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PETROGENESIS OF U-, Th-, Mo-, and REE-BEARING PEGMATITES,
SKARNS, AND VEINS IN THE CENTRAL METASEDIMENTARY BELT
OF THE GRENVILLE PROVINCE, ONTARIO AND QUEBEC

by

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David Richard Lentz, Ottawa, Canada, 1992



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ABSTRACT

Field examination of late-tectonic, U-, Th-, Mo-, and REE-bearing pegmatites, skarns, and veins in the southwestern Grenville Province indicates that they are spatially and temporally related. Skarns and pegmatites have a common physical association, age, and textural similarity, however a direct spatial association with the veins is less common. These observations lead to a renewal of the hypothesis that the deposits were related to intrusion of the pegmatites and formation of the skarns.

The granitic pegmatites are related either to chemical fractionation of late-tectonic granitic plutons or mid-crustal anatectic melts with emplacement at the present structural level. This interpretation is based primarily on their discordant nature, late tectonic age, and moderately-evolved chemical composition. At the time of pegmatite emplacement the host rocks remained above 500°C based on published $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronologic data. Furthermore, published retrograde P-T paths are compatible with the pegmatites being intruded at approximately 400 MPa pressure. The average normative composition of many granitic pegmatites is coincident with the 400 MPa cotectic in the haplogranite system. The chemical evolution of the pegmatites is compatible with a fractional crystallization of K-feldspar, quartz, and plagioclase under water-undersaturated conditions. The complex mineralogy of pegmatites and the association with mineralization is interpreted in terms of metasomatic exchange (hybridization and skarnification). Volatile phase saturation of the pegmatite would substantially increase diffusion and/or infiltration reactions.

Endoskarns (within pegmatite) are dominated by calc-silicate minerals (Ca pyroxene, scapolite, andradite, and titanite) and have a similar origin to the hybridized pegmatites involving metasomatic reaction of the pegmatite and skarn by either

diffusion or infiltration of chemical components into the pegmatite. The quite common occurrence of Ca pyroxene and more rarely scapolite (marialite) may result from a desilication phenomena related to high chemical potentials of Ca and Mg within the outer margin of the pegmatite. Although rare, andradite has a similar occurrence to Ca pyroxene and is possibly related to a high chemical potential of O_2 in the pegmatite and the stability of the hedenbergite component (Fe^{2+}) of Ca pyroxene.

The exoskarns are dominantly primary (ie. related to the first episode of metasomatic transformation) with a mineralogical zonation which may be characterized as proximal to distal with relation to the pegmatite. The absence of calcite within the proximal skarn is explained in that the pegmatite-derived fluids were undersaturated in calcite resulting in dissolution. Calcite veins, with selvages of Ca pyroxene-tremolite-phlogopite and less commonly molybdenite and sulphides, represent distal primary skarn. Secondary tremolite-phlogopite-sulphide replacement veins occur within the primary skarn, presumably forming as late-stage fluids interacted with the primary skarn assemblages. The mineralogy of distal exoskarns is dominantly a function of the composition of the host rock.

Fluorite-apatite-calcite veins, occurring in silicate host rocks, have inclusions and selvages of coarse-grained biotite, K-feldspar, Ca amphibole, Ca pyroxene, and titanite with occasional magnetite, sulphides, and rare-element minerals. The relative proportions of fluorite, apatite, silicates, sulphides, and magnetite are quite variable within the calcite dominant veins.

Common minerals within the pegmatites, skarns, and veins facilitated a chemical comparison of these minerals. The colour of ferromagnesian phases, particularly Ca pyroxene and biotite/phlogopite was used in the field to describe the

relative iron contents of these phases. In general, iron was highest in the minerals associated with the pegmatites, and proximal skarn; more magnesium rich in the skarns not directly associated with a pegmatite. The fluorite-apatite-calcite veins contained iron-rich ferromagnesian phases most similar to the pegmatites and the proximal skarns. A chemical comparison of minerals common to the pegmatites, skarns, and veins (biotite/phlogopite, Ca amphibole, Ca pyroxene, calcite, and apatite) has shown that there is a chemical continuum between the three styles of mineralization with considerable overlap in major- and trace-element composition. The major- and trace-element composition of the vein minerals was intermediate between those from proximal skarns and pegmatites suggesting that the pegmatite-derived hydrothermal fluid was chemically modified by host-rock interaction during marble-hosted skarn formation.

Major- and trace-element distribution coefficients (K_D) for coexisting phases in veins and skarns are indistinguishable, although only a few elements (Fe, Mg, Mn, and Zn) have regular distributions. If indeed these distributions are temperature sensitive, this data would indicate similar temperature conditions for the formation for the skarns and veins. The elemental distribution coefficients between silicates and carbonates are irregular indicating that the carbonates continued to re-equilibrate with the fluid during skarn formation or that disequilibrium resulted due to kinetic problems of equilibrium fractionation between silicate and carbonate phases.

In a more detailed study of the Hunt Mo skarn, four zones have been identified in the exoskarn which is, in part, consistent with observations from many other skarns in the region. The proximal zone 1 assemblage is narrow, coarse-grained (< 1 metre), and dominantly composed of Fe-rich Ca pyroxene, scapolite (or microcline or albite), titanite,

pyrite, and molybdenite (rare quartz). The dominant skarn type, zone 2, is fine- to coarse-grained and consists of Fe-bearing Ca pyroxene, phlogopite/biotite, titanite, pyrite, and pyrrhotite, with irregular phlogopite (possibly secondary) veinlets throughout. Apatite is an accessory phase within zone 2 skarns. The third zone is composed of Ca pyroxene, phlogopite, and tremolite, and occasionally calcite and pyrite which are fine to medium grained. The fourth zone represents small veins hosted in graphite-bearing phlogopite-diopside-dolomite-calcite marble, and is dominated by fine- to medium-grained tremolite, phlogopite, calcite, pyrite ($\pm$ graphite). The relationship between zones 3 and 4 is rarely evident. The Hunt Mo skarn differs from skarns associated with uranium and thorium enrichment, in that there is occasionally primary chondrodite (or norbergite) and fluorite associated with the distal assemblage (zones 3 and 4). The absence of wollastonite and the observed sequence of assemblages are consistent with a temperature of formation between 575°C and 525°C at 400 MPa, with $X(\text{CO}_2)$ between 0.1 and 0.3 for the proximal skarn, and 0.2 to 0.4 for the distal skarn assemblages.

In general, carbon and oxygen isotopic analyses of calcite from pegmatites, skarns, veins, and marble indicate a spectrum from the marble ($\delta^{13}\text{C} = 2$ to 3‰ and $\delta^{18}\text{O} = +22$ to $+24\text{‰}$) to pegmatite ($\delta^{13}\text{C} = -3$ to -2‰ and $\delta^{18}\text{O} = +11$ to $+13\text{‰}$). This indicates that infiltration metasomatism and resultant decarbonation were responsible for the observed trends. Carbon isotopic values below this trend are interpreted to be a result of oxidation of isotopically light graphite. A few of the vein calcite samples have lower $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios than do calcites in most pegmatites and these are interpreted to have originated from the isotopically lighter pegmatites.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in calcite from pegmatites, skarns, and veins range between 0.7040 and 0.7065, with the pegmatites and the veins having the lowest ratios. The data are interpreted

to indicate hydrothermal mixing of pegmatite-derived strontium (0.704x) with marble-derived strontium (0.706x) with strontium abundance increasing due to saturation of calcite.

The spatial, temporal, petrochemical, and isotopic evidence support a related origin for the pegmatites, skarns, and veins. The separation of a silicate (Si, Al, Fe)-, rare-metal (Ti, U, Th, Mo, REE, Nb)-, and halogen (F, Cl)-rich volatile phase was responsible for the metasomatic alteration of the dolomitic marbles to form endoskarns and exoskarns. The chemical modification of the hydrothermal fluid as a result of skarn formation and the dissolution of calcite within the exoskarn is responsible for vein formation.

SOMMAIRE

Les travaux de terrain dans le sud-ouest de la province du Grenville nous indiquent que les pegmatites, skarns et veines tardi-tectoniques enrichies en U, Th, Mo et terres rares sont reliées spatialement et temporellement. Les skarns et pegmatites ont souvent en commun une association physique, un âge, et une similarité texturale, cependant l'association avec les veines est moins commune. Ces observations suggèrent que les dépôts sont associés à l'intrusion des pegmatites et à la formation des skarns.

Les pegmatites granitiques sont reliées soit à un fractionnement de plutons granitiques tardi-tectoniques ou à des fondus anatectiques. Cette interprétation repose principalement sur leur nature discordante, leur âge tectonique, et leur chimisme moyennement évolué. D'après les données thermochronologiques $^{40}\text{Ar}/^{39}\text{Ar}$, au temps de la mise en place des pegmatites, les roches encaissantes furent maintenus à des températures au dessus de 500°C . En plus, les trajectoires P-T rétrogrades publiés pour ces roches suggèrent une mise en place des pegmatites à une pression d'environ 400 MPa. La composition normative moyenne de plusieurs pegmatites granitiques coïncide avec la cotectique de 400 MPa dans le système des haplogranites. L'évolution géochimique des pegmatites est compatible avec une cristallisation fractionnée de feldspath potassique, quartz, et plagioclase sous des conditions sous-saturées en H_2O . La minéralogie complexe des pegmatites et leur association avec les minéralisations sont signes d'échanges métasomatiques (hybridation et skarnification). La saturation en phase volatile des pegmatites augmenterait substantiellement les réactions de diffusion ou d'infiltration.

Les endoskarns (c.à.d., à l'intérieur des pegmatites) sont composés d'une minéralogie calco-silicatée (c.à.d., pyroxène calcique, scapolite, andradite et titanite) et ont, comme les

pegmatites hybrides, une genèse métasomatique par infiltration ou diffusion de composantes chimiques vers le filon de pegmatite. La présence commune de pyroxène calcique, ou plus rarement de scapolite (marialite) résulte possiblement d'une désilicification associée aux potentiels chimiques élevés du Ca ou du Mg dans les bordures externes du filon de pegmatite. L'andradite est plutôt rare et est possiblement relié au potentiel élevé de l'oxygène dans la pegmatite et à la stabilité de la composante hedenbergite (Fe^{2+}) dans le pyroxène calcique.

Les exoskarns sont surtout primaires. Ils sont associés à la première transformation métasomatique et ont une disposition en zones minéralogiques qui peut être caractérisée de distale ou proximale relativement au filon. Dans le skarn proximal, la calcite est absente puisque les fluides dérivés de la pegmatite étaient sous-saturés. Plus loin, dans le skarn distal, on retrouve des veines de calcite avec des bordures de pyroxène calcique, trémolite et phlogopite avec parfois de la molybdénite et des sulfures. Dans les skarns primaires on retrouve des veines secondaires de trémolite, phlogopite et sulfures, qui représentent possiblement des remplacements du skarn primaire par des fluides tardifs. La minéralogie des exoskarns distaux est contrôlée surtout par la composition de la roche encaissante.

Les veines de fluorine, apatite et calcite que l'on retrouve dans les roches encaissantes silicatées ont des inclusions et des bordures à gros grains de biotite, feldspath potassique, amphibole calcique, pyroxène calcique, titanite et parfois aussi de magnétite, sulfures et de minéraux d'éléments rares. Les proportions de fluorine, apatite, silicates, sulfures et magnétite sont très variables dans les veines où domine la calcite.

Plusieurs minéraux communs aux pegmatites, veines et skarns, permettent une comparaison chimique de ces minéraux. La

couleur des minéraux ferromagnésiens fut utilisée, sur le terrain, afin de décrire approximativement la teneur en fer de ces phases. En général, les teneurs en fer furent les plus élevées dans les minéraux associés aux pegmatites et aux skarns proximaux, et les teneurs en magnésium furent les plus élevées dans les skarns qui n'étaient pas directement associés à une pegmatite. Les veines de fluorine, apatite et calcite sont composés de minéraux riches en fer semblables à ceux des pegmatites et des skarns proximaux. Une comparaison chimique des minéraux communs aux pegmatites, skarns et veines (biotite/phlogopite, amphibole calcique, pyroxène calcique, calcite et apatite) démontre l'existence d'un continuum chimique entre les trois styles de minéralisations et aussi d'un empiètement considérable entre les compositions d'éléments majeurs et traces. La composition des minéraux des veines est intermédiaire entre celles des skarns proximaux et des pegmatites, ce qui suggère que le fluide hydrothermal, dérivé des pegmatites, fut modifié chimiquement par une interaction avec les roches encaissantes durant la formation des skarns dans les marbres.

Les coefficients de partage (K_D) pour les éléments majeurs et traces des minéraux des veines et des skarns sont pratiquement identiques malgré que certains éléments démontrent des distributions irrégulières (Fe, Mg, Mn et Zn). La similarité des coefficients de partage pourrait indiquer que les veines et les skarns ont été précipités à des températures semblables, si ces coefficients sont sensibles aux températures. Les coefficients de partage d'éléments entre les minéraux silicatés et carbonatés sont irréguliers, indiquant que les carbonates ont soit continuer leur ré-équilibration avec les fluides durant la formation du skarn, ou qu'il existe un déséquilibre cinétique de fractionnement entre les silicates et les carbonates.

Une étude détaillée du skarn à molybdène Hunt permet de délimiter, comme dans plusieurs autres skarns de la région, quatres zones dans l'exoskarn. La zone 1, proximale, est étroite, à gros grain (< 1 mètre), et se compose surtout de pyroxène calcique riche en fer, scapolite (ou microcline, ou albite), titanite, pyrite et molybdénite (rarement le quartz). Le skarn principal, dans la zone 2, varie de grain fin à gros grain, et se compose de pyroxène calcique riche en fer, phlogopite/biotite, titanite, pyrite, et pyrrhotite avec des veines irrégulières de phlogopite qui sont possiblement secondaires. L'apatite est un minéral accessoire dans la zone 2. La zone 3 est composée de pyroxène calcique, phlogopite, trémolite et occasionnellement de calcite et de pyrite qui sont à grain fin. Finalement, la zone 4 est représenté par de petites veines de trémolite, phlogopite, calcite et pyrite ($\pm$ graphite) qui recoupe les marbres à phlogopite, diopside, dolomie et calcite. Les relations entre les skarns des zones 3 et 4 ne sont jamais clairement observées. Le skarn à molybdène Hunt se distingue des autres skarns qui ont des enrichissements en uranium ou thorium par la présence occasionnelle de chondrodite (ou norbergite) primaire et aussi par la présence de fluorine dans les assemblages distaux (zones 3 et 4). L'absence de wollastonite et la séquence d'assemblages que l'on observe suggèrent une genèse entre 575°C et 525°C à une pression de 400 MPa et $X(\text{CO}_2)$ entre 0.1 et 0.3 pour le skarn proximal et 0.2 et 0.4 pour le skarn distal.

En général, les rapports isotopiques du carbone et de l'oxygène de la calcite des pegmatites, skarns et marbres définissent un spectre continu des marbres ($\delta^{13}\text{C} = 2$ à 3‰ et $\delta^{18}\text{O} = +22$ à $+24\text{‰}$) aux pegmatites ($\delta^{13}\text{C} = -3$ à -2‰ et $\delta^{18}\text{O} = +11$ à $+13\text{‰}$). Ceci indique que le métasomatisme par infiltration et la décarbonation sont responsable de ces variations. Les rapports isotopiques du carbone inférieurs à ce spectre sont

interprétés comme étant les résultats de l'oxydation de la graphite. Quelques veines de calcite qui ont des rapports isotopiques du carbone et de l'oxygène plus légers que les pegmatites sont interprétés comme étant dérivés de pegmatites isotopiquement légères.

Les rapports $^{87}\text{Sr}/^{86}\text{Sr}$ de la calcite des pegmatites, skarns et veines varient entre 0.7040 et 0.7065, les valeurs les plus basses correspondant aux pegmatites. Ces données reflètent un mélange hydrothermal de strontium dérivé des pegmatites (0.704X) avec du strontium dérivé des marbres (0.706X), avec une augmentation de la teneur en strontium causée par la saturation de la calcite.

Les données spatiales, temporelles, géochimiques et isotopiques suggèrent une origine commune pour les pegmatites, skarns et veines. La séparation de minéraux silicatés (Si, Al, Fe), de minéraux enrichies en métaux rares (Ti, U, Th, Mo, terres rares, Nb), et d'une phase volatile enrichie en halogènes, est responsable l'altération métasomatique des marbres en endoskarns et exoskarns. La modification chimique du fluide hydrothermal, suite à la formation du skarn, et la dissolution de la calcite dans l'exoskarn sont responsables pour la formation des veines.

STATEMENT OF CONTRIBUTION

The principle objective of the thesis was to identify the relationship between U, Th, Mo, and REE-bearing pegmatites, skarns and fluorite-apatite-calcite veins in the Central Metasedimentary Belt of the Grenville Province. In order to establish this relationship, detailed examination of the pegmatites, skarns, and veins was required. As a preliminary part of this study, radioelement (K, U, Th) analyses of pegmatite, skarns, and veins was used to establish the chemical and possibly petrogenetic relationship between occurrences (Appendix 7).

The petrogenesis of the pegmatites is re-evaluated in light of our current understanding of pegmatite genesis. The graphic texture of granitic pegmatites (Appendix 5) suggests a diffusion-controlled growth model. Reconnaissance compositional analysis of biotites from zoned, partially-zoned and unzoned Grenville pegmatites was to clarify the fractionation processes occurring in the pegmatites. In addition, pegmatite compositions are used to evaluate phase equilibria in the pegmatites.

The compositions of mica, Ca pyroxene, amphibole, and calcite from pegmatites, skarns, and veins indicate a progressive evolution compatible with a petrogenetic relationship. The elemental distribution coefficients for coexisting minerals within skarns and veins suggests similar conditions of formation. The skarn assemblages and other geologic constraints help to define conditions of formation as, 575° to 525°C, 400 MPa, and $X(\text{CO}_2)$ 0.1 and 0.5.

The oxygen and carbon stable isotopic compositions of calcite in the pegmatites, skarns, veins, and marble indicate that infiltrative metasomatic introduction of SiO_2 has resulted in decarbonation and isotopic exchange of the marble with the pegmatite-derived fluid phase. The chemically-modified fluid is potentially responsible for deposition of fluorite,

apatite, and calcite and hydrothermal alteration of the vein. The Sr isotopic compositions of the calcite support this interpretation and help to discriminate the veins from carbonatites.

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CHAPTER 1

INTRODUCTION AND REGIONAL GEOLOGICAL SETTING

1.1 Introduction

1.1.1 Background and purpose

The purpose of this thesis is to examine the petrogenesis of uranium- and molybdenum-bearing skarns and fluorite-apatite-calcite veins in the Central Metasedimentary Belt (CMB) of the Grenville Structural Province. The origin of the pegmatites, skarns, and veins within the Grenville Province is of particular interest because of the past and potential economic and environmental significance of these deposits. Spatial, temporal, mineralogical, and geochemical evidence presented below indicates a related origin for these deposits rather than separate unrelated origins. Although the distribution of pegmatites, skarns, and veins is somewhat continuous throughout the Central Metasedimentary Belt, the mineralizing elements (U, Th, Mo, and REE) are concentrated in certain areas.

The U, Th, Mo mineral occurrences in the Bancroft area are subdivided into three main types (pegmatites, skarns, and veins) by Satterly (1957), and this classification is applicable to deposits throughout the Grenville Province (Table 1.1). These general subdivisions are retained, with minor modifications, in later articles by Lang et al. (1962), Hewitt (1967) and Masson and Gordon (1981). Numerous researchers have noted the close spatial relationship among pegmatite, skarn, and vein deposits and have provided detailed geologic and mineralogic descriptions of numerous deposits (Currie, 1951; Satterly, 1957; Shaw, 1958). Petrogenetic models for their origin have evolved since initial discovery of the deposits, coincident with our increased understanding of the structural, metamorphic, and thermochronologic evolution of the Grenville Province. Currently, there are several hypotheses for the origin of these deposits. A study

**Table 1.1 Uranium Deposits in the Grenville Province (from
Satterly (1957))**

1. Deposits in granite pegmatite
 - A. Zoned pegmatite
 - B. Unzoned pegmatite
 1. Red pegmatite
 2. White pegmatite
2. Metasomatic skarn deposits
 - A. Marble-hosted skarns
 1. Dolomitic marble-hosted skarns
 2. Calcitic marble-hosted skarns
 - B. Metamorphic pyroxenite-hosted skarns
3. Hydrothermal vein deposits
 - A. Fluorite-apatite-calcite veins
 1. Gneiss-hosted veins
 2. Amphibolite-hosted veins
 3. Marble-hosted veins
 4. Metamorphic pyroxenite-hosted veins

of the associated pegmatites is included in the present study because they play a role in the preferred magmatic-hydrothermal model for the formation of the skarns and fluorite-apatite-calcite veins. Hypotheses proposed for the origin of U-Mo pegmatite, skarns, and veins in the Grenville Province are:

PEGMATITE

- 1) crustal anatexis "in situ" (Allen, 1971; Tremblay, 1974; Storey and Vos, 1982; Ford, 1982, 1983)
- 2) hydrothermal replacement (Storey and Vos, 1982; Dr. S. Lumbers, personal communication)
- 3) magmatic-hydrothermal (Hewitt, 1967; Nishimori et al., 1978; Fowler, 1980; Storey and Vos, 1982; Fowler and Doig, 1983a and b)

SKARNS

- 1) late metamorphic-hydrothermal (Mo) (Shaw, 1958; Vokes, 1963, Karvinen, 1973; Carter et al., 1979; Masson and Gordon, 1982)
- 2) late magmatic-hydrothermal (U-Mo) (Currie, 1951; Satterly, 1957; Lang et al., 1962; Hewitt, 1967; Kreczmer, 1974; Nishimori et al., 1978; Masson and Gordon, 1982)

U-Mo FLUORITE-APATITE-CALCITE VEINS

- 1) igneous carbonatite (Spence, 1929; Heinrich, 1980; Storey and Vos, 1982; Dr. S. Lumbers, personal communication)
- 2) metamorphic-hydrothermal veins (Rowe, 1952; Karvinen, 1973; Carter et al., 1980; Masson and Gordon, 1982; Storey and Vos, 1982)
- 3) magmatic (pegmatite)-hydrothermal veins (Wilson, 1924; Ellsworth, 1932; Currie, 1951; Satterly, 1957; Powell, 1965; Hewitt, 1967; Nishimori et al., 1978; Storey and Vos, 1982).

The overall objective is to develop a well constrained and integrated model for the origin of Grenville Province uranium-

and molybdenum-bearing skarns and (fluorite)-apatite-calcite veins. The study represents a regional examination of numerous occurrences of each style of mineralization within the Central Metasedimentary Belt of the Grenville Province. This approach was warranted considering the diverse hypotheses for the origin of these occurrences formulated from individual study areas most of which were included in this regional study. The shortcomings of a regional synthesis were overcome by more detailed work on the occurrences in the Wilberforce area and the Dacre area, Ontario, and the Otter Lake area, Quebec although poor outcrop exposure hampered detailed examination of even these localities. The combination of these two approaches seems to have resulted in a more comprehensive understanding of the relationship between each of the three styles of deposits and the pressure, temperature, and fluid conditions associated with their formation. Field, petrographic, radiometric analysis, major- and trace-element geochemistry, and stable and radiogenic isotope evidence will be used to place further constraints on the model. Despite the fact that these rocks host some of Canada's first uranium and molybdenite producers, little detailed work evaluating their petrogenesis has been done, in part, due to the lack of application of detailed geochemical techniques for discriminating between various hypotheses.

1.1.2 Location

The radioactive deposits are dominantly found in the Wilberforce - Bancroft, Sharbot Lake - Perth, Griffith - Dacre, and the Renfrew areas of Ontario, and in the Grand Calumet Island - Otter Lake, Gatineau - Buckingham, Maniwaki, Mont Laurier, and the Baie Johan Beetz areas of Quebec. The study encompasses the observations from 124 localities throughout the Central Metasedimentary Belt (Figure 1.1 and 1.2) but in particular on two well known areas, the Wilberforce - Bancroft area, Ontario and the Otter Lake - Grand Calumet Island area, Quebec. A regional analysis of the

distribution of uraniferous and molybdeniferous pegmatites, skarns and apatite-calcite veins shows that they are confined to rocks that have achieved upper amphibolite grade of metamorphism (Figure 1.3). It is evident that skarns and fluorite-apatite vein occur predominantly within the Central Metasedimentary Belt implying a spatial relationship with the marbles.

1.1.3 Mining history

Apatite was mined from apatite-calcite veins and apatite-rich skarns at numerous localities in both Ontario and Quebec from the early 1870's. The largest mines were in the Buckingham - Gatineau area, Quebec and the Perth - Kingston area, Ontario (Spence, 1920; Storey and Vos, 1982).

Uraninite was initially discovered in the Wilberforce area (Richardson (Fission) fluorite-apatite-calcite vein) in 1922 during radium exploration (Ellsworth, 1932). Several uraniferous granite pegmatites (Faraday, Bicroft, Greyhawk, Dyno, and Halo) were briefly brought into production in the mid to late 1950's and closed shortly after with a total production of 5500 tons U_3O_8 at an average grade of 0.17 wt. % U_3O_8 with 0.02 to 0.2 wt. % ThO_2 (Robertson, 1978, 1981). Uranium was discovered in numerous pegmatite, skarn and vein deposits in the mid-1950's and several mines (Bicroft, Faraday, and Canadian Dyno pegmatite deposits) had a brief mining history, the largest of which was the Bicroft Mine near Cardiff, Ontario. In 1975, the Faraday uranium pegmatite mine reopened as the Madawaska Mines and operated until 1981 (Masson and Gordon, 1981). The deposit averages approximately 0.10 wt.% U_3O_8 with 5 260 000 tonnes of ore (Alexander, 1986) and represents the largest of the deposit types within the area. The Grenville radioactive pegmatites are similar to the low grade Rossing uranium deposit in southwest Namibia (Berning et al., 1976).

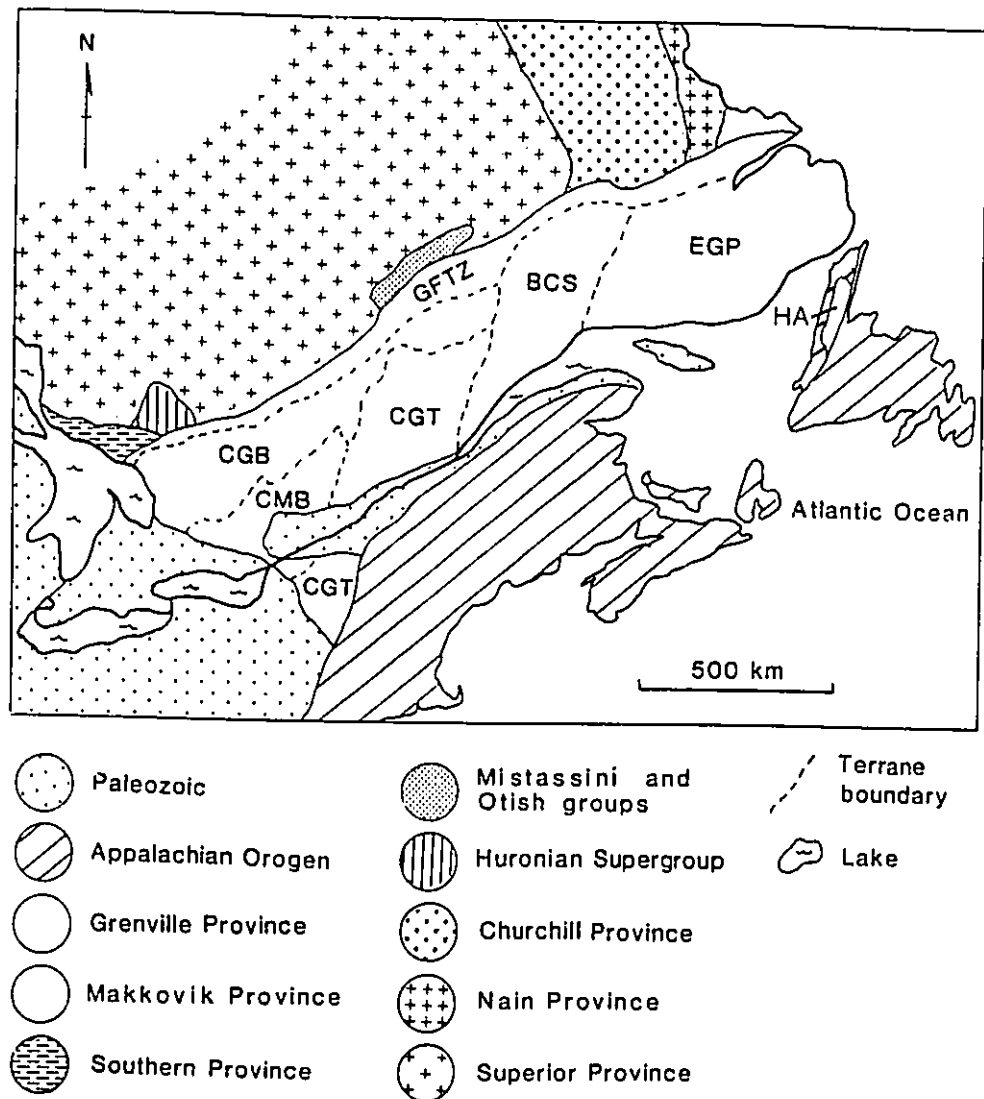
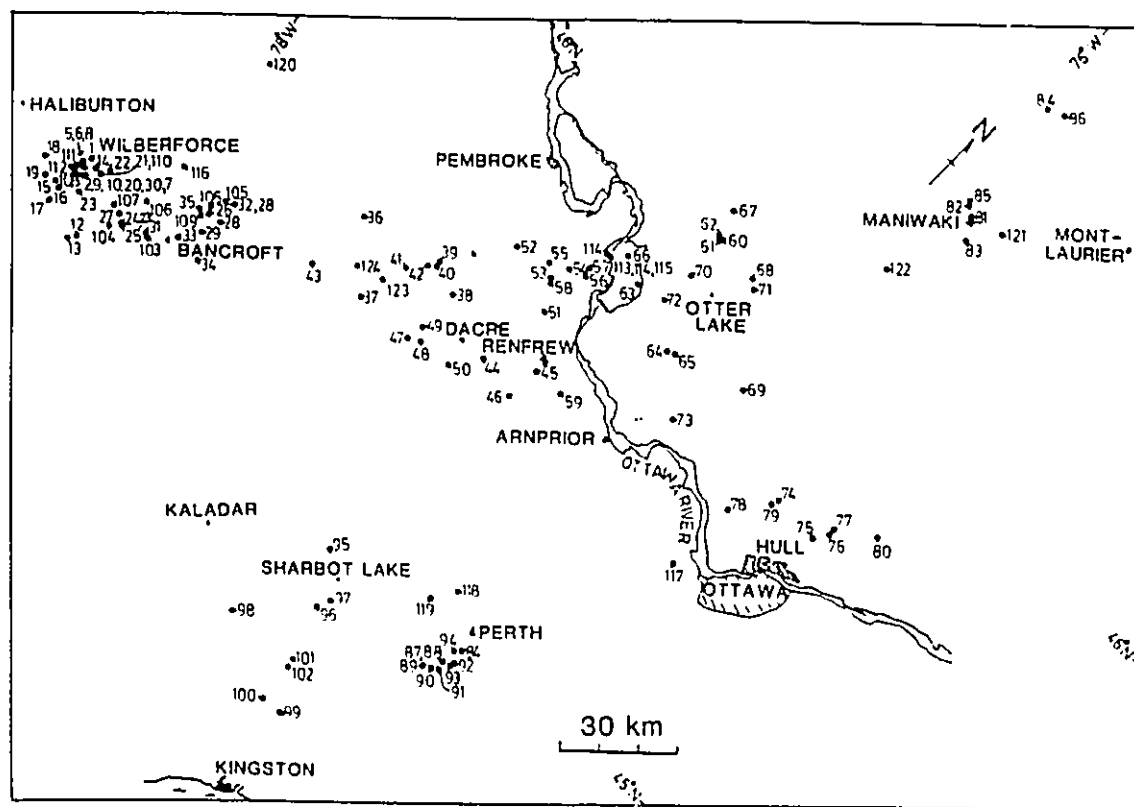


Figure 1.1 Sketch map of the Grenville Province and bordering areas. Subdivisions : EGP = Eastern Grenville Province; BCS = Baie Comeau Segment; GFTZ = Grenville Front Tectonic Zone; CGB = Central Gneiss Belt; CGT = Central Granulite Terrane; CMB = Central Metasedimentary Belt (CMB), (from Moore 1986, Fig. 1), and HA = Humber Allochthon.



1. Harcourt Mo skarn	42. Turner's Island apatite vein	84. Highway skarn
2. Halo U-Mo pegmatite/skarn	43. Liedke Mo skarn/vein	85. Maniwaki Mo skarn/vein
3. Field trip	44. Dugeon U pegmatite	86. Duver U pegmatite
4. Monti-Launer field trip	45. Belanger's Corner skarn	87. Otty Lake apatite vein
5. Desmond Mo-U skarn	46. Mountain Chute U pegmatite/skarn	88. Old Anthony mica skarn
6. Wilberforce Mo skarn	47. Sparn Mo-U pegmatite/skarn	89. Star Hill apatite skarn/vein
7. Joiner Mo-U skarn/vein	48. Sunset Mo skarn	90. Mica skarn
8. American Molybdenites Mo skarn	49. H.A. Legris U pegmatite	91. Silver Queen apatite skarn/vein
9. Cardiff South U skarn/vein	50. Hunt Mo pegmatite/skarn	92. Pentrite pegmatite
10. Cardiff West U occurrence	51. Field trip	93. Roger's apatite skarn/vein
11. Tory Hill field trip	52. Cole Mo skarn	94. McLaren apatite skarn/vein
12. Dyno Turn road cut pegmatite	53. Woornke No. 4 vein	95. Avery Mo skarn
13. Elmridge Mines skarn	54. Ross apatite vein	96. Eagle Lake apatite skarn/vein
14. Richardson (Fission) U vein	55. Rose Mo pegmatite	97. St. George apatite vein
15. Saranac zircon pegmatite/skarn	56. Elliot's apatite vein	98. Chilsom Mo skarn
16. Saranac East pegmatite	57. Vaughan U pegmatite/vein	99. Lacey mica skarn
17. Rare-Earth U pegmatite	58. Cobden apatite vein	100. Freeborn mica skarn
18. G. Padwell Mo skarn	59. Dempsey's U vein	101. Kingston Beresford mica skarn
19. Millar's apatite skarn/vein	60. Matie apatite-U vein	102. Richardson feldspar pegmatite
20. Cardiff A zone skarn/vein	61. Camo U pegmatite/skarn/vein	103. Greyhawk U pegmatite
21. Tripp & Montgomery U vein	62. Thorntale skarn, Huddersfield U	104. Bircroft U pegmatite
22. Clark Kuonle pegmatite/skarn	63. Dunraven U pegmatite	105. Genesee No. 2 pegmatite
23. Kemp Th. U skarn	64. Kirkham Mo pegmatite/skarn/vein	106. Bapile Lake skarn
24. Howard-Kerr U pegmatite/skarn	65. Quebec Metals U pegmatite/skarn	107. Croft U pegmatite
25. Lockwood U skarn	66. Calumet U skarn/vein	108. Armac Mo pegmatite/skarn/vein
26. McDonald feldspar pegmatite	67. Squaw Lake Mo skarn/vein	109. McCormack feldspar pegmatite
27. Silver Crater skarn/vein	68. Brady Mo skarn	110. Road outcrop
28. Quirk U pegmatite/skarn	69. Bain Mo-U pegmatite/skarn/vein	111. Cockle Lake U skarn
29. South State U skarn	70. Utchfield Mo skarn/vein	112. Essonville-Wilberforce U skarn
30. Cardiff North Zone skarn vein	71. Clapham Mo skarn	113. Barrage Rocher-Fendu U skarn/vein
31. Madawaska U pegmatite	72. Lawless Lake U skarn/vein	114. Sullivan Island carbonatite
32. Normingo U skarn	73. Moss Mo pegmatite	115. Calumet Contact U skarn/vein
33. Eagles Nest vein	74. Dacey apatite skarn/vein	116. Maynooth pegmatite
34. Urban Quebec U pegmatite/skarn	75. Phosphate Queen apatite skarn/vein	117. South March feldspar pegmatite
35. Hybla skarn	76. Jackson-Rae apatite vein	118. Perth feldspar pegmatite
36. Rockingham U pegmatite/skarn	77. Blackburn apatite vein	119. Kirkham Mo-U pegmatite
37. Jamieson Mo skarn/vein	78. Chaput-Payne Mo skarn/vein	120. Cornet quartz pegmatite
38. Gratton Twp. U pegmatite/skarn	79. Vavasour apatite skarn/vein	121. Acme Mo pegmatite
39. Meany apatite vein	80. Emerald apatite skarn/vein	122. Blue Sea feldspar pegmatite
40. Smart apatite skarn/vein	81. McShaffrey U pegmatite	123. Road outcrop
41. Opoongo U pegmatite/skarn	82. Cligan U skarn	124. Wall Gem Be pegmatite
	83. Opicawa U pegmatite	125. Field Trip
		126. New Armstrong pegmatite
		127. Kermac-Chibougamau U pegmatite

Figure 1.2 Pegmatites, skarns, and veins examined by the writer within the southwestern Grenville Province. Numbers denoted as field trips are not located on the map (3, 4, and 51).

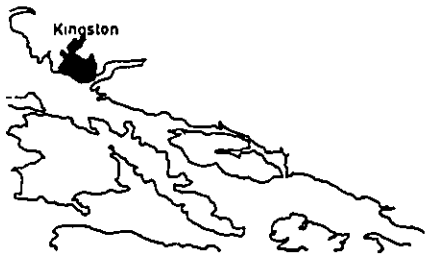
Figure 1.3 Regional compilation of uraniferous and molybdeniferous pegmatites, skarns, and fluorite-apatite-calcite veins in the southwestern Grenville Province (see pocket in back).

Haliburton

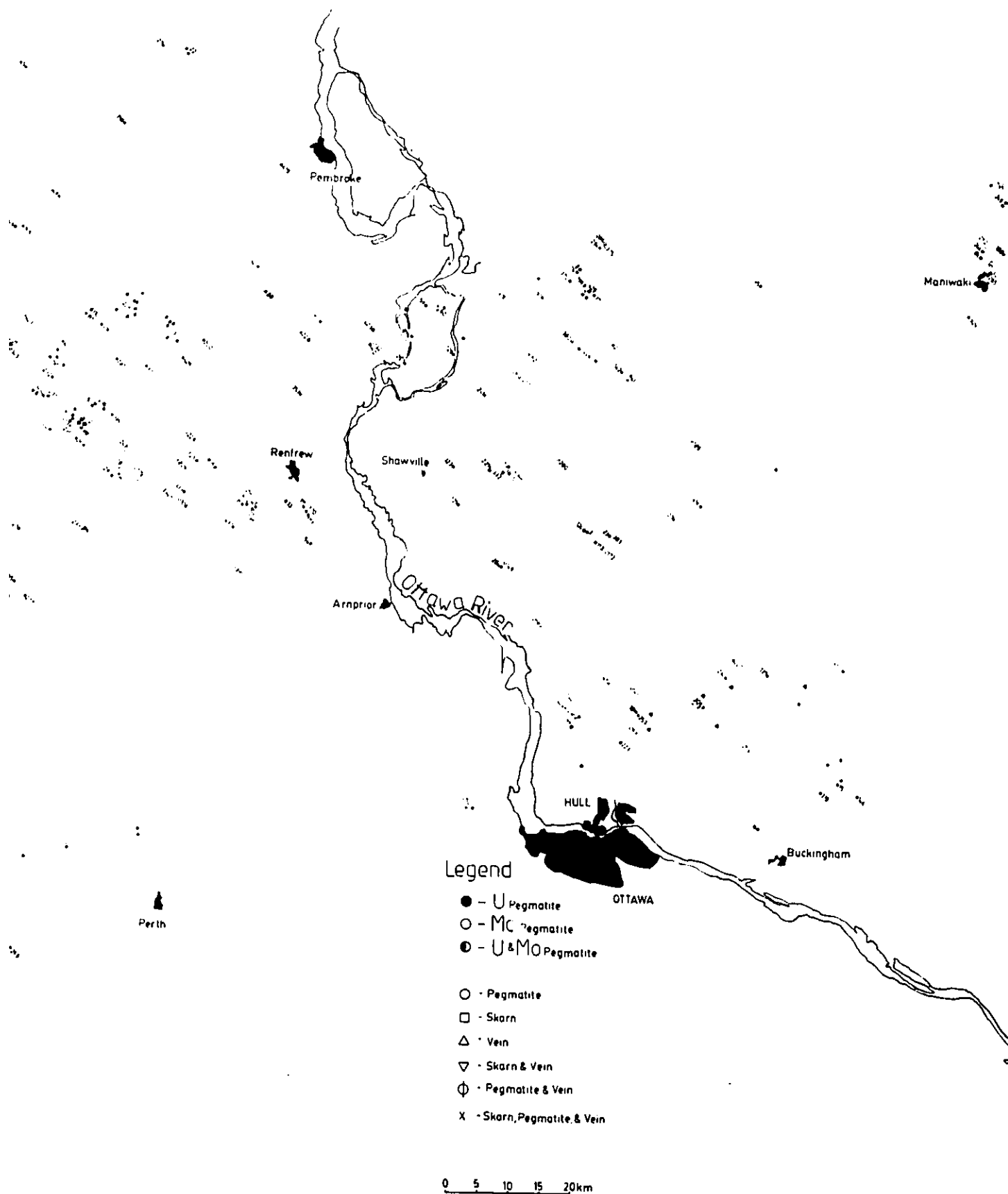
Barry's Bay

Bancroft

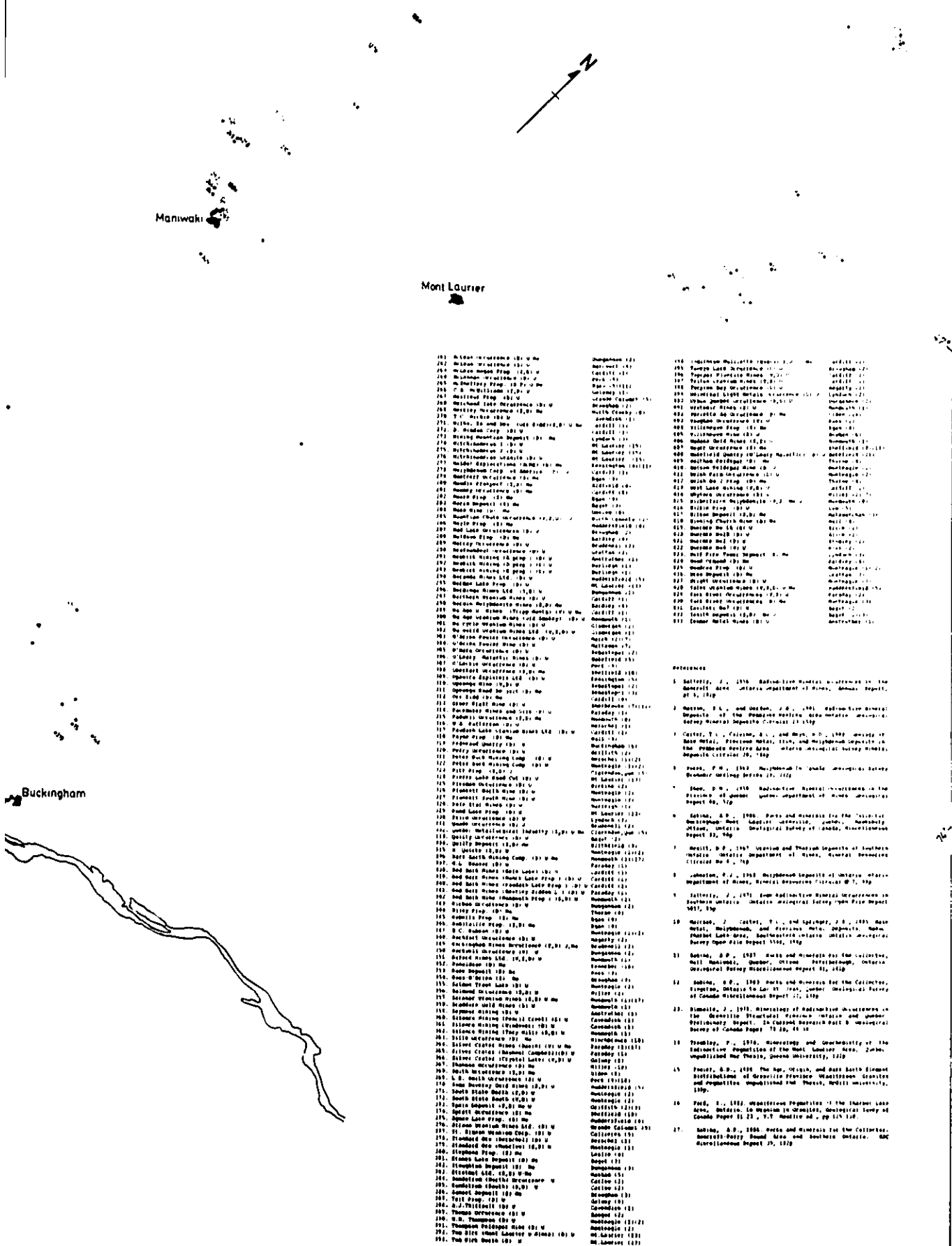
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Location Map of Uranium and Molybdenum Pegmatite, Skarn, and Vein Deposits of the southwest Grenville Province



The southwest Grenville Province



Molybdenum was mined during the First World War at numerous small deposits. The largest was the Moss Mine near Quyon, Quebec (Vokes, 1963). The Moss Mo Mine is not typical of most of the Mo deposits in the Grenville particularly since all others are hosted in skarns (Hunt, Spain, Bain, and Chislom deposits), skarnoid rocks (American Molybdenites, Kirkham, and Bain, and Spain deposits), and apatite-calcite veins (Joiner, and Kirkham) (Eardley-Wilmot, 1925; Johnston, 1968; Karvinen, 1973; Carter et al., 1980).

K-feldspar was mined from the large zoned pegmatites during the 1920's, and 30's for potash although the very large Back feldspar mine near Buckingham, Quebec operated until 1974 (D.D. Hogarth, personal communication). These deposits have been described in detail by de Schmid (1916), Spence (1930), Hewitt (1967), and Storey and Vos (1981b).

Phlogopite was mined from the skarn deposits and the vein deposits in the late 1910's and 1920's (de Schmid, 1912, Spence, 1929; Hoadley, 1960; Storey and Vos, 1981b) although the Vavasour mica deposit was operated until 1964 (D.D. Hogarth, personal communication).

1.1.4 Previous work

There has been considerable work done on all types and styles of uranium and molybdenum mineralization in the Grenville Province, but few detailed geologic, mineralogic, and geochemical studies have been carried out in recent years. Several compilation studies have, however, contributed significantly to the understanding of the deposits.

Satterly (1957) and Hewitt (1967) have suggested that the fluids related to the pegmatite were responsible for the formation of the skarns and veins. This hypothesis was shared by Currie (1951), Nishimori et al. (1977), Masson and Gordon (1981), and Lentz (1989). Karvinen (1973) suggested that the pegmatites were unrelated to the Mo-bearing skarns and vein deposits and instead proposed a metamorphic-hydrothermal model for their formation. Satterly (1957) noted that the Silver

Crater biotite-hornblende-apatite-calcite vein or metasomatically altered marble deposit was mineralogically similar to carbonatites. Heinrich (1966) noted the similarities of these fluorite-apatite-calcite veins with carbonatites but conceded with the evidence for an origin related to the skarns and pegmatites and called them carbonic deposits to exemplify their different origin. The Silver Crater deposit was classified as a carbonatite (Robertson, 1978, 1981). The apatite-calcite veins have also been interpreted as carbonatites (Lumbers, personal communication; Mungall, 1989) because in a few areas of the Grenville the veins are not visibly associated with pegmatites and skarns. Masson and Gordon (1981) have described the fenite-like pyroxene alteration mantling these veins which has been interpreted as fenites by Lumbers (1988) and Mungall (1989). Lentz (1989) has suggested that the Ca pyroxene is a result of calcium and magnesium metasomatism from a chemically-modified hydrothermal pegmatite-derived fluids as a result of skarn formation in the marbles. This hypothesis explains the spatial distribution, the temporal relationship, and radioactive nature of these deposits. The enrichment of both uranium and thorium, in similar proportions [Th/U] within the pegmatites, skarns, and veins suggests that uranium was mobilized in the tetravalent (U^{4+}) state at the magmatic stage.

Apatite deposits throughout the Grenville Province were first studied in detail by de Schmid (1912) and Spence (1920). de Schmid (1912) suggested that the apatite-calcite deposits represented pegmatitic segregations associated with mafic (Ca pyroxene-phlogopite-scapolite-plagioclase-titanite) intrusive rocks. A Ca pyroxene-rich rock, referred to by later researchers as clinopyroxenite, was believed to be intrusive because it commonly had sharp boundaries with the host rock gneisses, and the fact that the clinopyroxenite had no fabric suggested a post-Grenville origin. Landes (1938) studied

these deposits (Perth-Kingston and Gatineau-Buckingham Area) and concluded that the granite pegmatites were the origin of the hydrothermal fluids which interacted with marbles to produce apatite-calcite veins by a process of contact metamorphism. Currie (1951) suggested that the close spatial relationship of the pegmatites, skarns, and veins in the Perth area indicated a magmatic-hydrothermal origin. Rowe (1952) concluded that the Richardson (Fission) uranium-bearing, fluorite-apatite-calcite deposit was formed by high temperature hydrothermal fluids focussed along a large fracture system which was supported by Guillet (1964). Satterly (1957) proposed a magmatic-hydrothermal origin for the radioactive skarns and apatite-calcite veins because of their relationship to radioactive pegmatite bodies and their relative disposition within the Grenville gneisses. Shaw (1958) and Shaw et al. (1963) noted the radioactive-element and association between the pegmatites, skarns, and veins within the Otter Lake - Maniwaki area of Quebec and decided the skarn and vein deposits were a metamorphic phenomena because the mineralogy was similar to the host rocks; the pegmatites were thought to be of anatectic origin. Lafontaine (1980) also proposed a metamorphic origin on similar grounds. Storey and Vos (1981) distinguish between apatite-calcite veins with a pegmatite association and apatite-bearing marble which are described in some Grenville localities (eg. Legris occurrence; Dacre, Ontario). Masson and Gordon (1981) favour an early epigenetic uranium mineralization and/or a synmetamorphic-hydrothermal model for the origin of the apatite-calcite veins although they emphasize the spatial relationship between the granites and the uranium mineralization.

The molybdenum skarns were studied by Wilson (1924) and based on geologic association were assigned a magmatic-hydrothermal origin. Eardley-Wilmot (1925) also suggested a magmatic origin for these deposits. At the Spain Mo-U deposit, Vokes

(1963) noted that an unmineralized granite pegmatite intruded into a Mo-bearing Ca pyroxene-K-feldspar pegmatite. Therefore, he suggested that the pegmatite dikes were unrelated to the Mo skarns. Similar reasoning was used by Karvinen (1973) in an extensive study of the Mo skarn deposits in the Grenville Province. He proposed a metamorphic-hydrothermal origin for these deposits related to devolatilization of the supracrustal gneisses. Many of the deposits included in that study (Joiner and Spain deposits) are apatite-calcite veins hosted in Ca pyroxene-feldspar gneisses. Karvinen (1973) did not realize that these were veins and that the "mineralized pegmatite" are actually Mo-bearing calcite-Ca pyroxene-K-feldspar vein associated with the skarn. Carter et al. (1979) compiled information on the Mo deposits in Ontario and concurred with the findings of Karvinen (1973). Kreczmer (1974) and Salvi (1987) proposed a magmatic-hydrothermal model for the Hunt Mo skarn and granite, Zenith Mo-U skarn and pegmatite deposit.

The uranium- and thorium-bearing skarns have been investigated by numerous researchers. Satterly (1957) examined, in considerable detail, all known deposits of the Bancroft area and found considerable evidence for a magmatic-hydrothermal origin for the uranium (molybdenum) skarns and veins. Hewitt (1967) supported Satterly's petrogenetic model. Shaw (1958) and Shaw et al. (1963) documented a similar petrogenetic relationship to the pegmatites but described them as a metamorphic-hydrothermal phenomena. Lang et al. (1962) studied the deposits and supported a magmatic-hydrothermal origin for their formation. Nishimori et al. (1978) examined these uranium and thorium deposits and found the deposits are most consistent with a magmatic-hydrothermal origin related to the radioactive granite pegmatites. Masson and Gordon (1981) have suggested that these radioactive skarns have formed by metamorphic-hydrothermal fluids in some cases and by interaction with pegmatites where the association is most

obvious. Haynes (1986) has suggested a magmatic-hydrothermal origin for the radioactive skarn (tactites) associated with pegmatites.

A further complication is the confusion concerning the titanite-phlogopite-scapolite-bearing clinopyroxenites in the Grenville Province. These units are commonly regional in extent and possibly represent a metamorphosed impure siliceous dolomite as proposed by van de Kamp (1968). It is possible that primary apatite may be associated with the clinopyroxenite and associated marble (Storey and Vos, 1981b; Dupuy, 1992). This apatite could be metasomatically scavenged during magmatic fluid (not just pegmatite) infiltration and interaction resulting in the coarse-grained, vein-style alteration which is typical of the large apatite deposits.

Unfortunately, many of the petrogenetic studies of these deposits were done in isolation of other studies hence all the information present was not available to the researchers. The significance of the granitic pegmatites to the petrogenesis of the skarns and fluorite-apatite-calcite veins has warranted a more detailed examination of their petrogenesis (Chapter 2). The re-examination of the pegmatites and research on the petrogenesis of the uranium- and molybdenum-bearing skarns, and veins has resulted in the development by the author of a more coherent model for the origin of all these deposits which adequately explains their disposition, spatial relationships, age, radioelement and molybdenum association, and mineralogical and chemical similarity (Figure 1.4).

1.1.5 World-wide occurrences of phlogopite skarn and apatite veins

Although the U-, Th-, and Mo-bearing phlogopite-, albite (or scapolite)- Ca pyroxene skarns, and biotite-Ca pyroxene-amphibole-fluorite-apatite-calcite veins may seem to be a very restricted style of mineral occurrence, in fact they are not. In Canada, Ca pyroxene is associated with phlogopite and calcite both in veins and skarns near Lake Harbour, Baffin

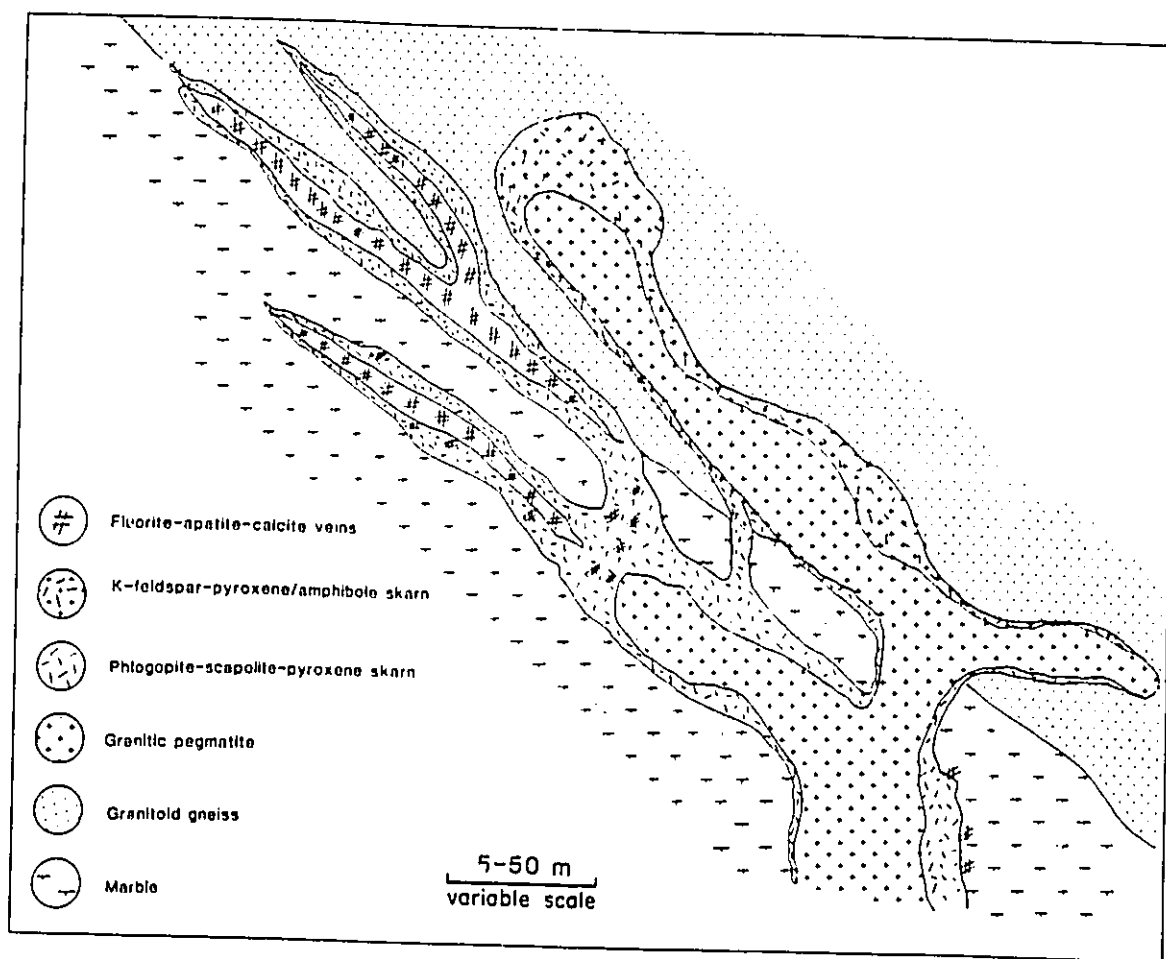


Figure 1.4 Schematic diagram of the spatial relationship between pegmatites, skarns, and veins in the Central Metasedimentary Belt of the southwestern Grenville Province.

Island. Scapolite, tremolite, and titanite are associated with Ca pyroxene in the skarns. Compared to the Grenville suite, the rocks are depleted in iron, being grey to white but the mineral assemblage is similar (Davison, 1959; D.D. Hogarth, personal communication). The best known of these deposits occur in the south-central U.S.S.R were very large phlogopite and apatite occurrences have been mined west of Lake Baikal (Hogarth, 1970). Korzhinskii (1947) proposed that the apatite and phlogopite occurrences were derived by pegmatite-dolomitic marble interactions. Guliy (1989) has described both apatite-silicate and apatite-carbonate deposits from Precambrian metamorphic rocks of the Aldan crystalline shield in southern Yakutia, U.S.S.R.. These deposits were interpreted as meta-evaporite deposits originally dominated by impure cherty dolomite, which resulted in a metamorphic mineralogy similar to the Grenville clinopyroxenites ("metamorphic pyroxenites") as well as the skarns. There are numerous U-Th skarn and apatite-bearing veins in southeastern Madagascar which were mined for apatite and phlogopite at the same time as those here in Canada. However, the grade of material and the traditional wages made the Madagascar deposits more viable. The host rocks are similar to those described as the clinopyroxenites or "metamorphic pyroxenites" which had endured granulite facies conditions (Moine et al., 1985). Although the mechanism for the formation of these deposits is related to metamorphic/metasomatic alteration, details of the metasomatic process are poorly described. Apatite-phlogopite deposits also occur in granulite grade rocks in southeastern India in the Ghats mobile belt and similar rocks in Sri Lanka. Rao and Narendra (1986) present geologic and chemical evidence to propose that these deposits were formed by interaction of marbles with hydrothermal emanations from pink granites. In Norway, apatite "dikes" with a similar mineral assemblage to those examined in this study (including abundant clinopyroxene, common titanite, less common monazite and xenotime) are formed

in amphibolite to granulite grade gneisses (Neumann, 1960). Granitic pegmatites have a similar disposition to the apatite veins but are thought to be younger because in one instance an apatite xenolith was identified within a pegmatite. However, the veins have never been seen cross cutting the pegmatites (Morton, 1960). Interestingly, carbonates are rare in the apatite veins and there is no marble in the vicinity of the deposits, although in the same area Dahlgren et al. (in prep) recognized boudinaged dolomite veins (Asen dolomite is 3 m wide) which are related to charnockite intrusions and granulites in the Bamle Shear Belt, South Norway. These veins may host apatite (Bugge, 1965) and are associated with albitization ($\pm$ scapolitization) of the wall rocks. Although these veins have been proposed to be of carbonatite origin (Heinrich, 1980), Dahlgren et al. (in prep) proposed that volatiles evolved from crystallization of deep level charnockite as responsible for the formation of the dolomite veins. Thorium-rich, apatite-bearing veins (< 0.3 m wide) with Ca pyroxene, carbonate, amphibole, feldspar, scapolite, and minor allanite occur at Nisikkatch Lake, northern Saskatchewan (Hogarth, 1957). There are numerous other occurrences of apatite-bearing hydrothermal veins in high grade gneiss terranes.

Magnetite veins occur northeast of Stormy Lake, along the Dysart-Glamorgan line (Adams and Barlow, 1910) although there association is unknown. The Kiruna magnetite-apatite deposits of Sweden have many similar characteristics to the fluorite-apatite-calcite veins in the Grenville Province. Actinolitic amphibole (minor chlorite) and albite (rare scapolite) form the selvages to these very large deposits (Parák, 1985). As with the deposits examined in this study, Kiruna deposits were originally hypothesized to be of magmatic-intrusive origin although Parák (1985) has proposed a hydrothermal origin for these deposits based on alteration evidence. Hildebrand (1986) proposed that the Kiruna-type deposits in the Great

Bear Magmatic zone were derived from volatiles related to cogenetic subvolcanic plutons. The arguments presented for a hydrothermal origin for the fluorite-apatite-calcite veins related to pegmatite emplacement and skarn formation are not unequivocal but the cumulative evidence is compelling for a related origin.

1.2 Regional geological setting

1.2.1 Introduction

The Central Metasedimentary Belt (CMB) of the Grenville Province has been subdivided into several structural domains including the Bancroft Terrane, Elsevier Terrane, Frontenac Terrane and the Mont Laurier Terrane and is bounded to the northwest by Central Gneiss Belt (CGB) and to the southeast by the Central Granulite Terrane (CGT) (Figure 1.5). Tectonometamorphic subdivisions of the Grenville Province have been proposed by Rivers et al. (1989). The CMB is dominantly composed of a metamorphosed supracrustal succession of volcanic and sedimentary origin intruded by compositionally variable plutonic rocks throughout the Grenville Orogeny.

1.2.2 Geology and lithologies

The Wilberforce-Bancroft area has been mapped by Hewitt (1959) (Cardiff and Faraday Twp.), Armstrong and Gittins (1969) (Glamorgan and Monmouth Twp.), Bright (1980) (Eels Lake) and Bright (1983a, b) (Centre Lake), Hewitt (1955) (Monteagle and Carlow Twp.), Masson, (1982a and b) (Bancroft East and West). Breaks and Thivierge (1985) and Lumbers (1982) compiled and remapped most of the Bancroft-Renfrew area at 1:100 000 scale. The Otter Lake-Grand Calumet Island area was mapped by Shaw (1955) and Kretz (1957a,b, 1977).

Within the CMB, metavolcanic rocks range in composition from mafic (amphibolite) to felsic (quartz-feldspar gneisses). The metasedimentary rocks include metapelites, calc-silicate gneisses, amphibolites, quartzites, and marbles. It has been suggested that metamorphic pyroxenite was formed by the metamorphic (metasomatic) interaction of narrow marbles

(dolomitic) with hybrid granitic gneisses producing an assemblage consisting of Ca pyroxene, phlogopite, scapolite, plagioclase, apatite, and titanite (Satterly, 1956). Granitization and syenitization of Grenville gneisses has also been recognized particularly where para- and orthogneisses are transformed by potash metasomatism (Satterly, 1956; Kretz, 1977). Interestingly however, in Monmouth Township the partially to completely metasomatised quartz-feldspar gneisses, metapyroxenites, and amphibolites (Satterly, 1957) are associated with large scale zoned to unzoned granite pegmatites. However, Kretz (1977) has noted the presence of numerous pegmatites in the areas characterized by alkali metasomatism. The large extent of the metapyroxenites (clinopyroxenites) throughout the Grenville Province suggests primary origin (ie. metamorphosed siliceous dolomites), however their proximity to quartz-feldspar gneiss makes them more susceptible to further metasomatic transformation by numerous mechanisms.

Alkalic gneisses are located within the Bancroft terrane south of the Central Metasedimentary Belt Boundary Zone (CMBBZ) of Davidson (1986) but are located within the zone as it was defined earlier by Wynne-Edwards (1972). These rocks have received considerable attention in an attempt to discriminate between the alkalic igneous origin or the metasomatic origin involving supracrustal rocks and the marble (Floor, 1974).

The supracrustal gneisses have well developed fabrics within the high-grade portions of the Grenville Province. The well developed fabric (aligned minerals, gneissic texture, and schistosity) parallel the rock contacts many of which have been inferred to be lithologic contacts (S_0) particularly contacts with marbles (Kretz, 1977). It seems that many other marble contacts are indeed tectonic especially in the Bancroft area (Masson, 1982 a and b; Bright, 1983; van der Pluijm and

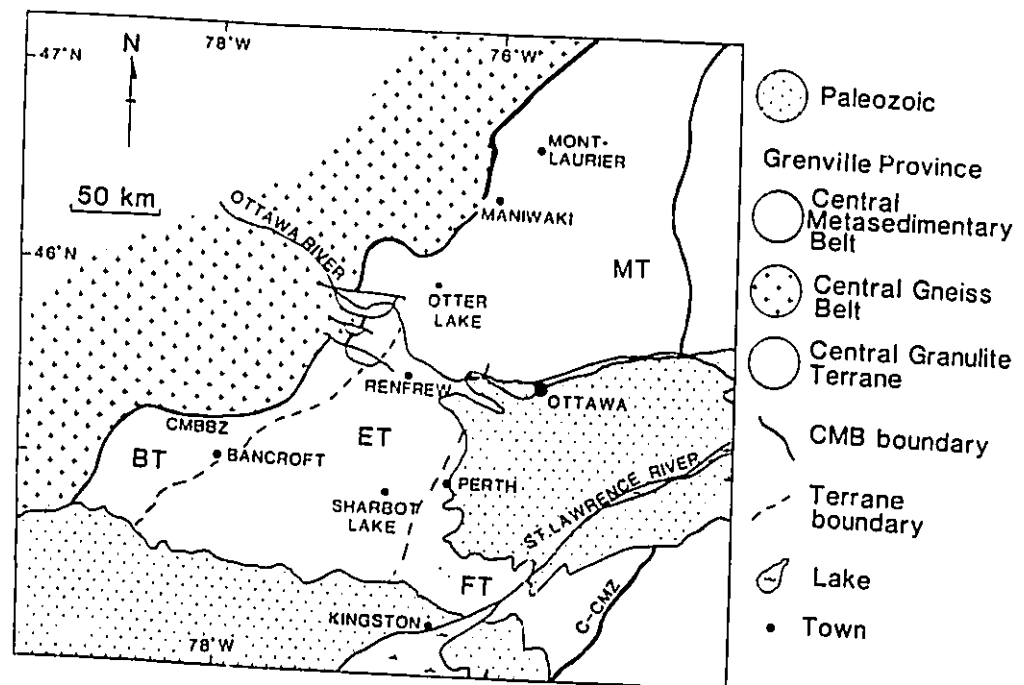


Figure 1.5 Distribution of terranes in the southwestern Grenville Province (from Davidson 1986, Fig. 1). CMBZ = Central Metasedimentary Belt Boundary Zone; C-CMZ = Colton-Carthage Mylonite Zone; BT = Bancroft Terrane; ET = Elzevier Terrane; FT = Frontenac Terrane; MT = Mont Laurier.

Carlson, 1989; Carlson et al., 1990). Several areas dominated by quartz-feldspar gneisses are similar to the rocks of the Ontario Gneiss Belt to the north hence may represent basement to the supracrustal rocks (Cardiff Dome, Cheddar Dome, etc.) (Wynne-Edwards, 1972) but no reliable evidence has yet substantiated this correlation (Davidson, 1986).

1.2.3 Plutonic rocks

The metaplutonic rocks range in composition from ultramafic rocks to gabbroic to granitic rocks and more rarely alkaline to peralkaline but are dominated by a suite of tonalitic intrusions particularly in the eastern Ontario (Lumbers, 1982). The regional studies cited above provide a general understanding of the sequence of intrusions within any particular area and details concerning their mineralogy and composition. Wu and Kerrich (1986) and Corriveau et al. (1990) examined the petrogenesis of many of the dominant intrusive rocks throughout the CMB and subdivided them into pre- and post-tectonic intrusive rocks, as well as, calc-alkaline, alkaline, and peralkaline types. They evaluated the petrogenesis of these granitoids using major-element compositional data and oxygen and strontium isotope evidence. More numerous detailed studies of these intrusive rocks illustrate the complex intrusive history in the CMB.

Most of the intrusive rocks are pre- to syn-metamorphic which is supported by the fabric development within these bodies. A more penetrative fabric and gneissosity is developed within the premetamorphic intrusive units, whereas syn- to late-metamorphic intrusions generally are massive to weakly foliated. The latest Grenvillian intrusive rocks are the granites and granite pegmatites which are commonly massive, with a gneissic fabric rarely developed along the marginal zones.

1.2.4 Structural history

The structural development in the Grenville Structural Province is complex. Rarely are F_1 folds preserved, isoclinal and intrafolial folds may represent the vestiges of the earliest phase of folding. The S_1 fabric is invariably parallel (transposed) to the S_0 , hence is commonly used in the absence of S_0 relationships. The development of F_2 folds refolds the S_1 (S_0) fabric resulting in open to tight (more rarely isoclinal) folds and local repetition of the stratigraphy and/or development of a dome and basin structure. The axial planes of these folds vary considerably in dip and plunge (undulatory) even on a local scale. A penetrative S_2 fabric is rarely developed axial planar to the F_2 folds but minor amounts of planar metamorphic minerals (biotite) may form parallel to F_2 axial plane. The metamorphism definitely spans the development of both F_1 and F_2 folds. F_3 folds are minor producing open folds which warp the axial plane of the F_2 folds.

The thrust zones developed at the base of the CMB define the base of the Central Metasedimentary Belt Boundary Zone (CMBBZ) (Davidson, 1986). This high strain zone seems to represent the basal decollement of the CMB and is probably cryptically present throughout the Grenville stratigraphy. The basal coarse clastic sequence defined by Lumbers (1982) may represent highly strained gneisses with boudins (Davidson, 1986). Kinematic indicators support crustal imbrication of the supracrustal rocks toward the northwest (Davidson, 1986; van der Pluijm and Carlson, 1989). In the Bancroft-Wilberforce area, numerous large scale structural breaks have been mapped as fault zones (Masson, 1982a and b) and thrusts and fault zones (Bright, 1983a, b). Some of the large scale fault zones have been used to subdivide the CMB into various terranes based on lithologic, structural, and metamorphic similarities. The Bancroft Terrane is defined as the northwestern most portion of the CMB bounded to the northwest by the CMBBZ and

to the south by the York River Shear Zone (McArthur Mills Line). The CMB extends, somewhat ambiguously, into Quebec (Davidson, 1986), whereas Wynne-Edwards (1972) has suggested that the northern boundary of the CMB was the McArthur's Mill Line. This zone extends into the Quebec segment of the Grenville up to Mont Laurier (Wynne-Edwards, 1972).

Late-tectonic structures are loci for the emplacement and disposition of the late-tectonic granitic pegmatites within the Grenville Province. The late stage development of shallow dipping normal faults along marble contacts in the Wilberforce area are the locus of intense shearing (Bright, 1980; van der Pluijm and Carlson, 1989; Carlson et al., 1990). In the Tory Hill, Cardiff and Bancroft areas similar relationships are found. The granite pegmatites commonly intrude the Grenville rocks along these high strain zones. The localization of these zones along the margins of the granitoid domes may explain the anomalous abundance of the granite pegmatites associated with these areas and the development of *lit par lit* gneisses (Evans, 1966). The localization of granitic melts along the late high strain zones which are undergoing extension late in the Grenville orogeny is compatible with their late tectonic nature (Fyson et al., 1979; Bedell, 1982; Habib, 1982). Intrusion of pegmatitic melts in these shear zones may explain the development of shearing and locally boudinaging of the pegmatites as was noted by Fyson et al. (1979) and Habib (1982). The pegmatites intrude the hanging walls of several of these late-stage shear zones. The competency of the host rocks may control the distribution of granite pegmatites in the Grenville Province. Bedell (1982) has suggested that the gabbro which hosts the Faraday uraniferous pegmatite deformed in a dilatant manner allowing the pegmatite to be emplaced.

Throughout the southwestern part of the Grenville Province, east to southeast trending normal faults disrupt the stratigraphy. In the Wilberforce area, Bright (1983a and b)

has noted the development of numerous late faults. In the Renfrew area, Lumbers (1982) has documented the faults responsible for the development of the Ottawa graben structure. In the Grand Calumet Island - Otter Lake area, Kretz (1980) suggested that these faults may be responsible for the exposure of lower metamorphic grade of the rocks in the Ottawa Valley.

1.2.5 Metamorphic history

The metamorphic grade of the rocks in the Grenville Province is variable from low upper greenschist grade (low) to amphibolite grade (medium) to granulite (high) (Figure 1.6). The Bancroft terrane is middle to upper amphibolite facies in contrast to the Elzevir terrane (greenschist-lower amphibolite facies) to the south and the upper amphibolite to granulite facies gneisses of the Central Gneiss Belt (CGB) to the north. Metamorphic distinctions between the Bancroft and Elzevir terranes become more obscure near Flower Station (Moore and Thompson, 1980) where metasedimentary rocks in the Flinton Group achieve upper amphibolite grades. The metamorphic assemblages in the Otter Lake area are variable from upper amphibolite facies to (locally) granulite facies (Kretz, 1977). In general, it has been shown that peak metamorphism was achieved during F_1 folding and persisted through F_2 and F_3 folding. A more detailed account of the metamorphic geology is reviewed with the petrogenesis of the skarns in Chapter 3.

1.2.6 Cardiff-Monmouth area

This area has numerous deposits of uranium, thorium, molybdenum, REE, apatite, and fluorite which made this area particularly key to this research project. Figure 1.7 represents a geological synopsis of the two maps produced by Bright (1980a and b). Many of the mineral occurrences were described by Satterly (1956) and Karvinen (1973). In this area, it can be seen that the pegmatites, and fluorite-apatite-calcite veins strike parallel to the regional fabric

although they may crosscut the dip fabric locally. The pegmatites are most common in the granitoid gneisses (orthogneisses) and the highest grade U pegmatites occur within the paragneisses. The smaller clinopyroxenite units are grouped with the marbles where they are closely associated with marble or with paragneisses. The Cardiff fluorite deposits are concordant to discordant fluorite-apatite-calcite veins hosted predominantly in hanging-wall granitoid gneisses above an eastward-dipping (30° to 40°) graphite-bearing, diopside marble (Figure 1.7). The marble-gneiss contact is the locus of intense shearing which produces a cryptocrystalline carbonate mylonite which has evidence of extension (Carlson et al., 1990). The mylonite is intruded by pegmatites and replaced by skarns and fluorite-apatite-calcite veins which are in turn mylonitized.

1.2.7 Dacre area

There are several deposits in the vicinity of Dacre of which the Hunt Deposit (#50) has the best exposure and is well known. The Spain U-Mo skarn, pegmatite (#47), Sunset Mo skarn (#48), Legris U pegmatite (# 49) and Dudgeon radioactive pegmatite (#44; just east of map south of highway 132) were also examined. The Lepine Mo skarn, Maloney Mo skarn, Charron Mo skarn, Guiney Mo skarn, Ross-O'Brien Mo skarn, Kiley Mo pegmatite and Lafleur's Lake Mo skarn are a few of the other occurrences (Carter et al., 1980) in the area. Figure 1.8 is a summary geological map (after Lumbers 1982) of the area illustrating the regional distribution of these occurrences close to the marbles. Although the occurrences are dominantly skarns and pegmatites, numerous small crosscutting veins may be found along roadcuts which may be related to these deposits.

1.2.8 Otter Lake - Kazabazua area

The Yates uranium deposits (# 60, 61, 62) are located west of Sandy Creek which is north of Otter Lake, Quebec. The good

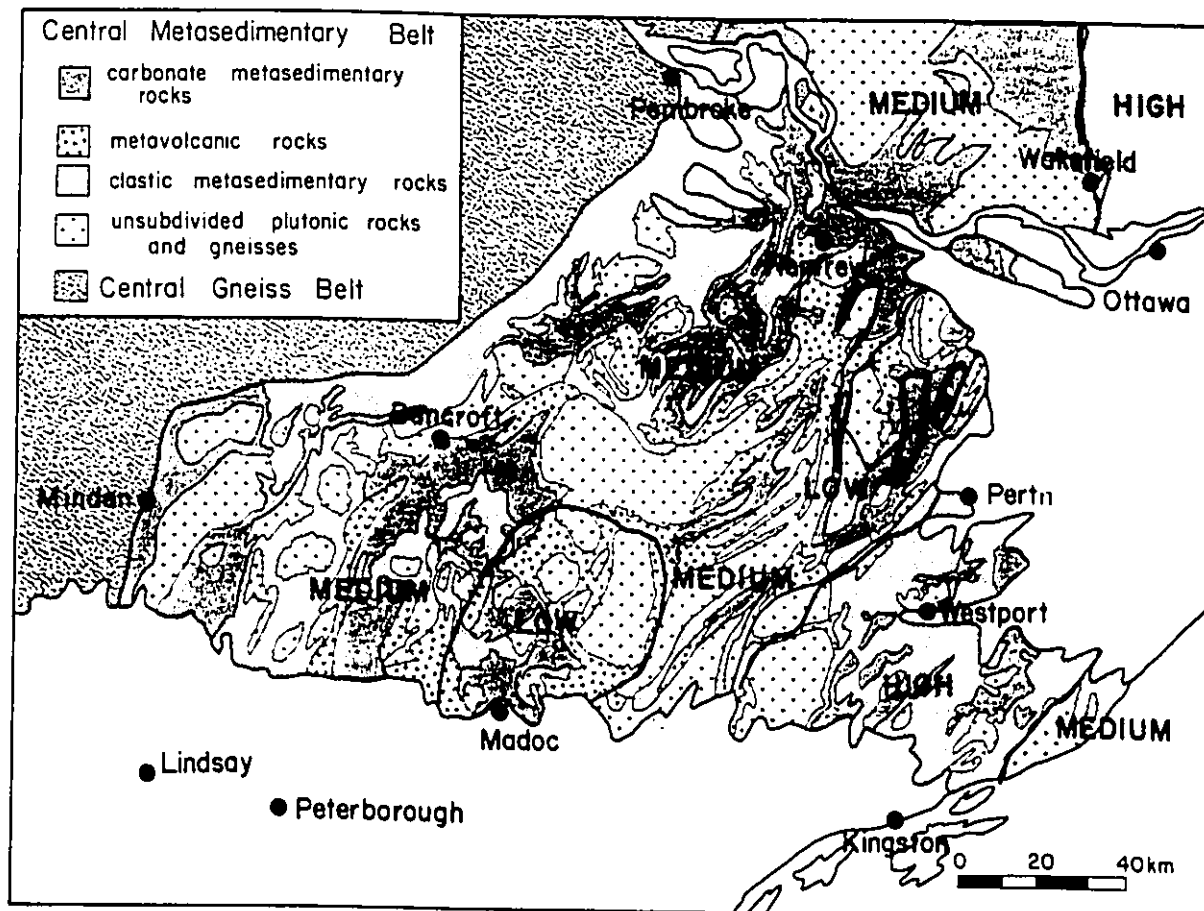


Figure 1.6 Generalized geology map of the Central Metasedimentary Belt of the southwest Grenville Province of Ontario and Quebec (after Easton et al., 1986). WHITE = Paleozoic. Low (greenschist), medium (amphibolite), and high (granulite) refer to metamorphic grade. Many generalization made by original author are inaccurate.

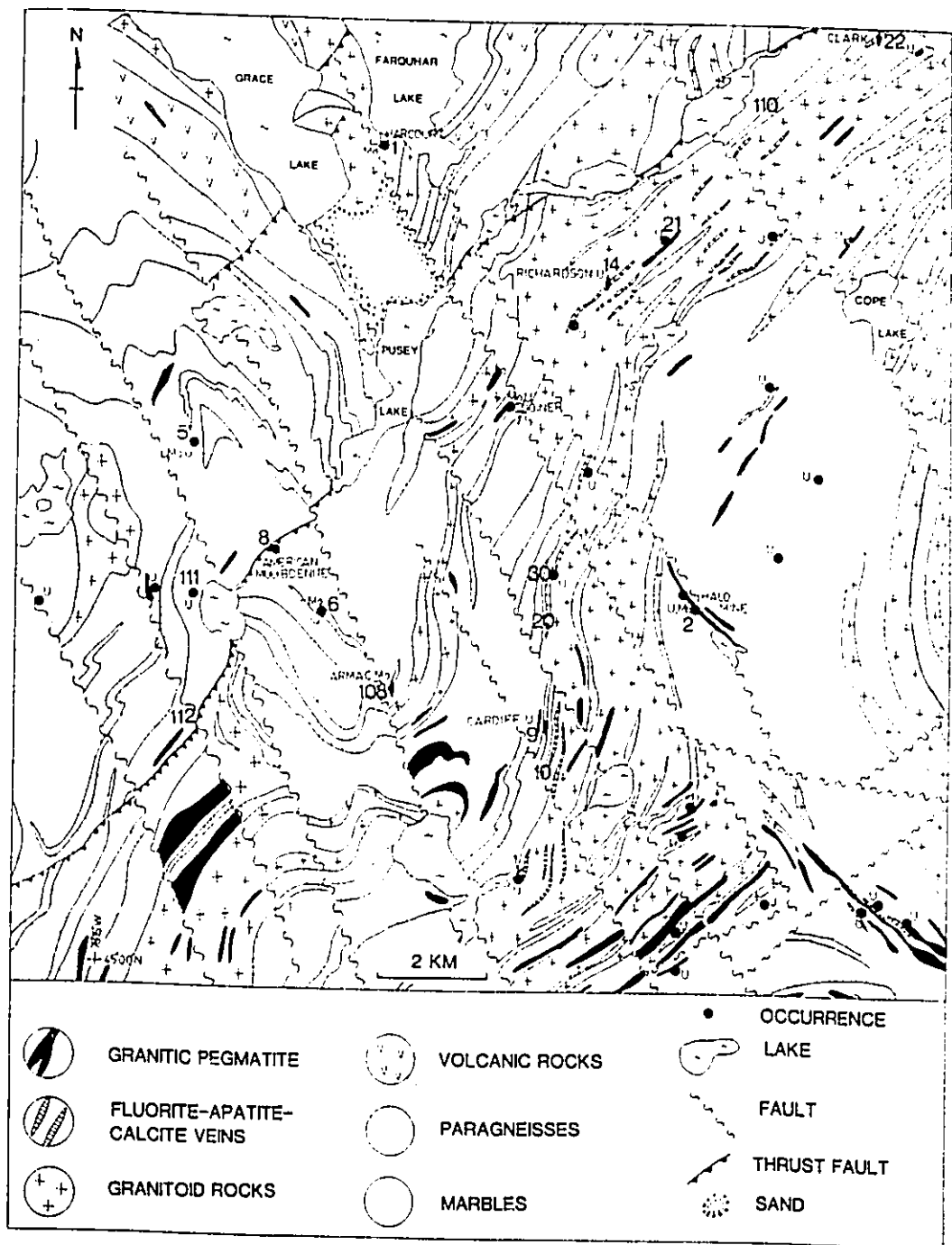


Figure 1.7 General geology map of the Wilberforce area (Cardiff and Monmouth Townships) of Ontario (from Bright 1980a and b). Deposits 1 - Harcourt Mo skarn; 2 - Halo U-Mo pegmatite; 5 Desmond U-Mo skarn; 6 - Mo-U skarn; 7 - Joiner Mo-U vein; 8 - American Molybdenites Mo skarn; 9, 20, 30 - Cardiff U-Mo pegmatite, skarn, and vein; 10 - Liscombe vein; 14 - Richardson U vein; 21 - Tripp U vein; 22 - Clark skarn, pegmatite; 108 - Acmac Mo skarn, pegmatite; 111 - Cockle Lake U skarn, pegmatite; 112 - Road U skarn.

exposure of the Yates deposits (Camp I and II) and their similarity with other uranium deposits in the Grenville Province made them particularly amenable to further study. Kretz (1957, 1977) studied the regional geology of this part of Quebec (Figure 1.9) while Shaw (1958) examined the Yates and other uranium deposits of western Quebec.

1.2.9 Geochronologic considerations

The locally discordant nature of the U-Mo granitic pegmatites, skarns, and veins and the lack of a penetrative metamorphic fabric strongly suggests a late- to post-tectonic origin for these deposits. The development of a penetrative fabric (mylonite or shear) occurs locally along the margins of some granitic pegmatites in the Bancroft area (Hanmer and van Breeman, 1985; Fyson et al., 1979; Habib, 1982; Masson and Gordon, 1981) indicates that deformation continued after emplacement of the granite pegmatites along normal faults which are interpreted as reactivated thrust faults (van der Pluijm and Carlson, 1989). The development of a mylonite fabric is also found in skarns (Shaw, 1958; Guillet, 1964; Masson and Gordon, 1981), and veins (Satterly, 1956; Rowe, 1958; Shaw, 1958; Lafontaine, 1979; Masson and Gordon, 1981; Storey and Vos, 1981). Mylonitic fabric indicates continued deformation well after the main Grenville metamorphic event during a period of crustal extension (Carlson et al., 1990). The granitic pegmatites were emplaced within and above these structurally active zones.

Any discussion of radiogenic isotopic dating of the Grenville pegmatites, skarns, and veins should be considered within the context of the radiogenic isotopic dating of other rocks in the Grenville Province in order to facilitate a comparison of age relationships and field observations. Radiogenic isotopic dates from the Grenville Province are compiled and interpreted by Easton (1986). Each of the isotopic dating methods used has different susceptibility to being reset (ie. loss of

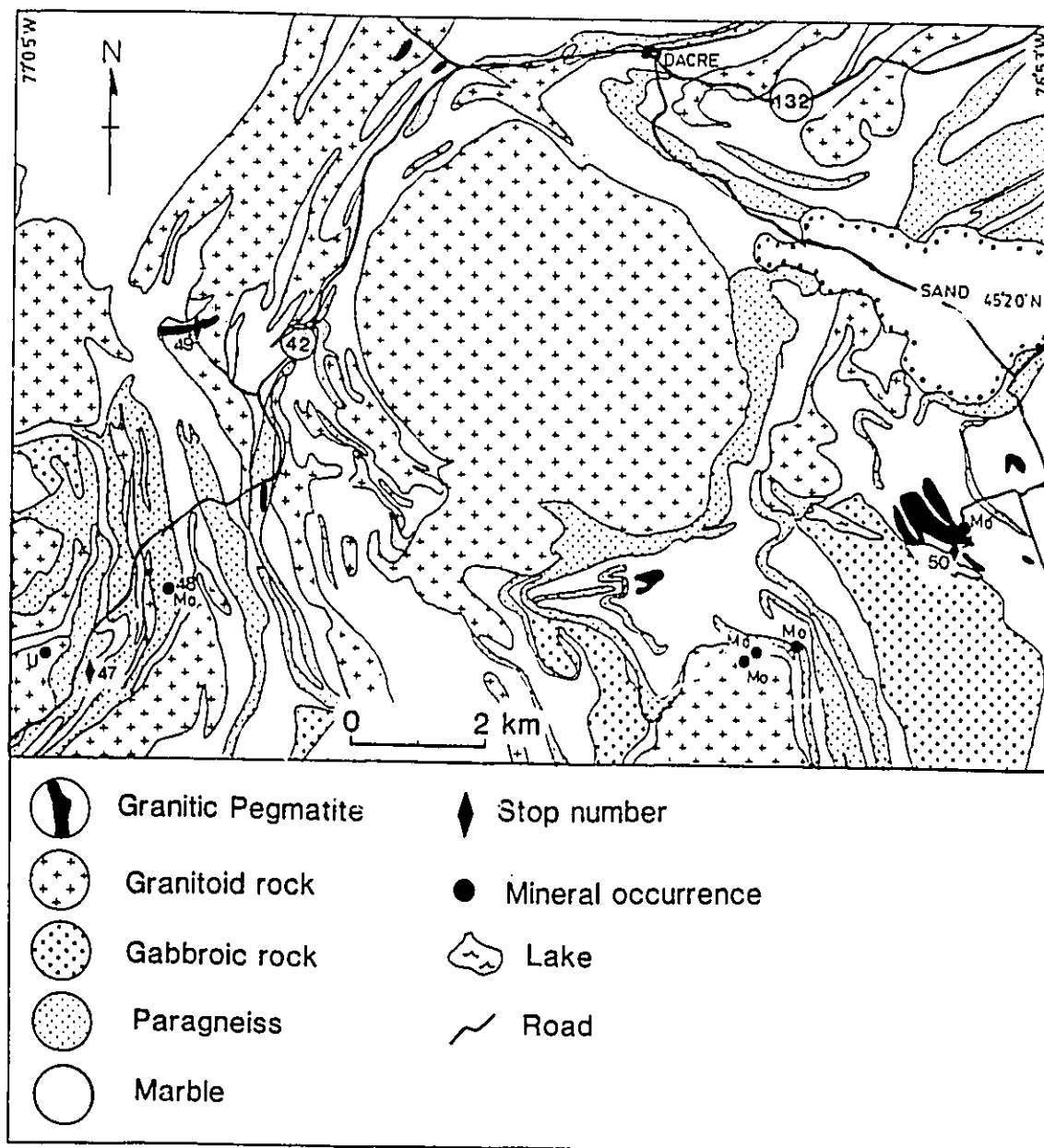


Figure 1.8 General geology map of the Dacre area west of Renfrew, Ontario (after Lumbers, 1982). The deposits are 47 Spain Mo-U pegmatite; 48 - Sunset Mo skarn; 49 - Legris U pegmatite; 50 - Hunt Mo skarn, pegmatite.

radiogenic daughters) which influences the interpretation of the age data (Easton, 1986).

With regard to the Bancroft area, where abundant data are available, Easton (1986) has indicated that there was a period of sedimentation and volcanism between 1280 and 1250 Ma (deposition of the Grenville Supergroup) followed by a metamorphic episode (Elzevirian orogeny) and plutonic emplacement of granodiorite, gabbro, diorite, and nepheline syenites) ending at approximately 1220 Ma. The Grenville Supracrustal package was metamorphosed at approximately 1170 to 1150 Ma. This event was followed by another period of plutonic activity between 1120 and 1100 Ma which reset all Rb/Sr (whole rock) systematics. This was followed by another period of post-tectonic felsic plutonic activity between 1090 and 1070 Ma (Corriveau et al. 1990) with the intervening period (1100 to 1090 Ma) being uplifted with the formation of the Flinton group metasedimentary package and further metamorphism (Ottawan Orogeny) of the Grenville Supergroup rocks. Pegmatites were intruded between 1060 and 1010 Ma, well after the main period of deformation and metamorphism. The greater spread of age data from pegmatites, skarns, and veins in Table 1.2 are interpreted to be a result of isotopic closure problems (daughter isotope migration) during slow cooling of the Grenville Province (Berger and York, 1981) and the presence of xenocrystic zircons. Grenville Orogenic cycle includes all of these events.

Radiogenic isotope dates have been compiled for mineralized pegmatites, skarns, and veins within the Central Metasedimentary Belt, as well as, the Baie Johan Beetz area uraniferous pegmatites (Eastern Quebec) (Table 1.2). The range in ages is in part due to the isotope systematics and technologic capabilities at the time the research was carried out. The concordia ages seem to be the most reliable although concordia ages derived from several different areas or inheritance of pre-existing zircons from the metamorphic rocks

Table 1.2 Summary of geochronologic data for pegmatites, skarns, and veins in the southwestern Grenville Province

(Ma)	Mineral	Place	Method	Reference
821	U on titanite in peg.	Mont Laurier	207/206 Pb	Rimsaite (1985)
849	biotite in pegmatite	Bancroft	K/Ar	Aldrich et al.(1958)
852	zircon in pegmatite	Mont Laurier	207/206 Pb	Rimsaite (1985)
879	biotite in pegmatite	Cardiff Twp.	K/Ar	Lowdon (1960)
905	biotite in skarn	Cardiff Twp.	K/Ar	Lowdon (1960)
912	perthite in pegmatite	Balmat	Rb/Sr (0.703)	Doe (1962)
915	biotite in granite	McArthur Mills	K/Ar	Lowdon (1960)
917	wr. pegmatite	Lac Montango	Rb/Sr	Fowler (1980)
920	biotite in vein	Fission mine	K/Ar	Aldrich et al.(1958)
924	wr. pegmatite	Lac Edmond	Rb/Sr	Fowler (1980)
925	bio. pegmatite	Monteagle twp.	K/Ar	Lowdon (1960)
928	wr. pegmatite	Mitchinamascus	Rb/Sr	Fowler (1980)
928	wr. granite	Turgeon	Rb/Sr	Fowler (1980)
938	wr. pegmatite	Mitchinamascus	Rb/Sr	Fowler (1980)
955	uraninite in peg.	Bicroft mine	ave. Pb	Lowdon (1960)
955	biotite in skarn/vein	Cardiff mine	K/Ar	Aldrich et al.(1958)
959	wr. pegmatite	Bancroft	Rb/Sr	Fowler (1980)
968	biotite in pegmatite	Bancroft	Rb/Sr	Aldrich et al.(1958)
971	U on titanite in peg.	Bancroft	207/206 Pb	Rimsaite (1981b)
975	thorianite in peg.	Mentor deposit	ave. Pb	Lowdon (1960)
976	zircon in pegmatite	Faraday mine	207/206 Pb	Rimsaite (1981a)
977	biotite in vein	Fission mine	Rb/Sr	Aldrich et al.(1958)
977	wr. granite	Guenette	Rb/Sr	Fowler (1980)
980	discordia pegmatite	Bancroft	U/Pb	Rimsaite (1981b)
980	U in skarn	Nu-Age deposit	207/206 Pb	Lowdon (1960)
983	zircon in pegmatite	Mont Laurier	207/206 Pb	Rimsaite (1985)
988	wr. aplite	Mitchinamascus	Rb/Sr	Fowler (1980)
990	U on feld. in peg.	B.Johan Beetz	207/206 Pb	Rimsaite (1981b)
990	thor. in pegmatite	Mentor deposit	207/206 Pb	Lowdon (1960)
992	U on monz. in peg.	B. Johan Beetz	207/206 Pb	Rimsaite (1981b)
992	zircon in pegmatite	Faraday mine	207/206 Pb	Rimsaite (1981a)
995	alt. uran. in peg.	Bancroft	207/206 Pb	Rimsaite (1981b)
995	monazite in peg.	B.Johan Beetz	207/206 Pb	Rimsaite (1981b)
997	uraninite in skarn	Cardiff mine	207/206 Pb	Aldrich et al.(1958)
1000	thor. in skarn	Camex deposit	ave. Pb	Lowdon (1960)
1000	uraninite in peg.	Bicroft mine	ave. Pb	Lowdon (1960)
1003	euxenite in peg.	Calabogie	207/206 Pb	Collins et al.(1954)
1005	uraninite in peg.	Bicroft mine	ave. Pb	Lowdon (1960)
1009	biotite in skarn/vein	Cardiff mine	Rb/Sr	Aldrich et al.(1958)
1010	phl. in pegmatite	Balmat, N.Y.	K/Ar	Doe (1962)
1011	zircon in peg.	Faraday mine	207/206 Pb	Rimsaite (1981a)
1013	zircon in peg.	Mont Laurier	207/206 Pb	Rimsaite (1985)
1016	uraninite in skarn	Wilberforce	207/206 Pb	Collins et al.(1954)
1019	zircon in pegmatite	Faraday mine	207/206 Pb	Rimsaite (1981a)
1020	uraninite in peg.	Faraday mine	207/206 Pb	Lowdon (1960)
1020	concordia pegmatite	Faraday mine	U/Pb	Rimsaite (1981a)
1021	zircon in pegmatite	Faraday mine	207/206 Pb	Rimsaite (1981a)
1025	uraninite in skarn	Nu-Age deposit	207/206 Pb	Lowdon (1960)
1029	biotite. in peg.	Faraday mine	K/Ar	Lowdon (1960)
1031	U on bio. in peg.	Mont Laurier	207/206 Pb	Rimsaite (1985)
1033	allanite in peg.	B.Johan Beetz	207/206 Pb	Rimsaite (1981b)
1034	uraninite in skarn	Wilberforce	207/206 Pb	Collins et al.(1954)
1040	thorianite in skarn	Normingo deposit	207/206 Pb	Lowdon (1960)
1040	uraninite in skarn	Cardiff mine	207/206 Pb	Lowdon (1960)
1045	uraninite in peg.	Faraday mine	ave. Pb	Lowdon (1960)
1052	uraninite in vein	Bancroft	207/206 Pb	Rimsaite (1981b)
1053	zircon in pegmatite	Mont Laurier	207/206 Pb	Rimsaite (1985)
1056	phlogopite in vein	Cardiff mine	K/Ar	Lowdon (1960)
1063	uraninite in vein	Fission mine	207/206 Pb	Aldrich et al.(1958)
1065	uraninite in peg.	Bicroft mine	ave. Pb	Lowdon (1960)
1068	uraninite in skarn	Wilberforce	207/206 Pb	Collins et al.(1954)
1072	thorite in skarn	Bancroft	207/206 Pb	Rimsaite (1981b)
1077	phlogopite in peg.	Balmat	Rb/Sr (0.703)	Doe (1962)
1079	muscovite in peg.	Balmat	Rb/Sr (0.703)	Doe (1962)
1085	phlogopite in skarn	Normingo deposit	207/206 Pb	Lowdon (1960)
1087	uraninite in skarn	Wilberforce	207/206 Pb	Collins et al.(1954)
1088	U on bio. in peg.	Bancroft	207/206 Pb	Rimsaite (1981b)
1090	uraninite in peg.	Faraday mine	207/206 Pb	Lowdon (1960)
1090	discordia peg.	Bancroft all samples	U/Pb	Rimsaite (1981b)
1130	K-feldspar in peg.	Balmat	Rb/Sr (0.703)	Doe (1962)
1192	K-feldspar in peg.	Balmat	Rb/Sr (0.703)	Doe (1962)
1197	U on feld. in peg.	Bancroft	207/206 Pb	Rimsaite (1981b)

or syn-tectonic intrusive rocks may be responsible for the unrealistic 1090 Ma upper intercept age (Rimsaite, 1981b). The 1020 Ma concordia age from the Faraday pegmatite (Madawaska Mines) seems very reasonable in light of other pegmatite dates. The recalculated $^{207}\text{Pb}/^{206}\text{Pb}$ ratios on uraniferous minerals also give reasonable age estimates.

The Rb/Sr whole-rock ages are younger than both the concordia and $^{207}\text{Pb}/^{206}\text{Pb}$ age data indicating that even whole-rock Rb/Sr systematics remain open to Sr until further cooling ($< 500^\circ\text{C}$) of the Grenville Province possibly due to high Rb content and low Sr content in the pegmatites and/or recrystallization (exsolution, ordering). The recalculated K/Ar ages from biotite and phlogopite in pegmatites and skarns (Easton, 1986) are commonly in agreement with the lower ages of these minerals in the Bancroft terrane of the Grenville Province. Thermochronologic $^{40}\text{Ar}/^{39}\text{Ar}$ cooling curves for the Grenville Province, as well as K-Ar dating indicate that cooling of the Central Metasedimentary Belt was considerably slow subsequent to the Ottawa Orogeny. Within the Bancroft terrane the $^{40}\text{Ar}/^{39}\text{Ar}$ dates from metamorphic hornblendes (closure temperature range of 550 to 500°C) retained ages of approximately 980 Ma whereas biotites retain an age of 920 to 930 Ma (closure temperature of 350°C) suggesting a prolonged period of thermal activity (slow uplift?) from the Ottawa Orogeny to post pegmatite emplacement. Further thermochronologic research by Mike Cosca (personal communication) confirmed these findings and concluded that the Grenville Province was probably uplifted very slowly. This indicates that the pegmatites were emplaced into a portion of the crust, which remained at lower to middle amphibolite facies conditions subsequent to the middle to upper amphibolite facies conditions imposed by the Ottawa orogeny (1100 to 1090 Ma).

The most reliable ages of pegmatites, skarns, and veins overlap with 19 samples yielding ages between 1010 to 1060 Ma (Table 1.2). These dates support late-tectonic pegmatite emplacement ages between 1060 and 1010 Ma which is 30 to 80 Ma after the Ottawa Orogeny but before considerable cooling of the Grenville supracrustal rocks.

