elements occur at very nearly the same wavelength.

Errors caused by Microinhomogeneities: Analytical points are normally selected optically. Reflected light examination while often allowing distinction between different phases, gives information only on what is at the surface. In microprobe analysis, the primarily excited volume extends some depth below the surface. Thus hidden beneath the surface may lie a whole range of hazards -- gas, liquid or glass "bubbles", micro-inclusions of other minerals, exsolution lamellae etc., and every straightforward grain boundaries. The material actually analyzed is the average of everything within the excited volume.

For the present work errors caused by matrix effects, and by the instrumental effects have been calculated and corrected by the used computer programs. The performed selective remeasuring of standards helped to diminish errors caused by changes in instrumental behaviour.