1.3 Summary

The pegmatites, skarns, and veins have a long mining and exploration history, in particular, molybdenum mining during World War 1 and uranium mining in the late 1950's and again in the late 1970's.

There are several hypotheses for the petrogenesis of late-tectonic Grenville pegmatites including; (1) *in situ* anatexis of Grenville gneisses, (2) middle to lower crustal partial melting of Grenville gneisses and fractionation to emplacement level, (3) late fractionations during granite magmatism, and (4) hydrothermal replacements of Grenville gneisses.

There are two main hypotheses for the origin of Mo skarns including a metamorphic-metasomatic origin related to regional devolatilization and pegmatite-related metasomatic deposits. It is generally agreed to that the uraniferous skarns are related to the rare-metal granitic pegmatites although a syngenetic, evaporite-related origin has been proposed for the origin of silicated marbles (Haynes, 1986).

The petrogenesis of the fluorite-apatite-calcite veins is particularly controversial because of their similarity to carbonatites. However, metamorphic mobilization of carbonates during pegmatite hydrothermal activity has been generally accepted until recent years.

The lithotectonic, structural, and metamorphic evolution of the Grenville Province (Grenville Orogenic Cycle) is complex. There is considerable geologic and geochronologic evidence to suggest that the pegmatites were emplaced during late-tectonic denudation of the Grenville Province. Late-tectonic granitic pegmatites were emplaced within the vicinity and along late-

tectonic faults and, in some instances, were inturn sheared along their margins. The pegmatites, skarns, and veins are spatially related in many areas. A review of geochronologic data indicate overlapping ages, which lends furthur support for a cogenetic origin.

CHAPTER 2
PETROGENESIS OF GRANITIC PEGMATITES
IN THE SOUTHWESTERN GRENVILLE PROVINCE

2.1 Introduction

Uranium-, molybdenum, and rare-earth element (REE)-bearing granitic pegmatites (rare-metal pegmatites) occur throughout the Central Metasedimentary Belt of the Grenville Structural Province (Figure 1.2). Among these pegmatites are, in Ontario, the Faraday (U, Mo), Bicroft (U), Dyno (U), and Halo (U, Mo) pegmatites in the Bancroft area and the Richardson and Orser-Kraft (U) pegmatites near Perth. In Quebec, the most well known pegmatites are the Dunraven (U), and Struan (U) pegmatites on Grand Calumet Island and the Acme (Mo, U), and Blue Sea pegmatite near Maniwaki. In addition to U and Mo, some contain thorium, rare-earth elements (REE), and niobium. This chapter summarizes field, textural, mineralogical, chemical, and metallogenic characteristics of several pegmatite bodies with emphasis on the petrogenesis of uranium, thorium, and molybdenum, and REE mineralization. An increased understanding of pegmatite formation is essential in help resolve petrogenetic aspects of the skarns and fluorite-apatite-calcite veins.

2.2 Description of granitic pegmatites

2.2.1 Introduction

Numerous granitic pegmatite localities in the Grenville Province were examined (Figure 1.3) including several other localities (#129 to #135). This represents a very small proportion of the millions of pegmatites which occur within the southwestern Grenville Province. The geology of some of the pegmatites has been extensively described by Masson and

Gordon (1981), Storey and Vos (1981b), and Hewitt (1967); hence only a brief discussion is necessary.

Granitic pegmatites occur both as sills and dikes with respect to the predominant fabric and lithologic layering developed within the host rock. They range in size from small (10 centimetres wide) to very large (few 100 metres wide). One of the largest is the Faraday pegmatite swarm which is greater than 5 kilometers long and cumulatively greater than 500 metres wide in places. The dikes were evidently granitic melts intruded along structurally weak zones, particularly faults and shear zones bounding large competent domains resulting in a preferred orientation of many of the pegmatites within individual districts (Hewitt, 1967; Masson and Gordon, 1981; Storey and Vos, 1981b). Some pegmatites were formed during early stages of the Grenville Orogeny and as a result are highly deformed. In contrast, the late tectonic granitic pegmatites are relatively undeformed, and commonly intrude brittle zones within competent lithologies. This resulted in the emplacement of the larger granitic pegmatite dikes as was the case for the Faraday pegmatite, emplaced into a metagabbro (Bedell, 1982). Lumbers (1982) noted that the pegmatites occur in small swarms, and tend to follow late, open folds formed during the culmination of the Grenville deformation. The granitic pegmatite - host rock contact zones were commonly affected by syn- to post-emplacement shearing (mylonitization) (compatible with emplacement in structurally active zones). The shearing has been associated with further enrichment of uranium in the pegmatites contact zone (ie. Faraday) (Masson and Gordon, 1981; Habib, 1982).

The pegmatites are dominantly composed of quartz, K-feldspar, plagioclase, and a ferromagnesium phase (simple type) although reaction of the pegmatite with the host rock produces a complex variety of minerals including: pyroxene, amphibole, biotite, titanite, magnetite, sulphides, allanite, zircon, garnet, monazite, pyrochlore-group minerals and, of

course, the uranium and thorium phases (complex type) (Hewitt, 1967; Masson and Gordon, 1981; Storey and Vos, 1981).

2.2.2 Pegmatite textures

The granitic pegmatites occur as zoned and unzoned bodies. The zoned granite pegmatites occur only rarely in a few pegmatite districts, and have developed their zoning to various degrees, for example, the MacDonald pegmatite (Hybla field; Figure 2.1) and Wall Gem pegmatite (Quadeville field; Figure 2.2). In some dikes the zones may be described as border, wall, intermediate, and core zones can be recognized based on the distribution of minerals and texture in the dike. The grain size within the border and wall zones ranges from fine to medium (pegmatitic) grained (0.5 to 10 cm). The ferromagnesium silicates are subhedral to euhedral, the feldspars are subhedral, and the quartz is dominantly anhedral although late quartz veins may have euhedral crystal forms. The texture shows extreme variations in grain size. In the zoned pegmatites, the border and wall zone are fine to medium grained with rare ferromagnesium minerals (Ca pyroxene, hornblende, biotite, and garnet) and commonly have graphic texture. The intermediate zone is medium to coarse grained (plagioclase, K-feldspar, quartz, biotite and/or magnetite) and texturally heterogeneous. The core is usually very coarse-grained quartz and microcline with rare calcite (Hewitt, 1967; Masson and Gordon, 1981; Storey and Vos, 1981b).

Unzoned granitic pegmatite bodies range in width from 10 cm to 50 m and have anastomosing strike lengths that may exceed 1 km (eg. Faraday pegmatite, Croft pegmatite (Figure 2.3) and Halo pegmatite (Figure 2.4)). They are dominantly fine-grained pegmatitic with average sizes of 1 to 3 cm with an equigranular texture. However, within some bodies, the grain size is variable with no relationship to pegmatite contacts, and varies from aplitic to medium-grained pegmatitic texture.

In a few instances, aplite dikes and stocks are associated with granitic pegmatites in the region. In Quebec, Fowler (1980), Fowler and Doig (1983a), Rimsaite (1985) noted aplites in the Mont Laurier area, and Shaw (1958) and Savard (1974), have described the convoluted aplite texture in the Dunraven pegmatite on Grand Calumet Island (Plate 2.1), and Hogarth (1966), Vistelius et al. (1983), and Cousineau (1986) have studied aplite in the Gatineau area. Ford (1982) noted aplite textured rock in association with texturally heterogeneous portions of granite pegmatites in the Sharbot Lake area, Rimsaite (1980) noted uraniferous aplite in the Bancroft area, and the author has noted aplites at the Hunt Mo skarn deposit, Renfrew, Ontario.

Myrmekitic texture has been observed at several localities where plagioclase has evidently replaced K-feldspar as irregular grains (Pride, 1974; Tremblay, 1974; Hervet, 1979).

Graphic and granophyric quartz and K-feldspar intergrowths are commonly present in the unzoned granitic pegmatites, and in border and wall zones of zoned pegmatites. The scale of the intergrowths may be extremely variable (Plate 2.2). The quartz forms plates, angular rods, and blebs within the larger K-feldspar crystals particularly in the medium-grained granitic pegmatite, whereas rods, blebs, and wormy forms are more common in finer grained varieties. Graphic and granophyric pegmatite is commonly found near the transition from mineralized portions of the pegmatite and/or host rocks to unmineralized granite pegmatite, and near the transition between unzoned to zoned pegmatite. It has been shown that diffusion-controlled growth kinetics are responsible for the formation of graphic texture in Grenville pegmatites (Appendix 6; Lentz and Fowler, in press).

2.2.3 Pegmatite/host rock interaction

The contacts of the granite pegmatites with the host rock gneisses are quite variable from sharp to gradational. The diffuse pegmatite contact zones are mineralogically

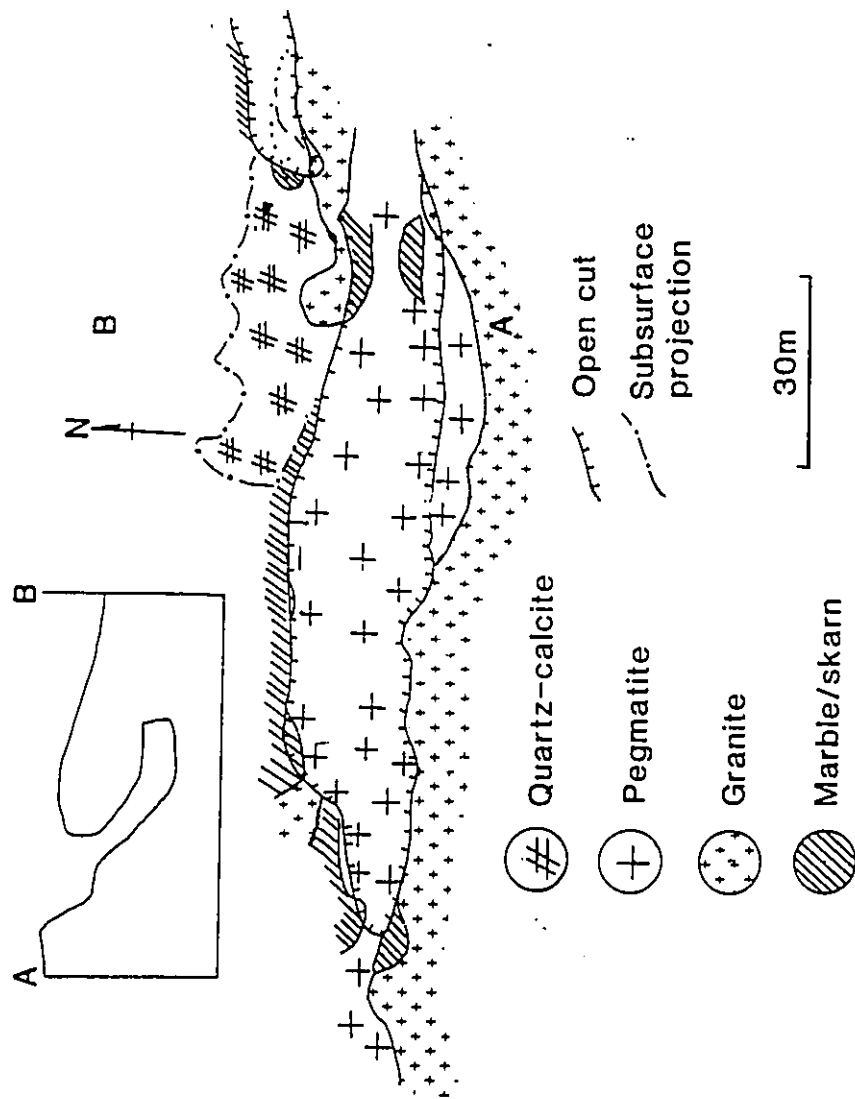


Figure 2.1

MacDonald zoned pegmatite located near Hybla, Ontario northeast of Bancroft, Ontario (after Hewitt, 1967). A portion of the map is a projection of the underground workings (deposit # 26).

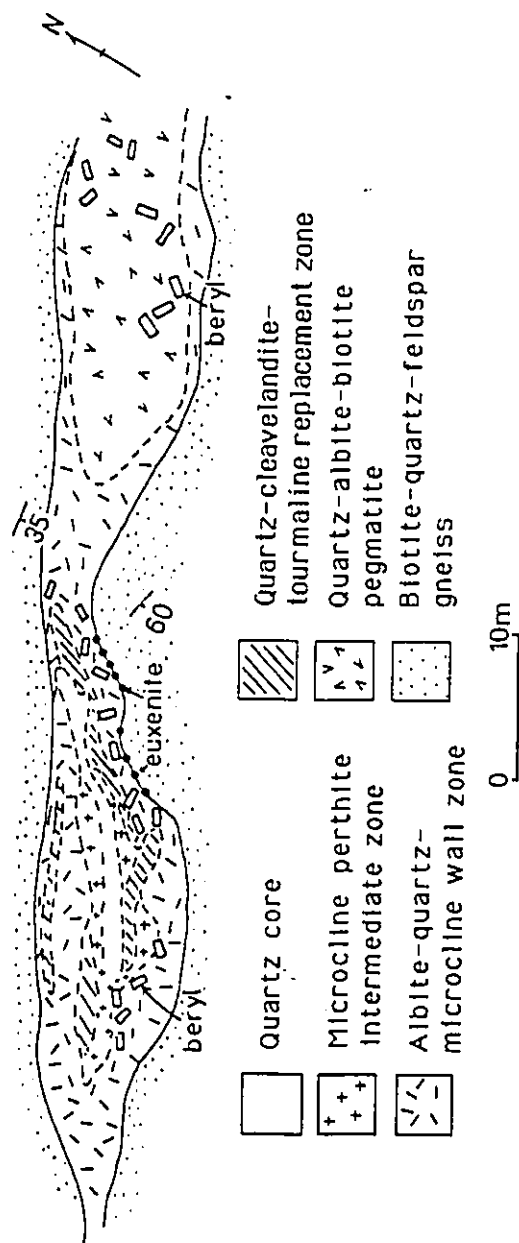


Figure 2.2 Wall Gem zoned beryllium pegmatite located just north of Quadeville, Ontario (after Hewitt, 1967) (deposit # 124.)

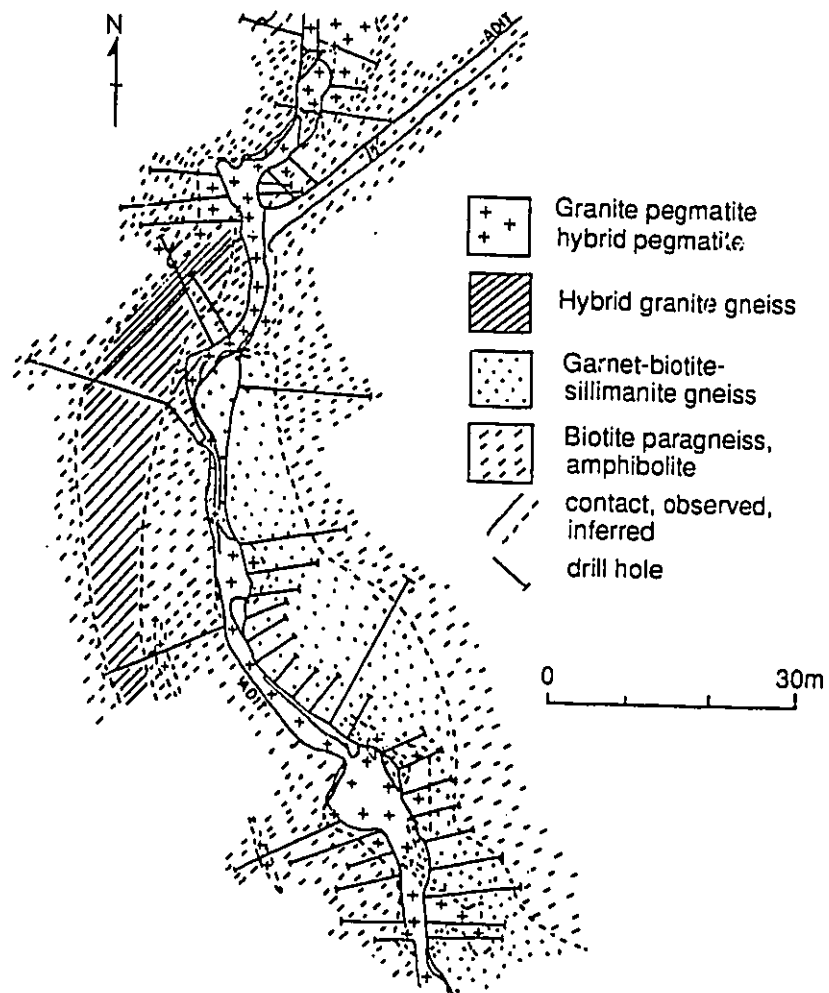


Figure 2.3 Croft uraniferous unzoned pegmatite located north west of Cardiff, Ontario (after Satterly, 1957) (deposit # 106).

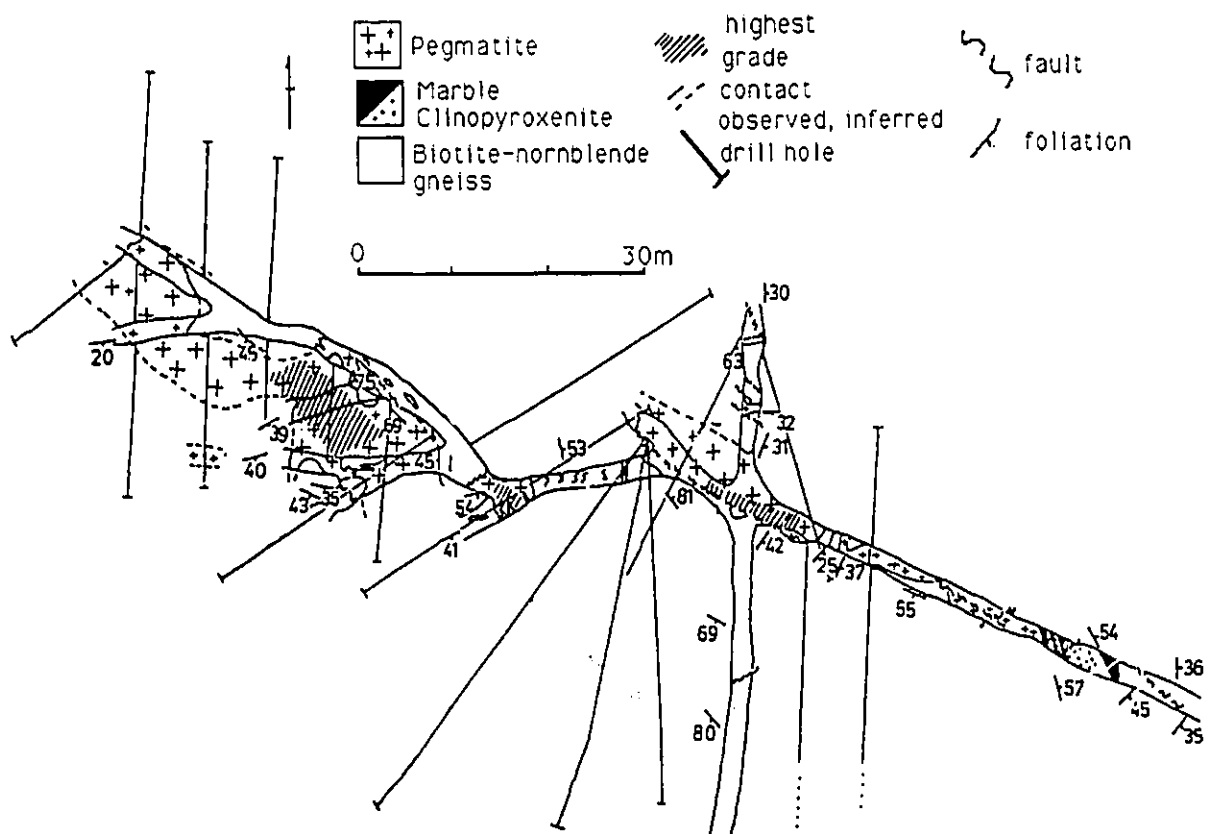


Figure 2.4 Halo uranium-molybdenum unzoned pegmatite located south of Wilberforce, Ontario (deposit # 2) (after Satterly, 1957).

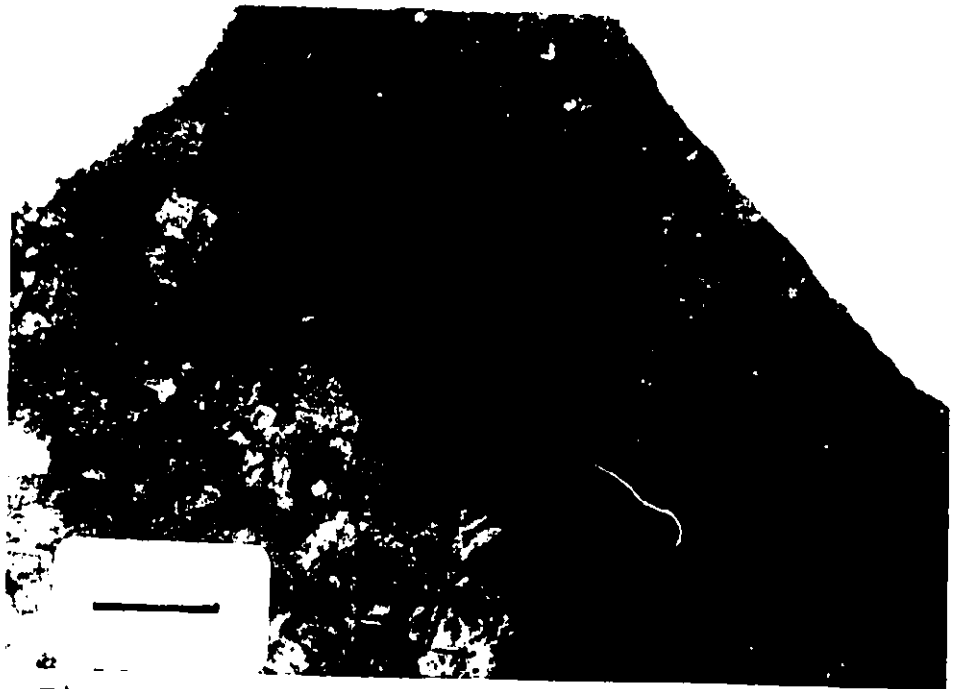


Plate 2.1

Fine-grained, layered aplite from the Dunraven uranium pegmatite, Grand Calumet Island, P.Q. (deposit # 63). Scale bar is 1 cm long.

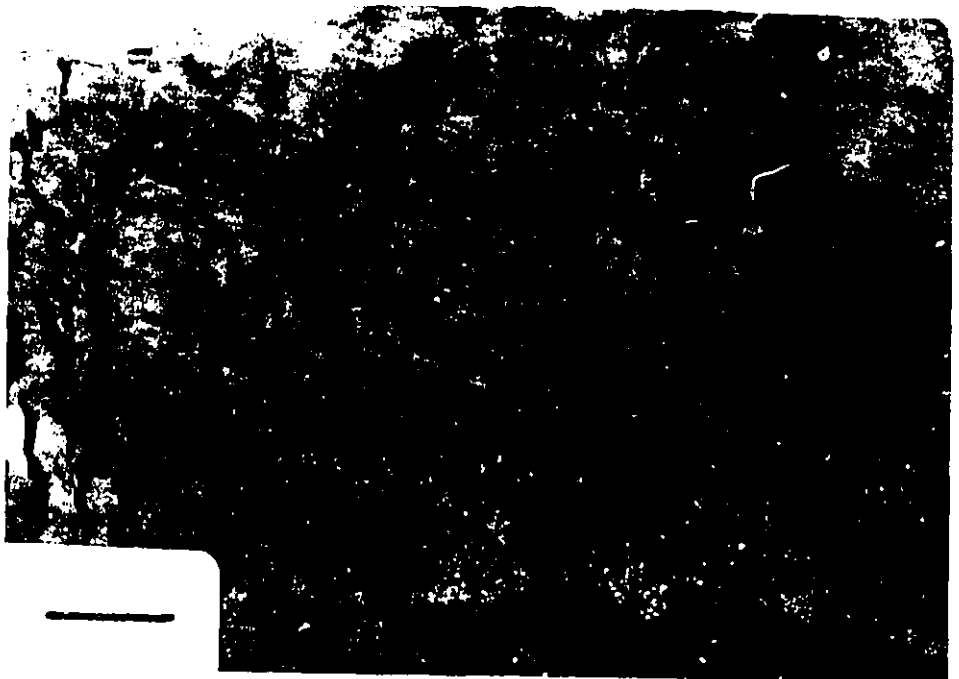


Plate 2.2

Fine-grained graphic granite pegmatite, Legris uranium deposit, Dacre, Ontario (deposit # 49). Scale bar is 1 cm long.

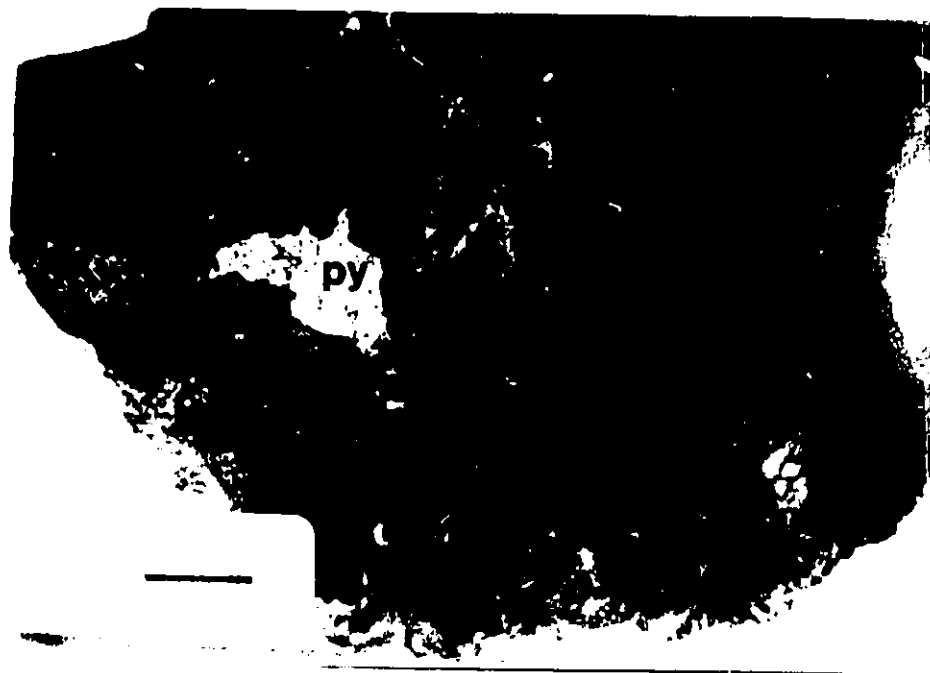


Plate 2.3

Hybrid pyrite-bearing biotite pegmatite (margin), Halo uranium deposit, Wilberforce, Ont. (deposit # 2). Scale bar is 1 cm long.

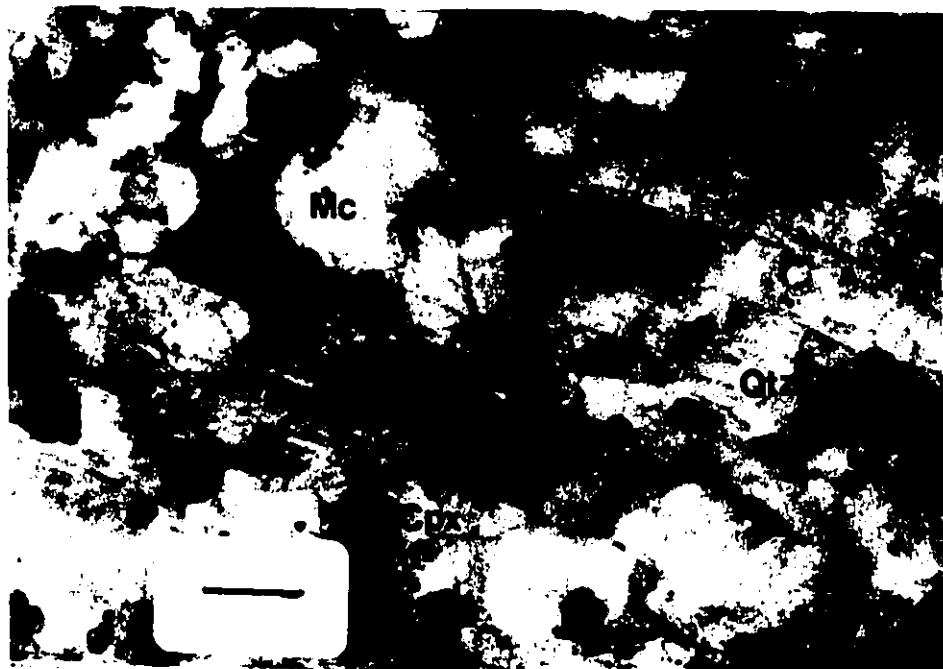


Plate 2.4

Hybrid Ca pyroxene-bearing white granitic pegmatite, Saranac zircon deposit, Wilberforce, Ontario (deposit # 15). Scale bar is 1 cm long.

heterogeneous (biotite, hornblende, aegirine-augite, magnetite, allanite, titanite, and zircon and more rarely uraninite, uranothorite, and molybdenite) and are here referred to as hybrid pegmatite. Hybridization is evident in the Faraday pegmatite but many other examples have also been described (Satterly, 1956; Vokes, 1963; Lang et al., 1971; Habib, 1982; Masson and Gordon, 1981; Rimsaite, 1982, 1983, 1985a, and b). The hybrid portions of zoned pegmatites occur along the wall zone and to a lesser extent in the intermediate zone with euxenite, allanite, REE zircon (cyrtolite), and REE garnet (yttrian andradite) forming the radioactive portion of the assemblage (Ellsworth, 1932; Storey and Vos, 1981b). Generally, the concordant pegmatites have reacted more completely with the host rocks than have the discordant pegmatites (Satterly, 1957; Hewitt, 1967; Tremblay, 1974; Masson and Gordon, 1981; Haynes, 1986).

The reaction zones may have formed by three main mechanisms : 1) a xenocrystic origin with growth and/or recrystallization at pegmatite temperatures, 2) assimilation of the host rock by partial melting, subsequent mixing, and crystallization, and 3) endoskarns produced in response to the interaction of the pegmatite and the host rock by the hydrothermal fluids at both hypersolidus or subsolidus temperatures. The first two processes are indistinguishable in the field. The later process may be described as a metasomatic exchange reaction between pegmatite and skarn (some of these reactions will be examined in chapter 5).

The hybridization process is evident in gneisses with a high mafic mineral content, particularly amphibolites, and biotite gneisses (Plate 2.3). As an example granite pegmatites hosted by biotite-bearing gneisses commonly contain biotite reaction zones and large biotite crystals.

Endoskarns are most evident where pegmatites intrude carbonate-bearing supracrustal rocks commonly resulting in a Ca pyroxene-feldspar (K-feldspar, plagioclase, and/or

scapolite) assemblage along the margins of the pegmatite. Diopside-bearing pegmatites occur at the Cardiff Uranium Mines (northeast of the shaft), along the margin of the Hunt Mo pegmatite; Camp zone pegmatite at the Yates Mine; and within the Saranac zircon-bearing pegmatite (Plate 2.4). The metasomatic interaction between pegmatite and wall rocks is usually associated with the protore enrichment of uranium and thorium (Habib, 1982; Haynes, 1986; Lentz, 1991a).

The pegmatites are commonly grouped into white and pink (red) varieties. The red pegmatites have feldspars with very fine-grained, earthy hematization (secondary alteration?).

The granitic pegmatite bodies are commonly white to very light pink when hosted in carbonate-bearing metasediments or metapyroxenites (Satterly, 1957; Shaw, 1958; Tremblay, 1974; Carter et al., 1979; Masson and Gordon, 1981; Storey and Vos, 1981b; Habib, 1982; Rimsaite, 1985) (Plate 2.1d). There are several processes which could explain the absence of earthy hematization (white feldspars) including : i) decreasing the redox state of the pegmatite fluids in the subsolidus because of the low redox state of the marbles (commonly sulphide and graphite bearing) (Masson and Gordon, 1981), ii) decreasing the activity of water by the interaction with the marble, and iii) lack of subsolidus oxidation by circulating oxygenated fluid. The white pegmatites commonly contain orthoclase in contrast to the usual microcline assemblage in the pegmatites (Storey and Vos, 1981b; Tremblay, 1974). Retention of the more disordered form of K-feldspar may be related to the low water fugacity during crystallization or the impermeable nature of marbles.

These hybrid features have been interpreted by many researchers as "melanosome" related to the pegmatitic "leucosome". Alternatively, metasomatic exchange with the wall rocks (hybridization and/or skarnification) is responsible for the complex mineralogy and textures at the margins of the pegmatites.

The hybrid pegmatite, the evidence of local partial melting, and association with upper amphibolite grade metamorphism have been interpreted as evidence for an *in situ* anatectic origin of the granitic pegmatite melts (Robinson, 1960; Evans, 1966; Allen, 1971; Tremblay, 1974; Masson and Gordon, 1981; Storey and Vos, 1981b; Ford, 1982, 1983). However, the discordant nature of these pegmatites, the disproportionate amount of "melanosome" to pegmatite "leucosome", the abundance of rare-metals, and the geochronologic relationships between peak metamorphism and rare-metal pegmatite emplacement do not support this hypothesis.

The commonly sharp contact with the host rock is compatible with emplacement as melt. The granitic composition is approximately that of the haplogranite minimum, and crystallization of dominantly anhydrous silicates will result in volatile enrichment of the melt. The development of aplitic and graphic texture and the development of the coarse-grain size suggests that volatile phase separation occurred in some pegmatites during intermediate stages of crystallization indicating considerable volatile enrichment preceding emplacement (Lentz and Fowler, in press; Appendix 5). The separation of the volatile phase from the melt may be controlled by the density of exsolved fluid and the nature of the wall rocks. The retention of the fluids could lead to mineralized zones, recrystallization, and re-equilibration of assemblages within the pegmatite. In some areas, fracture fillings of quartz and/or muscovite may be found crosscutting the pegmatites.

2.3. Pegmatite mineralogy

2.3.1 Quartz

Quartz may be clear to milky coloured to blue (in charnockitic pegmatite) and has a variable abundance. Subgrain development of quartz along grain boundaries, and undulose extinction are common. Turbid black to grey quartz is

associated with radioactive minerals, in particular, allanite, zircon, uraninite, uranothorite, euxenite, and betafite and is due to gamma radiation effecting electron transfer related to structural defects (Fron del, 1962; Martin, 1982). Quartz colouration next to K-feldspar in zoned pegmatites (MacDonald zoned pegmatite) could also be due to Al substitution in Si sites (Storey and Vos, 1981b) as described by Martin (1982).

2.3.2 Feldspars

Plagioclase is subordinate to K-feldspar and varies in composition from Ab 80 to Ab 98 based on thin section determinations on twinned feldspar (symmetrical zone). This is complimented by chemical analyses of plagioclase from pegmatites in the study area (Table 2.1). Three of the analyses are from the Quadeville Be pegmatite which represents the most chemically fractionated pegmatite in this study. These plagioclases have an average of 11% An, 86% Ab, and 3% Or typical for most pegmatites. The three plagioclase samples from the Quadeville Be pegmatite have an average of 61 ppm barium, 174 ppm strontium, and only 19 ppm rubidium.

Microcline is usually the most abundant mineral in the granitic pegmatites. The feldspar is coloured various shades of pink to red reflecting the degree of earthy hematization (turbidity) of the feldspar. The reddish K-feldspar is most commonly associated with magnetite-bearing radioactive pegmatites. Bluish greenish perthitic amazonite occurs in several highly fractionated pegmatities (e.g. Blue Sea #122, and Evans Lou #131). The development of tartan twinning indicates that ordering has occurred in almost all pegmatites indicating that crystallization took place above the microcline-orthoclase inversion temperature. However, granitic pegmatites intruding carbonate-bearing metasedimentary rocks contain white intermediate microcline (Roy, 1990). The development of the entire range of perthite types is typical of these pegmatites. Microperthite, cryptoperthite, mesoperthite and perthite are all represented

in the pegmatites even within single crystals representing continued exsolution during slow cooling of the originally hypersolvus feldspar. The development of graphic texture definitely preceeds feldspar exsolution with cryptoperthite developed within fine- to coarse-grained graphic quartz- K-feldspar intergrowth. Table 2.2 presents a few chemical analyses of K-feldspar from granitic pegmatites which are similar in composition to K-feldspars from other Grenville pegmatites (Table 2.3; Appendix 5). This data indicates an approximate average of 3 % anorthite (An), 26% albite (Ab), and 71% orthoclase (Or) for these feldspars.

There is a trend of Rb enrichment and Sr and Ba depletion in the K-feldspar indicative of the degree of fractionation of these pegmatites (Goad, 1990). In a detailed study of K-feldspar compositions (800 samples from 277 localities) of granitic pegmatites from the Grenville Province of southern Ontario, Goad (1990) found that the pegmatites have low Li (ave. 3 ppm (range <1 to 50 ppm)), Rb (ave. 400 ppm (70 to 5000 ppm)) and Cs (ave. 10 ppm (<1 to 170 ppm)) and high Ba (ave. 500 ppm (3 to 10 000 ppm)) indicating that they are variable and poorly fractionated. The Rb, Ba, and Sr abundances are dominantly influenced by feldspar fractionation (Goad, 1990).

2.3.3 Ferromagnesian silicates

Biotite is the most common ferromagnesium phase in the pegmatite and is particularly abundant if the pegmatite is hosted in biotite-bearing gneiss. The grain size varies from fine to coarse grained (pegmatitic) and there is in general an increases in size toward the central portion of the bodies. Biotite comprises less than 5 volume percent of the granitic pegmatite except along the margins. The biotite occurs mostly as fine- to coarse-grained books within an unzoned pegmatite. Biotite is characteristic of all textural varieties and may coexist with amazonite, tourmaline, and fluorite. Biotite formed at relatively early stages of pegmatite crystallization

Table 2.1 Chemical analyses of plagioclase from pegmatites

(wt.%)	1	2	3	4	5	6	7
SiO ₂	63.6	64.6	65.9	66.3	66.7	67.37	66.74
Al ₂ O ₃	22.75	22.04	21.1	19.9	19.85	19.96	20.88
Fe ₂ O ₃	0.05	~	0.21	0.11	0.10	0.00	0.00
CaO	2.40	2.94	1.92	0.91	0.67	0.75	1.67
Na ₂ O	8.82	9.28	10.50	10.74	10.81	11.20	10.69
K ₂ O	2.12	1.27	0.94	0.49	0.27	0.13	0.25
Total	99.74	100.13	100.57	98.45	98.4	99.41	100.23

Notes: Chemical analysis No. 1 is from MacDonald Mine (Spence, 1932), 2 is from the Watson Mine (Walker, 1932), and 3, 4, and 5 are from antiperthitic plagioclase separates from the Quadeville pegmatite (this study), 6 and 7 from Davis nepheline pegmatite near Bancroft (Sylvester and Anderson, 1976).

Table 2.2 Chemical analyses of microcline from pegmatites

(wt.%)	1	2	3	4
SiO ₂	64.6	64.60	65.4	65.30
Al ₂ O ₃	19.3	19.14	19.7	18.48
Fe ₂ O ₃	0.09	0.06	0.0	0.00
CaO	0.0	0.0	0.11	0.04
Na ₂ O	2.67	2.96	2.85	0.64
K ₂ O	12.35	13.02	12.2	16.01
Total	99.0	99.8	100.3	100.5

Notes: Analyses 1 & 2 - MacDonald Mine (Spence, 1932), 3 - Quadeville Be pegmatite (Storey and Vos, 1981b), 4 Davis nepheline pegmatite near Bancroft (Sylvester and Anderson, 1976).

Table 2.3 Chemical analyses of perthitic microcline and a muscovite (130-1M) from selected Grenville pegmatites

Smp	4C	116A	117-E	118	119-2	120D1	121H	122C	130-1	130-1M
wt. %										
SiO ₂	64.7	63.2	63.9	64.8	65.0	64.7	63.3	65.2	65.1	46.3
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.49
Al ₂ O ₃	18.33	20.21	18.42	17.90	18.52	18.19	19.56	18.50	18.53	32.87
Fe ₂ O ₃	0.17	0.16	0.10	0.07	0.07	0.05	1.13	0.05	0.03	4.07
MnO	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.00	0.01	0.05
MgO	0.13	0.05	0.00	0.00	0.05	0.03	0.00	0.12	0.10	1.07
CaO	0.12	1.40	0.11	0.11	0.26	0.10	0.27	0.09	0.08	0.04
Na ₂ O	2.2	5.2	1.9	2.2	2.4	2.1	3.9	3.2	2.3	0.7
K ₂ O	13.13	7.66	13.50	12.82	12.23	13.00	9.88	12.26	12.91	10.72
P ₂ O ₅	0.02	0.01	0.00	0.01	0.00	0.00	0.01	0.01	0.01	0.00
S	0.04	0.04	0.05	0.04	0.01	0.00	0.06	0.08	0.02	0.00
Total*	98.8	97.9	98.0	98.0	98.6	98.2	98.1	99.5	99.1	96.6
ppm										
Ba	1220	3510	1650	690	1990	1190	19410	150	200	80
Cr	14	8	12	19	21	22	2	9	23	31
Zr	7	33	6	3	0	0	95	2	0	2
Sr	342	1518	417	168	464	273	5242	36	53	2
Rb	374	295	418	368	182	367	112	1946	767	1770
Zn	60	.88	109	50	0	0	49	70	C	56

Notes: K-feldspars separates analysed using fused disk on a Phillips PW1410 XRF at the University of Ottawa; Totals do not include Ba, Sr, Rh contents; Pb in amazonite samples was not analysed and Na₂O may be partially volatilized during fusion accounting for low totals. The sample numbers refer to locations (Figure 1.2).

because biotite may be enclosed in graphic granite pegmatite (e.g. Blue Sea pegmatite). The zoned Wall Gem beryllium pegmatite is concordantly hosted in biotite-bearing quartz-feldspar gneiss and amphibolite. Biotite is concentrated in the border zone of the pegmatite.

Tremblay (1974) noted that biotite forms aggregates within the pegmatites of the Mont Laurier area and crystals may show a preferred orientation parallel to the margins of the dike. The biotite may be primary phase crystallizing from the melt and/or a result of host rock contamination (xenocrystic) and recrystallization (hybridization).

Twenty two chemical analyses of biotite from nine Grenville pegmatites will be discussed with respect to the petrogenesis of the skarns and fluorite-apatite-calcite veins in the Grenville (Section 3.3). This data have also been used to illustrate the effects of differentiation, hybridization, and volatile phase separation in the pegmatite as biotite is a sensitive indicator to changes of crystallization conditions within the melt (Lentz, in prep; Appendix 6). The following discussion will be restricted to previously published analytical data (Table 2.4). The hybrid nature of ferromagnesian minerals within the marginal zones of late-tectonic granitic pegmatites of the Grenville Province has been noted by numerous researchers. Rimsaite (1982) reported 2 biotite-phlogopite samples, one from the Bancroft area, and the other from the Baie-Johan-Beetz area of which the later has a significantly higher Al_2O_3 content (17.6 wt.%) than the average of this study (14.5 wt.%). Armstrong and Gittins (1969) found similarly high Al_2O_3 contents (17.5 wt.%) for biotite hosted in a hybrid nepheline pegmatite (Table 2.4). Rimsaite (1984) obtained biotite analyses from the Mont Laurier pegmatites similar to those of this study. Rimsaite (1980) analysed the REE content of biotite from a pegmatite in the Bancroft area, which contained abundant microinclusions

Table 2.4 Chemical analyses of biotite and phlogopite from Grenville pegmatites (previous studies)

<u>Smpl</u> <u>wt. %</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>
SiO ₂	36.8	37.5	34.6	34.3	41.9	41.3	37.3	33.2	34.1	40.8	41.9	39.6	32.8
TiO ₂	3.3	3.3	3.4	3.3	-	-	-	2.21	2.50	0.5	0.9	1.9	1.5
Al ₂ O ₃	15.3	15.6	16.3	15.0	10.4	13.1	17.6	17.5	19.25	10.0	10.4	10.6	16.8
Fe ₂ O ₃	5.5	5.0	10.1	6.4	6.3	2.1	4.4	3.2	-	2.1	6.31	3.8	7.2
FeO	16.3	16.7	14.6	14.1	0.5	11.8	16.6	23.1	26.98	13.85	10.50	15.22	22.36
MnO	0.7	0.7	0.4	0.3	-	-	-	0.51	0.58	0.4	0.5	0.5	0.9
MgO	9.0	8.9	6.6	9.0	1.3	16.2	7.9	7.45	4.14	16.3	14.3	14.6	5.8
CaO	0.0	0.0	0.2	1.7	0.2	0.5	0.1	0.06	0.15	0.00	0.22	0.2	0.2
Na ₂ O	0.0	0.0	0.0	0.0	0.1	0.1	0.5	0.54	0.06	0.3	0.12	0.3	0.3
K ₂ O	9.0	8.7	8.9	7.9	9.7	9.1	8.4	8.96	10.00	9.7	9.9	9.5	9.3
H ₂ O	3.2	3.4	3.6	5.0	-	-	-	3.67	3.86	2.8	1.5	1.9	3.7
Cl	0.15	0.18	0.20	0.1	-	-	-	-	-	-	-	-	-
F	0.85	1.30	0.40	0.3	-	-	-	-	-	3.73	3.67	3.63	0.55
O=Cl	0.13	0.04	0.05	0.02	-	-	-	-	-	-	-	-	-
O=F	0.36	0.55	0.17	0.13	-	-	-	-	-	1.6	1.54	1.5	0.2
Total	99.6	100.7	99.1	97.3	93.4	94.2	92.8	100.4	101.6	98.9	100.2	100.2	101.2
ppm													
Ba	300	200	300	300	-	-	-	-	-	tr	400	tr	tr
Rb	1000	1000	700	600	8010	730	1525	-	-	2000	6000	2500	600
Zn	500	500	500	400	-	-	-	-	-	1500	900	1500	1400

Notes: Samples # 1, 2, 3, 4 from Mont Laurier (Rimsaite, 1985), 5, 6 from Bancroft, and 7 from Baie-Johan-Beetz (Rimsaite, 1982), and 8 from Wilberforce (Armstrong and Gittins, 1969), 9 average biotite from the Davis nepheline pegmatite near Bancroft (Sylvester and Anderson, 1976), 10 from Cardiff pegmatite & gneiss, 11 from radioactive pegmatite Faraday twp. (Bancroft), 12 from pegmatite in skarn Cardiff twp., and 13 from radioactive pegmatite Mentor deposit, Monteagle twp. (Bancroft) (Rimsaite, 1967).

and obtained La (2000 ppm), Ce (3200 ppm), Nd (1000 ppm), Sm (300 ppm), Eu (20 ppm), Dy (502 ppm), Ho (140 ppm), Er (650 ppm), Tm (150 ppm), Yb (2450 ppm), Y (2450 ppm), and Th (1400 ppm).

Hornblende is common in granitic pegmatites with grain size coincident with that of quartz and feldspar. Hornblende is confined mainly to the contact zones of some pegmatites (e.g. Richardson feldspar deposit). Hornblende-bearing pegmatites are most commonly hosted in hornblende gneisses, amphibolites and/or carbonate-bearing gneisses. Rimsaite (1982) has reported a hornblende analysis from the margin of an U-bearing granitic pegmatite in the Bancroft area, and found it to be iron-rich, with $\text{FeO} = 11.3 \text{ wt.}\%$ and $\text{Fe}_2\text{O}_3 = 7.2 \text{ wt.}\%$. In the same area, Rimsaite (1982) reported the composition of a hornblende in a migmatitic gneiss, which contained 11.8 weight percent FeO and 2.1 weight percent Fe_2O_3 , indicating that the pegmatite hornblende contained more iron and is oxidized compared to the host gneiss.

Ca pyroxene is medium to dark green in colour and occurs primarily in the metasomatized margin (hybrid/skarn) of granitic pegmatites. In the endocontact zones of the pegmatite, Ca pyroxene is not normally associated with quartz. It seems likely that Ca pyroxene is formed at the expense of quartz commonly occurring with an assemblage of K-feldspar, plagioclase or scapolite, and titanite. Desilication of the pegmatite may also occur to a limited extent in response to hybridization with the marble (Wyllie, 1974). One chemical analysis of Ca pyroxene is presented (Table 3.3) from the Camp zone, Yates deposit indicating that it is iron-rich compared to Ca pyroxenes in the skarns and veins.

2.3.4 Minor minerals

Apatite is rare in granite pegmatite bodies from the Grenville Province but has been reported by Rimsaite (1984) from the Baie-Johan-Beetz area. Apatite is associated with

the marginal parts of the pegmatites with ferromagnesium minerals (Sempels, 1971; Pride, 1974). Along the contact with the ACME Mo pegmatite east of Maniwaki, apatite (samples 121J and 121I) occurs with an assemblage of K-feldspar-biotite-calcite. Apatite from the ACME pegmatite had 0.01 wt.% MnO which was higher than in apatite in the skarns and veins (Appendix 3.7). Yttrian fluorapatite was found in the quartz core of the Evans Lou quarry near Poltimore, Quebec (Miles et al., 1971) and was later recovered from the wall zone of the same pegmatite body. Hogarth (1989) found that apatite from pegmatites has a higher Mn content than apatite from skarns.

Calcite occurs within and along the margins of a few granitic pegmatites. It varies in colour from white to orange. The composition of calcite is relatively uniform with slight variations in CaO (53.5 to 56.0 wt.%), MgO (0.0 to 0.56 wt.%), FeO (0.28 to 0.73 wt.%), MnO (0.11 to 0.50), Na₂O (0.00 to 0.42 wt.%), Ba (80 to 330 ppm), Sr (670 to 2090 ppm) and Y (140 to 460 ppm) contents (Table 2.4).

Magnetite is common as small (< 1cm) equant, euhedral crystals disseminated in the radioactive pegmatites particularly in the Bancroft area. The magnetite is usually associated with intense hematization of the pegmatite feldspars, normally near the contacts of the pegmatite (Rimsaite, 1980; Masson and Gordon, 1981; Ford, 1982; Rimsaite, 1982; Rimsaite, 1985) where there is a high proportion of mafic constituents.

Euhedral titanite (sphene) is a common accessory phase particularly along margins of the granite and nepheline pegmatites. Chemical analysis of titanite from the uranium mineralized pegmatites indicate an average SiO₂ = 30.3 wt.%, TiO₂ = 29.4 wt.%, Al₂O₃ = 5.6 wt.%, CaO = 27.4 wt.%, MgO = 0.2 wt.%, FeO = 2.2 wt.%, and Nb₂O₅ = 1.75 wt.% (Lafontaine, 1979; Habib, 1982), whereas Sylvester and Anderson (1976) found lower SiO₂ (29.6 wt.%), Al₂O₃ (2.34 wt.%), and FeO (0.70 wt.%)

Table 2.5 Chemical composition of calcite

Sample	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
CO ₂ wt. %	43.9	44.8	44.5	43.3	44.2	42.1	43.7
CaO	55.43	56.0	55.8	53.5	56.3	51.5	54.1
Na ₂ O	-	0.00	0.13	0.42	0.07	0.49	0.14
FeO	0.28	0.35	0.25	0.73	0.02	0.95	0.70
MgO	-	0.44	0.40	0.45	0.00	0.56	0.41
MnO	0.21	0.11	0.14	0.50	0.03	0.85	0.42
SiO ₂	0.03	0.03	0.04	0.1	0.07	2.7	0.08
SrO	-	0.13	0.08	0.25	0.02	0.02	0.26
Total	99.8	101.9	101.4	99.3	100.7	99.3	99.8
Ba ppm	-	330	80	130	40	40	80
Y	-	140	330	50	0	80	210

Notes: Sample # 1 from MacDonald Mine (Walker and Parsons, 1923); (This study) 2 & 3 are from the MacDonald Mine (#26 G and H); 4 & 5 are from the Faraday Mine; 6 - New Armstrong pegmatite (#126); 7 - Kenmac-Chibougamou pegmatite (#127).

and higher TiO_2 (36.09 wt.%) and CaO (27.83 wt.%) contents in a nepheline pegmatite near Bancroft, Ontario.

Zircon is common, forming small (millimetre) euhedral crystals. The zircon is usually associated with the marginal phases of the pegmatite. Cyrtolite was described by Ellsworth (1932) from the Hybla pegmatites near Bancroft. Robinson (1979) noted that cyrtolite from a pegmatite in Hastings County (Bancroft area) which had high total RE_2O_3 (4.72 wt.%) of any zircon. Rimsaite (1980) found much lower total RE_2O_3 ($\approx$ 0.2 wt.%) in zircon from Bancroft. Habib (1982) and Rimsaite (1984) have analysed zircons and obtained average $\text{SiO}_2 = 32.0$ (wt.%), $\text{TiO}_2 = 0.01$ (wt.%), $\text{Fe}_2\text{O}_3 = 0.45$ (wt.%), $\text{CaO} = 1.0$ (wt.%), $\text{ZrO}_2 = 61.4$ (wt.%), and $\text{Nb}_2\text{O}_5 = 0.6$ (wt.%) contents on two zircons. Uranium contents vary from 0.05 to 6.34 weight percent and thorium contents vary from 0.007 to 0.55 weight percent (Rimsaite, 1985a). Hurley and Fairbairn (1957) determined a range from 0.081 to 2.522 wt.% uranium and 0.001 to 0.384 wt.% thorium from 10 zircons taken throughout Ontario.

Allanite is associated with the marginal zones of the granite pegmatite and hosts the bulk of the REE in the pegmatites. The grain size varies considerably from millimeters to less than 1 meter (eg. MacDonald Mine). Frondel (1964) determined the REE content of some Grenville allanites. MacFarlane (1987) obtained 26 chemical analyses of allanite from Grenville pegmatites. From 23 granite pegmatites, he quoted mean values of $\text{SiO}_2 = 32.1$ (wt.%), $\text{TiO}_2 = 0.82$ (wt.%), $\text{Al}_2\text{O}_3 = 15.27$ (wt.%), $\text{Fe}_2\text{O}_3 = 16.39$ (wt.%), $\text{MnO} = 0.4$ (wt.%), $\text{MgO} = 0.63$ (wt.%), $\text{CaO} = 11.36$ (wt.%), $\text{La}_2\text{O}_3 = 6.42$ (wt.%), $\text{Ce}_2\text{O}_3 = 9.71$ (wt.%), $\text{Pr}_2\text{O}_3 = 0.89$ (wt.%), $\text{Nd}_2\text{O}_3 = 2.46$ (wt.%), $\text{Sm}_2\text{O}_3 = 0.15$ (wt.%), $\text{Gd}_2\text{O}_3 = 0.07$ (wt.%), $\text{Y}_2\text{O}_3 = 0.02$ (wt.%), and $\text{ThO}_2 = 0.84$ (wt.%) contents for these allanites. Habib (1982), Rimsaite (1982) and Rimsaite (1980) obtained similar

chemical analyses (less complete) on allanites from the Bancroft area.

There are numerous studies on the mineralogy of these radioactive deposits in the Grenville Province including those of Ellsworth (1932), Rowe (1952) Robinson and Sabina (1955), Hurley and Fairbairn (1957); Robinson and Abbey (1957), Satterly (1957), Heinrich, 1959; Habib, (1982); Rimsaite (1980, 1981a, b, 1982, 1983a, b, 1984, 1985, 1986). The radioelement content and the U/Th ratio strongly affects the composition and occurrences of radioactive minerals. The dominant radioactive minerals are uraninite, uranothorite, thorite, pyrochlore-group minerals (pyrochlore, betafite, microlite), fergusonite, euxenite, allanite (REE epidote), cyrtolite, monazite, samarskite, gadolinite, spencite, and titanite (Satterly, 1957; Hewitt, 1967; Traill, 1970, 1974; Hogarth et al., 1972). Uraninite from pegmatites, granites, and syenite dikes generally has less than 10 wt.% ThO_2 , fluorite-apatite-calcite veins and mica pyroxenite skarns have 10 to 18 wt.% ThO_2 , and silicated marbles generally have greater than 20 wt.% ThO_2 (Robinson and Sabina, 1955). Tremblay (1974) found similarly low ThO_2 (< 10 wt. %) in uraninites from Mont Laurier pegmatites. Rimsaite (1986a) noted that uraninite formed in association with biotite and amphibole (magmatic stage) contained 9.3 wt. % ThO_2 and 70.1 wt. % UO_2 , which is partly replaced by Y-Fe uranothorite (19.5 wt. % UO_2 , 36 wt. % ThO_2 , and 1 wt. % Y_2O_3). Secondary uraninite associated with chloritized ferromagnesium minerals has 3.9 wt. % ThO_2 , and 4.8 wt. % Y_2O_3 . Dr. J. Rimsaite has found in many instances, particularly in association with pegmatites, that secondary mobilization of uranium from minerals is responsible for the complex variation in uranium and thorium abundances within an individual deposit. This is particularly significant with secondary enrichment of uranium along shear zones occurring in the margins of the pegmatites (Habib, 1982). Robinson and

Abbey (1957) found uranothorite to have an average 10.0 % (1s = 2.2; n = 5) in pegmatites from the Grenville. Tremblay (1974) found approximately 17 wt.% U in pegmatite-hosted uranothorites. Habib (1982) analysed 12 uranothorites from the Cardiff pegmatites (ave. 15.2 % UO_2). Hurley and Fairbairn (1957) determined uranium and thorium contents of zircons from 10 localities in the Grenville with average abundances of 5276 ppm (1s = 7355) and 1134 (1s = 1337), respectively. Tremblay (1974) found 0.2 to 0.5 wt. % uranium in pegmatite zircons. Dr. J. Rimsaite conducted numerous analyses on the abundance of uranium, thorium, and rare elements in numerous trace oxide minerals and silicate minerals in the Grenville deposits. Rimsaite (1980) analysed a titanite from a radioactive Mont Laurier pegmatite which had 0.29 wt.% U, and 0.55 wt.% Th, and Rimsaite (1982) noted a titanite from a granitoid rock near Bancroft with 0.03 wt.% U, and undetermined Th. Lafontaine (1980) observed the thorianite and thorite at the Yates deposit although uraninite was also found and cores of uraninite in thorianite.

2.4 Composition of granitic pegmatites

In an attempt to understand the processes occurring during pegmatite emplacement and subsequent formation of skarn, a literature review of the chemical composition of granite pegmatites, aplites, and associated hybrid zones has been compiled (Appendix 3.6). Samples have been grouped to obtain an average composition from any particular area. This study presents additional whole-rock XRF analyses on uranium-bearing granite pegmatites throughout the southwestern Grenville Province (Table 2.6).

There are several difficulties in determining the chemical composition of pegmatite bodies, especially the sampling problem. Approximately 2 to 5 kilogram samples of fine-grained pegmatite were taken for analysis, although a composite sample of fine-grained pegmatite from the border zone of the

MacDonald pegmatite was used. An additional problem is whether the sample represents the part of the liquid line of descent or fractionated product of the crystallization process. For example, it has been noted that normative anorthite content of the granitic pegmatite increases with increasing proportion of modal albite particularly in the marginal zones of the pegmatites (Sempels, 1971; Pride, 1974; Hervet, 1979) indicating early crystallization of plagioclase in the marginal zones or hybridization during emplacement. In this study, unzoned, fine-grained granitic pegmatite and the fine-grained border zone of zoned granitic pegmatites were sampled. Several of the samples represent hybrid varieties of pegmatite.

The range encountered in this and previous studies is: SiO_2 (74 - 76 wt.%), Al_2O_3 (13.0 - 15), FeO_T (0.0 - 2.0), MgO (0.0 - 0.3), CaO (0.5 - 1.0), K_2O (4.0 - 7.0), Na_2O (2.0 - 4.0), and TiO_2 (0.0 - 0.2) (Figures 2.5, 2.6, and 2.7). The variation diagrams illustrate the chemical composition of all these pegmatites with the oxide trends of Al_2O_3 , Na_2O , and K_2O and SiO_2 , reflecting the relative abundance of quartz and feldspar. There is an inverse correlation between the SiO_2 abundance and FeO_T , MgO , MnO , TiO_2 , and CaO content (Figures 2.5 and 2.6), due to high abundances of these elements result from the presence of Ca pyroxene, hornblende, biotite, plagioclase, magnetite, and titanite in the mode. (Fowler, 1980; Habib, 1982; Rimsaite, 1982, 1985, 1983, 1982).

The Rb/K and Ba/K ratios are fairly uniform for most samples except those low in K_2O which occur in the marginal zones of the pegmatite (Figure 2.7). Strontium content is not systematically related to SiO_2 content but there is a weak enrichment trend related to CaO content of the pegmatite (Figure 2.6 and 2.7). The ternary Rb-Ba-Sr plot (El Bouseily and El Sokkary, 1975) illustrates that the pegmatite

TABLE 2.6 Whole-rock major- and trace-element chemical analyses of granitic pegmatites from the southwestern Grenville Province, Ontario and Quebec.

Sample	2C	3D	4A	4B	13A	13B	15A	16B	26	49	50	63A	102A	107	116	118
wt. %																
SiO ₂	64.8	72.7	74.5	74.5	77.0	73.7	78.5	75.0	75.7	69.9	72.9	76.7	72.9	73.8	72.0	71.1
TiO ₂	0.20	0.01	0.08	0.04	0.01	0.68	0.06	0.05	0.07	0.31	0.16	0.03	0.03	0.06	0.02	0.02
Al ₂ O ₃	13.57	13.90	12.45	13.39	12.53	12.65	11.16	12.90	12.80	12.23	13.36	12.78	14.88	13.13	15.43	14.55
FeO _T	4.16	0.19	2.80	0.54	0.25	0.67	0.30	1.13	0.22	3.21	1.14	0.55	0.43	0.50	0.40	0.40
MnO	0.07	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.09	0.02	0.02	0.01	0.01	0.01	0.01
MgO	1.67	0.08	0.22	0.25	0.13	0.36	0.14	0.14	0.15	0.21	0.29	0.16	0.12	0.17	0.26	0.18
CaO	2.39	0.34	1.53	0.82	0.06	2.30	0.58	0.66	0.59	3.74	0.72	0.84	1.20	0.99	2.34	0.19
Na ₂ O	1.78	3.02	3.02	2.63	4.29	5.53	1.62	5.14	3.32	4.82	3.09	4.11	4.57	4.27	5.78	2.07
K ₂ O	8.13	7.68	3.97	6.82	4.84	1.06	6.69	2.78	6.20	2.60	6.06	3.57	5.06	4.58	1.48	10.17
P ₂ O ₅	0.04	0.01	0.01	0.01	0.00	0.02	0.00	0.00	0.01	0.00	0.02	0.00	0.00	0.02	0.01	0.02
Total	97.6	97.9	99.0	99.1	99.2	97.1	99.4	98.0	99.1	98.2	98.0	98.9	99.3	97.5	97.8	98.7
ppm																
Ba	1350	1470	450	840	190	110	630	60	740	170	270	90	180	500	510	610
Nb	34	0	4	0	3	285	5	297	6	101	18	7	5	15	0	0
Rb	353	354	111	196	370	51	220	166	261	161	201	312	135	233	48	343
Sr	430	551	243	278	68	231	865	53	430	398	192	77	129	159	1101	153
Y	81	10	29	7	0	412	12	246	17	1354	42	18	11	25	5	13
Zn	61	89	17	51	0	61	7	21	75	3	13	18	6	92	56	59
Zr	15	414	104	18	0	190	832	183	24	3501	46	56	26	73	40	6
q	17.24	24.91	38.15	31.02	33.21	33.47	42.00	32.80	31.47	26.71	29.83	37.09	24.32	29.57	27.38	19.59
c	-	-	0.43	0.21	0.15	-	0.20	0.24	-	-	0.46	0.63	-	0.02	0.09	-
or	48.05	45.37	23.46	40.28	28.60	6.24	39.54	16.43	36.60	15.37	35.31	21.10	29.90	27.04	48.89	60.08
ab	15.06	25.55	25.55	22.25	36.30	46.53	13.71	43.49	28.07	40.79	26.15	34.78	38.67	36.11	11.54	17.51
an	5.03	1.62	7.53	4.00	0.30	6.53	2.88	3.27	1.71	4.06	3.44	4.17	5.15	3.13	-	0.37
hy	1.94	0.20	0.55	0.62	0.32	0.03	0.35	0.35	0.03	-	0.72	0.40	0.03	-	0.65	0.30
di	4.79	-	-	-	-	1.85	-	-	0.74	1.13	-	-	0.58	0.92	-	0.32
wo	-	-	-	-	-	-	-	-	-	5.14	-	-	-	0.13	-	-
mt	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
li	0.15	0.02	0.04	0.02	0.02	0.02	0.02	0.04	0.02	0.19	0.04	0.04	0.02	0.02	0.02	0.02
hm	4.62	0.21	3.11	0.60	0.28	0.74	0.33	1.25	0.24	3.56	1.27	0.61	0.48	0.55	0.45	0.44
ru	-	-	0.06	0.03	-	-	0.05	0.03	-	-	0.14	0.01	-	-	-	-
ti	-	-	-	-	-	1.63	-	-	-	0.51	-	-	0.05	-	0.01	-
xp	0.09	0.02	0.02	0.02	-	0.04	-	-	0.02	-	0.05	-	-	0.04	0.02	0.04

Notes: Chemical analyses of bulk pegmatite samples were obtained on fused disks with a PW 1420 XRF unit in the University of Ottawa Geochemistry Laboratory. The detection limit of trace elements is 10 ppm therefore elements below this are only qualitative, at best. The spectral lines for Y and Nb are affected by U and Th contents which were not quantified and are therefore preliminary values. Samples located on Figure 1.2.

compositions are only moderately-evolved chemically (Figure 2.8).

The average composition is granite based on the quartz, K-feldspar, and plagioclase normative compositions which ranges between metaluminous and peraluminous (with 6.63 % normative diopside to 3.44% normative corundum) (Table 2.6 ; Figure 2.9). As previously noted, extreme compositional variation of the pegmatite represents hybrid pegmatite or a non-representative sample or other causes. The samples with high normative diopside content (UU series; Appendix 3.6) were from altered pegmatites (Habib, 1982) or alkali pegmatites (Armstrong and Gittins, 1969). The corundum-normative samples are usually biotite bearing which in several cases were possibly affected by interaction with the wall rock. Generally, there is an increased plagioclase content in the margins and higher K-feldspar in the intermediate and core zones (e.g. Sempels, 1971; Pride, 1974).

The low abundance of anorthite in the norm allows utilization of the simplified quartz - orthoclase - albite eutectic for estimating crystallization conditions. Luth et al. (1964) located the quartz-feldspar equilibria at 500 MPa (Qtz = 28% (eutectic; 650°C) to 36% at Qtz-Or (cotectic; 735°C)). Similarly, Tuttle and Bowen (1958) located the quartz-feldspar eutectic at a pressure of 300 MPa (Qtz = 33% (eutectic; 665°C) to 42% at Qtz-Or (cotectic; 745°C)). It is estimated that the pegmatites crystallized at approximately 400 MPa (300 to 500 MPa) because normative quartz, K-feldspar, and albite are clustered in the vicinity of the quartz-K-feldspar cotectic (Figure 2.10).

There are several other factors which affect the phase relations of the granitic melt which may account for some of the scatter in Figure 2.10. Fluorine (estimated < 1 wt.% in the melt) reduces the liquidus and solidus temperatures (below 650°C) while expanding the quartz field between 10 and 15 % at

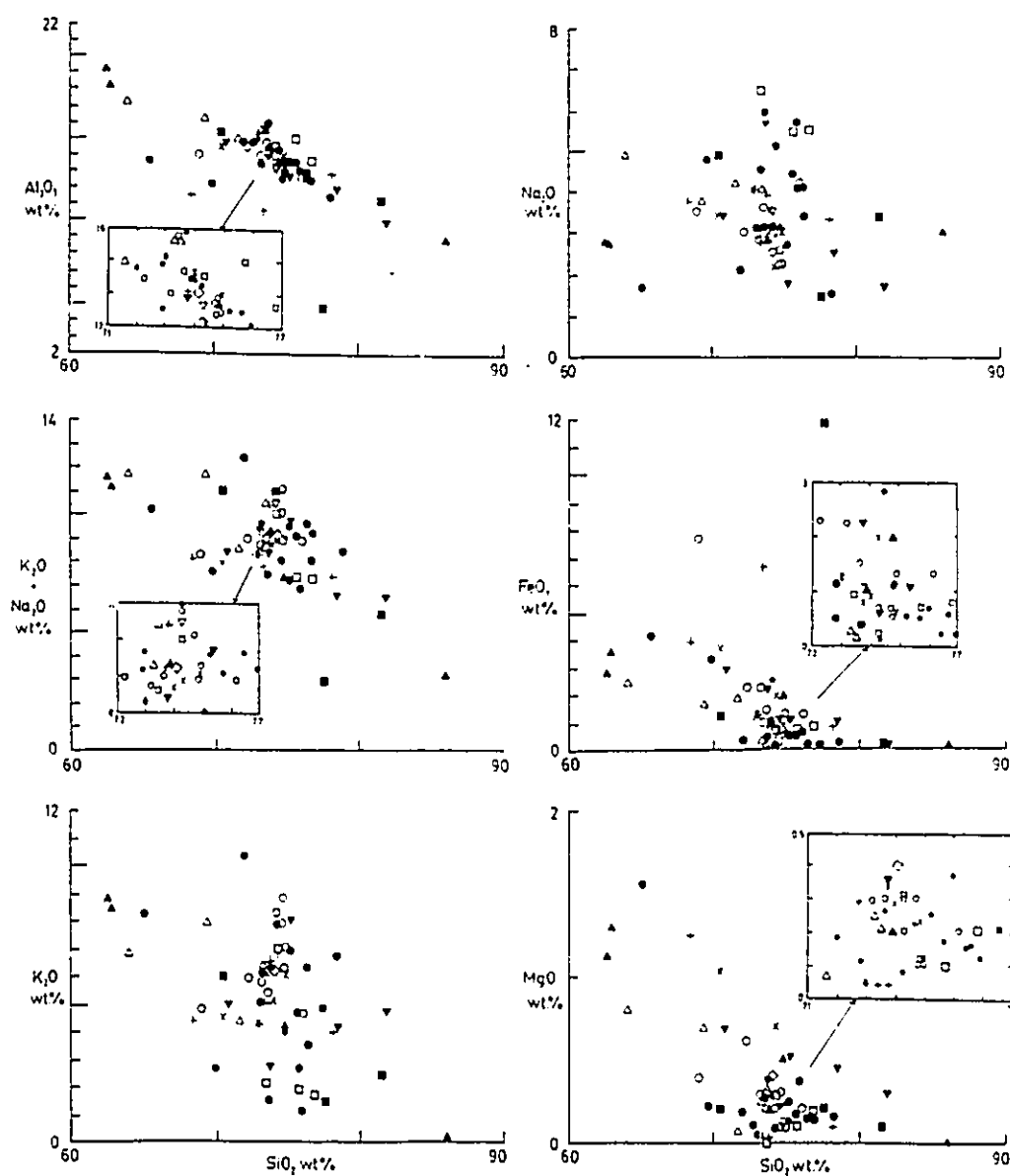


Figure 2.5 The whole-rock variation of Al_2O_3 , $\text{K}_2\text{O}+\text{Na}_2\text{O}$, K_2O , Na_2O , FeO_T , and MgO (wt.%) versus SiO_2 (wt.%) of Grenville pegmatites. Symbols: x - Ford (1983, #1); o - Fowler (1980, #2); □ - Rimsaite (1983) (#3); ▲ - Rimsaite (1985) (#4); ■ - Rimsaite (1984) (#5); ▼ - Tremblay (1974) (#6); ▽ - Hervert (1979) (#7); * - Cousineau (1986) (#8); + - Habib (1982) (#9), ◇ - Bottomley (1988) (#10); Δ - Armstrong and Gittins (1969) (#11) (Appendix 3.6); ● - this study (#12) (Table 2.6).

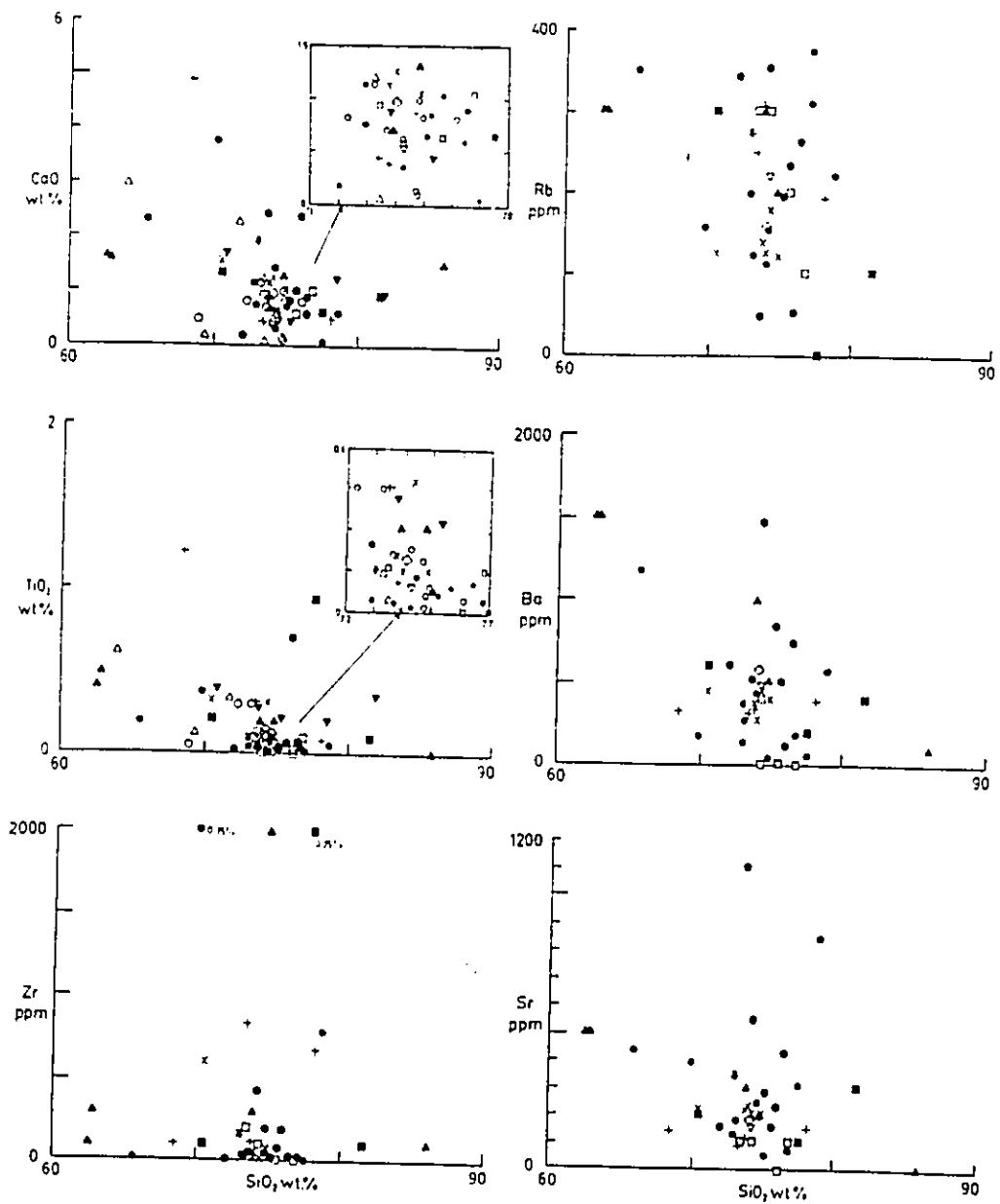


Figure 2.6 The whole-rock variation of CaO (wt.%), TiO₂ (wt.%), Zr (ppm), Rb (ppm), Ba (ppm), and Sr (ppm) versus SiO₂ (wt.%) for granitic pegmatites (Table 2.6; appendix 3.6). See Figure 2.5 for symbols.

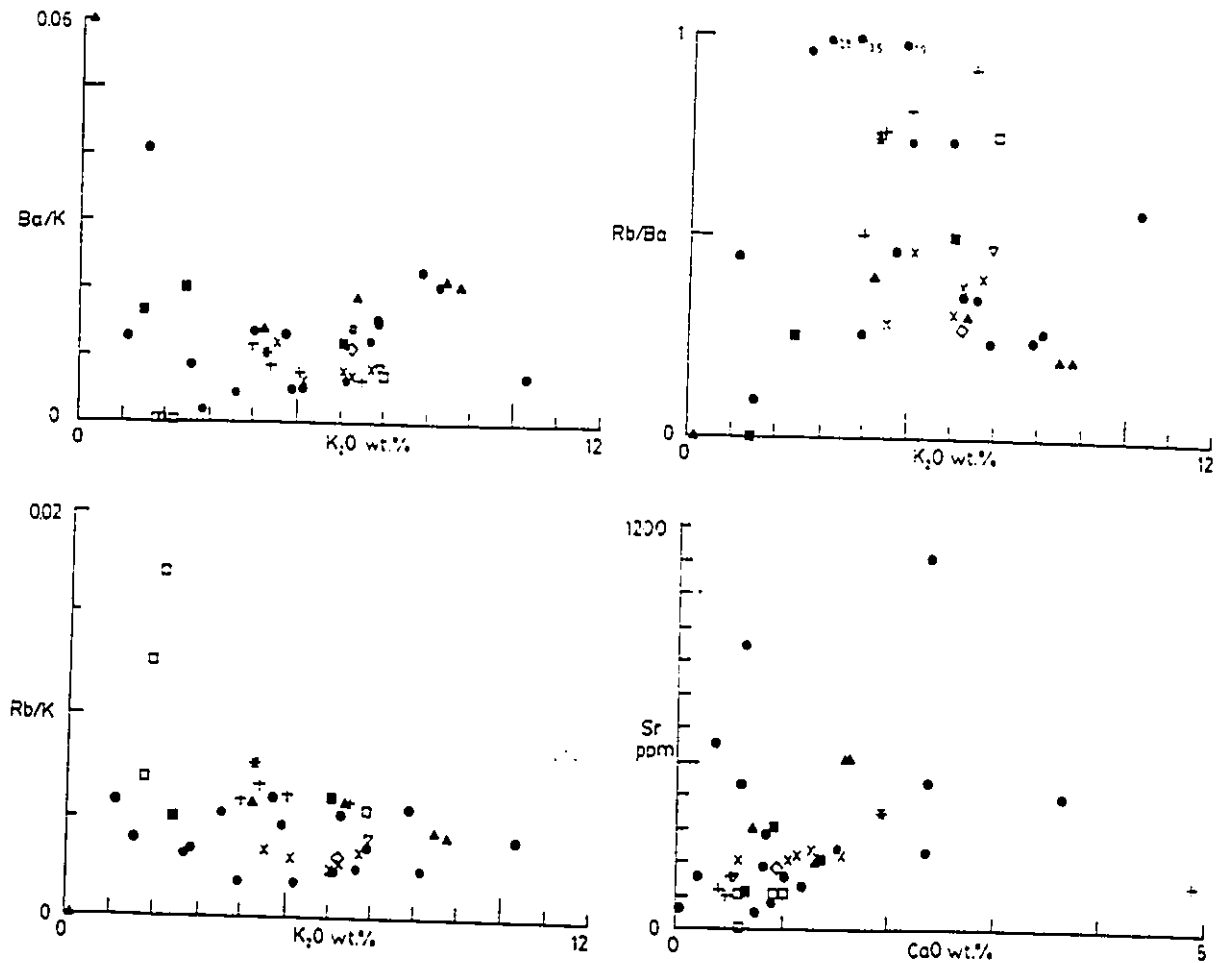


Figure 2.7 The whole-rock ratio of Ba/K, Rb/K, and Rb/Ba versus K_2O (wt.%) and Sr (ppm) versus CaO (wt.%) for Grenville pegmatites (Table 2.6; Appendix 3.6). See Figure 2.5 for symbols.

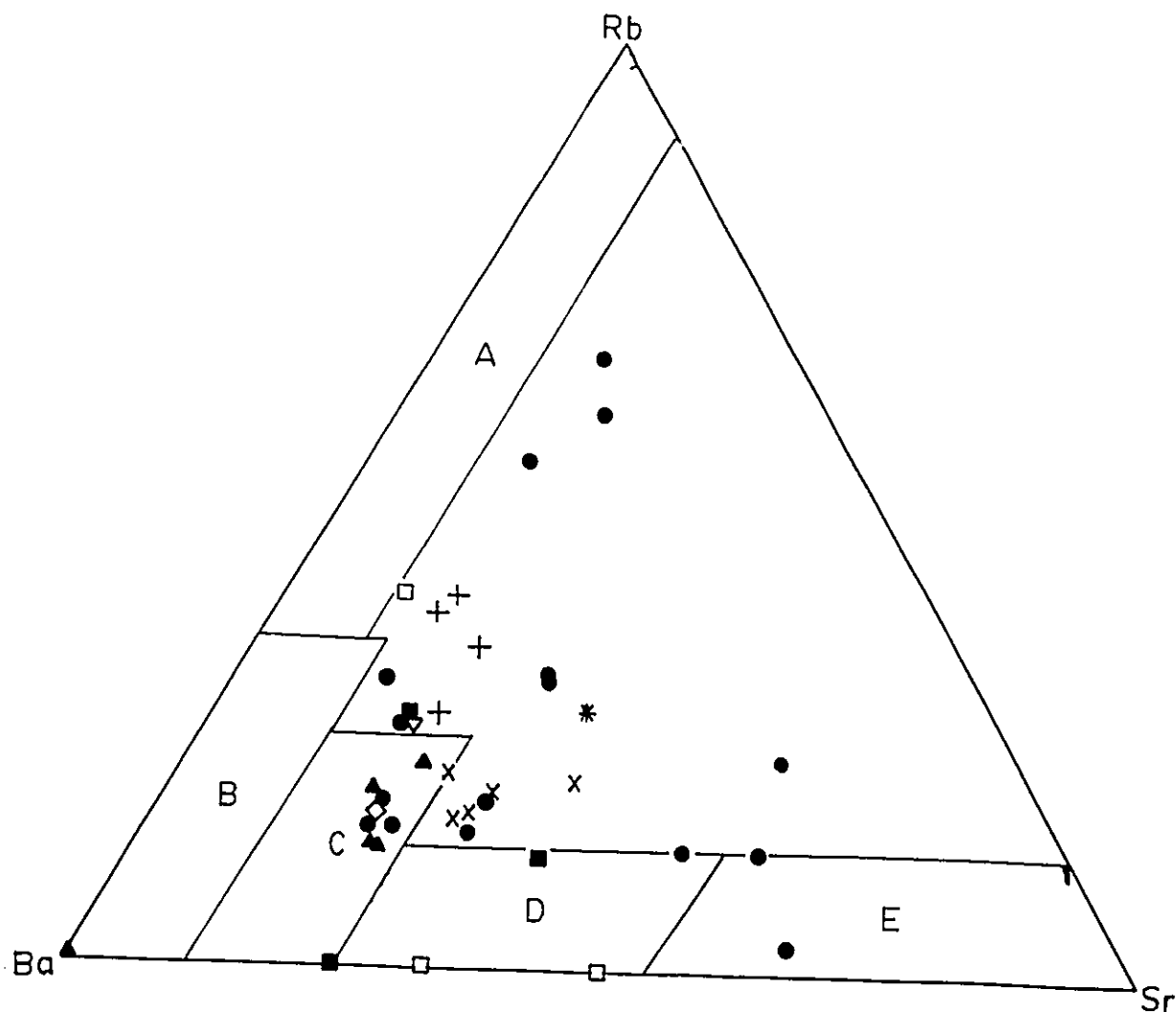


Figure 2.8 Rb-Ba-Sr ternary diagram illustrating the compositional variation of the Grenville pegmatites (Table 2.6; appendix 3.6). A - Strongly differentiated granites; B - Normal granites; C - Anomalous granites; D - Quartz diorites and granodiorites; E - Diorites (El Bousley and El Sokkary, 1975); see Figure 2.5 for symbols.

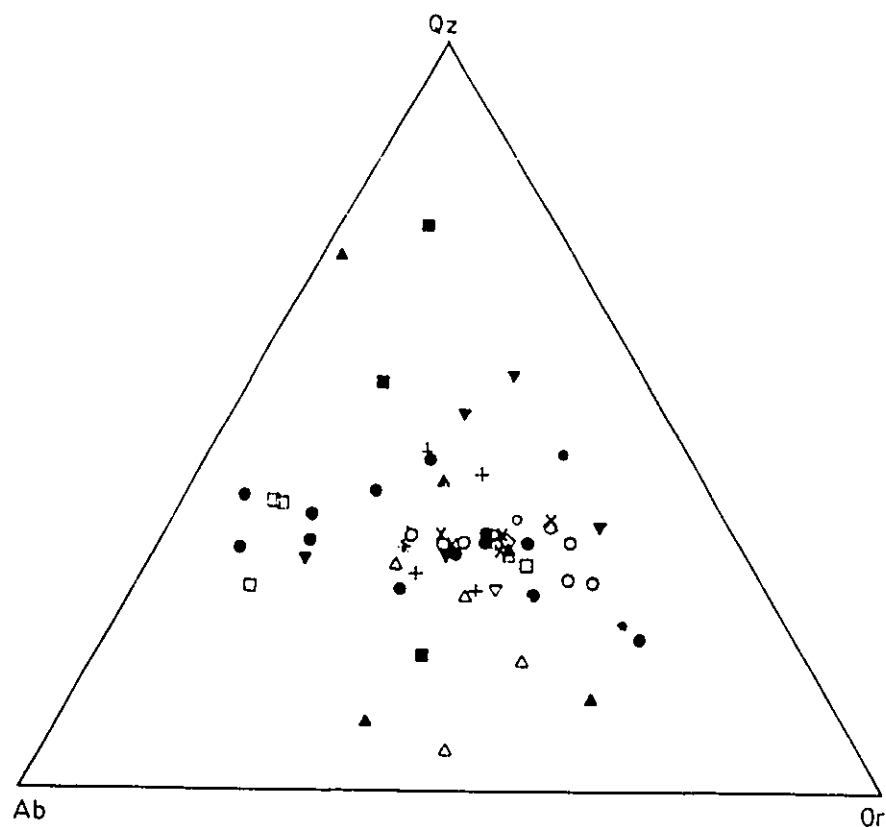


Figure 2.9 The distribution of a) normative quartz (Qz), albite (Ab), and orthoclase (Or) (Table 2.6 and appendix 3.6). The points away from the center represent altered pegmatites, which usually contain high Fe and Mg. See Figure 2.5 for symbols. By far most of the samples are represented by the near eutectic composition considering that many of the samples are averages.

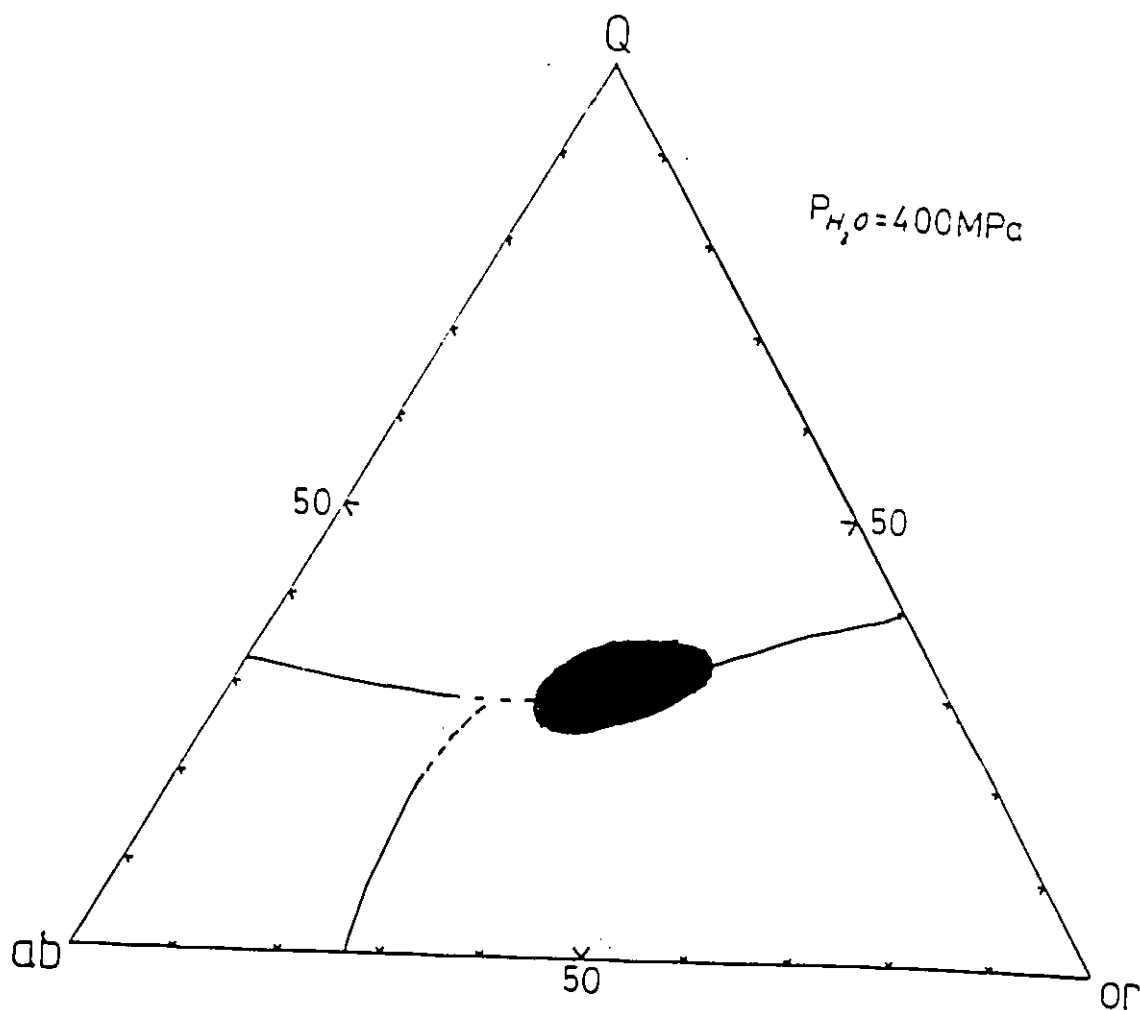


Figure 2.10

Phase equilibria in the Quartz (q) - K-feldspar (or) - Albite (ab) H_2O ternary system at 400 MPa (approximate) from Luth et al. (1964). Patterned area represents most of the pegmatite data (*Figure 2.9) from the Grenville pegmatite samples compiled. *Note that the samples represent an average of many samples.

the expense of feldspar (Wyllie and Tuttle, 1961; Manning, 1981) with the addition of 4 weight percent HF. Wyllie and Tuttle (1959) noted that increasing the partial pressure of CO_2 raises the granite solidus. This phenomena may be responsible for the premature crystallization of pegmatites in carbonate-bearing lithologies.

2.5 Isotopic considerations

The following discussion of stable and radiogenic isotope systematics of the pegmatites is brief as a more detailed understanding of the isotopes systematics in skarns is required to fully appreciate the information. Oxygen and carbon isotope analysis of calcite from 6 of the pegmatites indicate a tight cluster near $\delta^{18}\text{O} = 12\text{‰}$ and $\delta^{13}\text{C} = -2.8\text{‰}$ (Table 2.7). Generally, there is a covariation in ^{18}O and ^{13}C isotopes. The calcite within the pegmatites is suspected to have crystallized from a late stage chemically-modified hydrothermal fluid at about 550°C. The oxygen isotope fractionation between H_2O and calcite ($\delta_{\text{c}} - \delta_{\text{cc}}$) is 1.2‰ @ 550°C (O'Neil et al., 1969) (0° to 500°C) however, the graphical representation of the curve by Friedman and O'Neil (1977) indicates a fractionation of 2.5‰. The fluid coexisting with the calcite would have an approximate $\delta^{18}\text{O}_{\text{H}_2\text{O}} = 10.8\text{‰}$. At 550°C the carbon isotope fractionation between CO_2 and calcite is 2.5‰ (Bottinga, 1969) corresponding to a $\delta^{13}\text{C}_{\text{CO}_2}$ composition of 0‰. The calcite hosted with quartz in the core of a partially zoned pegmatite at the MacDonald feldspar deposit has a $\delta^{18}\text{O} = 12.2$, therefore quartz in equilibrium with this calcite would have $\delta^{18}\text{O} = 11.25\text{‰}$ which is higher than pegmatites examined by Shieh and Schwarcz (1974) of 8 to 9‰. The calculated carbon isotopic composition of the CO_2 is similar to marine marble (Dienes and Gold, 1969; Shieh and Taylor, 1969). The $\delta^{13}\text{C}$ of calcite from the pegmatite is evidence for the CO_2 infiltration into the pegmatite. The decarbonated CO_2 produced during skarn formation in the

Table 2.7 Oxygen and carbon isotope analyses of calcite from pegmatites

	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	$^{87}\text{Sr}/^{86}\text{Sr}$
MacDonald Pegmatite (26F)	12.01	-2.25	
MacDonald Pegmatite (26G)	12.44	-1.61	0.7041
MacDonald Pegmatite (26H)	12.26	-2.13	
ACME Mo Pegmatite (121H)	11.53	-2.92	
ACME Mo Pegmatite (121J)	11.36	-3.04	0.7041
Faraday U Pegmatite	11.92	-2.30	
Faraday Pegmatite (126)	15.08	-3.38	
N. Armstrong Pegmatite (127)	13.46	-2.21	0.7053
Kenmac-			
Chibougamau Pegmatite (128)	8.34	-5.15	0.7202

Average $\delta^{18}\text{O}$ = 12.04, 1s = 1.80 ‰ and $\delta^{13}\text{C}$ = -2.78, 1s = 1.04 ‰

dolomitic marbles could be entrained into the pegmatite by traveling down chemical potential, and possibly pressure, gradients within the fluid phase. Shieh and Schwarz (1974) determined the oxygen isotopic composition of Grenville pegmatite minerals and host gneisses within the Central Gneiss Belt and found that coexisting mineral temperatures were low for the pegmatites. They also noted that the pegmatites and gneisses were isotopically light and suggested that an isotopically primitive, externally-derived fluid was responsible and may have been involved in the production of the partial melts. In a detailed analysis of isotopic and compositional systematics of granitoid rocks in the Grenville Province, Wu and Kerrick (1986) found that the Algonquin batholith has an average of $\delta^{18}\text{O}$ between 7 and 8 similar to the White lake pluton. The Cheddar granitoid gneiss is slightly higher with an average of $\delta^{18}\text{O} = 8.8$ (Wu and Kerrick, 1986). These are all possible protoliths for the granitic pegmatites.

A low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was found for 3 calcites from these Grenville pegmatites and one moderately high sample (128) (Table 2.6). This complements the interpolated initial strontium isotopic signatures (ca. 0.705) of uraniferous Grenville pegmatites presented by Fowler and Doig (1983a) and the low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.704) of anhydrite from the Faraday uranium-bearing granitic pegmatite (Rimsaite, 1982). Fowler and Doig (1983a) have interpreted their isotopic data as evidence for a radiogenically primitive source for the pegmatites. These initial strontium values of the pegmatites are too low to have originated from a paragneiss protolith but is compatible with the isotopic systematics of Grenville basement gneisses (Bell and Blenkinsop, 1980; Wu and Kerrick, 1986).

2.6 Discussion

2.6.1 Origin of Grenville pegmatites

The origin of the uranium-, molybdenum-, and REE-bearing granitic pegmatites is still poorly understood. The dikes are similar to other uranium and REE pegmatites emplaced at moderate depths (lower mesabyssal) (Strong, 1988) which have been hypothesized to be of either local anatectic and igneous origin in many other areas (Černý, 1982b). There are dominantly four hypotheses for the origin of these granitic pegmatites: 1) *in situ* anatectic (proximal to source protolith) (Allen, 1971; Tremblay, 1974; Masson and Gordon, 1981; Storey and Vos, 1981b; Habib, 1982; Ford, 1982, 1983), 2) partial melting and fractional crystallization of a partial melt derived at depth (middle to lower crust or mantle? source (Nishimori et al., 1978; Masson and Gordon, 1981), 3) granite-pegmatite association (Fowler, 1980; Fowler and Doig, 1983a), and 4) hydrothermal formation (S. Lumbers, personnel communication).

With respect to the first hypotheses, there is considerable evidence for "in situ" partial melting: 1) development of migmatites, melanosomes, and leucosomes within some gneisses of the CMB, CGB, and the CGT, 2) the greater abundance of pegmatites in the quartz feldspar gneisses than other rock types (Lumbers, 1982) suggesting a compositional control to their formation, 3) development of melanocratic selvages on the mineralized pegmatites, and 4) granitic pegmatites are only associated with rocks exceeding middle amphibolite grade implying a relationship to metamorphic grade. In several studies, the composition of migmatitic gneisses hosting granitic pegmatites was examined in order to evaluate the possibility of an *in situ* anatectic origin for the pegmatites (Allen, 1971; Tremblay, 1974; Herver, 1979; Masson and Gordon, 1981; Ford, 1983).

However, there are other considerations: 1) The development of leucosomes and melanosomes do not imply partial melting of the gneisses during local peak metamorphic conditions. In addition, the mineralized pegmatites have significantly

younger ages (ca. 980-1030 Ma; Easton (1986) or ca. 1040-1070 Ma; Heaman and Lammers (1987)) compared to the Ottawa Orogeny (ca. 1090 to 1100 Ma; Easton, 1986) 2) Pegmatites are definitely more numerous within quartz-feldspar gneisses but this is to be expected since with any degree of hybridization and/or contamination with mafic or carbonate rocks could chemically modify the granitic melt resulting in crystallization. Mafic gneisses, amphibolites and marbles may act as compositional barriers to these low temperature granitic melts (Fowler, 1989) 3) The process of hybridization and/or skarnification (H/S) associated with the mineralizing process produces assemblages which crudely resemble melanosome. Considering that these zones are indeed the richest in uranium, thorium, REE, and occasionally molybdenum, far exceeding original host rock abundances, lends support for a more complex origin. 4) Retrograde pressure-temperature-time relationships (Martignole, 1986) indicate pressures of 400 MPa (4 kb) and 500°C during the time of pegmatite emplacement, which are themselves not sufficient to form partial melts.

In general, the late-tectonic granites exposed in the Grenville Province have slightly older ages (>1070 Ma; Corriveau et al. 1990) but this does not preclude granites at depth. Fowler and Doig (1983a) noticed the primitive strontium isotopic signatures of both the late-tectonic granitic plutons and pegmatites. This could indicate that these granitoids remained hot and were remobilized during subsequent uplift thus inheriting the primitive isotopic signature. Corriveau et al. (1990) has recently described alkaline granitoid rocks in the region which have ages between 1100 and 1070 based on U-Pb zircon geochronology, which significantly narrows the age discrepancy between the pegmatites and the granitoid rocks.

A hydrothermal origin has been proposed for the origin of some of these pegmatites; this proposal, however, is not analogous to the hydrothermal-structural hypothesis of Gresens (1967a and b). This hypothesis has merit in certain instances: 1) mineralogic similarities with the quartz-feldspar gneiss, 2) zoned nature, 3) gradational but discordant contact with host rock, 4) absence of a granitic textured border and wall zone in the zoned varieties, and 5) high proportion of quartz to feldspar within the whole pegmatite body. In many instances, pervasive recrystallization and grain growth within the gneisses are associated with the metasomatic halo of a granitic pegmatite or a fluorite-apatite-calcite vein. These "pegmatites" have been designated as metasomatized wall rocks. Although there are major element similarities between the pegmatites and the migmatitic gneisses, the trace elements and the abundance of uranium, thorium, and REE indicate considerable fractionation of these rare-metal pegmatites. The chemical composition of these pegmatites is also very similar to pegmatites reviewed by Černý (1982a, 1982b), radioactive pegmatites (Ayres and Černý, 1982) and uranium, REE pegmatites (Kuzmenko et al., 1976). Fluorine is definitely an additional component considering that the micas are fluorine-bearing and portions of the pegmatite, and contact zones host abundant fluorite alteration.

2.6.2 Pressure and temperature considerations

The pegmatites are hosted in middle and upper amphibolite facies to, more rarely, granulite facies rocks of the Central Metasedimentary Belt. The granitic pegmatites are late tectonic, therefore the temperature and pressure conditions prevailing at the time of emplacement were not peak regional metamorphic conditions. The alteration minerals (microcline, albite, scapolite, Ca pyroxene, hornblende, biotite, sphene, etc.) associated with the pegmatite margins (exocontact ± endocontact wall zone) are similar to amphibolite facies

assemblages hence the equilibration temperature of the wall-rock assemblage was close to the peak metamorphic conditions (Ottawan Orogeny).

The distribution of elements between coexisting minerals in pegmatites may be regular to irregular depending on the cation/site behaviour in the minerals; with proper calibrations regular distributions could be used as potential geothermometers (Kretz, 1970). The distribution of Rb in coexisting phlogopite and K-feldspar (sanidine) has been determined experimentally at various temperatures (2 kbar) (Beswick, 1973). Lentz (in prep; Appendix 6) has used the distribution of Rb between biotite and K-feldspar to calculate an approximate equilibration temperature (600°C) which may represent crystallization conditions.

Fluid inclusions in quartz, fluorite, and calcite from the Hybla Pegmatite field, including the MacDonald (zoned pegmatite) Feldspar Mine, near Bancroft, Ontario provide rough pressure constraints under which the zoned pegmatite formed (Peach, 1951). A re-evaluation of the ten fluid inclusion decrepitation analyses of quartz gives a mean value of 322°C ($\pm 15^\circ\text{C}$); calcite yields values about 40°C lower. Decrepitation temperatures are generally lower than the true homogenization temperature so 300°C was chosen as a reasonable value of the liquid-vapour (L-V) homogenization temperature. At this temperature pure H_2O corresponds to a density of approximately 0.70 g/cm³. The isochore for a fluid density of 0.7 g/cm³ intersects 300 MPa, 400 MPa, and 500 MPa pressures at approximately temperatures of 580°, 670°C, and 790°C, respectively (Roedder, 1984). A temperature of 580°C and a pressure of 300 MPa seem to be the most reasonable for the conditions of crystallization of the MacDonald zoned pegmatite.

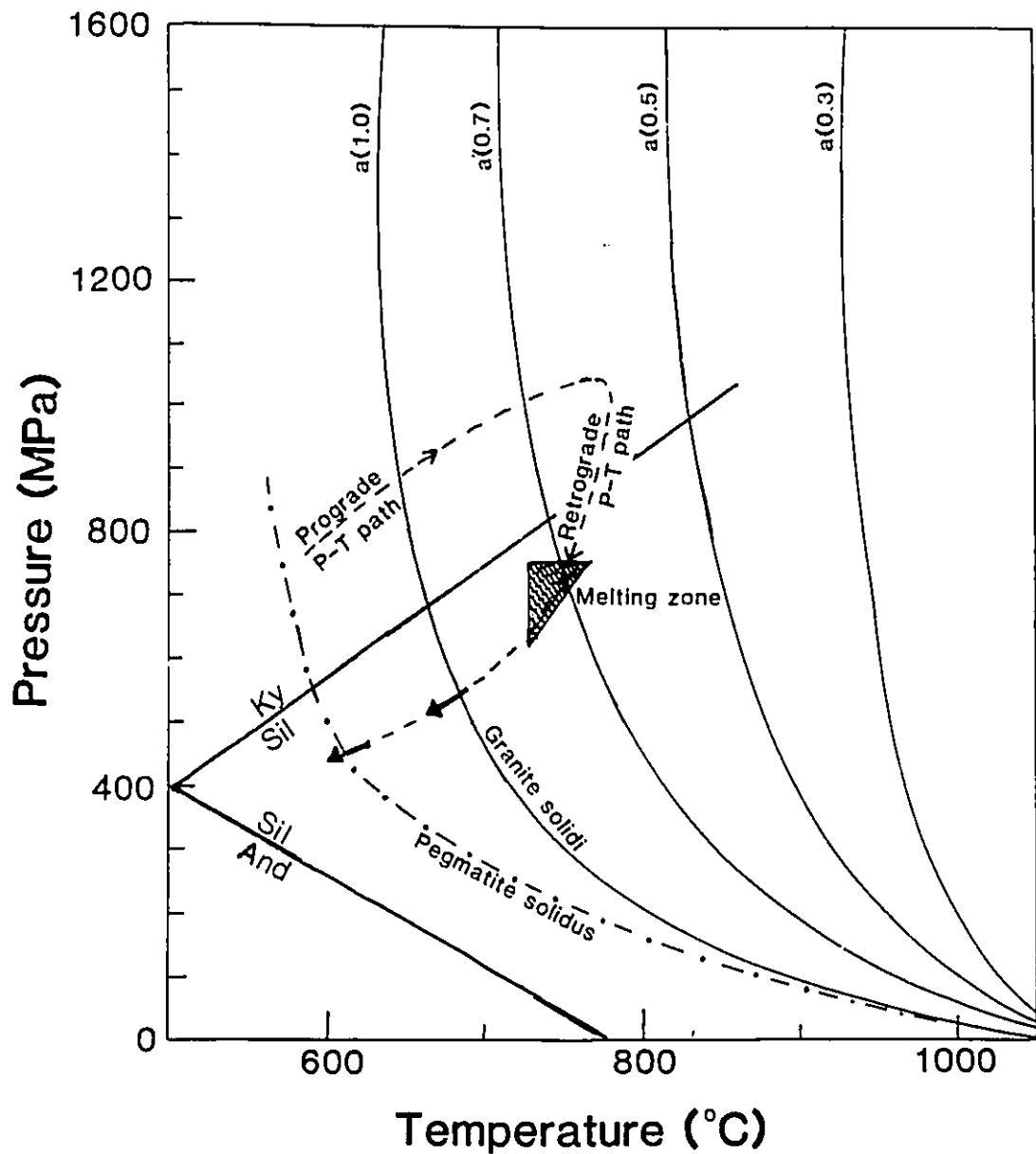


Figure 2.11 Pressure-temperature diagram indicating a possible zone of partial melting and a path of liquid ascent to the pegmatite emplacement depth of 400 MPa. The granite solidus is from Burnham (1979). The proposed pegmatite solidus is similar to the Harding pegmatite (Strong, 1988). Retrograde P-T curve is similar that estimated by Martignole (1986) for the Maniwaki-Morin area, Quebec.

2.6.3 A revised hypothesis

There are two possible mechanisms for the generation of late tectonic partial melts: 1) introduction of volatiles into volatile-understaturated gneisses and 2) late-tectonic uplift along a pressure-temperature path (isothermal?) which crosses volatile-undersaturated melting curves, and/or metamorphic dehydration curves. There is no evidence for the underplating of the Grenville Province during the time of late-tectonic granite pegmatite emplacement.

The retrograde pressure-temperature path would have to be almost isothermal for a portion of the cycle in order to cross the steep anhydrous melting curves. Indares and Martignole (1984) and Martignole (1986) proposed an uplift path in the Maniwaki area (CGT) similar to the path of England and Thompson (1984) which has a retrograde path which could initiate partial melting in the deeper portions of that crustal segment. However, this may not apply to all of the Grenville Province.

A tentative hypothesis for the generation of the pegmatites would involve partial melting of middle to lower crustal rocks during regional uplift by intersecting H_2O undersaturated melting curves (Figure 2.11). This process may be accompanied by influx of external water (volatile saturated) derived by metamorphic dehydration/defluorination in the vicinity and at depth. It is well understood that the generation of volatile-saturated granite melts is extremely rare beyond the initial stages of partial melting (Brown and Fyfe, 1970; Wyllie, 1977; Winkler, 1979; Grant, 1985) hence most partial melting will be at reduced activities of H_2O . The generation of melts is most probably attributable to a combination of both processes, introduction of fluxes derived from metamorphic dehydration reactions and uplift along a pressure-temperature path conducive to generating lower crustal partial melts, similar to the process proposed by Strong and Hanmer (1981) and Černý

and Meintzer (1988). The generation of partial melts with volatile activities less than total pressure is key to their subsequent mobility and differentiation. The proposal for introduction of volatiles into the crust has some merit considering the stable isotopic results of Shieh and Schwarcz (1974) in gneisses and pegmatites of the Central Gneiss Belt (CGB), the low initial $^{87}\text{Sr}/^{86}\text{Sr}$ data on Grenville pegmatites (Fowler and Doig, 1983a), the strontium and oxygen isotopic compositions of Grenville basement gneisses (Wu and Kerrick, 1986), and the oxygen and strontium isotopic data found during this study (Chapter 4).

The presence of CO_2 in granulite facies rocks could be responsible for their lower H_2O activities which would affect the solidus temperature of the melts (Wyllie and Tuttle, 1959) similar to anhydrous melting conditions. The presence of fluorine however helps to reduce the melting temperature of the melts (Wyllie and Tuttle, 1961). Late tectonic hydrothermal solutions associated with emplacement of the late-tectonic granite pegmatites are seemingly responsible for the retrograde alteration of granulite to upper amphibolite assemblages in parts of the Grenville Province (Davidson, 1986). Further dehydration of upper amphibolite facies rocks may occur during regional uplift (Wyllie, 1977; Grant, 1985) which could be responsible for the introduction of fluids into volatile-undersaturated gneissic rocks could be responsible for the production of partial melts within portions of the CGB. These low temperature melts would begin crystallizing during their ascent to higher crustal levels. The melt derived by partial melting would also be depleted in Th, Zr, Y (U) since they are hosted in refractory minerals which remain in the melanosome (Weber et al., 1985; Sawyer, 1987; Sawyer and Barnes, 1988). However, melt/crystal partition coefficients for granitic compositions (Arth, 1976) and uranium (Dostal and Capedri, 1975) indicate that all these elements are

enriched during fractional crystallization of quartz and feldspar. Sawyer (1987) suggests that positive Eu anomalies in pegmatites (Quetico Belt, Northern Ontario) represent cumulate plagioclase during pegmatite fraction (filter pressing).

2.6.4 Fractional crystallization and vapour phase saturation

The Rb, Ba, and Sr content of the K-feldspars have similar trends to those presented by Černý et al. (1985) for other pegmatite deposits. Černý et al. (1985) have suggested that extreme enrichments of incompatible elements are produced by element partitioning from a melt to a coexisting volatile phase. The separation of a volatile phase during the emplacement and crystallization of granitic melts is possibly responsible for the further enrichment of U, Th, Mo, and REE in the pegmatites and skarn.

Fowler and Doig (1983b) have suggested that the REE distribution in Grenville pegmatites is a result of incongruent hydrothermal dissolution of calcic plagioclase rather than only due to fractional crystallization. Fowler and Doig (1983b) present evidence for hydrothermal alteration of the granitic pegmatites based on the relationship between Eu/Ce and U/Th ratios.

The presence of numerous salt-bearing fluid inclusions in apatite, and diopside in proximal skarn (Salvi, 1987) is evidence that the pegmatite-derived hydrothermal fluids were quite saline. Kilinc and Burnham (1972) have shown that chlorine is strongly partitioned into the vapour phase from a crystallizing melt. Holland (1972) found that the partition coefficients for Fe, Mn, and Zn between vapour and melt were directly a function of chloride concentration. Chlorine concentration was also a major factor in the high Fe solubilities determined in vapour/melt partitioning experiments (Whitney et al., 1985). In general, iron is enriched in the proximal skarns (chapter 3) and the increasing abundance of Fe, Mn, and Zn in biotite from the most evolved pegmatites (Lentz, in prep; Appendix 6) could be interpreted

in terms of the hydrothermal mobility of these elements as chloride complexes.

The association of fluorite, fluoroapatite, and fluorine-rich micas with the most U, Th, and REE enriched pegmatites is formidable evidence of HF in the magmatically-derived hydrothermal fluid. HF remains dissociated even to high temperatures ($< 500\text{ }^{\circ}\text{C}$) favouring F^- as a hard complexing ligand (Holland and Malinin, 1979). Based on the mineral assemblages, the fluids derived from the pegmatites would have weakly acidic to weakly alkaline pH's which would offset the role of HF in the mobilization of the high-field-strength elements. Experimental studies indicate that HF is more strongly partitioned in favour of the melt phase during initial crystallization but as volatile phase separation proceeds HF is evolved (Burnham, 1979). Flynn and Burnham (1978) determined that higher concentrations of chlorine and fluorine increased the partitioning of REE into the coexisting fluid, particularly divalent Eu, at lower pressures. In all cases however, the REE partitioned strongly into the glass. Unfortunately, these models are not realistic since with increasing crystallization of quartz and feldspar the concentration of REE in the melt will increase with greater strain on the melt structure (octahedral sites) hence vapour/melt partition coefficients will tend to increase as crystallization proceeds. Keppler and Wyllie (1990, 1991) have experimentally determined that at magmatic temperatures uranium is partitioned more strongly into a vapour phase coexisting with a granitic melt with high activities of HCl and HF whereas only high HF activities are responsible for enhance partitioning of Th into the vapour phase. This has implications on the differential mobilization of uranium and thorium during volatile phase separation.

The presence of the carbonate in several pegmatites indicates that CO_2 was present in the pegmatite-derived

hydrothermal fluid probably due to infiltration of CO_2 from the skarn environment. Flynn and Burnham (1978) noted that CO_2 did not enhance REE partitioning as was commonly believed. However, this may be influenced by the moderate pH conditions of the experiment where H_2CO_3 is stable at high temperatures. Unfortunately, no information is available on complex alkali carbonate complexes.

Hydroxide complexes are responsible for the mobilization of many major-elements (Si, Al, Ca, Mg, etc.) and trace-elements (Ti, Y, Zr, U, Th, Sn, REE) in some environments at intermediate to high pH's. Candela and Holland (1984) have determined the vapour/melt partition coefficients for Cu and Mo in granitic melts. They found that the partitioning of molybdenum is independent of chlorine and fluorine concentration in the experiment (molybdate species) whereas Cu was strongly partitioned into the vapour with increasing chloride concentrations.

It seems that the numerous ligands (F^- , Cl^- , and OH^-) and their abundance within the granitic pegmatites of the Grenville Province would play a major role in the mineralization process during volatile phase saturation.

The formation of uranium, thorium, REE, and molybdenum mineralization in association with the chemical evolution of the pegmatites which is a combination of protolith abundance, partial melting, fractional crystallization (and hybridization) and volatile phase separation.

2.7 Conclusions

- 1) The discordant and undeformed nature of many of the granitic pegmatites is compatible with their late-tectonic origin.
- 2) Geologic constraints and previous geochronological data indicate that the rare-metal pegmatites are late-tectonic (ca. 1020 to 1060 Ma) with respect to the Ottawa orogeny (ca. 1090 Ma; Easton, 1986).
- 3) The simple pegmatites are dominated by

quartz, feldspar and possibly a ferromagnesium mineral whereas complex pegmatites contain more numerous complex assemblages, which were formed by metasomatic interaction (hybridization) with the wall rocks. Hybridization is particularly evident in pegmatite sills.

4) Anomalous abundances of rare metals (U, Th, Mo, REE, and Nb) are normally associated with the contact zone (endoskarn or hybridized) of the pegmatites (e.g. Faraday U pegmatite deposit).

5) The presence of aplites, graphic texture, and the transition from unzoned to zoned granitic pegmatites is evidence of the evolution of a fluid phase from these pegmatites.

6) Geological, geochemical, and geochronological evidence has been presented that favours ultrametamorphism of radiogenically primitive rocks at depth possibly related to quasi-isothermal uplift after the Grenville (Ottawan) orogeny. However, a relationship to fractionated alkaline granitoid rocks may be associated with the introduction of heat from possibly late-stage evolved melts.

6) A review of whole-rock compositional data indicates moderate chemical evolution of the pegmatites. Although, the composition of the source protolith and fractional partial melting may produce a slightly evolved granitic melt, these rare-metal pegmatites are more chemically evolved than in situ pegmatitic melts indicating that quartz and feldspar fractionation is, at least, partially responsible for the chemical evolution of the pegmatites.

7) In general, normative quartz, albite, and K-feldspar contents are roughly coincident with the haplogranite equilibria at 400 MPa which indicates that the granitic pegmatite crystallized between 600° and 650°C.

8) Mineralogic and compositional data support metasomatic interaction of pegmatite melts with the wall rocks

(hybridization/skarnification) resulting in crystallization and in some instances rare-metal precipitation.

9) Trace-element enrichments in zoned pegmatites may be related to volatile- phase separation. The strong enrichment in uranium, thorium, molybdenum, niobium, and REE within the marginal zones of some pegmatites is directly related to the factors affecting pegmatite evolution particularly the hybridization and volatile-phase separation of H₂O-rich fluid containing HCl and HF.

Field, mineralogical and textural observations on the U-, Th-, Mo-, and REE-bearing Grenville pegmatites suggests that partial melting, fractional crystallization, hybridization, and volatile-phase separation are all responsible to some degree for the complex nature of these pegmatites.

CHAPTER 3

GEOLOGY AND PETROLOGY OF URANIUM-, THORIUM-, AND MOLYBDENUM-BEARING

SKARNS AND VEINS IN THE CENTRAL METASEDIMENTARY BELT OF THE GRENVILLE PROVINCE

3.1 Introduction and geological setting

3.1.1 Introduction

3.1.1.1 Scope of study

The petrogenesis of late-tectonic, uranium-, thorium-, and molybdenum-bearing skarns in the Grenville Province is problematic. The examination of numerous deposits may contribute to the overall understanding of their petrogenesis and may reveal similarities between various types of deposits including those without uranium, thorium, or molybdenum minerals.

In this chapter, data on the spatial distribution, temporal association, mineralogy, and textures of skarns and fluorite-apatite-calcite veins are reviewed and evidence presented for a genetic relation among them. Chemical compositions of minerals common to pegmatites, skarns, and veins are examined for inter-element comparisons. Inter-mineral element comparison (distribution coefficients) has been used to examine equilibrium between coexisting phases and determine differences in elemental distributions which may be associated with different temperatures of formation. Distributions of fluorine and chlorine in phlogopite and apatite were also examined on selected samples for purposes of geothermometry and determining halogen-element fugacity ratios. General aspects of the phase equilibria of contact skarns are examined to help constrain the conditions of skarn formation. Metasomatic reactions are briefly examined within the skarns and veins which may account for the somewhat peculiar mineral assemblages observed in these rocks.

The U and Th distribution between pegmatites, skarns, and fluorite-apatite-calcite veins on a local and regional scale is interpreted as additional evidence supporting a chemical association between these deposit types (Lentz, 1991a).

3.1.1.2 Terminology

A brief review of skarn (Zharikov, 1970; Einaudi et al., 1981) and vein terminology will be given to help clarify ensuing discussions. The term "skarn" originated as a Scandinavian mining word for calc-silicate gangue associated with Fe-ore and sulphide deposits (in Archean rocks) especially where these occur in marble or limestone. In recent years, it is generally agreed that "skarn" should be applied to Ca-Fe-Mg-Mn silicate assemblages formed by the replacement of carbonate-bearing rocks. There are three dominant types: i) those formed by near-isochemical regional or contact metamorphism of siliceous carbonates, ii) those formed by exchange of silicate rocks with carbonate-bearing rocks (bimetasomatic skarn), and iii) those formed by infiltrative metasomatism (Si, Al, Fe) of carbonate-bearing rocks which would include both magmatic- and metamorphic-metasomatic skarns. Zharikov (1970) provided a definition of skarns:

"Skarns (magmatic) are limy-magnesian-ferruginous metasomatic silicates and aluminosilicates formed in high-temperature zones of contact halos of intrusions by interactions implemented by magmatogenic solutions between carbonate rocks and magma or intrusives or other aluminosilicate rocks."

However, bimetasomatic skarns are also formed by the chemical exchange between unlike lithologies due to reciprocal diffusion of elements. Magmatic (magmatic-metasomatic) exoskarn (exomorphic) is formed by replacement of carbonate-bearing rocks during infiltration of magmatic-hydrothermal solutions. Magmatic endoskarn (endomorphic) is formed by the metasomatic replacement of igneous rock responsible for the skarn development. Metamorphic-metasomatic skarns are formed

by solute-bearing metamorphic-hydrothermal fluids formed during regional metamorphic dehydration reactions interacting with carbonate-bearing lithologies to produce calc-silicates. Skarnoid rocks are the products of metasomatic replacement of carbonate or carbonate and aluminosilicate rocks. Silicated marble is a unique term (Satterly, 1957) for marble-hosted skarns with an appreciable amount of calcite forming the matrix to the silicate minerals (> 20 vol.% calcite) whereas the skarns do not have matrix supporting this much calcite. The author prefers a broader definition of skarns than the definitions outlined above. As it is used in this study, skarn is a rock consisting of calc-silicate and associated minerals which by interpretation formed by metasomatic replacement of pre-existing minerals. This differs from other definitions because the host rock may not be marble, but clinopyroxenite, amphibolite, or gneiss. This definition is favoured because in many areas the alteration is so extensive that the original protolith is commonly obscured. Within a particular area, this results in skarn assemblages within different units which are very similar. In this study, these calc-silicate-bearing assemblages are generally coarser grained than the host rock in which they have formed. Metasomatite is used to refer to hydrothermally-altered gneisses which produced an assemblage of microcline, or albite, Ca pyroxene, hornblende, phlogopite/biotite, titanite, and more rarely quartz without calc-silicates. Primary skarn assemblage refers to the assemblages formed during the first episode of metasomatic replacement whereas secondary refers to those assemblages which are definitely later and crosscut and/or replace primary assemblages. Abbreviations used in this section are those proposed by Kretz (1983) unless otherwise indicated.

In this study, vein is used to represent a two dimensional feature cross-cutting which may be either a dilatant fracture space filling (ie. calcite, fluorite) or a replacement of the

host rock (ie. Ca pyroxene replacement of marble). In a general sense, the fracture filling derives no components from the host rock to the fracture. The term vein-dyke for the fluorite-apatite-calcite veins (or bodies) was coined by Ellsworth (1932) and has been continually used in the literature until recently (cf. Hogarth, 1989). The ambiguous nature of this term captures the uncertainty of origin (magmatic or hydrothermal) for these bodies. The overwhelming preliminary evidence for a hydrothermal origin for these bodies has led the author to refer to them simply as veins to avoid any further ambiguity.

3.1.1.3 Previous research

Field studies of these deposits began with deSchmid (1912), Spence (1929), Spence and Carnochan (1930), Landes (1938), Currie (1951), Satterly (1957), Shaw (1958), and Vokes (1963). These studies were continued by Carter et al. (1979), Storey and Vos (1981), and Masson and Gordon (1981). The major mineralogic and geochemical studies of the silicate and carbonate fractions of these skarns including evaluation of thermodynamic equilibrium began with Kretz (1960), Shaw et al. (1963), Shaw et al. (1965), Haughton (1971), and Karvinen (1973). Strontium isotopic studies of Grenville marbles, skarns, and veins was made by Powell (1965), and Gittins et al. (1969).

There are two important points to clarify; there is considerable confusion as a result of similarity of skarns and primary clinopyroxenite (pyroxene granofels) host rocks. In this study, the latter are interpreted as having formed by separate processes. Fine-grained clinopyroxenites and related plagioclase-Ca pyroxene gneisses are commonly interlayered with marbles, calc-silicate marbles, and Ca pyroxene-bearing, quartz-feldspar gneisses (van de Kamp, 1968). These units are interpreted as products of metamorphism of impure siliceous dolomites (van de Kamp, 1968) and not interpreted as skarns. However, the mineralogy is similar between these primary units

and the pegmatite- and vein-related skarns. The absence of layer-parallel fabric, coarse grain size, and the exotic mineralogy are a few of the main distinguishing features.

Metasomatic alteration of quartz-feldspar gneisses to an assemblage of Ca pyroxene, hornblende, microcline, and titanite with interstitial fluorite, calcite, and apatite within the vicinity of the pegmatites has commonly been confused with the textural and mineralogical similar alteration selvage (skarn) associated with fluorite-apatite-calcite veins. These assemblages have also been misinterpreted as syenite. The vein-related and pegmatite-related alteration of the gneiss was recognized as "syenitized gneiss" exemplifying its metasomatic origin. Without the surface exposure of the pegmatite or vein, these coarse-grained alteration assemblages are virtually indistinguishable.

3.1.1.4 General aspects of skarns

There are numerous complex petrochemical aspects to the examination of skarns. These include the examination of elemental associations, petrology, mineral parageneses, mineral compositions, mineral and fluid equilibria, elemental distribution, and mechanisms of skarn formation. In this study, an attempt was made to integrate many of these aspects because they are all important in evaluating the petrogenesis of the skarns and fluorite-apatite-calcite veins. At this point, a brief account of previous research into the various facets of skarn geology will be given especially those studies pertaining to the petrogenesis of these Grenville skarns.

There is voluminous literature critical to evaluating the petrogenesis of skarns. It is important to note that most of these studies are on mineralized skarns and therefore a certain amount of the academic emphasis is related to the process of mineralization. Many common aspects of skarn petrogenesis are examined in the studies on mineralized and non-mineralized skarns utilizing similar analytical

techniques. There are several key papers on the petrogenesis of skarns that were invaluable in this study. They include the exhaustive compilation of elemental associations, mineral compositional data and mineral equilibria by Zharkov (1970) and Einaudi et al. (1981). There are numerous experimental and thermodynamic studies of mineral equilibria that were particularly helpful to this study. These include: Wintsch (1975), Taylor and Liou (1978), Walther and Helgeson (1980), Bowers and Helgeson (1983), Luce et al. (1985). The GEOCALC program, formulated at the University of British Columbia, was used to calculate some mineral equilibria (Berman et al., 1985, 1988, 1989). A few particularly key papers examining mineral equilibria and petrogenesis in contact skarns were useful; Shay (1975), Kerrick (1977), Walther (1983), Bowman et al. (1984), and Frisch and Helgeson (1984). A common theme throughout these papers is that contact skarns formed by decarbonation of marbles and that they may be modelled using chemical potential diagrams. Also, a static fluid phase was responsible for the transfer of elements, but H₂O infiltration was occurring in only some instances. Previous studies of elemental partitioning between coexisting minerals by Kretz (1960), McIntrye (1963) and Kretz (1980) were particularly useful in the examination of mineral-chemical equilibria. A reconnaissance fluid inclusion study of the Grenville Zenith Mo-U skarn deposit by Salvi (1987) indicated saturation in several salts with no obvious CO₂ present. The examination of stable isotope systematics in contact skarns by Shieh and Taylor (1969), Taylor and O'Neil (1977), and Bowman et al. (1985), and Taylor and Bucher-Nurminen (1986) helped considerably in the examination and interpretation of the stable isotope systematics in the skarns and veins examined in this study. Most of these authors found that a decrease in the ¹⁸O and ¹³C content of minerals toward the intrusive rock that required infiltration of an isotopically light H₂O-rich

fluid to produce the isotopic spectrum observed. Solubility data on quartz and alkali feldspar (Anderson and Burnham, 1983), magnetite (Chou and Eugster, 1977), calcite (Fien and Walther, 1987, 1989), fluorite (Richardson and Holland, 1979a and b), and apatite (Dernov-Pegarev and Malinin, 1985) helped contribute to the understanding of the skarn and vein petrogenesis. The integration of all these aspects contributes to a better understanding of skarn and vein petrogenesis.

3.1.2 Local geology

3.1.2.1 Introduction

The Wilberforce and Dacre areas of Ontario and the Yates area near Sandy Creek, Quebec have been the focus of the present research; additional data were obtained at the Faraday U-Mo Mine, MacDonald pegmatite, South State U skarn, Spain U-Mo pegmatite and skarn, Hunt Mo pegmatite and skarn, and the Zenith Mo (U) pegmatite and skarn deposits of Ontario and the Bain Mo-U skarn and pegmatite, Kirkham (Quebec Metallurgical Industry) Mo-U-Th skarn, vein, and pegmatite, Bear Lake (Leidke) Mo skarn and vein, and the deposits on the northern part of Grand Calumet Island in Quebec (Figure 1.2 and 1.3).

The field observations of numerous previous researchers, particularly their maps, have contributed significantly to the present study.

3.1.2.2 Cardiff-Monmouth area

Numerous deposits of uranium, thorium, molybdenum, REE, apatite, and fluorite occur in the Cardiff-Monmouth area, northwest of Bancroft and many of these were described by Satterly (1957). The Harcourt Mo skarn, American Molybdenite Mo skarn, and the Joiner Mo (U) apatite-calcite vein were studied by Karvinen (1973). The petrogenesis of the Richardson (Fission) uranium fluorite-apatite vein deposit was investigated by Rowe (1952). An investigation of fluorite deposits from the Cardiff (U) deposit, Richardson (U) deposit, Tripp deposit, Montgomery deposit, and Clark deposit was

carried out by Guillet (1964). The spatial relationship between pegmatites, skarns, and fluorite-apatite-calcite veins is evident in the vicinity of the Cardiff deposits particularly at the C Zone (Figures 3.1a and b) and at the Acmac Mo deposit, 1 kilometre southwest of Wilberforce. The Cardiff fluorite deposits are concordant to discordant fluorite-apatite-calcite veins hosted predominantly in granitoid gneisses (hanging wall) above an eastward dipping (30° to 40°C) graphite-bearing, diopside marble (Figure 3.1a). The marble-gneiss contact is the locus of intense shearing which produces a cryptocrystalline carbonate mylonite which has evidence of extension (Carlson et al., 1990). The mylonite is intruded by pegmatites and replaced by skarns and fluorite-apatite-calcite veins. These are in turn mylonitized. Five zones were identified by Guillet (1964) "A", "B", "C", "E", and "F" (Figure 3.1) all of which occur in the vicinity of the gneiss-marble contact. The concordant, gneiss-hosted fluorite-apatite-calcite veins are also mylonitized. Pegmatitic K-feldspar, pyroxene, hornblende, and magnetite mantle the gneiss-hosted fluorite-apatite-calcite vein. Small simple granite pegmatites and hybrid diopside-bearing granitoid pegmatites intrude marble along the contact at the base of an escarpment.

3.1.2.3 Dacre area

There are several deposits in the vicinity of Dacre of which the Hunt deposit Mo (#50) is well exposed and best known. Besides the Hunt deposit, the Spain U-Mo skarn (#47), Sunset Mo skarn (#48), Legris U pegmatite (# 49) and Dudgeon radioactive pegmatite (#44) were examined. The Lepine Mo skarn, Maloney Mo skarn, Charron Mo skarn, Guiney Mo skarn, Ross-O'Brien Mo skarn, Kiley Mo pegmatite and Lafleur's Lake Mo skarn are a few of the other occurrences (Carter et al., 1980) in the area.

3.1.2.4 Otter Lake area

The Yates uranium deposits are located west of Sandy Creek which is north of Otter Lake, Quebec. The good exposure of the Yates deposits (Camp I and II) and their similarity with other uranium deposits in the Grenville Province made them particularly amenable to further study. Kretz (1957, 1977) studied the regional geology of this part of Quebec while Shaw (1958) examined the Yates and other uranium deposits of western Quebec. Lafontaine (1980) examined the geology, mineralogy, and mineral compositions (including radioactive minerals) of the Yates deposits.

The Camp I zone is two hundred meters west of the Camp II zone and both are located 1 km southwest of the Matte zone. The Camp I zone is dominated by small phlogopite veins (0.1 to 0.3 m) hosted in a clinopyroxenite. A trench has exposed a weakly radioactive, narrow diopside-bearing granitoid pegmatite (several metres wide) which has associated marginal titanite-scapolite-pyroxene skarn and phlogopite-pyroxene skarn with calcite-phlogopite-pyroxene veins hosted in the clinopyroxenite (Figure 3.2a).

The Camp II zone is a moderately radioactive, coarse-grained silicated marble located at the contact between an amphibole gneiss and a biotite-quartz-feldspar gneiss, exposed in a few pits (Figure 3.2b).

The Matte zone is a dominantly concordant, radioactive, fluorite-apatite-calcite vein formed along the contact between a hanging wall biotite-quartz-feldspar gneiss and a narrow foot wall of amphibole-plagioclase gneiss (Figure 3.2c). The vein has a variable thickness (0 to 5 m) along strike and moderate dip. Medium- to coarse-grained titanite-apatite-phlogopite-scapolite-pyroxene skarn mantles the vein representing a replacement of the host amphibole-plagioclase gneiss. Medium- to coarse-grained titanite-apatite-pyroxene-microcline replace the biotite-quartz-feldspar gneisses marginal to the fluorite-apatite-calcite vein.

3.2 Skarns

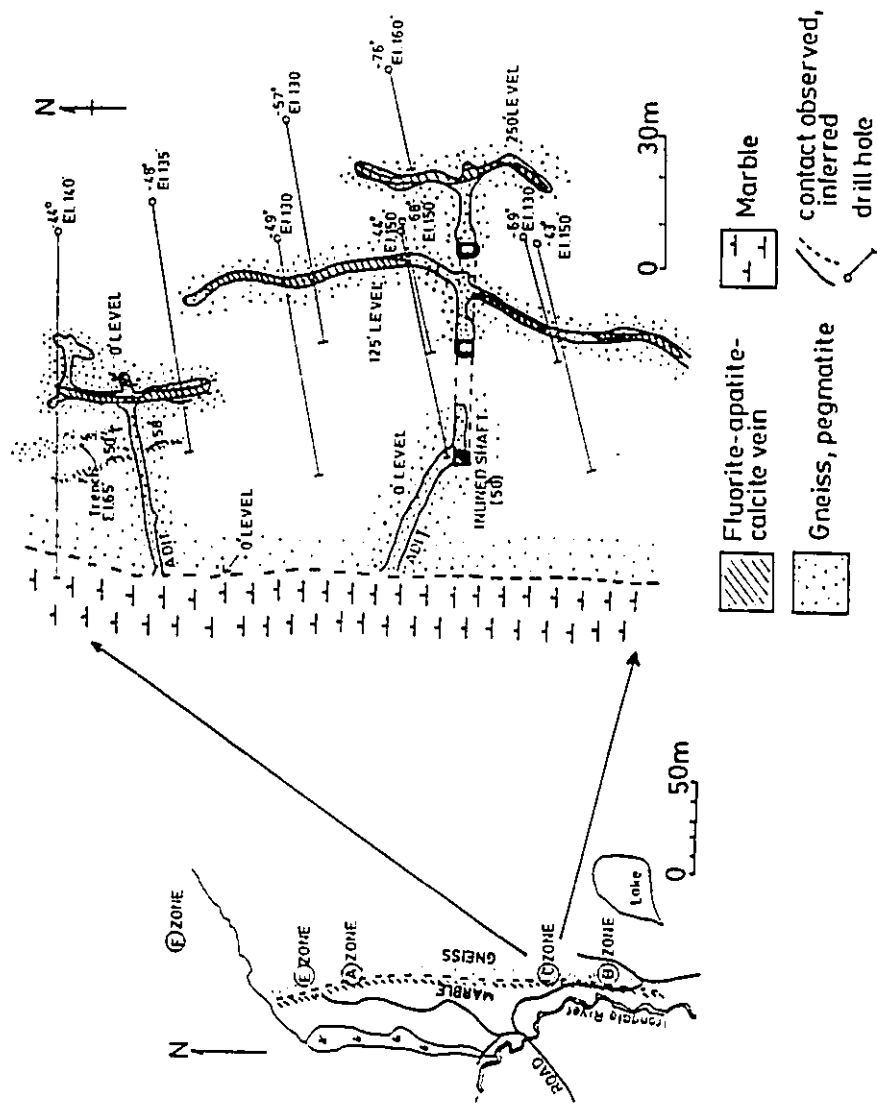


Figure 3.1 Cardiff fluorite deposits, A. Location of Cardiff "A", "B", "C", "E", "F" zones; B. Geology of Cardiff "C" zone (# 9), Cardiff township, ON (after Guillet (1964)).

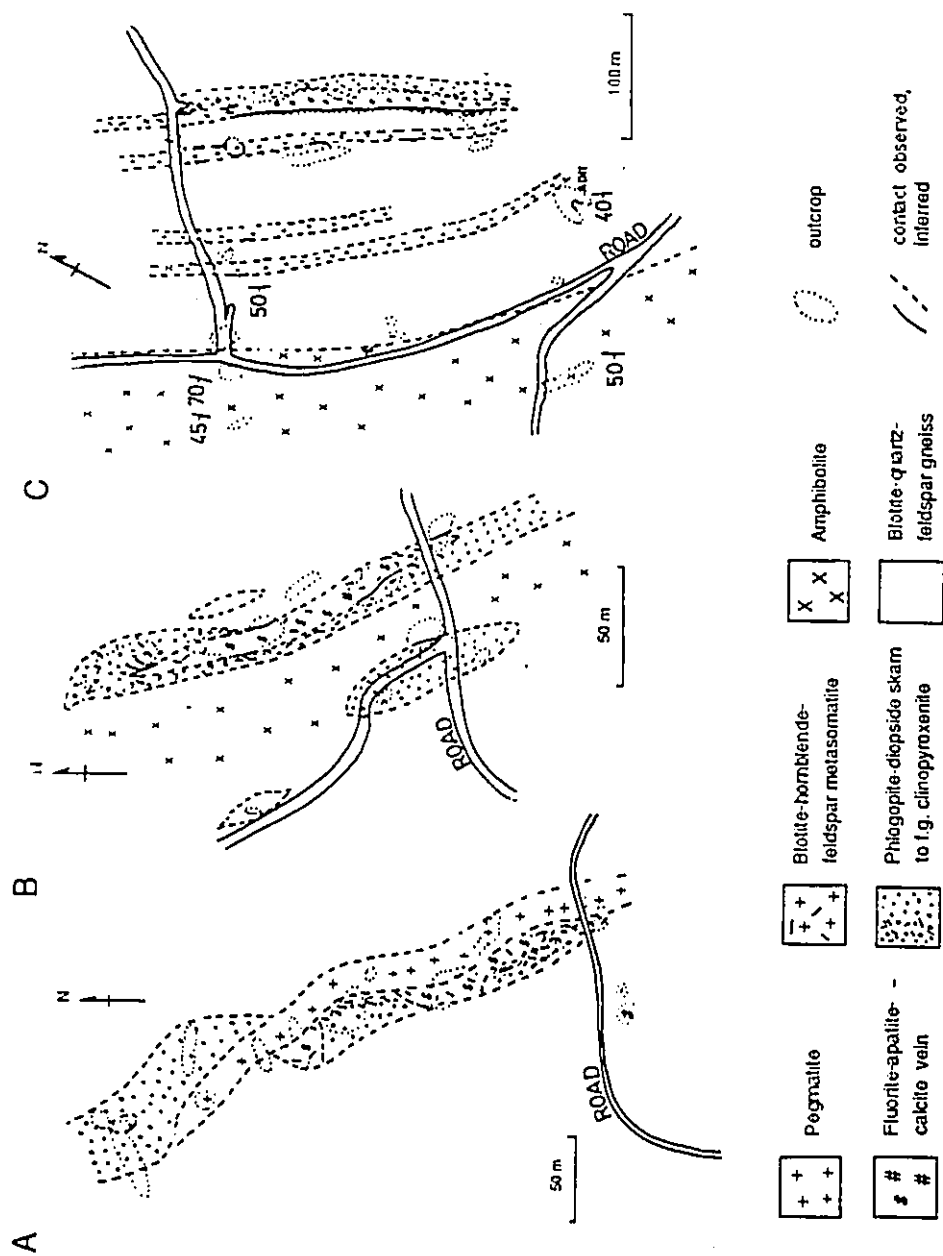


Figure 3.2 Geology of the Yates uranium deposits, A. Camp I zone (after Shaw (1958)), B. Camp II zone and C. Matte zone (after Lafontaine (1980)).

3.2.1 Introduction

The skarns and apatite-calcite veins can be subdivided into several groups based on their host rock. These comprise: i) clinopyroxenite-hosted, ii) marble-hosted, iii) amphibolite-hosted, and iv) gneiss-hosted skarns and veins and represent the dominant rock types within the Grenville Province. The compositional differences within these subdivisions will also affect the mineralogy and composition of the skarn alteration as was noted by previous researchers. Many of the descriptions of the skarns from each of these environments are similar to those from veins, which attest the similarity of these deposits.

3.2.2 Clinopyroxenite-hosted skarns

Clinopyroxenite has a high proportion of Ca pyroxene with plagioclase and/or scapolite. The protolith of pyroxene-scapolite gneiss has been interpreted as a mixture of carbonates and silicates (impure siliceous dolomites) which were metamorphosed to a diopside-rich assemblage (van de Kamp, 1968). This unit may be classified as skarn because it may have formed during regional metamorphism. However, to distinguish them from the late-tectonic metasomatic skarns they have simply been termed clinopyroxenite or diopsidite to exemplify its primary sedimentary origin. Pyrite and/or pyrrhotite are commonly finely disseminated in clinopyroxenite but account for less than a percent of the mode. Ca pyroxene is usually light green in colour whereas skarn Ca pyroxene ranges from a very light green to a dark green colour reflecting the compositional range $Di_{100} Hd_0$ to $Di_{50} Hd_{50}$ (diopside).

The coarse-grained assemblages, in and along the margins with granite pegmatites or hybrid granite pegmatites, are dominantly composed of Ca pyroxene, scapolite, plagioclase, K-feldspar, titanite. These bodies grade outward into a coarse-grained pyroxene-phlogopite assemblage and subsequently into

phlogopite veins unless there is a significant primary component of scapolite, plagioclase, K-feldspar or phlogopite in the primary clinopyroxenite. The pegmatite which intrudes clinopyroxenite in the Camp I zone of the Yates deposit has many of the features characteristic of the associated skarns (Figure 3.2a). The Acmac molybdenum deposit is located just west of the Cardiff "C" zone which is a granitic pegmatite with graphic texture which intrudes a stratabound clinopyroxenite unit in marble. Coarse-grained titanite-scapolite-Ca pyroxene skarn is associated along the margin with coarse-grained, phlogopite-pyroxene skarn and pyroxene- and phlogopite-bearing, apatite-calcite veins occur at some distance away from the contact. Salvi (1987) examined the Zenith uranium-molybdenum deposit, which is a coarse-grained feldspar-Ca pyroxene replacement skarn (Plate 3.3) formed along the contact of a graphic granite pegmatite and a clinopyroxenite. At the Quebec Metallurgical Industry's uranium occurrence, granitic pegmatite intruded a fine- to medium-grained clinopyroxenite which is hosted in silicated marble (Figure 3.3). A coarse-grained uranium-bearing, titanite-phlogopite-scapolite-Ca pyroxene assemblage is formed along the contact zones with the pegmatite.

At the Cardiff "C" zone, diopside-bearing granitoid pegmatite intruded a scapolite-Ca pyroxene gneiss with only minor interaction along the contact. At the Camp I zone of the Yates uranium mine, a marginal titanite-scapolite-Ca pyroxene skarn with distal phlogopite vein is hosted in clinopyroxenite at the margin with a titanite- and pyroxene-bearing granite pegmatite (Figure 3.4b; Plate 3.1). In the same area, phlogopite forms the outer portion of the scapolite-Ca pyroxene skarn (Figure 3.5a). At the Camp zone, scapolite is associated with Ca pyroxene in the endocontact zone of a small pegmatite (Figure 3.5b). Ca pyroxene-scapolite veins with marginal phlogopite are common in the Camp Zone (Plate 3.2). Feldspar-Ca pyroxene skarn is associated with the contact zone

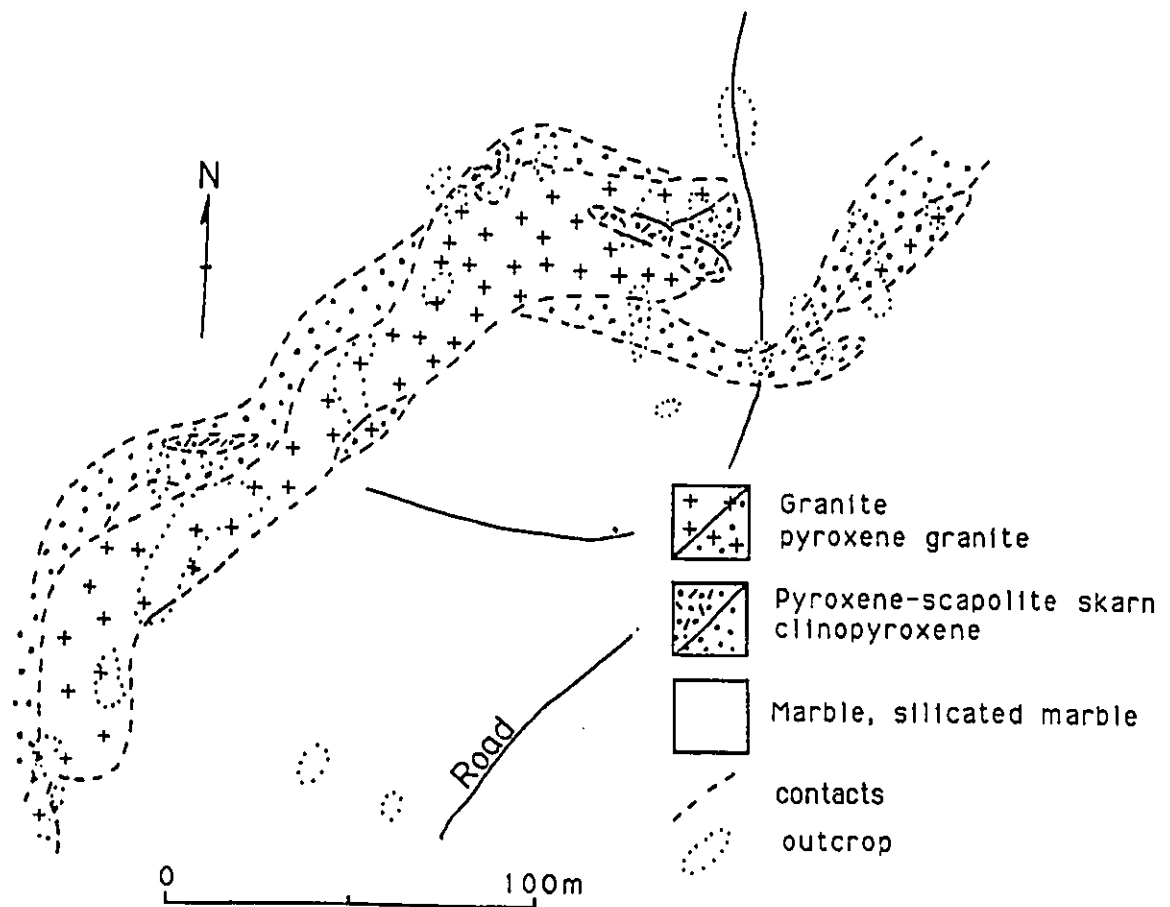


Figure 3.3 Geology of the Quebec Metallurgical Industry's uranium pegmatite and skarn deposit (after Shaw, 1958), or Kirkham west deposit, near Charteris, P.Q..

of several pegmatites for example the Quebec Metallurgical Industry's uranium occurrence (Figure 3.3; Shaw, 1958).

Primary tremolite is associated with phlogopite and scapolite which are hosted in Ca pyroxene skarn near the Camp I zone (Plate 3.4). At the Desmond U-Mo deposit north of Wilberforce, several quartz-calcite-tremolite veins are hosted in clinopyroxenite (Plate 3.5) and are similar to the phlogopite-feldspar-tremolite skarn veins hosted in clinopyroxenite at Rockingham uranium occurrence west of Barry's Bay (Plate 3.6). However, secondary tremolite-actinolite replace some of the primary Ca pyroxene-rich skarn assemblages.

3.2.3 Marble-hosted skarn

The skarns produced in marble are predominantly a function of the abundance of dolomite within the marble. The virtual absence of wollastonite in the skarns indicates that wollastonite-forming conditions were not attained. However, the absence of wollastonite may be due to compositional constraints in the proximal skarn. As previously mentioned, the silicated marbles (silicated marble skarns) are distinguished from other skarns by the presence of interstitial calcite. Marginal skarns with granite pegmatites and vein skarns produce an assemblage which is in equilibrium with the temperature, pressure, and activities of volatile and aqueous species. The presence of silicated marble (metasomatically altered Ca pyroxene- and phlogopite-rich calcite marble) along the roof zone and margins of the granite pegmatite suggest a genetic relationship (South State, Yates, Bicroft, Kemp, and Grand Calumet deposits).

The skarns may be decimetres to 10's of metres wide if hosted in dolomitic marble, whereas silicated marble can be much larger. The Cardiff "C" zone has several well developed examples of contact marble skarns with pegmatite where hybrid pyroxene granitic pegmatite has a fine-grained diopside exoskarn (Figure 3.7a). The endoskarns are dominantly

pyroxene-bearing with or without a replacement of primary feldspars by K-feldspar, plagioclase, or scapolite. At the contact (proximal exoskarn), the coarse-grained assemblage Ca pyroxene-feldspar (K-feldspar, plagioclase, and/or scapolite) grades into monomineralic diopside or diopside and phlogopite and then more distally into an assemblage of diopside, tremolite, phlogopite and calcite then into an assemblage of tremolite-phlogopite-calcite-dolomite and the distal assemblage, graphite-norbergite-phlogopite-calcite-dolomite marble (Figure 3.7b; Plate 3.9). At the Cardiff "C" zone, several stages of skarnification were identified. Marble-hosted, medium- to coarse-grained vein skarns with minor interstitial calcite are hosted in graphite-bearing diopside-phlogopite marble (Figure 3.8a; Plate 3.10). Several of the skarn veins are dominated by calcite and phlogopite with minor diopside. Fine-grained calcite-phlogopite-diopside marginal skarn envelops coarse-grained quartz-phlogopite-feldspar-pyroxene skarn veins (Figure 3.8b). At the Camp II zone, a medium-grained diopside-rich marble has numerous coarse-grained, scapolite-phlogopite-pyroxene veins.

It is not uncommon to find a humite-group mineral (norbergite or chondrodite; XRD identification) disseminated in dolomite-bearing phlogopite-calcite marbles in proximity to radioactive skarns. It is associated with a few of the skarn localities (Wilberforce, Grand Calumet, Otter Lake and Maniwaki) which interestingly are the few areas with rare-metal-enriched, fluorite-bearing skarns, and fluorite-apatite-calcite veins. Marble-hosted skarns in other areas of the CMB rarely contain humite-group minerals. Bourne (1974) and Kretz (1980) found clinohumite, chondrodite, and humite in regionally metamorphosed calcite-dolomite marble.

Commonly, the silicated marble is coarser grained than the host marble and rarely have a fabric indicating recrystallization and growth of calcite in the altered marble. It contains no dolomite and a higher proportion of diopside

and/or phlogopite. The calcite is yellow to orange. The Camp II zone of the Yates deposit is a good example of silicated marble (Figure 3.1b; Plate 3.11). The South State uranium deposit northeast of Bancroft has many of the characteristics of silicated marbles with coarse-grained calc-silicates in coloured calcite. The Québec Metallurgical Industries uranium pegmatite is partially hosted in silicated marble (Figure 3.3).

The Hunt molybdenum deposit is a marble- and amphibolite/clinopyroxenite-hosted marginal skarn associated with a fine-grained granite pegmatite (Figure 3.9). The granitic pegmatite is texturally heterogeneous with locally developed graphic granite and aplite. A marginal molybdenite-bearing, titanite-scapolite (K-feldspar)-Ca pyroxene assemblage (proximal) (<1 m) occurs beside the pegmatite with minor scapolite-pyroxene endoskarn (0.1 to 1 m). A phlogopite-pyroxene $\pm$ calcite assemblage is prominent further from the contact (distal) (1 - 10 m) and distal coarse-grained calcite-phlogopite-tremolite veins are hosted in phlogopite-dolomite-calcite marble. Pink calcite veins with coarse-grained phlogopite-diopside selvages are hosted in the skarn. Later, retrograde pyrite/pyrrhotite-bearing phlogopite-tremolite veins replace earlier pyroxene-rich skarn assemblages. Molybdenite is associated with both the primary skarn and the retrograde veins. Unfortunately, poor exposure precludes detailed analysis of the distribution of skarn minerals.

3.2.4 Amphibolite- and gneiss-hosted metasomatic rocks

The mineralogy and composition of metasomatically-altered amphibolites and gneisses are mainly a function of the wall rock composition but are also related to the composition of the fluid responsible for the replacement processes. The fluid composition is responsible for many of the alteration assemblages produced adjacent to the pegmatites.

Various types of metasomatic rocks form depending on their relationship to the granite pegmatite or the modification of

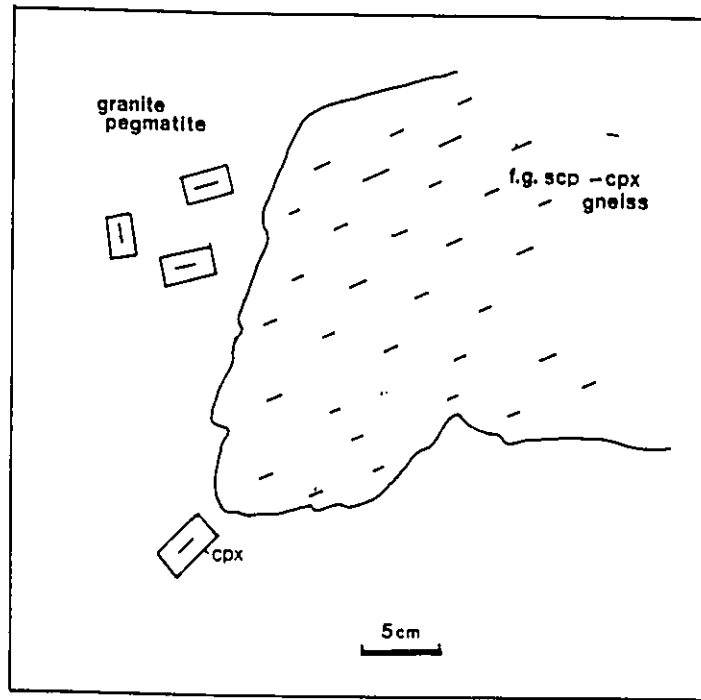


Figure 3.4 A) Sketch of hybrid Ca pyroxene-bearing white granite pegmatite hosting a xenolith of fine-grained scapolite-pyroxene gneiss, Cardiff deposit "C" zone (# 9), Wilberforce, ON.

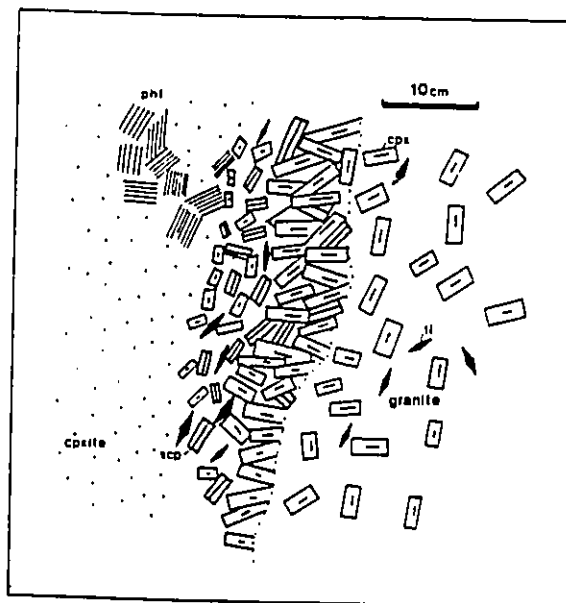


Figure 3.4 B) Sketch of titanite-scapolite-Ca pyroxene marginal skarn with granite pegmatite with phlogopite vein hosted in medium-grained clinopyroxenite, Camp I zone (# 61), Yates deposit, Huddersfield, P.Q..

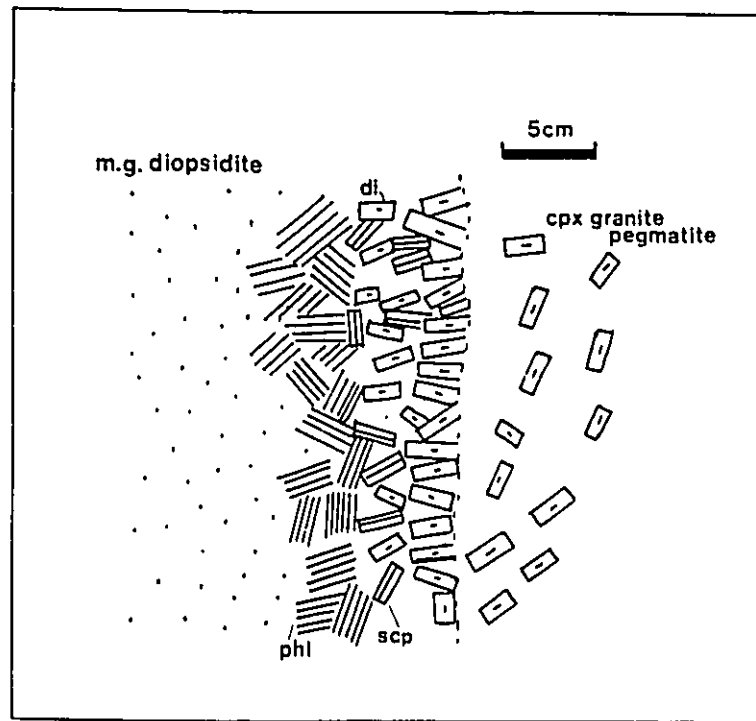


Figure 3.5 A) Sketch of Ca pyroxene-bearing granite pegmatite with marginal phlogopite-scapolite-Ca pyroxene skarn hosted in medium-grained clinopyroxenite, Camp I zone (# 61), Yates deposit, Huddersfield, P.Q..

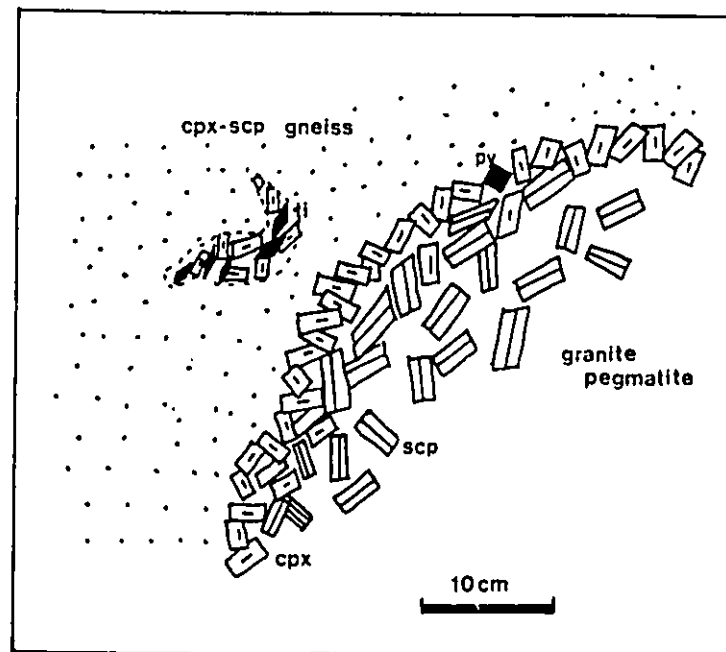


Figure 3.5 B) Sketch of Ca pyroxene- and scapolite-bearing granitic pegmatite with skarn hosted in Ca pyroxene-scapolite gneiss, Camp I zone (# 61), Yates deposit, P.Q..



Plate 3.1 Ca pyroxene-bearing pegmatite with marginal Ca pyroxene-scapolite skarn with outer phlogopite zone (right) hosted in clinopyroxenite (not visible), Camp I zone (# 61), Yates deposit, Huddersfield township, P.Q.. Scale is 1 cm long.

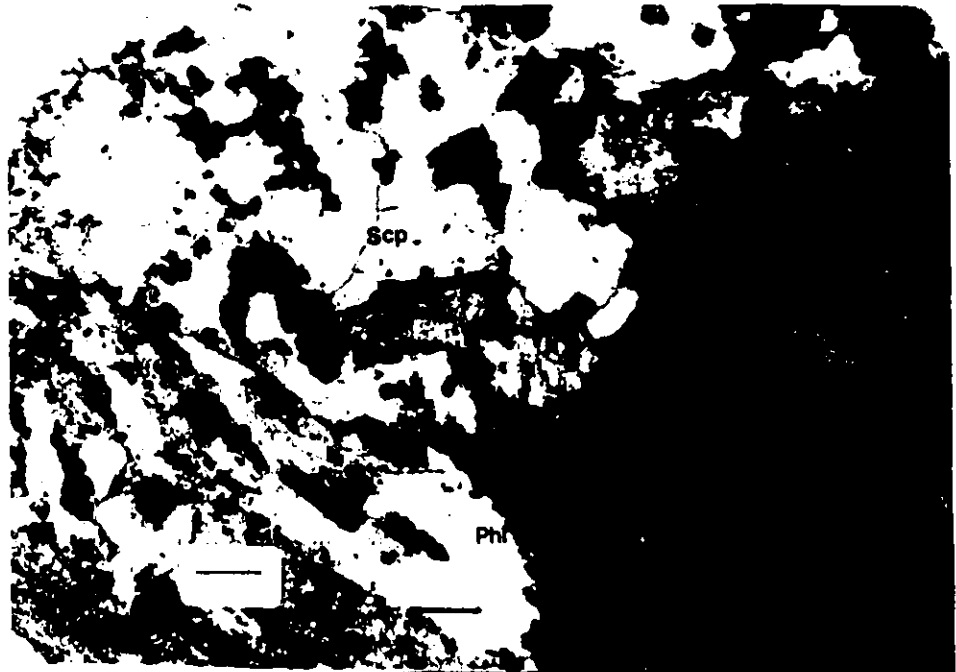


Plate 3.2 Coarse-grained Ca pyroxene-scapolite exoskarn with phlogopite selvage hosted in medium-grained clinopyroxenite, Camp I zone (# 61), Yates deposit, Huddersfield township, P.Q. Scale is 1 cm long.



Plate 3.3 Phlogopite-microcline-Ca pyroxene skarn marginal to granite pegmatite and hosted in a clinopyroxenite and marble sequence, Zenith Mo-U deposit located southwest of Renfrew, ON (S. Salvi sample). Scale is 1 cm long.

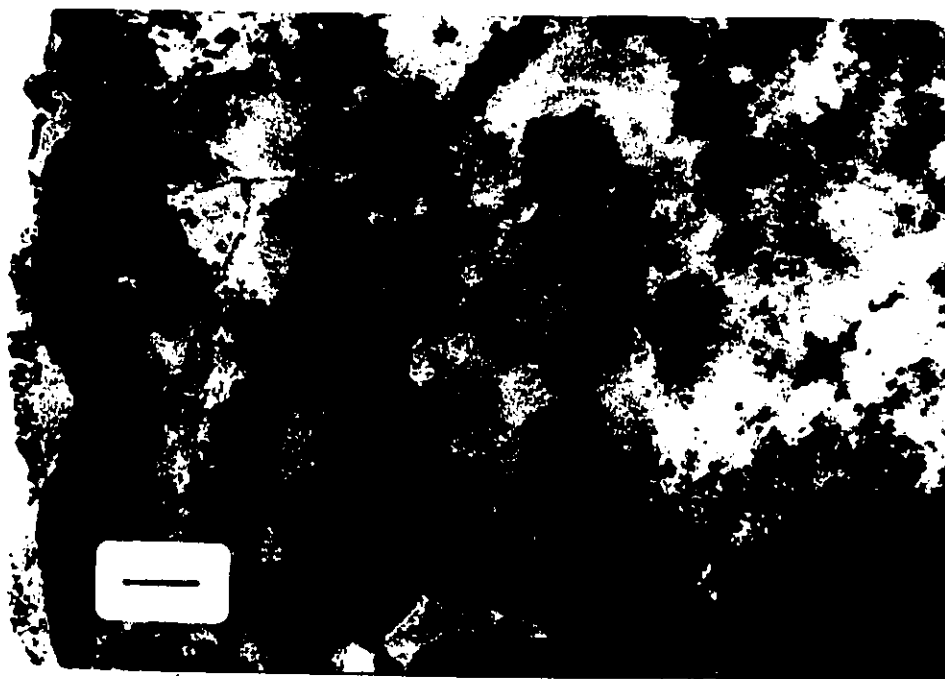


Plate 3.4 Phlogopite-bearing, scapolite-tremolite replacement skarn hosted in scapolite-Ca pyroxene skarn, Camp zone (# 62), Yates deposit, Huddersfield township, P.Q.. Scale is 1 cm long.

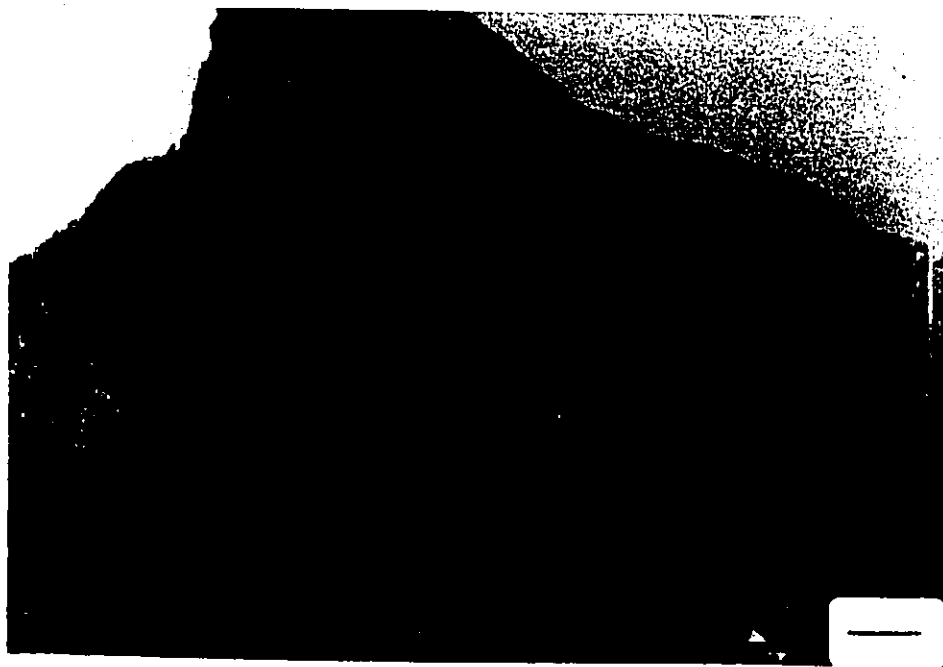


Plate 3.5 Coarse-grained quartz-calcite-tremolite vein hosted in fine-grained diopsidite, Desmond U-Mo occurrence (# 5), located north of Wilberforce, ON. Scale is 1 cm long.

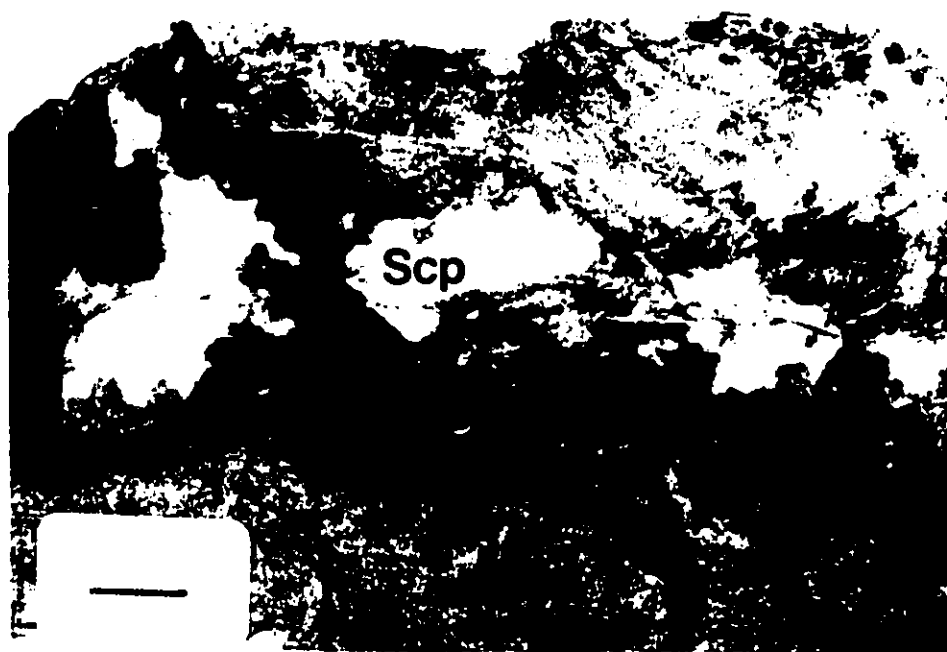


Plate 3.6 Coarse-grained phlogopite-feldspar-tremolite vein hosted in medium-grained diopsidite, Rockingham U occurrence (# 36), east of Barry's Bay, ON. Scale is 1 cm long.

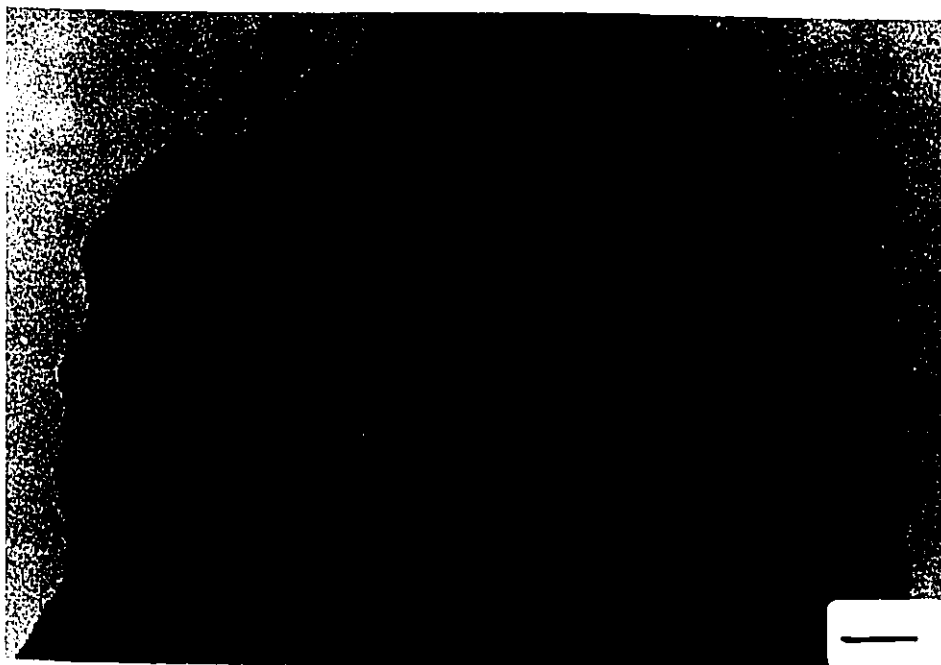


Plate 3.7 Salmon pink calcite-phlogopite vein hosted in medium-grained clinopyroxenite, Camp I zone (# 62), Yates deposit, Huddersfield township, P.Q.. Scale is 1 cm long.

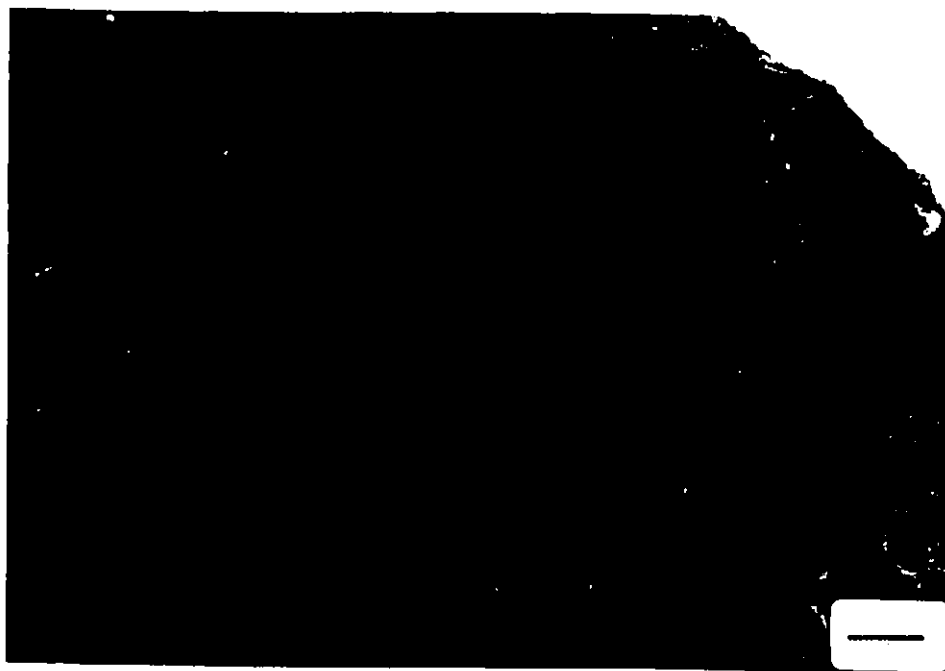


Plate 3.8 Coarse-grained diopside-bearing, (orange) calcite vein with phlogopite selvage hosted in medium-grained phlogopite-bearing diopsidite, Camp II zone (# 62), Yates deposit, Huddersfield township, P.Q.. Scale is 1 cm long.

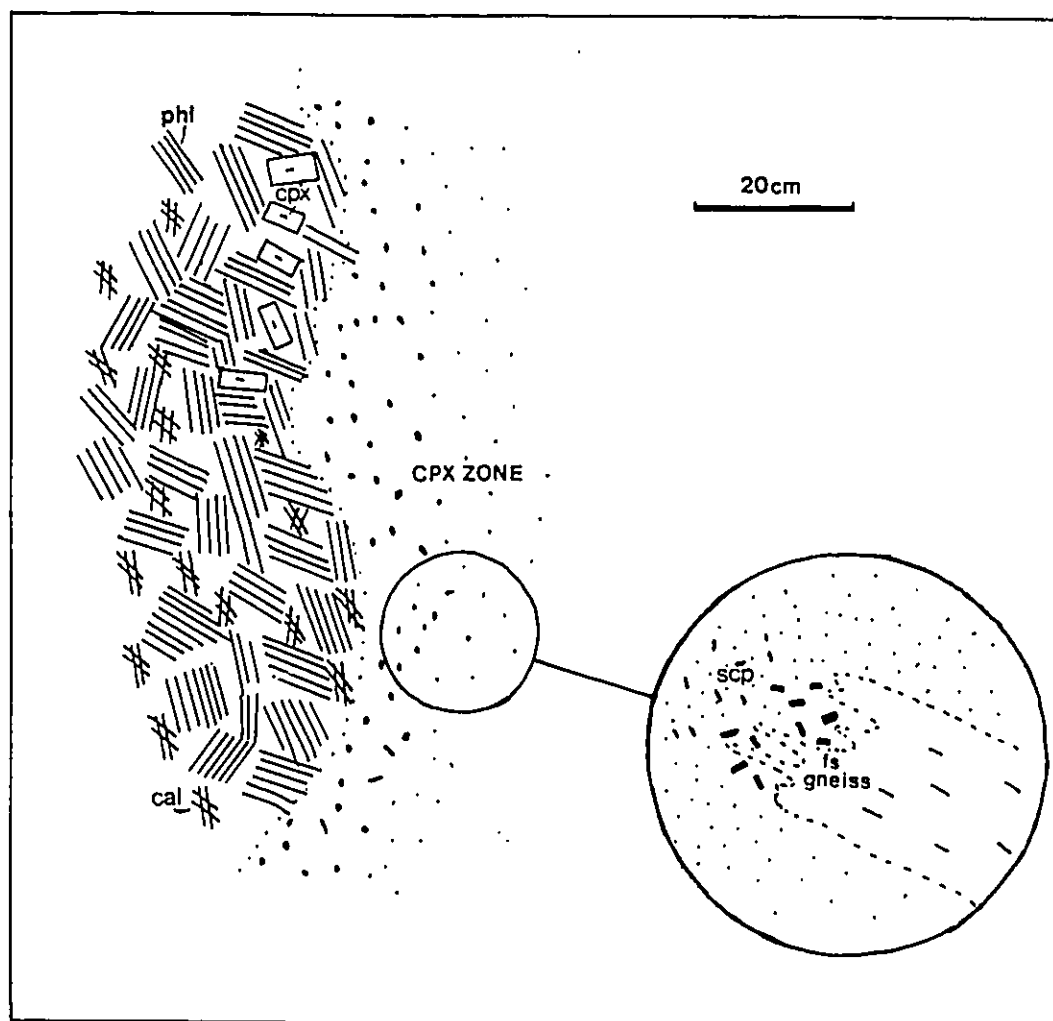


Figure 3.6 Sketch of coarse-grained phlogopite-calcite vein with a phlogopite-Ca pyroxene selvage hosted in an altered Ca pyroxene-scapolite gneiss, Camp I zone (# 61), Yates deposit, Huddersfield township, P.Q.. Inset illustrates the replacement of plagioclase gneiss by a coarser grained assemblage of scapolite and pyroxene.

the hydrothermal fluid by interaction with marble/skarn. The composition of the host rocks is the primary control of the alteration assemblages produced as was true for the marble- and clinopyroxenite-hosted skarns. There is a general increase in the proportion of feldspar and phlogopite toward the pegmatites and veins, coincident with an increase in grain size. Several of these features have been briefly discussed in Chapter 2.

The gneisses and amphibolites are commonly altered to a coarse-grained assemblage rich in biotite, feldspars, and/or scapolite particularly along the margins of the pegmatite, which in many cases is confused with pegmatites (see Chapter 2). In general, there is an increase in the modal proportion of feldspar and/or scapolite in these proximal exoskarn. The largest and highest grade uranium deposits are hosted in the marginal zones of amphibolite-hosted granite pegmatites (Faraday, Dyno, Bicroft, "REE", Greyhawk, and Halo deposits).

The Clark fluorite deposit near Harcourt (just east of Wilberforce) is associated with a graphic granite pegmatite which intrudes hornblende-plagioclase gneisses and granitoid gneisses and calc-silicate gneisses (Figure 3.10). Fluorite is associated with hydrothermally replaced gneisses which are dominated by an assemblage of coarse-grained titanite-apatite-scapolite-Ca pyroxene. The metasomatic assemblage grades indistinguishably into a hybrid pyroxene-K-feldspar pegmatite and then to a graphic granite pegmatite, which illustrates the spatial relationship of the granite pegmatite and the metasomatically-replaced gneisses.

The Quadeville beryl pegmatite has a coarse-grained biotite-rich selvage replacing a narrow amphibolite along the north wall of the open cut. In addition, coarse-grained feldspar veins commonly replace fine-grained, biotite-bearing granitic gneiss.

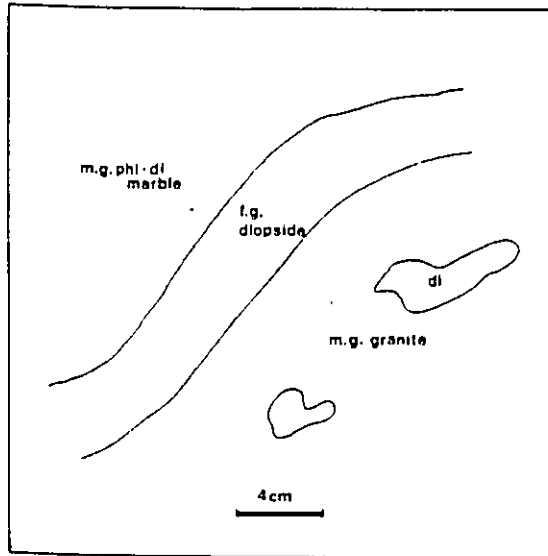


Figure 3.7 A) Sketch of medium-grained granite with a medium-grained diopside skarn selvage and xenoliths of diopside hosted in medium-grained phlogopite-diopside marble, Cardiff "C" zone (# 9), Wilberforce, ON.

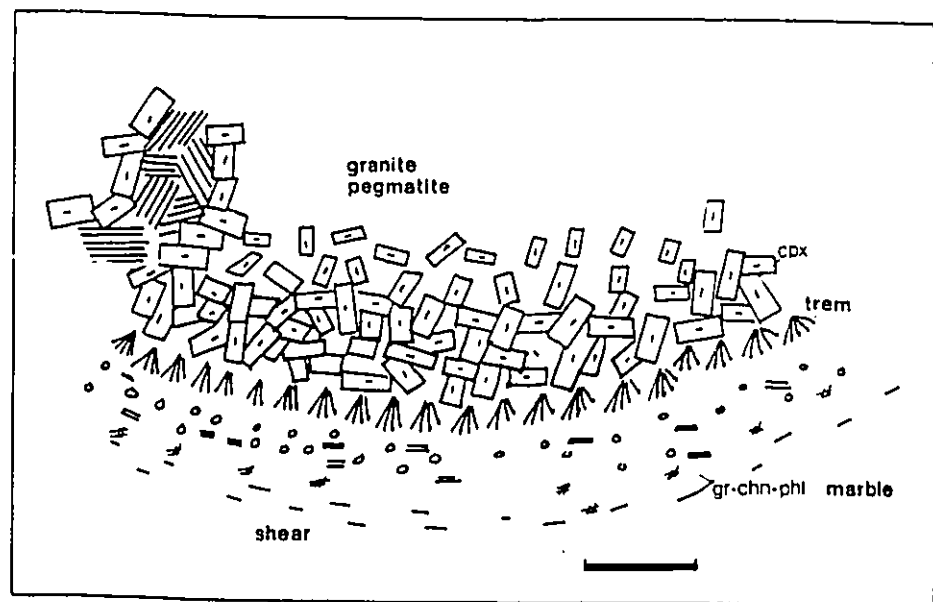


Figure 3.7 B) Sketch of diopside-bearing granitic pegmatite with zoned marginal skarn hosted in a phlogopite-norbergite marble (altered?), north of Cardiff "C" zone (# 9), Wilberforce, ON. The skarn is bounded by sheared marble. Scale bar is 1 m.

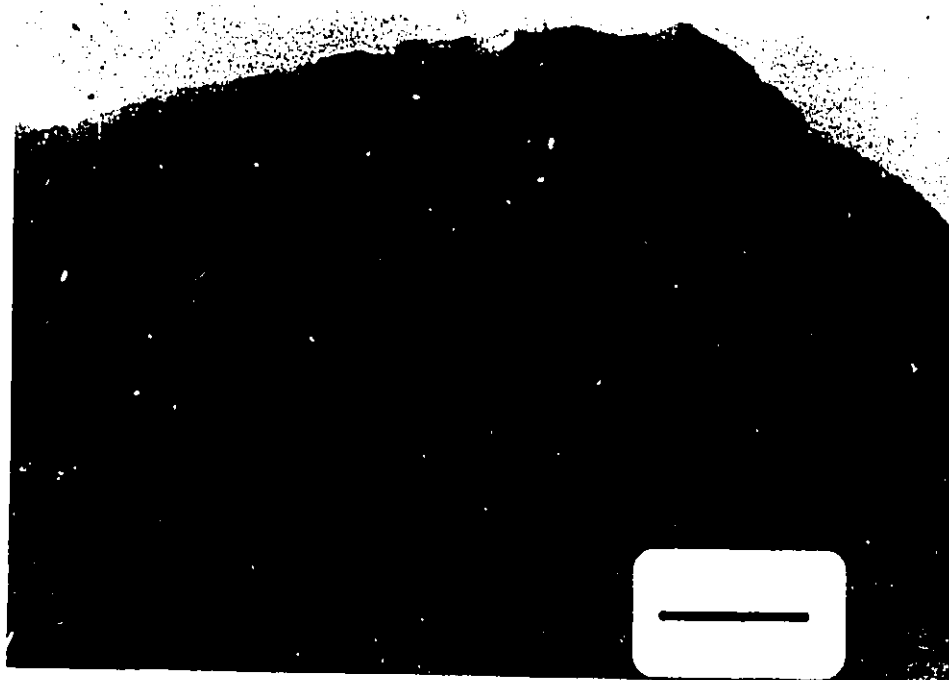


Plate 3.9 Medium-grained graphite-bearing, phlogopite-chondrodite (norbergite ?) calcite-dolomite marble, Cardiff "C" zone (# 9), Wilberforce, ON. Scale is 1 cm long.

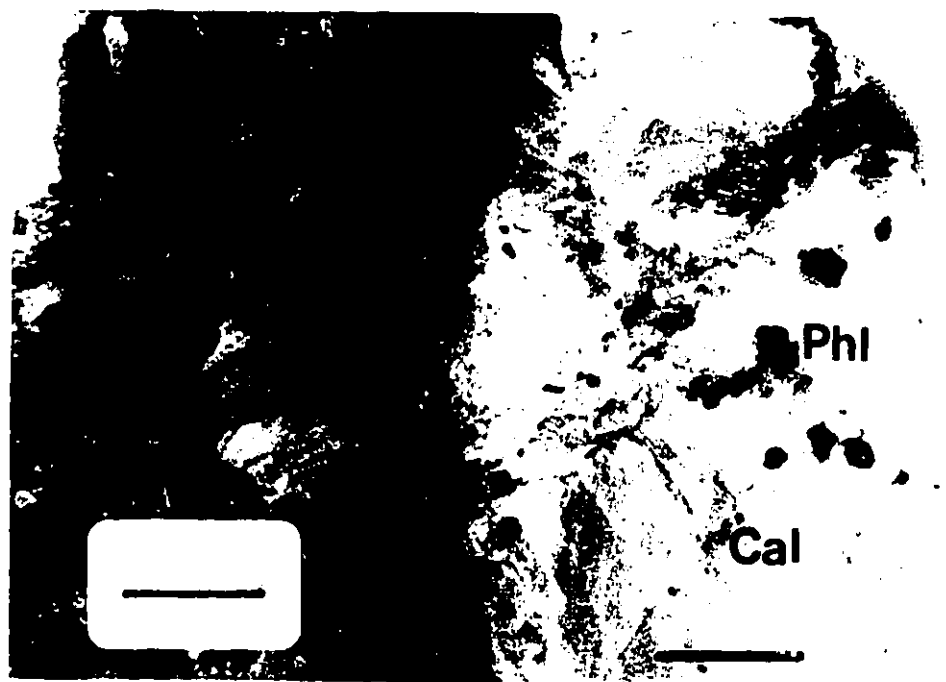


Plate 3.10 Calcite-phlogopite-diopside-scapolite skarn vein in coarse-grained phlogopite-calcite marble,

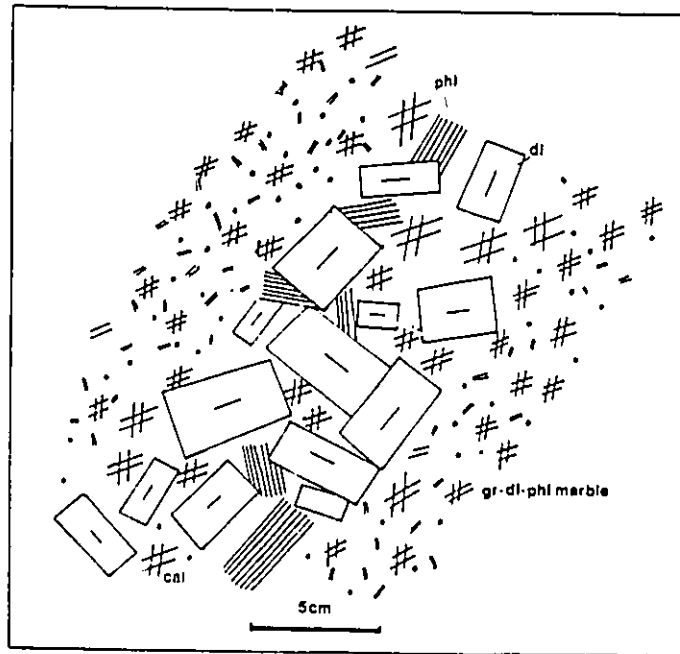


Figure 3.8 A) Sketch of coarse-grained calcite-phlogopite-diopside skarn vein hosted in graphite-bearing diopside-phlogopite marble, Cardiff "C" zone (# 9), Wilberforce, ON.

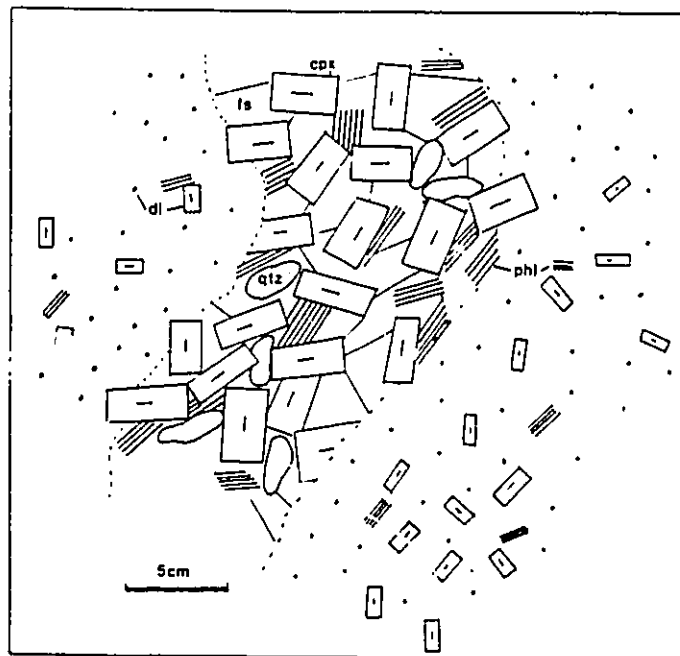


Figure 3.8 B) Sketch of coarse-grained quartz-bearing, phlogopite-feldspar-pyroxene vein hosted in marginal phlogopite-bearing diopside skarn, Cardiff "C" zone (# 9), Wilberforce, ON.

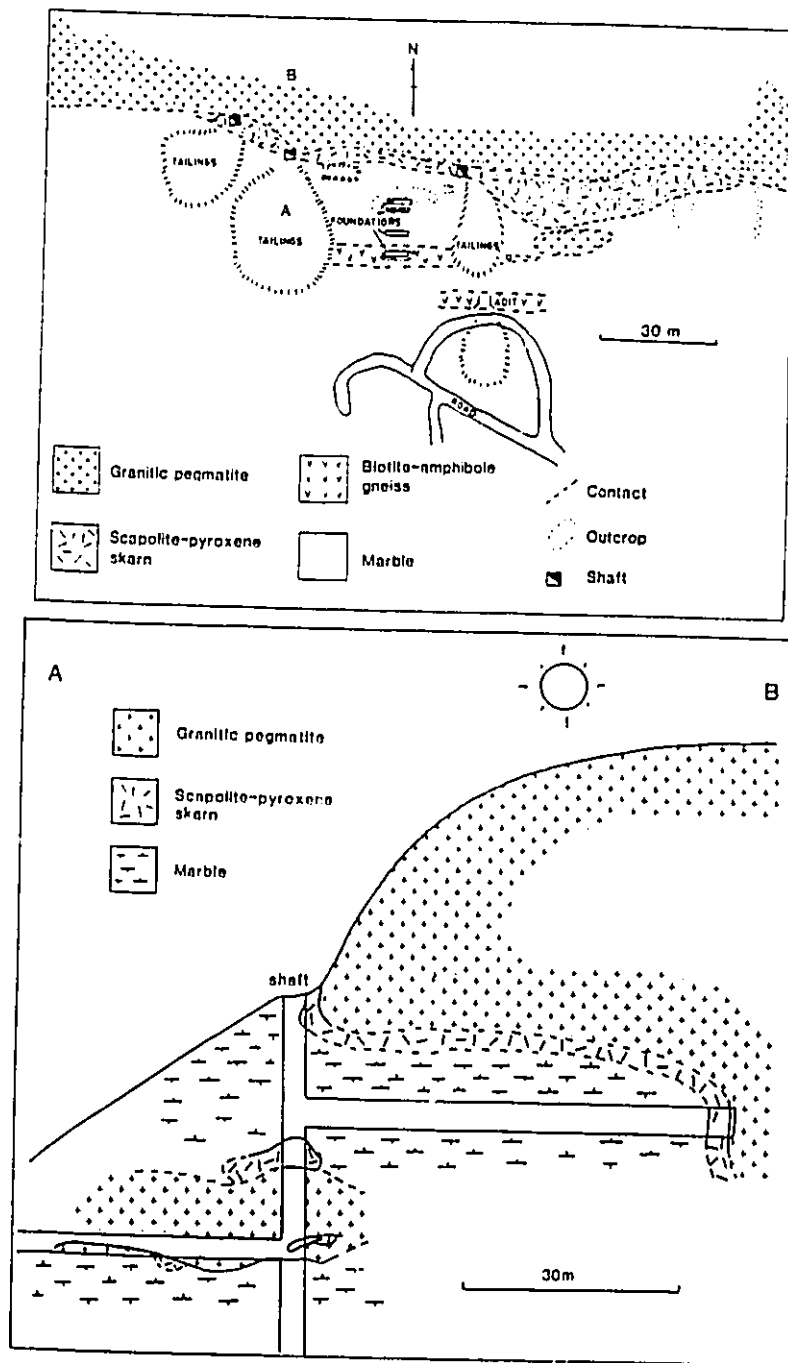


Figure 3.9 A) Geological plan of the Hunt Mo skarn deposit and B) geological section (A - B) of the west portion of the deposit (# 50). The deposit is located south of Dacre, ON (after Carter et al. 1980).

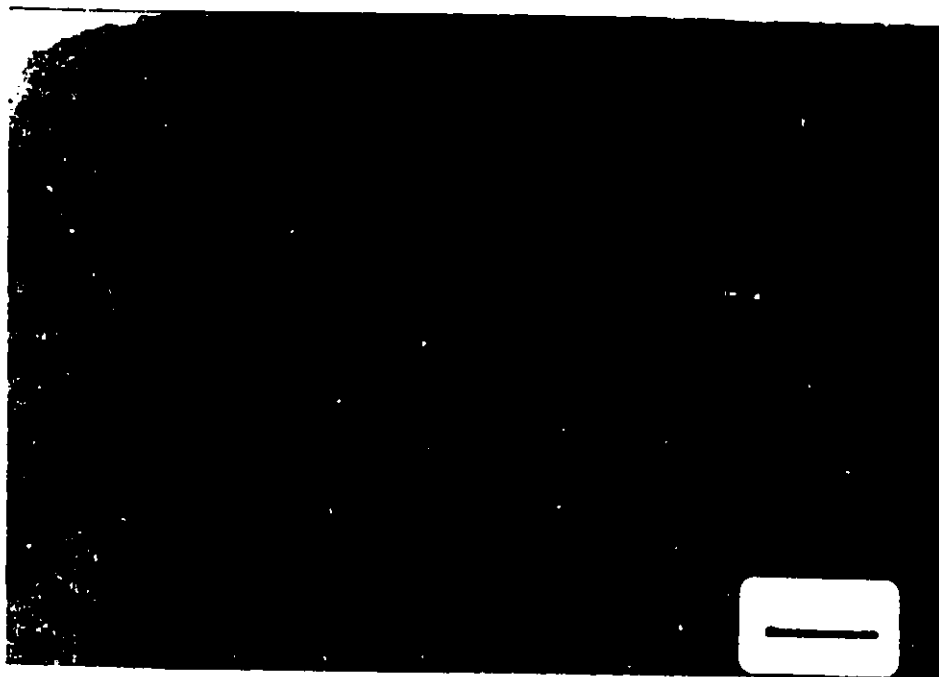


Plate 3.11 Medium-grained, phlogopite-diopside-calcite skarn/vein in phlogopite-calcite-diopside skarn, Camp II zone (# 62), Yates deposit, Huddersfield township, P.Q. Scale is 1 cm long.



Plate 3.12 Coarse-grained diopside-pink calcite vein hosted in phlogopite-calcite-diopside skarn, northwest of Camp I zone (# 61), Yates deposit, Huddersfield township, P.Q. Scale is 1 cm long.

3.2.5 Discussion

The clinopyroxenites (diopsidites) are commonly medium-grained, equigranular, and monomineralic (> 90%) with minor plagioclase, scapolite and/or disseminated phlogopite. There are several types of pyroxene-rich rocks which may not always be readily distinguished in the field. These include: 1) primary, fine-grained Ca pyroxene-rich units derived from the metamorphism of impure siliceous dolomites and are termed clinopyroxenites, 2) secondary, fine- to coarse-grained Ca pyroxene-rich rocks derived by metasomatic interaction of carbonate rocks with other rocks and/or solute-bearing fluids of various origins. There are numerous possible mechanisms for the metasomatic transformation of rocks to produce Ca pyroxene-rich rock.

Wilson (1921) used the term "metamorphic pyroxenites" to distinguish the clinopyroxenite of metamorphic parentage from igneous pyroxenite, and Lacroix used the term pyroxenolite (Dr. J. Martignole, personal communication). The clinopyroxenites do not have a well developed layer-parallel fabric although units hosted within them often have a foliation (pyroxene granofels). Clinopyroxenite commonly occurs along the boundary between quartz-feldspar gneiss and marble but are also found within marble. The origin of these units is uncertain although several hypotheses include: i) regional metamorphic-metasomatic reaction between gneiss and marble, ii) magmatic skarn if the quartz-feldspar gneisses are of magmatic origin, and iii) a primary unit representing impure siliceous dolomites. The last possibility is the most compelling considering the large size and thickness of these units and the weak foliation developed particularly in gneisses enclosed in the clinopyroxenites and their gradational contact relationships with other units (several meters). In a comparative analysis of gneiss compositions, van de Kamp (1968) noted the chemical similarity between the pyroxene-scapolite gneisses and the carbonate-silicate

gneisses. He suggested that the Ca pyroxene-scapolite gneisses were decarbonated primary lithologies (siliceous dolomites ?) with introduced chlorine, lead and zinc. Villeneuve (1977) examined five Ca pyroxene-bearing rocks within the Gatineau Park and found that three represented metamorphosed siliceous marbles and coarse-grained Ca pyroxene-rich zones within these units have been metasomatically modified by the emplacement of calcite-rich vein and pegmatites. Using the abundance of compatible elements (Ni, Cr, V, Co, Cu, Sc), Villeneuve (1977) distinguished a ultramafic protolith from a marble protolith. Furthermore, he could identify metasomatically-altered clinopyroxenite of mafic igneous parentage that transformed to amphibole skarn by a pegmatite-derived hydrothermal fluid. Warnock (1978) has suggested that the calc-silicate rocks are metamorphosed impure calcareous metasediments whereas coarse-grained phlogopite-cpx-apatite-calcite zones represent metasomatically-altered calc-silicate rocks. It is important as well to know that pre-tectonic Ca pyroxene-magnetite skarn deposits are formed along the contacts with large granitoid intrusions (Carter et al., 1980). Karvinen (1973) suggested that the clinopyroxenite was derived by interaction of the marble with the gneiss. Karvinen (1973) thought the common occurrence of pegmatites, skarns, and veins within these fine- to medium-grained clinopyroxenites was evidence for a metamorphic-hydrothermal origin for the Mo skarns. However, many of these skarns are Ca pyroxene alteration marginal to apatite-calcite veins or magmatic skarn replacements of amphibolite. This suggests that there are numerous possible origins for Ca pyroxene-rich units within the Grenville Province.

In an examination of apatite and mica deposits in Quebec, Landes (1938) noted the spatial association between pegmatites and apatite-mica veins in clinopyroxenites.

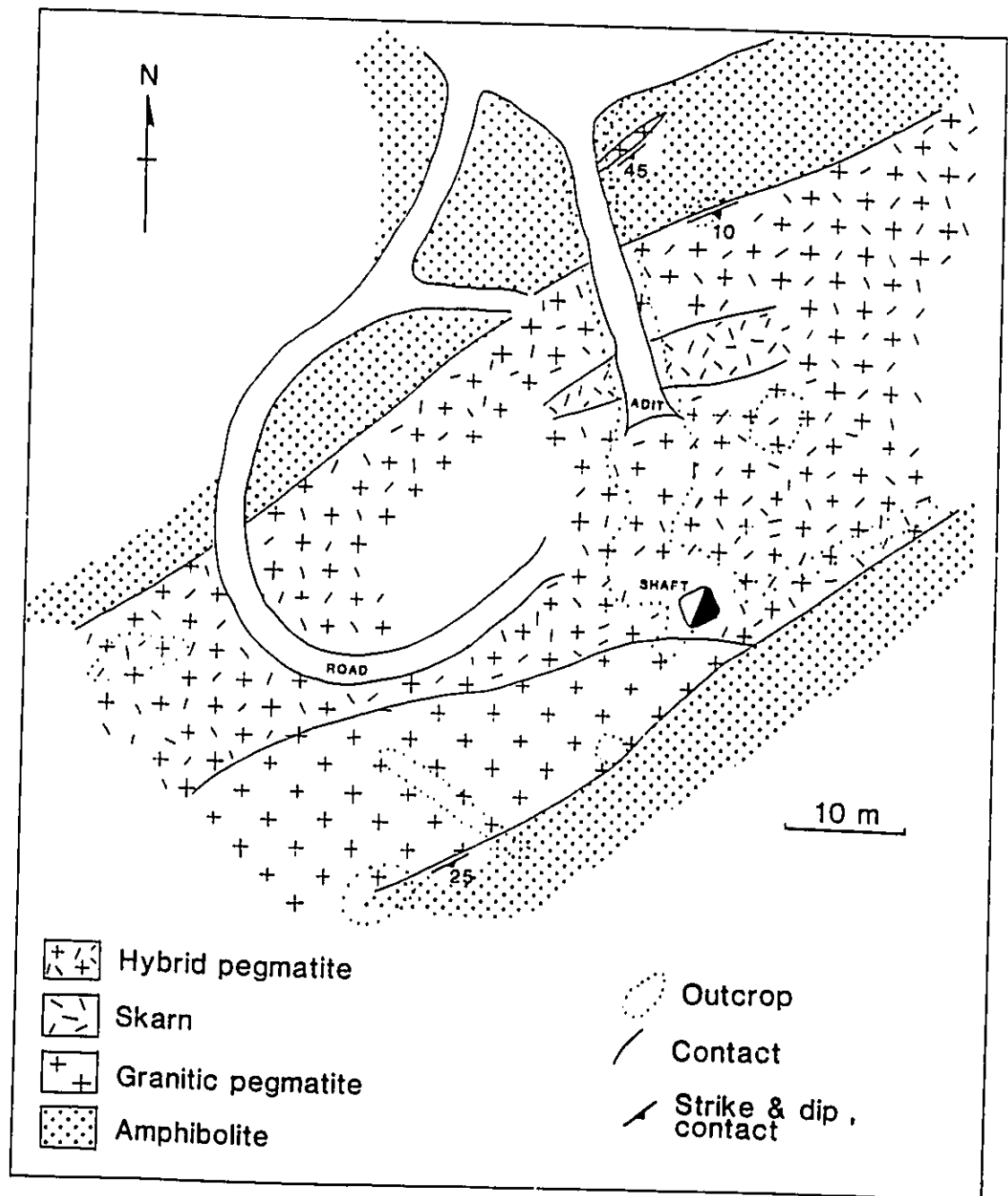


Figure 3.10 Geology of the Clark fluorite-U occurrence located near Harcourt, ON (after Guillet, 1964).

Currie (1951) has suggested that the skarns in the Perth area formed by interaction of pegmatite-derived fluids with marble. A contact metamorphic origin was proposed for the Ca pyroxenite-rich rocks by Shaw et al. (1963) and Shaw et al. (1965) possibly formed by metamorphism of impure marble. Interestingly, they noted the spatial relationship of the skarns with the granitic pegmatite.

Karvinen (1973) has subdivided the coarse-grained skarns into scapolite- and feldspar-Ca pyroxene skarns. The feldspar skarns may be either plagioclase or K-feldspar and may even vary within the deposit.

Kretz (1980) has described the marble-hosted skarns as minor marble, noting their textural differences and compositional differences and has ascribed a metamorphic-metasomatic origin to their formation. Shaw et al. (1965) examined two zoned radioactive skarns mantling granitic bodies in the Fort Coulange and Grand Calumet Island area. Stratabound and discordant skarns are mineralogically similar to primary calc-silicate marble. Lafontaine (1980) also examined the marble-hosted skarns and veins in the Yates area and noted the mineralogical similarity to metamorphic assemblages hence has described them as forming by a metamorphic-hydrothermal mechanism. Haynes (1986) concurred with the magmatic-hydrothermal origin for the formation of the uraniferous skarns. In addition, he attributed the presence of humite-group minerals in U- and Th-rich marble to a sabbka-type environment in the absence of a spatial relationship to skarn. However, the presence of anomalous U and Th concentrations favour an origin related to the skarns, particularly since Th is not concentrated in a sabbka-type environment.

The metasomatic reaction zones with these pegmatites are particularly significant since they host the highest concentration of U, Th, Mo, Nb, and REE elements (Habib, 1982; Rimsaite, 1982, 1983a, 1985). The ferromagnesium-rich assemblage along the margins of the granite pegmatites has

commonly been described as a reaction zone between the granite pegmatite and the amphibolite (Satterly, 1957; Hewitt, 1967; Masson and Gordon, 1981b; Storey and Vos, 1981; Habib, 1982; Rimsaite, 1982, 1983, 1985) and hosts the highest grade uranium mineralization (e.g. Faraday U pegmatite deposit). This alteration is a complex metasomatic process of hybridization and/or skarnification. Although different, the processes of hybridization and skarnification are difficult to separate because the result is indistinguishable. The hybridization processes (see Chapter 2) would involve the incorporation of wallrock components by mixing of solids and/or melts. The higher volatile-saturated melting temperature of amphibolite compared to the granite pegmatite strongly suggests that the minerals were mechanically incorporated and subsequently recrystallized while the pegmatite melt continued to evolve and crystallize. However, skarnification would involve the of deuteritic fluids derived from the melt with the wall rock to produce these alteration assemblages. A combination of these two processes is most likely.

3.3 Fluorite-apatite-calcite veins

3.3.1 Introduction

As was noted for the skarns, the fluorite-apatite-calcite veins have alteration assemblages mantling them which may be described as skarns (silicate skarn or skarnoid rock). However, in order to distinguish them, they have been described separately. The descriptions of the textural details and mineral assemblages are applicable to the vein alteration.

The veins are composed of variable proportions of fluorite, apatite, and calcite and are up to a few hundred metres long and a few metres wide. They are most commonly subparallel to the primary metamorphic fabric of the host rocks or more discordant bodies which pinch and swell along both dip and strike. The veins seem to have formed along structural

discontinuities (shear zones) which, in many instances, have been sheared (reactivated) subsequent to vein formation. Fluorite-apatite-calcite veins have variable proportions of fluorite and apatite which are less abundant than calcite. This calcite is normally grey, yellow, orange or pink. Apatite is usually more abundant than fluorite, however, some portions of the Cardiff "C" zone have a higher proportion of fluorite (Plate 3.13). The distribution of alteration assemblages is very heterogeneous within and along the margins of the veins. The alteration assemblages produced are partially a function of host rock composition, like the skarns, and therefore have been subdivided into clinopyroxenite-hosted, marble-hosted, amphibolite-hosted, and gneiss-hosted veins.

3.3.2 Clinopyroxenite-hosted veins

Apatite-calcite veins hosted in clinopyroxenite represent some of the largest apatite (e.g. Silver Queen apatite deposit, Perth area) and phlogopite deposits (e.g. Lacey Mine, Kingston area) in the region. In the Camp I zone, of the Yates uranium mine, disseminated and vein, of calcite-phlogopite occur within clinopyroxenite (Plate 3.7 and 3.8). Coarse-grained phlogopite and Ca pyroxene with interstitial calcite commonly form veins in the clinopyroxenite (Figure 3.6). The pyroxene along the margins becomes coarser grained and pre-existing pyroxene-plagioclase gneiss is transformed into pyroxenite suggesting that some clinopyroxenites may be of metasomatic origin. The association of phlogopite with apatite-calcite veins hosted in clinopyroxenite is common to numerous larger deposits particularly in the Perth area (e.g. McLaren apatite deposit; Plate 3.7), Gatineau area (e.g. Dacey apatite-phlogopite Mine) and the area north of Kingston (e.g. Lacey phlogopite deposit; Plate 3.8).

3.3.3 Marble-hosted veins

The formation of (fluorite-apatite) calcite veins in marble produces an assemblage similar to silicated marble (Plate 3.12). The apatite-rich, phlogopite-diopside-calcite marble,

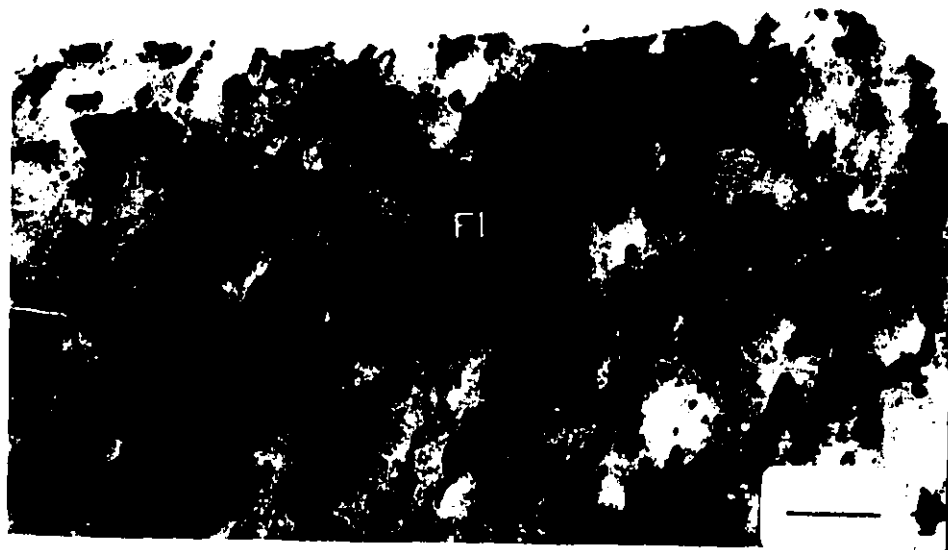


Plate 3.13 Coarse-grained apatite-fluorite-calcite vein from Cardiff "B" zone (# 9 & 10) hosted in gneiss, Wilberforce, ON. Scale is 1 cm long.

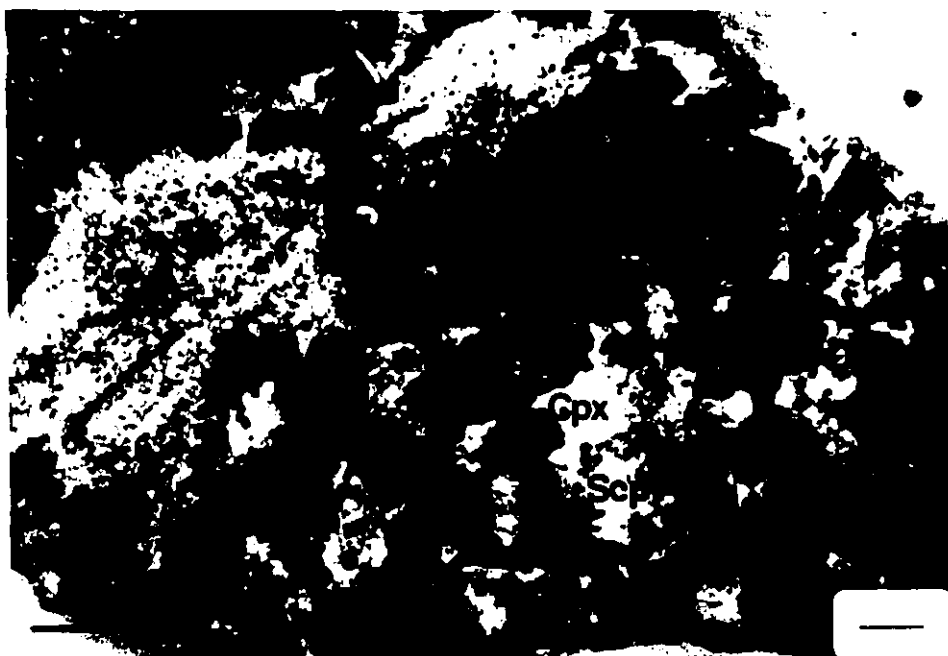


Plate 3.14 Fragment of scapolite-pyroxene gneiss (originally amphibole-plagioclase gneiss ?) enclosed and partially replaced by coarse-grained apatite-fluorite-pyroxene assemblage (skarn), Matte zone (# 60), Yates deposit, Huddersfield township, P.Q. Scale is 1 cm long.

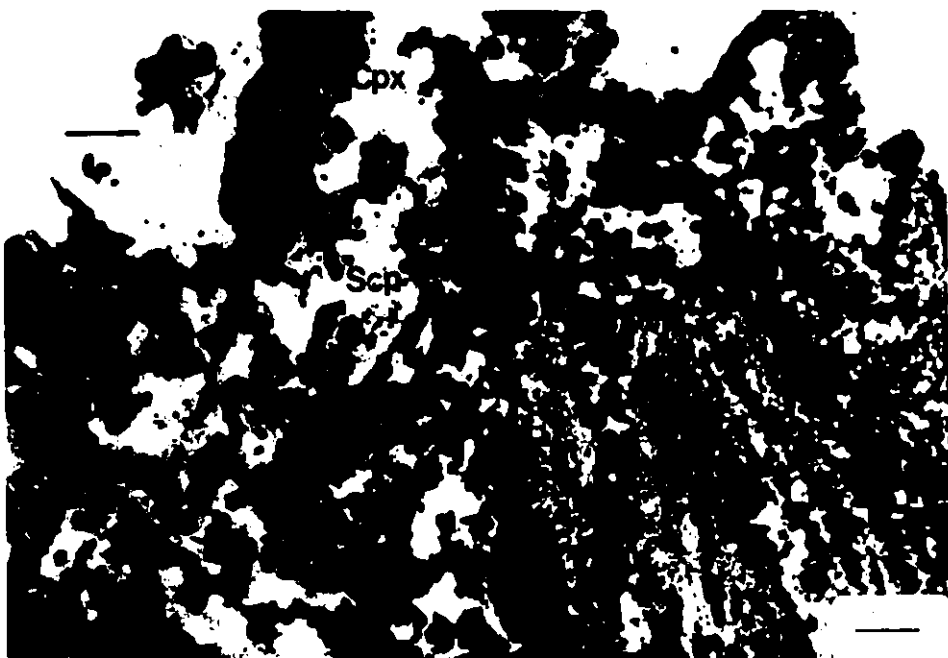


Plate 3.15 Coarse-grained calcite-fluorite-apatite with pyroxene replacing gneissic fragment (opposite side of slab Plate 14), Matte zone (# 60), Yates deposit, Huddersfield township, P.Q. Scale is 1 cm long.

located 10 m north of the Legris uranium pegmatite, has been interpreted as a primary apatite marble (Storey and Vos, 1981b). The proportion of silicates to calcite in the silicated marble reflects several factors; 1) the original proportion of silicates and dolomite within the marble before skarnification and 2) the proportion of calcite removed or introduced during skarnification.

3.3.4 Amphibolite- and gneiss-hosted veins (metasomatite)

The reaction zones on the margin amphibolite-hosted veins commonly produces medium- to coarse-grained major Ca pyroxene, biotite/phlogopite, amphibole, minor scapolite, plagioclase, and/or K-feldspar, fluorite, apatite, calcite, and accessory pyrite, pyrrhotite, magnetite, molybdenite as replacements of the fine-grained amphibolite assemblage. The footwall fine-grained Ca pyroxene-scapolite gneiss at the Matte zone of the Yates deposit may be an altered amphibole-plagioclase gneiss (Figure 3.11). The assemblage increases in grain size toward the vein to the point where the minerals (scapolite, Ca pyroxene, hornblende, apatite, titanite) are readily identifiable. Generally, the proportion of Ca pyroxene increases with an increase in grain size and proximity to the vein. Plates 3.14 and 3.15 represent opposite sides of a rock slab from the altered margin of the fluorite-apatite-calcite vein with gneissic fabric distinguishable in the least altered portion of the slab (Plate 3.14). Remnant fine-grained portions may be identified within the coarser grained assemblage (Plate 3.15). The Silver Crater deposit is an apatite-calcite vein hosted in a fine-grained, biotite-bearing hornblende-plagioclase gneiss (Figure 3.12). The vein is discontinuous along strike and dips moderately eastward. The host gneiss is altered to an assemblage of biotite-hornblende-albite with a noticeable increase in grain size along the margins with the apatite-calcite vein. Albite replaces the oligoclase in the altered zone and biotite replaces coarse-grained hornblende (Plate 3.16) accounting for the abundant

very coarse-grained biotite within and along the margins of the vein. Betafite is associated with the coarse-grained marginal assemblage.

The Tripp uraninite-bearing fluorite-apatite-calcite vein, like the Richardson fluorite-uranium deposit to the northeast, is hosted in intercalated amphibolites and feldspathic gneisses (Figure 3.13). The biotite-hornblende-K-feldspar assemblage mantles the vein and seems to replace the feldspathic gneisses. However a coarse-grained assemblage of biotite and hornblende occurs along the vein margin next to amphibolite.

Usually, gneiss-hosted metasomatic assemblages (granite- and/or pegmatite-hosted veins) are dominated by the prevalent feldspar in the gneiss. On the south side of the Cardiff "B" zone a fluorite-apatite-calcite vein is mantled by a coarse-grained assemblage of titanite-magnetite-pyroxene-K-feldspar which replaces a pyroxene-K-feldspar gneiss (Figure 3.13; 3.14a). The fluorite-apatite-calcite veins in the vicinity of the marble-gneiss contact form veins within granites and pegmatites which intrude the marbles. Phlogopite-scapolite-Ca pyroxene forms selvages on granitoid fragments within apatite-calcite veins at the Cardiff "C" zone (Figure 3.14). In addition to the common assemblage, primary tremolite, i.e. tremolite derived from prograde reactions, may occur with titanite, Ca pyroxene, and scapolite as the replacement assemblage associated with calcite veins particularly in the vicinity of marble (Figure 3.15).

The Richardson (Fission) uraninite-bearing, fluorite-apatite-calcite vein is situated along strike northeast of the Cardiff deposits and the Joiner molybdenite-bearing apatite-calcite vein. It is well exposed in old trenches and underground workings, which reveal the effects of recrystallization and alteration of the host gneiss and amphibolite. Rowe (1952) noted the replacement of the host gneisses by feldspathizing fluids during the progressive

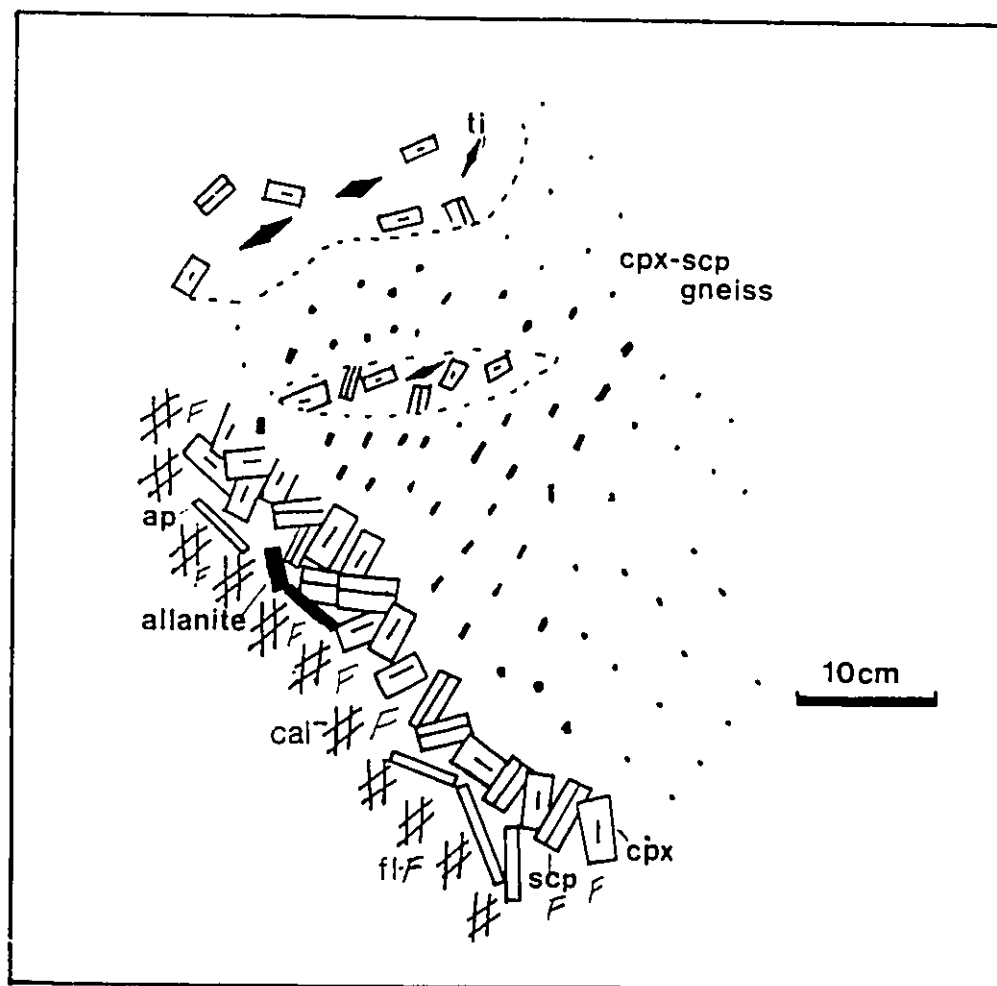


Figure 3.11 Fluorite-apatite-calcite vein with apatite-pyroxene-scapolite selvage hosted in altered pyroxene-scapolite gneiss, Matte zone (# 60), Yates deposit, Huddersfield township, P.Q..

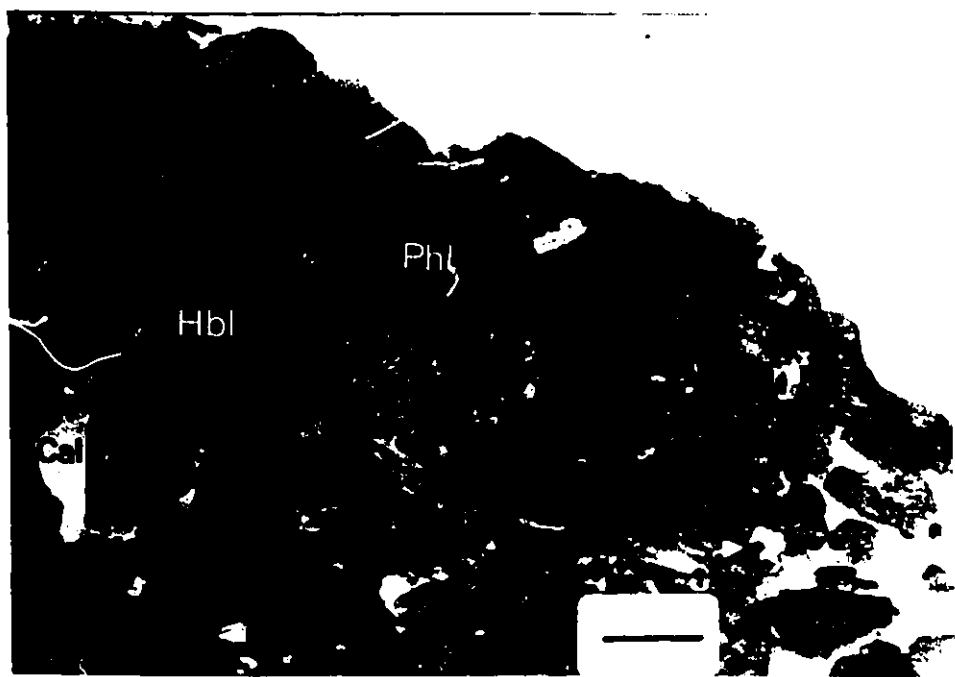


Plate 3.16 Coarse-grained hornblende-scapolite beside a (apatite-) calcite vein, biotite occurs as dark patches with hornblende, Silver Crater mica deposit (# 27), Cardiff township, ON.

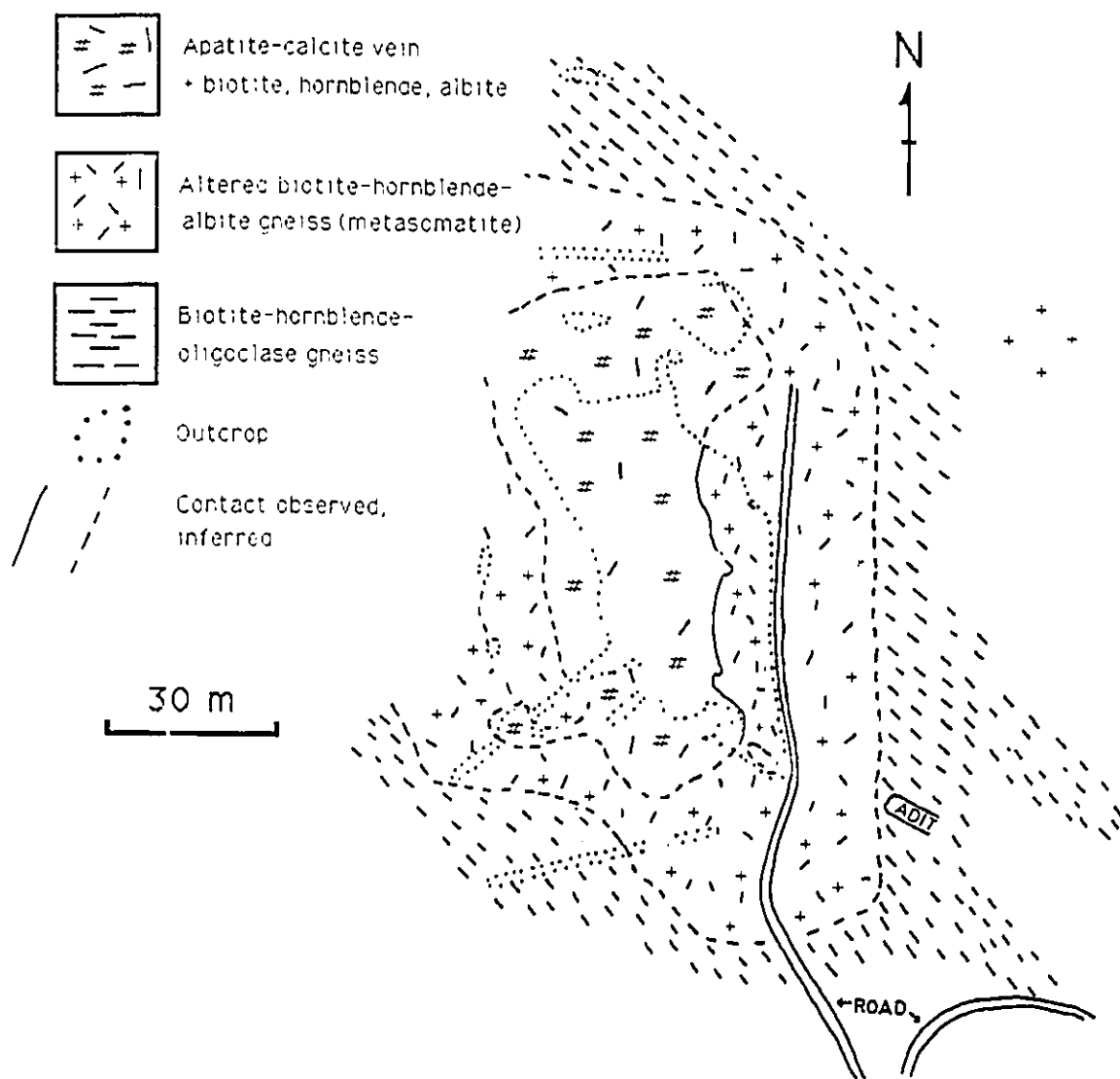


Figure 3.12 Silver Crater deposit (# 27), Cardiff township, ON (after Satterly, 1957).

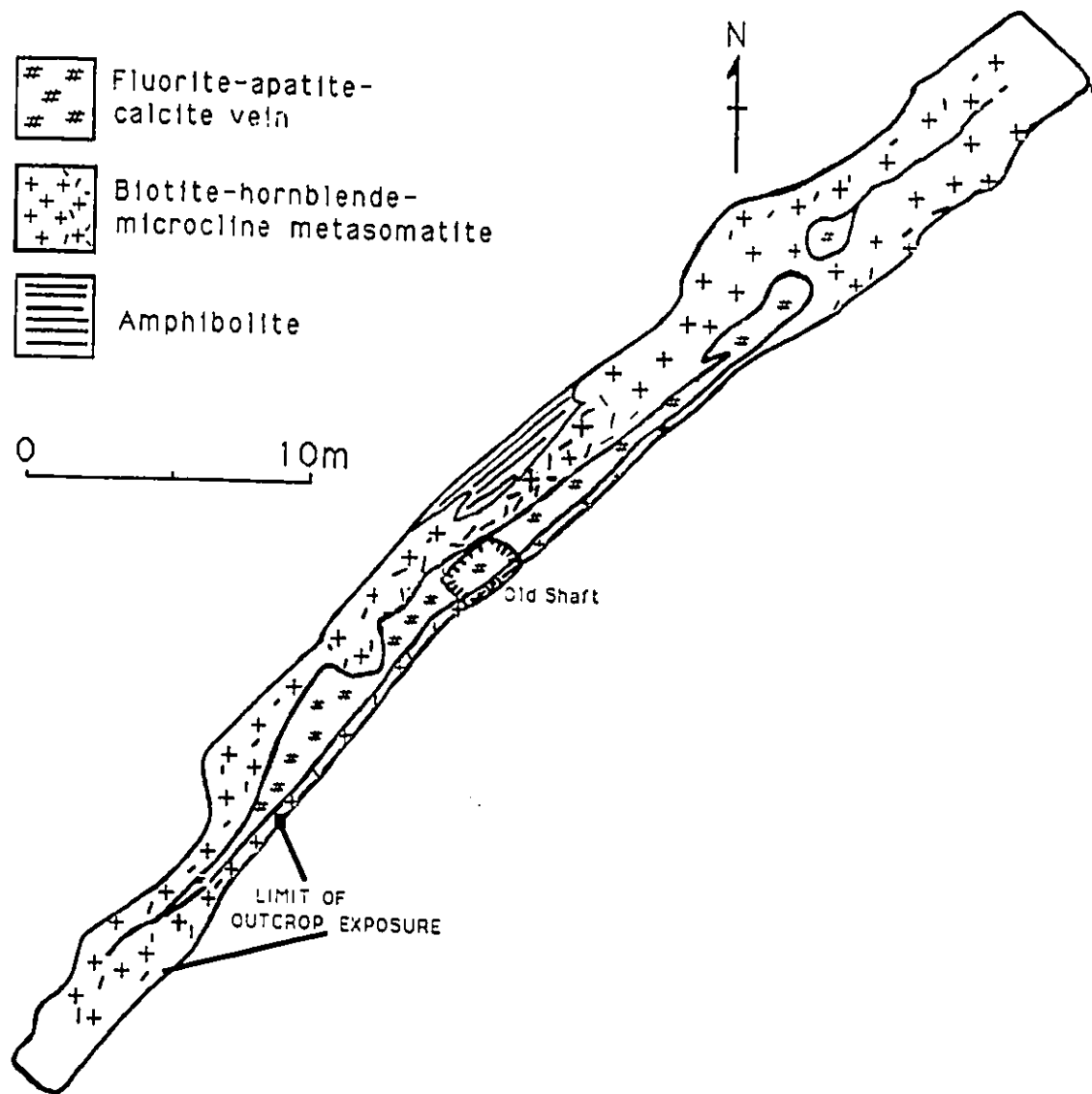


Figure 3.13 Tripp uranium deposit, Cardiff township, ON (after Satterly, 1957).

development of the fluorite-apatite-calcite vein which has resulted in incomplete and often discontinuous zoning away from the fluorite-apatite-calcite vein.

Medium-green Ca pyroxene is the dominant type of alteration associated with the apatite-calcite veins. In some instances, quartz and feldspar are replaced by Ca pyroxene (Plate 3.17) and may replace host rock fragments almost entirely (Plate 3.18). Light green pyroxene (diopside) replaces granite pegmatite along the margins of apatite-calcite veins particularly in the vicinity of marble. Along the margin of a calcite vein the assemblage phlogopite-scapolite-Ca pyroxene seems to replace the host rock with only minor textural modification suggesting molecular replacement (Plate 3.19). The texture is subsequently modified by recrystallization and an increase in grain size.

3.3.5 Discussion

The brief descriptions of the mineral assemblages associated with the fluorite-apatite-calcite veins indicate that they are very complex. The alteration assemblages represent a partial to complete chemical reaction of the host rock in response to the presence of a chemically-reactive hydrothermal fluid. The complex and often conflicting mineral parageneses are a result of the dynamic effects of the changing chemical and physical nature of the hydrothermal fluid. Several hypotheses have been proposed for the petrogenesis of the fluorite-apatite-calcite veins which reflect the interpretation of the related alteration assemblages. These include: 1) a hydrothermal origin related to carbonatites and/or mafic magmas, 2) a regional metamorphic-metasomatic origin, 3) a pegmatite-hydrothermal origin involving hydrothermal mobilization of marble carbonates.

A hydrothermal origin was first proposed by deSchmid (1912) in a study of mica deposits in the Grenville Province of Ontario and Quebec. However, the alteration assemblage of phlogopite-scapolite-pyroxene was interpreted as a mafic

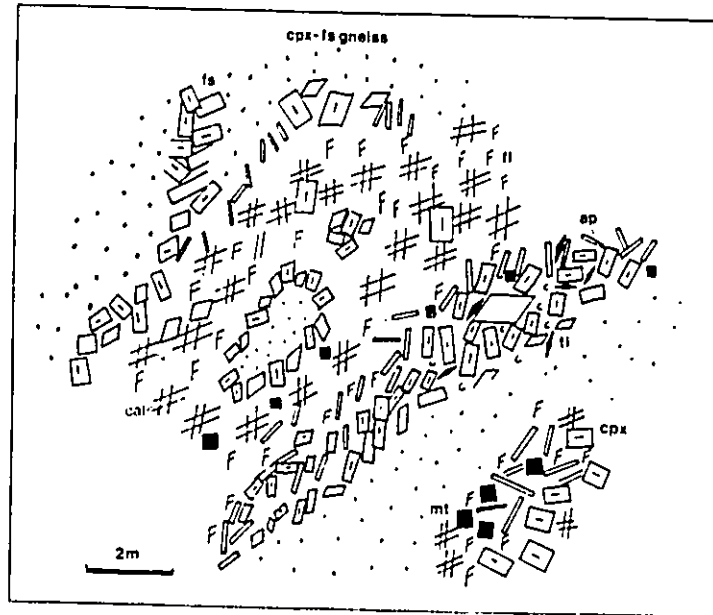


Figure 3.14 A) Apatite-fluorite-calcite vein with titanite- and magnetite-bearing pyroxene-feldspar selvage hosted in altered pyroxene-feldspar gneiss, Cardiff "B" zone (# 9), Cardiff township, ON.

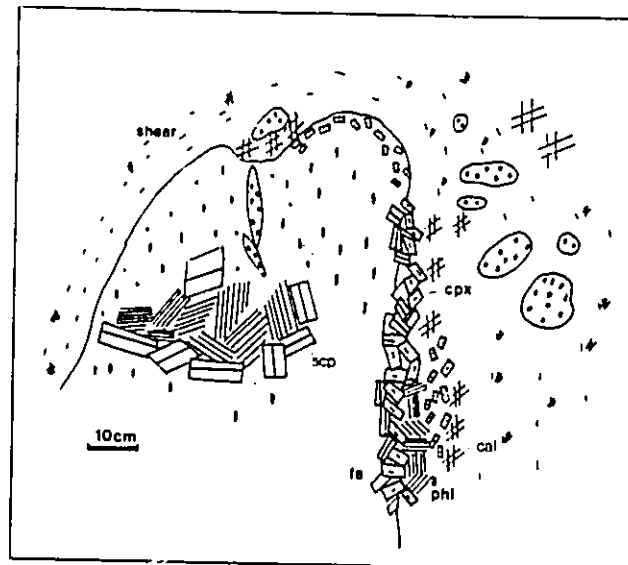


Figure 3.14 B) Granitoid xenolith partially replaced by phlogopite-scapolite vein with a phlogopite-scapolite-pyroxene selvage hosted in a sheared calcite vein, north of the Cardiff "C" zone (# 9). Cardiff township, ON.

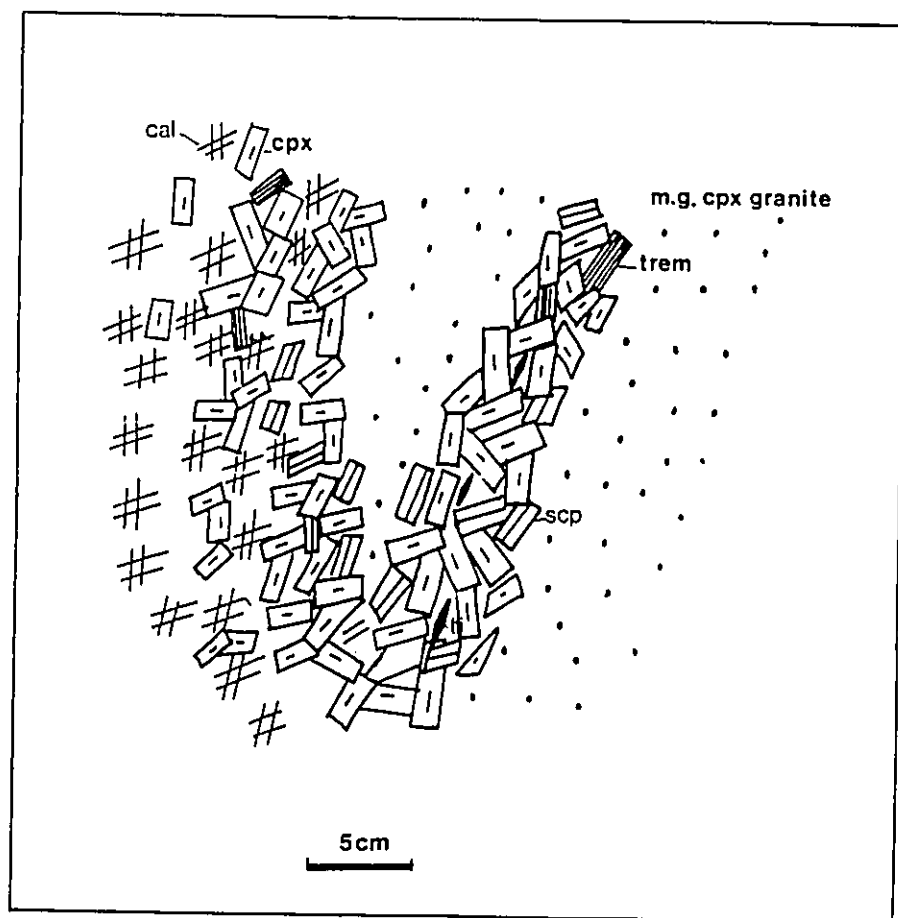


Figure 3.15 Coarse-grained titanite-tremolite-scapolite-pyroxene vein and selvage replacing pyroxene-bearing granitoid rock related to calcite vein, north of Cardiff "C" zone (# 61), Cardiff township, ON.



Plate 3.17 Apatite-fluorite-calcite vein with coarse-grained pyroxene selvage hosted in altered pyroxene-K-feldspar gneiss, Vaughan uranium occurrence, north of Forester Falls (# 57), ON. Scale is 1 cm long.



Plate 3.18 Apatite-fluorite-calcite vein with partially altered gneiss fragments, Ca pyroxene and K-feldspar fragments, Matte zone (# 60), Yates deposit, Huddersfield township, P.Q.. Scale is 1 cm long.

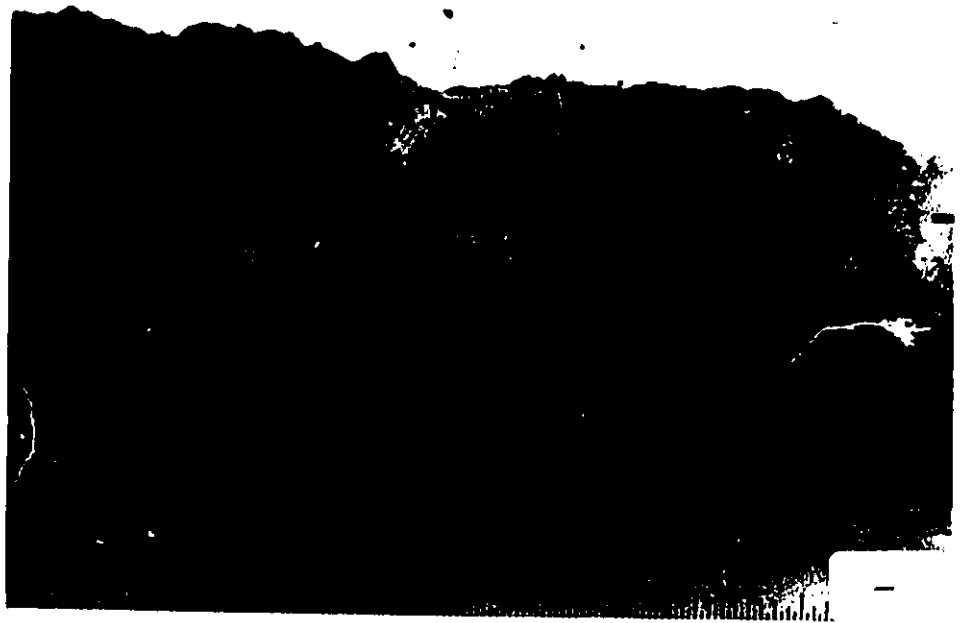


Plate 3.19 Orange calcite vein with marginal scapolite hosted in a phlogopite-Ca pyroxene-scapolite replacement zone after granitoid rock, Litchfield (Leslie Lake) Mo occurrence, Otter Lake, P.Q. Scale is 1 cm long.

igneous intrusion and the apatite-calcite veins were thought to represent volatile emanations from the solidification of the phlogopite-scapolite-Ca pyroxene "magma". Spence and Carnochan (1930) examined the uraninite-bearing "syenite pegmatites" associated with apatite and calcite, as well as pyroxenite, in the Wilberforce area and interpreted the "pyroxenites" (clinopyroxenites) as basic igneous magmas. Heinrich (1966) notes the similarity between these deposits and carbonatites but calls them carbonatic veins because of their association with pegmatite and skarns. Heinrich (1966) noted the resemblance of the veins to carbonatites but was reluctant to describe them as such because of the abundant evidence for a hydrothermal origin. Subsequently, however, he simply referred to them as carbonatites. In a review of Ontario uranium deposits, Robertson (1981) classified the Silver Crater as a carbonatite. Lumbers (personal communication) and Mungall (1989) have suggested that the veins are carbonatites instead of large hydrothermal calcite veins and that the pyroxene alteration is actually fenitization. The pyroxene alteration associated with the apatite-calcite veins has been described as fenite-like alteration by Masson and Gordon (1981) in their study of uranium deposits in the Pembroke-Renfrew area. Similarly, Storey and Vos (1981b) described the alteration as fenite-like because the host rock is replaced, in part, by a pyroxene-rich assemblage.

In a regional geological study of the Fort Coulonge-Otter lake-Kazabazua area of western Quebec, Kretz (1977) suggested that the skarns were related to regional metamorphism. Similarly, Lafontaine (1980) concluded that the skarns and veins were related to the expulsion of volatiles during regional metamorphism. In a geochemical study of apatite from marble, skarns, veins, and carbonatites from Hull and Templeton townships, Quebec, Hogarth (1988) found a low Sr

content in apatites from skarns and veins compared to the carbonatites.

In an examination of molybdenum deposits, Wilson (1924) suggested that the metapyroxenite was a contact metamorphic phenomena with limestone. In several instances, this relationship may be observed, particularly the Hunt Mo deposit (Figure 3.12). At the time of investigation, the term contact metamorphism included metasomatic transformation of the marble (limestone). In a geological and petrological study of the phlogopite-apatite deposits of western Quebec, Landes (1938) indicates that the phlogopite-apatite deposits are related to the magmatic-hydrothermal activity of pegmatites. He suggested that contaminated pegmatite resulted from the interaction of marbles with the pegmatite which cause desilicification of the granitic pegmatite, resulting in diopside crystallization (endoskarn).

Numerous earlier researchers noted the association of pegmatites, skarns, and apatite-calcite veins. In the township of North Burgess (south of Perth, Ontario), Currie (1951) mapped phlogopite-apatite deposits and found a spatial and temporal relationship between the apatite-calcite vein, pyroxenite, and pegmatites. This led Currie (1951) to suggest a contact metamorphic origin for the veins related to the intrusion of the pegmatites. Rowe (1952) favoured a hydrothermal origin for the Richardson (Fission) uraninite-bearing, fluorite-apatite-calcite vein near Wilberforce. Satterly (1957) proposed a magmatic-hydrothermal origin for the veins related to the pegmatites based on a field study of the uranium mineralization in the Bancroft area. In a study of the uranium deposits in western Quebec, Shaw (1958) and Shaw *et al.* (1963) indicated that the pyroxenites were associated with pegmatites but related the phenomena to regional metamorphism. In a study of scapolite-bearing skarns Shaw *et al.* (1965) proposed a contact metamorphic origin for

these skarns because of the spacial relation to a granitic pegmatite.

The spatial distribution and mineralogic (Fe-rich Ca pyroxene, scapolite, albite, K-feldspar hornblende, biotite, titanite) and textural similarities (coarse-grained nature) of the pegmatite-related skarns and the fluorite-apatite-calcite veins are interpreted as evidence for a related origin. This petrogenetic relationship suggests that the metasomatic fluid responsible for the formation of the veins and skarn was pegmatite-derived, but had been chemically modified during interaction with marble.

CHAPTER 4

CHEMICAL COMPOSITION OF SKARN AND VEIN MINERALS

4.1 Introduction

The variation in skarn mineralogy and mineral-chemical composition is here seen as a reflection of the interaction between a chemically evolving hydrothermal fluid and the compositionally variable host rocks (marbles, clinopyroxenite, amphibolites, and gneisses) as was emphasized in the previous section. In general, field examination of the pegmatites, skarns, and veins indicate that there is a progression from Fe-rich to Fe-poor assemblages (mica, pyroxene, amphibole) consistent with their spatial relationship to pegmatite bodies. This suggests that the iron-bearing, pegmatite-derived metasomatic fluid became depleted in iron during interaction with the wall rocks. Major- and trace-element chemical analyses of minerals from pegmatites, skarns, veins, and host rocks is used to; i) characterize the chemical evolution and variation of these assemblages, ii) compare compositions with previous studies, and iii) determine distribution coefficients (K_D) and elemental distributions between skarn minerals. The analytical methods are described in appendix 1.1. The samples are 3 mm to 10 cm sized crystals which were separated with tweezers, under the binocular microscope in many instances, washed with dilute nitric acid until effervescence stopped (10 to 120 seconds), washed with distilled water, and air dried under a hot lamp. The complete chemical analyses are given to indicate the limited extent of contamination by other phases (> 99 volume percent pure mineral).

4.2 Phlogopite/biotite

4.2.1.1 Introduction

This study of the chemical composition of phlogopite/biotite is a supplement to Dr. J. Rimsaite's investigation of micas in uraniferous, thoriferous, and molybdeniferous skarns and veins within the Central Metasedimentary Belt of the Grenville Province (Rimsaite, 1967). In the present study, the major- and trace-element analyses were obtained by XRF analysis (appendix 1) for 8 occurrences in marble, 8 in silicated marble, 42 in skarns (marble/clinopyroxenite hosted), 8 in apatite-calcite veins (amphibolite-gneiss hosted), and from pegmatites, dominantly from the Wilberforce and Yates areas, but also from other deposits in the Central Metasedimentary Belt.

4.2.1.2 Compositional zoning in micas

It is important to consider the extent to which zoning or other compositional variation exists in the mica crystals. A large phlogopite crystal (16.75 cm x 10.5 cm) from the Dacey skarn/vein locality was separated into 9 segments (Figure 4.1) and chemically analysed by XRF (Figure 4.2). Hand specimen examination of the phlogopite indicated that it was not zoned. Of the nine samples analysed, the outer most sample 1 was contaminated with minor quartz hence was not considered in this discussion. Similarly, a coarse-grained biotite crystal (2.5 cm to 3 cm diameter) from the Silver Crater mica-apatite-calcite locality was cut concentrically from the core into 4 zones and chemically analysed by XRF (Figure 4.2). The average and standard deviation were calculated for each mica (Table 4.1). The chemical variation represented by the standard deviation (s) reflects variations in the mica composition within the crystal. Compositional zoning in the Dacey phlogopite and the Silver Crater biotite were plotted with analytical errors (Appendix 1.2). Instrumental error was tested based on 8 replicate analyses of a standard (BR), 5 replicate analyses of a fused phlogopite (sample 6B), and 2 replicate analyses of a fused biotite (sample 27B) and are

quoted as a coefficient of variation at 1 standard deviation (see Appendix 2 for details).

The standard deviations for the raw and normalized data are quite low indicating that there is only minor chemical zonation developed in the micas (Table 4.1). However, in the Dacey phlogopite Al_2O_3 decreases slightly toward the margins whereas CaO increases almost two fold from core to margin. The calcium content of the phlogopite is probably a result of contamination with calcite within the vicinity of the rim. Contamination of calcite would account for the decrease in Al_2O_3 within the mica. Barium and Rb decrease near the margin but Rb is quite irregular. The Silver Crater biotite is also weakly zoned with a decrease in FeO at the margin coincident with an increase in MgO . TiO_2 decreases systematically from core to margin (2.2 to 1.95 wt.%). In other crystals from the Dacey mine, rutile occurs as very fine-grained, oriented needles within the phlogopite and is possibly an exsolution product (D.D. Hogarth, personal communication). This zoning study shows that barium decreases from core to margin but previous barium analyses on this mica by the author were considerably lower and the difference has not been explained. In the author's opinion, bulk-crystal analyses seem to properly represent the chemical composition of the micas.

4.2.1.3 Compositional variation in the micas

The average chemical compositions of each of the 5 types are presented in Table 4.2 from compositional data listed in Appendix 3.1. Compositional data is used to calculate mineral formula (Minfile program; Affifi and Essene, 1985) which will be used in the subsequent discussion. There are some major-element and trace-element differences between the five types of micas (Table 4.2a; Figure 4.4 and 4.5). The $\text{Si}^{4+\text{IV}}$ content of the mica in the marbles and skarns is similar but lower than mica in the veins and the pegmatites (Figure 4.4). The tetrahedral Si content decreases with increasing $\text{Fe}/(\text{Fe}+\text{Mg})$.

Table 4.1 Average chemical compositions two zoned micas

	Dacey phlogopite		Silver Crater biotite	
	ave.	1s	ave.	1s
n	8		4	
SiO ₂	41.0	0.4	38.9	0.3
TiO ₂	1.57	0.05	2.10	0.13
Al ₂ O ₃	13.01	0.16	11.02	0.13
FeO	3.75	0.06	17.88	0.38
MgO	23.85	0.22	13.86	0.15
MnO	0.04	0.00	0.87	0.02
CaO	0.31	0.08	0.06	0.03
Na ₂ O	0.32	0.03	0.56	0.07
K ₂ O	9.95	0.07	9.37	0.08
P ₂ O ₅	0.01	0.01	0.01	0.01
S	0.02	0.01	0.01	0.01
Total	94.1	0.7	94.9	1.1
ppm				
Ba	3770	250	930	70
Cr	36	7	83	6
Zr	<10		<10	
Sr	39	7	<10	
Rb	689	11	484	9
Y	<10		<10	
Nb	104	13	108	8
Zn	320	23	632	41
Ni	<10		<10	
V	16	4	116	4

Notes: 1s is an estimate of one standard deviation. n - number of samples.

A

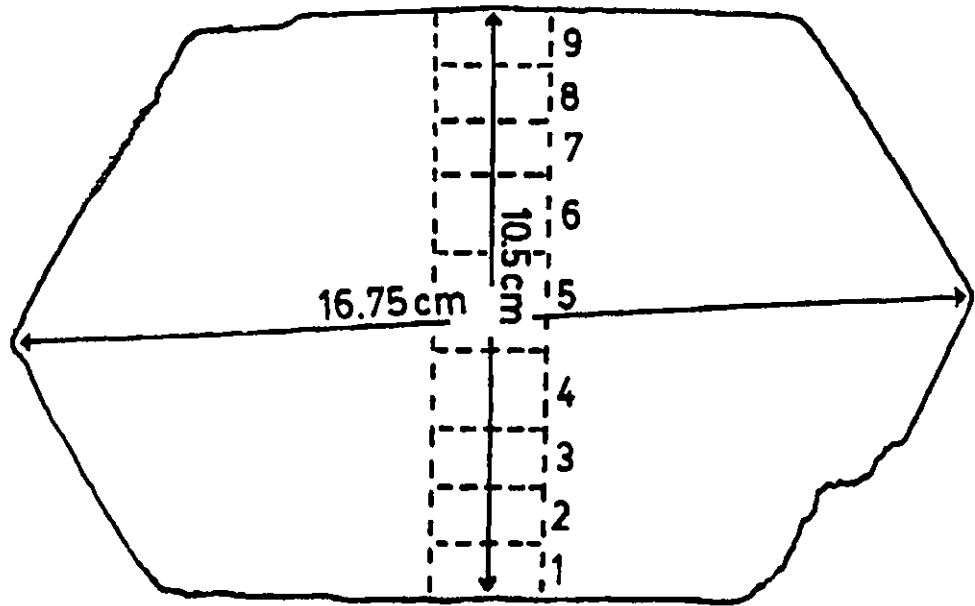


Figure 4.1 A) Sample numbers located on a sketch from zoning profile study of the Dacey phlogopite crystal (# 74), Canton, Quebec.

B

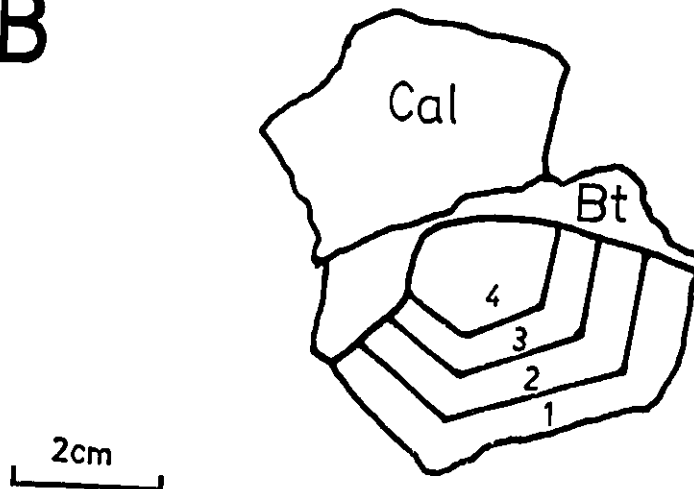


Figure 4.1 B) Sample numbers located on a sketch from a concentric zoning study on a Silver Crater biotite crystal (# 27), Cardiff Township, Ontario.

The mica in the veins have the lowest Al^{3+} but the Al content of the pegmatite-hosted mica increases with increasing Fe/(Fe+Mg) ratio up to 2.6 cations. The trioctahedral mica from veins and pegmatites have the highest Fe and Mn content with a strong positive correlation between them. The Ti^{VI} content of micas is high in the veins and pegmatites and increases sympathetically with Fe/(Fe+Mg) ratio and inversely with silica. The Ca^{2+} , K^+ , and Na^+ (A site) are variable and low in all types, particularly pegmatites, suggesting the presence of H_3O^+ or NH_4^+ or an A-site vacancy. However, partial volatilization of alkalis eduring sample preparation cannot be ruled out. A few trace elements vary systematically in micas from marble, through silicate marble, skarn, vein to pegmatites: generally, Rb, Nb, Zn, and Ni, increase whereas Sr decreases. The abundance of the remaining trace elements (Ba, Cr, V, Zr, and Y) is variable and, of these Zr and Y may be contaminant elements (Appendix 3.1). Abundances of some of these elements are shown on figure 4.5. The plots of trace elements Rb versus Ba and Zn reveal a weak inverse relationship for Rb and Ba but a positive correlation for Rb and Zn. The plots of Zn versus Ba and V indicate a crude but inverse relationship between Zn and Ba and no obvious relationship between Zn and V. However, the variation in other trace elements is erratic within and between mica types precluding further analysis.

4.2.1.4 Mica compositions (previous work)

Kretz (1980) obtained 21 partial analyses of phlogopites from marble and 6 from minor marble which represent metasomatized marble (Table 4.2b). Phlogopite separates from metasomatized minor marble have a higher Fe/(Fe+Mg) ratio and MnO contents than separates from the majority of the marble. In a study of distribution coefficients, Kretz (1960) partially analyzed 11 Grenville skarn phlogopites (Table

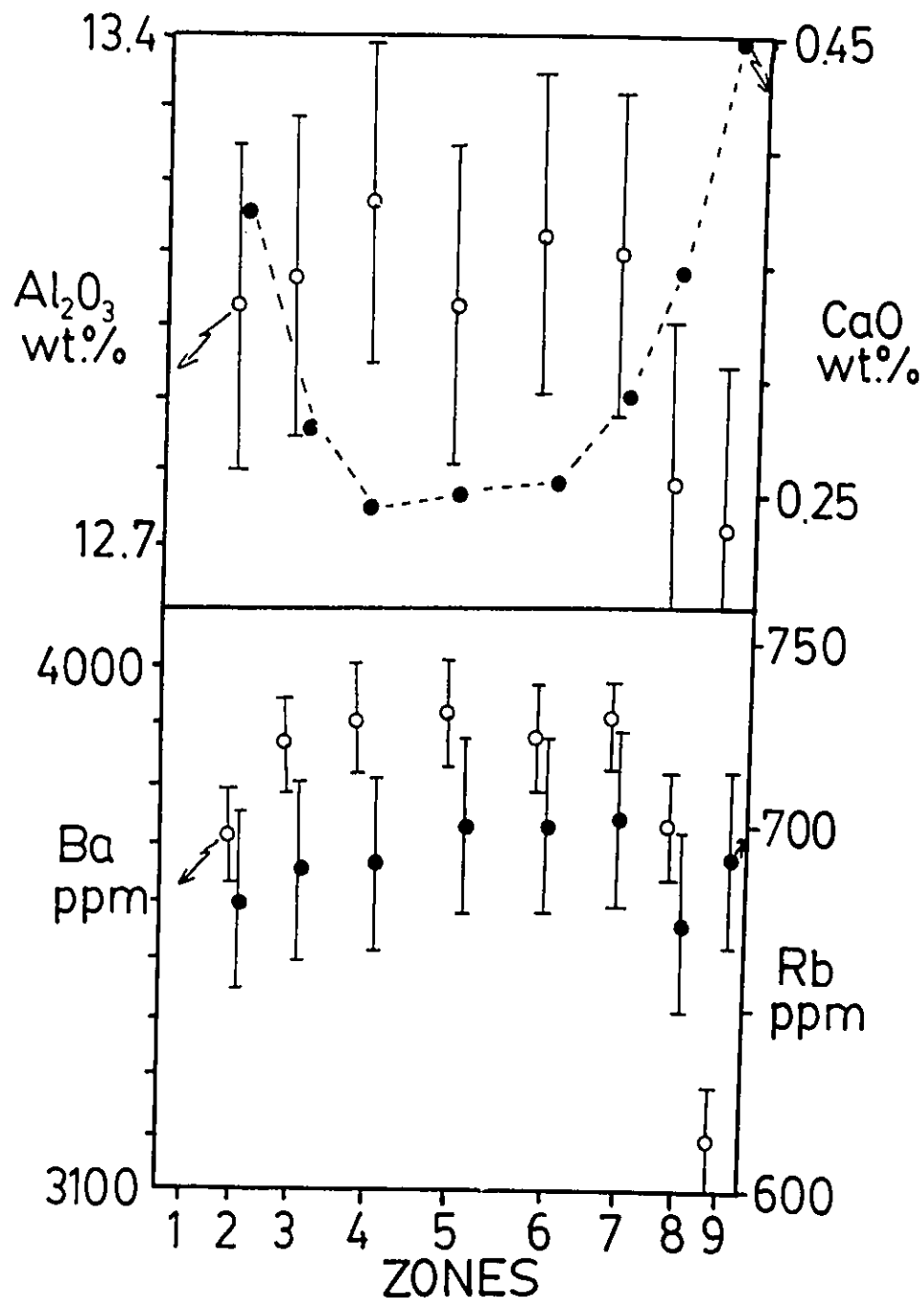


Figure 4.2

Compositional zonation of Al₂O₃ wt.% (O), CaO wt.% (●), Ba ppm (O), and Rb ppm (●) of a phlogopite crystal from the Dacey Mica Mine with 8 samples along a profile (Figure 4.1a). Error bars represent analytical error (2s) based on coefficient of variation derived from replicate analysis of SY-2 (Appendix 1.2).

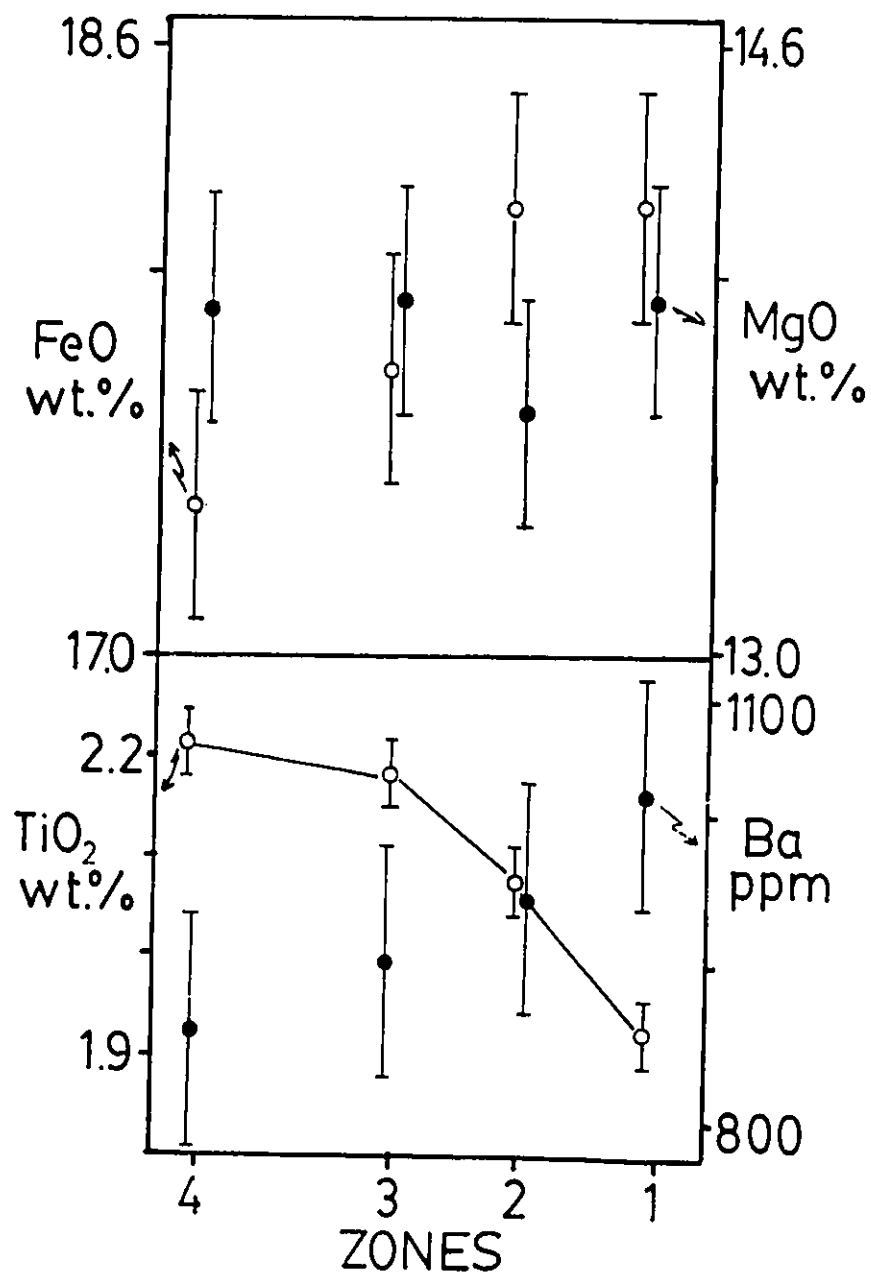


Figure 4.3 Compositional zonation of FeO wt.% (O), MgO wt.% (•), TiO₂ wt.% (O), and Ba ppm (•) of a biotite crystal from the Silver Crater biotite (sample 27C) with 4 concentric zones (see Figure 4.1b). Error bars represent analytical error (2s) based on coefficient of variation derived from replicate analysis of SY-2 (Appendix 1.2).

Table 4.2a Average chemical composition of trioctahedral micas (this study)

Host n wt. %	marble 8 (1s)		silicated marbles 8 (1s)		skarn 42 (1s)		ap-cc vein 8 (1s)		pegmatite 13 (1s)	
SiO ₂	41.3	0.9	41.5	0.9	41.8	1.45	40.3	1.4	37.7	1.3
TiO ₂	0.57	0.41	0.33	0.31	0.47	0.34	1.31	0.61	2.27	0.74
Al ₂ O ₃	12.84	1.18	12.45	1.13	12.19	1.51	11.16	0.48	14.53	1.17
FeO	1.50	0.81	2.48	1.48	4.00	2.77	13.95	4.13	19.33	2.15
MgO	26.89	1.33	25.97	1.40	24.26	1.95	17.24	2.93	10.25	3.66
MnO	0.01	0.01	0.02	0.01	0.06	0.04	0.32	0.26	0.80	0.37
CaO	0.50	0.38	0.20	0.09	0.30	0.28	0.49	0.67	0.23	0.30
Na ₂ O	0.68	0.53	0.45	0.17	0.40	0.29	0.38	0.23	0.11	0.09
K ₂ O	9.35	0.68	9.71	0.15	9.70	0.43	9.54	0.20	9.00	0.86
P ₂ O ₅	0.07	0.11	0.02	0.01	0.02	0.03	0.05	0.09	0.01	0.01
S	0.04	0.02	0.03	0.02	0.03	0.01	0.03	0.02	0.03	0.01
Total	93.8		93.2		93.2		94.8		94.3	
ppm										
Ba	2790	2140	3430	1010	2820	1490	1840	820	1440	2270
Cr	50	23	25	18	37	31	95	67	40	17
Zr	55	62	17	27	43	123	43	41	8	19
Sr	82	131	60	39	65	144	29	31	13	10
Rb	390	278	823	265	895	367	892	382	2623	2003
Y	7	7	8	3	41	131	23	23	31	21
Nb	6	3	4	5	18	26	51	42	363	366
Zn	151	72	192	120	276	108	677	304	791	560
Ni	5	9	15	16	27	42	42	67	62	43
V	70	55	33	42	44	47	83	44	86	76

Notes: n = number of samples. 1s is an estimate of one standard deviation.
Data presented in appendix 3.1.

Table 4.2b Average chemical composition of micas (previous work)

Host	marble	minor marble		skarn		vein		gneiss		skarn		vein		skarn		vein	
Ref.	1	1	6	2	5	2	2	2	2	3	1	3	4	5	11	6	2
No.	21 (1s)	-	(1s)	-	41.9	41.1	36.7	43.74	39.44	0.60	-	-	40.1	0.86	-	42.8	-
SiO ₂	-	-	-	-	-	0.4	4.2	0.20	1.22	0.13	-	-	0.47	0.79	-	0.55	-
TiO ₂	-	-	-	-	-	11.1	14.1	13.74	13.35	1.03	-	-	14.22	13.5	1.8	9.7	-
Al ₂ O ₃	13.80	0.93	13.30	1.13	10.7	-	-	0.38	2.48	1.77	-	-	2.35	-	-	0.3	-
Fe ₂ O ₃	0.36	0.34	1.08	0.37	-	-	-	0.10	3.69	4.15	-	-	2.75	3.0	3.5	4.07	-
FeO	1.18	1.13	3.72	1.19	1.5	8.4	18.4	0.10	23.08	3.17	-	-	23.8	23.9	2.7	24.3	-
MgO	25.81	1.64	23.17	1.67	27.6	21.1	12.0	26.27	0.05	0.02	-	-	0.1	0.03	0.01	0.05	-
MnO	0.00	0.00	0.02	0.02	0.0	0.0	0.0	0.60	0.00	0.00	-	-	0.6	-	-	0.95	-
CaO	0.66	0.35	0.27	0.37	0.0	0.0	0.0	1.89	0.00	0.00	-	-	0.32	0.41	0.19	0.6	-
Na ₂ O	0.69	0.41	0.26	0.09	0.4	0.4	0.0	1.00	2.58	0.39	-	-	9.75	9.4	0.31	9.95	-
K ₂ O	8.64	0.65	9.20	0.19	9.4	10.0	9.5	7.06	9.99	0.50	-	-	3.25	-	-	5.0	-
F	-	-	-	-	-	-	-	0.66	2.95	.57	-	-	2.4	-	-	1.7	-
H ₂ O+	-	-	-	-	-	-	-	3.52	1.94	.49	-	-	0.3	-	-	0.35	-
H ₂ O-	-	-	-	-	-	-	-	0.47	0.43	0.13	-	-	1.8	-	-	2.2	-
O=F	-	-	-	-	-	-	-	0.20	1.20	-	-	-	99.5	-	-	98.6	-
Total	-	-	-	-	-	-	-	98.6	100.0	-	-	-	-	-	-	-	-

Notes: Ref. = references number: 1-Kretz (1980), 2-Lafontaine (1980), 3-Shaw et al. (1965), 4-Hogarth et al. (1970), 5-Kretz (1960), 6-Rimsaite (1967) (BaO > 0.5 wt.%, V₂O₅ ranges from below detection to 0.02 wt.%) (Totals not calculated on incomplete analyses). n = number of samples. Dashes represent no analysis provided. 1s is an estimate of one standard deviation.

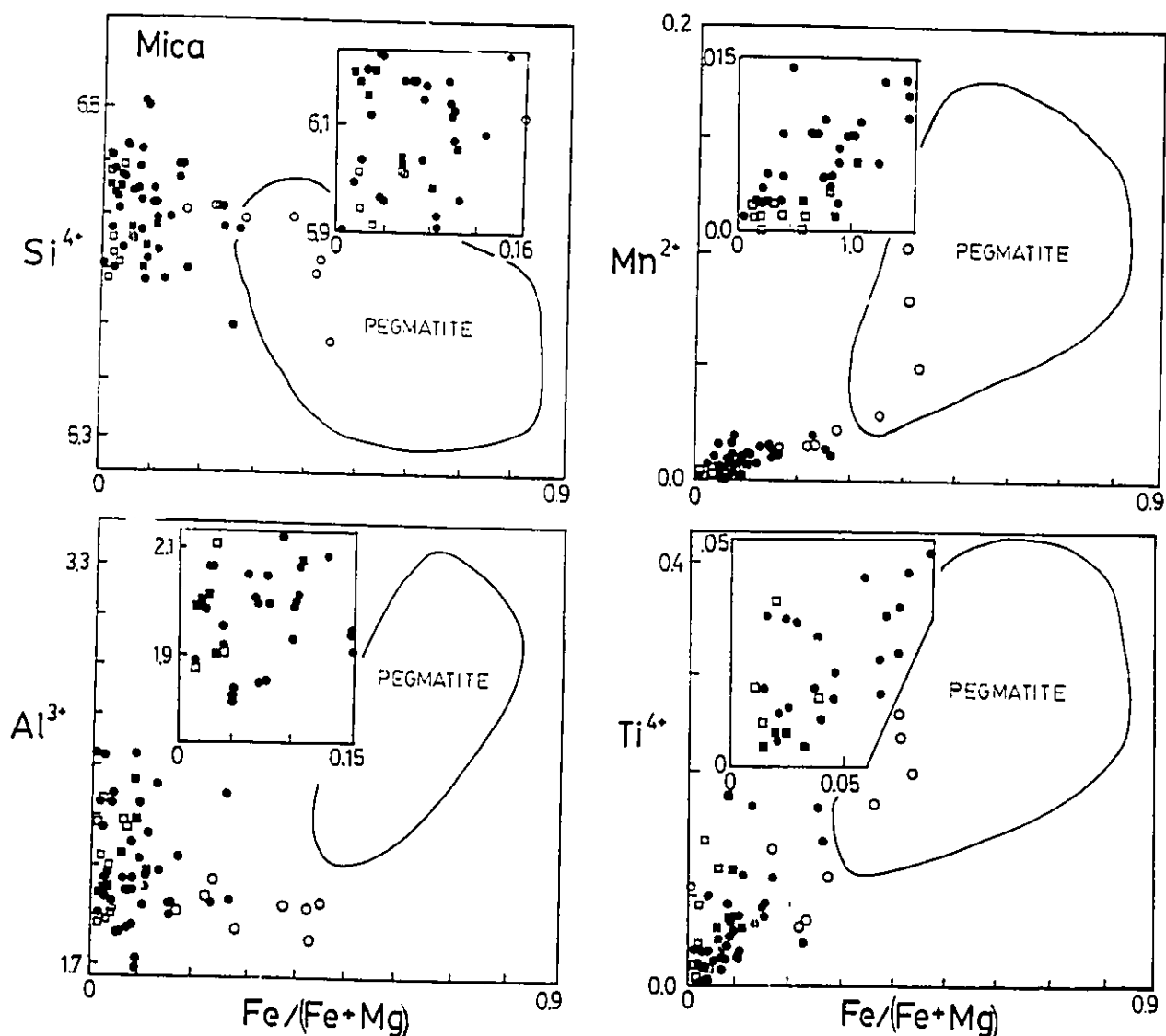


Figure 4.4 Major and trace-element variation (Si^{4+} , Al^{3+} , Mn^{2+} , and Ti^{4+}) versus $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio in micas from marble ($\square$), silicated marble ($\blacksquare$), skarns ($\bullet$), and veins ($\circ$) as well as one unrelated carbonatite (C). Si, Al, Ti, Mn plotted with respect to 44 charges. Data presented in appendix 3.1. The pegmatite field is derived from the biotite study in appendix 6 and includes 22 analyses.

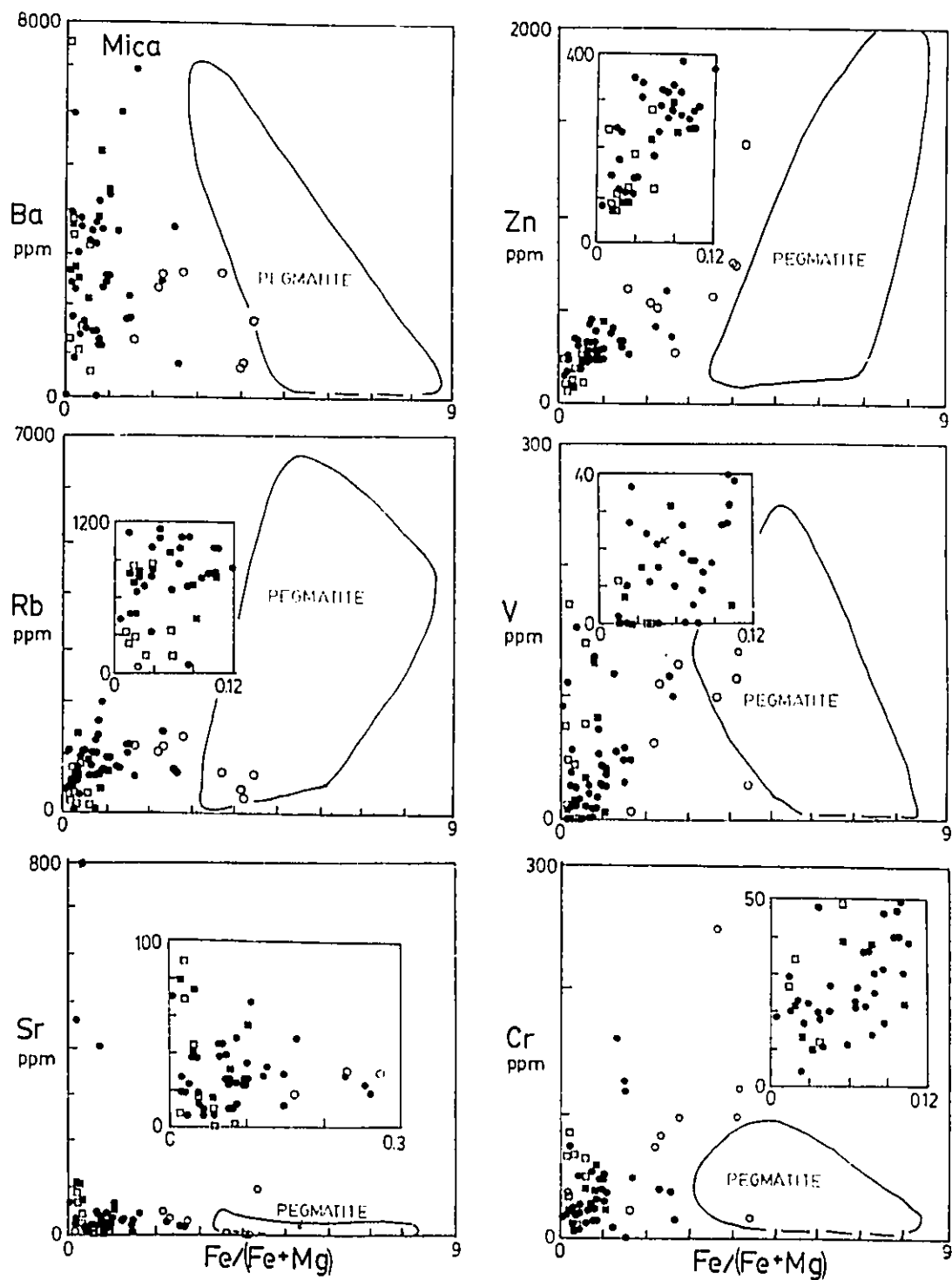


Figure 4.5 Trace-element variation (Ba, Rb, Sr, Zn, V, and Cr) versus $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio in micas from marble ($\square$), silicated marble ($\blacksquare$), skarns ($\bullet$), veins ($\circ$), and carbonatite (C). Data presented in appendix 3.1. The pegmatite field is derived from the biotite study in appendix 6 and includes 22 analyses.

4.2b). These phlogopites have high MgO, Al₂O₃, TiO₂, MnO, and BaO (> 5000 ppm) contents.

At the Yates uranium skarn and vein deposits, Lafontaine (1980) compared phlogopite from skarn and veins with biotite in gneiss. He found the fluorite-apatite-calcite veins at the Matte zone to be Fe rich relative to the skarn phlogopites at the Camp zone but both of these micas contained less Fe, Al, Ti, and more Si and Mg than the biotite in gneiss (Table 4.2b). Shaw et al. (1965) presented a complete analysis of phlogopite from a contact skarn phlogopite from Gib Lake near Fort Coulange (Table 4.2b). Hogarth et al. (1970) compared biabsorbtion, Mossbauer spectra, and chemical compositions for 3 phlogopites from veins and 2 from carbonatites. They found than the phlogopite from carbonatite contained tetrahedral Fe³⁺; the vein phlogopites have no tetrahedral Fe³⁺.

4.2.2 Ca pyroxene compositions

4.2.2.1 Introduction

Numerous researchers have examined the properties of Ca pyroxenes from marble, skarns, and veins. In the present study, the major- and trace-element compositions of pyroxene from silicated marbles (5), skarns (22), and apatite-calcite veins (4) have been determined on mineral separates (>99 % pure) (Table 4.3a). Other major and trace elements are more variable between the types of deposits. Pyroxene nomenclature is that of Morimoto (1989). All the Ca pyroxene analyses pass the test for tetrahedral occupancy ($Si^{IV} + Al^{IV} > 1.979$) indicating good chemical analysis (Robinson, 1980).

4.2.2.2 Compositional variation of Ca pyroxenes (this study)

The average composition of Ca pyroxenes was calculated for each rock type from data summarized in Appendix 3.2. Compositional data were used to calculate mineral formula (Minfile version 2, Affifi and Essene, 1985). The data are summarized in Table 4.3b and plotted with respect to iron content. The Fe/(Fe+Mg) ratio reflects the light to dark

green colour intensity change observed within the field. Fe^{3+} was assigned to unfilled ($\text{Si}_{\text{IV}} + \text{Al}_{\text{IV}}$) tetrahedral site. The Fe^{3+} content of the Ca pyroxenes was calculated with the minfile program and range from 0 to 0.05 tetrahedral ions per standard formula unit ABZ_2O_6 .

The 32 chemical analyses indicate that all the samples may be considered Ca pyroxenes (Figure 4.6A; Morimoto 1989) and fall within or close to the diopside field on the Ca pyroxene quadrilateral (Figure 4.6B). The Na+K content remains less than 7% (0.07 ions per formula unit) of the available A ions in the ideal structure except for the Ca pyroxene hosted in pegmatite (62A-1P) which has 0.12 ions per formula unit.

In general, cationic proportions of Al^{IV} , Al^{VI} , Mn^{VI} , and Ti^{VI} positively correlate with $\text{Fe}/(\text{Fe}+\text{Mg})$ content. As seen in Appendix 3.2, there is insufficient aluminum to fill the tetrahedral positions which accounts for the negative Al^{IV} in some analyses (2 positions - Si cations - Al cations). The positive correlation between the Al^{IV} vacancies (0 to 0.055) and $\text{Fe}/(\text{Fe}+\text{Mg})$ suggests a relationship (Figure 4.7). Iron increases at the expense of Mn in moving from silicated marbles to skarns to veins, similar to the other silicates. The irregular titanium variation may be due to a compositional variation not considered or some submicroscopic titanite contamination which cannot be ruled out. Zinc and V show the strongest positive relationships with iron (Figure 4.8). The other trace constituents (Ba, Sr, Y, and Cr) are more irregular with respect to $\text{Fe}/(\text{Fe}+\text{Mg})$ content.

4.2.2.3 Compositional variation in Ca pyroxene (previous work)

In a study of molybdenum skarn deposits, Karvinen (1973) examined the compositions of Ca pyroxene from skarns and skarnoid gneiss and found that the skarnoid gneiss was enriched in iron over the skarn Ca pyroxene. This could indicate a host rock control on the mineral composition. Lafontaine (1980) noted that a dark green Ca pyroxene formed

**Table 4.3a Average chemical composition of Ca pyroxenes
(this study)**

Host n	sil. marble 5 (1s)		skarn 22 (1s)		ap-cc vein pegmatite 4 (1s) 1		
wt. %							
SiO ₂	53.3	1.00	53.0	1.1	51.5	0.55	50.8
TiO ₂	0.06	0.03	0.06	0.07	0.14	0.11	0.16
Al ₂ O ₃	0.81	0.40	0.81	0.50	0.86	0.30	2.31
FeOT*	4.16	3.66	5.38	3.56	7.37	3.71	12.65
MgO	16.46	3.19	13.67	4.66	13.61	2.77	9.98
MnO	0.22	0.20	0.22	0.12	0.24	0.10	0.46
CaO	22.92	1.02	23.20	1.06	23.67	0.70	21.13
Na ₂ O	0.44	0.23	0.52	0.24	0.51	0.24	1.46
K ₂ O	0.10	0.09	0.06	0.05	0.04	0.02	0.12
P ₂ O ₅	0.00	0.00	0.00	0.01	0.01	0.01	0.00
S	0.03	0.01	0.03	0.01	0.04	0.01	0.00
Total	98.5		96.9		98.1		99.2
Ba ppm	75	24	96	37	82	15	86
Cr	25	21	52	59	41	19	44
Zr	169		22	22	19	17	30
Sr	85	41	92	91	119	27	52
Rb	5	9	4	18	0	0	0
Y	35	24	33	37	27	10	40
Nb	17	25	1	5	7	8	0
Zn	236	233	194	101	264	116	263
Ni	0	0	0	0	3	3	63
V	59	65	97	68	103	54	168

Notes: All Fe as total FeO. n = number of samples. Pegmatite sample (# 62A-1P) not included in appendix. 1s is an estimate of one standard deviation.

Table 4.3b Average chemical composition of pyroxenes (previous work)

Host	marble	marble	gneiss	skarn	skarn	vein	vein	skarn	vein
Ref.	1	9	2	2	3	3	4	5	5
n	(1s)	(1s)	(1s)	(1s)	(1s)	(1s)	(1s)	(1s)	(1s)
wt. %									
SiO ₂	-	-	52.3	0.5	54.6	0.7	54.1	52.5	53.58
TiO ₂	-	-	0.0	0.0	0.0	0.0	-	-	0.07
Al ₂ O ₃	0.46	0.35	1.39	0.47	1.3	0.3	0.4	1.1	1.20
Fe ₂ O ₃	1.11	0.78	1.90	1.09	-	1.8	2.9	1.20	0.72
FeO	5.94	5.63	6.48	3.86	11.3	2.0	3.5	7.4	4.18
MgO	14.53	4.26	12.91	3.13	11.3	1.5	16.2	12.1	14.85
MnO	0.09	0.07	0.13	0.08	0.3	0.3	0.2	0.3	0.19
CaO	23.08	0.89	22.73	1.10	22.3	0.5	23.8	23.7	23.87
Na ₂ O	0.16	0.10	0.43	0.16	1.1	0.2	0.3	0.8	0.54
K ₂ O	0.02	0.00	0.03	0.01	0.1	0.0	0.1	-	0.04
H ₂ O	-	-	-	-	-	-	-	-	0.15
Total			100.0	100.0	100.0	99.2	100.8	100.1	100.5
									100.5

Notes: Ref. = references: 1-Kretz (1980); 2-Karvinen (1973); 3-Lafontaine (1980); 4-Shaw et al. (1963); 5-Hogarth (1988). n = number of samples. 1s is an estimate of one standard deviation.

within the Matte zone fluorite-apatite-calcite vein was higher in Fe, Na, Al, and Mn and lower in Mg compared to medium green Ca pyroxene in the the Camp zone skarn.

Shaw et al. (1963) noted that marble, skarn, and pegmatite pyroxenes belonged to the diopside-hedenbergite series of which the veins and pegmatites were higher in the hedenbergitic component. The pyroxenes were characteristically low in Ti^{4+} and Al^{3+} . Trace-element data on pyroxene from gneisses, syenite, pegmatite, skarns and veins has been determined by Shaw et al. (1963) and Moxham (1960) (Table 4.3c). The few trace-elements examined in this study are similar in abundance and range to those presented in Shaw et al. (1963).

Pyroxenes from skarn and apatite-calcite veins from the Gatineau area have high Al^{3+} and Ti^{4+} contents (Hogarth, 1988) possibly indicative of high metamorphic grade (granulite?) during vein formation. Pyroxene from the veins are richer in iron than those in the skarns.

Kretz (1980) found that the pyroxene in the majority of the marble samples contained less than 10 % of the hedenbergite component whereas the diopsides in the minor marble samples contained more iron (Table 4.3b). In a study of Grenville skarn minerals, Kretz (1960) performed partial chemical analyses on 10 Ca pyroxenes. They had low TiO_2 (0.062 wt.% ave. (0.035 wt.%, 1s)), Al_2O_3 (1.6 wt.% (0.8)), FeO_t (2.2 wt.% (1.7)), Na_2O (0.37 wt.% (0.11)), K_2O (0.10 wt.% (0.10)), BaO (0.01 wt.% (0.01)), and high MgO (16.7 wt.% (1.2)).

4.2.2.4 Discussion

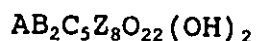
It is evident from this study and previous research that the composition of the Ca pyroxene is related to the host environment. Ca pyroxene hosted in the veins and the pegmatite have a greater hedenbergite component as was surmised from observation of mineral colour in the field. In all cases, the Ca pyroxene falls within the Ca-Mg-Fe

quadrilateral and had low aluminum content except those samples that were formed under granulite grade conditions as noted by Hogarth (1988). The Na_2O content of Ca pyroxene is similar for silicated marble, skarns, and fluorite-apatite-calcite veins and thus suggests that there is no obvious alkalinity difference between their environments during their formation. The remaining major- and trace-elements are either the same within sample variance, or there are no systematic trends with respect to deposit types on a regional scale. However, on a local scale, the chemical variation may be more systematic.

4.2.3 Amphibole compositions

A few bulk-crystal chemical analyses of amphiboles have been determined from skarns (7) and fluorite-apatite-calcite veins (2) (Table 4.4a). There was a problem with obtaining very pure mineral separates with the binocular microscope because of the complex mixture of minerals, in particular biotite and scapolite (?), but the amphibole fraction is believed to be at least 95% pure. Mineral formulas were calculated for each of the chemical analyses on the basis 46 charges (Appendix 3.4; Minfile version 2; Affifi and Essene, 1985). The program calculates the required H_2O to fit the mineral formula since no data were available on H, F, Cl contents of amphibole.

The standard amphibole formula:



Seven samples are Ca amphiboles ($(\text{Ca}+\text{Na})_{\text{B}} \geq 1.34$ and $\text{Na}_{\text{B}} \leq 0.67$) according to the classification of Leake (1978) (Figure 4.9); however, several of the analyses do not pass the criteria for a good chemical analysis (Robinson et al., 1982) because of the Ca in T site (112B-3) and A site (62E, 64C) and A site site occupancy greater than 1 (14D, 27C). Note 19C and 27C have 0.88 and 0.80 ions Na in B and are therefore not

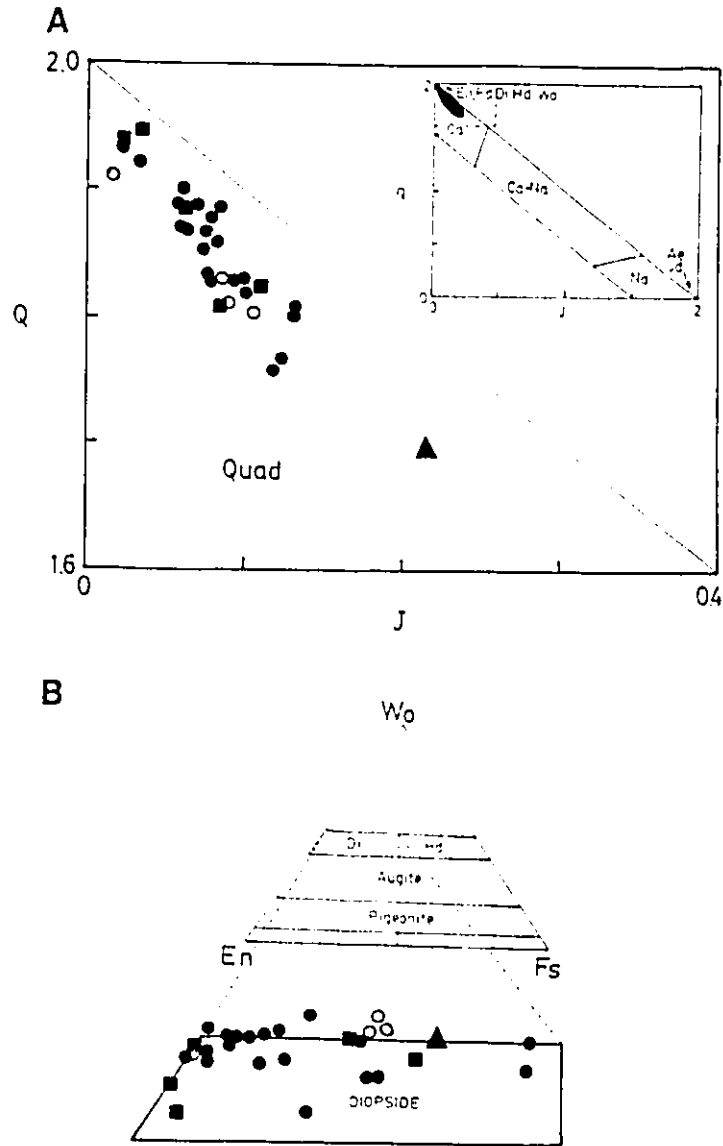


Figure 4.6 A) Q ($Ca^{2+}+Mg^{2+}+Fe^{2+}$) versus J ($2Na^{+}$) pyroxene discrimination diagram (Morimoto 1989) with three fields describing the pyroxene quadrilateral (Ca pyroxene), Ca-Na pyroxene, and Na pyroxene. B) Enstatite-Ferrosilite-Diopside-Hedenbergite quadrilateral for low Na pyroxenes. Symbols are in figure 4.4.

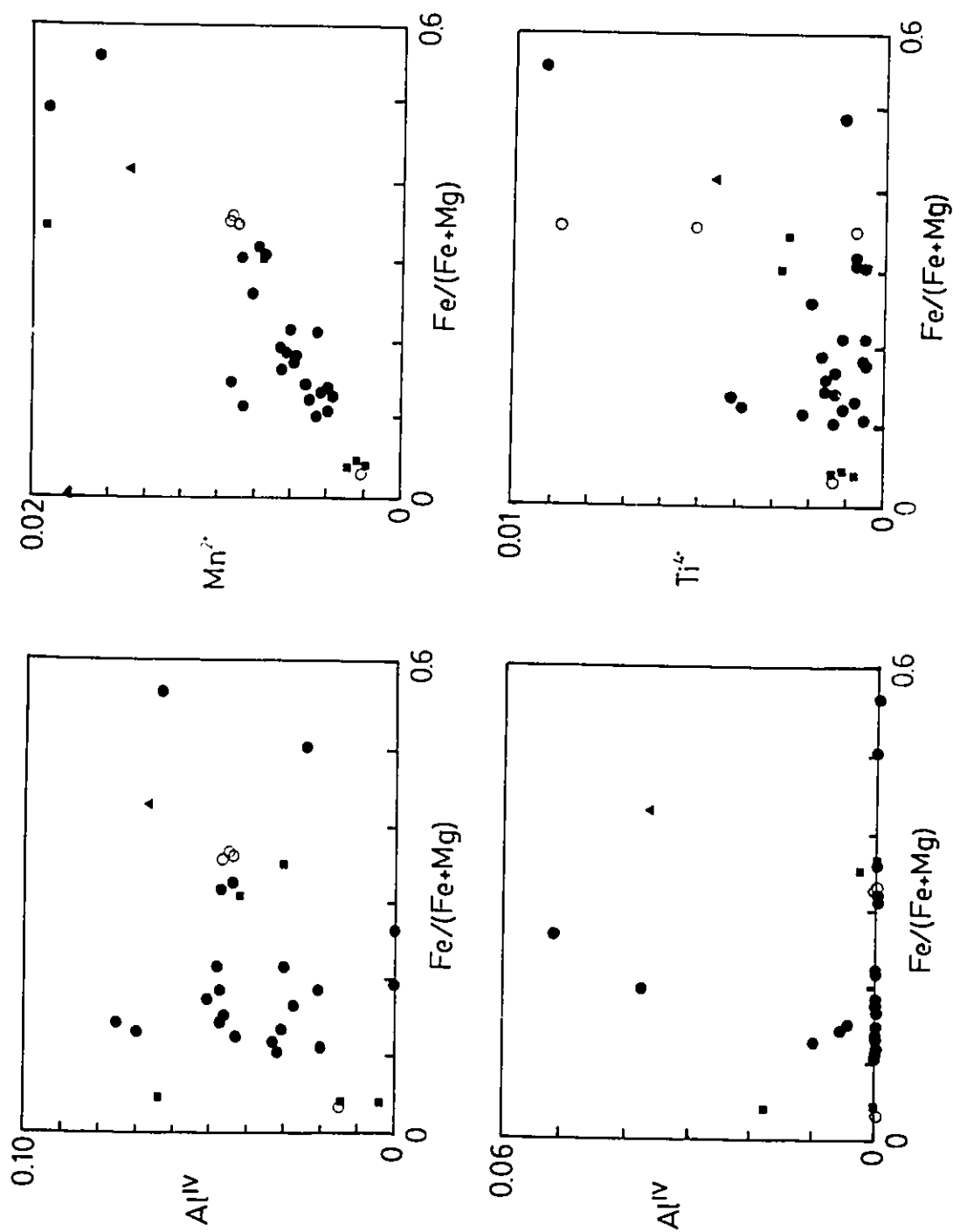


Figure 4.7 Major-element compositions (Al^{IV} , Al^{VI} , Mn^{2+} , and Ti^{4+}) versus $Fe/(Fe+Mg)$ in Ca pyroxenes from silicified marble, skarns, veins, and a pegmatite. Data located in appendix 3.2.

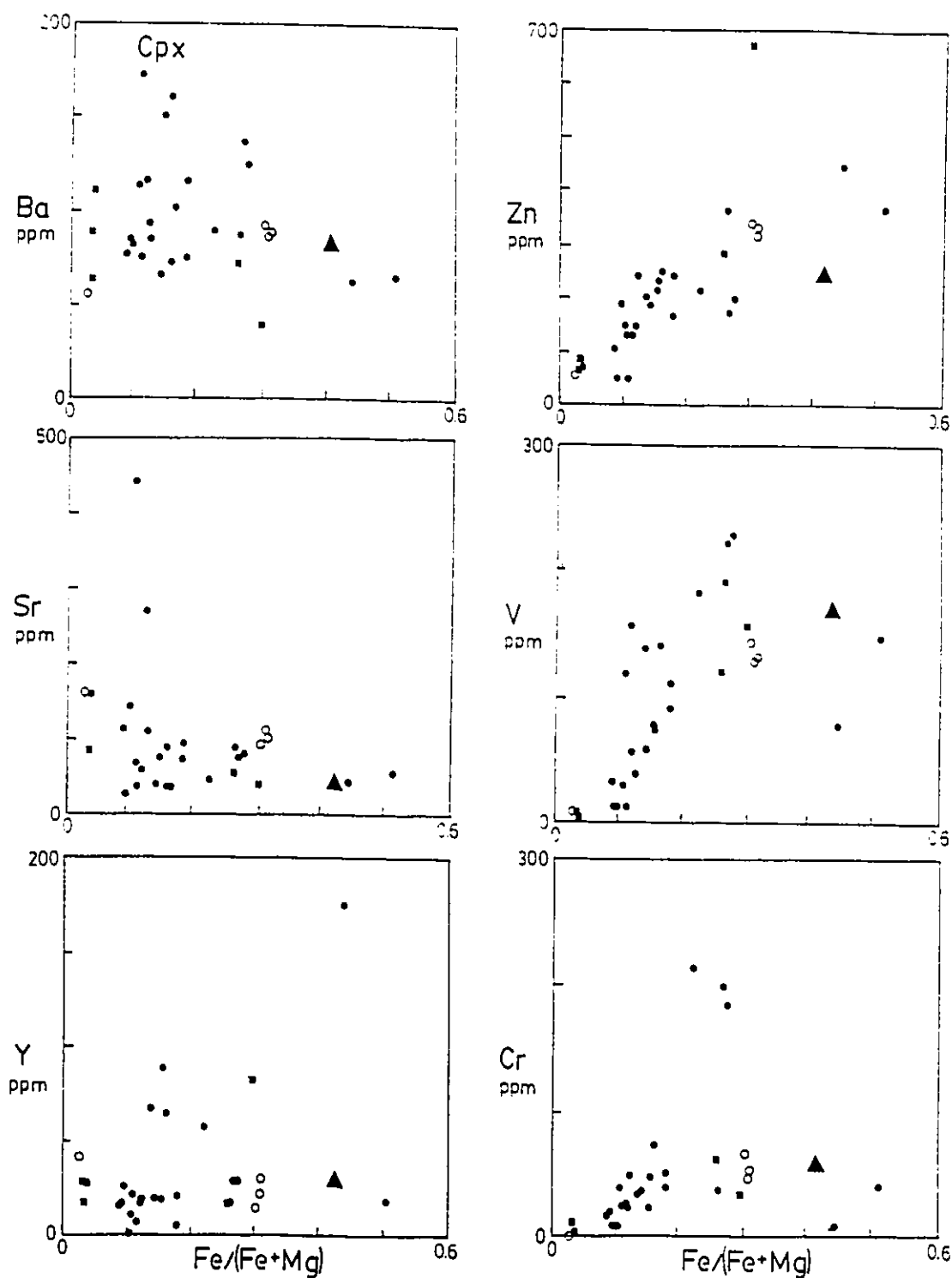


Figure 4.8 Trace-element composition (Ba, Sr, Y, Zn, V, and Cr) versus Fe/(Fe+Mg) ratio of Ca pyroxenes from silicated marble, skarns, veins and a pegmatite. Data presented in appendix 3.2.

Table 4.3c Tabulated trace-element composition of "skarn" pyroxene (Shaw et al. 1963)

	Mean	Range
B	20	7-89
Be	3.5	tr-19
Ga	11	tr-27
Cr	32	tr-210
Ti	309	150-930
Li	63	tr-160
Ni	13	1-39
Co	15	4-45
Cu	4.5	tr-15
V	32	7-76
Zr	38	10-68
Mn	1350	590-2800
Sc	8.9	tr-48
Y	9.1	tr-30
Sr	70	17-120
Ba	15	tr-65
Rb	8	tr-32

Notes: Data includes pyroxenes from granodiorites, syenites, pegmatites, gneisses, skarns, and veins. tr = below detection limit.

calcic amphiboles. In addition, the amount of Na and K in the A site is much higher than normal suggesting that these amphiboles were not compositionally pure and/or the environment was alkaline. Unfortunately, no optical examination of these amphiboles was done hence amphibole exsolution products may have been analysed which could account for amphiboles with intermediate aluminum compositions or the presence of impurities. It is also interesting that no tremolites were analysed due to the apparently high abundance of Na in the A site. The uncertainty in the amphibole analyses precludes a detailed analysis of their compositions.

The amphibole compositions are variable, with the veins being lower in Mg^{2+} and higher in Ti^{4+} , Fe^{2+} , and Mn^{2+} than the skarn amphiboles. The Al^{3+} content is quite variable in the skarns and vein-hosted amphiboles. The two Na-Ca amphiboles from apatite calcite veins are richer in Cr, Zr, Y, Nb, and Zn than those from skarn which may, in part, be contamination.

Kretz (1980) found that the majority of the amphiboles in the marble had a high Mg/Fe ratio in comparison to the metasomatized minor marble similar to other silicate phases (Table 4.4). Shaw et al. (1963) report a Mg-rich calcic amphibole analysis from the Gib Lake marble-hosted contact skarn. Hogarth (1988) examined a Ca amphibole from a skarn finding low Al with moderate iron, high Fe^{3+}/Fe^{2+} and Mn.

It is evident from this study and previous work that the amphiboles are particularly sensitive indicators of the conditions under which they formed. Although there are small differences in the composition between the skarn amphiboles and vein amphiboles, it seems to reflect the differences in the host rock environment. The Na-Ca amphiboles have a alkaline trend which is common to igneous rocks but are not obviously similar to Na amphiboles related to fenite alteration associated with a carbonatite.

Table 4.4 Average chemical composition of amphiboles

Host Ref. n	skarn 1 7	(ls)	vein 1 2	(ls)	skarn 2	(ls)	marble 3 8	(ls)	min. marble 3 4	skarn 4 1	vein 5 1
SiO ₂ wt. %	48.4	5.4	43.6	2.5	-	-	-	-	-	48.3	56.3
TiO ₂	0.17	0.08	0.91	0.01	0.26	0.34	-	-	-	0.13	0.10
Al ₂ O ₃	8.66	5.91	7.36	1.45	10.1	6.2	7.81	6.26	8.40	11.17	0.55
Fe ₂ O ₃	4.32	3.75	21.49	1.72	-	-	0.89	0.76	6.23	3.02	4.79
FeO	-	-	-	-	3.7	2.7	0.94	0.79	6.51	3.20	2.82
MgO	19.54	2.45	9.30	1.32	18.5	2.5	21.34	1.64	15.23	5.33	19.55
MnO	0.12	0.09	0.95	0.27	0.08	0.04	0.02	0.02	0.05	0.05	0.22
CaO	11.09	1.91	7.91	2.07	-	-	13.11	1.13	12.50	0.52	9.23
Na ₂ O	3.24	1.15	4.59	1.47	2.06	1.35	1.66	0.95	1.14	0.57	2.09
K ₂ O	1.23	0.34	1.43	0.27	1.10	0.61	0.67	0.32	0.97	0.60	0.94
P ₂ O ₅	0.00	0.00	0.00	0.00	-	-	-	-	-	0.02	-
S	0.04	0.01	0.04	0.01	-	-	-	-	-	-	-
H ₂ O+	-	-	-	-	-	-	-	-	-	-	-
F	-	-	-	-	-	-	-	-	-	1.59	1.77
F=O	-	-	-	-	-	-	-	-	-	0.36	0.75
Total	96.8	-	97.5	-	-	-	-	-	-	98.8	98.5
Ba ppm	135	70	70	10	200	150	-	-	-	-	-
Cr	29	13	102	50	-	-	-	-	-	-	-
Zr	81	62	377	170	-	-	-	-	-	-	-
Sr	144	163	59	27	-	-	-	-	-	-	-
Rb	10	7	26	26	-	-	-	-	-	-	-
Y	36	32	76	19	-	-	-	-	-	-	-
Nb	15	9	88	23	-	-	-	-	-	-	-
Zn	173	110	769	267	-	-	-	-	-	-	-
Ni	2	6	0	0	-	-	-	-	-	-	-
V	111	173	193	96	100	100	-	-	-	-	-

Notes: Ref. = references: 1-This study (appendix 3.3); 2-Kretz (1960); 3-Kretz (1980); 4-Shaw et al. (1965); 5-Hogarth (1988). n = number of samples. Dashes indicate no analysis. ls is an estimate of one standard deviation.

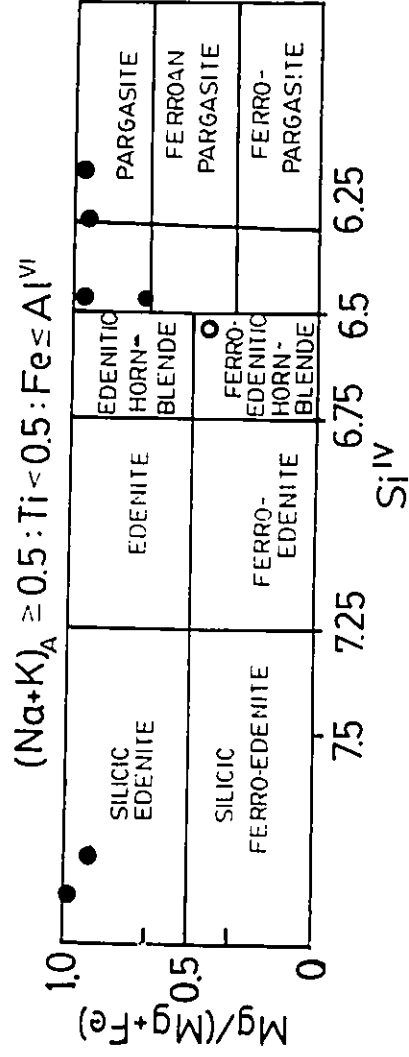


Figure 4.9 Si in standard formula unit versus Mg/(Mg+Fe) composition of Ca amphibole from skarns (●) and veins (○) with the nomenclature after Leake (1978). See appendix 3.3 for tabulated data.

4.2.4 Scapolite compositions

A petrochemical study of scapolite is beyond the scope of this research. However, it is essential to consider the research presented to date on scapolite because this mineral is prevalent in many of the gneisses, skarns, and veins under consideration. Most of the compositions lie within the dipyre ($\text{Ma}_{25}\text{Me}_{75}$) to mizzonite ($\text{Ma}_{75}\text{Me}_{25}$) range (Shaw et al., 1963). The pegmatite-hosted scapolite has the highest marialite content ($\text{Ma}_{80.6}$) where as the skarns have the highest meionite contents (Table 4.5).

Karvinen (1973) analysed scapolites from several skarns (some coexisting with plagioclase) finding mainly intermediate compositions. Generally, scapolites from Mo-bearing skarns seem to be in disequilibrium with the coexisting plagioclase because of the absence of a systematic chemical relationship between scapolite and plagioclase. The scapolite hosted in the hedenbergite gneisses have consistently higher calcium contents than those in the skarns (Karvinen, 1973).

Shaw et al. (1965) chemically analysed a scapolite (dipyre) from a proximal exoskarn zone at Gib Lake, Quebec. Haughton (1971) examined numerous scapolite-plagioclase pairs in the skarns from the Grenville Province and found that the scapolites were usually richer in calcium than the coexisting plagioclase. Hogarth (1988) analysed a scapolite (calcic mizzonite) from a skarn-hosted apatite vein near Gatineau, Quebec. Kretz (1980) noted that scapolite is commonly present in the metasomatic minor marbles.

The chemical analyses of scapolite presented by Shaw (1960) were subdivided into various rock types, based on the description provided, in order to identify differences in scapolite composition from various environments. The subdivisions include: gneiss (including granulite), marble, skarn (including veins), and pegmatite (includes syenite).

Table 4.5a Average chemical composition of scapolite

Host	skarn		gneiss		peg	skarn		skarn	skarn	vein	
Ref.	1		1		1	2		3	4	5	
n	3 (1s)		2 (1s)		1	6 (1s)		1	5 (1s)		1
SiO ₂	50.2	2.8	50.3	6.2	57.9	56.8	2.2	55.4	51.7	0.9	46.3
TiO ₂	0.03	0.01	0.04	0.04	0.01	-	-	tr	0.00	0.01	0.01
Al ₂ O ₃	24.79	1.32	25.52	3.78	21.62	22.2	0.66	22.89	23.66	0.74	27.40
Fe ₂ O ₃	0.15	0.08	0.10	0.02	0.07	-	-	0.00	0.09	0.05	0.00
MgO	0.40	0.53	0.24	0.29	0.03	-	-	0.30	0.13	0.13	0.02
MnO	tr	-	0.00	0.00	0.01	-	-	0.00	0.01	0.00	0.00
CaO	12.37	1.70	15.76	8.2 ^a	4.81	7.4	1.6	7.72	11.16	0.87	16.02
Na ₂ O	5.69	1.64	5.50	4.32	10.50	8.4	1.1	9.36	6.78	0.75	3.71
K ₂ O	1.01	0.15	1.65	0.80	1.16	0.9	0.2	0.22	0.87	0.18	0.26
SO ₃	0.98	0.38	0.67	0.39	0.03	0.3	0.2	0.18	0.96	0.23	1.32
H ₂ O	0.62	0.70	0.64	0.72	0.50	-	-	0.25	0.22	0.08	-
CO ₂	2.36	0.27	2.28	0.83	1.11	1.5	0.4	1.85	2.47	0.52	-
F	0.06	0.05	0.00	0.01	0.00	-	-	0.00	0.00	0.00	-
Cl	1.36	0.70	1.12	1.51	2.96	2.4	0.3	2.30	1.67	0.21	0.48
F=O	0.03	0.02	-	-	-	-	-	-	-	-	-
Cl=O	0.31		0.25		0.67	0.54		0.52	0.38		0.11
Total	99.7		103.3		99.3	99.4		100.0	99.3		95.7

Notes: Ref. = references: 1-Shaw et al.(1963); 2-Karvinen (1973)(21 samples from 6 localities); 3-Shaw et al. (1965); 4-Haughton (1971)(Samples ON3B, Q30, CA63A, Q26, Q13A)(0.19 wt.% SrO); 5-Hogarth (1988)(0.34 wt.% SrO, 0.03 BaO wt.%). 1s is an estimate of one standard deviation. n = number of samples.

Table 4.5b Trace-element compositions of Grenville scapolite (from Shaw, 1960)

Host	Gneiss		Marble		Skarn/vein		Pegmatite	
n	14	(1s)	3	(1s)	18	(1s)	3	(1s)
Na wt. %	4.9	1.0	4.8	1.5	4.7	1.7	7.1	1.7
Ca	8.3	2.6	8.7	3.4	8.8	3.0	4.7	1.3
K	0.7	0.3	1.2	0.0	0.9	0.4	1.7	-
ppm								
Sr	2043	700	1467	165	2263	1159	248	91
Ba	103	53	250	234	159	136	17	2
Rb	17	7	20	6	25	29	7	-
Mg	1113	1153	1117	1261	1916	2447	510	459
Mn	47	15	25	7	52	18	109	37
Li	55	44	55	40	45	29	80	25
Ti	91	130	19	17	100	160	31	20
Cu	3	1	4	2	3	2	15	6
B	18	17	52	48	36	59	13	12
Be	8	6	7	2	8	7	24	17
Ga	36	11	28	9	35	16	41	18
Pb	56	35	48	34	47	23	34	13

Notes: This data was summarized according to the descriptions provided in Shaw (1960). n = number of samples. Grenville Province "skarn" deposits a part of a larger study on scapolite compositions and stability.

There is considerable overlap in the composition of scapolite from various environments based on the averages and standard deviations presented in Table 4.5b. The pegmatite-hosted scapolites are sodic (marialite-rich) and have low Sr contents (Table 4.5b).

4.2.5 Titanite composition

Titanite (sphene) is a common accessory phase in silicated marbles, skarns, veins and hybrid/skarn pegmatites in the Grenville Province. A single titanite analysis was performed to identify any trace-element anomalies (Table 4.6). The titanite has high Y, Nb, Zr, and Sr with respect to the other silicate, phosphate, and carbonate minerals analysed.

Lafontaine (1980) suggested that skarn and pegmatite titanite were more aluminous than gneiss-hosted titanite. Kretz (1980) found that titanite was a common phase (approximately 1 percent) in minor marble, and its higher abundance with respect to the majority of marble occurrences indicated that Ti was metasomatically introduced. Prince (1938) noted high Fe in titanite from the Turner's Island apatite-calcite vein. Storey and Vos (1981a) analysed a few titanite chips from the Turner's Island apatite veins and found them to contain 1700 ppm Y, 1890 ppm Zr, 119 ppm U, 700 ppm La, 5000 ppm Ce, 6000 ppm Nd, <100 ppm Eu, and 150 ppm Yb.

There are no obvious major-element differences in titanite composition from the various environments. However, rare elements (including REE, Y, Nb, etc.) may reveal more systematic chemical variation between these environments. Mungall (1989) analysed the REE content of titanite associated with the Sullivan Island carbonatite and noted strong LREE enrichment and total REE enrichment with respect to the host carbonatite and fenite.

3.2.6 Allanite compositions

Allanite has been found in numerous skarns, veins, and pegmatites within the Grenville Province. Lafontaine (1980) analysed an allanite from the Matte zone fluorite-apatite-calcite vein of the Yates deposit and from an associated amphibole

Table 4.6 Average chemical composition of titanite

Host	skarn	vein	marble		pegm	gneiss	vein
Ref.	1	2	3		2	2	4
n	1	2	6	(1s)	1	1	1
SiO ₂ wt. %	24.8	30.4	-	-	30.3	32.8	28.8
TiO ₂	31.7	30.0	-	-	29.6	36.8	32.8
Al ₂ O ₃	7.9	5.6	3.67	1.15	5.6	1.9	6.32
FeCr	1.2	1.5	1.16	0.60	1.5	1.0	3.5
MgO	0.7	0.3	0.12	0.04	0.2	0.5	-
MnO	0.0	-	0.013	0.006	-	-	0.03
CaO	32.6	27.7	27.6	0.7	27.5	27.6	28.0
Na ₂ O	0.8	0.0	0.073	0.027	0.2	0.0	-
K ₂ O	-	0.2	-	-	-	-	-
P ₂ O ₅	0.0	-	-	-	-	-	-
S	-	0.1	-	-	-	-	-
Total	100.0	95.5			95.3	100.6	99.4
Ba ppm	0	-	-	-	-	-	-
Cr	0	-	-	-	-	-	-
Zr	670	-	-	-	-	-	-
Sr	188	-	-	-	-	-	-
Rb	0	-	-	-	-	-	-
Y	2510	-	-	-	-	-	-
Nb	1130	-	-	-	-	-	-
Zn	98	-	-	-	-	-	-
Ni	0	-	-	-	-	-	-
V	353	-	-	-	-	-	-

Notes: Ref. = reference; 1-This study, corrected for silica dilutant in XRF analysis and recalculated to 100% anhydrous (Ca, SiO₂, and TiO₂ are suspect); 2-Lafontaine (1980); 3-Kretz (1980); 4-Prince (1938). 1s is an estimate of one standard deviation.

gneiss. He found vein-hosted allanite to contain higher rare-earth elements (2 times) and less aluminum, iron, and titanium than an allanite from the amphibole gneiss.

In a microprobe study of allanite from 24 Grenville pegmatites and 9 apatite-calcite veins, MacFarlane (1987) found similar overall compositions except that the overall abundances of REE was less in allanite from the veins than in allanite from the pegmatites.

4.2.7 Apatite compositions

Apatite occurs as a minor phase in many of the silicated marbles, skarns, and veins but rarely in the pegmatite and marble. In addition to the XRF analyses quoted in Appendix 3.5, four samples containing apatite were analysed by the microprobe to test the biotite-apatite geothermometer (Table 4.13). Strontium was the only trace constituent analysed by the microprobe in these apatites. The data is very comparable to the same samples analysed by XRF hence were not included in the discussion.

Apatite is usually medium green with inclusions of rare minerals. The carbonatite apatite from Sullivan Island was notably high in iron and strontium compared to the other environments. At the Matte zone of the Yates deposit the red varieties of apatite represent hematized green apatite because reddish colour is symmetrical about fractures which have earthy hematite stain. Major- and minor-element contents of the apatites are quite similar between the various types except for the Fe_2O_3 content of the carbonatite-hosted apatite from Sullivan Island. However, the Fe_2O_3 content may be due to hematization of the apatite (Table 4.7a). The trace elements are slightly more variable, with the apatite from pegmatite weakly anomalous in barium. The carbonatite and pegmatite are enriched in strontium relative to the veins and skarns. The Y content of apatite from the skarns and veins is high and erratic possibly representing some contamination (xenotime ?).

Hogarth (1988) presented numerous bulk-crystal and microprobe analyses of fluorapatite from the skarns, veins, and a carbonatite from the Gatineau area, Quebec. The summary of analyses presented in Table 3.7b represent four bulk crystal analyses. In microprobe analyses, the fluoroapatite from the carbonatite/fenite sample had notably higher strontium (2.47 wt.%) and cerium (2900 ppm) contents than apatite from the skarns and veins (0.25 wt.% Sr and 1157 ppm Ce). A microprobe traverse of skarn apatite indicates minor increases in Si, S, and Na from the rim to core. Fluorine accounted for 75 to 98 % of the F, Cl, and OH ions. In a later study, Hogarth (1989) found that the carbonatite apatite was higher in strontium but however, apatite from the fields of skarns and pegmatite overlapped the abundance of apatite from skarn and pegmatite. The abundance of Mn is generally higher in pegmatites compared to marble, skarn, and carbonatite (Hogarth, 1989).

Hounsflow and Chao (1970) identified a rare occurrence of marble skarn-hosted chloroapatite in the Bob's Lake area west of Perth, Ontario. The apatites from the Yates deposit have similar Cl, F, and OH contents to the microprobe analyses of apatites analysed by Hogarth (1988). The apatite from the Yates deposits were considerably richer in La and Ce than those examined by Hogarth (1988).

Storey and Vos (1981a) suggested that one variety of apatite occurrence in the Central Metasedimentary Belt was apatite disseminated in marble (Legris deposit near Dacre, Ontario). Storey and Vos (1981a) performed 144 trace-element analyses on 144 selected marble samples in the Pembroke-Renfrew area and obtained a range in P_2O_5 of 0.01 to 0.16 wt. % with an average of 0.02 wt.%. Grant et al. (1989) chemically analysed 1912 marble (carbonate-bearing) samples from the Grenville Province of southeastern Ontario. They found that the calc-silicate calcite-dolomite marbles had the highest mean phosphorous contents (0.16 wt.% (0.13 wt.%, 1s) P_2O_5 , @ n = 21). The lowest mean P_2O_5 content

Table 4.7a Average chemical compositions of apatite (this study)

Host n	skarn 8	(1s)	vein 4	(1s)	pegm 1	carbonatite 1
wt. %						
SiO ₂	0.9	0.5	1.0	0.3	0.4	0.8
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	0.03	0.01	0.06	0.03	0.03	0.00
Fe ₂ O ₃	0.30	0.10	0.23	0.13	0.45	1.00
MgO	0.16	0.09	0.22	0.06	0.12	0.00
MnO	0.00	0.00	0.00	0.00	0.01	0.00
CaO	52.9	1.5	52.3	1.1	54.4	54.0
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
P ₂ O ₅	40.7	2.9	39.3	2.4	39.6	41.8
SO ₃	0.5	0.4	0.4	0.4	0.2	0.9
Total	95.5		93.5		95.2	98.5

ppm						
Ba	99	11	106	19	200	97
Zr	41	20	34	23	83	152
Sr	2408	1206	1753	879	5821	9333
Y	752	226	2283	1510	411	954
Zn	21	29	5	15	43	0

Notes: n = number of samples. High CaO and P₂O₅ are suspect because of lack of proper standards. All chemical analyses are in appendix 3.5. Is is an estimate of one standard deviation.

Table 4.7b Average chemical compositions of apatites (previous work)

Host Ref.	veins 1a	carbonatite 2	skarn 3	skarn 4	skarn 5	skarn 14	skarn/vein (1s)
n	4 (1s)	1	1	1	14	1.1	
SiO ₂ .%	0.9	0.2	1.1	-	1.2	1.1	
TiO ₂	0.00	0.00	-	-	-	-	
Al ₂ O ₃	0.05	0.05	-	-	0.06	0.03	
Fe ₂ O ₃	0.07	0.01	tr	0.13	0.04	0.15	0.19
MgO	0.12	0.05	-	0.01	0.01	-	-
MnO	0.01	0.01	N.D.	-	0.01	0.04	0.02
SrO	0.29	0.04	-	0.28	0.27	0.44	0.18
BaO	0.00	0.00	-	-	-	-	-
CaO	53.6	1.4	53.4	53.9	54.0	-	-
Na ₂ O	0.0	0.0	-	-	0.28	-	-
K ₂ O	0.0	0.0	-	-	-	-	-
P ₂ O ₅	39.4	1.1	41.2	38.26	38.37	-	-
SO ₃	0.5	0.2	-	-	0.72	-	-
Cl	-	-	6.2	-	0.02	-	-
F	-	-	0.13	3.92	3.30	-	-
H ₂ O+	-	-	0.09	0.29	0.14	-	-
CO ₂	-	-	-	0.88	2.10	-	-
F=O	-	-	0.05	1.65	1.39	-	-
Cl=O	-	-	1.40	-	-	-	-
Total	94.9	99.6	99.6	100.4	-	-	-
Zr ppm	65	10	-	-	-	-	-
Y	195	115	-	1200	1400	2360	1260
V	10	0	-	-	-	-	-

Notes: Ref. = references: 1 - Hogarth (1988) (Sample AP 7, AP 8, AP 11, AP 14) (516 ppm La, 1157 ppm Ce); 2 - Hounslow and Chao (1970), 3 - Trzcienski et al. (1974) (0.44 wt. % La₂O₃, 1.23 wt. % Ce₂O₃); 4 - Cruft et al. (1965) (0.35 wt.% La₂O₃, 0.96 wt.% Ce₂O₃); 5 - Cruft (1966) (3832 ppm La (1s = 2098 ppm); 7297 ppm Ce (1s = 3876 ppm)). 1s is an estimate of one standard deviation. N.D. means not detected.

was 0.03 wt.% (0.04 wt.% ls) in siliceous calcite marble. The highest value was in a calcite marble with 6.0 wt. % P_2O_5 (Grant et al., 1989). Hogarth (1988) noted the occurrence of an apatite marble near St. Rose Templeton Township, Quebec with up to 5.4 wt.% P_2O_5 (D.D. Hogarth, personal communication). The abundance of phosphorous is usually low in Grenville marble hence hydrothermal fluids must be involved in the enrichment of apatite in skarns and, particularly, fluorite-apatite-calcite veins. The phosphorous abundance in the marble may be a major factor in the presence or absence of apatite within the calcite veins.

4.2.8 Calcite composition

Calcite occurs in silicated marble, skarns, and veins and more rarely in pegmatites. Calcite is variably coloured (white, grey, beige, yellow, orange, and pink) within these rocks probably reflecting chemical variations or inclusions. Calcite separates from 7 samples of dolomite-calcite marble, 8 from silicated marble, 53 from skarns, 17 from veins, 10 from pegmatites, and a carbonatite were analysed by atomic absorption and DCP analysis (Table 3.8a; Appendix 3.4); several calcite samples were re-analysed by XRF in order to determine the reliability of the method on carbonates, (which was found to be good) and identify trace-element constituents.

In general, the calcite from marble has higher magnesium than associated silicated marble and skarn. The calcite from pegmatites and veins is low in Mg. There is an overall average increase in Mn content of calcite from marble, silicated marble, skarn, vein to pegmatite. Iron is highest in the vein calcite and lowest in the marble-hosted calcite. Barium and strontium are highest in the pegmatite calcite, but barium is erratic in calcite from the other four rock types. Strontium is lowest in marble and silicated marble whereas intermediate Sr abundances occur in skarn- and vein-hosted calcite. Yttrium is highest in vein and pegmatite calcite. The two samples of grey calcite (microscopic magnetite inclusions) from the Sullivan Island

carbonatite (deposit # 114) are chemically indistinguishable from calcite from pegmatite and veins except for the very high strontium contents (Figures 4.10 and 4.11; Table 4.8a). The plots of strontium versus MnO, Na, Ba, and Y are much more scattered (Figure 4.11).

Individual calcite analyses were plotted against FeO content because of the common variation in iron contents (Figure 4.10). These plots illustrate the internal variation within and between calcite types. There is a poor correlation between FeO and MnO and FeO and Y content. The vein calcites have high Fe, Mn, Na, Sr, and Y (Figures 4.10 and 4.11).

In a study of marbles from the Pontiac region of Quebec, Kretz (1980) distinguished two types of marble, major marble and minor marble. He proposed that the minor marble represents metasomatized varieties of major marble. On average the pink calcite from the minor marble is lower in Mg and higher in Fe and Sr than calcite in the major marble.

Shaw et al. (1963) noted that calcite recrystallized and changed colour from white to grey to pink from the marble into the skarn. They investigated, in detail, the major- and trace-element calcite compositions in Grenville skarns, veins, and marble. Silica, alumina, and titania are thought to be submicroscopic contaminants of the calcite samples or analytical errors. Generally, calcite from skarns, veins, and pegmatites have higher abundances of Sr, Mn, Fe, and Pb and lower Mg than the marble. It was proposed that the pink colouration of calcite is due to the Mn or Fe content (Shaw et al. 1963). Chemical analyses of 6 calcite samples from radioactive skarns by Dr. J. Satterly are quoted by Shaw et al. (1963) and confirm the calcite compositions determined by Shaw et al. (1963). In addition, yttrium ranged from 200 to 800 ppm in calcite compared to the low amount in marbles. Boron and barium contents of skarn calcite were similar to marble calcite. Numerous other elements were investigated but were not detected (<1-5 ppm). The calcite data from Shaw et al. (1963) has been subdivided into skarns, veins,

and pegmatites based on sample descriptions. The majority of the data is very similar between types but reveals a small increase in the average magnesium content from skarns to veins to pegmatites. The average iron content of the veins is higher than the skarns and pegmatites.

St. Onge (1977) petrographically and chemically examined marble from Onslow township, Quebec. He found that the average Mn content of the marbles was 400 ppm and probably primary in origin. The average strontium content was 710 ppm with the highest contents being in pink calcite marble at the margin with the Onslow syenite complex, which intrudes marble.

Grant et al. (1989) examined and analysed 1912 whole-rock samples of Grenville marble from southeastern Ontario for 19 elements. They subdivided the marbles into 16 groups depending on SiO_2 , CaO , and MgO contents. The average of eighty seven calcitic marble samples has been tabulated for comparison (Table 4.8b).

In general, there is a slight enrichment of FeO and MnO and a decrease in MgO from marbles to skarns to veins to pegmatites as was noted for the silicate minerals. There is a slight enrichment in Ba, Sr, Na, and Y from the marbles to the skarns, veins and pegmatites.

4.2.9 Discussion

The major- and trace-element composition of mica, pyroxene, amphibole, and calcite have been presented from various environments marble, silicated marble, skarns, veins, pegmatites, and a carbonatite. In the field the depth of colour of minerals was readily discernable, qualitatively reflecting variation in the iron content. In general, it was noticed that mica and calc-silicate minerals from skarn were darker when in proximity to the pegmatite bodies compatible with a spatial and genetic relationship of skarn to the pegmatite. The high iron content of these minerals within the pegmatites supports this relationship.

Table 4.8a Compositions of calcite separates (this study)

Host n	marble 7	sil. marble (1s) 8	skarn (1s) 53	vein (1s) 17	pegmatite (1s) 10	carbonatite (1s) 1
wt. %						
CaO	51.6	53.5	55.1	51.6	55.8	47.6
MgO	2.61	1.29	1.20	0.32	0.22	0.38
MnO	0.03	0.10	0.14	0.26	0.32	0.17
FeO	0.37	0.12	0.47	0.98	0.79	0.85
CO ₂ *	43.6	43.8	44.9	41.6	43.7	38.4
Total	98.2	99.3	101.8	94.8	100.8	87.4
ppm						
Ba	52	63	111	89	118	103
Sr	748	997	1738	669	1977	1075
Na	63	34	109	76	137	95
Y	95	135	270	344	161	122

Notes: n = number of samples. CaO, MnO, MgO, FeO, Na, and Zn were determined by atomic absorption spectroscopy, Y, Sr, and Ba were determined by DCP spectroscopy; * CO₂ calculated; It is evident that poor CaO analyses are responsible for the poor total (Appendix 3.4). 1s is an estimate of one standard deviation.

Table 4.8b Calcite compositions (previous work)

Host Ref.	marble 1	marble 11	marble (1s) 3	skarn 2	vein 18	vein (1s) 2	pegmatite 2	pegmatite (1s) 2	cc marble 3	pegmatite 4
n	34	(1s)	(1s)	(1s)	(1s)	(1s)	(1s)	(1s)	(1s)	(1s)
SiO ₂	-	-	-	0.205	0.158	0.603	0.203	0.567	0.203	1.48
TiO ₂	-	-	-	0.001	0.000	0.002	0.000	0.002	0.000	0.02
Al ₂ O ₃	-	-	-	0.036	0.038	0.082	0.005	0.039	0.005	0.40
FeO	0.19	0.16	0.39	0.369	0.134	0.559	0.109	0.302	0.109	0.20
MgO	2.04	0.73	0.65	0.332	0.120	0.744	0.854	1.136	0.854	1.21
MnO	0.05	0.03	0.06	0.155	0.075	0.216	0.020	0.135	0.020	0.03
CaO	52.7	1.3	53.1	-	-	-	-	-	-	57.22
SrO	0.06	0.05	0.14	0.414	0.232	0.228	0.333	0.448	0.333	2.74
BaO	-	-	-	0.004	0.004	0.006	0.004	0.005	0.004	0.106
Na ₂ O	-	-	-	-	-	-	-	-	-	0.098
K ₂ O	-	-	-	-	-	-	-	-	-	0.018
P ₂ O ₅	-	-	-	-	-	-	-	-	-	0.01
Total	55.5	-	54.3	-	-	-	-	-	-	0.07
										0.08
										0.09
										0.64
										59.38
										55.95

Notes: Ref. = references: 1-Kretz (1980); 2-Shaw et al. (1963) (average 21 ppm B, 22 ppm Pb, and 53 ppm Ba); 3-Grant et al. (1989) for calcite-rich marbles; 4-Walker and Parsons (1923) pink calcite associated with betafite "ellsworthite", MacDonald feldspar mine (43.9% CO₂) (Totals not calculated on samples without CaO determination). n = number of samples. 1s is an estimate of one standard deviation.

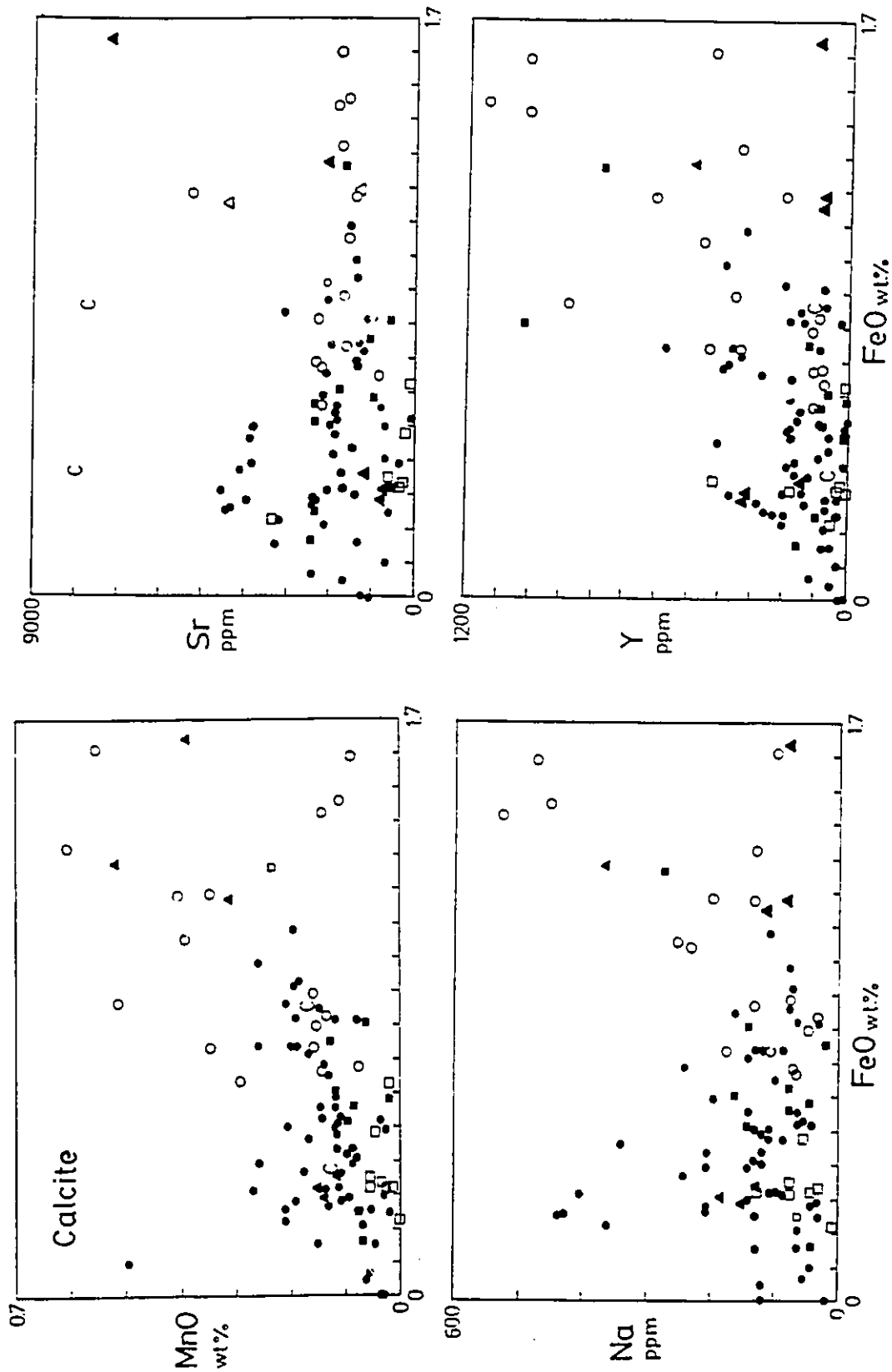


Figure 4.10 Compositional variation of MnO, Na, Sr, and Y content versus FeO content in calcites from marble ($\square$), silicified marble ($\circ$), skarns ($\bullet$), veins ($\triangle$), pegmatites ($\blacktriangle$), and carbonatite (C) (see Appendix 3.4).

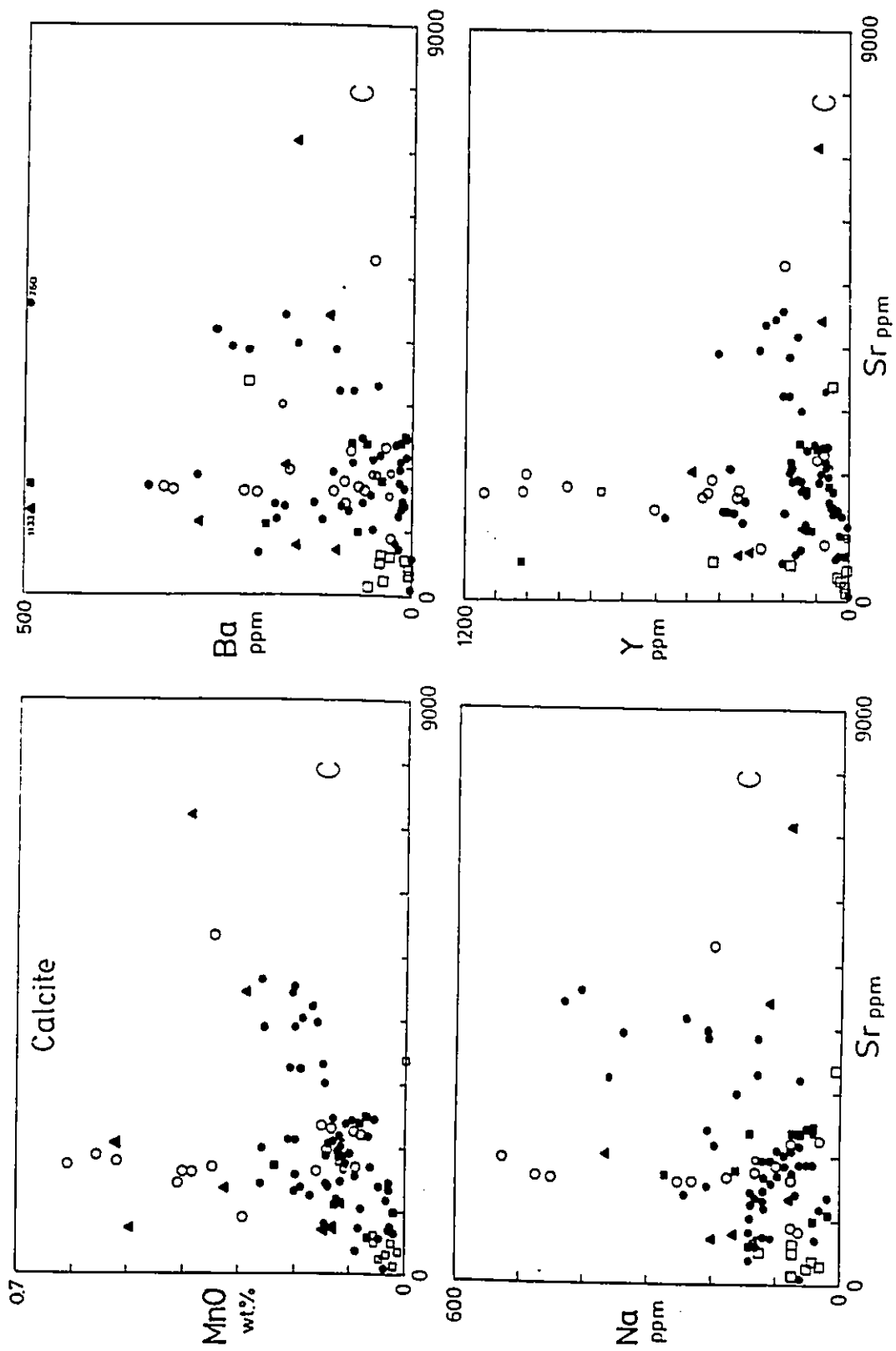


Figure 4.11 Compositional variation of MnO, Na, Ba, and Y content versus Sr content in calcites from marble (□), silicified marble (■), skarns (●), veins (○), pegmatites (▲), and carbonatite (C) (see Appendix 3.4).

The poor outcrop exposure and preservation in many areas examined precluded a detailed traverse from proximal to distal skarn hence only general inferences may be made from the regional compilation of data.

Mineral compositions from pegmatites, skarns and veins were also compared with those of carbonatites. Mineral separates from the Sullivan Island carbonatite and comparison with compositions from the literature was used to discriminate between pseudocarbonatites and carbonatite.

In order to identify other systematic elemental variations, mineral compositions were plotted with respect to variations in $\text{Fe}/(\text{Fe}+\text{Mg})$. The compositional data was compared from the various environments and in a few instances the data show a continuum between marble, silicated marble, skarns, veins, and pegmatites.

The phlogopite/biotite compositions indicate covariation of MnO , TiO_2 , Rb , Y , Nb , Zn , and V with an increase in $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio with the veins and pegmatites having the highest iron contents.

This is consistent with the chemical compositions of biotite within the Grenville pegmatites (Lentz, in prep; Appendix 6). In general, there are no obvious major-element differences between micas from these pegmatites, skarns, and veins and carbonatite- or fenite-hosted mica analyses from the literature (Rimsaite, 1969; Heathcote and McCormack, 1989) except possibly the high content of Ti and low content of Al in the latter although these features are not common in late-stage carbonatite micas.

It was observed that Ca pyroxene, the principal skarn mineral, varied in colour from dark green to very light green coincident with spatial variation from endoskarn and proximal exoskarn to the distal exoskarn. Unfortunately, only one Ca pyroxene was analysed from a pegmatite (Camp zone, Yates deposit) hence the variation in iron content between marbles and pegmatites is poorly constrained. However, there is a coherent covariation of Mn , Ti , Al , Zn , and V with $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio of the Ca pyroxene.

The low aluminum content of the Ca pyroxene is consistent with the middle to upper amphibolite grade conditions of formation. The uniformly low content of Ti and Na in Ca pyroxene from the veins are not consistent with most early magmatic pyroxenes from a carbonatite.

Amphibole compositions are particularly sensitive to changes in the formation conditions. Unfortunately, few amphiboles were chemically analysed from skarns and veins. The problem of separating biotite and scapolite from the amphiboles precluded very pure mineral separates (> 95%) which may have been responsible for the inconsistencies found in the mineral formula. All the samples were calcic amphiboles but two were sodic-calcic amphibole. The aluminum content was quite variable with no observed discontinuity gap between actinolite (low Al) and paragonitic hornblende (high Al) compositions probably as a result of whole-mineral analysis. The vein amphiboles had the highest iron contents.

The Ca amphibole compositions are not typical of carbonatitic amphiboles. Na-Ca and Na amphiboles are characteristic of carbonatites based on data presented by Hogarth (1989). Ca amphiboles of the tremolite-actinolite series have not been definitely established in carbonatites and even edenite compositions are very rare. Uncertainties in the exact amphibole compositions preclude a more detailed discussion.

Apatite from silicated marbles, skarns, veins, and pegmatites is indistinguishable in major- and trace-element composition except for the 0.01 wt.% MnO observed in the pegmatite-hosted apatite. A comparison of these apatite compositions with the apatite from the Sullivan Island carbonatite indicate that the latter is much richer in strontium. This is consistent with the Mn-Sr diagram which discriminates between apatites from marbles, skarns, pegmatites, and carbonatites presented by Hogarth (1989).

Calcite compositions are particularly useful geochemical indicators because of their presence in all environments examined. As noted previously, metasomatic alteration of calcite

results in bleaching of buff marble calcite concurrent with recrystallization possibly due to the oxidation of fine graphite. There is a pronounced colour variation in calcite from silicated marbles, skarns, veins, and pegmatites. For example, the calcite within the core zone of the MacDonald pegmatite is orange, yellow and grey coloured. The calcite within the pegmatites and the veins is generally the highest in iron. The covariation of FeO with MnO and V is quite pronounced. In general, the Sr content of the calcite from the pegmatites, veins, skarns, and marble is less than 3000 ppm, however, calcite in the MacDonald pegmatite has a high Sr composition (5000 ppm) which approaches the abundance of the carbonatite sample. The veins have less than 2000 ppm Sr on average whereas the skarns have between 1000 and 4000 ppm Sr. Strontium content of calcite and apatite is particularly useful in discriminating between carbonatite and vein calcite. The calcite data will be further discussed in conjunction with the isotopic data in chapter 6.

4.3 Intercrystalline element distributions

4.3.1 Introduction

The present study includes the analysis of major- and trace-element distributions between coexisting minerals from the silicated marble, skarns, veins, pegmatites, and a carbonatite. This includes 16 mica (biotite-phlogopite)/pyroxene, 7 biotite/amphibole, 48 mica/calcite, 20 pyroxene/calcite, 8 amphibole/calcite and 14 apatite/calcite pairs. The average distribution coefficients (K_D) have been computed for the silicate pairs and selected pairs are plotted.

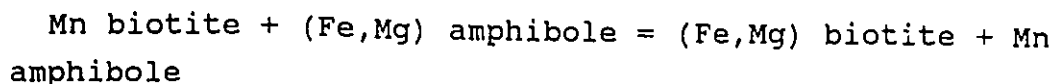
An important aspect of the study involved discriminating the origin of skarns and the fluorite-apatite-calcite veins. Separate symbols have been used to differentiate between silicated marble, skarns and apatite-calcite veins in order to identify any differences if they exist.

Distribution coefficients are principally a function of temperature and composition and are much less sensitive to

pressure (Kretz 1961; McIntire 1963; Burns, 1970). It has been established that the skarns and veins formed between 500° and 600°C at approximately 400 MPa (4 kb) pressure. Under equilibrium conditions, the distribution of elements between coexisting phases should be regular, particularly if similar sites are available in both phases.

4.3.2 Thermodynamic considerations

The exchange of Mn between biotite and amphibole may be expressed as follows:



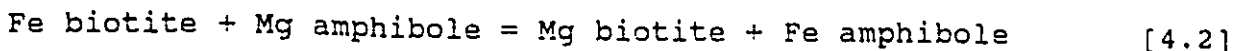
$$\text{At equilibrium } K_D = X_{\text{Bt}} / (1 - X_{\text{Bt}}) / X_{\text{Amp}} / (1 - X_{\text{Amp}}) = X_{\text{Bt}} / X_{\text{Amp}} \quad [4.1a]$$

$$X_{\text{Bt}} / X_{\text{Amp}} = Q \exp(\Delta G / RT) = f(T, P, \text{Mg:Fe}) \quad [4.1b]$$

$$Q = \text{constant}$$

$$K_D = X_{\text{Bt}}^{\text{Mn}} / X_{\text{Amp}}^{\text{Mn}} \quad \text{where: } X^{\text{Mn}} = \text{Mn} / (\text{Mn} + \text{Mg} + \text{Fe}) \quad [4.1c]$$

The Fe-Mg exchange reaction with biotite and amphibole (equation 3.2) is:



$$K_D = (X_{\text{Bt}} / (1 - X_{\text{Bt}})) / (X_{\text{Amp}} / (1 - X_{\text{Amp}})) \quad \text{where: } X = \text{Fe} / (\text{Fe} + \text{Mg})$$

An irregular distribution may be due to 1) non-equilibrium conditions, 2) an interfering element(s) or 3) contamination of the phases by microscopic inclusions.

4.3.3 Equilibrium considerations

There are numerous explanations for chemical disequilibrium between coexisting phases. The coarse-grained nature of the minerals examined may suggest chemical communication between phases. However, the metasomatic origin of the samples suggests that chemical equilibrium may not have been achieved because of non-cogenetic mineral parageneses. The kinetic tendency for a secondary phase to inherit the chemical characteristics of the primary phase complicates matters and may be responsible for

distribution coefficients near unity. The inheritance of elements may be perturbed by the saturation or undersaturation of that element in the hydrothermal fluid resulting in elemental distributions deviating from unity. If recrystallization occurs subsequent to replacement, equilibrium may be approached. In most cases, the phases observed seemed to be in equilibrium, but in several instances this was definitely not so based on this study.

The concentration of an element or a combination of elements may affect the distribution of other elements within coexisting minerals (Kretz 1959, 1960). The strong chemical variation within the minerals examined could be particularly useful in identifying these effects.

It is important at this stage to recognize the possible effects of contamination on the samples analysed. Although the mineral samples were cleaned to greater than 99 percent purity mineral by hand picking and washed briefly in dilute nitric acid, it is still probable that some minor contamination has occurred, particularly in the amphiboles. An example would be the presence of 0.5 % titanite in biotite which could add 0.16 wt.% CaO, 0.16 wt.% TiO₂, 13 ppm Y, 6 ppm Nb, and 3 ppm Zr to the composition of biotite. Biotite was a minor contaminant of amphibole in several instances but was generally less than 1 volume percent. The effect of contamination on the samples may be responsible for some of the less systematic elemental distributions between minerals.

The principal octahedral components Fe and Mg in biotite, Ca-Na amphibole and Ca pyroxene are expressed as ratios, for example Fe in biotite is expressed as biotite $[Fe] = Fe^{2+}/(Fe^{2+}+Mg)$ in order to evaluate the distribution of these elements. Similarly, Fe in calcite is expressed as calcite $[Fe] = Fe/(Ca+Mg+Mn+Fe)$.

4.3.4 Elemental distributions among mica, Ca pyroxene, and Ca-Na amphibole

4.3.4.1 Description of data

The elemental distributions for 16 mica/Ca pyroxene and 7 mica/Ca-Na amphibole pairs will be examined. The distribution of the principal octahedral cations Fe, Mg, Mn and Ti with the exception of Al has been analysed. The Ca pyroxene has less than 1.87 wt.% Al_2O_3 ; hence variations in distributions are probably not a function of this variable. The distribution of Al between biotite and amphibole is irregular. The regular distribution of Fe and Mg between mica, Ca pyroxene and Ca-Na amphibole is indicative of an approach to equilibrium. The $K_D^{\text{Bt/Cp}}$ for Fe and Mg in sample 50C and 50D-1 are anomalous possibly representing non equilibrium. The average [Fe] $K_D^{\text{Bt/Cp}} = 0.5$ and $K_D^{\text{Bt/Amp}} = 0.65$ (Figures 4.12 and 4.13). The distribution of MnO and TiO_2 in mica/amphibole pairs are regular however, the mica/pyroxene distributions are more irregular (Figure 4.14). The trace-metal distributions in mica/pyroxene pairs are more irregular than the major elements but less so for mica/amphibole pairs (Figure 4.15, 4.16, 4.17, and 4.18). The distributions of Ba and Zn seem to be the most regular of the trace elements. The distribution of Cr is quite regular in both mica/pyroxene and mica/amphibole pairs. The Sr K_D in mica/pyroxene pairs changes from an average of 0.44 to approximately 1.0 in phlogopitic micas which may be a result of slightly higher Ca content in contaminant calcite in mica.

Within the coexisting silicates there was no obvious difference in the distribution coefficient between minerals from samples designated as silicated marbles, skarns, and veins which indicates that they formed under similar temperature conditions or that the temperature effect was small.

In a similar study of Grenville skarns, Kretz (1960) examined elemental distributions between biotite and Ca pyroxene and amphibole. As in this study, Kretz (1960) found that the distribution of Al_2O_3 wt.% between biotite/pyroxene pairs is very irregular. A biotite/pyroxene $KD_{[\text{Fe}]}$ of 1.5 was determined for low Al pyroxenes which differs from this study ($K_{D\text{Fe}}^{\text{Bt/Cp}} = 0.8$). This difference may be, in part, due to the Fe-F avoidance since

Table 4.9 Elemental distributions between mica, Ca pyroxene, and amphibole

Pairs	Bt/Cp	Bt/Amp	Bt/Amp *
n	16	7	14
Ref.	1	1	2
Fe/(Fe+Mg)	0.50 $\pm$ 0.10	0.65 $\pm$ 0.22	0.9
MnO	0.38 $\pm$ 0.14	0.45 $\pm$ 0.09	0.31
TiO ₂	9.1 $\pm$ 6.90	1.71 $\pm$ 0.40	2.06
Ba	26.0 $\pm$ 9.0	17.2 $\pm$ 4.2	
Cr	1.50 $\pm$ 1.56	0.64 $\pm$ 0.19	0.8 **
Zr	2.28 $\pm$ 4.83	0.10 $\pm$ 0.14	
Sr	0.44 $\pm$ 0.30	0.60 $\pm$ 0.50	
Rb	---	---	
Y	0.61 $\pm$ 0.38	78.5 $\pm$ 46.4	
Nb	---	0.62 $\pm$ 0.50	
Zn	---	1.09 $\pm$ 0.53	
V	1.78 $\pm$ 0.90	1.39 $\pm$ 0.40	
	0.59 $\pm$ 0.57	0.34 $\pm$ 0.24	0.83

Notes: Ref. = reference: 1- this study; 2- Kretz (1959), ** estimated (n = 13) Kretz (1959). n = number of samples.
 $\pm = (t_{\alpha/2} \times 1s)/\sqrt{n}$ (Kretz, 1985; Le Maitre, 1982).

these samples are, in general, fluorine-rich which would lower the affinity of mica to concentrate Fe. A $K_D^{[Mn]^{Bt/Cp}}$ of approximately 0.25 is very similar to this study ($K_D = 0.31$). In Grenville marbles, a $[Mn] K_D^{Bt/Cp} = 0.14$ was determined (Kretz, 1980). Kretz (1960) found a slightly irregular Ti distribution between biotite and pyroxene.

Within the silicate-silicate reactions, there were no obvious differences between the elemental distributions for silicated marble skarns, skarns and fluorite-apatite-calcite veins. This suggests that the temperature conditions which led to vein formation were similar to the skarns if K_D was temperature sensitive.

In a study of Grenville gneisses, Kretz (1959; 1978) found elemental distributions between biotite/hornblende pairs similar to those found in this study. The distribution of Fe in this study is intermediate between the values obtained by Kretz (1960) for Al-rich and Al-poor amphiboles. In this study the $[Fe] K_D$ for the three lowest Al amphiboles is between 0.65 and 1 which could be due to the rejection of Fe from mica due to higher fluorine contents. The three most Al amphiboles have a lower K_D is close to the 0.46 value obtained by Kretz (1960) (Table 4.9). The variation in K_D for Fe and Mg with respect to Al content of amphibole (Kretz, 1960) was not found in this study. Larkin (1971) found a regular Mn distribution of 0.58 ($n = 7$) in Grenville skarns. The $[Mn] K_D$ is also close to that found by Kretz (1960) but differs from $[Mn] K_D^{Bt/Amp} = 0.19$ in Grenville marbles (Kretz, 1960).

Kretz (1959, 1960) determined that Ba was distributed in the following manner biotite > amphibole > pyroxene which was also found in this study. In comparison, Kretz (1959, 1960) found that V is concentrated in amphibole > biotite > pyroxene which is different to this study; amphibole > pyroxene > biotite.

4.3.4.2 Crystal-chemical factors

The effects of ionic radius, charge and crystal-field effects are responsible for the elemental distributions observed. It is important to realize that the proportion of octahedral sites to cations in the root formula of Ca pyroxene (25%), amphibole (33%) and biotite (37.5%) is not the same hence may be partially responsible for the partitioning of octahedrally-co-ordinated elements. In general, there are 1.5 times the number of octahedral ions in biotite compared to pyroxene, and 1.14 times the number of these ions in biotite compared to amphibole. This should also be kept in mind for XII-co-ordinated elements. Figure 4.19 illustrates the controls charge and radius have on the distributions of the first series transition elements. The octahedrally-co-ordinated ionic radii are from Shannon (1976) and the high spin state radii were used for the Fe^{2+} and Mn^{2+} . The smaller divalent Zn^{2+} prefer the biotite over pyroxene and amphibole whereas the larger divalent cations Fe^{2+} and Mn^{2+} favour the amphibole and pyroxene over coexisting biotite. With the octahedral site correction factor (1.5 times) for biotite/pyroxene distributions, Cr^{3+} , V^{3+} , Zn^{2+} , Fe^{2+} and Mn^{2+} all prefer the octahedral sites in pyroxene. Similarly, the octahedral site correction (0.85) for biotite/amphibole indicates that Cr^{3+} , V^{3+} , Fe^{2+} and Mn^{2+} partition more strongly into amphibole whereas Ti^{4+} and Zn^{2+} favour biotite. The distributions for each octahedrally co-ordinated element are not significantly different for biotite/pyroxene and biotite/amphibole pairs precluding further discussion on different characteristics of the sites between these minerals.

An examination of the octahedral site preference energy with respect to the distribution coefficient for the first series transition elements revealed no significant relationship even for elements with the same charge and similar ionic radii.

4.3.4.3 Elemental distributions among calcite and mica, Ca pyroxene, and Ca-Na amphibole

The silicates are much richer in [Fe] than coexisting calcite (10 to 40 times) and have a moderately regular distribution.

$$[\text{Fe}/(\text{Fe}+\text{Mg})]_{\text{silicate}} > [\text{Fe}/(\text{Fe}+\text{Mg})]_{\text{calcite}}$$

Similarly, [Mg] has a slightly irregular distribution and the silicate is variably enriched (20 to 140 times) in Mg compared to calcite. [Mn] is regularly distributed with an average biotite/calcite $K_D = 1.1$ except for two samples from the Silver Crater phlogopite-apatite-calcite vein which have a distribution coefficient of approximately 10. Similarly, the distribution of [Mn] between amphibole and calcite is 1.9 ($1\% = 0.5$; $n = 6$) but the sample from the Silver Crater has a [Mn] $K_D = 22$. The distribution of Na and Ba between calcite and amphibole is slightly irregular but between pyroxene and calcite Na distribution is irregular. Strontium is more abundant in calcite than in coexisting pyroxene and has a fairly regular distribution. Yttrium is irregularly distributed in all samples with no apparent relationship to the presence of an additional element. The irregular distributions are most likely a result of a later paragenesis for the calcite in the skarns and the veins with the exception of the silicated marble skarns which remained saturated in calcite throughout metasomatic alteration.

Kretz (1980) examined the distribution of Fe, Mn, and Sr between calcite and phlogopite, Ca amphibole, and Ca pyroxene in Grenville major and minor (metasomatized) marbles. The distribution of [Fe] in the major marbles is somewhat regular suggesting an approach to equilibrium. However, the minor marbles that are richer in [Fe] also deviate from an equilibrium distribution suggesting non-equilibrium conditions (Kretz, 1980). The range in the weight ratio of these elements in calcite to that in the coexisting phlogopite, Ca pyroxene, and amphibole in the marbles overlaps with those determined in this study. Kretz (1980) suggested that calcite-silicate exchange equilibrium was only rarely achieved in the minor marbles because of their metasomatic origin.

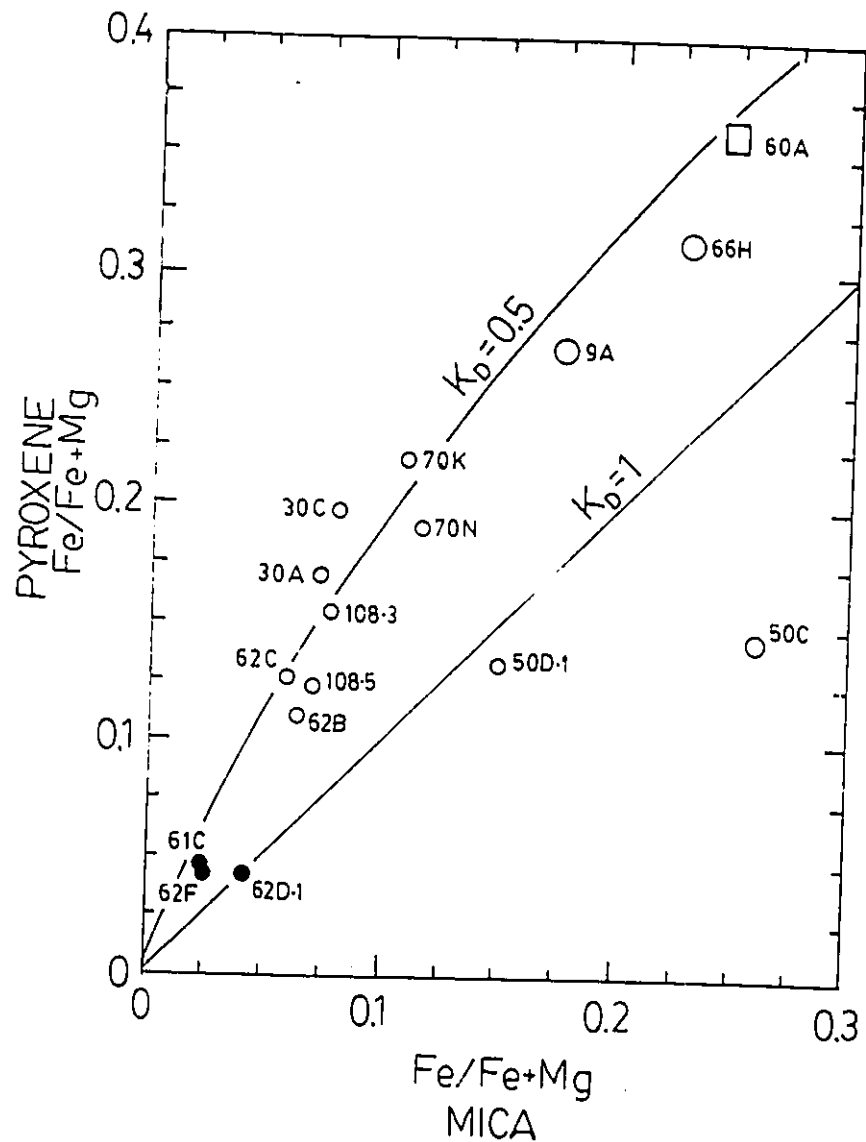


Figure 4.12 Distribution of Fe/(Fe+Mg) between coexisting mica and Ca pyroxene. Symbols are silicated marble (●), skarns (○), and veins (□). Errors are within the size of the sample spot and represent a 95% confidence interval using coefficient of variation derived from the zoning study of zoning in micas.

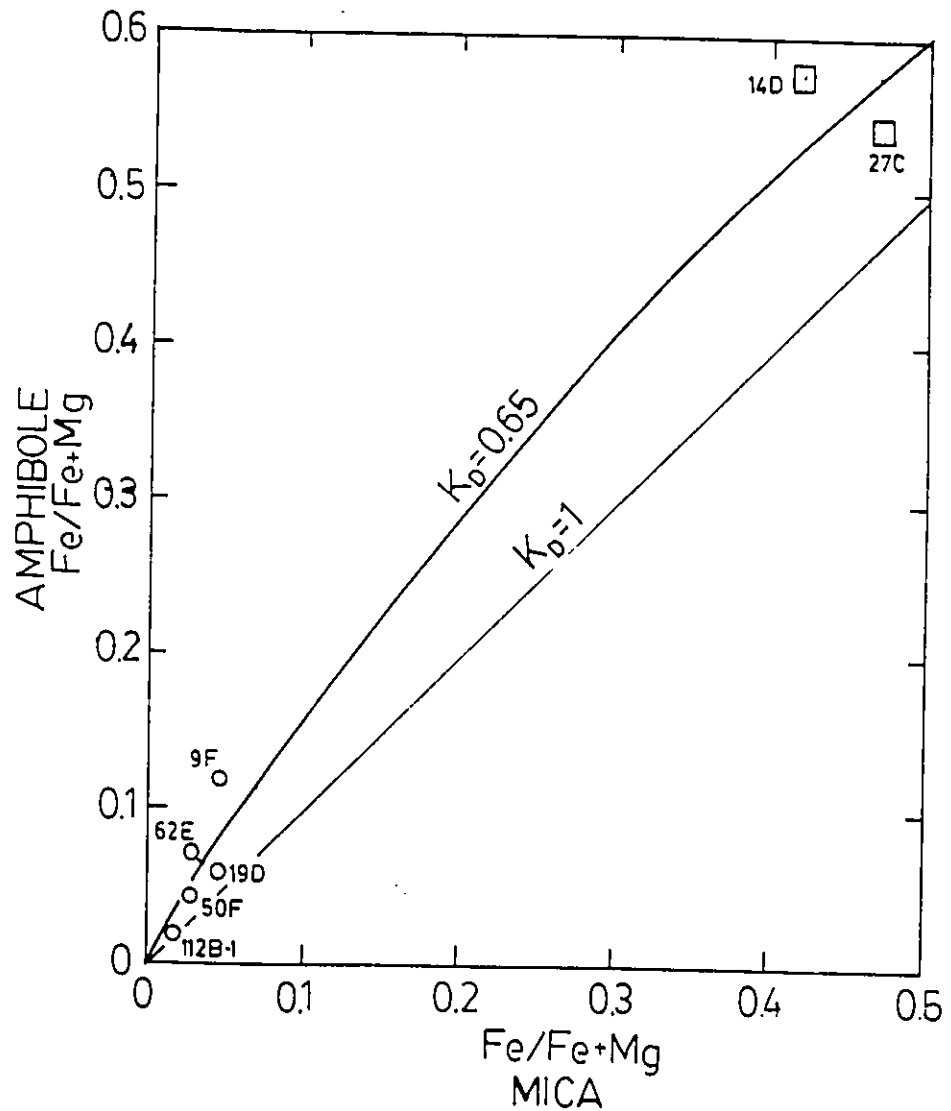


Figure 4.13 Distribution of Fe/(Fe+Mg) between coexisting mica and amphibole. Symbols are silicated marble (●), skarns (○), and veins (□). Errors are within the size of the sample spot and represent a 95% confidence interval using coefficient of variation derived from the zoning study of zoning in micas.

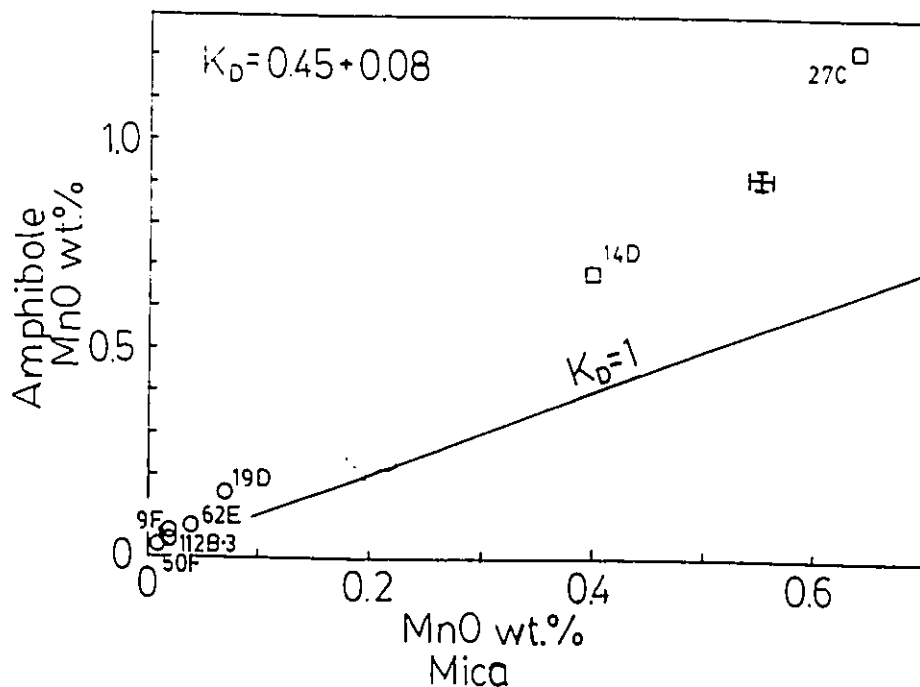
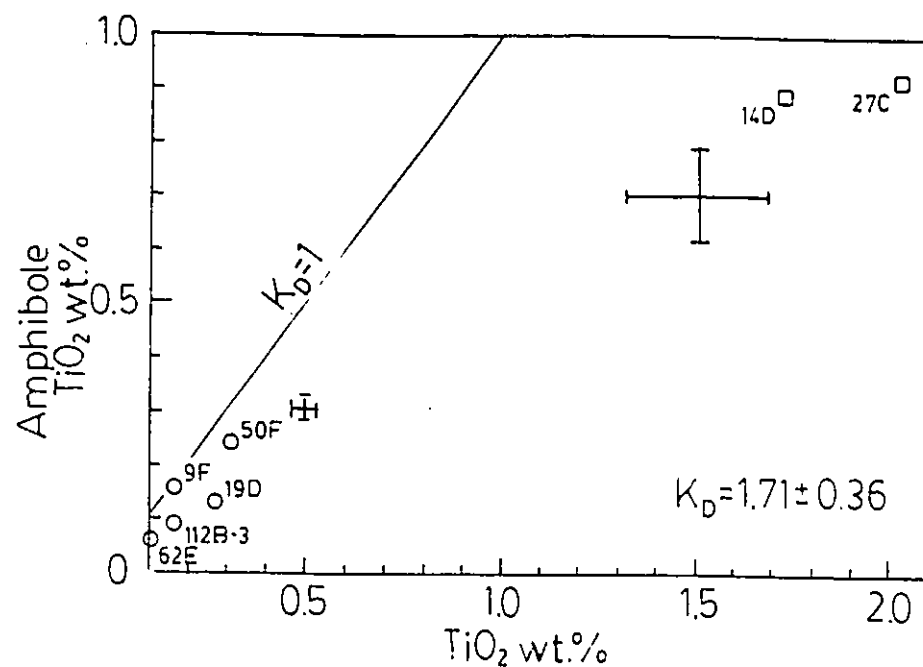


Figure 4.14 A) Distribution of TiO_2 between mica and Ca pyroxene.
 B) Distribution of MnO between mica and Ca pyroxene. Symbols are silicated marble ($\bullet$), skarns ($\circ$), and veins ($\square$). Error bars represent a 95% confidence interval using c_v derived from the zoning study of micas.

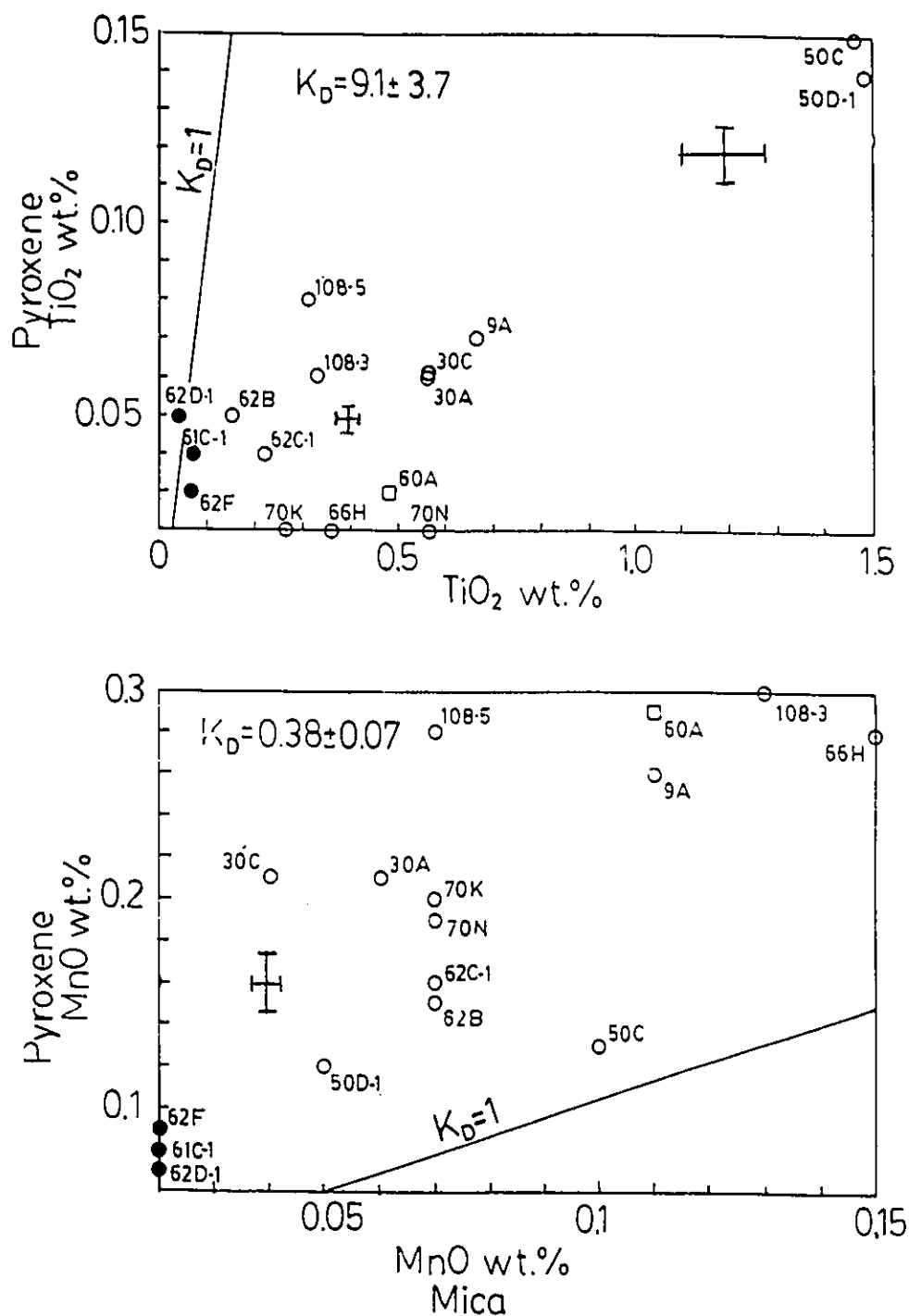


Figure 4.15 A) Distribution of TiO₂ between mica and amphibole. B) Distribution of MnO between mica and amphibole. Symbols are silicated marble (●), skarns (○), and veins (□). Error bars represent a 95% confidence interval using cv derived from the zoning study of micas.

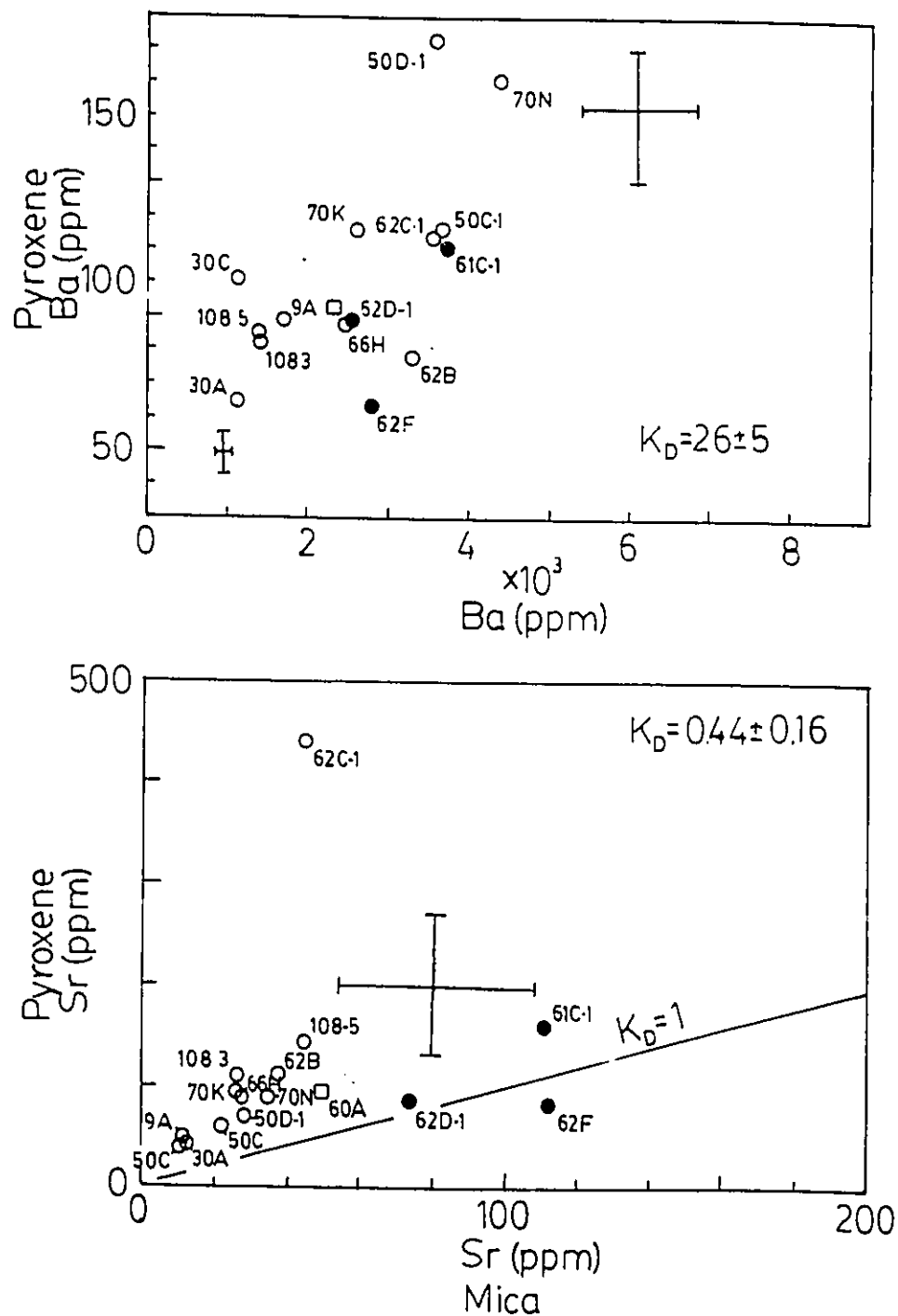


Figure 4.16 A) Distribution of barium between mica and Ca pyroxene. B) Distribution of strontium between mica and Ca pyroxene. Symbols are silicated marble (●), skarns (○), and veins (□). Errors bars represent a 95% confidence interval using cv derived from the zoning study in micas.

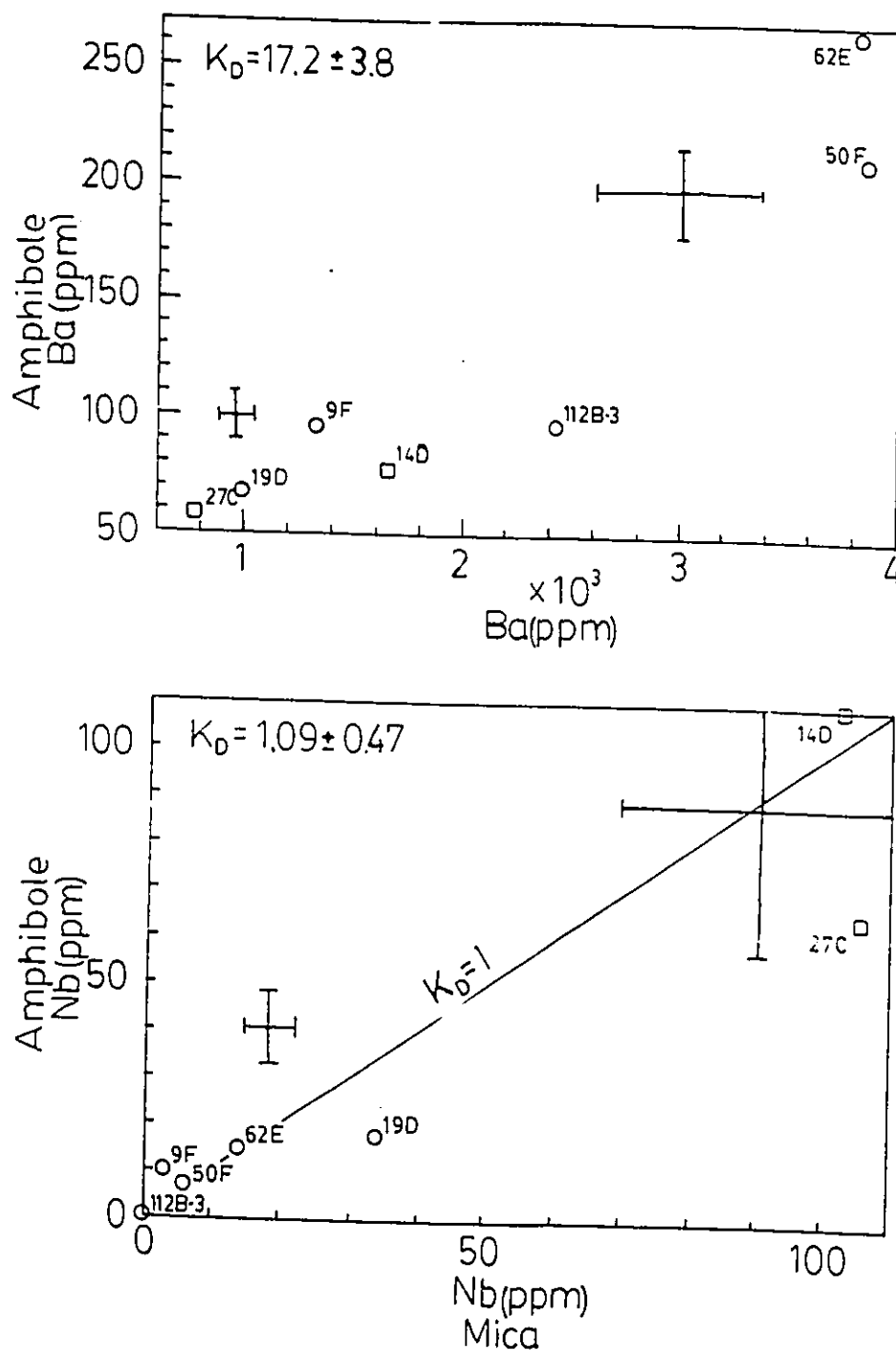


Figure 4.17 A) Distribution of barium between mica and amphibole.
 B) Distribution of niobium between mica and amphibole. Symbols are silicified marble (●), skarns (○), and veins (□). Error bars represent a 95% confidence interval using cv derived from the zoning study in micas.

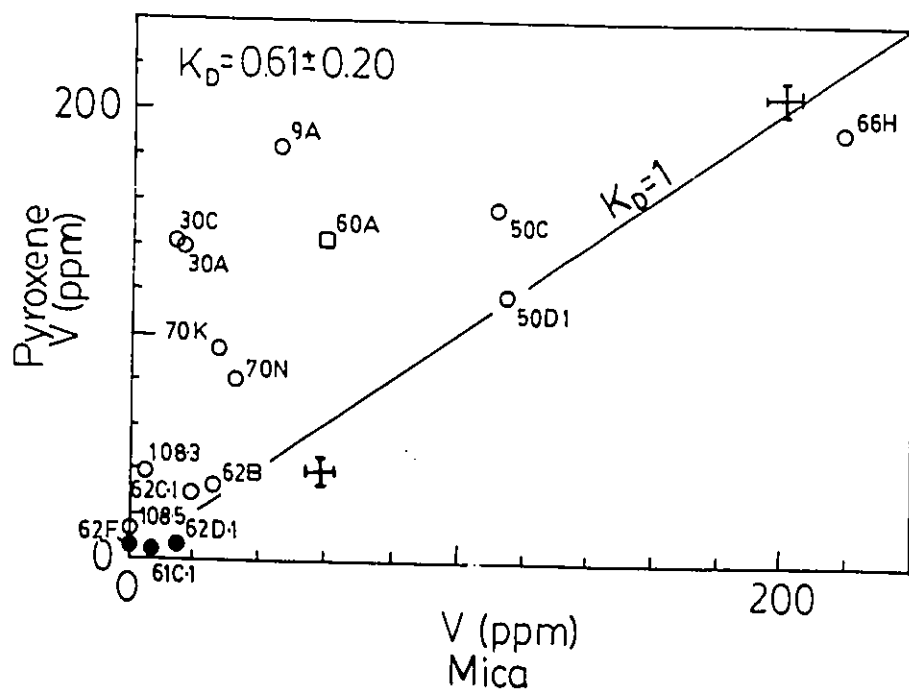
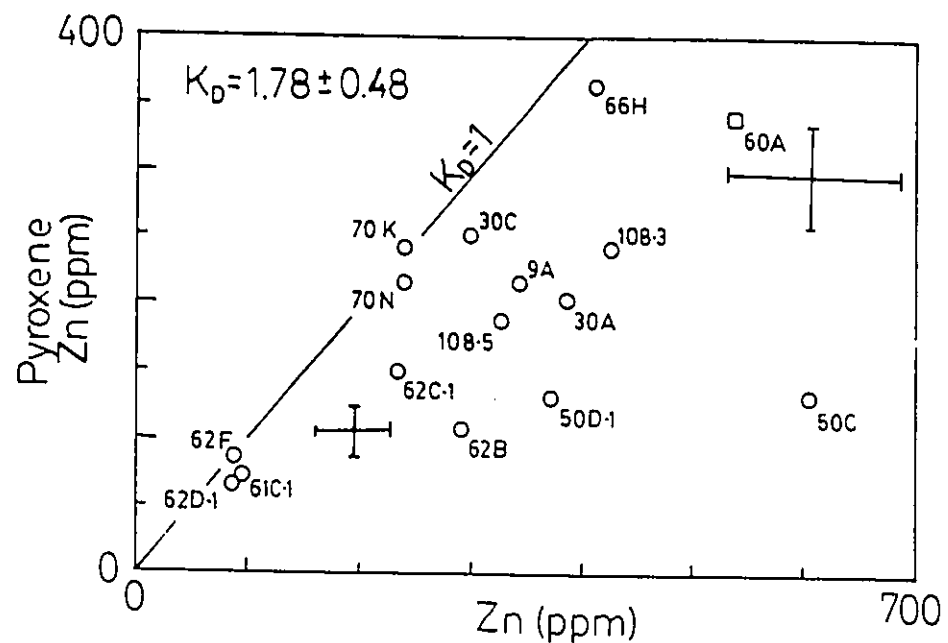


Figure 4.18 A) Distribution of zinc between mica and Ca pyroxene.
B) Distribution of vanadium between mica and Ca pyroxene. Symbols are silicated marble (●), skarns (○), and veins (□). Errors bars represent a 95% confidence interval using cv derived from the zoning study in micas.

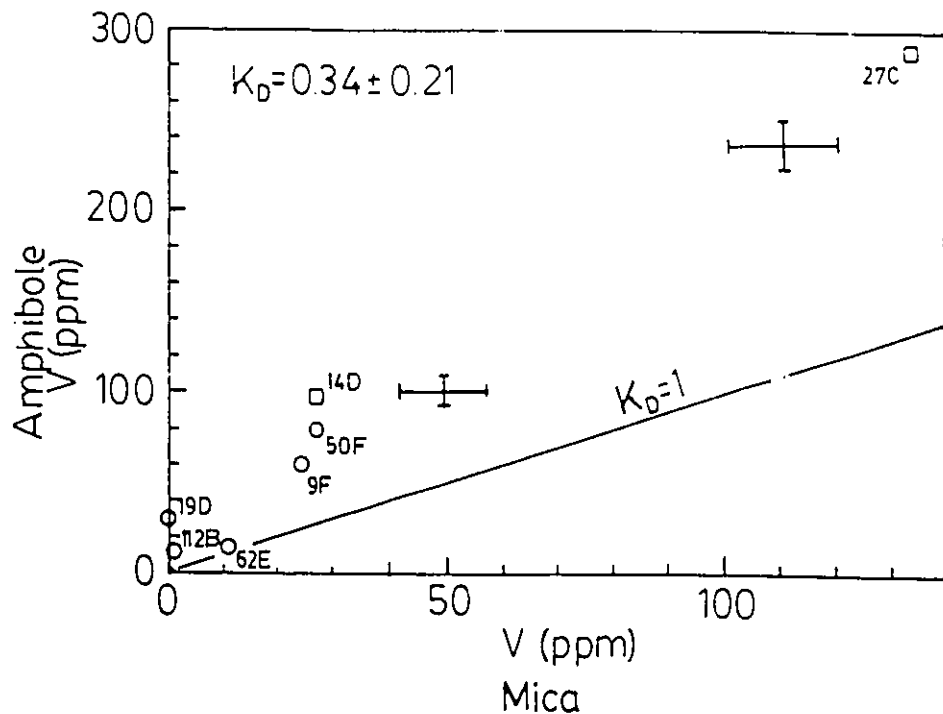
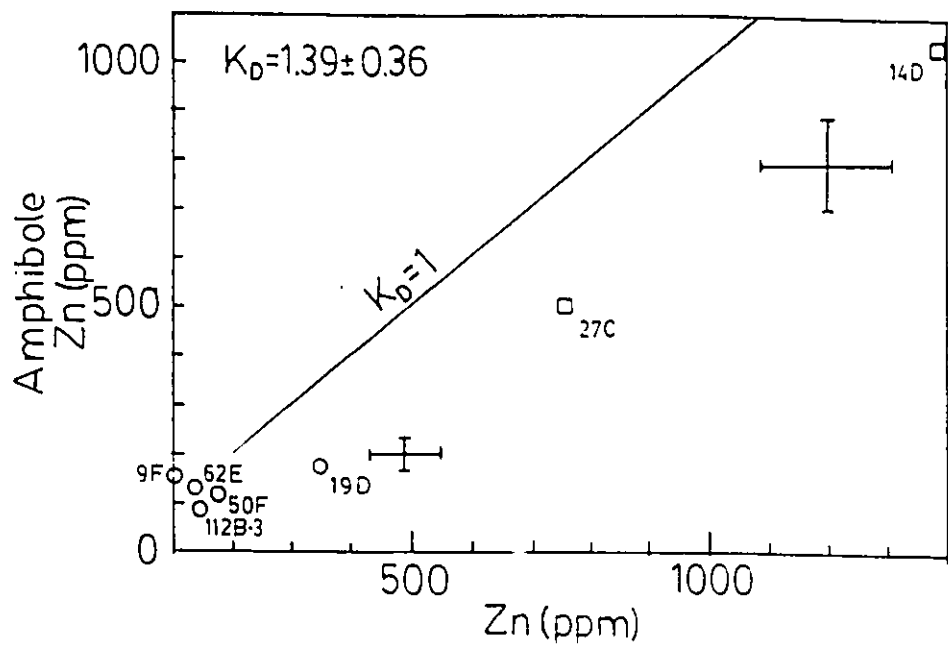


Figure 4.19 A) Distribution of zinc between mica and amphibole. B) Distribution of vanadium between mica and amphibole. Symbols are silicated marble (●), skarns (○), and veins (□). Error bars represent a 95% confidence interval using c_v derived from the zoning study in micas.

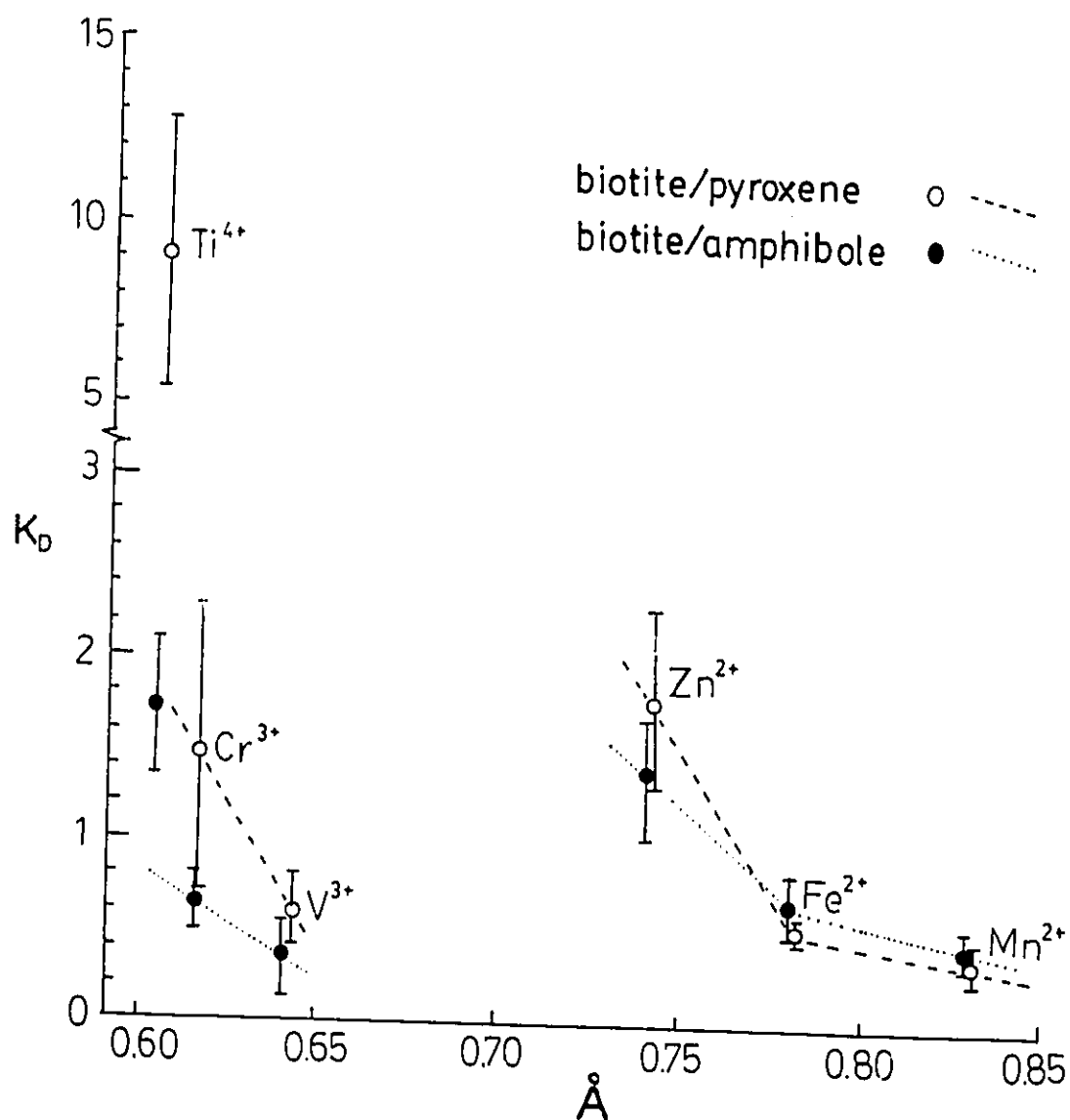


Figure 4.20 Distribution coefficients for Ti^{4+} , Cr^{3+} , V^{3+} , Zn^{2+} , Fe^{2+} and Mn^{2+} for biotite/Ca pyroxene pairs (open symbols) and biotite/amphibole pairs (solid). Ionic radii are from Shannon (1976). High spin state radii were used for Fe^{2+} and Mn^{2+} cations. Error bars represent a 95% confidence interval using standard deviation for set of pairs.

Table 4.10 Distribution of elements between mica, Ca pyroxene, Ca-Na amphibole, and apatite and calcite (this study)

Pairs No.	Bt/Cal		Cp/Cal		Amp/Cal		Ap/Cal	
	48		20		8		14	
	ave.	1s	ave.	1s	ave.	1s	ave.	1s
[Fe]	17	12	28	14	26	7	0.15	0.12
[Mg]	86	67	102	45	68	23	0.81	0.81
[Mn]	1.1	1.8	4.2	1.5	4.4	6.5	---	--
Na	---	--	52	36	160	72	---	--
Ba	107	132	2.9	2.6	8.6	11	1.9	1.1
Sr	---	--	0.04	0.01	0.07	0.07	0.94	0.53
Y	0.14	0.19	0.26	0.26	0.26	0.29	22	37

Notes: No. = number of samples. [Fe] = Fe/(Fe+Mg+Mn), [Mg] = Mg/(Fe+Mg+Mn), [Mn] = Mn/(Fe+Mg+Mn). Samples below detection. 1s is an estimate of one standard deviation.

4.3.5 Distribution of elements between apatite and calcite

The irregular distributions for [Fe], [Mg] and [Mn] may be attributed to the very low (detection limit) abundances for these elements in apatite (Table 3.10). Ferric iron is the dominant form of iron in apatite at higher abundances (Hogarth, 1989), hence the presence of magnetite may explain the 1.0 wt.% Fe_2O_3 in apatite from the Sullivan Island carbonatite. Barium and yttrium have moderately irregular distributions and no systematic relationship to the abundance of another element was found. Yttrium is very high in apatite from samples 21A and 14A resulting in a large apatite/calcite distribution which can only be accounted for by the presence of inclusions as other elemental distributions approach equilibrium values. Strontium is regularly distributed between apatite and calcite for 14 of 15 samples ($D = 0.81$; $1s = 0.17$). The Vaughan uraniferous fluorite-apatite-calcite vein occurrence (57B) has low Sr calcite which results in a high apatite/calcite distribution of 2.85 which is yet unexplained.

As was found with the silicates, there were no obvious differences in the elemental distributions for calcite with silicates or apatite between the skarns and veins. This may indicate similar temperature conditions during formation or poor temperature sensitivity of the elemental distribution.

4.4 Distribution of halogen and hydroxyl components

The volatiles H_2O , HF, and HCl can affect the stability of some skarn minerals, in particular, mica, amphibole and apatite. This is a preliminary examination of the halogen and hydroxyl components of micas and apatites in a marble (50A, 49C?), skarns (9I, 9K, 49C, 50C, 50D, 50F, 62B-1, 62B-2, 113), veins (14B-2, 14B-3, 113B) and a carbonatite (114). Major- and trace-elements were determined with the energy dispersive spectroscopy (EDS) and Cl and F were determined with wavelength dispersive spectroscopy (WDS), both with 100 second integration times. Most of the analyses were analysed from rim to core at several places on the

polished thin section. In general, no zoning was found except for TiO_2 in a few cases. Usually, the analytical data for each sample section was averaged unless distinct elemental differences existed between various areas. The chemical analyses of mica and apatite are summarized in Tables 4.11 and 4.13.

The hydroxyl component of mica and apatite was assumed to be the remainder after halogen sites were filled. Ideally, trioctahedral mica has 4 hydroxyl sites and apatite has 1 hydroxyl site. However, these sites may not be completely filled. In apatite two fluorine atoms may replace an oxygen atom thus excluding hydroxyl from the structure (ie. 14B-3, 113B).

The phlogopite, annite, and siderophyllite components ($X(\text{Phl})$, $X(\text{Ann})$ and $X(\text{Sd})$) of the mica were calculated based on the Fe, Mg, and Al content of mica. Similarly, $X(\text{F})$, $X(\text{Cl})$ and $X(\text{OH})$ were calculated on the relative hydroxyl site occupancy (Figures 4.21 and 4.22). These were used to determine the fluorine intercept value $\text{IV}(\text{F})$, chlorine intercept value $\text{IV}(\text{Cl})$, hydroxyl intercept value $\text{IV}(\text{OH})$ and the fluorine/chlorine intercept value $\text{IV}(\text{F/Cl})$ (Table 4.12). These intercept values are a correction for the effects of the octahedral site cations on the hydroxyl components of the mica.

The $\text{IV}(\text{F})$ value approaches 0 at the highest concentrations of fluorine in the micas. Munoz (1984) presents an equation for the fluorine intercept value (equation 4.3), chlorine intercept value (equation 4.4) and F/Cl intercept value (equation 4.5).

$$\text{IV}(\text{F})_{\text{bl}} = 1.52 X_{\text{Phl}} + 0.42 X_{\text{Ann}} + 0.20 X_{\text{Sld}} - \log (X_{\text{F}}/X_{\text{OH}}) \quad [4.3]$$

$$\text{IV}(\text{Cl})_{\text{bl}} = -5.01 - 1.93 X_{\text{Phl}} - \log (X_{\text{Cl}}/X_{\text{OH}}) \quad [4.4]$$

$$\begin{aligned} \text{IV}(\text{F/Cl})_{\text{bl}} = & 3.45 X_{\text{Phl}} + 0.41 X_{\text{Ann}} + 0.20 X_{\text{Sld}} \\ & - \log (X_{\text{F}}/X_{\text{Cl}}) + 5.01 \end{aligned} \quad [4.5]$$

In addition, the $\text{IV}(\text{F/Cl})$ value is the ratio between $\text{IV}(\text{F})$ and $\text{IV}(\text{Cl})$ (Table 4.12). Equations 4.6, 4.7, and 4.8 use the intercept values to compute relative fugacities given a formation temperature.

$$\log [f(\text{H}_2\text{O})/f(\text{HF})] = 2100/T + \text{IV}(\text{F}) \quad [4.6]$$

Table 4.11a Microprobe analyses of phlogopite and biotite from marble, skarns, and veins (this study)

Sample Type	9I	1s	9K	1s	14B2	1s	14B3	1s	49C	1s	50A	50C	50D	1s	50F	1s
	3		3		4		4		1		1	3	3		3	
	6		8		3		3		6		6	1	7		4	
SiO ₂	44.4	0.3	43.2	0.2	39.7	0.13	38.3	0.2	36.8	0.4	40.4	38.2	40.0	0.4	40.7	0.1
TiO ₂	0.31	0.06	0.22	0.06	1.26	0.04	1.47	0.04	1.92	0.18	1.34	1.43	1.53	0.22	0.60	0.06
Al ₂ O ₃	11.83	0.28	12.16	0.16	11.48	0.11	11.84	0.15	14.49	0.12	15.69	15.27	15.39	0.21	16.29	0.15
FeO	2.51	0.13	0.66	0.10	16.29	0.40	18.13	0.18	20.97	0.61	1.62	10.82	5.25	0.13	1.09	0.08
MgO	25.6	0.4	28.13	0.50	15.34	0.09	13.82	0.17	12.95	0.26	25.91	19.69	24.29	0.31	27.42	0.10
MnO	0.08	0.05	0.09	0.04	0.29	0.03	0.42	0.06	0.22	0.06	0.08	0.22	0.09	0.07	0.11	0.07
CaO	0.04	0.04	0.03	0.02	0.00	0.00	0.02	0.03	0.08	0.05	0.05	0.00	0.02	0.02	0.00	0.00
Na ₂ O	0.00	0.00	0.27	0.21	0.42	0.16	0.21	0.25	0.51	0.26	0.25	0.49	0.38	0.27	1.00	0.11
K ₂ O	10.53	0.18	10.11	0.21	9.69	0.10	9.76	0.13	9.55	0.20	10.00	9.57	9.82	0.10	9.00	0.10
Cl	0.13	0.09	0.01	0.01	0.25	0.02	0.27	0.02	0.19	0.02	0.06	0.22	0.11	0.03	0.03	0.02
F	5.18	0.20	4.72	0.29	3.62	0.02	3.38	0.10	0.41	0.08	1.43	1.22	1.12	0.07	1.33	0.08
O=F	2.18		1.99		1.52		1.42		0.60		0.17	0.43	0.47		0.56	
O=Cl	0.03		0.00		0.06		0.06		0.01		0.04	0.05	0.02		0.01	
Total	100.1		99.6		98.9		98.4		99.8		101.5	100.0	101.2		100.6	
Si IV	6.21		6.03		6.02		5.92		5.55		5.65	5.57	5.61		5.61	
Al IV	1.79		1.97		1.98		2.08		2.45		2.35	2.43	2.39		2.39	
T Site	8.00		8.00		8.00		8.00		8.00		8.00	8.00	8.00		8.00	
Al VI	0.16		0.03		0.08		0.08		0.13		0.24	0.20	0.16		0.25	
Fe VI	0.29		0.08		2.07		2.34		2.65		0.19	1.32	0.62		0.13	
Mg VI	5.34		5.86		3.47		3.18		2.91		5.40	4.29	5.08		5.63	
Mn VI	0.01		0.01		0.04		0.05		0.03		0.01	0.03	0.01		0.01	
Ti VI	0.03		0.02		0.14		0.17		0.13		0.14	0.16	0.16		0.06	
O Site	5.84		6.00		5.80		5.83		5.93		5.98	5.99	6.02		6.09	
Ca XII	0.01		0.00		0.00		0.00		0.01		0.01	0.00	0.00		0.00	
Na XII	0.00		0.07		0.12		0.06		0.15		0.07	0.14	0.10		0.27	
K XII	1.88		1.80		1.88		1.92		1.84		1.78	1.78	1.76		1.58	
A Site	1.89		1.88		2.00		1.99		2.00		1.86	1.92	1.86		1.85	
OH	1.68		1.91		2.20		2.28		3.76		3.35	3.47	3.48		3.41	
F	2.29		2.08		1.74		1.65		0.20		0.63	0.47	0.50		0.58	
Cl	0.03		0.00		0.06		0.07		0.05		0.01	0.05	0.03		0.01	

Notes: Type description: 1- marble; 263-skarn; 4-vein; 5-pyroxene; 6-carbonatite. n = number of sample points. Formula is based on 44 positive charges. s is an estimate of the standard deviation. Major-elements analyses were obtained by energy dispersive spectrometry (EDAX) and F and Cl were obtained by (WDS) microprobe at 9.5 nanoamps on the Cambridge microprobe by Peter Jones at the Department of Earth Sciences, Carleton University, Ottawa, Ontario.

Table 4.11b Microprobe analyses of phlogopite from marble, skarns, and veins

Sample Type n	62A1 3 3	1s 0.2 0.05 0.09 0.12 0.04 0.01 0.00 0.18 0.02 0.12	62A2 3 1	113 4 5	1s 0.21 0.08 0.15 0.14 0.16 0.07 0.03 0.08 0.05 0.02 0.10	113B 4 7	1s 0.3 0.12 0.15 0.20 0.18 0.08 0.00 0.06 0.15 0.02 0.11	114 6 7	1s 0.3 0.07 0.25 0.58 0.53 0.02 0.00 0.13 0.11 0.04 0.27 0.11	9K 3 1
SiO ₂	43.2	0.2	42.7	42.2	0.21	39.1	0.3	38.9	0.3	34.0
TiO ₂	0.24	0.05	0.22	0.80	0.08	1.42	0.12	1.25	0.07	0.45
Al ₂ O ₃	12.44	0.09	12.30	12.72	0.15	12.76	0.15	11.96	0.25	0.14
FeO	3.44	0.12	3.36	1.91	0.14	13.27	0.20	12.91	0.58	1.78
MgO	26.21	0.04	25.56	26.92	0.16	18.58	0.18	18.46	0.53	58.7
MnO	0.14	0.04	0.00	0.13	0.07	0.12	0.08	0.05	0.02	0.12
CaO	0.01	0.01	0.04	0.03	0.03	0.00	0.00	0.00	0.00	0.07
Na ₂ O	0.00	0.00	0.00	0.30	0.08	0.03	0.06	0.13	0.13	0.00
K ₂ O	10.53	0.18	10.19	9.61	0.05	9.74	0.15	9.56	0.11	0.04
Cl	0.07	0.02	0.10	0.04	0.02	0.23	0.02	0.27	0.04	0.00
F	4.68	0.12	4.63	4.49	0.10	2.70	0.11	4.08	0.11	7.01
O=F	1.97		1.95	1.89		1.14		1.72		2.95
O=Cl	0.02		0.02	0.01		0.05		0.06		
Total	101.0		99.1	99.4		99.5		97.8		99.4
Si IV	6.03		6.06	5.94		5.81		5.89		2.00
Al IV	1.97		1.94	2.06		2.19		2.11		0.01
T Site	8.00		8.00	8.00		8.00		8.00		2.01
Al VI	0.08		0.12	0.05		0.05		0.02		0.00
Fe VI	0.40		0.40	0.22		1.65		1.63		0.09
Mg VI	5.45		5.41	5.65		4.12		4.16		5.16
Mn VI	0.02		0.00	0.02		0.02		0.01		0.01
Ti VI	0.03		0.02	0.08		0.16		0.14		0.03
O Site	5.98		5.96	6.02		5.98		5.96		5.33
Ca XII	0.00		0.01	0.00		0.00		0.00		0.00
Na XII	0.00		0.00	0.08		0.01		0.04		0.00
K XII	1.87		1.85	1.72		1.85		1.84		0.00
A Site	1.88		1.85	1.81		1.85		1.88		0.00
OH	1.92		1.90	1.99		2.67		1.98		0.65
F	2.07		2.08	2.00		1.27		1.95		1.31
Cl	0.02		0.02	0.01		0.06		0.07		0.00

Notes: Type description: 1- marble; 2&3-skarn; 4-vein; 5-pegmatite; 6-carbonatite. n = number of sample points. Sample 9K is chondrodite. Formula is based on 44 positive charges. 1s is an estimate of one standard deviation. Major-elements analyses were obtained by energy dispersive spectrometry (EDAX) and F and Cl were obtained by (WDS) microprobe at an operating current of 9.5 nanoamps on the Cambridge microprobe by Peter Jones at the Department of Earth Sciences, Carleton University, Ottawa, Ontario.

Table 4.12 Fluorine X(F), Chlorine X(Cl) and F/Cl intercept values

	X(Phl)	X(Ann)	X(Sid)	X(F)	X(OH)	X(Cl)	IV(F)	IV(Cl)	IV(F/Cl)	H ₂ O/HF	H ₂ O/HCl	HCl/HF
9I	0.914	0.050	0.027	0.573	0.420	0.008	1.29	-5.05	6.33	6900	16.0	430
9K	0.977	0.013	0.005	0.520	0.478	0.000	1.46			10200		
14B-2	0.598	0.357	0.014	0.435	0.550	0.015	1.18	-4.60	5.76	5300	45.5	120
14B-3	0.545	0.401	0.014	0.413	0.570	0.0175	1.14	-4.55	5.69	5000	49.7	101
49C	0.491	0.447	0.022	0.050	0.940	0.0125	2.18	-4.09	6.29	53800	144.2	370
50A	0.903	0.032	0.040	0.158	0.838	0.0025	2.13	-4.31	6.35	47700	89.1	500
50C	0.716	0.220	0.033	0.118	0.868	0.0125	2.04	-4.57	6.60	39200	49.0	800
50D	0.844	0.103	0.027	0.125	0.870	0.0075	2.18	-4.60	6.75	53300	45.2	1180
50F	0.924	0.021	0.041	0.145	0.853	0.0025	2.20	-4.34	6.45	56100	82.8	680
62A-1	0.911	0.067	0.013	0.518	0.480	0.005	1.39	-4.79	6.17	8700	29.7	290
62A-2	0.908	0.067	0.020	0.520	0.475	0.005	1.38	-4.78	6.16	8500	29.7	290
113	0.939	0.276	0.008	0.500	0.498	0.003	1.45	-4.60	5.97	10000	45.2	220
113B	0.689	0.276	0.008	0.318	0.668	0.015	1.48	-4.69	6.18	10900	36.9	300
114	0.698	0.273	0.003	0.488	0.495	0.0175	1.18	-4.92	6.09	5400	21.9	250

Notes: X(Phl) = mole fraction of phlogopite; X(Ann) = mole fraction of annite; X(Sid) = mole fraction of siderophyllite. H₂O, HCl and HF denotes f(H₂O), f(HCl) and f(HF) derived from equations 4, 5 and 6 at 550°C. IV(F), IV(Cl), and IV(F/Cl) are intercept values (see text) as described by Munoz (1984).

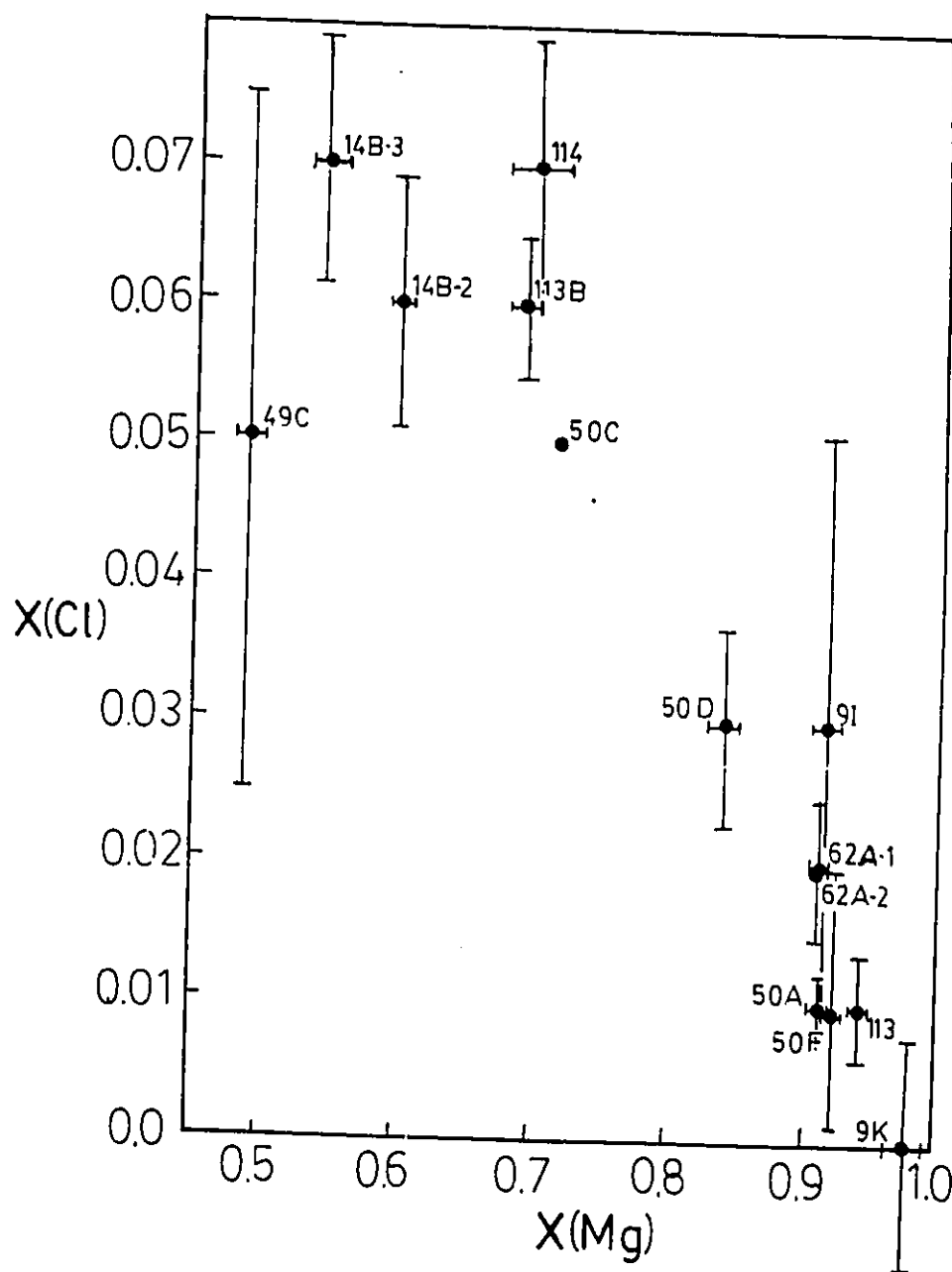


Figure 4.21 X(Mg) versus X(Cl) content of phlogopite and biotites from skarns and veins (Table 4.11). 2s error bars represent a 95% confidence level.

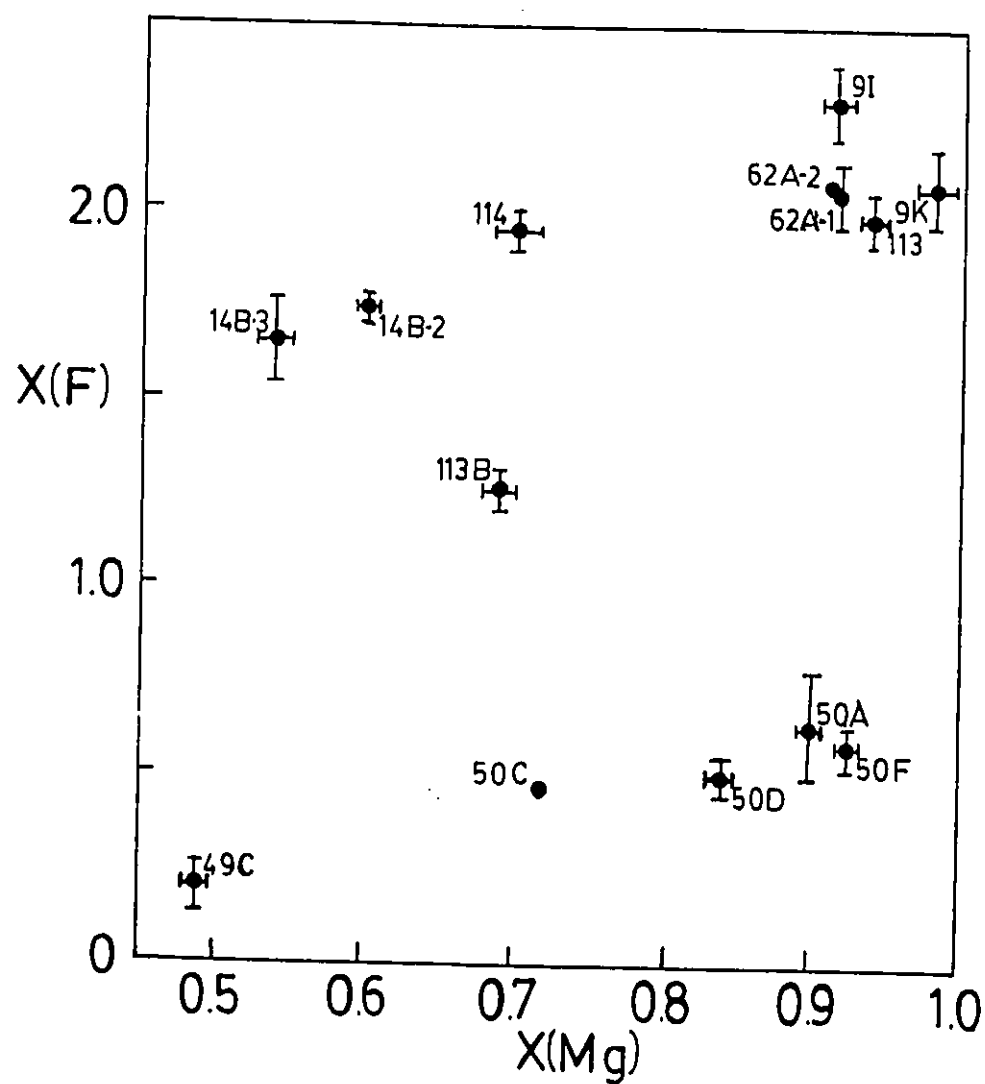


Figure 4.22 X(Mg) versus X(F) content of phlogopite and biotite from skarns and veins (Table 4.11). 2s error bars represent a 95% confidence interval.

Table 4.13 Microprobe analyses of apatite

Smpl	14B3	1s	49C	1s	113B	1s	114	1s
Type	4		1		4		6	
n	6		3		4		9	
CaO	54.3	0.4	55.0	0.1	54.1	0.3	53.1	0.2
SrO	0.16	0.01	-	-	-	-	1.27	0.04
P ₂ O ₅	40.8	0.2	41.5	0.5	39.7	0.4	39.7	0.4
Cl	0.03	0.03	0.09	0.02	0.09	0.01	0.05	0.02
F	3.93	0.05	3.54	0.14	3.84	0.13	3.54	0.23
O=F	1.65	-	1.49	-	1.62	-	1.49	-
O=Cl	0.03	-	0.01	-	0.02	-	-	-
Total	97.6		98.7		95.9		96.1	
Ca	5.01		5.03		5.09		5.02	
Sr	0.01		-		-		0.07	
P	2.98		3.00		2.95		2.96	
Cl	0.004		0.013		0.013		0.007	
F	1.07		0.95		1.07		0.99	
OH	-		0.03		-		-	

Notes: Type description; 1 - marble, 2 & 3 - skarn, 4 - vein; 5 - pegmatite, 6 - carbonatite. - below detection limit; n = number of sample points; Formula is based on 25 positive charges. 1s is an estimate of one standard deviation.

$$\log [f(\text{H}_2\text{O})/f(\text{HF})] = 5151/T + \text{IV}(\text{Cl}) \quad [4.7]$$

$$\log[f(\text{HCl})/f(\text{HF})] = -3051/T + \text{IV}(\text{F/Cl}) \quad [4.8]$$

The fluorine and chlorine intercept values obtained in this study from the Wilberforce, Otter Lake and Grand Calumet Island localities are similar to rare-metal skarns (Munoz, 1984). The Hunt Mo skarn (50C, 50D and 50F) has different intercept values compared to the other Grenville skarns examined but are similar to porphyry Cu-Mo deposits (Munoz, 1984). The Sullivan Island carbonatite has $\text{IV}(\text{F})$, $\text{IV}(\text{Cl})$ and $\text{IV}(\text{F/Cl})$ values indistinguishable from the skarns and veins (Table 4.12). However, the carbonatite apatite is very rich in strontium compared to the veins. Samples 14-B3 was the only sample analysed where phlogopite-biotite coexisted with fluorite, calcite, and apatite but phlogopite in sample 9K coexisted with chondrodite. Although these samples are not the highest $X(\text{F})$ content they are high. The presence of calcite and fluorite would buffer the fugacities of HF and H_2CO_3 . It is interesting to note that mica from the sample that is saturated with fluorite and calcite has a lower $X(\text{F})$ than the fluorphlogopite ($X(\text{F}) = 0.96$) analysed by Peterson et al. (1987) from a Balmat area marble which achieved granulite grade conditions. This may be due to the presence of CaCO_3 .

With an average temperature of 550°C (823.15 K) the relative fugacities may be computed (Table 4.12) including the carbonatite from Sullivan Island (114) although it may not have crystallized near 550°C . In general, the skarns and veins from the Wilberforce area (9I, 9K, 14B-2, 14B-3), Otter Lake (62A-1, 62B-2) and Grand Calumet Island (113, 113B) have an average $f(\text{H}_2\text{O})/f(\text{HF}) = 5000 - 10\,000$. With the exception of sample 50A (marble) and 9I (skarn), the $f(\text{H}_2\text{O})/f(\text{HF})$ ratio is between 1.47 and 2.18. Munoz (1984) has suggested that the most meaningful data is the $f(\text{HCl})/f(\text{HF})$ because of the assumption of OH filling the remaining hydroxyl site not occupied by halogens which were measured. The $f(\text{HCl})/f(\text{HF})$

ratio ranges between 180 to 300 for the Otter Lake and Grand Calumet Island samples. The samples from the Hunt Mo skarn deposit and associated marble have consistently high $f(\text{H}_2\text{O})/f(\text{HF})$ ratios (41 000 to 55 000) and high $f(\text{HCl})/f(\text{HF})$ ratios (440 to 1 100).

Calculated $f(\text{F}_2)$ for fluids coexisting with F-rich micas, and amphiboles saturated with fluorine are very low. Fluorine remains a minor component of the fluid in rocks of the Adirondacks (New York) (Valley et al., 1990). Therefore, the presence of F-rich phases and fluorite do not implicitly imply the coexistence with a F-rich vapour phase.

The partitioning of halogens and hydroxyl constituents between coexisting trioctahedral mica and apatite is a potential geothermometer (Stormer and Carmicheal, 1971; Ludington, 1978). Ludington (1978) presented an equation for the equilibrium constant for F-OH exchange which is a function of temperature (equations 4.9 and 4.10).

$$\log K^* = \log[X_F/X_{OH}]_{Ap} + \log [X_{OH}/X_F]_{Bt} - 1.107(X_{Ann}) - 1.444(X_{Sd}) \quad [4.9]$$

$$T(K) = 1100/\log K^* \quad [4.10]$$

Only 4 samples have coexisting mica and apatite. Sample 14B-3 has coexisting fluorite and calcite with apatite which are very high in fluorine (ie. no Cl detected) which precludes the analysis of temperatures. The remaining two samples have calculated $\log K^*$ values equal to 2.21 and 2.08 for samples 49C and 114, respectively, which corresponds to temperatures of 225°C and 256°C. There are several plausible explanations for the low temperatures including continued exchange to low temperature, disequilibrium due to secondary alteration or the inaccuracy of the method due to low abundances of hydroxyl which was low in the first place.

CHAPTER 5

METAMORPHIC AND METASOMATIC CONDITIONS FOR SKARN FORMATION

5.1. Introduction

Field, petrographic, and chemical examination of the U, Th, Mo, and REE deposits indicate several reoccurring processes common to clinopyroxenite- and marble-hosted skarns, and fluorite-apatite-calcite veins. Metamorphic equilibria will be considered to establish the stability of the metasomatic assemblages. Subsequently, the dominant metasomatic reactions (to form clinopyroxene, phlogopite, apatite, and scapolite) will be further defined with implications for the formation of the various deposit types.

For the areas under consideration, the regional metamorphic grade reached upper amphibolite to granulite facies coincident with the culmination of the Grenville orogenic cycle (Ottawan Orogeny; 1100-1090 Ma) as was outlined briefly in Chapter 1. However, upper amphibolite to granulite grade conditions were achieved at least 50 Ma prior to the emplacement of the pegmatites and formation of the skarns and fluorite-apatite-calcite veins (1020-1060 Ma) during uplift of the crust (see chapter 1). The host rock temperatures at this period of time do not differ greatly from those of the metamorphic peak (650°C) explaining the similarity between regional metamorphic assemblages and contact metasomatic assemblages.

The late-tectonic age of the pegmatites, skarns, and veins precludes the involvement of regional metamorphic volatiles being directly responsible for the formation of the skarns and veins, unless metamorphic devolatilization occurred during quasi-isothermal uplift. Furthermore, the heat associated with pegmatite emplacement cannot produce further decarbonation or dehydration reactions in the host rocks because the host rocks already achieved at least upper amphibolite facies conditions during regional metamorphism.

As previously discussed, thermochronological considerations indicate that host rocks were approximately 500° to 550°C while at high pressure during pegmatite emplacement. In addition, the granitic pegmatites have solidus temperatures on the order of 600° to 650°C at $P(H_2O) = 400$ MPa. This helps to constrain the pressure of skarn and fluorite-apatite-calcite vein formation. The temperature of formation of skarns and veins should be between the pegmatite solidus temperature (600° to 650°C) and the temperature of the host rocks (500° to 550°C). The temperature gradient from a pegmatite into the distal contact skarn environment may have been relatively small hence would not be a primary factor in the variation in mineral assemblages within the skarn.

5.2 Conditions of skarn formation

5.2.1 Introduction

The metamorphic/metasomatic phase relations have been examined in a regional perspective rather than with respect to any particular locality. A detailed analysis of the phase equilibria of any particular skarn is beyond the scope of this research. However, the mineralogical similarities among skarns and veins throughout the area indicates that they may have formed under similar conditions. Therefore the following presentation represents only a general discussion of the skarn phase equilibria not specific to any particular locality. The generally narrow compositional variation in Fe/(Fe+Mg) ratio and Al content in phlogopites and Ca pyroxenes from the skarns supports these simplifications. General constraints on temperature, pressure, bulk, and volatile phase compositions are evaluated based on common assemblages observed. Some possible reactions are presented to explain the formation of phases within the skarns.

As previously mentioned, the difference between silicated marble and skarn is the high proportion of calcite in silicated marbles. The absence of calcite in the Ca pyroxene-

rich assemblage might indicate that dolomite was the only carbonate present. However, the common occurrence of calcite in the marbles distal to the skarns indicates that calcite was dissolved and removed during skarnification. If the original proportion of calcite in the marble was too low to saturate the fluid phase the resultant skarn is devoid of primary skarn calcite whereas silicated marble/skarns and some distal skarns remain saturated in calcite.

In general, silica, alkalis, alumina, and volatiles are introduced metasomatically during skarnification of the marble based on the replacement of marble by calc-silicates and aluminosilicates. Species of metasomatic origin are denoted with a subscript (aq) indicating an aqueous species. Chlorine (Cl) ligands may be responsible for complexing the chalcophile elements (Fe, Mn, Zn) and LREE, fluorine for other high field strength elements (HFSE) (Si, Al, Ti, HREE), as well as carbonate (CO_3^{2-}) and phosphate ions (P_2O_5). However, hydroxyl ligands have the potential of mobilizing most cations and are particularly stable in an alkali environment. Regardless of the ligand responsible for the mobilization of cationic constituents, OH^- will be used to represent the species for simplicity.

It is very important to realize that these mineral stability diagrams were calculated under the assumption of a pure $\text{H}_2\text{O}-\text{CO}_2$ fluid phase. The effect of salts on the $\text{H}_2\text{O}-\text{CO}_2$ fluid phase has been investigated by Bowers and Helgeson (1983). The activities of these species produce a shift in the position of calc-silicate equilibria toward the H_2O -rich axes (at the conditions under consideration) because of increased CO_2 activity. It seems likely that H_2O and CO_2 immiscibility probably occurred in these skarns because of the high salt contents evident from the presence of scapolite (dipyre) and the daughter salts in the fluid inclusions (Salvi, 1987). Therefore, the calculated $X(\text{CO}_2)$ for the proximal and distal

skarns are preliminary upper estimates for the CO₂ content of the H₂O-rich fluid.

There are several implications of H₂O-CO₂ immiscibility in the skarns. It is probable that the salt content of the original pegmatite-derived fluid was moderate to high in salt (ie. > 20 wt.% equivalent NaCl) or even saturated (Salvi, 1987). The CO₂ evolved from the skarn during metasomatic decarbonation of the marble would be incorporated into the H₂O-rich fluid until saturation of the fluid in CO₂ after which it would exist as a separate volatile phase. It is also interesting that at 550°C and 400 MPa the CO₂ fluid has a density near 0.95 g/cm³ whereas pure H₂O has a density of 0.85 g/cm³ but with 25 wt.% dissolved salt the density of the H₂O fluid approaches that of the CO₂ fluid with which it coexists. Therefore, coexisting H₂O-CO₂ immiscible fluids may have profound effects on the mineral stabilities (Bowers and Helgeson, 1983) and possibly solubilities of components within each fluid. Unfortunately, no evidence for this CO₂-rich fluid was found in the fluid inclusion study of Salvi (1987).

5.2.2 Stability of calc-silicate minerals

Marble-hosted marginal (to pegmatites) and vein skarns have diopside, phlogopite, scapolite, titanite, and, more rarely, tremolite as part of the skarn assemblage. Diopside is present in the proximal contact zones with either scapolite, plagioclase, or more rarely with K-feldspar. Toward the marble, the assemblage diopside-phlogopite becomes more dominant. The diopside-phlogopite is transitional into an assemblage of diopside-tremolite-phlogopite. The abundance of phlogopite tends to decrease toward the distal tremolite-rich zone. The tremolite-rich marginal or vein exoskarn abruptly terminates against the marbles.

Carbonates associated with silicated marbles, skarns, and veins are invariably lower in Mg, with variable Fe, Mn, and Sr contents compared to the marbles. Therefore the dolomite

component of calcite is low possibly due to the interaction with siliceous fluids.

The absence of wollastonite, except in a few rare instances, and the coexistence of quartz and calcite in some skarn veins indicate that the conditions for wollastonite formation were not achieved (Figure 5.1). However, the bulk composition is such that quartz and calcite do not occur together in the proximal skarn because of calcite dissolution. Therefore the absence of wollastonite may be simply related of the undersaturation in calcite in the proximal skarns. However, the presence of quartz and calcite in a few skarn veins (e.g. Desmond U-Mo skarn and Litchfield Mo skarn) attests to the instability of wollastonite in some places.

The principle reactant in the marble to form the calc-silicate minerals in skarns is dolomite and $\text{CaMg}(\text{CO}_3)_2$ dolomite component in calcite. Diopside is the most common Ca-Mg silicate mineral within the skarns (commonly > 90 vol. %), hence its stability is of particular importance in the consideration of skarn formation.

In numerous instances, chondrodite or norbergite have been found within silicated marbles and skarns as previously discussed. It is evident that humite group minerals are related to some of the skarns and formed metasomatically by the introduction of fluorine into the marbles. However, Bourne (1974) has also characterized the presence of humite group minerals as a primary regional metamorphic products in Grenville marbles.

The calc-silicate equilibria may be considered with respect to the simple Ca-Mg-Si-O-H-C diagram (Figure 5.1) because of the dominance of calc-silicates in these skarns. The presence or absence of calcite may be portrayed on the CaO-MgO-SiO_2 ternary diagram. The variation in the bulk composition of the skarn may be represented by a tie line extending from quartz to an appropriate composition along the dolomite-calcite join.

This represents the metasomatic introduction of dissolved silica from the pegmatite into the marble. Therefore the proximal assemblage should be rich in quartz and calc-silicate phases and devoid of dolomite and calcite whereas the distal assemblages should contain few calc-silicate minerals and calcite.

Tremolite is commonly a primary mineral in the distal skarns commonly coexisting with calcite and more rarely with quartz. Therefore, the rare coexistence of tremolite, quartz, and calcite represents conditions of distal skarn formation (Figure 5.1).

In general, forsterite is absent from the skarns. This may indicate higher $X(\text{CO}_2)$ in the distal skarn near the reaction with dolomite but this could also be due to the increased stability of fluortremolite. The occurrence of humite group minerals chondrodite and/or norbergite could also explain the absence of forsterite in some of the skarns.

The skarn assemblages are consistent with an approximate temperature of 550° to 575°C and an $X(\text{CO}_2)$ between 0.1 and 0.3 for most of the skarn although the proximal assemblages are poorly constrained.

Quartz is not commonly associated with diopside in the proximal skarn although this is expected based on the bulk composition (CaO-MgO-SiO_2 ternary). This would suggest that silica solubility is only affected by reaction with dolomite during calc-silicate formation. The calc-silicate-forming metasomatic reactions are more clearly illustrated in chemical potential diagrams. The metasomatic introduction of silica, reaction of dolomite with associated decarbonation, and dissolution of calcite at these temperatures and pressures are the principal factors influencing the skarn mineralogy. A schematic Ca^{2+} and $\text{Si}(\text{OH})_4$ activity diagram with dolomite (@ 575°C, 400 MPa, and $X(\text{CO}_2) = 0.3$) illustrates the relative stabilities of the calc-silicate minerals with respect to

dolomite (Figure 5.2). Figure 5.2 illustrates the calcite saturated equilibria (curve a) and undersaturated equilibria (curve b) and their relation to the stability of calc-silicate minerals.

In many pegmatite-related skarns, K-feldspar (albite or scapolite), phlogopite, diopside, tremolite, calcite, and titanite are the dominant assemblages and are most appropriately portrayed on a magnesite-calcite-quartz-K-feldspar tetrahedron (Figure 5.3) but the complexity precludes a strait forward analysis in temperature- $X(\text{CO}_2)$ space. Additional components (K & Al) are needed to explain the presence of the K-feldspar or phlogopite in the skarns and veins. The temperature versus $X(\text{CO}_2)$ equilibria in the system Ca-Mg-Si-Al-K-C-H are portrayed in Figure 5.4. Unfortunately, this diagram portrays only calcite saturated equilibria hence is of limited use in the analysis of the mineral stabilities were there is an undersaturation of calcite.

The SiO_2 - KAlSi_3O_8 - $\text{CaMg}(\text{CO}_3)_2$ ternary diagram is used to illustrate the calcite saturated equilibria in Figure 5.3. The bulk compositional range may be represented by a tie line from the quartz-K-feldspar binary composition based on approximated relative quartz and feldspar solubilities (Anderson and Burnham, 1983), to the dolomite apex. The sequence of mineral assemblages quartz-K-feldspar-diopside-calcite (1), K-feldspar-diopside-phlogopite-calcite (2), phlogopite-diopside-tremolite-calcite (3), and phlogopite-tremolite-dolomite-calcite (4) are similar to the zoning sequence observed in the skarns except that calcite is usually undersaturated in the first two zones. At the Hunt Mo skarn South of Dacre, Ontario (deposit 50), the first and second assemblages are proximal assemblages and later (3 and 4) as distal assemblages. The variation of these ternary components may be responsible for the formation of the observed assemblages present but the metasomatic introduction of SiO_2

and KAlSi_3O_8 into the exocontact environment, the reaction with dolomite exclusively, and the degree of calcite saturation are prominent factors in evaluating the mineral equilibria.

5.2.3 Stability of phlogopite and K-feldspar

The pegmatite-related skarn may be described as a sequence of reactions from proximal to distal skarn and may be subdivided into zones. Within the calcite-magnesite-K-feldspar-quartz tetrahedron, bulk compositional variations are reflected in the skarn mineralogy (Figure 5.3). The calcite-absent skarn assemblages follow a path of calc-silicate formation that reflects the undersaturation of calcite. Such a path might produce an early assemblage of K-feldspar (plagioclase or scapolite)-diopside-calcite but continued interaction with a siliceous, calcite-undersaturated fluid will produce a K-feldspar-diopside assemblage. This process may explain the absence of tremolite with diopside in the proximal skarns because of the calcium-rich bulk composition (Figure 5.3). The proximal K-feldspar-pyroxene $\pm$ quartz assemblage (zone 1) and diopside-phlogopite $\pm$ K-feldspar (zone 2) indicates conditions above the initial diopside formation above tremolite-quartz-calcite breakdown reaction (Figures 5.1 and 5.2). The assemblage diopside-phlogopite-tremolite $\pm$ calcite (zone 3) field is characteristic of the skarns intermediate to distal skarns and are more closely associated with unaltered marble (distal) (Figure 5.3). Distal skarn is characterized by an assemblage of tremolite-phlogopite-calcite (zone 4). Humite minerals in the marbles in the vicinity of skarn may have a metasomatic origin.

A schematic μSi versus μAl diagram illustrates the compositional variation and relative mineral stabilities in the skarn (Figure 5.5). A bulk compositional variation from a quartz-K-feldspar assemblage to the dolomite apex intersects a sequence of zones (1 to 4) as outlined above. The chemical potential variation of silicon and aluminum can successfully

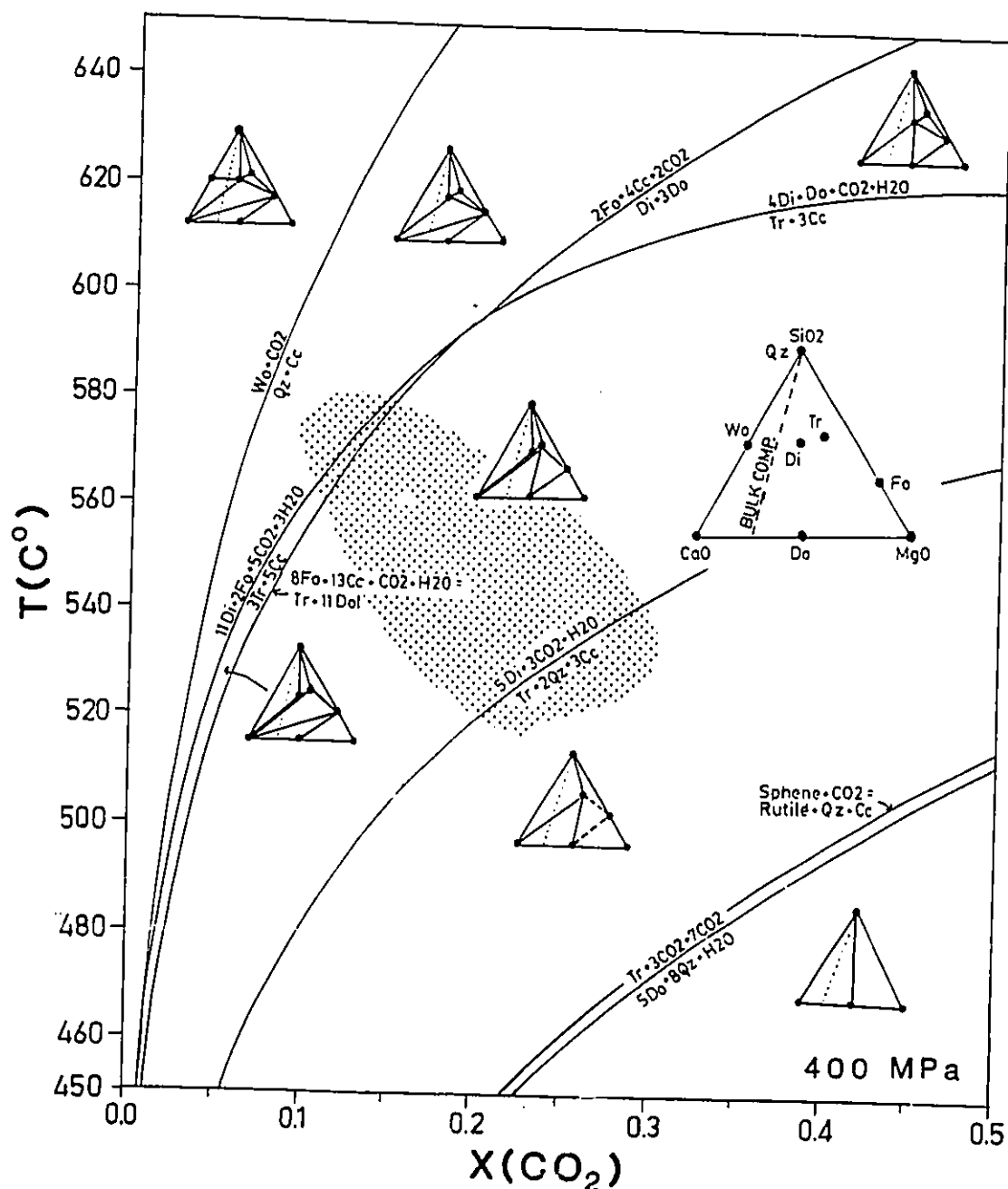


Figure 5.1 Temperature- $X(\text{CO}_2)$ diagram at 400 MPa pressure in the system Ca-Mg-Si-O-C-H; geocalc program; Berman et al. (1985); Perkins et al. (1986). Stippled area represents the approximated range of formation conditions for the proximal to distal skarns. For this and subsequent diagrams, the thermodynamic data (Perkins et al., 1986) was compiled and modified from direct experimental (various authors) and thermochemical (various authors) data.

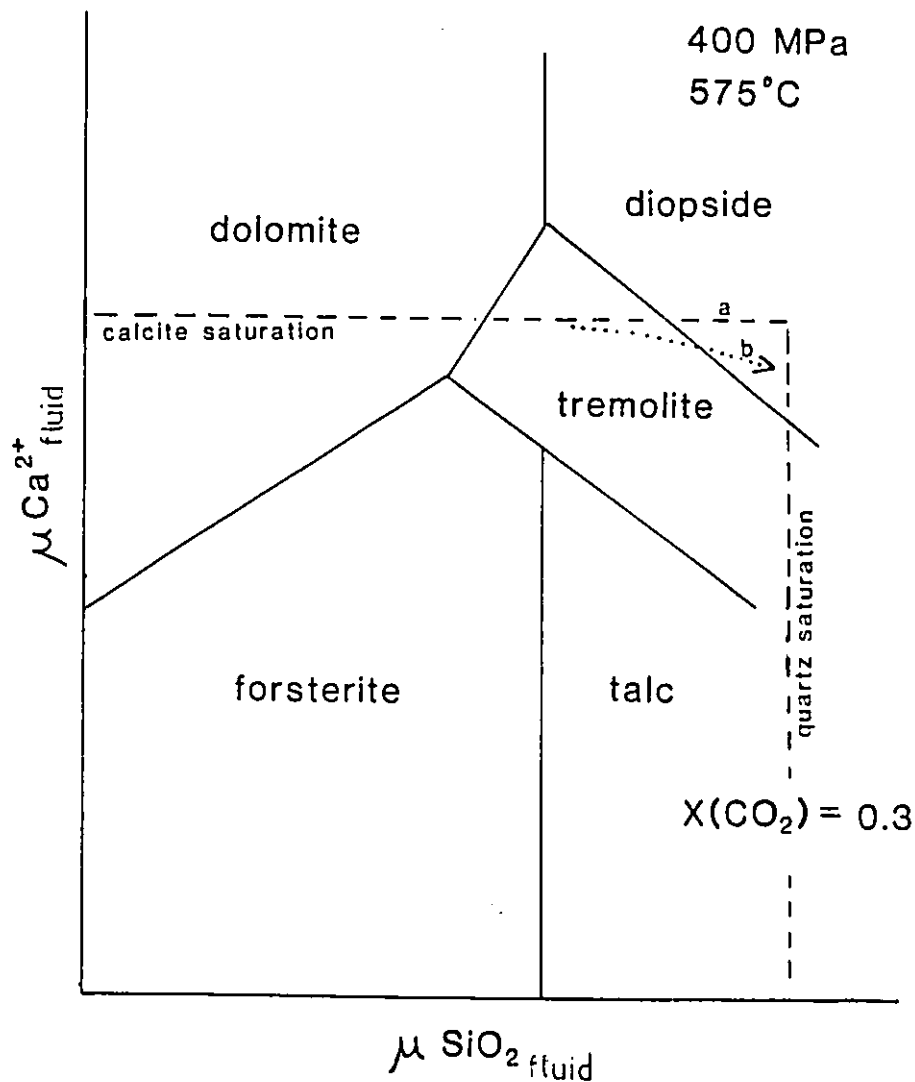


Figure 5.2 Schematic μCa^{2+} versus μSiO_2 diagram in the system Ca-Mg-Si-O-H-C at 575°C, 400 MPa, and $X(\text{CO}_2) = 0.3$ (see figure 5.1) illustrating the relative stabilities of the calc-silicate minerals, and the affect of calcite saturation (curve a) and undersaturation (curve b) and quartz saturation (modified from Walther and Helgeson, 1980).

model the metasomatic interaction of dolomitic marble with the pegmatites.

In general, the mineral assemblages observed in the proximal skarns are consistent with a temperature of 575°C and $X(\text{CO}_2) = 0.1$ to 0.3 whereas the distal skarns which have primary tremolite and no K-feldspar formed at approximately 550°C at a $X(\text{CO}_2) = 0.1$ to 0.5 at 400 MPa pressure. Unfortunately limited variation in bulk compositions preclude a more definitive characterization of the conditions of skarn formation.

5.2.4 Scapolite stability

Scapolite is a common product in the contact metasomatic skarns (Shaw et al., 1965; Zharikov, 1970; Shay, 1975). Zharikov (1970) described scapolite equilibria in skarns. Shaw (1960) described scapolite crystal-chemistry from scapolite within the Grenville Province. In further detail, Shaw et al. (1963), Shaw et al. (1965), Haughton (1971), and Karvinen (1973) described the scapolite in Grenville skarns. In most cases, plagioclase is more sodic than coexisting scapolite (Karvinen, 1973). This suggests that plagioclase compositions more sodic than those in equilibrium with scapolite are stable without coexisting scapolite. Alternatively, scapolite compositions more calcic than those coexisting with plagioclase should exist without coexisting plagioclase. Therefore, the presence of scapolite and/or feldspar is a function of the resultant bulk composition of the skarn and feldspar which is an interplay of original bulk composition and metasomatic transformation. It is not uncommon to have feldspars and scapolite in the same deposit (ie. Hunt Mo deposit) although these minerals probably do not represent an equilibrium assemblage.

Although the two end-members are marialite (3 Albite + NaCl) and meionite (3 Anorthite + CaCO_3), they rarely occur in nature. Instead, dipyre and mizzonite are common in these

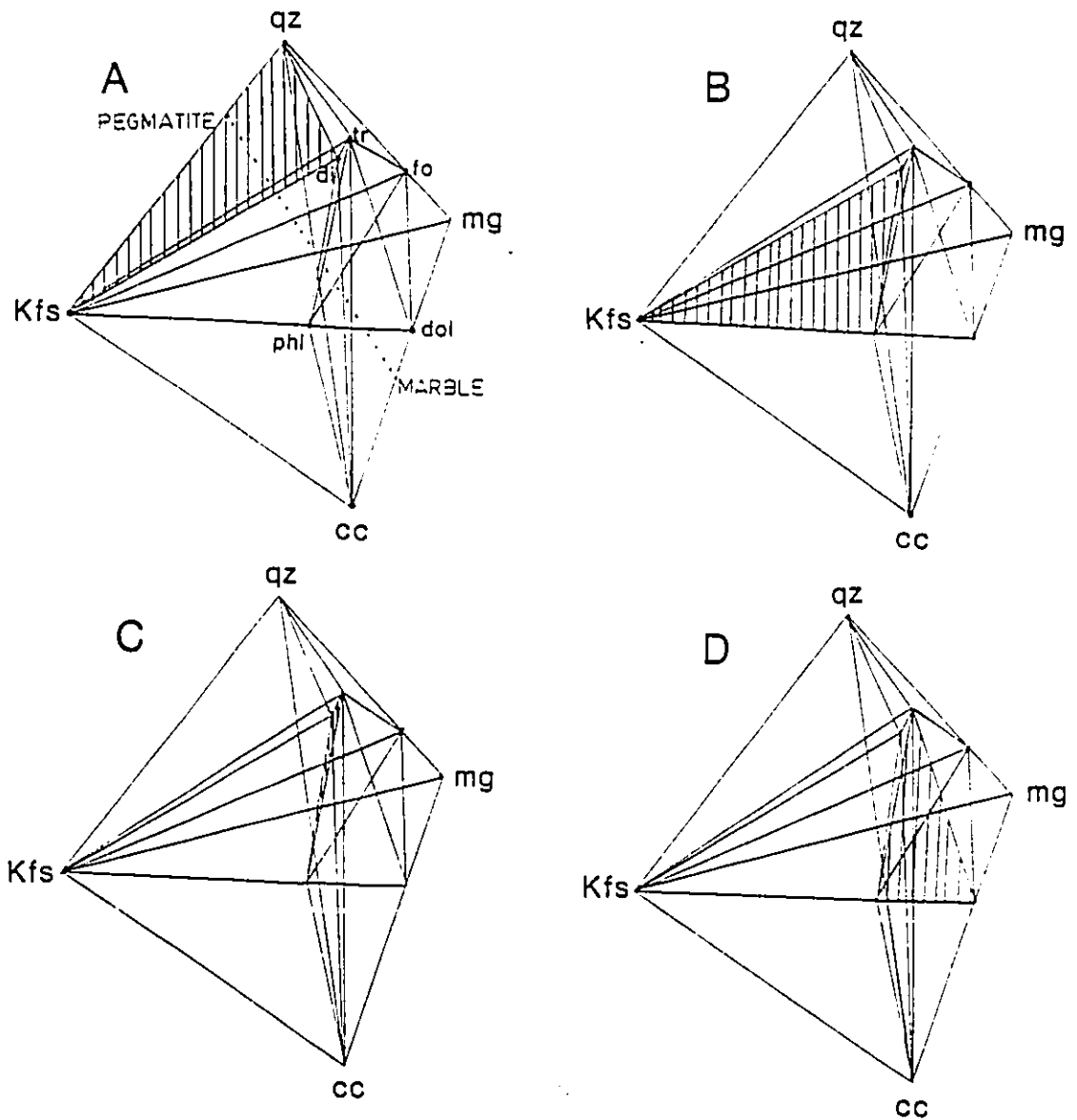


Figure 5.3 Topology of stable mineral assemblages in the multi-component system CaO , MgO (FeO), KAlSi_3O_8 , Al_2O_3 , SiO_2 at the temperature and pressure of skarn formation. The striped pattern represents the stable assemblage in each of the four recognized zones. Field A - endoskarn assemblages, B - proximal exoskarn assemblages, C & D - distal exoskarn assemblages. Symbols: cc = calcite, Kfs - microcline, mg = magnesite, qz = quartz, di = diopside, dol = dolomite, tr = tremolite, phl = phlogopite, fo = forsterite. Pegmatite = fluid in equilibrium with pegmatite. Marble = estimate of a hypothetical marble composition.

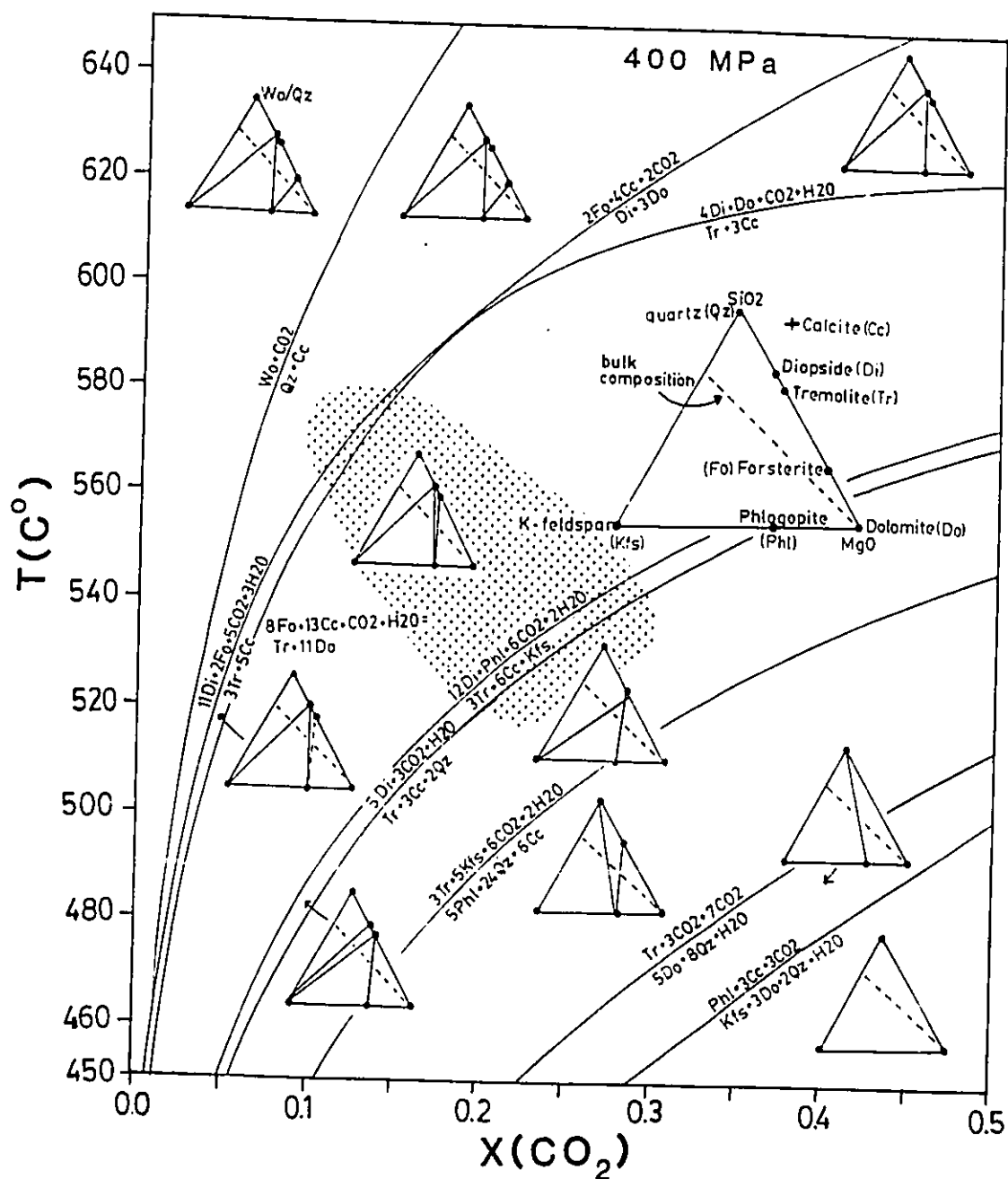


Figure 5.4 Temperature- $X(\text{CO}_2)$ diagram at 400 MPa pressure in the system Ca-Mg-Si-K-O-C-H; geocalc program; Berman et al. (1985); Perkins et al. (1986). Stippled area represents the approximate stabilities of the proximal to distal skarns. The dashed tie line represents the bulk compositional variation from a pegmatite fluid to the apex of the principle reactant phase (dolomite).

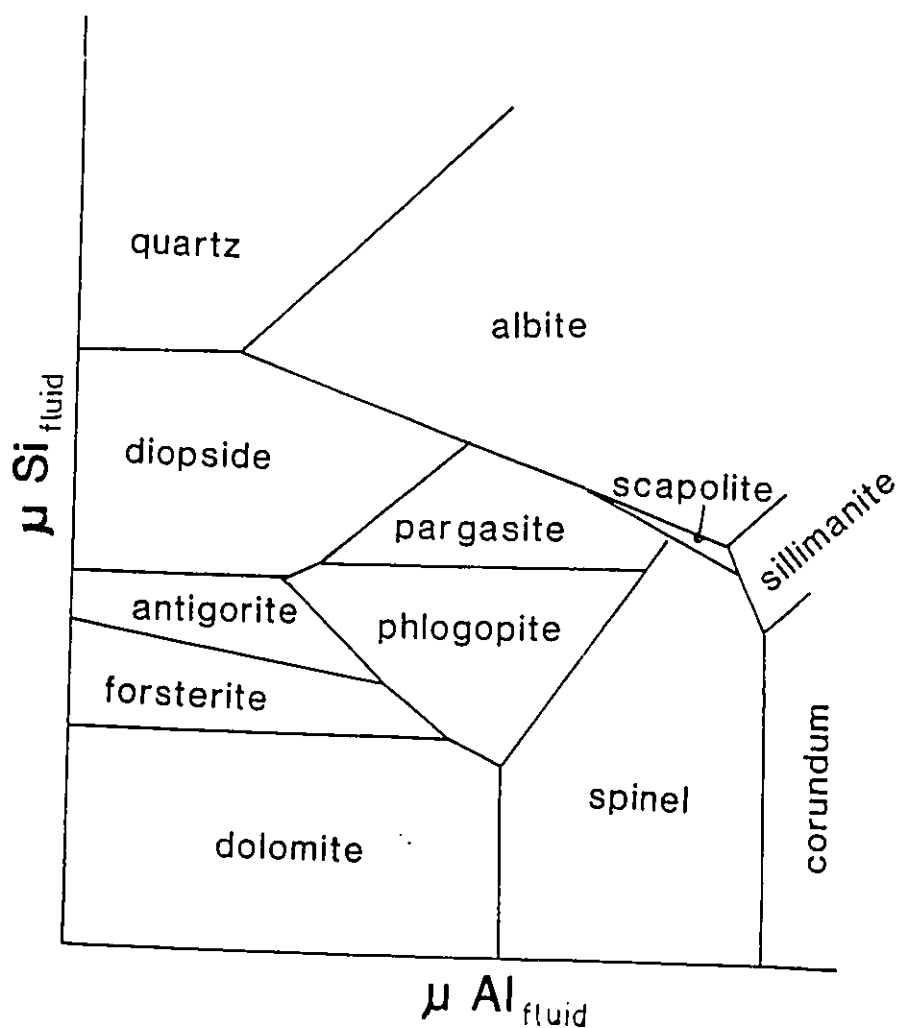


Figure 5.5 Schematic μ_{Si} versus μ_{Al} diagram with variable $a[\text{Ca}^{2+}]$, $a[\text{K}^+]$, and $X(\text{CO}_2)$ at high temperature and pressure (after Shaw et al., 1965) illustrating the possible variation in composition represented by various zones.

skarns (Shaw et al., 1963). As discussed in the previous section on the stability of feldspar, the stability of scapolite was primarily due to resultant intermediate Na-Ca contents of scapolite. The stability of albite and NaCl must be greater than marialite and similarly the stability of meionite is less than anorthite and calcite. Orville (1975) and Ellis (1978) determined that albite and NaCl were more stable than marialite at conditions as high as 750°C and 400 MPa but that intermediate compositions were indeed stable. Goldsmith and Newton (1977) found that anorthite + calcite is more stable than meionite up to 870°C (pressure independent). The lack of thermochemical data for intermediate compositions of scapolite precludes a detailed analysis of their stability but generalizations in terms of metasomatic processes may be made from end-member reactions to explain the absence of anorthite, zoisite and grossularite in the skarn assemblage. Figure 5.6 illustrates the stabilities of anorthite, zoisite, and grossularite in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$, however, the absence of these minerals suggests that the stability of the intermediate scapolite compositions (dipyre/mizzonite) is greater than these minerals. Other calc-silicate equilibria indicated that the skarns formed at temperatures between 550° and 575°C at 400 MPa and $X(\text{CO}_2)$ between 0.1 and 0.3, therefore the assemblages anorthite-calcite-quartz are expected to be stable with respect to zoisite and grossularite. Therefore, the stability of scapolite is principally related to the plagioclase composition as discussed earlier, although the following discussion will include scapolite relative to grossularite and zoisite stability for completeness.

Meionite has a stability field on the high $X(\text{CO}_2)$ (> 0.5 $X\text{CO}_2$) side of the zoisite-anorthite equilibria (Figure 5.6). It seems scapolite stability precludes the presence of zoisite, anorthite, calcite, and grossularite. Although the end-member equation (5.1) is displaced to the left at these

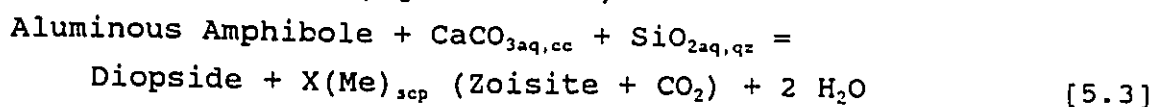
temperature and pressure conditions, intermediate compositions (dipyre and mizzonite) may account for all of



the calcium in the rock. Similarly, the reaction (5.2) may destabilize zoisite relative to intermediate scapolite compositions which explains the absence of zoisite from the primary skarn assemblage. However, zoisite is occasionally present in secondary replacements of scapolite.



Analogously, a reaction to produce zoisite may be changed to stabilize scapolite (equation 5.3).



The absence of grossularite from the skarn assemblages may be accounted for by transformations to form scapolite. The analysis of zoisite stability with respect to scapolite also pertains to the stability of grossularite.

Zharikov (1970) indicated that the distribution of Ca and Na between scapolite and plagioclase was a function of temperature and pressure of formation. In general, the scapolites are more calcic than coexisting plagioclase under the highest pressure conditions (Zharkov, 1970). The data presented by Shaw et al. (1963), Haughton (1971), and Karvinen (1973) do not represent equilibrium because of irregular partition of components between plagioclase and scapolite but are consistent with a higher pressure of formation relative to epizonal skarns. Zharkov (1970) attributes the distribution of sodium and calcium in coexisting scapolite and plagioclase to variations in the partial pressure of CO_2 . Kwak (1977) presented evidence for regional metamorphic scapolite and showed that the meionite component increased with increasing grade.

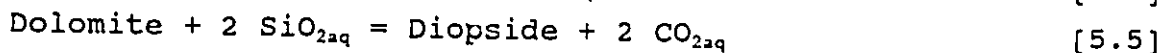
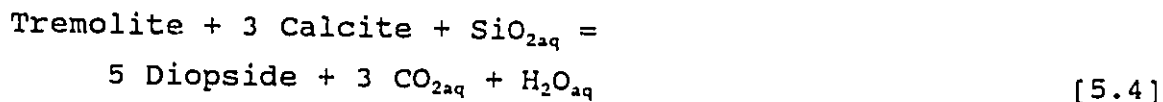
5.3 Metasomatic replacement processes

5.3.1 Introduction

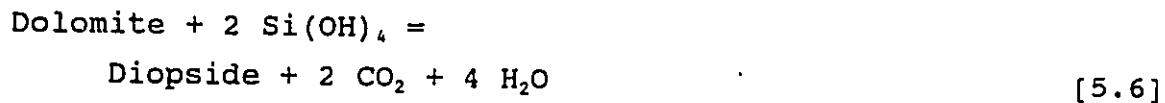
It is evident from the petrographic description of the skarns and veins that metasomatic alteration of pre-existing host rock and skarn assemblages is responsible for the complex mineral paragenesis. An attempt has been made to explain a few of the most common metasomatic transformations using balanced metasomatic reactions. There are numerous possible reactions which may be responsible for the formation of pyroxene, amphibole, phlogopite, and apatite within the host rock marbles, clinopyroxenite, gneisses, and amphibolites. It is evident in an examination of the skarns and veins that even the elements that are considered immobile (Al and Ti) are quite mobile. Constant volume (mineral volumes), or constant elemental abundances were used as endmember constraints for these reactions. They represent the possible range of chemical constraints on the metasomatic transformations involved in the skarns and veins.

5.3.2 Metasomatic Ca pyroxene-forming reactions

There are two simple reactions for the metasomatic formation of diopside in marble:



In both cases, diopside forms in response to the introduction of silica as either the Si(OH)_4 or SiF_4 complex (Figure 3.7 and 3.8). The Si(OH)_4 complex may be simply written as $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$; hence the $2\text{H}_2\text{O}$ seems redundant to the equilibria but adds to the volatile constituents on the product side of the reaction:



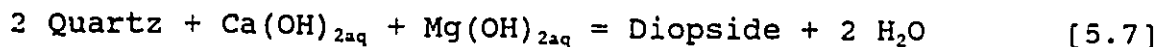
The formation of a mixed volatile phase may seem important ($2 \text{ H}_2\text{O} + \text{CO}_2$) but it is important to consider that the low solubility of silica in H_2O (fluid) indicates that there must have been much more H_2O fluid present than that released by

the destabilization of the $\text{Si}(\text{OH})_4$ (silica) complex. Primary tremolite is not formed in the proximal skarn because the assemblage tremolite + calcite + SiO_2 is unstable with respect to diopside at the initial conditions of skarn formation.

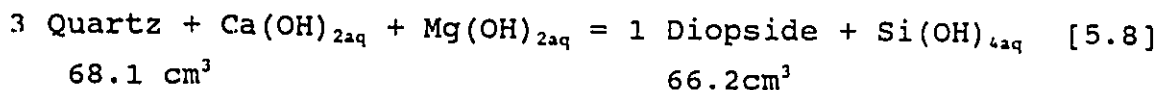
The variation in Fe, Mn, Al, and Mg pyroxene composition affects its stability and characterizes its environment of formation. In general, skarn pyroxenes are Mg-rich with low Fe, Mn, and Al approximating diopside composition. Pegmatite-hosted pyroxenes have higher Fe and Al coincident with lower Mg contents. There are two possibilities for the formation of pyroxene in granitic pegmatites: i) diopside or dolomite may be included mechanically into the magma or ii) metasomatically introduced $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ from reactions in the exoskarn environment react with quartz or silica in the melt to produce diopside. The smaller proportion of or absence of quartz in diopside-bearing pegmatites implicates the latter process. The Ca pyroxene chemically analysed from pegmatite is salitic diopside with a medium to dark green colour. It is slightly more aluminous as a result of equilibration with the microcline at high temperature.

Along the margins of apatite-calcite veins or within the proximal endoskarn environment pyroxene may replace quartz (fenite-like alteration; Plate 3.17 and 3.18):

i) Constant silicon



ii) Constant Oxygen + Volume



Thus coupled calcium and magnesium metasomatism could transform quartz into Ca pyroxene, which is consistent with the formation of the endoskarns and Ca pyroxene along the selvages of fluorite-apatite-calcite veins.

Analogous to the replacement of quartz by Ca pyroxene is the replacement of feldspar by Ca pyroxene at advanced stages of

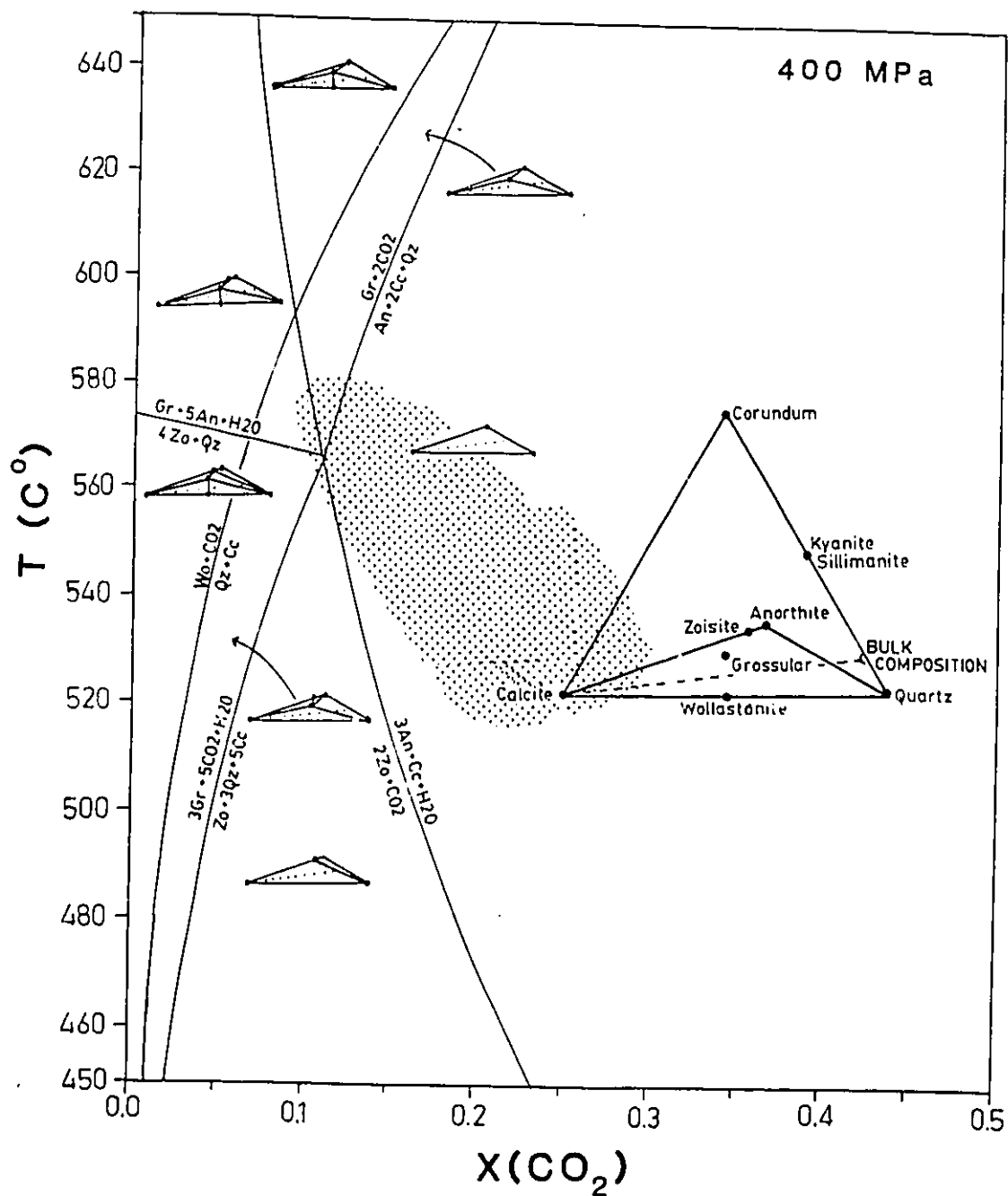
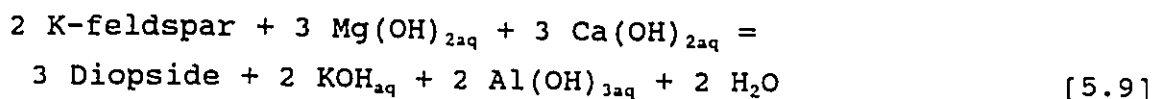


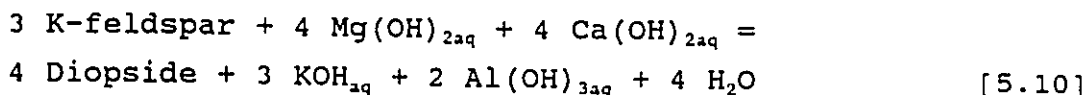
Figure 5.6 Temperature versus $X(\text{CO}_2)$ diagram illustrating the system Ca-Al-Si-C-H-O at 400 MPa pressure; geocalc program; Berman et al. (1985); Perkins et al. (1986). Stippled area represents the approximate conditions of formation of proximal skarns.

alteration to produce Ca pyroxene mantles about apatite-calcite veins (Plate 3.17); replacement of this kind has not been observed in the proximal endoskarns. Generally, the alteration of quartz to pyroxene precedes feldspar alteration (reactions 5.9, 5.10, and 5.11). If the volume of pyroxene is similar to the volume of feldspar after alteration then approximately 3 moles of microcline are required to produce 5 moles of diopside.

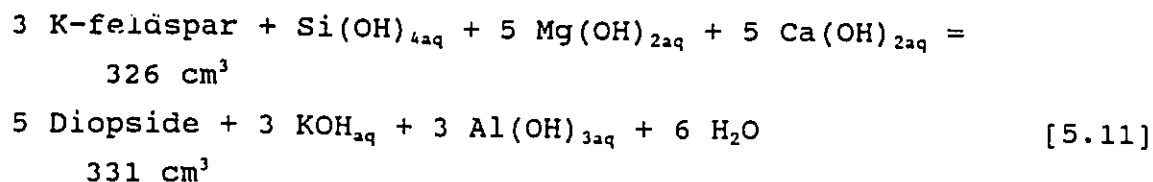
i) Constant silicon



ii) Constant oxygen



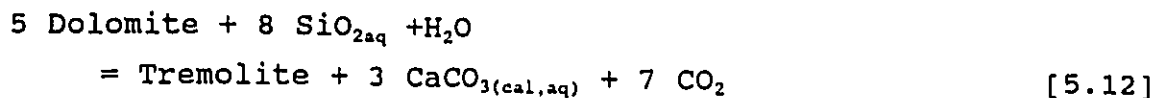
iii) Constant volume



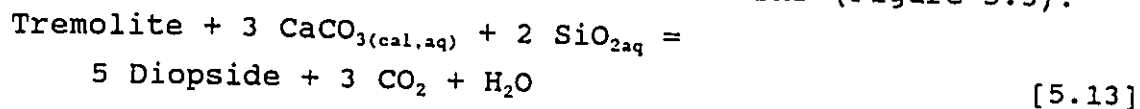
The pyroxenes in the exoskarn environment associated with scapolite, and/or feldspar are, in general, richer in aluminum compared to Ca pyroxenes not coexisting with feldspar or scapolite. Also, the pyroxenes associated with feldspar/scapolite forming selvages on fluorite-apatite-calcite veins have slightly higher Al contents.

5.3.3 Metasomatic tremolite-forming reactions

The stabilization of primary tremolite with diopside is not common except in marble-hosted skarns which may indicate the conditions controlling the formation of tremolite (Figure 3.7b). The silica introduced into dolomitic marble reacts to form tremolite if the conditions are such that tremolite is stable (Figure 5.1):

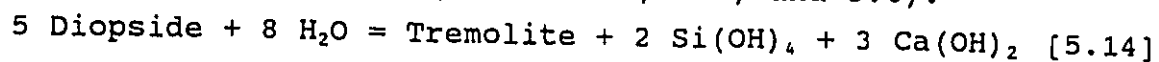


Calcite may be totally solubilized (undersaturated) or partially solubilized (saturated) during skarn formation. Although this is a decarbonation reaction, the CO_2 is diluted by the influx of volatiles (H_2O , HF , H_3PO_4). A low activity of $\text{SiO}_{2\text{aq}}$ and/or calcite/ $\text{CaCO}_{3\text{aq}}$ is responsible for the increasing proportion of tremolite in the distal skarns (Figure 5.3):



It may be possible that the proportion of CO_2 (XCO_2) in the fluid is high enough to inhibit the formation of diopside (Figure 5.1). In addition to these other considerations, the formation of fluortremolite rather than hydroxy-tremolite would increase the stability of tremolite at the expense of diopside.

Tremolite replacement zones and veins are formed by the replacement of diopside in the skarn or clinopyroxenite and are a common late-stage phenomena in the development of some of these skarn. Quartz, calcite, phlogopite, feldspar (scapolite), titanite, and/or sulphides may be present with the secondary tremolite, however, monomineralic tremolite is most common. Intuitively, constant silica content and approximately constant volume are most reasonable for possible tremolitization reactions. A simple hydration reaction involving the partial or complete removal of quartz and/or calcite may be involved depending on the degree of saturation of these two components (Plates 3.4, 3.5, and 3.6):



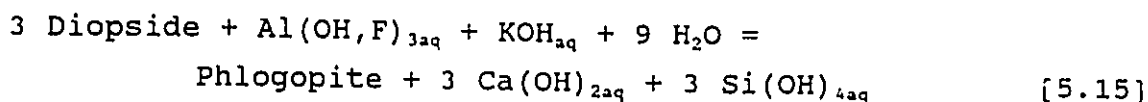
If the partial pressure of CO_2 is high enough then calcite may become a part of the alteration assemblage. Cermignani and Anderson (1973) found a secondary tremolite and calcite assemblage after diopside in a skarn near Tweed, Ontario. In some instances a secondary assemblage of tremolite-calcite-quartz may be associated with the carbonation and hydration of diopside which is the inverse of the prograde diopside-forming

reaction. This is consistent with lower temperatures and/or higher CO₂ activities in the retrograde hydrothermal fluid. An alternative mechanism for the tremolitization of diopside involving a variation in the chemical potentials of magnesium and calcium are also possible.

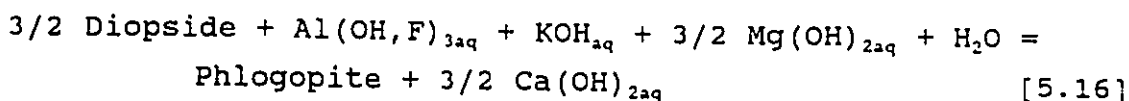
5.3.4 Metasomatic phlogopite-forming reactions

Commonly, phlogopite replaces diopside in the vicinity of marginal skarns and along the selvages of apatite-calcite veins and is a process common to skarns and veins. In many instances phlogopite seems to be the only product, and forms veins within the clinopyroxenite (Plates 3.1, 3.2, 3.7, and 3.12 and Figures 3.4 and 3.5). Phlogopite mantling and forming veinlets in diopside grains is evidence for replacement. Several possible reactions are as follows:

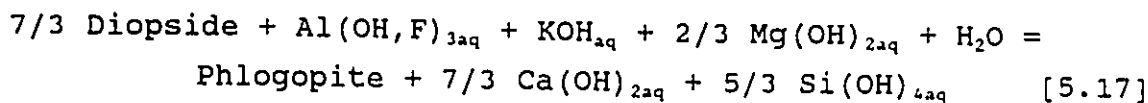
i) Conserve magnesium



ii) Conserve silicon

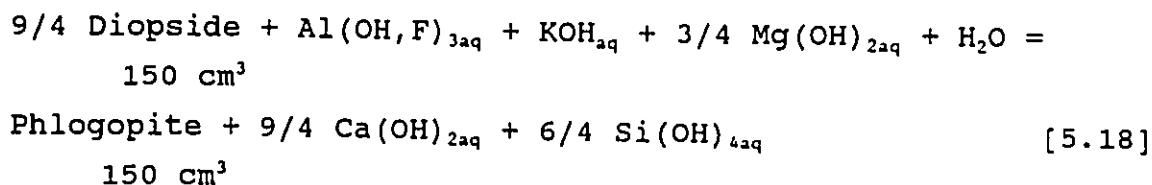


iii) Conserve oxygen



iv) Constant volume

Approximately 9/4 moles of diopside would be required to form 1 mole of phlogopite if this process was one of constant volume.



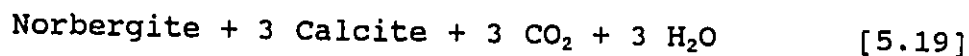
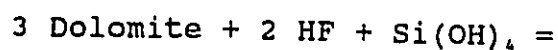
All reactions involve the addition of aluminum, alkalis, and water with the removal of calcium. Reactions involving the removal of silica are not preferred since high silica contents

must involve aluminum mobility. Therefore the constant silica reaction seems the most reasonable.

5.3.5 Metasomatic humite mineral-forming reactions

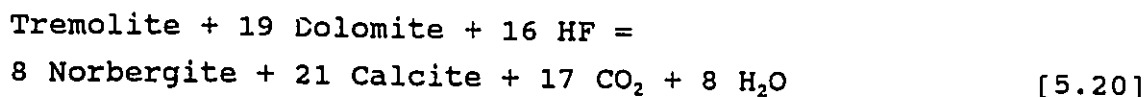
The absence of forsterite may indicate that the stability of forsterite has not been reached or that the composition of the skarn is such that forsterite is not stable. Coincident with the high fugacities of H_2O which may stabilize forsterite at moderate temperatures are high activities of SiO_2 which may preclude the formation of forsterite. Krezcmer (1974) identified forsterite in the marble in the vicinity of the Hunt Mo skarn deposit but its relationship to the skarn is not known.

Humite-group minerals are spatially associated with these skarns in numerous occurrences including the Wilberforce and Yates areas (Plate 3.9 and Figure 3.7). Chondrodite and norbergite are associated with these metasomatized Grenville marbles and the chondrodite where analysed was found to be fluorine-rich (Table 4.11). Simple metasomatic reactions will be written with the fluorine end-member. The disseminated distribution in the marble skarn suggests the replacement of a pre-existing calc-silicate phase (tremolite, diopside, or forsterite) by the introduction of fluorine at low activities of SiO_2 at the pressure and temperature conditions of skarnification. This would not favour the reaction (5.19) (below), which involves the introduction of $Si(OH)_4$ into dolomite but rather involve reactions with pre-existing calc-silicates:

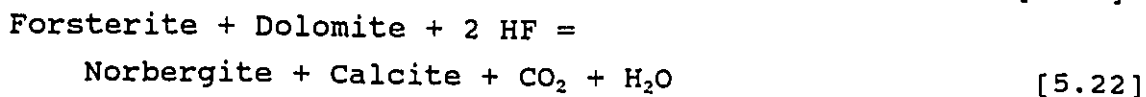
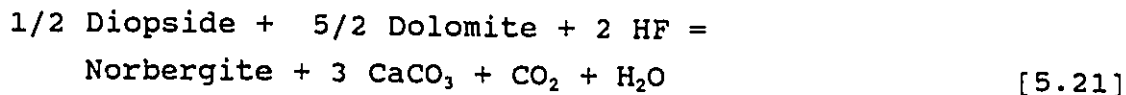


The formation of norbergite may involve replacement of primary hydroxy-tremolite or fluortremolite in the marble with addition of fluorine. The reaction may either involve aqueous magnesium hydroxide which is derived from previous skarn-forming reactions or dolomite component of calcite or as

dolomite which occurs in the marble (reaction 5.20). The reactions are written to conserve silica between the reactants and products:



However, the reaction may be written with diopside or forsterite and dolomite if these form part of the primary calc-silicate assemblages (reactions 5.21 and 5.22):



Whatever the mechanism for the formation of humite-group minerals, it seems reasonable to conclude that their stability is related to the higher fugacity of fluorine in the outer portions of certain skarns. The stability of norbergite or chondrodite may explain the absence of forsterite in the distal metasomatic portions of the skarn.

5.3.6 Metasomatic feldspar-forming reactions

K-feldspar (perthitic microcline) is present with plagioclase (albite) with Ca pyroxene in proximal contact skarns and along the selvages of fluorite-apatite-calcite veins. The stability of feldspars (perthitic microcline or albitic plagioclase) in these environments provides clues to their formation conditions. Karvinen (1973) found that the presence of feldspar (microcline or albite) rather than scapolite was a particularly distinguishing feature in the field and separated the deposits investigated into scapolite-bearing and feldspar-bearing skarns. It is quite evident that the stability of feldspar is affected by the stability of scapolite.

The coexistence of oligoclase and perthitic microcline in numerous pegmatites (Chapter 2) indicates that the mineralogy is not dominated by metasomatic phenomena. In many cases the

supercritical fluid evolved from the crystallizing pegmatite should have alkali element contents approaching that of the crystal-melt compositions at magmatic temperatures (Burnham and Ohmoto, 1980). However, the quartz to feldspar ratio changes with decrease in pressure, temperature, and interaction with the host rocks. It seems reasonable to expect that interaction of the metasomatic fluid with the compositionally heterogeneous host rocks (marbles, amphibolites, clinopyroxenites, gneisses) has the most profound influence of the presence of perthitic microcline, albite or scapolite in skarn.

Albitic plagioclase is just as common as either perthitic microcline or scapolite in these skarns. Albite ($An \leq 10$) occurs at the American Molybdenites deposit, the Sunset Mo deposit ($An \leq 27$), and Spain Mo-U deposit (Karvinen, 1973; this study).

Perthitic microcline is quite common in proximal skarns occurring with Ca pyroxene and more rarely with tremolite (ie. Hunt Mo deposit). The proportion of microcline generally increases with proximity to the granitic pegmatite. The perthitic lamella are not as prominent in the skarns as in other instances, particularly in some pegmatites. The kinetics of albite exsolution from the microcline during cooling may be affected by the environment (higher CO_2 activity).

Perthitic microcline and albitic plagioclase rarely occur together in the skarns. Therefore, it seems likely that Na-K protolysis reactions affect the stability of these two feldspars (Karvinen, 1973). Orville (1963) established the approximate stability fields of microcline and albite between 400° and 700°C at 2 kilobars (200 MPa) with respect to the molar ratio m_{KCl}/m_{NaCl} . At 550°C the K-feldspar-albite equilibrium occurs at approximately $m_{KCl}/m_{NaCl} = 0.32$ (2 N solutions) and increases with increasing temperature however

these ratios are affected by pressure and normality of the solution. Orville (1963) found that an increase in pressure tends to reduce the K/Na ratio of the fluid in equilibrium with the coexisting feldspars. Lagache (1984) presented data on the K-feldspar-albite equilibria at 600°C and 2 kilobars (200 MPa) in 1 normal solutions and found an approximate $m_{KCl}/m_{NaCl} = 0.2$. The miscibility between K-feldspar and albite is increased considerably with an increase in temperature. Therefore it is possible that complete miscibility is approached under the conditions of skarn formation.

The plagioclase-fluid equilibria indicate that the fluid is much more sodic than the coexisting plagioclase (Orville, 1972; Lagache, 1984). An increase in pressure tends to increase the stability of calcic plagioclase component with respect to the fluid phase as observed with K-feldspar-albite equilibria (Lagache, 1984). This suggests that the presence of albitic plagioclase in the proximal exoskarns reflects very high Na/Ca and Na/K ratios in the metasomatic fluid. The absence of intermediate plagioclase compositions in the skarns attests to the higher stability of dypyrlic and mizzonitic scapolite due to higher activities of Cl^- and $CaCO_3$. Therefore, the presence of scapolite in the skarns is partially indicative of higher Ca/Na and Ca/K ratios in the host rock and metasomatic fluid.

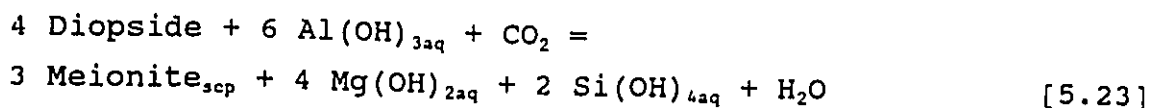
The absence of muscovite or paragonite ($\pm$ quartz) in the skarns may be due to several factors. The bulk composition is not aluminous for the skarn rocks. It is possible that lower activities of H_2O due to dilution with CO_2 are responsible for the stabilization of K-feldspar and aluminosilicate although the latter is not present. The absence of muscovite and sillimanite in the skarns could be due to original bulk compositional limitations or that high alkali elements (K, Na) and/or a normal to alkaline pH in the hydrothermal fluid (Eugster, 1970; Wintsch, 1975).

5.3.7 Metasomatic scapolite-forming reactions

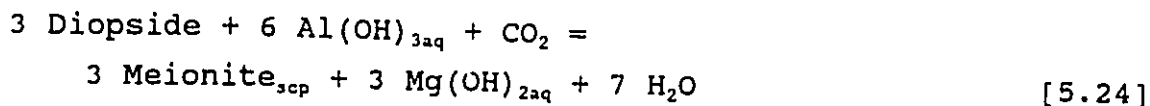
Scapolite is a common phase observed in the proximal skarns (Plates 3.1, and 3.10 and Figures 3.4, 3.5, 3.6) and the marginal zones of apatite-calcite veins (Plates 3.14, 3.15, and 3.19, and Figures 3.11, 3.14, and 3.15). This discussion relates to the obvious metasomatic formation of scapolite which is compositionally variable between diopside and mizzonite. It was not obvious from the petrographic observations whether scapolite replaces Ca pyroxene or occurs as an void infilling. Within the margins of skarn veins, apatite-calcite veins, and within endoskarn scapolite is observed replacing pre-existing K-feldspar and plagioclase (Plates 3.14, 3.15, and 3.19 and Figures 3.6, 3.11, 3.14, and 3.15). This was briefly discussed with respect to the stability of feldspars.

Scapolitization within marginal skarns may occur as either deposition of scapolite from solution and/or replacement of pyroxene. It is evident that hydrothermal deposition is possible as veins of scapolite occur in marbles (Plate 3.6, and 3.10). However, the replacement of calc-silicates does occur particularly in clinopyroxenites and requires the chemical transformation of calc-silicates to scapolite by metasomatic introduction of aluminum (Plate 3.1, 3.2, 3.4, 3.6, 3.10, 3.14, and 3.15). There are numerous possible processes which could account for this transformation of which only a few possibilities are presented:

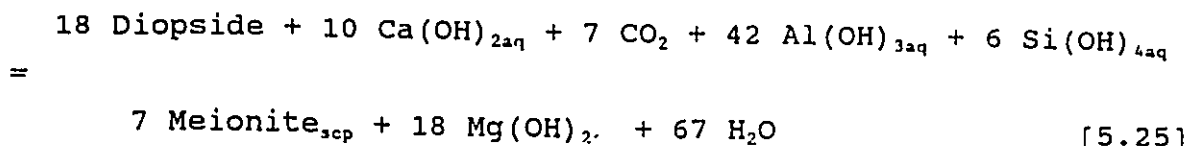
i) Conserve Calcium



ii) Conserve Silica

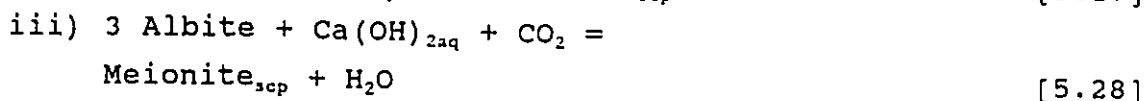
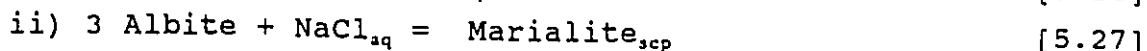
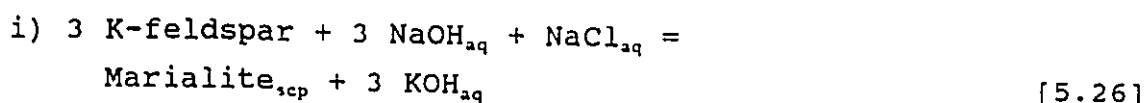


iii) Constant Volume



In all cases aluminum is metasomatically introduced but calcium, magnesium and silica are also mobile in a few of the end-member reactions.

In endoskarns, scapolite replaces the feldspathic portion of the granitic pegmatite and is probably coincident with diopside replacements after quartz and feldspar. The formation of scapolite within the skarns may be represented by several reactions:



These reactions are a function of the calcium content of the primary plagioclase being replaced and the Na/Ca ratio and the CO₂ content of a fluid phase that has been reincorporated into the solidified pegmatite.

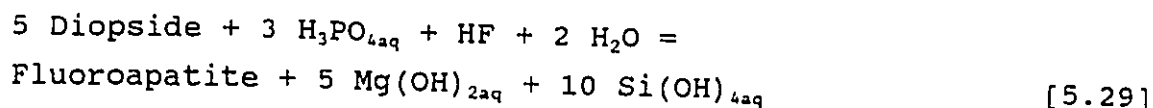
Haughton (1971) determined that plagioclase coexisting with scapolite was usually higher in sodic component in these skarns. Karvinen (1973) also noted that the proportion of meionite in scapolite from these skarns was related to the host rock composition and was generally more calcic than coexisting plagioclase although equilibrium was not well established between these minerals. The study of scapolite-plagioclase equilibria in these skarns and associated gneisses revealed an approach to equilibrium which may be interpreted as metasomatic alteration and re-equilibration of scapolite- and plagioclase-bearing assemblages.

5.3.8 Metasomatic apatite-forming reactions

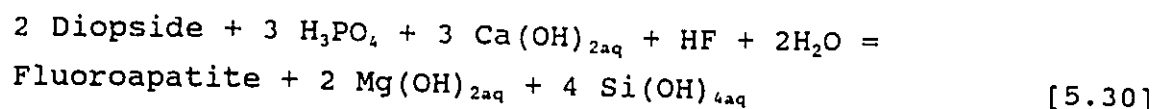
Apatitization of clinopyroxenite may occur by either of two processes: i) deposition of apatite from solution into void

space or replace pyroxene and ii) deposition of H_3PO_4 from solution by dissolution of pyroxene. The deposition of apatite is possible considering the high solubility of apatite in high temperature saline solutions (see Chapter 7). However, H_3PO_4 may be partially responsible for apatite formation by deriving Ca from pyroxene during alteration particularly since many of the skarns have associated pervasive apatite zones:

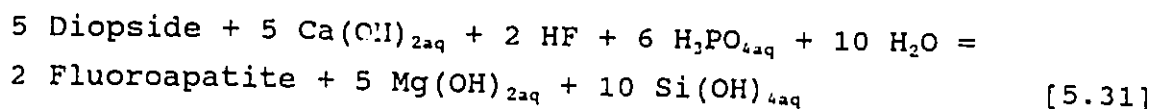
i) Constant Calcium



ii) Constant Oxygen

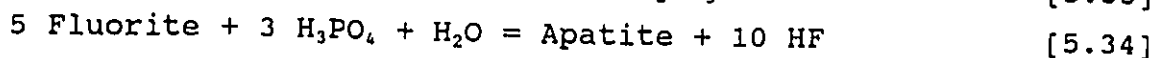
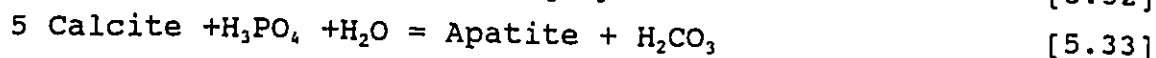
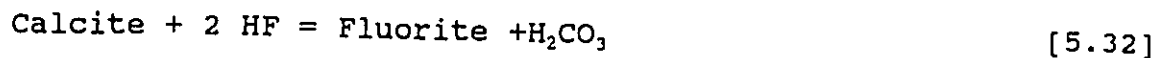


iii) Constant Volume



The reaction involving constant calcium (reaction 5.29) involves solely the addition of phosphorous, fluorine, and water and the removal of magnesium and silica. The hydrothermal fluid must be undersaturated with silica but overall the process is not incompatible with skarn-forming fluids.

The occurrence of calcite, apatite-calcite, fluorite-calcite, and fluorite-apatite-calcite veins and skarns may be explained by metasomatic variations in the H_2O , H_2CO_3 , HF , H_3PO_4 activities in the hydrothermal fluid. The variation of these components are a function of the fluid source, and subsequent crustal interactions. If the two principal volatile species are H_2O and CO_2 then at fixed $X(\text{CO}_2)$ the stabilities of fluorite, apatite, and calcite are a function of the relative activities of HF and H_3PO_4 in the fluid:



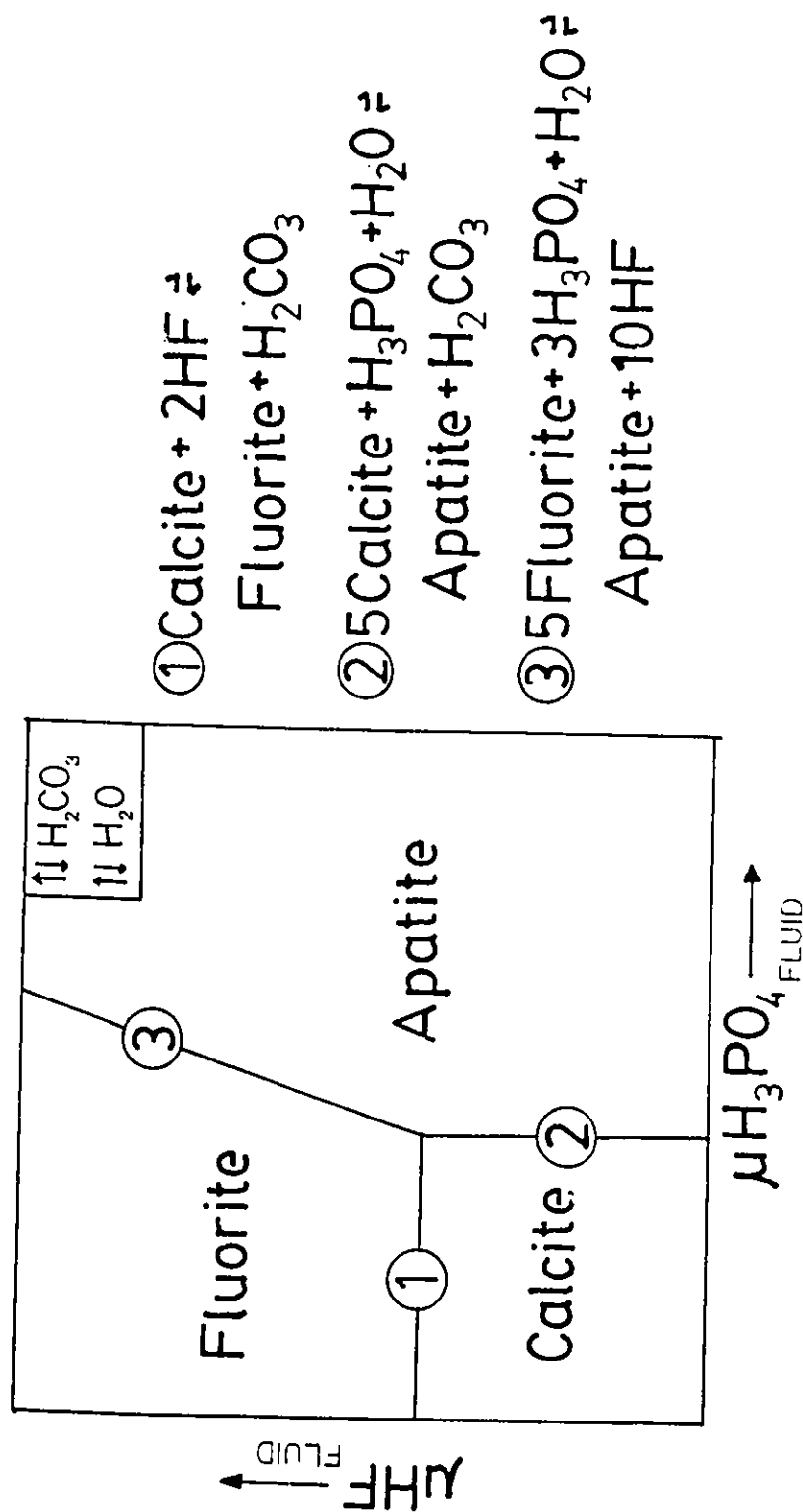


Figure 5.7 Schematic μHF and $\mu\text{H}_3\text{PO}_4$ diagram with variable H_2O and H_2CO_3 activities illustrating the relative stabilities of calcite, apatite, and fluorite.

These reactions have been written involving hydroxyapatite and would change slightly if fluorapatite were considered. Figure 5.7 illustrates the relative stabilities of fluorite and apatite with respect to calcite. The deposition of calcite from the hydrothermal fluid may be responsible for the increase in the chemical potentials of HF and H_3PO_4 in the evolving hydrothermal fluid.

5.4 Stability of sulfide, silicate, and carbonate minerals

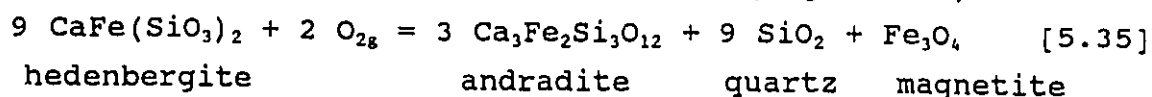
The approximate temperature and pressure conditions of skarn formation are 550°C (820 K) & 400 MPa (4 kb), however, most of the relevant oxidation and sulphidation equilibria have been determined at 200 MPa (2 kb). Therefore, the following discussion of this equilibria represents a preliminary estimate of the conditions of skarn formation. In general, the exoskarns contain low Fe diopside and phlogopite, pyrite, pyrrhotite, molybdenite, titanite, U-Th minerals, and REE-bearing minerals, as well as microcline or scapolite, indicative of fairly reducing conditions possibly imposed by the marbles, which are sometimes graphite-bearing. The endoskarn or hybridized marginal portions of the pegmatites commonly have more diverse assemblages.

The presence of pyrite, pyrrhotite, and low iron calc-silicates and the absence of garnet, magnetite, and hematite in most exoskarns is evidence of the reduced nature of the exoskarns, particularly the molybdenite-bearing skarns. Fe-rich diopside, pyrite, and magnetite (not always coexisting) also occur in the marginal zones of marble-hosted pegmatites (Plates 2.4 and 3.1). The coexistence of Fe-rich diopside ($0.25 < X_{Hd} < 0.5$) with pyrite and pyrrhotite in sulphide-bearing skarns is compatible with the sulphide equilibria. These assemblage indicate a low to moderate $f(S_2)$ and low $f(O_2)$ associated with skarn formation (Figure 5.8). Gamble (1982) determined that pyrite and pyrrhotite coexist at a $\log f[S_2]$ equal to -3.18. This value is comparable to the conditions

determined for the pyrite-pyrrhotite-magnetite buffer (Robie, Hemingway, and Fisher, 1979); $\log f(S_2) = -3.9$ and $\log f(O_2) = -18.4$ based on thermochemical data. The common occurrence of pyrite and pyrrhotite with Ca pyroxene of intermediate diopside contents in the molybdenite-bearing exoskarns suggests that these are appropriate conditions for exoskarn formation.

Andradite occurs in several granitic pegmatites particularly along the marginal zones near the host rock. Gamble (1982) located the hedenbergite invariant breakdown reaction to andradite + pyrrhotite + magnetite + quartz (reaction 5.35) at $\log f(S_2) = -4.5$ and $\log f(O_2) = -19.6$. However, this approximates to $\log f(S_2) = -5.0$ and $\log f(O_2) = -19.3$ with respect to the sulphide and oxide equilibria of Robie and Waldbaum (1968) (Figure 5.8). Similarly, the hedenbergite-diopside_{ss} ($X_{Hd} = 0.25$ & $X_{Di} = 0.75$) invariant break down to andradite + pyrite + magnetite + quartz occurs at approximately $\log f(S_2) = -3.8$ and $\log f(O_2) = -18.3$ indicating that the diopside component increases the stability of Ca pyroxene into the pyrite and magnetite fields.

Yttrian andradite occurs with quartz and magnetite in the hybrid zones of granitic pegmatites (eg. MacDonald (deposit # 26) and Legris (deposit # 49)). The presence of andradite garnet with magnetite and quartz is indicative of a higher fugacity of oxygen in several endoskarns (Figure 5.8).



The mantling of Fe-rich Ca pyroxene by andradite has been noted at the Legris deposit indicating that the $f(O_2)$ is approximately 10^{-18} to 10^{-19} at $f(S_2) < 10^{-4}$ at the Legris deposit. Kasowski and Hogarth (1968) examined the composition of yttrian andradite from several pegmatite/skarn localities in Quebec. The absence of andradite in the exoskarn environment

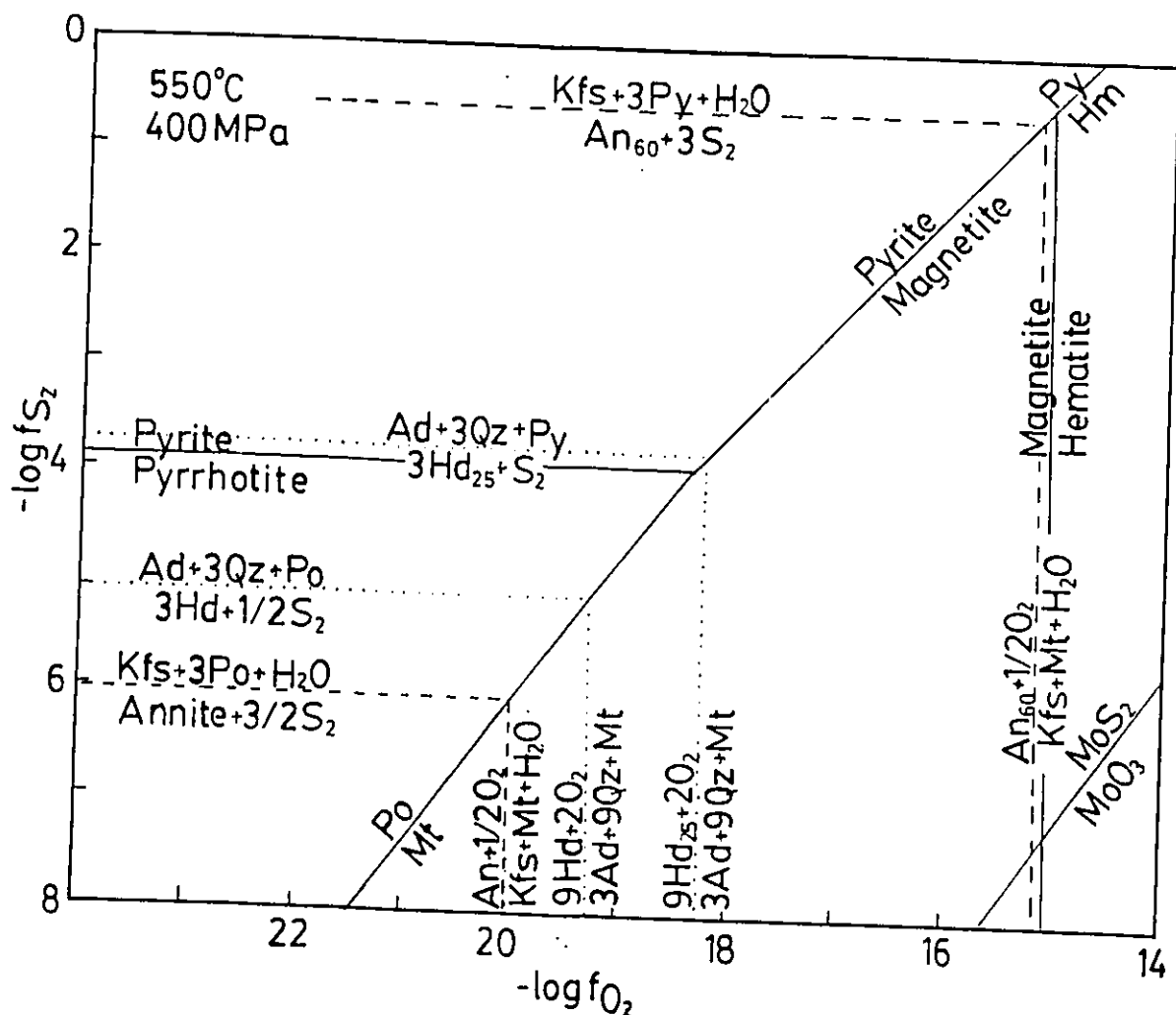
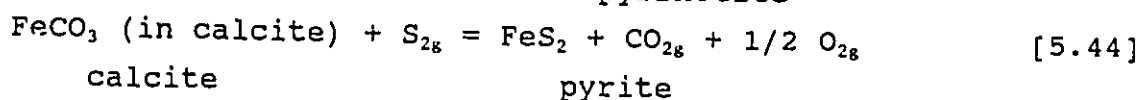
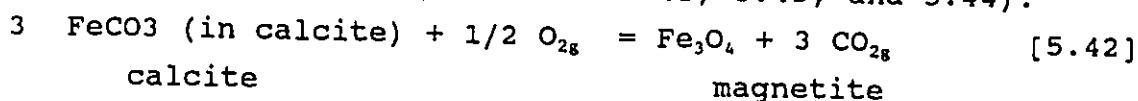
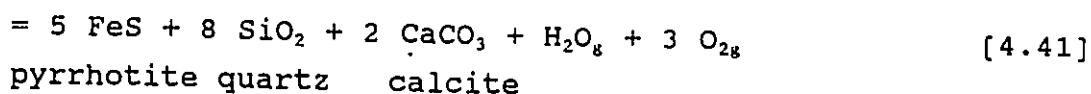
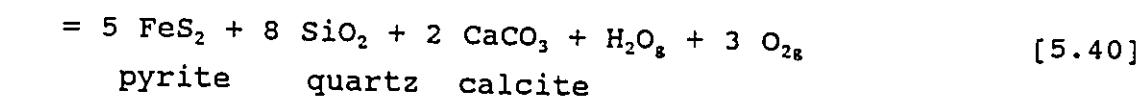


Figure 5.8

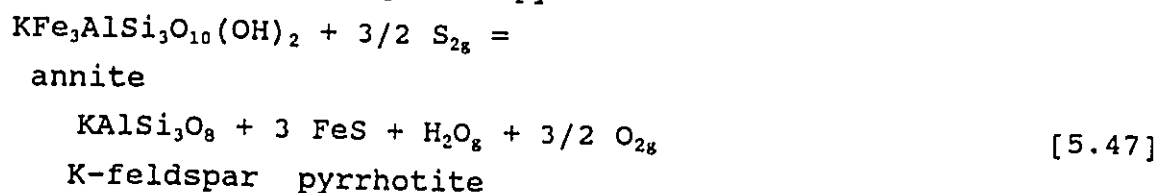
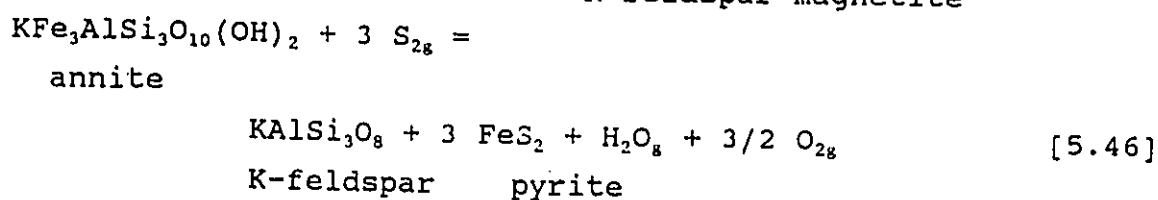
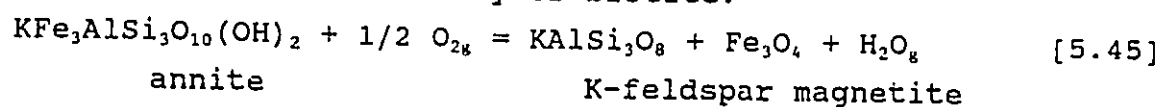
Log $f(S_2)$ and Log $f(O_2)$ diagram at 550°C at 200 MPa for molybdenite (MoO_3), molybdenite, pyrite, pyrrhotite, magnetite, and hematite (solid lines; Robie, Hemingway, and Fisher, 1979), the mineral stabilities of hedenbergite, andradite, quartz, and sulphide assemblage (dotted lines) are located approximately based on data by Gamble et al. (1982) & Liou (1974). The relative stability of hydroxybiotite, sanidine, and magnetite (dashed lines) are from Wones and Eugster (1965).



Generally, the calcic pyroxenes hosted within a granitic pegmatite or in the vicinity of the contact are Fe-rich ($0.25 < X_{Hd} < 0.50$). The occasional presence of andradite in the vicinity of the contact zones of granitic pegmatites and carbonate host rocks suggests that the most Fe-rich calcic pyroxenes were unstable under the higher $f(O_2)$ conditions. The absence of andradite in the exoskarns attests to their Mg-rich composition and/or the low $f(O_2)$ conditions. The assemblage magnetite + quartz + calcite is uncommon in the exoskarn indicating low $f(O_2)$ conditions and/or $X(CO_2) \leq 0.2$ compositions of the skarn fluid phase. Therefore, the composition of the skarn fluid seems to be evolving to lower temperatures and $f(O_2)$ conditions as a result of host rock interaction.

(endoskarn) and proximal exoskarn (e.g. Hunt deposit) may also be used to help constrain the conditions of formation.

The hydroxybiotite breakdown reaction to sanidine + magnetite + gas occurs at $\log f(\text{O}_2) = -19.8$ (equation 5.45; Wones and Eugster, 1965) which corresponds to an approximate $\log f(\text{S}_2) = -6.0$ for sanidine + quartz + pyrite + pyrrhotite (reactions 5.46 and 5.47). The stability of biotite is greatly enhanced with an increase in the phlogopite component. Wones and Eugster (1965) found that the stability field of hydroxybiotite ($X_{\text{Ann}} = 0.60$ & $X_{\text{Phl}} = 0.40$) was expanded to the hematite-magnetite stability field. This corresponds to an approximate $\log f(\text{S}_2) = -0.5$ for the formation of sanidine + quartz + pyrite (reaction 5.46; $X_{\text{Ann}} = 0.60$). This may explain the common presence of annite ($X_{\text{Ann}} = 0.5-0.6$) with K-feldspar, magnetite and/or pyrite at the pegmatite contacts (eg. Halo U-Mo pegmatite-skarn deposit). Rutherford (1973) found that aluminum increased the stability field of biotite. Fluorine also increases the stability of biotite.



In general, the hydrothermal fluid responsible for the hybridization and skarnification (endoskarn) or the granitic pegmatite seems to have been at a high oxidation state based on the presence of biotite ($X_{0.6}$) + magnetite +/- pyrite (@ 630°C; $\log f(\text{O}_2) = -15.7$; Wones and Eugster, 1965). At 550°C the $f(\text{O}_2)$ is 10^{-15} with a $f(\text{S}_2)$ equal to $10^{-0.5}$ (e.g. Halo U-Mo

pegmatite and skarn deposit; Plate 2.3). This is very close to the hematite-magnetite-pyrite invariant point (Figure 5.8). Pyrite was also present in an aplite at the Hunt Mo deposit. In an examination of the chemical composition of biotites within the pegmatites, similar conditions were determined. This is interpreted to have resulted from magmatic oxidation induced by volatile phase separation (Lentz, in prep; appendix 6). Therefore, in general the fluids derived from the pegmatites are quite oxidizing in contrast to the exoskarn environment which is quite reducing. Although preliminary, the granitic pegmatite may have a moderate $f(S_2)$ which may be a possible source for the sulphur in the deposits.

The mineral assemblages within the veins are more poorly constrained. In some instances, microcline occurs with magnetite, biotite, and paragenetic hornblende (e.g. Richardson U-fl deposit # 14), and Fe-rich diopside and pyrite. In many instances, the biotite compositions ($\pm$ magnetite) (annite 20-50; Figure 4.4) indicative of high $f(O_2)$ conditions analogous to the pegmatites. The similarity among the endoskarn and fluorite-apatite-calcite vein selvage assemblages indicates that the metasomatic fluid responsible for the formation of the veins was similar to that in equilibrium with the margins of the pegmatite.

5.5 Mechanisms of skarn formation

5.5.1 Introduction

It is quite evident from the spatial relationships of some vein and contact skarns with granitic pegmatites that they formed by the metasomatic introduction of components into the host rock environment (exocontact). There are dominantly two possible mechanisms for the metasomatic transport into the host rocks: 1) diffusion metasomatism and 2) infiltrative metasomatism (Korzhinski, 1947, 1959). Diffusion metasomatism involves the movement of constituents down chemical potential gradients with no net physical transfer of the medium in which

net transfer occurs whereas infiltration metasomatism involves the net physical transfer of components in a fluid phase.

5.5.2 Physical considerations

In order to model skarn formation by a diffusion mechanism, many parameters must be defined. It has been established with a certain degree of confidence that skarns of the present study formed (ca. 1020 to 1050 Ma) at approximately 575°C and 400 Mpa. It is also known that the Grenville Province rocks cooled below approximately 400°C at approximately 920 to 950 Ma, therefore the host rock temperatures remained very high for approximately 100 million years (3.2×10^{15} seconds) subsequent to intrusion of the pegmatites (Chapter 1). It is possible that some of the exoskarns and endoskarns formed by the long-term bimetasomatic diffusion of constituents between the chemically-dissimilar pegmatites and dolomitic marbles particularly those symmetrically distributed about the contact zone. Figure 5.10 illustrates the hypothetical compositional variation in proximal and distal skarn between a pegmatite and a dolomite marble resulting from simple solid state diffusion.

There are two end-member considerations in diffusion metasomatism; solid-state diffusion and fluid-state diffusion. In general, diffusion is related to the existence of dislocations, vacancies, substitutional impurities, and interstitial impurities in crystalline materials by the motion of vacancies and interstitial cations (Vernon, 1973). It is generally accepted that surface diffusion rates and grain-boundary diffusion rates are greater than volume diffusion through the rock at lower temperatures because of the presence of a fluid phase (Vernon, 1973; Brady, 1983).

Korzhinski (1970) has shown that there are many common features in the products of diffusion and infiltration metasomatism: 1) they have sharp reaction boundaries between zones, 2) generally, they have the same number of reaction zones if pressure and temperature are constant, 3) complete

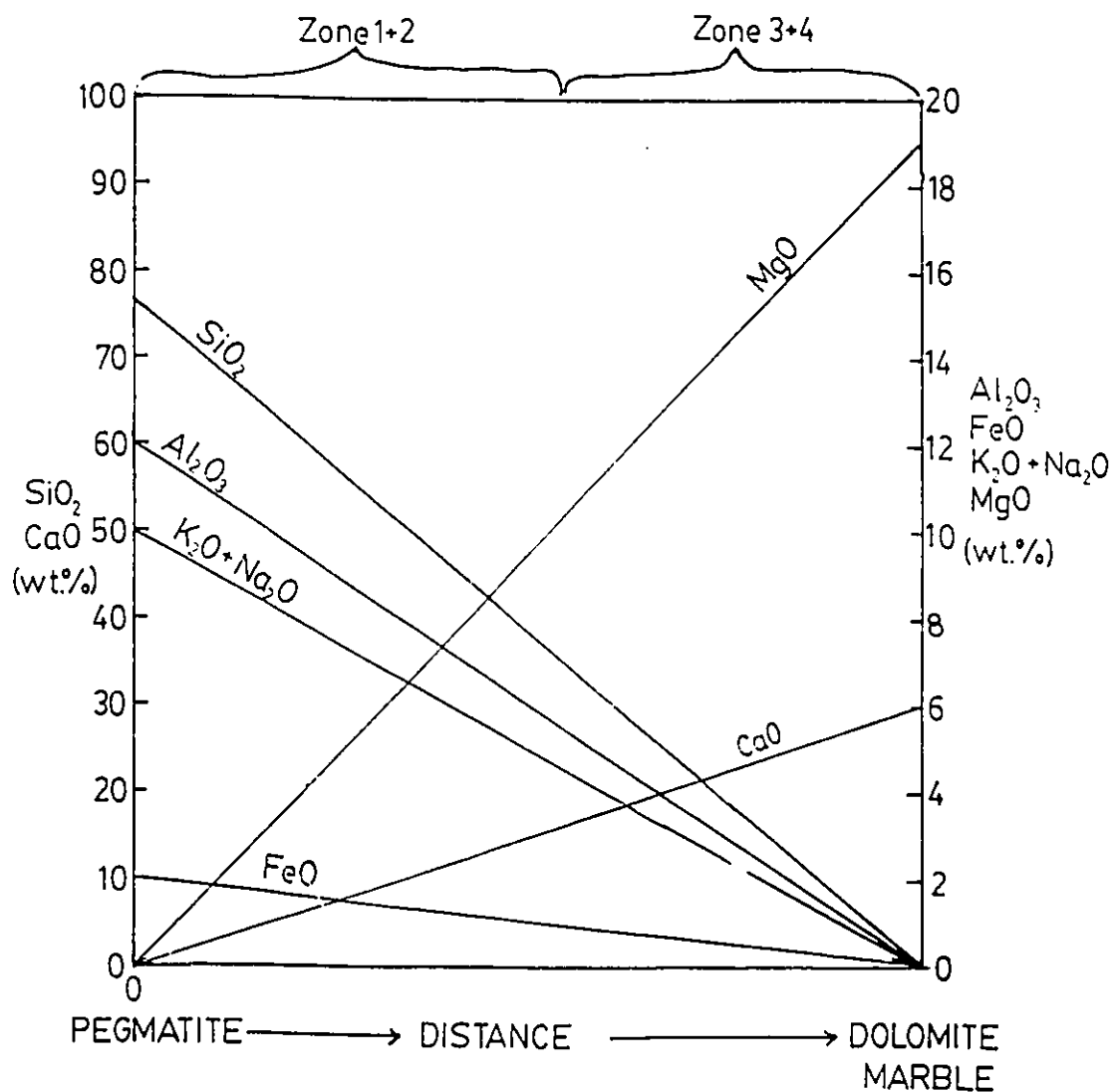


Figure 5.10 Estimation of chemical composition of proximal and distal skarns between a pegmatite and a dolomite marble formed by solid-state diffusion.

mobility of components will result in a monomineralic rock. There are also several important distinguishing features between diffusion and infiltrative metasomatism. Diffusion metasomatism cannot account for the existence of minerals/components in the reactant environment which do not exist in the source environment. If a fluid phase exists, the chemical composition of the fluid phase will change along the chemical potential gradient in diffusion-controlled metasomatic replacement zones whereas in infiltration-controlled metasomatic replacement zones, the fluid should be constant within an individual zone (Korzhinski, 1970). Therefore diffusion metasomatism would result in a gradual compositional variation from proximal to distal skarn, which is not consistent with the skarns examined in this study. Under the conditions of skarn formation, calcite does not react to form wollastonite; therefore primary calcite should remain in skarns formed by diffusion metasomatism.

If solid-state or fluid-state diffusion are responsible for the formation of skarn, then the reaction zones should be symmetrical on either side of the pegmatite and marble. The development of a symmetrical reaction zone between pegmatite and marbles would be conditional on the equal diffusivities of components into the pegmatite and conversely into the marble. However, this is complicated with calcium and magnesium, the principle components reacting with quartz, diffusing into the pegmatite (endoskarn) to form Ca pyroxene whereas silica diffusion outwards into the marble is responsible for exoskarn formation of Ca pyroxene. Coupled calcium and magnesium diffusion should be faster than silica diffusion because of their small charge/radius ratio, therefore the endoskarn should be volumetrically greater than the exoskarn if diffusion is the predominant mechanism for the formation of skarn. However, the volumetric ratio of exoskarn to endoskarn is usually greater than one and may be up to ten times (e.g. Hunt Mo deposit) which supports an infiltrative

fluid responsible for metasomatically introducing components into the skarn, in particular SiO_2 .

The formation of endoskarn within the pegmatite is variable from very small (< 10 cm) at the Hunt deposit to quite large at the Cardiff "C" zone diopside-bearing pegmatite (1 to 2 metres). It is possible that the endoskarns formed by desilication of the granitic pegmatite by the introduction of calcium and magnesium which reacted with the quartz to produce Ca pyroxene (ie. diopside pegmatite at the Camp zone, Yates deposit). This process may occur in response to simple solid state diffusion, fluid-state diffusion and/or incorporation of a chemically-modified skarn fluid into the granitic pegmatite.

The irregular morphology of contact skarns is evidence for infiltrative metasomatic transfer of components from the pegmatite into the host rocks. For instance, the Hunt Mo skarn is localized discontinuously along the contact between the pegmatite and the marble/amphibolite sequence. The pegmatite/marble contact is very sharp (< few centimetres) around much of the pegmatite body. The formation of exoskarns is principally controlled by the chemical or physical transfer of silica into the dolomitic marbles. The diffusion of silica would be the rate-controlling step because of its high charge and moderate size.

The presence of veins within the skarns and host rocks may be interpreted as evidence for infiltration metasomatism but it is possible, although unlikely, that the presence of a stagnant fluid within a fracture may enhance elemental diffusion along the structure. Formation of phases within the fracture may occur with supersaturation of that component irrespective of the mechanism of transport. The strong buoyancy effect of a fluid within a pre-existing structure and the general instability of open fractures (maintained) at the pressures under consideration preclude the existence of a

stagnant fluid except possibly in very small fractures. However, this will be considered as an end-member case.

5.5.3 A diffusion metasomatism model

Hoffman (1980) presents diffusion equations and reviews diffusion literature appropriate for the evaluation of diffusion metasomatism in these skarns.

The flux of components (J) by diffusion is estimated from Fick's law (equation 5.48).

$$J = -D \, dc/dx \quad [5.48]$$

where D is the diffusion coefficient (cm^2/s), c is the concentration in moles/ cm^3 , and x is the distance in centimetres.

Diffusion of a component is principally a function of media, temperature and pressure. The Arrhenius equation relates the diffusion coefficient to temperature (equation 5.49).

$$D = D_0 \exp (E/RT) \quad [5.49]$$

where D_0 is the frequency factor, E is the activation energy, R is the gas constant, and T is temperature. The effect of pressure is quite small with respect to temperature except if a fluid is considered (Walton, 1960; Ildefonse and Gaggis, 1976).

The linear diffusion of a component may be modelled with equation (5.50).

$$c(x,t) = (c_1 - c_0)/2 (1 - \text{erf} (x/2\sqrt{Dt})) \quad [5.50]$$

where c_0 is the concentration in the host rock and c_1 is the concentration in the source rock, x and t are as in equation 1 and $\text{erf} (x)$ is the probability integral. This equation is most appropriate for the modelling of the interaction between two chemically distinct and reactive bodies.

Although not well established, Si^{4+} diffusion in the solid state is on the order of 1×10^{-13} to $1 \times 10^{-15} \text{ cm}^2/\text{s}$ (Hoffman, 1980). However, Si^{4+} diffusion in a supercritical H_2O fluid is $3 \times 10^{-4} \text{ cm}^2/\text{s}$ at the temperatures and pressures under

consideration (Walton, 1960; Ildefonse and Gabis, 1976) although porosity and permeability must be considered.

Total porosity (ϕ_T) is the sum of flow porosity (ϕ_F), diffusion porosity (ϕ_D), and residual porosity (ϕ_R) (Norton and Knapp, 1977). An upper estimate of total porosity (ϕ_T) is less than 10^{-3} percent of the rock (Norton and Knapp, 1977). Unfortunately, the porosity data is unavailable at the pressure and temperature conditions of skarn formation but it seems reasonable that they would be significantly smaller. The net diffusion coefficient of 70 weight percent silica in rock with 0.001 % H_2O is approximately $3 \times 10^{-9} \text{ cm}^2/\text{s}$, which is about 10 000 times greater than solid-state diffusion of silica.

Silica concentration was calculated as a function of distance from the pegmatite-marble contact for fluid-state diffusion ($3 \times 10^{-9} \text{ cm}^2/\text{s}$) and solid-state diffusion ($1 \times 10^{-13} \text{ cm}^2/\text{s}$) for 10 Ma (3.1536×10^{14} seconds) and 100 Ma (3.1536×10^{15} seconds) (Table 5.14). The silica content of the pegmatite is estimated to be 75 weight percent of which approximately 30 weight percent is quartz. Under the conditions for proximal skarn formation in this study, reaction of a pegmatite with a dolomite marble (0 wt.% SiO_2) will form a Ca pyroxene skarn with Ca pyroxene constituting approximately 50 wt.% SiO_2 . Therefore, approximately 50 % of the silica calculated in the exoskarn will indicate the proportion of pyroxene formed due to silica diffusion if Ca pyroxene is the only calc-silicate formed (simplification). These calculations give maximum thicknesses for the formation of (symmetrical?) exoskarns and endoskarns by fluid-state and solid-state diffusion metasomatism. It is evident from Table 3.14 that solid-state diffusion can only be responsible for the formation of narrow reaction skarns (< 0.5 metres). If the porosity is as high 0.001 % of the rock at these temperatures and pressures then a H_2O -rich fluid phase can

Table 5.1 Linear of silica diffusion between two bulk compositions*

Fluid-state diffusion ($3 \times 10^{-9} \text{ cm}^2/\text{s}$)					
<u>years</u>	<u>50 cm</u>	<u>100 cm</u>	<u>200 cm</u>	<u>500 cm</u>	
10^7		36.4 wt%	35.3 wt%	33.2 wt%	26.9 wt%
10^8		37.5 wt%	37.5 wt%	37.5 wt%	37.5 wt%
Solid-state diffusion ($1 \times 10^{-13} \text{ cm}^2/\text{s}$)					
<u>years</u>	<u>50 cm</u>	<u>100 cm</u>	<u>200 cm</u>	<u>500 cm</u>	
10^7		0.0 wt%	0.0 wt%	0.0 wt%	0.0 wt%
10^8		1.7 wt%	0.003 wt%	0.0 wt%	0.0 wt%

Notes: $c_0 = 0$ weight percent, $c_1 = 75$ weight percent, $(c_0 + c_1)/2 = 37.5$ weight percent SiO_2 ; Silica content of pegmatite (75 wt.%) and dolomite marble (0 wt.%).

significantly enhance diffusion and produce large reaction zones.

5.5.4 An infiltration metasomatism model

The volatile phase saturation and separation of a fluid phase from crystallizing granitic pegmatites may be responsible for the net transfer of reactant material from the pegmatite into the exocontact environment. It is reasonable to suspect that the granitic pegmatite contains approximately 10 weight percent H_2O in addition to other volatile constituents. The density difference between the melt (2.3 g/cm^3) and the supercritical H_2O -rich fluid (0.8 g/cm^3) at 600°C and 400 MPa is approximately 1.5 grams per cm^3 , therefore, the fluid constitutes 30 volume percent of the pegmatite melt. Anderson and Burnham (1983) have determined quartz ($\approx 1.1 \text{ wt.}\%$) and feldspar ($\approx 0.5 \text{ wt.}\%$) solubilities at these conditions. Therefore approximately 0.16 weight percent (quartz and feldspar constituents) of the saturated portion of the pegmatite is hydrothermally transported into the exocontact zone of the pegmatite. It is possible to form calc-silicate minerals at very low activities of dissolved silica. In general, quartz solubilities decrease on the order of 45 % with a decrease in temperature from 600°C to 500°C in contrasts to the 85 % decrease in feldspar solubility. A decrease in pressure from 400 to 300 MPa decreases quartz solubility by 15 % and feldspar solubility by 85% (cf. Anderson and Burnham, 1983). This could account for the presence of quartz and feldspar (or scapolite) veins in the exocontact environment and explain the much low proportion of feldspathic constituents to Ca pyroxene in the proximal skarn. The lower proportion of aluminum to silica in the skarn cannot be simply explained by diffusion metasomatism because aluminum (under ideal conditions) should diffuse at a faster rate than silica.

The presence of faults and fractures allow for geostatic pressures less than the lithostatic pressure of 400 Mpa. These pressure differences allow the movement of fluids from areas of high pressure to those of low pressure (usually upward and outward) away from the intrusions contact. The difference in density of a supercritical fluid phase ($\text{H}_2\text{O} + \text{salt} + \text{CO}_2 \approx 1 \text{ g/cm}^3$) and crystalline host rock (2.8 g/cm^3) is responsible for the buoyant physical transfer of the fluid (not trapped along grain boundaries) beyond the granitic pegmatite into the exocontact environment and along pre-existing faults and fractures.

5.6 Discussion

There are numerous factors to consider in the analysis of mineral stabilities within the skarns including: temperature, pressure, bulk composition, critical behavior of fluid, $X(\text{CO}_2)$, $X(\text{H}_2\text{O})$, $X(\text{F})$, salt content etc. Estimates of temperature (550°C) and pressure (400 Mpa) were made primarily based on geological and geochronological constraints. These upper amphibolite facies skarn conditions are comparable to the pre-existing regional metamorphic assemblage.

The distribution of major and trace elements between coexisting phases indicates that the silicates, in particular phlogopite/biotite, amphibole, and Ca pyroxene, have regular distributions of $\text{Fe}/(\text{Fe}+\text{Mg})$, Mn, Zn, and V. The other elements examined have more irregular distributions possibly due to non-equilibrium processes governing their incorporation into the mineral, lack of retention of equilibrium, and poor analytical method (whole mineral). There are no obvious differences in the regular elemental distributions between phlogopite/biotite, amphibole and Ca pyroxene indicating similar temperatures of formation for the skarns and the veins if indeed they are temperature sensitive. The distribution of F and Cl in phlogopite and apatite indicated that the uraniferous and thoriferous skarns, especially in the systems

saturated with fluorite, were generally higher in fluorine compared to molybdenite-only deposits. The phlogopites from the Hunt Mo skarn have relatively low $f(\text{HF})/f(\text{H}_2\text{O})$ ratios in comparison to the other skarns and veins examined, possibly indicating that the lack of HF was responsible for the low U, Th, and REE content of this skarn.

Skarns formed within marble have an assemblage of Ca-pyroxene, scapolite and/or feldspar, and titanite in the proximal exoskarn environment (zone 1). The zone 1 assemblage abruptly changes to a Ca pyroxene, phlogopite (Mg biotite), and titanite assemblage (zone 2). The transition from zone 1 to zone 2 is marked by the appearance of trioctahedral mica at the expense of feldspar or scapolite. Zone 3 is considered a distal skarn and is characterized by the appearance of primary skarn tremolite occurring with phlogopite, calcite and more rarely Ca pyroxene. The outer most zone which occurs in contact with the dolomitic marble and is most commonly characterized by an assemblage of tremolite, calcite, and occasionally graphite if graphite is present within the marble. At the Cardiff and Yates deposits, in particular, the distal zones may contain humite-group minerals with phlogopite, calcite, dolomite, and graphite. Skarns formed within the clinopyroxenites have assemblages similar to zones 1 and 2 in the marble-hosted skarns, but rarely have primary tremolite.

An analysis of the mineral stabilities is complicated by the high variance assemblages. Therefore, the conditions of formation are considered preliminary. The proximal assemblages are compatible with temperatures of 550° to 575°C, and an $X(\text{CO}_2)$ of 0.1 to 0.3 at 400 MPa. The absence of wollastonite within the proximal zones is probably due to bulk compositional considerations where calcite has been dissolved in the proximal environment. Therefore, the low $X(\text{CO}_2)$ limit is an estimate. However, the presence of coexisting calcite

and quartz within late veins indicates that wollastonite is not stable in distal veins and retrograde assemblages due either to high CO_2 activities or to lower temperatures. The tremolite-bearing distal assemblages are indicative of higher $X(\text{CO}_2)$ and/or lower temperature conditions.

The spatial and temporal relationships of the skarns to the pegmatite are quite evident in a many instances. The overall concentric nature of zones 1 to 4 from the pegmatite suggests a metasomatic origin for these skarns related to the pegmatite. The variation in bulk composition of the skarn from zone 1 to 4 is compatible with the metasomatic exchange of components with the pegmatite. Dolomite seems to be the dominant phase involved in metasomatic decarbonation reactions. The introduction of alkalis, alumina, and silica into the exoskarn environment react with dolomite to produce the assemblage in zone 4. This is in turn replaced by zone 3 due to higher activities of the metasomatic constituents toward the source pegmatite. This process is repeated as the pegmatite is approached. The formation of Ca pyroxene in the endoskarn attests the metasomatic exchange with the marble/skarn and forms alteration of quartz to Ca pyroxene and/or alteration of feldspar to scapolite. The zonation may be examined with respect to variation in the chemical potentials of the pegmatite constituents (Si, Al, K, Na, Fe, Ti, and H_2O) and the marble constituents (Mg, Ca, and CO_2).

The relative stability of K-feldspar, albite, and scapolite is examined within the proximal endoskarn and exoskarn. It seems that the stability of scapolite is related to the original skarn protolith and to the moderate to high salinity of the metasomatising fluid. The common occurrence of phlogopite within the intermediate and distal skarn zones led to a more detailed analysis of the K-feldspar-bearing proximal skarn assemblage.

Secondary tremolite and phlogopite may form veins within the primary skarn assemblage. Tremolitization and possibly phlogopitization are considered retrograde processes replacing Ca pyroxene-rich skarn and clinopyroxenite. These retrograde processes probably formed at ambient host rock temperature near 500° and possibly higher CO₂ fugacities.

The numerous uncertainties including temperature and the effect of salinity on the chemical potential of H₂O and CO₂ (Bowers and Helgeson, 1983) preclude more detailed constraints of the CO₂ content, but it is probable that CO₂ immiscibility occurs which obscures the temperature X(CO₂) relations because the activity of CO₂ is locally higher at any given CO₂ content.

It is evident from the analysis of the paragenesis and petrogenesis of the numerous phases present within the skarns, and the apatite-calcite veins, that temperature and pressure control the stability of the minerals. Metasomatic processes are responsible for the compositional transformations occurring within the skarns and the apatite-calcite veins.

Metasomatic transformation of quartz to Ca pyroxene within the endoskarn and within the margins (selvage quartz-feldspar gneiss) of apatite-calcite veins may be explained by high chemical potentials of calcium and magnesium within the chemically-modified hydrothermal fluid. A metasomatic fluid with considerable calcite in solution (high Ca and H₂CO₃), and with high magnesium activities, is compatible with the hydrothermal fluid which formed the skarns.

In this system, all elements, including those considered to be the most immobile (ie. aluminum, titanium, etc.), are mobile to a much greater degree under the conditions of skarn and vein formation. It is probable that many of the elements considered most immobile are incorporated into coexisting phases, if present, or only locally transported away from the zone of alteration. These chemically-modified fluids were involved in reactions subsequent to the particular alteration

process being examined. Consequently, the infiltrating metasomatic fluid attempts to reach equilibrium with the host rocks. Unfortunately, the complexity of these processes precludes a more detailed analysis.

Pyrite, pyrrhotite, and molybdenite were commonly observed within primary and secondary calc-silicate exoskarn assemblages. Within the proximal skarns and the apatite-calcite veins, the iron-rich minerals are affected by the high $f(S_2)$ and $f(O_2)$ conditions resulting in more magnesium-rich minerals coexisting with magnetite, pyrite and/or pyrrhotite. The common occurrence of coexisting low-Fe Ca pyroxene ($Hd_{25}Di_{75}$) with pyrite and/or pyrrhotite within the skarn without magnetite indicates $\log f(O_2) < -18$ and $\log f(S_2) \leq -4$ at 550°C and 400 MPa. In all cases, exoskarn assemblages are reduced, with no andradite formed. The absence of graphite within these skarns indicates that either graphite has been dissolved as methane (CH_4) in the skarn, and/or the graphite has been oxidized to CO_2 . In addition, Fe-rich diopside occurs in the margins of several marble-hosted pegmatites (Yates and Camp deposits).

The formation of andradite with magnetite within the endoskarns of a few pegmatites (MacDonald and Legree) indicates lower $f(S_2)$ and higher $f(O_2)$ conditions than most endoskarn and exoskarn assemblages. The presence of K-feldspar (microcline), magnetite, and mica (annite = 60) is common within the margins of the pegmatites (endoskarn?), occasionally with pyrite present, indicates approximate fluid conditions of $\log f(O_2) = -15$ and an upper limit for $\log f(S_2) = -0.5$. In general, the pegmatites and their fluids have a higher oxidation potential than the host rocks. The transformation of graphite in the marble to methane and may be responsible for the reduced nature of the exoskarn.

The mineral assemblages within the veins are more poorly constrained although a microcline-bearing assemblages

containing magnetite and biotite, Fe-rich diopside and pyrite, and pargasitic hornblende and biotite may be found. In many instances, the biotite compositions (with magnetite) approach to those in the pegmatites (annite 60) indicative of high $f(\text{O}_2)$ conditions analogous to the pegmatites. Within the selvage of the pegmatites, the presence of biotite, microcline, and magnetite $\pm$ pyrite suggests that high $f(\text{O}_2)$ and possibly moderate $f(\text{S}_2)$ conditions are typical of the pegmatites. The similarity among the endoskarn and fluorite-apatite-calcite vein selvage assemblages indicates that the metasomatic fluid responsible for the formation of the veins was, in part, chemically similar to that in equilibrium with the margins of the pegmatite.

It is evident that these mineralized skarns formed by metasomatic alteration of the marble. Shaw et al. (1965) proposed that a radioactive scapolite-bearing skarn formed by metasomatic exchange between the marble and a quartzofeldspathic rock. They used mass balance calculations and chemical potential diagrams to explain the zonal paragenesis of the skarn in terms of diffusion metasomatism. They seemed to favour the presence of a fluid phase because of the existence of quartzofeldspathic boudins in marbles without appreciable skarn developed. As outlined previously, Karvinen (1973) proposed a metamorphic-hydrothermal origin for the molybdenite-bearing skarns related to the metasomatic transfer of components from quartzofeldspathic gneisses into the marble during metamorphic dehydration reactions. He also examined the mass balance considerations for the formation of the marble-hosted skarn and related hedenbergite-feldspar gneisses.

In addition to the mineralizing elements, the aforementioned studies proposed the metasomatic transfer of silicon, aluminum, and alkali elements from the quartz-feldspar rock into the marble, and the addition of magnesium, and calcium to quartz-feldspar rock. Although bimetasomatic

transfer of elements between the two rock types is implied in both studies, an infiltrative fluid phase must also have been responsible for skarn. The presence of veins supports this hypothesis. Therefore, Ca pyroxene formation within the quartz-feldspar gneiss will occur only if calcium and magnesium diffuse opposite to fluid movement, or if the infiltrative fluid is migrating along the contact region, facilitating mixing and exchange with both the marble and gneiss lithologies.

This study concurs with some of the observations made by Karvinen (1973) with respect to the relationship between the skarns and the hedenbergite-feldspar gneisses and the metasomatic nature of the skarns. The formation of molybdenite-sulphide-bearing Ca pyroxene-feldspar (scapolite) veins in a gneiss in the vicinity of skarns is compelling evidence for a related origin. However, instead of a metamorphic-fluid responsible for the infiltrative transfer of components into the marble, a pegmatite-derived fluid has been proposed based on spatial, temporal, and geochemical evidence outlined previously. This fluid was primarily responsible for skarn formation but also enhances the chemical reaction between the marble, skarn, and gneiss by both diffusion and infiltration metasomatism. The presence of calcite ($\pm$ apatite, fluorite, sulphides etc.) veins in the marbles and the gneisses attests to the infiltrative nature of the fluids.

Geochemical modelling of diffusion metasomatism indicates that a fluid would have to have been present for an unreasonably long period of time in order to form even a small bimetasomatic skarn. This explains the absence of skarn between quartz-feldspar boudins and marble. However, fluid-enhanced diffusion metasomatism may be responsible for the formation of some skarns in the Grenville Province because of the long duration of high temperature metamorphism.

Several important factors suggest that U- and Mo-bearing skarns formed by infiltration of a pegmatite-derived

hydrothermal fluid. The disproportionate nature of exoskarn and endoskarn, the presence of veins in the exocontact environment and occasionally in the endocontact environment (pegmatite), the presence of relatively sharp marble/pegmatite contacts, the greater mobility of silica compared to alumina, and the high concentration of U, Th, Mo, and REE in the contact and exocontact region support an infiltrative fluid related to the pegmatite.

CHAPTER 6

ISOTOPIC CHARACTERISTICS OF PEGMATITES, SKARNS, AND VEINS

6.1 Introduction

Stable (C & O) and radiogenic (Sr) isotopes (in addition to the major- and trace-elements; Chapter 4) were determined on primary calcite in pegmatites, skarns, and veins from the Grenville Province (Appendix 3.6). As with previous parts of the study, rocks from which calcites were sampled have been classified as marbles, silicated marbles, skarns, veins, pegmatites, and the Sullivan Island carbonatite (sample 114-1 and 114-2). Calcite was separated from coarse-grained feldspar pegmatite (26) samples from the Kenmac-Chibougamou (127) and the New Armstrong (126) properties collected by Dr. Lang (Geological Survey of Canada collection; 65744 and 65745, respectively). Unfortunately, no field investigation of these localities was undertaken hence the designation "pegmatite" is tentative.

Only primary calcite was sampled in this study. It was distinguished from calcite with possible secondary alteration effects by selecting crystalline calcite with a grain size similar to silicate components, uniformity of colour, absence of veinlets and freshness of silicate components. Also, isotopic and chemical uniformity of calcites within many localities (deposit 26; n = 5, deposit 30; n = 4, deposit 60; n = 4, deposit 70; n = 6, deposit 121; n = 3) is evidence for the absence of secondary alteration of calcite studied.

There are several objectives of this study: 1) characterize the isotopic variation within and between the various environments that calcite was formed; 2) define isotopic and chemical trends that may have petrogenetic significance; and 3) attempt to isotopically distinguish between fluorite-apatite-calcite veins (vein-dikes) and carbonatites (appendix 3.6).

Due to limited exposure, it was impossible to confine the study to the details of one particular skarn-vein system. Several skarns, however, were sufficiently sampled to illustrate the range in isotopic composition possible at any particular locality.

6.2 Stable Isotope Systematics

6.2.1 Analytical methods

Calcite and graphite samples were separated by hand picking and pulverized in a ceramic crucible. In all cases except one, dolomite does not coexist with calcite. The carbon and oxygen isotope compositions of calcite were determined on CO_2 released by reaction of 10 mg calcite with 100% phosphoric acid at 25°C for at least 4 hours (McCrea, 1950). $\delta^{13}\text{C}$ values are reported with respect to Pee Dee Belemnite (PDB), and $\delta^{18}\text{O}$ values are reported with respect to Standard Mean Ocean Water (SMOW). The instrumental precision of both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is less than 0.1 ‰ (per mil) but external precision is slightly larger. Fractionation factors for the phosphoric acid digestion were those of Sharma and Clayton (1965) and corrected by Clayton (1972, in Friedman and O'Neil, 1977). Graphite (1 mg) was burned with CuO at 1050°C for 15 minutes to form CO_2 . Mass spectrometre analyses and CO_2 extractions were performed in the Ottawa-Carleton Isotope Geochemistry Laboratory at the University of Ottawa.

6.2.2 Carbon and oxygen isotopic compositions

6.2.2.1 Marbles

Nine isotopic determinations were made on calcite from marble. Seven have compositional data; three from the Wilberforce area (9G, 9K-1, 9M), two from the Hunt skarn deposit (50A, 50P), and two from the Otter Lake area (1423A-80, 1374-3; sampled by Dr. Ralph Kretz). The two marbles from the Hunt deposit have lower $\delta^{13}\text{C}$ (-0.14 & 0.74) and $\delta^{18}\text{O}$ (18.95 & 19.94) than the few other marbles analysed (Appendix 3.4). These samples may not represent the pristine isotopic

Table 6.1 Graphite-calcite isotopic pairs in marbles and skarns

	$\delta^{13}\text{C}_{\text{gr}}$	$\delta^{13}\text{C}_{\text{cc}}$	$\delta^{18}\text{O}_{\text{cc}}$	$\Delta^{13}\text{C}_{\text{cc-gr}}$
9G	-2.7	1.60	21.59	4.30
9J	-2.24	1.53	22.58	3.77
9M	-1.17	2.68	24.35	3.85
30E	-1.98	0.69	16.60	2.67
50E	-4.20	0.68	21.04	4.88
50P	-3.53	0.74	19.94	4.27

Notes: Samples 9G, 9J, and 9M are from the Cardiff fl-U "C" zone, 30E is from the Cardiff fl-U "A" zone, and 50A and 50E are from Hunt deposit. Samples 30E and 50E are graphite-bearing skarns.

composition of marbles because of their proximity to the Hunt granite pegmatite. Sheppard and Schwarz (1970) found that calcite from Grenville marbles have a $\delta^{13}\text{C}$ range -2 to 5 and a $\delta^{18}\text{O}$ range of 20 to 26. This range $\delta^{13}\text{C}$ is larger than the range observed in this study.

Graphite was analysed from six marble samples that have coexisting calcite (Table 6.1). The carbon isotopic fractionation between calcite and graphite has been used with some success by Valley and O'Neil (1981) in Grenville marbles. However, the small fractionations in these samples yield unreasonable temperatures, greater than 750°C, using the calculated equilibrium fractionation factors derived by Bottinga (1969). This may be explained by the preferential depletion of ^{13}C in calcite during decarbonation reactions while the graphite remained refractory. It is interesting to note that sample 30E has the lowest $\delta^{18}\text{O}$ in calcite and the lowest carbon isotope fractionation factor (Table 6.1). As it will become apparent later, C in graphite is on average 4 ‰ lighter than C in the coexisting marble calcite.

6.2.2.2 Granitic pegmatite

It is suspected that the pegmatite-derived fluid is responsible for the decarbonation reactions resulting from silica metasomatism in the skarn and isotopic and chemical exchange with the skarn calcites. Therefore, it is important to document the isotopic characteristics of the rare-metal granitic pegmatites that are most closely associated with the skarn and vein deposits.

Ten calcite samples from six different pegmatites including three from the MacDonald feldspar deposit and three from the ACME Mo deposit, have a tight cluster of $\delta^{18}\text{O}$ from 11.3 to 12.4 and $\delta^{13}\text{C}$ from -1.6 to -3.0. The designation of samples 126, 127 and 128 as "pegmatite" is tentative, pending a field confirmation, hence the data have not been included in this discussion. The fluid in equilibrium with calcite (average

$\delta^{13}\text{C} = -3$ and $\delta^{18}\text{O} = 11.5$ at 600°C) had an isotopic composition of $\delta^{13}\text{C} = -0.5$ and a $\delta^{18}\text{O} = 10.6$ based on $\alpha_{\text{CO}_2\text{-calcite}}$ for carbon from Bottinga (1969) and $\alpha_{\text{H}_2\text{O-calcite}}$ for oxygen from Friedman and O'Neil (1977). A combination of isotope fractionation factors was used for calcite- H_2O because of the absence of a calibration above 500°C ($\alpha_{\text{quartz-H}_2\text{O}}$; Clayton, 1972 in Friedman and O'Neil, 1977; Matsuhisa et al., 1979; $\alpha_{\text{quartz-calcite}}$, Matthews et al., 1983).

Calcite in the MacDonald pegmatite has very similar isotopic composition ($\delta^{18}\text{O} = 12.01$ to 12.44 and $\delta^{13}\text{C} = -2.25$ to -1.61 ; 26F, G, H) to calcite from skarn ($\delta^{18}\text{O} = 12.81$ and $\delta\text{C} = -1.47$; 26A) and silicated marble ($\delta^{18}\text{O} = 12.34$ ‰ and $\delta^{13}\text{C} = -1.84$ ‰, 26B) at this locality. It is possible that the calcite in the pegmatite was derived from the skarns inheriting some of the isotopic characteristics of the exoskarn calcite. However, the ACME Mo granitic pegmatite is hosted in biotite-hornblende-quartz-feldspar gneiss and contains calcite at the contact between the pegmatite and gneiss. The absence of marble in the immediate vicinity of the ACME pegmatite would suggest that the isotopic composition of the calcite ($\delta^{18}\text{O} = 11.4$ to 11.5 and $\delta^{13}\text{C} = -3.0$ to -2.7) may more closely reflect the characteristics of the pegmatite. The δ values for oxygen and carbon of calcite from this locality are slightly lower than the MacDonald pegmatite. The inferred whole-rock oxygen isotopic composition of the MacDonald and ACME pegmatites is 3 to 4 per mil heavier than most of the pegmatites investigated by Shieh and Schwarz (1974) in the western portion of the Central Metasedimentary Belt and the Central Gneiss Belt. This indicates that the granitic melts were derived from a gneissic sedimentary or low temperature altered volcanic protolith, or contaminated by marine carbonates in during intrusion.

6.2.2.3 Silicated marbles and skarns

Skarn calcites have a large range in both carbon and oxygen

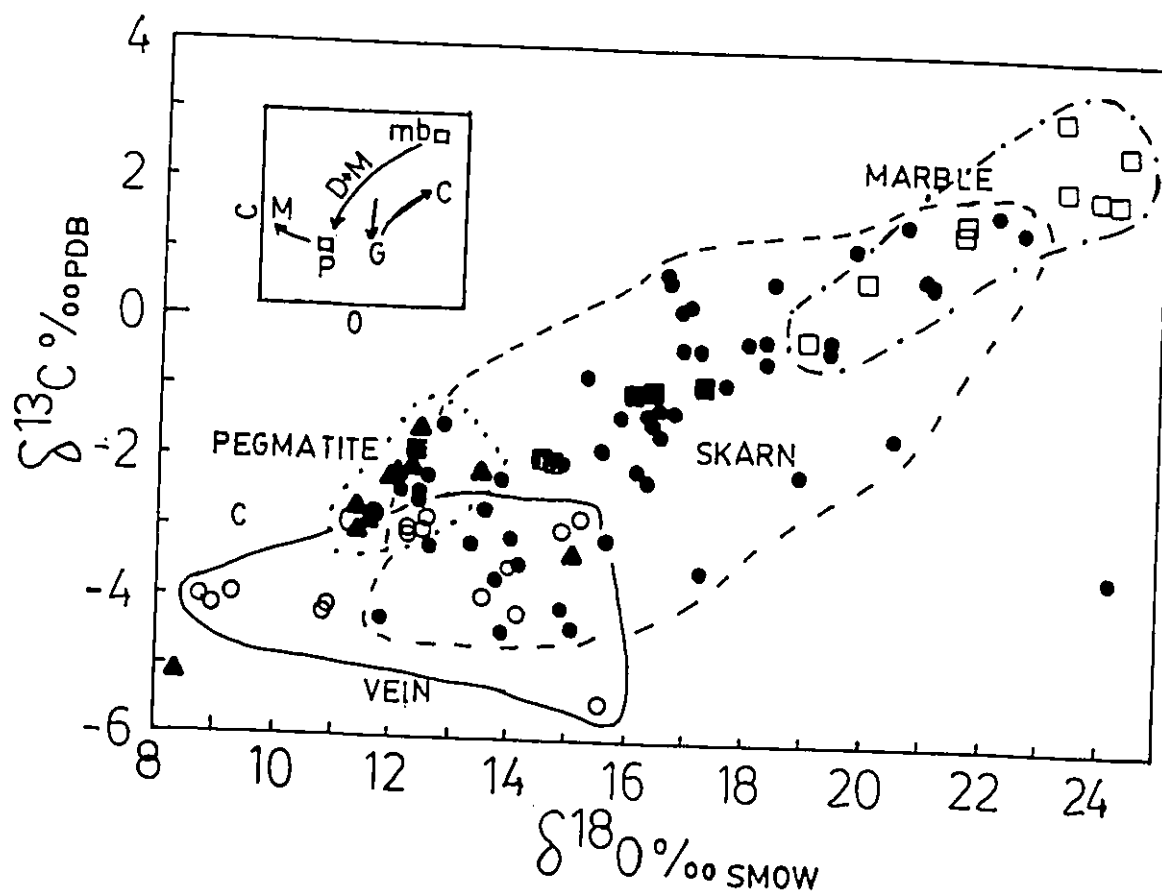


Figure 6.1 Plot of $\delta^{13}\text{C}$ (PDB) versus $\delta^{18}\text{O}$ (SMOW) for calcite from of marble ($\square$), skarn ($\bullet$), silicated marble ($\blacksquare$), vein ($\circ$), pegmatite ($\blacktriangle$), and carbonatite ($\circ$). The inset (after Taylor, 1987) represents various isotopic trend lines including: decarbonation and metasomatic exchange (D & M), graphite oxidation (G), meteoric involvement (M), cooling in the presence of a fluid of uniform isotopic composition (C).

isotopic composition ($\delta^{18}\text{O} = 11.5$ to 22 and $\delta^{13}\text{C} = -5$ to 2) extending between the marble and pegmatite (Figure 6.1). This range extends from the marbles ($\delta^{13}\text{C} = +2$ to $+3$ and $\delta^{18}\text{O} = +23$ to $+24$) to pegmatites ($\delta^{13}\text{C} = -1$ to -3 and $\delta^{18}\text{O} = 11.5$ to 12.5). In general, calcite in the silicated marbles ($\delta^{18}\text{O} = 16.3 \pm 3.2$ ‰ and $\delta^{13}\text{C} = -0.8 \pm 1.7$ ‰; $n = 6$) and skarns ($\delta^{18}\text{O} = 16.3 \pm 0.9$ ‰ and $\delta^{13}\text{C} = -1.5 \pm 0.5$ ‰; $n = 52$) has a range of values between the marbles and pegmatites. Silicated marbles have a trend similar to the skarn calcites and overlap in isotopic composition with the skarns. The high proportion of calcite within silicated marbles was also involved in the isotopic exchange processes involved in skarn formation. The average oxygen isotopic compositions of silicated marbles and skarns are coincidentally identical. The carbon isotopic composition of the few calcite samples from silicated marble is slightly heavier than the average skarn calcite.

In addition, numerous skarn calcite samples have $\delta^{13}\text{C}$ less than calcite from the MacDonald and ACME pegmatites indicating an additional source of isotopically light carbon. One calcite sample (112) has a very light carbon isotopic composition. Interestingly, graphite is common in the marbles in the vicinity of this locality. Oxidation of graphite (4 per mil lighter than coexisting calcite) in the marbles to CO_2 would result in isotopically lighter CO_2 which interacted and precipitated calcite.

6.2.2.4 Fluorite-apatite-calcite veins

The calcite in fluorite-apatite-calcite veins encompasses a large isotopic range from $\delta^{18}\text{O} = 8.5$ to 15.5 and $\delta^{13}\text{C} = -5.5$ to -2.5 with an average $\delta^{18}\text{O} = 12.7 \pm 1.0$ ‰ and $\delta^{13}\text{C} = -3.4 \pm 0.5$ ‰ ($n = 15$). This trend overlaps the skarn spectrum and extends just beyond what is considered the average isotopic composition of the pegmatite (Figure 6.1).

The lower $^{13}\text{C}/^{12}\text{C}$ ratio of vein carbonates in comparison to the pegmatites may be related to the oxidation of graphite to

CO₂. Ten of the vein calcite samples have $\delta^{18}\text{O}$ greater than the average pegmatite and five samples have $\delta^{18}\text{O}$ less than the average pegmatite. The latter are from veins in the quartz-feldspar gneisses along strike of the Cardiff and Richardson deposits. The lower oxygen isotope ratios of vein calcite are problematic with respect to a possible simple binary mixture of pegmatite fluids and marble carbonates; formation of the skarns and the veins was a more complex phenomena.

There are several possibilities that could explain the lower $^{18}\text{O}/^{16}\text{O}$ ratios of a few vein calcites: 1) equilibration with a meteoric water; 2) the source pegmatites in the Cardiff area are isotopically lighter ($\delta^{18}\text{O} = 8$ to 9‰) than the MacDonald and ACME pegmatites, and 3) fluid interaction with isotopically light gneissic wall rocks ($\delta^{18}\text{O} < 9\text{‰}$) (primitive orthogneisses?). The textural and compositional uniformity and limited isotopic variability of the calcite samples does not favour any meteoric effect on the vein calcites. The few isotopic analyses of calcite from pegmatite may not properly characterize the oxygen isotopic composition of most pegmatites. This may be true considering the low oxygen isotopic compositions ($\delta^{18}\text{O} = 8$ to 9 ; quartz) of other Grenville pegmatites (Shieh and Schwarcz 1974). Fluid interaction and exchange with the host quartz-feldspar orthogneisses may lower the oxygen isotopic composition of the fluid resulting in lower $\delta^{18}\text{O}$ of calcite deposited from the fluid. The later two hypotheses are the most reasonable.

The carbon and oxygen isotope compositions of vein calcite are most similar to calcite within the pegmatites. This suggests that high fluid/rock ratios are required in the skarn ($F/R > 5$) in order to achieve isotopic compositions close to pegmatites if a simple binary mixing of the oxygen isotopes is a proper measure of the exchange process. This is compatible with the high amounts of fluid required to dissolve calcite from the skarn/marble and redeposit calcite into the veins.

6.2.5 Minor- and trace-element and isotopic systematics between pegmatites, skarns, veins and marbles.

There are several relationships between minor and trace elements and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in calcite. A significant covariation between MnO and FeO and much less so, if at all, for Na and Y with $\delta^{18}\text{O}$ was found for calcites from the various environments (Figure 6.2 and 6.3). In general, calcites from the marbles have the lowest MnO, FeO, Na, and Y contents and highest $\delta^{18}\text{O}$ values and calcites from the pegmatites have the highest MnO, FeO, Na, and Y contents and lowest $\delta^{18}\text{O}$ values. The veins have high MnO, FeO, Na, and Y contents and low $\delta^{18}\text{O}$ contents. The silicated marble and skarn calcites have intermediate minor- and trace-element contents between those of the pegmatites and marbles. The calcite in veins is compositionally and isotopically very similar to the calcite in the pegmatites. The compositional and isotopic systematics are consistent with an infiltration metasomatic origin for the skarns and veins related to fluids derived from the pegmatites.

6.2.3 Discussion

Stable isotopes have been used successfully to characterize the temperature and fluid evolution of skarns and marbles (Shieh and Taylor, 1969; Rye et al., 1976; Taylor and O'Neil, 1977; Lattanzi et al., 1980; Nabelek et al., 1984; Bowman et al., 1985; Brown et al., 1985; Taylor and Bucher-Nurminen, 1986; Valley, 1986; Valley et al., 1990). In many cases, the carbon and oxygen isotopic composition of skarns is beyond the range that can be explained solely by isochemical metamorphic decarbonation reactions (Valley, 1986). These detailed stable isotope studies of contact and vein skarns reveal some of the complex metasomatic processes involved in the skarnification. There are dominantly three processes responsible for the primary stable isotopic variation in magmatic skarns; 1) metamorphic decarbonation, 2) metasomatic exchange, and 3)

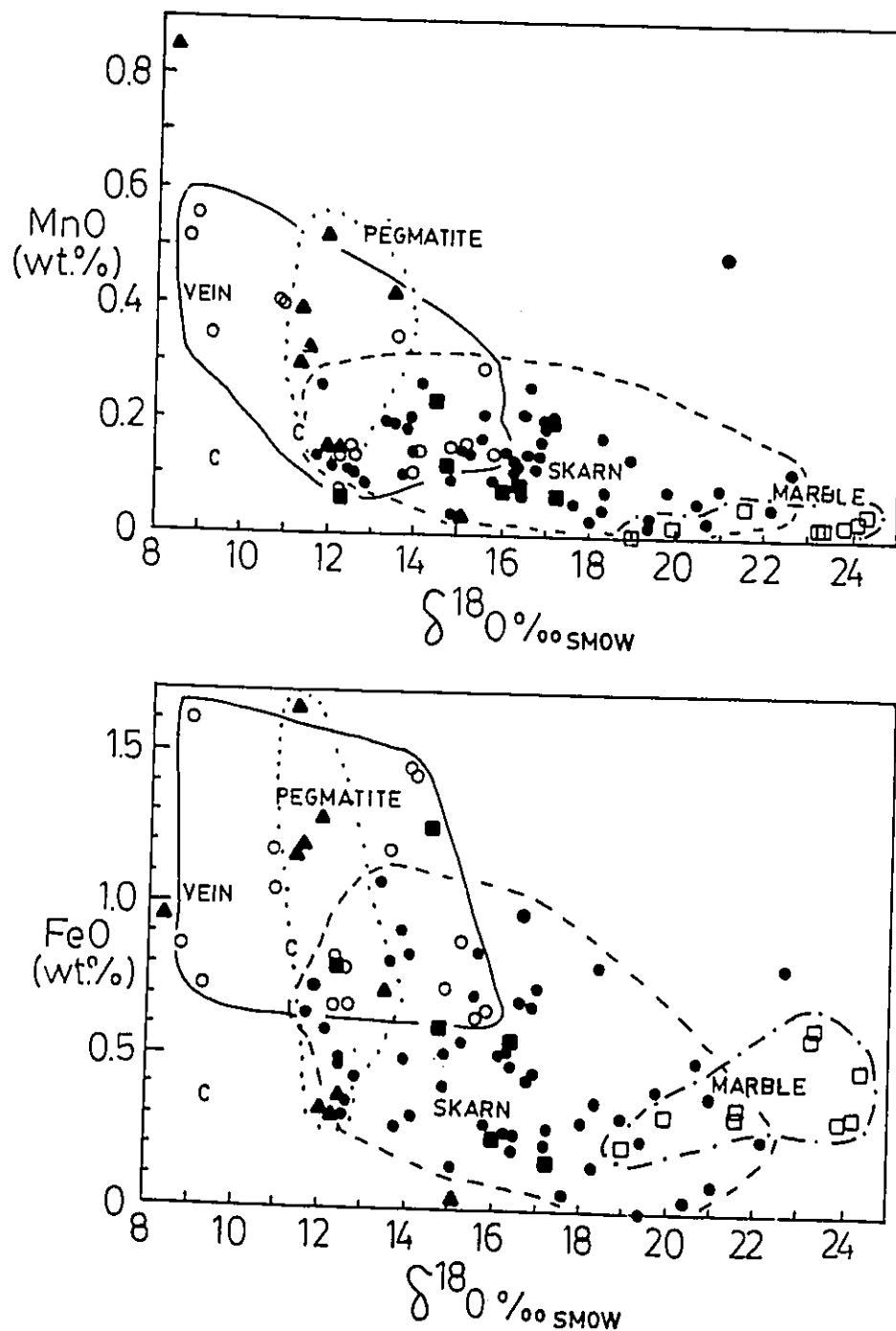


Figure 6.2 Plots of $\delta^{18}\text{O}$ (SMOW) versus MnO (wt.%) and FeO (wt.%) for marbles (□), skarns (●), silicated marbles (■), veins (○), pegmatites (▲), and carbonatites (c).

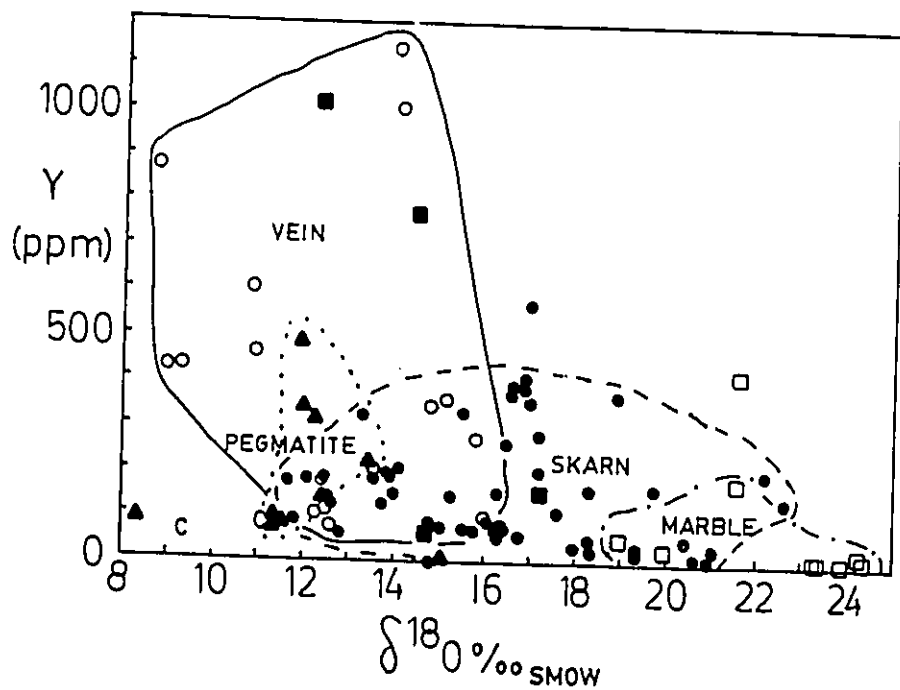
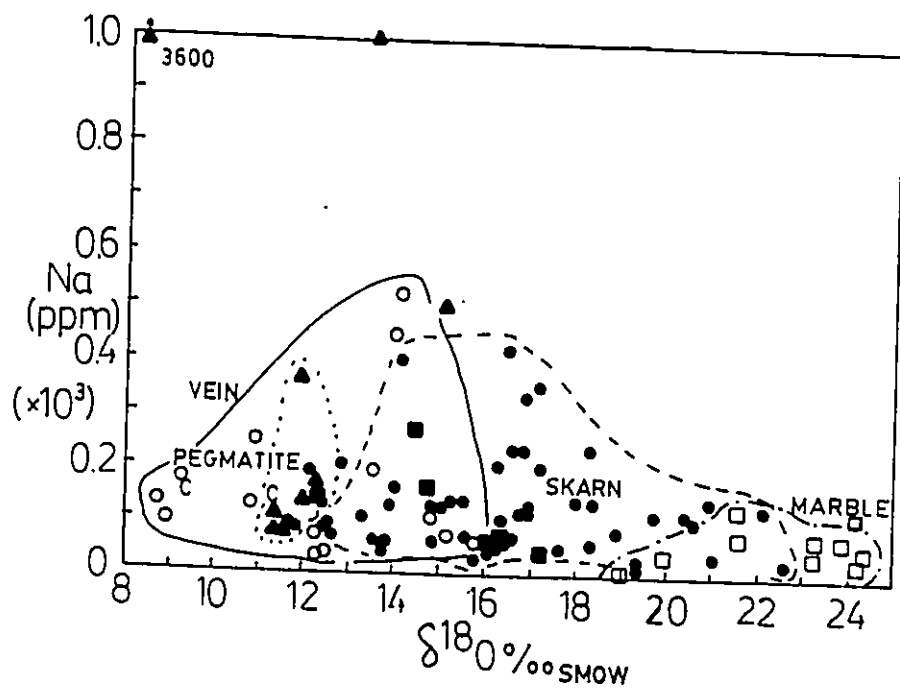


Figure 6.3 Plots of $\delta^{18}O$ (SMOW) versus Na (ppm) and Y (ppm) for marbles ($\square$), skarns ($\bullet$), silicated marbles ($\square$), veins (o), pegmatites ($\blacktriangle$), and carbonatites (c).

metasomatic induced decarbonation (silica metasomatism). With respect to the late-tectonic Grenville skarns, all the metamorphic decarbonation reactions occurred during the upper amphibolite grade regional metamorphism which preceded intrusion of the late-tectonic, U-, Th-, Mo- and REE-bearing granitic pegmatites. Therefore, metasomatic exchange and decarbonation related to silica metasomatism was probably responsible for the observed isotopic variation in the skarns and veins. The coupled oxygen and carbon isotopic shifts are indicative of a combination of decarbonation reactions (metamorphic or metasomatic) and metasomatic exchange of oxygen with the pegmatite-derived fluid. The "depletion ratio" ($\delta^{13}\text{C}/\delta^{18}\text{O}$) may be used to help constrain the mole fraction of CO_2 in the skarn forming fluid (Taylor and O'Neil, 1977; Nabelek et al., 1984; Taylor and Bucher-Nurminen, 1986; Valley, 1986).

As discussed earlier, the low $\delta^{18}\text{O}$ of calcite from some skarns and veins may have been partially inherited by metasomatic exchange with fluids exsolved from the pegmatite. However, it is possible that there was not enough CO_2 in the pegmatites to deplete the $\delta^{13}\text{C}$ in calcite to the lower values by simple binary mixing of pegmatite-derived CO_2 with the marbles. For instance, the fluid in equilibrium with the calcite in the core of the MacDonald pegmatite ($\delta^{13}\text{C} = -2.0\text{‰}$) would have a calculated $\delta^{13}\text{C} = -0.5\text{‰}$ at 600°C which is much heavier than "igneous (mantle) carbon" but compatible marine carbon or from decarbonation reactions. Carbon dioxide evolved from proximal contact skarn decarbonation reactions may have been entrained into the crystallizing pegmatite. The high chemical potential of CO_2 in the skarn versus the pegmatite would favour the movement of CO_2 down the chemical potential gradient into the H_2O -rich pegmatite. This would be substantiated by the similarity in the $\delta^{13}\text{C}$ values for calcite

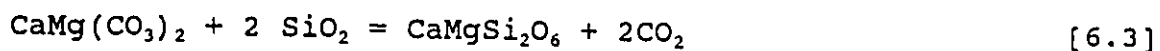
from the MacDonald pegmatite, skarn, and silicated marble skarn (deposit 26).

An alternative explanation for the low ^{13}C content of the skarn and vein calcites may be obtained by decarbonation reactions induced by silica metasomatism. Batch decarbonation may lower the $\delta^{13}\text{C}$ of residual calcite to a minimum value of -0.5 at $\alpha = 1.0025_{\text{cc-co}_2}$ (Bottinga, 1969) but Rayleigh decarbonation may possibly lower the $\delta^{13}\text{C}$ value to within the range of the pegmatites.

$$\delta_f = \delta_i - (1-F) 1000 \ln(\alpha) \quad \text{Batch decarbonation} \quad [6.1]$$

$$\delta_f = \delta_i + 1000(F^{\alpha-1} - 1) \quad \text{Continuous decarbonation (Rayleigh)} \quad [6.2]$$

Note: δ_f = final, δ_i = initial, F = portion calcite remaining
The batch and continuous devolatilization (decarbonation) equations were taken from Valley (1986). The end-member diopside forming reaction (1) allows 100% of the carbon to be driven from the rock (Figure 6.4).



The above reaction evolves 100% of the carbon but only evolves 40% of the oxygen with 60% remaining in the rock. This is termed the "calc-silicate limit" (Valley, 1986) as the endproduct is 100% diopside. Rayleigh decarbonation may be responsible for the substantial decrease in $\delta^{13}\text{C}$ of calcite from the skarns.

Theoretical calculations show that both batch and continuous decarbonation (Rayleigh) may substantially lower the $\delta^{18}\text{O}$ of carbonates and calc-silicates. However, these processes are essentially indistinguishable at the "calc-silicate limit" with F equal to 0.6 (Figure 6.4). In the end member case, it has been shown that continuous (Rayleigh) decarbonation of reaction 1 is insufficient to lower the $\delta^{18}\text{O}$ to values near the pegmatite because of the 60% oxygen remainder due to the "calc-silicate limit" (Bowman et al., 1985; Valley, 1986). Note that the equilibrium $\Delta_{\text{calcite-diopside}} = 2.3 \text{ ‰}$ at 550°C, hence calcite should be slightly heavier than coexisting diopside.

The isotopic composition of quartz was also not accounted for in the calculated decarbonation reactions in Figure 6.4. In the end-member case, this would involve a mixing of oxygen from premetamorphic detrital quartz (40%) and oxygen from dolomite (60%) (Reaction 6.3). If the quartz had a premetamorphic $\delta^{18}\text{O}$ value of 10 and dolomite had $\delta^{18}\text{O} = 24$, the whole-rock $\delta^{18}\text{O}$ isotopic composition of this hypothetical siliceous dolomitic marble would be 18.4 ‰. This could account for some of the isotopic variation of calcite in the marble and calc-silicate-rich skarn. The whole-rock oxygen isotopic composition of the siliceous dolomitic marble (18.4 ‰) combined with continuous decarbonation (2:1 quartz-dolomite mole ratio) could lower the $\delta^{18}\text{O}$ isotopic composition of the marble to 14.8 (Figure 6.4). This value is within the range of many of the skarns examined in this study but represents an extreme end-member value for simple decarbonation reactions. None the less, considering all the parameters, the oxygen isotopic composition of the skarns cannot be achieved solely by batch or continuous (Rayleigh) decarbonation of the marble.

Dissolved silica in the pegmatite-derived hydrothermal fluid may induce decarbonation analogous to the presence of premetamorphic quartz in a dolomitic marble. The isotopic composition of the dissolved silica (and fluid), inherited from the pegmatite, and H_2O -rich fluid will exchange with the dolomite analogous to detrital quartz resulting in a depletion of ^{18}O in the resultant skarn. The low $\Delta_{\text{quartz-H}_2\text{O}}$ (1.7 ‰) at 550°C, combined with the preliminary estimates made for the fluid in equilibrium with the pegmatite ($\delta^{18}\text{O} = 10.5$ ‰), would result in an end-member $\delta^{18}\text{O}$ for quartz of 12.2 ‰.

The simple binary mixing of dissolved silica in a fluid and carbonates may produce results similar to those of "isochemical" decarbonation of diopside-rich marble. However, silica metasomatism by an H_2O -rich, silica-bearing hydrothermal fluid has the capability of metasomatically

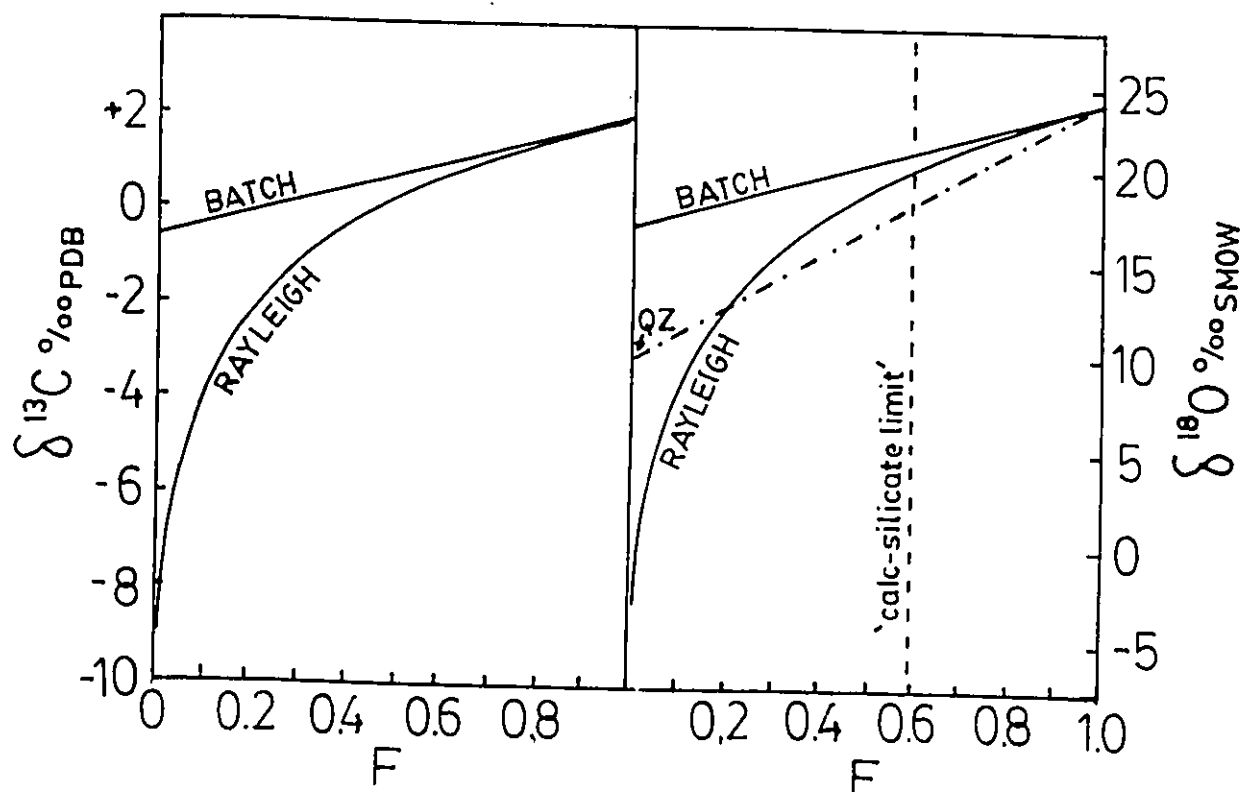


Figure 6.4 a) Plot showing variation of $\delta^{13}\text{C}$ versus F (fraction of carbonate remaining) for batch Batch and Rayleigh decarbonation processes between calcite and CO_2 at 550°C in a dolomite-quartz marble ($\delta^{13}\text{C} = +2$ and $\delta^{18}\text{O} = +24$). b) Plot showing variation of $\delta^{18}\text{O}$ versus F diagram illustrating Batch and Rayleigh decarbonation processes between CO_2 and diopside at 550°C , mixing of detrital quartz with dolomite, and the depletion factor (R) = 3.6 per mil at "calc-silicate limit" (reaction 1). An $\alpha_{\text{CO}_2\text{-diopside}} = 1.007$ was estimated from fractionations of calcite- CO_2 , albite-calcite and albite-diopside isotopic fractionations at 550°C (Bottinga, 1968; Matthews et al., 1983).

exchanging oxygen with the marbles. This could produce dramatic reduction in the $\delta^{18}\text{O}$ composition of marbles irrespective of the calc-silicate content. Metasomatic exchange is particularly applicable to the silicated marbles which have a high proportion of calcite remaining during metasomatic alteration. Fluid/rock (F/R) ratios were calculated by the following equations (Taylor, 1974).

$$\frac{F/R = \delta_f(\text{rock}) - \delta_f(\text{fluid})}{\delta_i(\text{fluid}) - \delta_f(\text{rock}) + \Delta} \quad \text{"closed system"} \quad [6.4]$$

Note: δ_f is final isotopic composition, δ_i is the initial isotopic composition, and $\Delta = \delta_f(\text{rock}) - \delta_f(\text{fluid})$.

$$F/R = \ln[(F/R)_{e-s} + 1] \quad \text{"open system"} \quad [6.5]$$

If an end-member calcite marble is metasomatically altered by pegmatite-derived hydrothermal fluids, the $\delta\text{O}_1(\text{rock}) = 24$ and $\delta\text{O}_1(\text{fluid}) = 10.6$, $\Delta_{\text{calcite-H}_2\text{O}} = 1.15 \text{ ‰}$ at 550°C . These were the parameters used to calculate fluid/rock ratios (Table 6.2).

In addition to the overall isotopic trend derived by decarbonation and metasomatic exchange, there are several calcites which have anomalous, isotopically light carbon beyond the limits of simple decarbonation and exchange phenomena (Figure 6.1). There are three possible explanations for the observed trend to lower $\delta^{13}\text{C}$ and/or higher $\delta^{18}\text{O}$; 1) Rayleigh decarbonation may have affected a certain set of samples greater causing some skarn calcites to have greater ^{13}C depletions than other skarn calcites, 2) cooling in the presence of a hydrothermal fluid of fixed isotopic composition, and 3) incorporation of graphite-derived CO_2 into the calcite would incorporate isotopically light carbon (see insert in Figure 6.1 after Taylor (1987)). Different extents of Rayleigh decarbonation may produce only small variations in the carbon isotopic signature with only moderate variation in oxygen isotopes. There is a negligible temperature gradient ($\Delta T < 100^\circ\text{C}$) outside the skarn forming environment hence

Table 6.2 Oxygen isotopic exchange between a calcite
marble and H₂O-rich, pegmatite-derived fluid
($\delta^{18}\text{O}$).

	"Closed system"		"Open system"	
F/R (atom%)	δ_{Fluid}	δ_{Rock}	δ_{Fluid}	δ_{Rock}
0.01	22.8	23.9	22.3	23.9
0.1	21.8	22.9	21.7	22.8
0.2	20.9	22.0	20.7	21.8
0.5	18.8	19.9	19.1	19.2
1.0	16.8	17.9	14.8	15.9
2.0	14.8	15.9	12.3	13.4
5.0	12.7	13.8	10.7	11.8
10.0	11.7	12.8	10.6	11.7
∞	10.6	11.7	10.6	11.7

Notes: Calculations have been derived for metasomatic exchange only (ie. decarbonation reactions are not considered.) $\Delta_{\text{H}_2\text{O-cc}} = 1.15$ at 550°C (Bottinga, 1969).

Table 6.3 $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ compositions of calcite at various fluid/rock ratios between a pegmatite-derived fluid and a calcite marble.

F/R	"Closed system"		"Open system"	
	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
0.01	1.94	23.9	1.94	23.9
0.1	1.45	22.9	1.43	22.8
0.2	1.0	22.0	0.91	21.8
0.5	0.0	19.9	-0.36	19.2
1.0	-1.0	17.9	-1.8	15.9
2.0	-2.0	15.9	-3.2	13.4
5.0	-3.0	13.8	-3.8	11.8
10.0	-3.46	12.8	-3.99	11.61
∞	-4	11.6	-4	11.6

Notes: These are calculated using ($\delta^{13}\text{C}$) $\Delta_{\text{CO}_2\text{-cc}} = -2.7\text{‰}$ and a ($\delta^{18}\text{O}$) $\Delta_{\text{H}_2\text{O-cc}} = 1.15\text{‰}$ (Bottinga, 1968) and a hypothetical endmember CO_2 content (100 %) for the $\delta^{13}\text{C}$ calculations. Curves reproduced in figure 6.5 are calculated for $X(\text{CO}_2) = 0.0, 0.2$ and 0.5 .

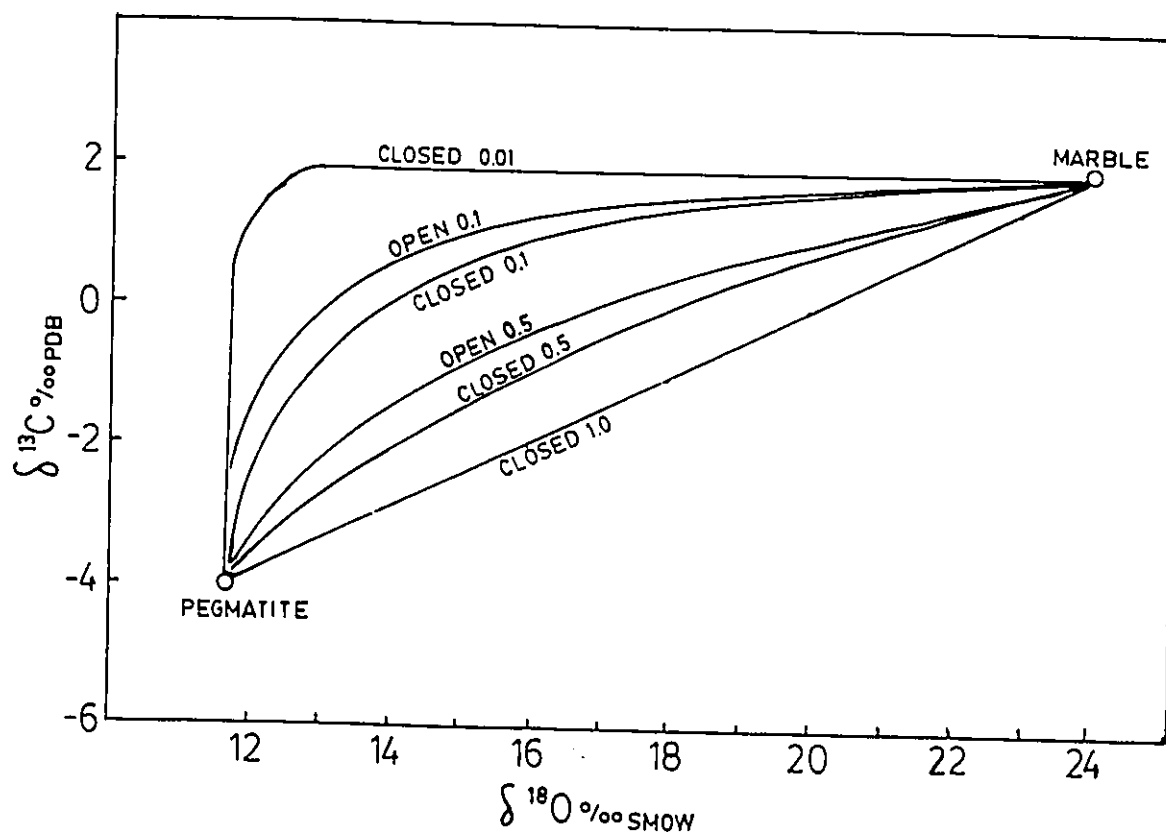


Figure 6.5 Plot of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ trend lines for various fluid/rock ratios (F/R) between a fluid in equilibrium calcite from pegmatite ($\delta^{13}\text{C} = -4 \text{ ‰}$ & $\delta^{18}\text{O} = 11.6 \text{ ‰}$) and marble ($\delta^{13}\text{C} = +2 \text{ ‰}$ & $\delta^{18}\text{O} = +24 \text{ ‰}$) at $X(\text{CO}_2) = 0.01, 0.1, 0.5,$ and 1.0 in both an open and closed system (see Table 4.4). Note: $(\text{F/R})_{\text{c.s.}}$ is the "closed system" value.

deposition of calcite from a cooling fluid is not reasonable. The presence of graphite in the marbles within the vicinity of skarns and the general absence of graphite in most skarns indicates that graphite is mobilized as CH_4 and/or CO_2 .

The presence of carbon derived from the oxidation of graphite precludes a detailed analysis of the mole fraction of CO_2 in the fluid. In general, the overall carbon and oxygen isotope array does not contradict the low $X(\text{CO}_2)$ (0.2 to 0.3) based on petrologic observations.

It is interesting to note that in a compilation of carbon and oxygen isotopic trends, Valley (1986) noted that they converge on the "carbonatite box" due to exchange and equilibration with granite-derived volatiles.

6.3. Strontium isotope systematics

6.3.1 Introduction

The radiogenic tracer isotope ^{87}Sr is particularly useful in evaluating the various sources of strontium (and possibly other constituents) in hydrothermal fluids (Faure, 1986). Unlike stable isotopes, heavy radiogenic isotopes, such as strontium, do not fractionate between the fluid phase and minerals, hence they reflect the composition of the rocks responsible for the strontium within the fluid. However, there are several considerations; 1) the effect of relative strontium abundance in various rocks, and 2) the abundance of radiogenic strontium produced from ^{87}Rb decay after deposition of the mineral under consideration. There is no detectable Rb in the calcites from this study (< 5 ppm) based on several XRF analyses, hence the strontium isotopic composition of calcite nearly reflects the composition of the fluid from which it was deposited.

The fractional enrichment of strontium during evolution of the hydrothermal solution may explain the low to moderate Sr content of calcite in the skarns and veins. The deposition of strontium-bearing minerals, in particular calcite, will

deplete the fluid in strontium. A distribution coefficient for $[Sr/Ca]_{\text{calcite}}/[Sr/Ca]_{H_2O} = 0.15$ has been determined in a calcite-saturated solution at low temperature (20°C ?) (Holland, 1966). Although the $Sr K_D$ calcite/solution will tend to decrease with increasing temperature, it is possible that Sr enrichment could occur as a result of calcite deposition (fractional crystallization of calcite) (See appendix 1.5 for analytical method).

6.3.2 Isotopic and compositional constraints on skarn and vein petrogenesis in the CMB of the Grenville Province

6.3.2.1 End-member compositions

There are several possible isotopic "end-members" for strontium that should be considered: 1) marbles, 2) granitic pegmatites, and 3) host rocks. The average strontium isotope composition of late Proterozoic marbles is well constrained between 0.7055 and 0.7065 (Veizer and Compston, 1976; Veizer et al., 1983). In a reconnaissance study of marbles, Storey and Vos (1981b) determined an average of 260 ± 60 ppm Sr in 150 marble samples from the Pembroke-Renfrew area. Seven of eight calcites from marbles analysed in this study have an average of 375 ± 174 ppm strontium. However, calcite from one marble sample near the Hunt pegmatite has 3355 ppm Sr.

Fowler and Doig (1983a) have determined that the initial strontium ratio of the uraniferous granitic pegmatites was around 0.705, similar to anhydrite from the Madawaska Mine pegmatite with a $^{87}Sr/^{86}Sr$ ratio of 0.704 (Rimsaite, 1982). The average strontium content of the granitic pegmatites is highly variable, but ranges from 100 - 300 ppm (Chapter 2). The low $^{87}Sr/^{86}Sr$ of the Grenville U-Mo-REE pegmatites is atypical for most rare-metal pegmatites which have much higher strontium isotopic initial ratios (Clark, 1982). The Sr isotope data strongly suggests partial melting of a primitive granitic

source rock with a low residence time in the crust or derived from the mantle (Fowler and Doig 1983a).

The host rock strontium isotopic compositions are very variable and dependant on strontium abundance, Rb contents and age. The host rock data is useful in evaluating the possible source protoliths of these pegmatites and characterize the host rocks for the veins. All available data has been collected on the Rb-Sr ages and initial strontium isotope ratios of host rocks in the southwestern Grenville Province (Table 4.5; Figure 6.6a and b). Using published whole-rock Rb-Sr ages, the average strontium ratios at a hypothetical time of pegmatite emplacement (1050 Ma) and closure (950 Ma cf. Fowler and Doig, 1983a) were computed by back calculation using the calculated initial strontium ratio, the last age of homogenization (Rb-Sr age), and the average Rb/Sr ratio of the host. These calculations indicate the average strontium initial ratio of the gneisses at the approximate time of pegmatite emplacement. In addition to determining possible protoliths for the pegmatite melts, this data may also be used to evaluate the numerous possible wall rock mixing end-members for the pegmatite-derived hydrothermal fluid, which was assumed to be responsible for skarn and fluorite-apatite-calcite vein formation.

Low strontium isotopic ratios are associated with mafic igneous rocks (low Rb) and felsic igneous rocks with short residence times in the crust before pegmatite emplacement. Of the 45 strontium isotopic data surveyed from the southern Grenville Province, 14 granitoid rocks and gneisses have an average 1050 Ma initial ratios (R') ($^{87}\text{Sr}/^{86}\text{Sr}$ ratio) ≤ 0.705 which is in the range observed for these late tectonic granitic pegmatites. In general, the more radiogenic strontium isotopic ratios are associated with gneisses which had longer residence times in the crust. The host rock gneisses commonly have a heterogenous Rb distribution, therefore, at the time of

emplacement the pegmatites had variable Sr isotopic signatures. The partial melting process has the effect of homogenizing the strontium isotopic signature of the source protolith, averaging different radiogenic strontium contents. The calculated $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (@ 950 Ma; R') is used as a lower limit for the age of the pegmatites. The younger Rb/Sr ages (< 1020 Ma) indicate strontium diffusion after pegmatite crystallization to 950 Ma. Interaction between the pegmatite and the crust may have occurred until the crust cooled substantially below the Rb/Sr closing temperature of 500°C.

The compilation of Rb/Sr data is also used to evaluate the possible sources of strontium of different isotopic composition, which could possibly affect the isotopic composition of the vein-forming hydrothermal fluids. These fluids may have exchanged strontium with the enclosing host rocks during crustal interaction preceding vein formation. Again, this process would have resulted in mixing pegmatite- and marble-derived strontium with strontium derived from the enclosing host rock gneisses. The $^{87}\text{Sr}/^{86}\text{Sr}$ signature of the host rocks may be incorporated into the fluid by inheritance due to fluid-host rock interaction. The $^{87}\text{Sr}/^{86}\text{Sr}$ value (R') was calculated indicative of the average isotope ratio at the average Rb/Sr abundance and time of vein formation (1050 Ma) (Table 6.4). Table 6.4 indicates that there are numerous possible strontium isotopic compositions for these gneisses ranging considerably in the radiogenic Sr isotope content. Unfortunately, there is no data for any of the areas investigated, including the Cardiff gneiss dome, which hosts many of the deposits in the Wilberforce area. However, it is reasonable to suggest that the syenitic orthogneisses of the Cardiff Dome had a Rb content and a residence time sufficiently long to produce radiogenic strontium at the time of vein formation. This could account for the radiogenic

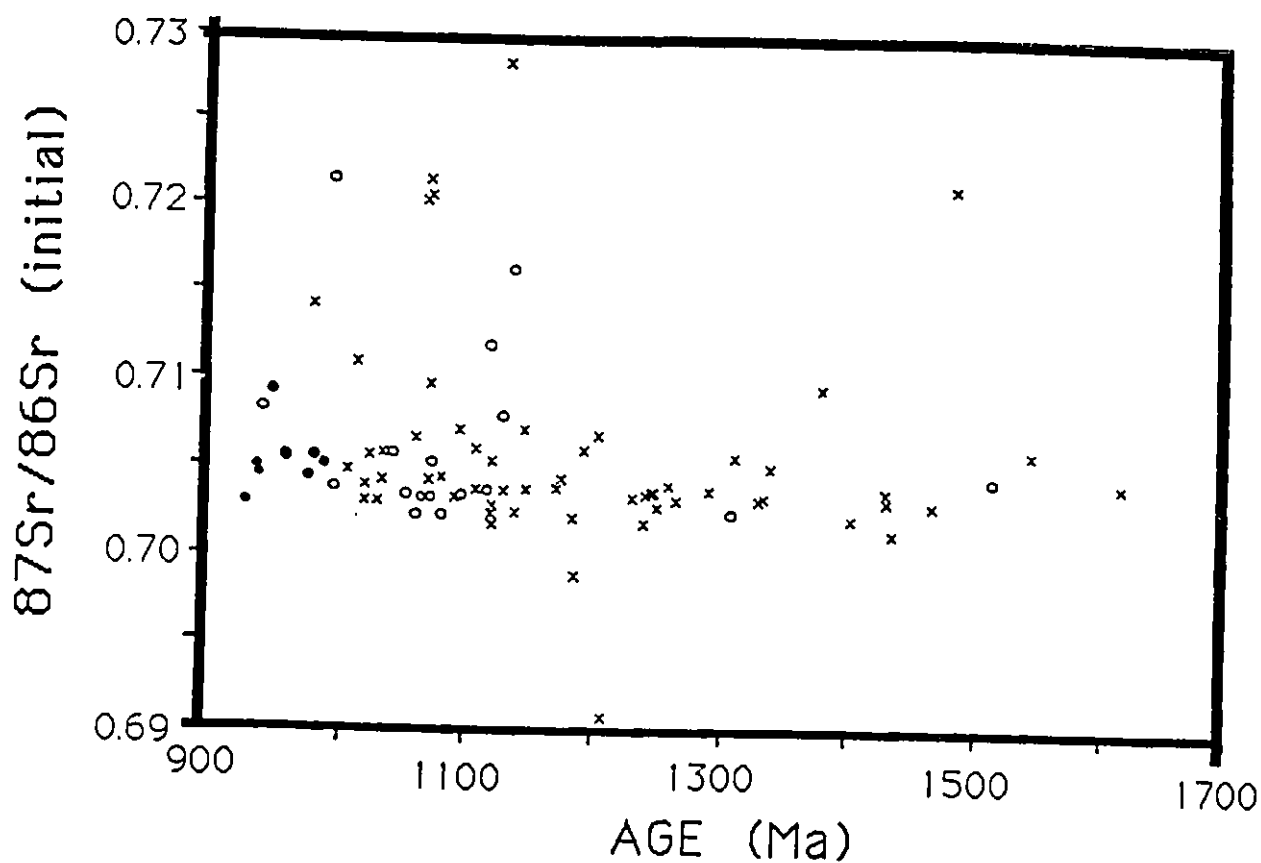


Figure 6.6 Average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of rocks at the last homogenization temperature in the southwestern Grenville Province from data listed in Table 4. The symbols are ● - pegmatites, o - granitoid gneisses, x - other gneisses.

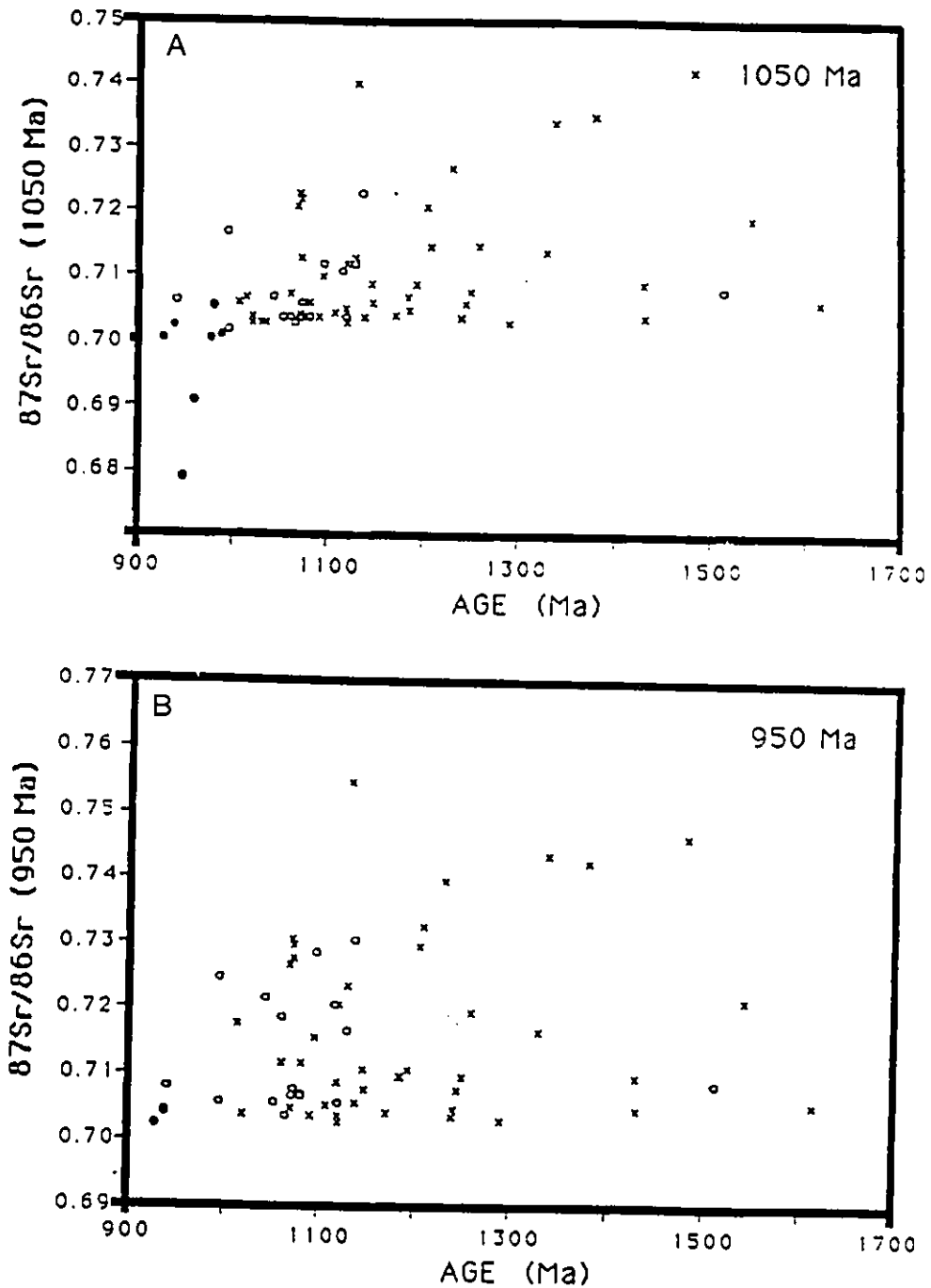


Figure 6.7 A) Calculated average $^{87}\text{Sr}/^{86}\text{Sr}$ isotope content of rocks at 1050 Ma and B) 950 Ma in the southwestern Grenville Province from data listed in Table 6.4. The symbols are ● - pegmatites, o - granitoid gneisses, x - other gneisses.

character of strontium in several skarn samples in the Wilberforce area.

6.3.2.2 Isotopic and compositional data from calcite in pegmatites, skarns, veins (this study)

The strontium isotopic ratios determined in this study compliment earlier work by expanding on the current data base. Figure 6.8 a and b illustrate the range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and abundances found in this study. Only one marble sample was analysed (0.7056) from the Cardiff Uranium mine area. Three calcite samples from pegmatites have low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with the exception of sample 128 (0.7202). An average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7060 ± 0.0021 was found for 9 skarns and 2 silicated marbles. Six fluorite-apatite-calcite vein samples have an $^{87}\text{Sr}/^{86}\text{Sr}$ average ratio of 0.7047 ± 0.0005 which is indistinguishable from the skarns and pegmatites. Figure 6.8 illustrates the range in $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr content of carbonates formed by mixing marble, and pegmatite, and gneisses and the variation in abundance due to hydrothermal fractionation.

6.3.3 Discussion

Only three skarn samples and one pegmatite have higher strontium isotopic ratios than those in the marble (sample 9G). In all 4 cases, the abundance of strontium is low, hence very susceptible to inheritance by interaction with the syenitic orthogneisses of the Cardiff gneiss dome. For the most part, the strontium abundances and isotopic ratios of calcite in the marbles, skarns, and veins are consistent with simple binary mixing between the pegmatite-derived hydrothermal fluid and the marble. It seems reasonable that the calcite in the veins represents most closely the strontium isotopic ratio of the pegmatites considering the high fluid-rock ratios that would be involved in hydrothermally transporting Ca, Sr and other components which form the fluorite-apatite-calcite veins.

There is only minor covariance of stable carbon and oxygen isotopes with the strontium isotope ratio of calcite. This data is consistent with the chemical interaction of marbles and pegmatites (Figures 6.9 and 6.10). There is a poor negative correlation between in $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio which is consistent with decarbonation accompanying infiltration metasomatism (Figure 6.10). Similarly, the small decrease in $\delta^{18}\text{O}$ with the strontium isotopic ratio is consistent with a metasomatic origin for the calcite (Figure 6.11). In general, there is little or no minor- and trace-element variation with $^{87}\text{Sr}/^{86}\text{Sr}$ content of the calcites. The major- and trace-element systematics of calcite suggest that pegmatite and marble are the principle contributors to the composition of calcite (Figures 6.12, 6.13, and 6.14). Unfortunately, the significant overlap in $^{87}\text{Sr}/^{86}\text{Sr}$ between pegmatites, skarns, and veins precludes a more detailed analysis of the origin of these elements.

The fluorite-apatite-calcite veins and skarns in the Wilberforce area have been previously studied using strontium isotopes. Powell (1965) examined 3 vein samples ($^{87}\text{Sr}/^{86}\text{Sr}$, 0.7049, 0.7047, and 0.7038) and a recrystallized marble (0.7048) from the Cardiff Uranium Mine property. Powell (1965) suggested that the veins were not carbonatites because the strontium isotopic ratio was too radiogenic and that crustal contamination of strontium was unreasonable to account for the radiogenic character of these veins. In a

Table 6.5 Compositional and isotopic variation of calcite from marble, skarn, vein, pegmatite, and carbonatite.

SmpType	CaO wt. %	MgO wt. %	MnO wt. %	FeO wt. %	Zn ppm	Sr ppm	Na ppm	Y ppm	Ba ppm	$\delta^{18}O$	$\delta^{13}C$	Sr*
9C 1	57.8	0.53	0.06	0.32	0	539	132	183	10	21.55	1.47	0.7056
20B 2	54.5	1.18	0.24	1.26	0	1694	275	777	495	14.46	-1.94	0.7048
26B 2	59.0	1.07	0.07	0.80	1	583	143	1023	34	12.34	-1.84	0.7043
9E 3	58.8	0.44	0.09	0.40	1	715	121	169	23	19.71	1.17	0.7066
9J 3	38.3	0.16	0.12	0.81	0	155	33	141	178	22.58	1.53	0.7050
9J-1 3	58.1	0.27	0.17	0.71	5	1221	143	338	19	15.51	-1.77	0.7090
19A 3	49.9	0.33	0.27	0.31	8	4576	407	210	759	14.11	-3.44	0.7040
20C 3	56.9	0.17	0.19	0.92	7	1364	66	201	11	13.82	-2.25	0.7051
26A 3	58.8	0.28	0.09	0.43	5	1529	209	65	32	12.81	-1.47	0.7040
30A 3	52.0	0.42	0.19	0.74	5	1375	132	362	92	16.94	0.30	0.7145
30B 3	55.8	0.43	0.14	0.68	4	1375	242	389	168	16.84	0.23	0.7048
9H 4	59.3	0.06	0.35	0.74	10	1661	176	436	70	9.26	-3.96	0.7042
9L 4	48.3	0.38	0.16	0.89	4	1628	77	362	61	15.19	-2.80	0.7049
10B 4	40.4	0.35	0.35	1.18	6	5280	198	207	53	13.54	-3.93	0.7050
14B 4	49.1	0.28	0.56	1.61	9	1859	99	426	53	8.92	-4.14	0.7045
21B 4	51.9	0.16	0.40	1.05	6	1606	253	464	218	10.91	-4.13	0.7042
27C 4	55.1	0.32	0.11	1.46	5	1650	451	1144	309	14.00	-3.47	0.7054
26G 5	57.2	0.07	0.11	0.36	0	1144	121	136	273	12.44	-1.61	0.7041
121J 5	59.7	0.2	0.29	1.15	3	4400	110	77	107	11.36	-3.04	0.7041
127 5	54.1	0.4	0.42	0.70	32	2190	1000	210	80	13.46	-2.21	0.7053
128 5	51.5	0.6	0.85	0.95	0	158	3600	80	40	8.34	-5.15	0.7202
114-1 6	60.0	0.22	0.13	0.36	4	8030	154	59	77	9.37	-2.88	0.7034

Notes: Type designations: 1 - marbles; 2 - silicated marbles; 3 - skarns; 4 - veins; 5 - pegmatites; 6 - carbonatites.

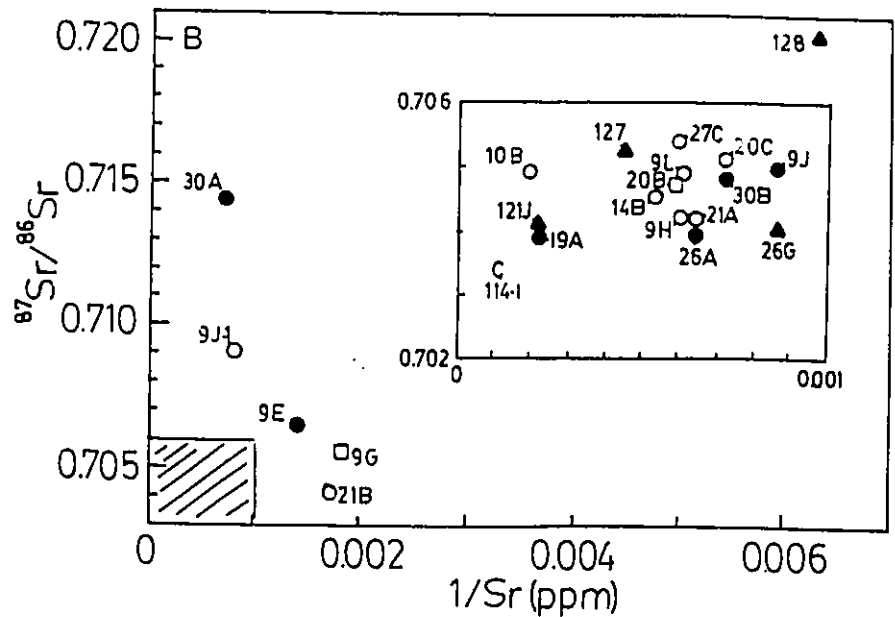
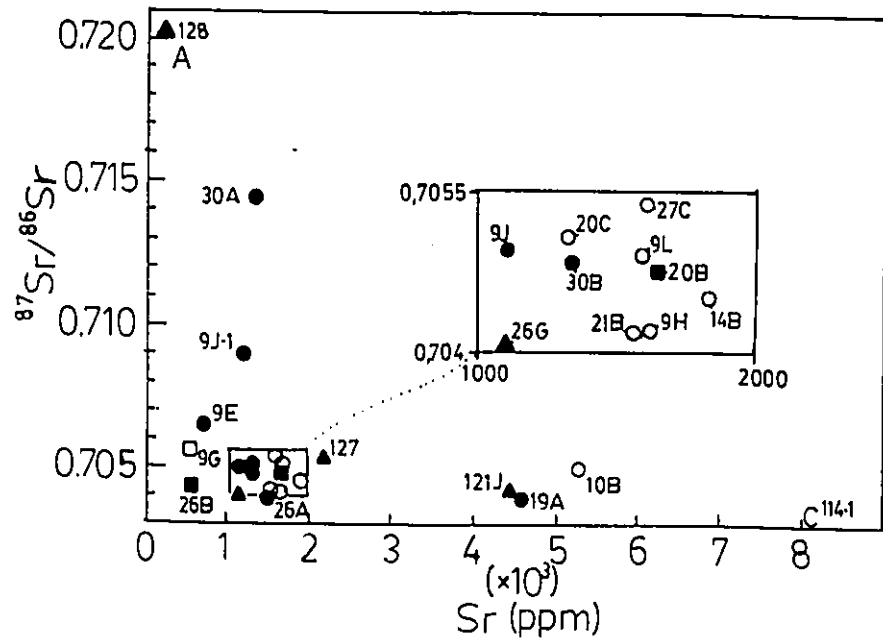


Figure 6.8 A) Plots of $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr (ppm) and B) $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ (ppm) variation of marbles ($\square$), skarns ($\bullet$), silicated marbles ($\blacksquare$), veins ($\circ$), pegmatites ($\blacktriangle$), and carbonatites (C). Numbers denote sample numbers.

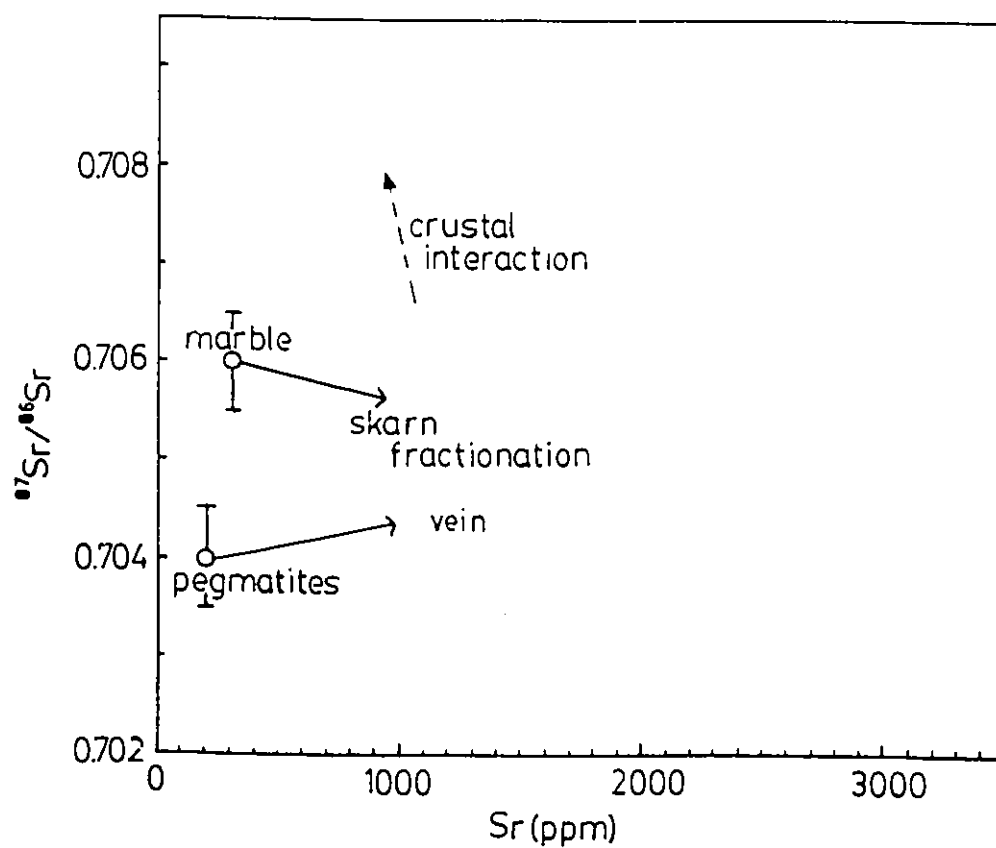


Figure 6.9 Plots of $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr (ppm) showing average values and ranges for pegmatites and marbles in addition to schematic trends resulting from calcite fractionation and crustal interaction.

complimentary study, Gittins et al. (1969) determined 15 strontium isotopic ratios from 10 samples of marbles and skarns in very close association with pegmatites in the Wilberforce-Tory Hill area, Ontario. The samples range from 0.7021 to 0.7090 ($^{87}\text{Sr}/^{86}\text{Sr}$) with an average of 0.7051 ± 0.0011 which are similar to fluorite-apatite-calcite veins determined by Powell (1965) and this study. Although, Gittins et al. (1969) used this as evidence that marbles cannot be distinguished from carbonatites, it does provide proof that skarns and probably the veins were derived from pegmatite-marble interaction and tend towards lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios consistent with low initial $^{87}\text{Sr}/^{86}\text{Sr}$ signatures of uraniferous pegmatites (Rimsaite, 1982; Fowler and Doig, 1983a, this study). Krogh and Hurley (1968) determined the initial strontium isotope ratio of 2 graphite-bearing diopside-scapolite marble skarns (0.7048 and 0.7050) of unknown parentage in the Kingston area. This indicates a lower strontium radiogenic signature than most late Proterozoic marbles indicative of interaction with a more primitive strontium source.

6.4 Pseudocarbonatites and carbonatite isotope systematics As just described, there is some evidence to support a magmatic-hydrothermal origin for these veins related to skarn formation. However, this contradicts the carbonatite hypothesis which has received considerable support in recent years (Dr. Sid Lumbers, personal communication, 1987; Mungall, 1989).

The compositions of the silicate minerals and calcite within the veins are similar to those analysed in pegmatites and skarns. The only element which seems to discriminate between the veins and carbonatites is strontium based on two analyses from the Sullivan Island carbonatite. The vein strontium in calcite seldomly exceeds 2000 ppm, whereas the Sullivan Island carbonatite averages 8000 ppm. This is similar to the average

strontium abundances quoted for carbonatites (6000 to 9000 ppm) (Kaputsin, 1982; Bell and Blenkinsop, 1989; Woolley and Kempe, 1989) and within the range 1000 to 30 000 ppm quoted by Woolley and Kempe, 1989). In carbonatites, the highest strontium abundances are a result of the fractionation of carbonatite melt which results in the very high strontium contents in the most evolved portions of a carbonatite. However, the fluorite-apatite-calcite veins have much lower strontium contents. In addition to the other evidence, stable and radiogenic isotope data provides some ways of discriminating between the magmatic-hydrothermal and carbonatite hypotheses. The stable isotope data for carbonatites is very complex due to post emplacement alteration processes and uncertainty of the temperature of formation (Taylor et al., 1967; Deines and Gold, 1973; Pineau et al., 1973; Galimov et al., 1974; Nelson et al., 1988; Deines, 1989). In a statistical analysis of carbon isotope compositions, Galimov et al. (1974) could discriminate between carbonatites and carbonatite-like silicate-calcite rocks. There is considerable overlap between the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic composition of carbonatites and the data obtained on calcite from pegmatites, skarns, and veins in this study. The Sullivan Island carbonatite (114-1 and 114-2) has carbon and oxygen isotope values which overlap with the pegmatites and veins from this study. The carbon isotope composition seems quite uniform near a value of $\delta^{13}\text{C} = -3$ whereas the $\delta^{18}\text{O}$ ranges from 9.4 and 11.3. This variation may be attributed to carbonatite contamination with the marble host rock in the area. The high strontium abundances of both carbonatites samples 114-1 and 114-2 (8030 and 7760 ppm, respectively) are similar to the average 7000 ppm strontium content of carbonatites quoted by Bell and Blenkinsop (1989). Sample 114-1 has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7034. Bell and Blenkinsop (1987; 1989) indicated that late Proterozoic carbonatites have

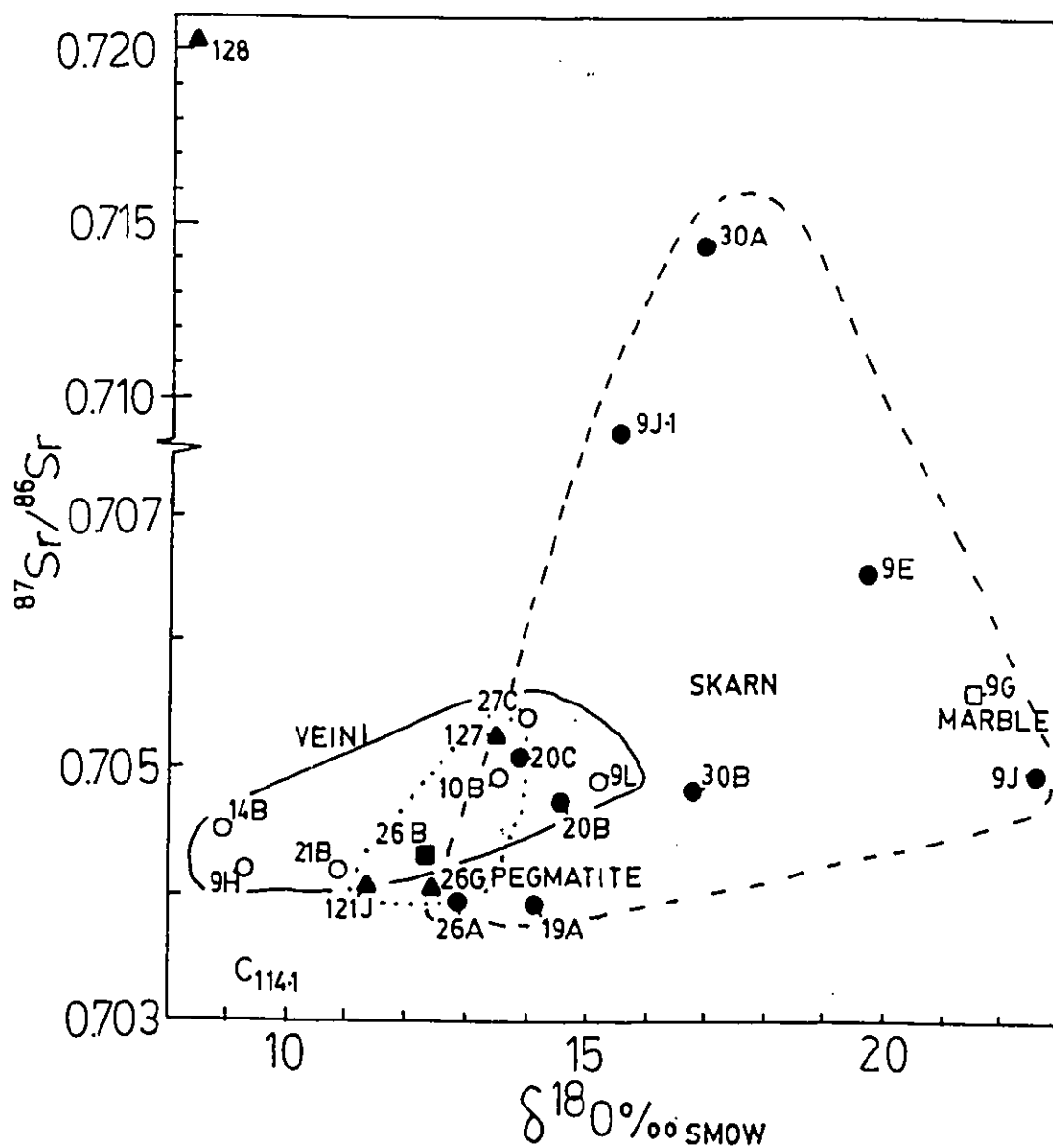


Figure 6.10 Plots of the variation in $\delta^{13}\text{C} \text{‰}$ (PDB) and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition of calcite from marble ($\square$), skarn ($\bullet$), silicated marble ($\blacksquare$), vein ($\circ$), pegmatite ($\blacktriangle$), and carbonatite (C).

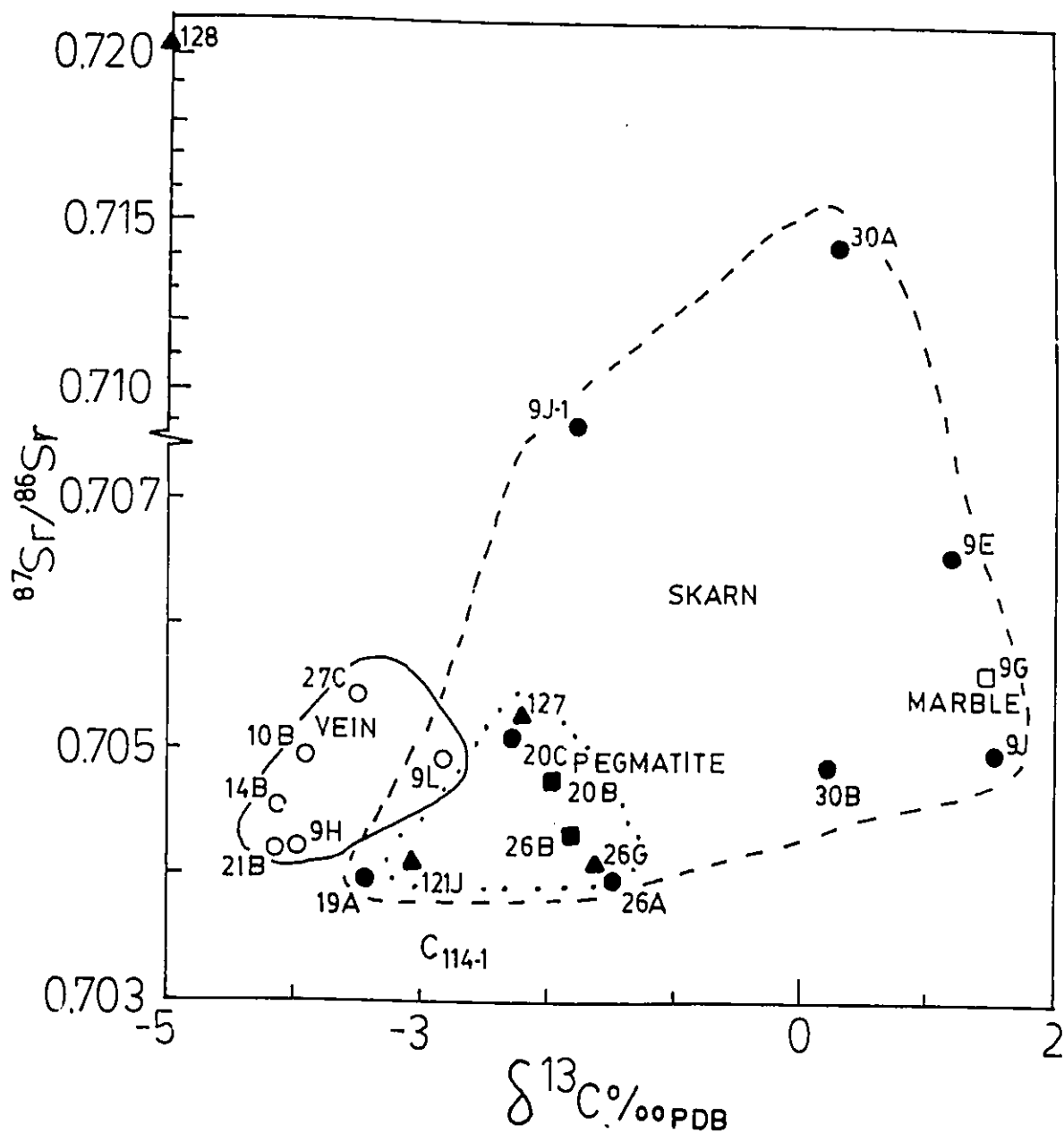


Figure 6.11 Plots of the variation in $\delta^{13}\text{C}$ o/o (SMOW) and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition of calcite from marble (□), skarn (●), silicated marble (■), vein (○), pegmatite (▲), and carbonatite (C).

$^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio between 0.7025 and 0.7035 although there are two North American samples which have a slightly more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio = 0.7037. However, it has been shown in several instances that crustal contamination can be involved in carbonatites (Bell and Blenkinsop, 1989), even though the high abundance of strontium (Powell et al., 1966; Kapustin, 1982; Woolley and Kempe, 1989) generally precludes contamination of radiogenic strontium from crustal sources.

The data obtained in this study shows a discrete, albeit small separation between the strontium isotope ratios of the carbonatite and those from the pegmatites, skarns, and veins. In addition, the Silver Crater apatite-calcite vein closely resembles a carbonatite but the high strontium isotope ratio obtained at this occurrence precludes a carbonatite origin.

6.5 Summary

The stable isotope characteristics within the "unaltered" marbles are typical of Grenville marbles with $\delta^{13}\text{C}$ ranging from -0.1 to 3.2 and $\delta^{18}\text{O}$ ranging from 19.0 to 24.4. Graphite coexisting with calcite had an average carbon isotopic composition 4 ‰ less than the calcite in marble. The calcite from the MacDonald and ACME pegmatites have a $\delta^{13}\text{C}$ = -3.0 to -1.0 and a $\delta^{18}\text{O}$ = 11.5 to 12.5. The silicated marbles and skarns have a range of stable isotopic compositions, which extend from the marbles to the pegmatites and veins. Calcite from the veins has a range of $\delta^{13}\text{C}$ from -5.5 to -2.5, and a $\delta^{18}\text{O}$ range from 8.5 to 15.5 that is isotopically similar to the pegmatite calcite.

The isotopically light carbon in calcite from the skarns and veins seems to have been derived from the oxidization of graphite to CO_2 during skarn formation. Incorporation of light carbon during metasomatic exchange and decarbonation processes precludes a detailed analysis of the CO_2 concentration in skarn- and vein-forming fluids. However, the isotopic data are consistent with petrographic observations

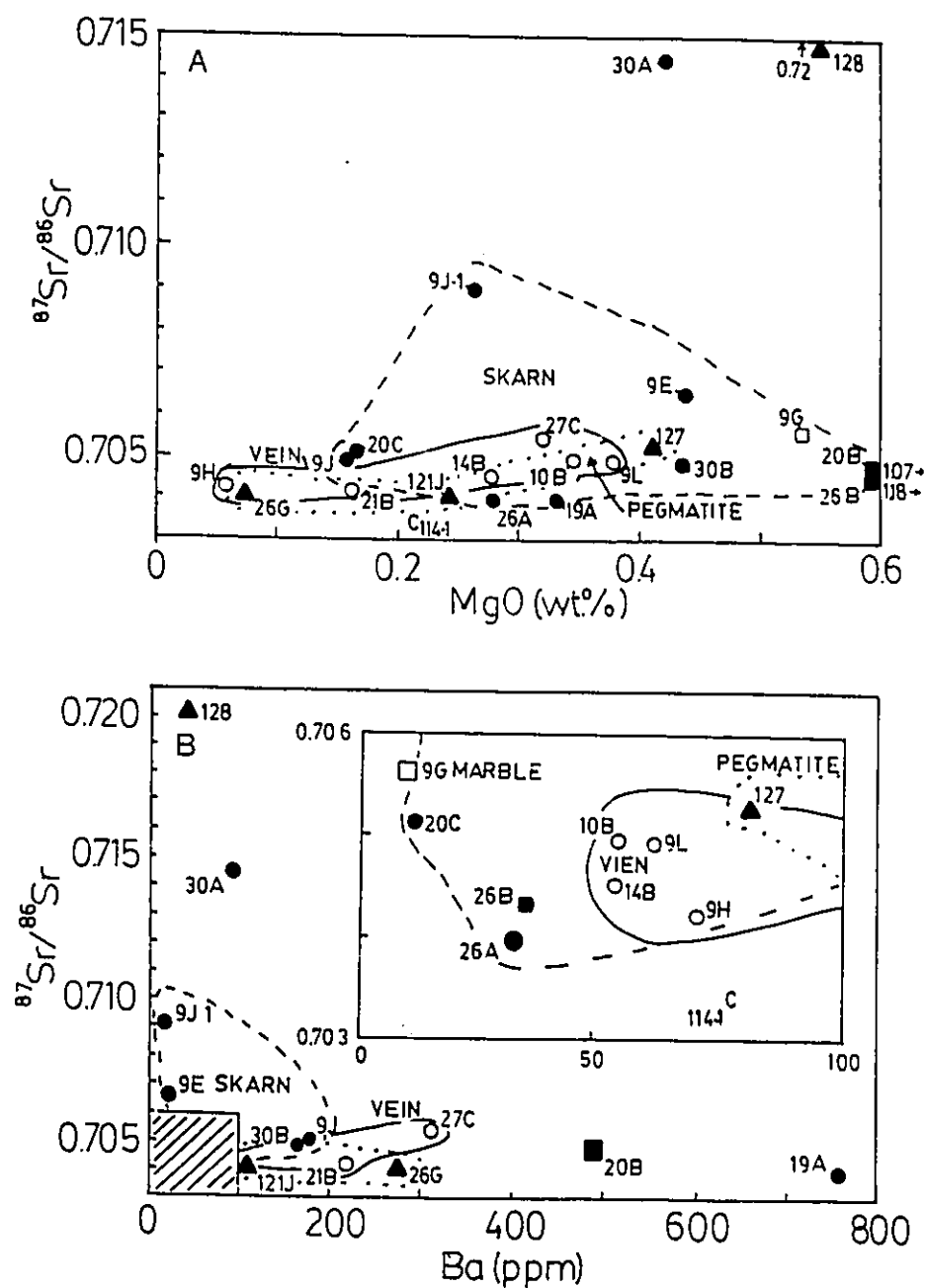


Figure 6.12 A) MgO (wt.%) versus $^{87}\text{Sr}/^{86}\text{Sr}$ and B) BaO (wt.%) versus $^{87}\text{Sr}/^{86}\text{Sr}$ compositional variation of calcites from marble ($\square$), skarn ($\bullet$), silicated marble ($\blacksquare$), vein ($\circ$), pegmatite ($\blacktriangle$), and carbonatite (C).

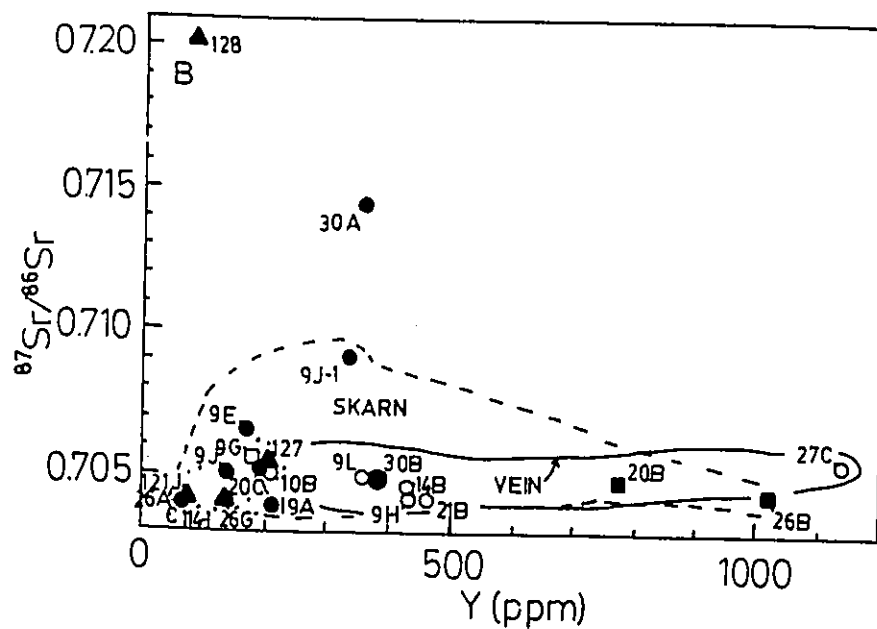
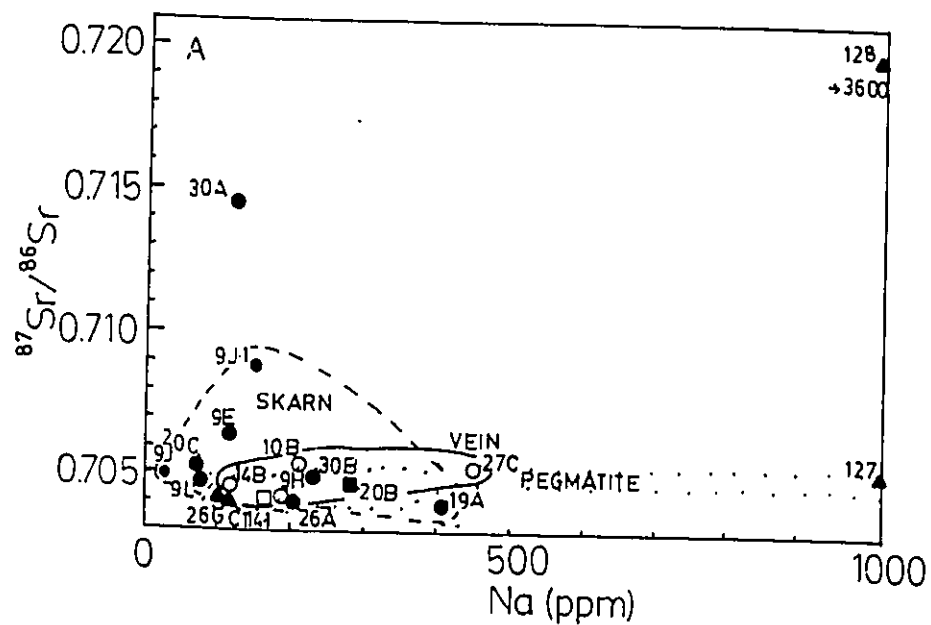


Figure 6.13 Plot of the variation in Na (ppm) and Y (ppm) versus $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in calcites from marble ($\square$), skarn ($\bullet$), silicated marble ($\blacksquare$), vein ($\circ$), pegmatite ($\blacktriangle$), and carbonatite ($\circ$).

that the $X(\text{CO}_2)$ of the metasomatic fluid ranges between 0.20 and 0.50. Preliminary estimates of the (H_2O) fluid/rock ratio for the silicated marbles and skarns are between 2 and 5. Calculated (H_2O) fluid/rock ratios for the calcite veins are greater than 5 to 10.

The covariation of carbon and oxygen isotope data on calcites from the pegmatites, silicated marbles, skarns, and veins are most consistent with metasomatic decarbonation reactions and isotopic exchange of a silicate-bearing, pegmatite-derived fluid with the Grenville marbles.

Strontium isotope ratios in calcite from pegmatites are low ($^{87}\text{Sr}/^{86}\text{Sr} = 0.704$ to 0.705) which is consistent with initial strontium isotope ratios calculated by Fowler and Doig (1983a). Calcite from silicated marbles, skarns, and veins have low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.704 to 0.706), which is slightly less to the same as the marbles. The compositional and stable and radiogenic isotopic data is consistent with a binary mixture of pegmatite and marble facilitated by a skarn forming, pegmatite-derived metasomatic fluid. Calcite saturation may have been responsible for fractional enrichment of strontium within the skarns and veins beyond the abundances found in the pegmatites and marbles.

Unfortunately, stable isotopic data cannot unequivocally discriminate between a pseudocarbonatites and a carbonatite origin for the fluorite-apatite-calcite veins. However, strontium isotopes combined with strontium content and stable isotopes on calcite show that all the data are compatible with a hydrothermal origin related to pegmatite emplacement and skarn formation. The strontium isotopic data obtained in this study compliments earlier work in the Wilberforce area supporting the hypothesis that the veins are genetically related to pegmatitic fluids.

CHAPTER 7

HYDROTHERMAL AND MELT EQUILIBRIA

7.1 Introduction

In order to appreciate the complex genetic considerations involved in metasomatic skarn and fluorite-apatite-calcite vein formation, it is essential to understand the factors affecting solubilities of components involved in these processes. It has been established that the pegmatites were emplaced at approximately 400 Mpa with solidus temperatures between 600° and 650°C. A conservative estimate of the proportion of fluid in the pegmatite near solidification is approximately 10 weight percent (approximately 20 to 25 vol.% of the pegmatite) (Strong, 1988; Lentz and Fowler, in press; appendix 5). Other gas species, HF and HCl, in addition to H₂O may be involved in the complexing of pegmatite components.

7.2 Pegmatite-derived components

The hydrothermal solubility of silicate components, in particular quartz and feldspar, are enhanced by high pressures and high alkali hydroxide concentrations (alkaline conditions) compared to the epizonal environment. Approximately, 1 to 2 wt.% dissolved quartz and feldspar are estimated to be dissolved in a supercritical fluid evolved from crystallizing granitic pegmatites at volatile phase saturation (second boiling) under these temperature and pressure conditions (Anderson and Burnham, 1983). Consequently, 0.1 to 0.2 weight percent of the entire pegmatite body is dissolved in the fluid evolved from the pegmatite.

Salvi (1987) noted the presence of numerous daughter salts in primary fluid inclusions in diopside and apatite from several of these skarns. Salt saturation may be achieved by subcritical separation of vapour and liquid phases at high pCO₂ conditions therefore we can only make very qualitative

estimates of fluid salinity. Burnham (1979) suggested an average of 17 weight percent salt for primary magmatic fluids, which may be applicable to these pegmatites. The presence of dipyre in the proximal exoskarn supports the presence of at least moderate salinities.

The presence of Ca pyroxene, scapolite, feldspars and occasionally quartz in the skarn environment is evidence for the metasomatic introduction of silicates (silica and aluminum) into the exopegmatite environment. There are numerous mechanisms which may be responsible for the deposition of dissolved silicate components from the pegmatite-derived metasomatic fluid including: 1) a decrease in geostatic pressure and temperature in the exopegmatite environment, 2) a decrease $P(\text{H}_2\text{O})$ with increasing CO_2 partial pressure, 3) low solubility of calc-silicate components, and 4) a decrease in alkali hydroxide species in the fluid due to metasomatic exchange with the exopegmatite rocks. In fact, each of these mechanisms may be contributing to the deposition of silicates in the exocontact environment.

In the field, it was noticed that there was a slight increase of iron in skarn and vein minerals, particularly calc-silicates and micas, reflected in their color intensity. Fe-chloride complexes (Whitney et al., 1985) are principally responsible for the introduction of Fe into the exopegmatite environment. Therefore, the partitioning of iron into the vapour phase evolved from the pegmatite would be sufficient to enrich proximal skarns and veins in iron. In at least some instances, the absence of Fe-silicates in the pegmatite could indicate that iron solubilities exceeded the iron content of the pegmatite.

Candela and Holland (1984) determined that molybdenum was principally complexed by hydroxide species and may be enhanced in the presence of alkali ions. Therefore, molybdenum would be partitioned into the pegmatite-derived fluid. Although

speculative, molybdenite deposition may be controlled by high sulphur partial pressures in the exocontact environment. However, changes in pressure, temperature, alkali hydroxide species, and oxidation conditions may all contribute to the deposition of molybdenite in the skarns, veins, and occasionally in the pegmatites. The low fluorine activities calculated from the skarn phlogopites at the Hunt Mo deposit imply that HF does not play a major role in the enrichment of molybdenum in the skarn.

The enrichment of both uranium, and thorium in pegmatites, skarns, and veins indicates that these metals were probably solubilized as tetravalent complexes. Hydroxide and fluoride complexing of tetravalent uranium and thorium (Park and Pohl, 1988) would be responsible for the high solubilities of these species within the pegmatites. Volatile phase saturation and separation from the crystallizing pegmatite would hydrothermally mobilize these metals into the exocontact environment. As discussed earlier, Keppler and Wyllie (1990, 1991) determined that fluorine was responsible for vapour/melt partitioning and hydrothermal complexing of tetravalent thorium and uranium at magmatic temperatures. However, chlorine complexing could only account for the mobility of uranium and not thorium. Although preliminary, the relatively low abundances of uranium and thorium and high abundance of molybdenite in the Hunt skarn may be evidence for fluorine complexing of uranium and thorium.

Holland (1972) has shown that partitioning of some chalcophile metals (Mn, Zn, and Cu) from a granitic melt into an evolving hydrothermal fluid is primarily a function of the chlorine content. The enrichment of Mn and Zn in skarn and vein minerals is evidence for the metasomatic introduction of these elements.

The presence of yttrium and rare-earth elements in skarns and veins, as well as pegmatites, is evidence for the hydrothermal transport of these elements. Yttrium content of

calc-silicates skarns is greater than the marbles and mica that form part of the skarns and veins have yttrium contents approaching the yttrium content of biotite in pegmatites. It is well known from the rare mineralogy of pegmatites, skarns, and veins that REE enriched in the skarns and veins. The presence of allanite, monazite, cyrtolite, pyrochlore mineral, columbite etc. indicate that all REE are complexed to some extent within the pegmatites and mobilized into the skarns and veins. Flynn and Burnham (1978) examined the REE fluid/melt (Spruce Pine pegmatite composition) partition coefficient and various chloride and fluoride concentrations. In all cases investigated, REE partitioned in favour of the melt. However, as silicate crystallization proceeds, fluid/melt ratios and REE contents of the melt possibly changing the K_D and resulting in an increase resulting in higher abundances in REE in the fluid. In a detailed analysis of REE distributions in pegmatites, Fowler and Doig (1983a) concluded that some of the REE were differentially mobilized due to oxidation conditions.

In summary, it seems reasonable to say that supercritical fluids derived from the volatile saturation of the crystallizing granitic pegmatite were responsible for the infiltrative metasomatic transfer of silica, aluminum, alkalis, and iron and rare-metal components in the genetically-related skarns and veins.

7.3 Solubilities of vein constituents

Understanding of mineral solubilities is critical to the study of the petrogenesis of the fluorite-aaptite-calcite veins at the conditions under which they formed. Unfortunately, many of the important parameters influencing the solubility of vein constituents are poorly understood. However, the absence of calcite in numerous silicate-rich skarns is strong evidence for the solution of calcite during skarn formation. Calcite solubility is probably not controlled by changing relative activities of calcium and

carbon dioxide because these parameters are not affected in the veins (ie. solubility product mechanism for calcite deposition). "Whole- mineral" calcite solubilities are suspected to cause the saturation of calcite within the veins. In fact, CO₂ boiling of the H₂O-rich, vein-forming fluid would decrease the CO₂ content of the fluid thus inhibiting calcite saturation if the increase of pH does not counteract the solubility characteristics. However, boiling could produce physiochemical changes in the fluid resulting in calcite saturation and deposition.

It is well known that calcite has a retrograde solubility at low pressure conditions (Sharp and Kennedy, 1965; Holland and Malinin, 1979). However, calcite solubility data (sparse) under low pCO₂ conditions at high pressures with alkali chloride and HCl indicate that calcite has a prograde solubility (> 300 MPa at low chlorinities; Dernov-Pegarev and Malinin, 1976; Dernov-Pegarev and Malinin, 1985; Fein and Walther, 1987, 1989). Preliminary examination of solubility data supports a decrease in temperature responsible for deposition of calcite within the veins with pressure playing a minor role.

Apatite is present predominantly within the veins but some apatite may be found in some silicated marbles and skarns. The phosphorous is probably derived from the exocontact environment (marbles, amphibolites, etc.) although a pegmatite origin cannot be ruled out at present. Although variable, the proportion of apatite to calcite in the veins is commonly 1 to 5. The increase in phosphorous abundance in fluid responsible for the formation of the apatite-calcite veins is enigmatic at present, although an approach to a hydrothermal eutectic may be responsible. Dernov-Pegarev and Malinin (1985) determined that apatite has a prograde solubility and that it is strongly a function of alkali carbonate content of the fluid.

Fluorite occurs in pegmatites, skarns, and veins with calc-

silicates, micas, and occasionally calcite. A solubility product mechanism may be responsible for fluorite saturation in the skarns environment but, analogous to calcite, fluorite deposition within the vein is probably controlled by "whole-mineral" solubilities. A comprehensive study of fluorite solubility was undertaken by Richardson and Holland (1979a and b). It was found that prograde fluorite solubility is directly a function of fluid salinity. A decrease in temperature is most likely responsible for the deposition of fluorite within the veins, whereas pressure seems to have a negligible effect on the solubility.

It is possible that fluctuations in the chemical potentials (μ) of H_2CO_3 , H_3PO_4 , and HF are responsible for the deposition of calcite, apatite and fluorite (Figure 5.7). It is possible that replacement of calcite by apatite or fluorite could occur within the vein by interaction with later fluids with a high $\mu\text{H}_3\text{PO}_4$ (apatite) and/or a high μHF (fluorite).

7.4 Melt equilibria of vein constituents

As discussed previously, the similarity of the fluorite-apatite-calcite veins to carbonatites has led many researchers to suspect that the fluorite, apatite, and calcite crystallized from a melt. The common absence of fluorite and/or apatite in the calcite veins may be construed as evidence for the hydrothermal origin rather than a eutectic melt origin because in many instances they do not represent minimum melt compositions. However, other researchers would simply involve fractionation of apatite or fluorite in the carbonatite magma, therefore it is essential to examine melt equilibria in similar systems. The melt equilibria will be examined from the stand point of crystallization of a carbonatitic magma and/or the possibility of hydrothermally melting of carbonate rocks during skarn formation. It is important to realize that hydrothermal melting of marbles will

only occur if the hydrothermal solubilities of calcite, apatite, and fluorite are exceeded.

The melt equilibria of the CaF_2 - $\text{Ca}(\text{OH})_2$ - CaCO_3 system was investigated by Gittins and Tuttle (1964) in order to evaluate the possibility of melting of limestone in metamorphic terranes. Their data indicate that a melt may be formed at temperatures as low as 550°C at 4 kbar (400 MPa) of a eutectic composition that includes a considerable proportion of portlandite ($\text{Ca}(\text{OH})_2$). However, the binary CaCO_3 - CaF_2 eutectic is approximately 850°C at 400 MPa. Therefore, the presence of portlandite is critical to the limestone melting hypothesis.

The addition of a few percent ($< 5\%$) $\text{Ca}_3(\text{PO}_4)_2$ (apatite) to the CaCO_3 - CaF_2 binary to form eutectic compositions produces a small decrease in temperature of the eutectic composition at 1 kbar (100 MPa) (850°C) but at 400 MPa a melt may be stable to temperatures between 800° and 830°C (Biggar, 1966). There is a considerable decrease in the eutectic composition with the addition of $\text{Ca}(\text{OH})_2$ to 575°C at 1 kbar (100 MPa).

The presence of $\text{Ca}(\text{OH})_2$ is of critical importance to the formation of a melt but there is no portlandite deposited in the veins. However, it is possible that $\text{Ca}(\text{OH})_2$ is converted to CaCO_3 under conditions of high CO_2 partial pressure. But, this is not realistic since portlandite and CO_2 readily form calcite and water which represents the H_2O -saturated, portlandite-absent equilibria. Therefore, it does not seem reasonable that the fluorite-apatite-calcite veins represent products of crystallization of carbonatitic magmas. However, the possibility that these occurrences represent the hydrothermal emanations of carbonatitic magmas must be entertained. As previously discussed, the strontium content is usually much higher in hydrothermal carbonatites by virtue of the fact that Sr^{2+} is a larger ion than Ca^{2+} , therefore behaving as an incompatible element in a carbonatitic melt.

Interestingly however, these calcites have Sr contents 2 to 3 times lower than most carbonatites.

It is interesting to speculate on the hydrothermal melting of Grenville marbles. The interaction of alkali hydroxide species in the pegmatite-derived hydrothermal fluid with the skarn releases $\text{Ca}(\text{OH})_2$, CaCl_2 , $\text{Mg}(\text{OH})_2$, and MgCl_2 etc., which are entrained in the chemically-modified hydrothermal fluid. These components are responsible for the metasomatic alteration of the wall rocks to produce calc-silicates. However, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ constitute a very small percentage of the fluid hence only a small proportion of melt might be produced with a large amount of skarn fluid. As indicated previously, the hydrothermal solubilities of calcite, apatite, and fluorite would undoubtedly exceed any melt fraction that might have been produced.

Preliminary evidence suggests that solubility of the vein constituents is prograde under the pressure and temperature conditions of skarn formation such that a decrease in the temperature during host rock interaction or a decrease in the geostatic pressure of the fluids is responsible for the deposition of these minerals in the veins and possibly in the skarns. The fluid responsible for the transport and deposition of the fluorite, apatite, and calcite within the veins and the complex metasomatic alteration mantling them has compositional, $f(\text{O}_2)$, and isotopic similarities to the pegmatites. If indeed, these fluids are pegmatite-derived chemically-modified skarn fluid, this indicates that high fluid/rock ratios were involved in the formation of the veins.

CHAPTER 8

SUMMARY AND CONCLUSIONS

8.1 Summary

The petrogenesis of the Grenville U-, Th-, Mo-, and REE-bearing pegmatites, silicated marbles, skarns, and veins has been examined by integrating geologic, tectonic, mineralogic, geochemical, geochronologic, and stable and radiogenic isotopic data. The overall objective was to propose a genetic model for skarn and vein formation consistent with all the evidence. There were several specific objectives of this study: 1) attempt to discriminate between the metamorphic-hydrothermal and pegmatite-hydrothermal hypotheses for the formation of the mineralized skarns, 2) characterize the environment in which the skarns were formed, and 3) determine the relationship between the mineralized fluorite-apatite-calcite veins and the skarns. Early on, it became apparent that the petrogenesis of the pegmatites was intimately related to skarn and vein formation hence more information was needed on the pegmatites. The investigation of pegmatite petrogenesis (Chapter 2) is an essential digression from the primary objectives evaluating the origin of the skarns and veins.

The evidence collected thus far is consistent with a petrogenesis of the silicated marbles, skarns, and veins genetically related to the emplacement of rare-metal granitic pegmatites.

Some of the important features of the pegmatites include:

- 1) From a regional and local perspective, there is considerable evidence for the spatial association of pegmatites, skarns, and veins within the Central Metasedimentary Belt of the Grenville Province.
- 2) Geologic, thermochronologic, and geochronologic dating of rare-metal granitic pegmatites, skarns, and veins indicate

that they formed late-tectonically between 1020 Ma and 1050 Ma during isothermal uplift of the Grenville Province.

3) Water-undersaturated partial melting of Grenville quartzofeldspathic gneisses possibly occurred in response to crustal denudation. A combination of partial melting and subsequent fractional crystallization were responsible for rare-metal enrichment of the pegmatite. Volatile phase separation occurred during crystallization of the initially water-undersaturated pegmatitic melt.

4) The rare-metal granitic pegmatites were emplaced into catazonal, middle to upper amphibolite facies rocks at wall rock temperatures of 500° to 550°C and pressures between 300 and 500 Mpa (ave. 400 Mpa).

5) Strontium isotope data from previous studies, plus several isotopic measurements in this study, indicate only a few possible source protoliths for the granitic pegmatites. If Grenville gneisses were the protolith then they either have low residence times in the crust or have low Rb contents. An alternate hypothesis is that the pegmatites are partial melts from the mantle.

In addition to the data on the pegmatites, there is abundant evidence for a pegmatite-related origin for the skarns and veins which includes:

1) The covariation in the abundance of uranium and thorium in pegmatites, skarns, and veins based on radiometric measurements provides qualitative evidence for a geochemical association among these deposits (Lentz, 1991; Appendix 7).

2) Field examination of minerals from pegmatites, skarns, and veins indicates an iron-enrichment trend based on color index. Mineral compositional data on phlogopite/biotite and Ca pyroxene from pegmatites, skarns, veins and marbles reveals minor-element and trace-element variation related to the enrichment of iron. The significance of Fe-enrichment coincident with enrichment in Mn, Ti, Al, Ba, Rb, Y, Zn, and V

is that these elements were derived from the crystallizing pegmatites.

3) The low Mg content of calcite from silicated marbles, skarns, and veins compared to marbles (high Mg and dolomite) is consistent with the interaction of a silica-rich pegmatite-derived fluid with the marbles. The more pronounced enrichments of some elements (Mn, Fe, Sr, and Y) in the skarns, veins, and pegmatites may be due to preferential CaCO_3 deposition (fractionation).

4) Mineral stabilities are compatible with upper amphibolite facies conditions. Primary skarn minerals formed at temperatures between 550 and 575°C and an estimated pressure of 400 MPa. The mineral assemblages of the proximal skarns (Ca pyroxene, phlogopite and/or feldspar and scapolite) were formed at low $X(\text{CO}_2)$ (0.2 to 0.3) conditions. The temperature difference between proximal and distal skarns is small ($< 100^\circ\text{C}$) relative to the epizonal environment because of the high temperature host rock environments in which these skarns are formed. The mineralogical difference between proximal and distal skarns (Ca pyroxene, tremolite, phlogopite, calcite) are probably due to variations in CO_2 partial pressure ($X(\text{CO}_2) = 0.3$ to 0.5).

5) The distribution of major and trace-elements among coexisting phlogopite/biotite, Ca pyroxene, and amphibole is consistent with an approach to equilibrium. There are no obvious differences between elemental distribution for minerals hosted in silicated marbles, skarns, and veins implying similar temperature conditions for these deposits.

6) Irregular elemental distributions between calcite and silicates indicate disequilibrium between the carbonates and silicates in the skarns and the veins. This may be interpreted as a later paragenesis for calcite in some skarns and veins or re-equilibration with later fluids. Low

temperature exchange is not probable because of the differences in the silicate versus carbonate structure.

7) Carbon and oxygen isotopic data was obtained on calcite from marbles, silicated marbles, skarns, and pegmatites. The data is consistent with an infiltrative metasomatic fluid (pegmatite-derived) responsible for decarbonation reactions and isotopic exchange. The $\delta^{13}\text{C}/\delta^{18}\text{O}$ ratio is consistent with an H_2O fluid with a $X(\text{CO}_2)$ between 0.2 and 0.5. Fluid/rock ratios for the skarns and silicated marbles are between 2 and 5 whereas fluid/rock ratios of the veins are generally greater than 5 which, in some instances make them isotopically indistinguishable from the pegmatites. Anomalously light carbon is interpreted to be the result of destabilization of graphite to methane or carbon dioxide during skarn formation.

8) Strontium isotope ratios of calcite from the various environments is consistent with a binary mixing of pegmatite strontium ($^{87}\text{Sr}/^{86}\text{Sr} = 0.704\text{--}0.705$) and with marble strontium ($^{87}\text{Sr}/^{86}\text{Sr} = 0.705\text{--}0.707$). The higher strontium isotopic ratios obtained on a few calcite from skarns and veins are probably due to fluid interaction with radiogenic crustal sources.

Cumulatively, there is formidable evidence for a pegmatite-related origin for these skarns. The chemically-modified fluid involved in skarn formation is responsible for the "fenite-like" alteration mantling the fluorite-apatite-calcite veins. The hydrothermal solubility of vein components is briefly examined.

Although not the primary objective of this study, the discrimination of a carbonatite versus a hydrothermal origin (pseudocarbonatite) for the fluorite-apatite-calcite veins arose in response to the increased popularity of the carbonatite hypothesis of these deposits. The fluorite-apatite-calcite veins examined in this study have many superficial similarities with carbonatites but there are several differences. Textural, temporal, mineralogical,

geochemical, and stable and radiogenic isotope evidence must be considered carefully and include:

- 1) Texturally, the fluorite-apatite-calcite veins are coarse-grained similar to the late-tectonic skarns and pegmatites.
- 2) In all cases, the fluorite-apatite-calcite veins occur near carbonate rocks of the Central Metasedimentary Belt of the Grenville Province.
- 3) There is a spatial association between pegmatites, skarns, and veins in most areas.
- 4) The fluorite-apatite-calcite veins are formed late tectonically concurrent with the skarns and pegmatites based on radiometric dates.
- 5) The fluorite-apatite-calcite veins have numerous minerals in common with the skarns. However, the silicate minerals hosted within the veins and along the selvages are slightly more sodic than the skarns and are more similar to the pegmatites.
- 6) The U, Th, Mo, and REE elements and minerals in the fluorite-apatite-calcite veins are also found in the skarns and the pegmatites.
- 7) There is definitely a difference between strontium content in pegmatites, skarns and veins (< 5000 ppm) whereas the Sullivan Island carbonatite has strontium exceeding 8000 ppm.
- 8) Stable isotope data is consistent with a metasomatic-hydrothermal origin for the fluorite-apatite-calcite veins since many of the stable isotopic characteristic of calcite overlap with the isotopic characteristic of the skarns.
- 9) The strontium isotope ratios of calcites from the veins are identical to those of calcite in pegmatite and skarn. In general, the Silver Crater phlogopite-bearing apatite-calcite vein (most similar to a carbonatite) has strontium isotopes which are very similar to marble values and much different from the Sullivan Island carbonatite from the Grenville Province.

In addition to compositional and isotopic data, the carbonatite melt equilibria for these assemblages were examined. If these assemblages originated as melts the temperatures would exceed 800°C which is not compatible to the observed metasomatic assemblages.

A review of some experimental data indicates that the vein constituents have a prograde solubility under the temperature and pressure conditions of skarn formation (575°C to 525°C & 400 MPa). Therefore, decreasing temperature resulting from host rock interaction and/or decreases in the geostatic pressure of the fluids could be responsible for the deposition of these minerals in the veins and skarns. The fluid responsible for the transport and deposition of the fluorite, apatite, and calcite within the veins and the complex metasomatic alteration mantling them has compositional, $f(\text{O}_2)$, and isotopic similarities to the pegmatites. If, indeed, these fluids were pegmatite-derived, they were chemically-modified skarn fluid due to high fluid/rock ratios involved in the formation of the veins.

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APPENDIX 1

ANALYTICAL METHODS

Appendix 1.1 Sample Preparation

The mineral separates were hand picked after coarse crushing of the hand specimen. A binocular microscope, tweezers, a long needle, and a hand magnet were used in the final stages of hand picking the samples particularly if there were abundant fine inclusions. The mica plates were separated with tweezers but were not pulverized for the fusion determination. Ca pyroxene, amphibole, K-feldspar, plagioclase, apatite, calcite and titanite were pulverized with a ceramic mortar and pestle. The silicate samples were washed in dilute nitric acid until all the calcite was dissolved then washed twice with tap water, and dried under a hot lamp.

A few whole rock samples of pegmatites were crushed in the jaw crusher and pulverized in the tungsten carbide swing mill to less than 200 mesh. The tungsten carbide swing mill may produce slight contamination in Co, Ti, and W.

Appendix 1.2 X-ray Fluorescence Techniques

The X-ray fluorescence disks were prepared by mixing 1.300 grams of powdered sample with 0.433 grams of LiCO_3 and 3.900 grams of $\text{Li}_2\text{B}_4\text{O}_7$ and then fused in platinum crucibles on the Classe fluxer.

X-ray fluorescence (XRF) analyses were performed on fused disks at the University of Ottawa on a Philips PW1410 X.R.F.. This technique provides information on SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MgO , MnO , CaO , Na_2O , K_2O , P_2O_5 , S, Ba, Cr, Zr, Sr, Rb, Y, Nb, Ni, and V composition of the minerals analysed. Duplicate analyses were done in order to test precision of the method and appropriate standard were used to correct for accuracy of the method. The analytical standards include SY-2, GA, DR-N, and BR were used as international standards (Abbey, 1983). A pure carbonate and phosphate were used for Ca, and P

determination in those minerals and BR for the remaining constituents.

Loss on ignition was not determined on these sample because of the small amount of sample in most instances hence the XRF totals were examined with respect to typical anhydrous totals in the mineral being analysed.

Appendix 1.3 Wet Chemical Techniques

Dilute 10% HCl was used to dissolve 0.5 grams of powdered calcite separates, filtered and brought up to 50 ml volumetric. The filter papers with the residue were ashed and reweighed in order to calculate the actual amount of dissolved calcite.

Major- and trace-elements were determined in duplicate on an Atomic Absorbtion Spectroscope (AAS) (Ca, Mg, Mn, Fe, Na, and Sr) and a Direct Current Plasma Spectrometer (DCP) (Y, Ba, and Mo) at the University of Ottawa Geochemical Laboratory. KCl was used as an activating agent for the enhanced detection of selected trace elements.

Appendix 1.4 Ferrous Iron Determinations

Selected micas were analysed in duplicate to determine the ferrous iron content using the ammonium metavanadate titration technique (modified Wilson method; Wilson, 1959) at the University of Ottawa. Ten ml of HF and 5 ml of ammonium meta vanadate was added to 0.2 grams of sample and allowed to digest for 1 to 2 days. The solution was then mixed with boric acid, ferrous ammonium sulfate, a phosphoric and sulfuric acid mixture and back titrated with a potassium dichromate solution. The amount of ferric iron was calculated by difference from the Fe_2O_3 determined by XRF. In general, duplicate determinations are were within 5% of each other.

Appendix 1.5 Strontium Isotopic Determinations

Strontium was separated from calcite separates for isotope analyses using ion exchange chromatography. Calcite samples were digested as previously described and 1 mL of digested

sample was added to glass columns (1.1 cm ID) packed with Bio Rad AG50W-X8 cation exchange resin (200-400 mesh, hydrogen form). The resin was eluted with about 70 mL of 2.5N HCl to remove Ca^{2+} and other ions prior to the elution of the Sr^{2+} fraction with about 30 mL of 2.5N HCl. The 2.5N HCl was prepared from 6.4N distilled HCl. The 2.5 N HCl was prepared from 6.4N distilled HCl provided by Carleton University. The exact volume increment containing the Sr^{2+} fraction was determined for each of the 4 columns used by calibration with suitable Sr standard solution prior to the actual sample separations. The collected solutions were evaporated to dryness at low temperature in teflon evaporation dishes then taken up to 2 mL of 2.5N HCl and transferred to cylindrical teflon sample holders. The solutions were evaporated to dryness, and analysed by a Finnigan-MAT 261 multi-collector mass spectrometer at Carleton University.

Appendix 1.6 Consideration of errors

In conjunction with the analysis of zoning within the micas, sample 6B and the standard BR were run several times (8 & 5) to estimate instrumental errors (Table A1-1). Accuracy and precision errors were determined on the BR rock standard of Centre Recherche Petrographiques et Geochimiques (France; CRPG) (Abbey, 1983) (Table A1-1). The trace-element variation within the BR standard are listed in Govindaraju and de la Roche (1977) and are within the limits of BR analysed at the University of Ottawa XRF laboratory.

The Canmet SY-2 (syenite-2) standard (Abbey, 1983) was used to estimate analytical errors (Table A1-2). The XRF method is accurate for all elements analysed falling within 1 standard deviation of the accepted value in all instances. In addition, the method is also very precise with coefficient of variations less than 1 for the major elements and less than 5 for the trace elements in most instances except for low abundance elements like Cr, Ni, and Zn.

The possible errors in the analysis of mineral separates by XRF include both instrumental errors, sample preparation errors, and possibly sample heterogeneity. It is generally accepted that the trace-elements below 10 ppm have unreliable accuracy although they may be fairly precise (Table A1-1); they value have been quoted in order to convey the extent of possible contamination within the mineral separate. Outer limits of precision should include the possiblility of local variation in composition, ie. sampling precision. Therefore, the variances associated with the Dacey phlogopite (Table A1-3) and the Silver Crater biotite (Table A1-4) were used (where appropriate) for calculation of limits of precision on the distribution coefficients calculated in Chapter 4.3.

Table A1-1 Analysis of Instrumental error

Sample No.	6B 5		BR 8		BR* ave.	(1s)
SiO ₂ wt. %	43.7	± 0.4	38.7	± 0.1	38.39	
TiO ₂	0.19	± 0.02	2.63	± 0.02	2.61	
Al ₂ O ₃	10.63	± 0.06	10.07	± 0.08	10.25	
FeO	2.41	± 0.02	12.86	± 0.04	12.94	
MgO	26.06	± 0.28	13.26	± 0.16	13.35	
MnO	0.12	± 0.02	0.20	± 0.00	0.20	
CaO	0.19	± 0.00	13.77	± 0.06	13.87	
Na ₂ O	0.18	± 0.10	2.95	± 0.04	3.07	
K ₂ O	10.28	± 0.08	1.39	± 0.00	1.41	
P ₂ O ₅	0.01	± 0.02	1.00	± 0.04	1.05	
S	0.05	± 0.00	0.04	± 0.00	0.04	
Total						
Ba ppm	1626	± 40	970	± 20	1050	(125)
Cr	22	± 4	345	± 6	380	(82)
Zr	5	± 4	258	± 6	250	(45)
Sr	5	± 4	1375	± 12	1320	(35)
Rb	1086	± 6	40	± 8	47	(17)
Y	13	± 6	29	± 4	30	(9)
Nb	4	± 2	124	± 3	100	(8)
Zn	326	± 34	156	± 46	150	(42)
Ni	10	± 8	260	± 8	260	(38)
V	2	± 6	213	± 10	240	(24)

* Replicate analysis of disk 6B was used for instrumental error estimates. BR is a CRPG standard run with samples and BR* is the accepted value based on Govindaraju and de la Roche (1977) (1s = quoted standard deviation for traces only between 1970 and 1976); ± = 2s (95% confidence level; Kretz, 1985; Le Maitre, 1982).

Table A1-2 Precision and accuracy of standard SY-2

	SY-2	2s	RV
n	10		
SiO ₂ wt. %	60.1 ± 0.4		60.9
TiO ₂	0.14 ± 0.01		0.15
Al ₂ O ₃	12.23 ± 0.20		12.15
Fe ₂ O _{3t}	6.25 ± 0.07		6.29
MgO	2.69 ± 0.10		2.61
MnO	0.33 ± 0.000		0.32
CaO	7.96 ± 0.12		8.00
Na ₂ O	4.37 ± 0.14		4.35
K ₂ O	4.52 ± 0.08		4.51
P ₂ O ₅	0.43 ± 0.03		0.42
S	0.02 ± 0.02		0.01
Ba ppm	470 ± 10		460
Cr	10 ± 16		10
Zr	269 ± 8		270
Sr	256 ± 14		270
Rb	222 ± 8		220
Nb	-	-	-
Y	123 ± 6		130
Zn	239 ± 64		250
Ni	2 ± 6		10
V	2 ± 3		213

Notes: SY-2 is the syenite standard; RV is the recommended value in Abbey, (1983); ± = 2s (95% confidence level, Kretz, 1985).

Table A1-3 Analysis of concentric zoning in the Silver Crater biotite (sample 27B)

Sample	1	2	3	4	ave.	s
SiO ₂ wt. %	38.7	38.5	39.2	39.1	39.9	0.3
TiO ₂	1.93	2.08	2.18	2.22	2.10	0.13
Al ₂ O ₃	10.92	10.90	11.17	11.10	11.02	0.13
FeO	17.39	17.77	18.18	18.18	17.88	0.36
MgO	13.91	13.63	13.92	13.97	13.86	0.15
MnO	0.85	0.86	0.88	0.88	0.87	0.02
CaO	0.11	0.04	0.05	0.05	0.06	0.03
Na ₂ O	0.51	0.50	0.63	0.61	0.56	0.07
K ₂ O	9.36	9.26	9.45	9.41	9.37	0.08
P ₂ O ₅	0.02	0.01	0.01	0.01	0.01	0.01
S	0.02	0.00	0.02	0.01	0.01	0.02
Total	94.1	93.9	96.0	95.8	94.9	
Ba ppm	1010	940	890	860	930	65
Cr	78	82	81	91	83	6
Zr	0	4	0	3	2	3
Sr	4	0	4	0	2	3
Rb	482	476	493	490	484	9
Y	11	0	0	0	0	
Nb	96	107	113	114	108	8
Zn	692	599	621	616	632	41
Ni	0	0	0	0	0	
V	114	111	121	117	116	4

Notes: 1 = outer zone, 4 = inner zone. ave. = average of 4 samples, s is an estimate of the standard deviation.

Table A1-4 Analysis of concentric zoning in the Dacey phlogopite

Sample	2	3	4	5	6	7	8	9	ave.	2s
SiO ₂ wt. %	41.5	41.7	41.1	41.1	40.9	40.6	40.5	40.9	41.0	± 0.8
TiO ₂	1.60	1.55	1.56	1.64	1.60	1.58	1.58	1.46	1.57	± 0.10
Al ₂ O ₃	13.03	13.07	13.18	13.03	13.13	13.10	12.78	12.74	13.10	± 0.32
FeO	3.42	3.44	3.39	3.41	3.40	3.40	3.30	3.30	3.38	± 0.12
MgO	23.98	23.78	23.99	23.69	23.92	23.75	23.48	24.21	23.85	± 0.44
MnO	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	± 0.00
CaO	0.38	0.28	0.24	0.25	0.26	0.29	0.34	0.46	0.31	± 0.16
Na ₂ O	0.34	0.35	0.28	0.33	0.36	0.31	0.32	0.27	0.32	± 0.06
K ₂ O	9.90	9.93	10.03	9.95	9.97	9.99	9.83	10.03	9.95	± 0.14
P ₂ O ₅	0.01	0.01	0.01	0.01	0.01	0.02	0.00	0.01	0.01	± 0.02
S	0.02	0.02	0.01	0.02	0.01	0.03	0.02	0.02	0.02	± 0.02
Total	94.8	94.7	94.5	94.0	94.2	93.7	92.7	93.9	94.1	
Ba ppm	3750	3900	3920	3930	3890	3890	3680	3190	3770	± 500
Cr	37	42	39	46	38	38	32	23	36	± 14
Zr	7	4	5	9	9	5	6	3	7	± 4
Sr	33	42	43	49	40	42	33	29	39	± 14
Rb	672	686	689	698	700	704	676	693	689	± 22
Y	2	0	5	7	5	7	6	11	5	± 6
Nb	101	102	105	115	112	116	104	76	104	± 26
Zn	334	311	343	281	301	348	311	329	320	± 46
Ni	0	0	0	5	0	2	0	2	1	± 4
V	15	22	18	12	12	22	13	16	16	± 8

Notes: Sample number 1 was omitted due to contamination with quartz; ave. = average of 8 analyses; ± = 2s (95% confidence level; Kretz, 1985; Le Maitre, 1982).

Table A1-5 Comparison of XRF and AA technique for the analysis of calcite separates

Sample	61D-1 XRF	61D-1 AA
SiO ₂	0.07	NA
TiO ₂	0.00	NA
Al ₂ O ₃	0.02	NA
FeO	0.25	0.25
MgO	1.56	1.4
MnO	0.08	0.08
CaO	54.2	58.1
Na ₂ O	0.31	0.005
K ₂ O	0.01	NA
P ₂ O ₅	0.00	NA
S	0.05	NA
Total	56.9	
Ba ppm	90	18
Cr	0	NA
Zr	32	NA
Sr	2480	2350
Rb	0	NA
Y	89	66
Nb	0	NA
Zn	8	5
Ni	0	NA
V	0	NA

Notes: NA = not analysed

APPENDIX 2

Appendix 2.1 Sample descriptions

Sample No.	Description
88-DL-4B	mt-bi granite pegmatite
88-DL-6A	phl-cc-cpx skarn vein
88-DL-6B	phl-cpx skarn zone
88-DL-9A	phl-cpx skarn vein
88-DL-9E	gr-zr-ti-phl-cc-cpx skarn
88-DL-9F	gr-cc-phl-trem skarn vein
88-DL-9G	gr-phl-cc(dol) marble
88-DL-9H	ap-fl-cc vein
88-DL-9J	allanite-gr-cc-phl-cpx-scaph skarn
88-DL-9J1	cc-phl-cpx skarn vein
88-DL-9J'	bi-ap-fl-cc vein
88-DL-9K-1	gr-chondrodite-phl-cc(dol) marble
88-DL-9L	phl-scaph-fl-ap-cc vein
88-DL-9M	gr-phl-chondrodite-cc(dol) marble
88-DL-10B	phl-ap-cc vein
88-DL-10C	phl-cc-tr skarn vein
88-DL-14A	Kfs-hb-fl-ap-cc vein
88-DL-14B	hb-fl-ap-cc vein
88-DL-14D	bi-hb-fl-ap-cc vein
88-DL-19A	cc-ap-tr skarn
88-DL-19C-1	phl-tr-skarn vein
88-DL-19C-2	phl-cc skarn
88-DL-19C-3	cc marble 5cm away from skarn vein
88-DL-19D	cc-phl-tr skarn vein
88-DL-20B	zr-gr-py-ti-cpx-ap-cc silicated marble
88-DL-20C	fl-ap-cc-cpx-scaph skarn/vein
88-DL-21A	cpx-fl-ap-cc vein
88-DL-21B	zr-mt-py-bi-Kfs-cc vein
88-DL-22B	fl-cpx-scaph-Kfs skarn/pegmatite
88-DL-22C	cpx-fl-ap-cc vein
88-DL-26A	phl-cpx-scaph-cc skarn
88-DL-26B	ti-cpx-cc silicated marble
88-DL-26F	cc vein in core of pegmatite
88-DL-26G	cc vein in core of pegmatite
88-DL-26H	cc vein in core of pegmatite
88-DL-27B	phl-(ap)-cc vein
88-DL-27C	phl-hbld-scaph-cc vein
88-DL-28C-1	phl-Kfs-ap-cc vein in cpx-scaph skarn
88-DL-30A	cpx-scaph-phl-cc skarn
88-DL-30B	phl-cc skarn
88-DL-30C	phl-cpx-cc skarn
88-DL-30E	gr-phl-cc skarn
88-DL-50A	phl-cc(dol) marble
88-DL-50B	phl-cc skarn
88-DL-50C	py-phl-cc-cpx skarn
88-DL-50D-1	phl-cpx-cc skarn

88-DL-50E	py-cpx skarn
88-DL-50F	py-cc-phl-tr skarn
88-DL-50J	py-cpx-cc skarn
88-DL-50L	py-bi-cc silicated marble
88-DL-50M	py-po-bi-cpx-cc skarn
88-DL-50N	phl-cc skarn vein in skarn
88-DL-50O	py-po-cpx-phl-cc skarn
88-DL-50P	gr-phl-cc marble
88-DL-50Q	py-cc-phl skarn vein
88-DL-50R-1	cc-phl skarn vein in skarn
88-DL-50R-2	gr-ap-cpx-phl silicated marble
88-DL-57B	phl-ap-fl-cc vein
88-DL-60	ap-cpx-cc vein
88-DL-60A	cpx-fl-ap-cc vein
88-DL-60B	qz-cc vein
88-DL-60D	cpx-fl-ap-cc vein
88-DL-60D-1	cpx-fl-ap-cc vein
88-DL-60G	cpx-fl-ap-cc vein
88-DL-61A	phl-trem-scaph skarn
88-DL-61C-1	cpx-phl-cc silicated marble
88-DL-61D-1	phl-cpx-cc silicated marble
88-DL-62A-1	ti-phl-cpx-scaph skarn
88-DL-62B	fl-phl-cc skarn vein
88-DL-62C-1	cpx-phl-cc skarn
88-DL-62D-1	cpx-cc silicated marble
88-DL-62E	phl-cc-cpx-scaph skarn
88-DL-62F	cc-phl cpx skarn
88-DL-62F-1	cpx-cc-phl skarn
88-DL-64C	cc-phl-cpx skarn
88-DL-64D	Mo-bearing, cpx-scaph-cc vein
88-DL-65A	py-phl-cc-cpx-scaph skarn
88-DL-65B	Mo-bearing, cc-pl-cpx skarn
88-DL-66C	cc-phl-cpx skarn
88-DL-66C-2	phl-cc skarn in skarn
88-DL-66D	chondrodite-phl-cc skarn
88-DL-66E	cc-phl-tr skarn vein in scaph-cpx skarn
88-DL-66H	py-phl-cc-scaph-cpx skarn vein
88-DL-70D	phl-qz-cc skarn vein in skarn
88-DL-70F	phl-scaph-cpx skarn
88-DL-70G	qz-cc-phl vein in cpx skarn
88-DL-70H	qz-cc-phl vein in skarn
88-DL-70I	qz-cc-phl vein in skarn
88-DL-70J	qz-phl-cc vein in skarn
88-DL-70K	ti-phl-scaph-cpx skarn vein
88-DL-70M	cc-phl-cpx skarn
88-DL-70N	phl-cpx-scaph skarn
88-DL-108-1	ap-cc-cpx vein in cpx skarn
88-DL-108-2	cc-phl-cpx skarn
88-DL-108-3	ti-cpx-phl-cc skarn
88-DL-108-4	phl-cpx skarn
88-DL-108-5	phl-cc silicated marble
88-DL-112B-3	py-cc skarn vein in silicated marble

88-DL-112C	gr-phl marble
88-DL-113-1	phl skarn
88-DL-113-3	phl-cpx-cc skarn
88-DL-113-4	ap-cc skarn? vein in clinopyroxenite
88-DL-113-5	ap-cc-phl-tr skarn vein in marble
88-DL-113-6	ap-phl-cc vein/skarn in amphibolite
88-DL-114-1	ap-mt-phl-cpx-cc carbonatite
88-DL-114-2	ap-cc carbonatite
88-DL-116C	biotite granitic pegmatite
88-DL-117E	biotite granitic pegmatite
88-DL-120B	biotite granitic pegmatite
88-DL-120C	biotite granitic pegmatite
88-DL-121H	Mo-bearing, cc-bi-Kfs pegmatite
88-DL-121I	mt-cc-ap-bi-Kfs pegmatite
88-DL-121J	ap-cc-bi vein in pegmatite
88-DL-122A	fl-bi-Kfs pegmatite
88-DL-122C	bi granite pegmatite
88-DL-124-4	allanite-fl-bi-granitic pegmatite
88-DL-124-7	biotite granitic pegmatite
88-DL-124-8	biotite-plag pegmatite
88-DL-126 collection)	cc-fs pegmatite (GSC sample, Robinson
88-DL-127 collection)	cc-fs pegmatite (GSC sample, Robinson
88-DL-128 collection)	cc-fs pegmatite (GSC sample, Robinson
223-57	phl marble (Kretz, 1980)
329-56	phl marble (Kretz, 1980)
1113-57	phl marble (Kretz, 1980)
1311-5B	phl marble (Kretz, 1980)
1374-3	phl marble (Kretz, 1980)
1423-80	bi in gneiss (Kretz sample)
GT1-5	bi-cc silicated marble

APPENDIX 3

Appendix 3.1a

Chemical composition of trioctahedral mica (XRF) with chemical formulas calculated with minfile program.

Sample Type	9G 1	9M 1	50P 1	66D 1	113-57 1	311-5B 1	1374-3 1	329-56 1	GT1-5 2	50L 2
wt. %										
SiO ₂	42.4	43.0	40.3	40.5	40.7	40.7	41.6	40.9	41.5	41.5
TiO ₂	0.14	0.09	0.66	0.17	0.93	0.45	0.97	0.34	0.98	0.48
Al ₂ O ₃	11.01	11.01	14.14	13.85	13.62	12.09	13.67	12.66	13.80	12.87
FeOt	1.81	0.69	0.95	0.56	3.93	4.93	2.79	0.96	2.68	2.75
MnO	0.01	0.01	-	0.02	0.01	0.05	0.01	0.01	-	0.02
MgO	25.74	27.55	26.38	29.36	24.26	24.12	25.43	27.90	25.32	26.12
BaO	0.17	0.14	0.39	0.85	0.59	0.50	0.06	0.43	0.36	0.23
CaO	0.22	0.57	0.46	0.83	0.16	0.18	0.18	0.29	0.10	0.06
Na ₂ O	0.77	0.37	1.00	1.72	0.17	0.28	0.01	1.01	0.10	0.58
K ₂ O	9.34	9.83	8.81	8.18	9.93	9.66	10.38	8.78	10.03	9.85
Rb ₂ O	0.10	0.02	0.03	0.04	0.05	0.08	0.01	0.09	0.04	0.10
H ₂ O*	3.76	3.80	3.80	3.84	3.72	3.72	3.75	3.82	3.75	3.75
Total	95.4	97.1	96.9	99.9	98.1	96.8	98.8	97.2	98.7	98.4
S wt. %	0.05	0.02	0.01	0.06	0.05	0.05	0.04	0.05	0.01	0.05
Ba ppm	1480	1250	3470	7550	5250	4440	526	3810	3230	2080
Cr	12	27	85	66	58	22	63	34	49	39
Zr	8	23	188	100	19	4	15	-	11	-
Sr	16	7	69	418	3	55	-	89	10	16
Rb	870	220	285	321	440	761	129	840	334	957
Y	22	2	5	17	5	5	3	2	-	8
Nb	6	-	5	4	9	3	7	6	11	5
Zn	188	86	106	240	234	433	116	69	283	221
Ni	28	-	4	-	58	4	4	6	-	12
V	-	11	171	74	80	5	138	47	75	31
#Si IV	7.09	7.00	6.56	6.33	6.70	6.80	6.73	6.61	6.72	6.75
#Al IV	0.91	1.00	1.44	1.67	1.30	1.20	1.27	1.39	1.28	1.25
T site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
#Al VI	1.26	1.11	1.28	0.88	1.33	1.18	1.33	1.03	1.36	1.21
#Ti VI	0.02	0.01	0.08	0.02	0.11	0.06	0.12	0.04	0.12	0.06
#Fe +2	0.25	0.09	0.13	0.07	0.54	0.69	0.38	0.13	0.36	0.37
#Mn +2	0.00	0.00	-	0.00	0.00	0.01	0.00	0.00	-	0.00
#Mg	6.42	6.68	6.40	6.84	5.94	6.01	6.13	6.72	6.12	6.33
O site	7.95	7.89	7.89	7.81	7.93	7.94	7.97	7.92	7.96	7.97
#Ba	0.01	0.01	0.02	0.05	0.04	0.03	0.00	0.03	0.02	0.01
#Ca	0.04	0.10	0.08	0.14	0.03	0.03	0.03	0.05	0.02	0.01
#Na	0.25	0.12	0.32	0.52	0.05	0.09	0.00	0.32	0.03	0.18
#K	1.99	2.04	1.83	1.63	2.08	2.06	2.14	1.81	2.07	2.04
#Rb	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.01
A site	2.30	2.27	2.25	2.34	2.21	2.22	2.18	2.21	2.15	2.26
#O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
#OH	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite, 7- gneiss; FeOt denotes total Fe expressed as FeO; H₂O calculated using minfile program; Trace-element contents below 10 ppm are precise but the accuracy is questionable; - below detection limit.

Appendix 3.1b

Chemical composition of trioctahedral mica (XRF) with
chemical formulas calculated with minfile program.

Sample Type	50R-2 2	61C-1 2	61D 2	62D-1 2	6B 3	9A 3	9C 3	9F 3	9I 3	9J-1 3
wt. %	---	---	---	---	---	---	---	---	---	---
SiO ₂	40.0	41.9	42.8	42.2	43.4	42.9	43.7	42.6	41.6	43.1
TiO ₂	0.55	0.07	0.04	0.04	0.19	0.66	0.14	0.16	0.56	0.67
Al ₂ O ₃	14.72	11.65	11.81	11.06	10.56	11.38	10.70	11.43	10.89	11.46
FeOt	3.71	0.94	0.73	1.60	2.15	6.55	2.18	1.74	6.68	6.61
MnO	0.03	0.02	0.01	0.02	0.12	0.11	0.12	0.02	0.08	0.10
MgO	24.32	26.99	27.58	27.26	25.29	21.26	25.61	25.58	21.30	21.40
BaO	0.43	0.42	0.30	0.29	0.18	0.19	0.17	0.15	0.19	0.19
CaO	0.36	0.22	0.28	0.19	0.19	0.26	0.24	1.28	0.49	0.11
Na ₂ O	0.31	0.55	0.65	0.45	0.28	0.22	0.23	0.86	0.12	0.18
K ₂ O	9.88	9.59	9.71	9.48	10.21	9.80	10.10	8.76	9.84	9.89
Rb ₂ O	0.08	0.08	0.09	0.16	0.12	0.12	0.13	0.08	0.14	0.14
H ₂ O	3.73	3.79	3.79	3.79	3.73	3.65	3.74	3.78	3.65	3.65
Total	98.1	96.2	97.8	96.6	96.4	97.1	97.1	96.4	95.5	97.5
S wt. %	0.03	0.01	0.01	0.02	0.05	0.04	0.04	0.05	0.03	0.02
Ba ppm	3860	3730	2680	2560	1600	1710	1510	1330	2140	1720
Cr	38	21	-	10	20	126	27	20	-	119
Zr	85	3	15	-	6	-	12	6	66	-
Sr	31	111	80	74	7	11	10	37	29	11
Rb	686	708	795	1424	1075	1115	1142	760	1241	1264
Y	9	5	12	11	12	5	11	29	262	12
Nb	14	-	-	-	4	24	4	3	42	28
Zn	299	97	75	89	338	343	308	106	315	336
Ni	6	9	7	11	8	17	14	10	63	17
V	123	7	-	15	-	46	15	24	28	56
#Si IV	6.55	6.90	6.92	6.92	7.24	7.27	7.22	7.01	7.17	7.27
#Al IV	1.45	1.10	1.08	1.08	0.76	0.73	0.78	0.99	0.83	0.73
T site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
#Al VI	1.39	1.16	1.18	1.06	1.32	1.54	1.30	1.23	1.38	1.55
#Ti VI	0.07	0.01	0.00	0.00	0.02	0.08	0.02	0.02	0.07	0.09
#Fe +2	0.51	0.13	0.10	0.22	0.30	0.93	0.30	0.24	0.96	0.93
#Mn +2	0.00	0.00	0.00	0.00	0.02	0.02	0.02	0.00	0.01	0.01
#Mg	5.94	6.63	6.65	6.66	6.29	5.37	6.31	6.28	5.47	5.38
O site	7.91	7.93	7.93	7.95	7.95	7.94	7.95	7.76	7.90	7.97
#Ba	0.03	0.03	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01
#Ca	0.06	0.04	0.05	0.03	0.03	0.05	0.04	0.23	0.09	0.02
#Na	0.10	0.18	0.20	0.14	0.09	0.07	0.07	0.27	0.04	0.06
#K	2.06	2.02	2.00	1.98	2.17	2.12	2.13	1.84	2.16	2.13
#Rb	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.02
A site	2.26	2.27	2.28	2.19	2.32	2.26	2.27	2.36	2.32	2.24
#O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
#OH	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite, 7-gneiss; FeOt denotes total Fe expressed as FeO; H₂O calculated using minfile program; Trace-element contents below 10 ppm are precise but the accuracy is questionable; - below detection limit.

Appendix 3.1c

Chemical composition of trioctahedral mica (XRF) with
chemical formulas calculated with minfile program.

Sample Type	9J 3	19C-1 3	19C-2 3	19D 3	28C-1 3	30A 3	30B 3	30C 3	50B 3	50C 3
wt. %										
SiO ₂	42.2	42.0	42.3	42.7	41.1	44.7	44.7	44.6	40.6	37.9
TiO ₂	0.39	0.12	0.11	0.27	1.18	0.56	0.54	0.56	0.73	1.46
Al ₂ O ₃	12.05	12.03	11.53	11.23	11.57	9.84	9.65	9.56	14.08	14.24
FeOt	2.77	1.21	1.00	1.86	11.91	3.99	3.59	3.65	1.76	11.77
MnO	0.01	0.04	0.03	0.07	0.08	0.06	0.03	0.04	0.01	0.10
MgO	25.17	26.02	25.91	26.30	18.75	23.14	23.09	23.27	25.40	19.44
BaO	0.38	0.26	0.19	0.11	0.08	0.13	0.13	0.13	0.41	0.41
CaO	0.69	0.14	0.21	0.13	0.63	0.20	0.18	0.28	1.05	0.58
Na ₂ O	0.29	0.65	0.63	0.56	0.28	-	0.27	0.23	0.45	0.13
K ₂ O	8.97	9.52	9.46	9.97	9.40	9.86	9.80	9.92	9.02	9.00
Rb ₂ O	0.07	0.08	0.07	0.11	0.08	0.23	0.18	0.15	0.04	0.09
H ₂ O	3.78	3.77	3.78	3.76	3.58	3.69	3.69	3.69	3.79	3.63
Total	96.8	95.9	95.2	97.1	98.7	96.4	95.8	96.1	97.3	98.7
S wt. %	0.01	0.03	0.03	0.03	0.03	0.05	0.05	0.03	0.04	0.04
Ba ppm	3360	2300	1710	990	720	1120	1190	1120	3650	3660
Cr	11	17	73	18	15	17	25	30	48	37
Zr	57	73	-	-	14	785	-	9	85	32
Sr	8	23	19	13	19	12	10	10	18	22
Rb	665	746	645	994	752	2073	1666	1400	318	805
Y	819	5	8	10	19	23	28	19	8	8
Nb	-	24	17	34	108	82	89	87	11	2
Zn	184	237	245	350	368	386	334	299	140	603
Ni	100	4	186	6	10	48	33	34	6	2
V	10	37	-	-	97	16	9	14	152	112
#Si IV	6.93	6.98	7.07	7.04	6.98	7.54	7.59	7.56	6.60	6.35
#Al IV	1.07	1.02	0.93	0.96	1.02	0.46	0.41	0.44	1.40	1.65
T site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
#Al VI	1.26	1.33	1.34	1.22	1.29	1.50	1.52	1.47	1.30	1.16
#Ti VI	0.05	0.01	0.01	0.03	0.15	0.07	0.07	0.07	0.09	0.18
#Fe +2	0.38	0.17	0.14	0.26	1.69	0.56	0.51	0.52	0.24	1.65
#Mn +2	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.01
#Mg	6.16	6.44	6.45	6.45	4.74	5.82	5.85	5.88	6.16	4.86
O site	7.85	7.96	7.95	7.97	7.88	7.96	7.96	7.94	7.79	7.87
#Ba	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.03
#Ca	0.12	0.02	0.04	0.02	0.11	0.04	0.03	0.05	0.18	0.10
#Na	0.09	0.21	0.20	0.18	0.09	-	0.09	0.08	0.14	0.04
#K	1.88	2.02	2.02	2.09	2.03	2.12	2.12	2.15	1.87	1.92
#Rb	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.00	0.01
A site	2.12	2.28	2.28	2.31	2.25	2.19	2.28	2.30	2.23	2.11
#O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
#OH	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite, 7-gneiss; FeOt denotes total Fe expressed as FeO; H₂O calculated using minfile program; Trace-element contents below 10 ppm are precise but the accuracy is questionable; - below detection limit.

Appendix 3.1d

Chemical composition of trioctahedral mica (XRF) with
chemical formulas calculated with minfile program.

Sample Type	50D-1 3	50F 3	50M 3	50N 3	50O 3	50Q 3	50R-1 3	61A 3	62A-1 3	62B 3
wt. %										
SiO ₂	39.9	40.6	40.2	40.5	41.0	41.7	39.4	40.6	41.7	42.1
TiO ₂	1.48	0.31	0.96	0.82	0.31	0.30	0.40	0.06	0.23	0.15
Al ₂ O ₃	14.64	15.47	14.06	15.48	14.13	12.16	15.33	13.26	12.00	11.70
FeOt	5.66	1.12	4.11	0.22	0.72	1.44	3.64	1.01	3.50	3.14
MnO	0.05	1.00	0.05	0.01	0.01	0.02	0.03	0.03	0.08	0.07
MgO	22.78	26.09	24.01	26.43	26.83	26.97	24.20	26.41	24.68	25.05
BaO	0.40	0.10	0.41	0.48	0.44	0.34	0.47	0.68	0.37	0.37
CaO	0.43	0.18	0.17	0.08	0.10	0.22	0.12	0.35	0.23	0.70
Na ₂ O	0.28	1.12	0.34	0.98	1.35	0.25	0.43	0.87	0.29	0.13
K ₂ O	9.38	8.67	9.69	9.21	8.77	9.86	9.88	9.17	10.08	9.90
Rb ₂ O	0.09	0.05	0.08	0.05	0.05	0.08	0.08	0.05	0.07	0.11
H ₂ O	3.70	3.81	3.72	3.80	3.80	3.79	3.73	3.79	3.72	3.74
Total	98.8	98.5	97.8	98.0	97.5	97.2	97.7	96.3	97.0	97.2
S wt. %	-	2.00	0.03	0.02	0.04	0.04	0.04	0.03	0.01	0.02
Ba ppm	3560	860	3620	4300	3930	3080	4180	6030	3300	3300
Cr	7	4	31	19	20	22	14	23	21	21
Zr	4	-	120	10	14	123	72	4	-	-
Sr	28	6	24	70	28	37	26	461	405	38
Rb	842	440	759	425	471	687	687	469	64	986
Y	15	6	8	6	6	7	6	4	214	7
Nb	4	6	14	14	10	4	14	8	-	2
Zn	372	175	322	81	80	115	279	111	266	290
Ni	3	-	-	-	32	-	-	-	13	11
V	115	27	69	90	109	56	128	10	17	26
#Si IV	6.54	6.49	6.62	6.53	6.64	6.81	6.48	6.69	6.94	6.95
#Al IV	1.46	1.51	1.38	1.47	1.36	1.19	1.52	1.31	1.06	1.05
T site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
#Al VI	1.37	1.41	1.35	1.47	1.34	1.14	1.46	1.26	1.29	1.23
#Ti VI	0.18	0.04	0.12	0.10	0.04	0.04	0.05	0.01	0.03	0.02
#Fe +2	0.78	0.15	0.57	0.03	0.10	0.20	0.50	0.14	0.49	0.43
#Mn +2	0.01	0.14	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01
#Mg	5.57	6.23	5.90	6.35	6.48	6.56	5.94	6.48	6.12	6.16
O site	7.90	7.96	7.94	7.96	7.95	7.94	7.95	7.89	7.93	7.85
#Ba	0.03	0.01	0.03	0.03	0.03	0.02	0.03	0.04	0.02	0.02
#Ca	0.08	0.03	0.03	0.01	0.02	0.04	0.02	0.06	0.04	0.12
#Na	0.09	0.35	0.11	0.31	0.42	0.08	0.14	0.28	0.09	0.04
#K	1.96	1.77	2.04	1.90	1.81	2.05	2.07	1.93	2.14	2.08
#Rb	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01
A site	2.16	2.16	2.21	2.25	2.29	2.20	2.27	2.32	2.30	2.29
#O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
#OH	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite, 7-gneiss; FeOt denotes total Fe expressed as FeO; H₂O calculated using minfile program; Trace-element contents below 10 ppm are precise but the accuracy is questionable; - below detection limit.

Appendix 3.1e

Chemical composition of trioctahedral mica (XRF) with chemical formulas calculated with minfile program.

Sample Type	62C-1 3	62E 3	62F 3	66C 3	66H 3	70F 3	70G 3	70H 3	70I 3	70K 3
wt. %										
SiO ₂	42.1	40.3	41.8	39.8	41.7	41.0	41.5	41.8	42.4	41.8
TiO ₂	0.22	0.10	0.07	0.44	0.36	0.92	0.28	0.26	0.24	0.26
Al ₂ O ₃	11.75	14.20	11.76	12.46	11.44	13.39	11.72	11.64	11.37	11.80
FeOt	3.10	1.88	1.22	4.36	10.51	5.10	4.85	4.71	4.67	4.81
MnO	0.07	0.04	0.02	0.02	0.15	0.08	0.07	0.07	0.07	0.07
MgO	24.98	25.80	27.10	25.48	19.99	24.16	24.13	24.46	24.72	24.53
BaO	0.40	0.43	0.31	0.26	0.28	0.49	0.29	0.28	0.28	0.29
CaO	0.45	0.11	0.11	0.77	0.13	0.07	0.05	0.04	0.05	0.08
Na ₂ O	0.15	0.79	0.63	0.14	0.22	0.28	0.26	0.33	0.33	0.10
K ₂ O	9.98	9.42	9.61	10.29	9.81	10.18	9.95	10.01	9.75	10.06
Rb ₂ O	0.09	0.09	0.09	0.08	0.17	0.11	0.09	0.09	0.09	0.09
H ₂ O	3.74	3.77	3.79	3.73	3.60	3.70	3.71	3.71	3.72	3.72
Total	97.0	96.9	96.5	97.9	98.3	99.5	96.9	97.4	97.7	97.6
S wt. %	0.01	0.02	0.03	0.05	0.02	0.02	0.04	0.03	0.02	0.03
Ba ppm	3560	3820	2820	2330	2480	4330	2600	2500	2480	2600
Cr	23	11	13	46	39	38	50	47	40	40
Zr	13	22	8	68	-	-	-	-	-	11
Sr	45	799	112	47	27	67	26	23	22	26
Rb	863	840	809	751	1509	986	788	782	784	792
Y	5	5	9	12	12	7	6	8	9	8
Nb	-	14	-	7	15	15	4	3	2	4
Zn	234	139	89	272	411	289	280	241	266	239
Ni	7	7	14	-	11	30	9	7	14	7
V	19	11	-	51	219	38	40	42	27	27
#Si IV	6.97	6.61	6.87	6.54	7.06	6.69	6.93	6.94	7.00	6.91
#Al IV	1.03	1.39	1.13	1.46	0.94	1.31	1.07	1.06	1.00	1.09
T site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
#Al VI	1.26	1.36	1.14	0.95	1.35	1.26	1.24	1.22	1.21	1.21
#Ti VI	0.03	0.01	0.01	0.05	0.05	0.11	0.04	0.03	0.03	0.03
#Fe +2	0.43	0.26	0.17	0.60	1.49	0.70	0.68	0.65	0.64	0.67
#Mn +2	0.01	0.01	0.00	0.00	0.02	0.01	0.01	0.01	0.01	0.01
#Mg	6.17	6.32	6.64	6.24	5.05	5.87	6.01	6.06	6.08	6.05
O site	7.89	7.95	7.96	7.85	7.96	7.96	7.97	7.97	7.97	7.97
#Ba	0.03	0.03	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02
#Ca	0.08	0.02	0.02	0.14	0.02	0.01	0.01	0.01	0.01	0.01
#Na	0.05	0.25	0.20	0.04	0.07	0.09	0.08	0.11	0.11	0.03
#K	2.11	1.97	2.01	2.16	2.12	2.12	2.12	2.12	2.05	2.12
#Rb	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01
A site	2.27	2.28	2.26	2.36	2.25	2.26	2.24	2.26	2.19	2.20
#O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
#OH	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite, 7-gneiss; FeOt denotes total Fe expressed as FeO; H₂O calculated using minfile program; Trace-element contents below 10 ppm are precise but the accuracy is questionable; - below detection limit.

Appendix 3.1f Chemical composition of trioctahedral mica (XRF) with chemical formulas calculated with minfile program.

Sample Type	70N 3	108-3 3	108-4 3	108-5 3	112B-3 3	113-1 3	113-6 3	10B 4	14D 4	21B 4
wt. %										
SiO ₂	41.4	44.2	42.1	42.9	42.7	41.4	40.2	41.5	37.2	40.9
TiO ₂	0.56	0.33	0.64	0.31	0.16	0.52	0.89	1.11	1.73	1.46
Al ₂ O ₃	12.17	11.00	11.70	10.76	10.90	12.30	12.79	11.14	11.30	11.21
FeOt	4.86	3.50	3.60	3.24	0.68	6.00	8.10	7.57	19.86	15.32
MnO	0.07	0.13	0.15	0.07	0.02	0.11	0.08	0.09	0.40	0.22
MgO	24.16	24.71	24.49	25.09	25.92	23.04	23.05	21.76	14.26	15.03
BaO	0.49	0.16	0.16	0.16	0.27	0.68	0.78	0.14	0.18	0.30
CaO	0.22	0.22	0.06	0.49	0.56	0.04	0.05	0.14	2.23	0.06
Na ₂ O	0.36	0.17	0.40	0.27	0.52	0.52	0.44	0.56	0.59	0.15
K ₂ O	10.11	10.24	10.03	9.90	9.88	9.94	9.79	9.79	9.38	9.43
Rb ₂ O	0.11	0.14	0.12	0.12	0.12	0.09	0.07	0.13	0.08	0.84
H ₂ O	3.69	3.71	3.71	3.73	3.76	3.66	3.66	3.63	3.44	3.46
Total	98.2	98.5	97.1	97.1	95.5	98.3	99.9	97.5	100.7	98.4
S wt. %	0.03	0.03	0.04	0.04	0.04	0.01	0.03	0.02	0.08	0.05
Ba ppm	4360	1390	1400	1410	2430	6070	6970	1240	1650	2710
Cr	30	53	36	26	29	161	49	25	17	250
Zr	-	199	-	-	-	2	5	117	74	11
Sr	35	26	23	45	19	33	47	18	99	7
Rb	998	1305	1094	1080	1118	813	670	1215	692	761
Y	20	15	6	12	10	5	17	13	80	10
Nb	8	13	20	4	-	2	-	32	103	37
Zn	239	427	450	327	144	402	263	612	1389	581
Ni	26	191	33	50	13	67	48	14	-	206
V	32	5	-	-	1	53	46	6	27	95
#Si IV	6.85	7.25	7.00	7.11	7.15	6.90	6.60	7.02	6.44	7.20
#Al IV	1.15	0.75	1.00	0.89	0.85	1.10	1.40	0.98	1.56	0.80
T site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
#Al VI	1.22	1.37	1.30	1.21	1.30	1.31	1.07	1.24	0.74	1.53
#Ti VI	0.07	0.04	0.08	0.04	0.02	0.07	0.11	0.14	0.23	0.19
#Fe +2	0.67	0.48	0.50	0.45	0.10	0.84	1.11	1.07	2.87	2.26
#Mn +2	0.01	0.02	0.02	0.01	0.00	0.02	0.01	0.01	0.06	0.03
#Mg	5.96	6.04	6.08	6.20	6.47	5.72	5.64	5.49	3.68	3.95
O site	7.93	7.95	7.98	7.90	7.88	7.95	7.94	7.97	7.57	7.97
#Ba	0.03	0.01	0.01	0.01	0.02	0.04	0.05	0.01	0.01	0.02
#Ca	0.04	0.04	0.01	0.09	0.10	0.01	0.01	0.03	0.41	0.01
#Na	0.12	0.05	0.13	0.09	0.17	0.17	0.14	0.18	0.20	0.05
#K	2.13	2.14	2.13	2.09	2.11	2.11	2.05	2.12	2.07	2.12
#Rb	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.09
A site	2.33	2.26	2.29	2.29	2.41	2.34	2.26	2.35	2.70	2.30
#O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
#OH	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite, 7-gneiss; FeOt denotes total Fe expressed as FeO; H₂O calculated using minfile program; Trace-element contents below 10 ppm are precise but the accuracy is questionable; - below detection limit.

Appendix 3.1g

Chemical composition of trioctahedral mica (XRF) with
chemical formulas calculated with minfile program.

Sample Type	27J 4	27C 4	57J 4	60A 4	60G 4	74D 4	4B 5	4C 5	116A 5	116B 5
wt. %	---	---	---	---	---	---	---	---	---	---
SiO ₂	39.0	39.7	41.2	41.4	41.2	41.0	35.4	36.2	37.5	37.9
TiO ₂	2.20	2.03	0.89	0.48	0.54	1.57	3.18	3.12	2.47	2.32
Al ₂ O ₃	11.10	10.32	10.69	11.51	12.04	13.01	15.72	16.19	14.38	14.71
FeOt	17.41	18.21	12.68	9.88	10.71	3.38	20.48	21.77	18.93	18.89
MnO	0.82	0.64	0.18	0.11	0.12	0.04	0.45	0.45	0.53	0.35
MgO	14.13	14.25	18.81	19.77	19.93	23.85	10.75	10.04	12.67	12.43
BaO	0.07	0.09	0.31	0.26	0.29	0.42	0.03	0.03	0.20	0.19
CaO	0.22	0.33	0.19	0.54	0.20	0.31	0.26	0.08	0.16	0.30
Na ₂ O	0.48	0.73	0.38	0.12	0.06	0.32	0.06	0.44	0.40	0.37
K ₂ O	9.36	9.27	9.59	9.68	9.85	9.95	8.36	9.06	9.59	9.08
Rb ₂ O	0.05	0.03	0.15	0.12	0.14	0.08	0.09	0.93	0.14	0.15
H ₂ O	3.45	3.44	3.56	3.61	3.61	3.70	3.44	3.36	3.42	3.44
Total	98.31	99.06	98.61	97.44	98.68	97.67	98.18	101.62	100.37	100.12
S wt. %	0.02	0.03	0.02	0.01	0.02	0.02	0.02	0.03	0.02	0.01
Ba ppm	650	770	2720	2330	2640	3770	220	270	1810	1700
Cr	98	120	97	73	83	36	20	19	64	46
Zr	4	2	4	61	68	7	20	3	-	45
Sr	-	-	29	50	30	39	7	4	14	14
Rb	445	273	1393	1115	1238	689	831	842	1301	1353
Y	9	12	32	17	12	5	19	26	36	50
Nb	102	106	4	9	14	104	141	364	108	231
Zn	757	754	281	536	508	320	269	274	438	312
Ni	-	-	11	28	78	1	19	17	69	74
V	111	134	122	60	107	16	110	120	112	106
#Si IV	6.91	7.00	7.04	7.05	6.95	6.81	6.28	6.34	6.54	6.59
#Al IV	1.09	1.00	0.96	0.95	1.05	1.19	1.72	1.66	1.46	1.41
T site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
#Al VI	1.23	1.14	1.20	1.37	1.34	1.35	1.57	1.69	1.50	1.61
#Ti VI	0.29	0.27	0.11	0.06	0.07	0.20	0.42	0.41	0.32	0.30
#Fe +2	2.58	2.68	1.81	1.41	1.51	0.47	3.04	3.19	2.76	2.75
#Mn +2	0.12	0.10	0.03	0.02	0.02	0.01	0.07	0.07	0.08	0.05
#Mg	3.73	3.74	4.79	5.03	5.01	5.90	2.85	2.62	3.30	3.22
O site	7.95	7.93	7.94	7.88	7.94	7.92	7.95	7.98	7.96	7.93
#Ba	0.01	0.01	0.02	0.02	0.02	0.03	0.00	0.00	0.01	0.01
#Ca	0.04	0.06	0.03	0.10	0.04	0.06	0.05	0.02	0.03	0.06
#Na	0.16	0.25	0.13	0.04	0.02	0.10	0.02	0.15	0.14	0.12
#K	2.11	2.08	2.09	2.11	2.12	2.11	1.89	2.03	2.13	2.01
#Rb	0.01	0.00	0.02	0.01	0.01	0.01	0.01	0.10	0.02	0.02
A site	2.33	2.40	2.29	2.28	2.21	2.30	1.98	2.30	2.33	2.22
#O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
#OH	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite, 7-gneiss; FeOt denotes total Fe expressed as FeO; H₂O calculated using minfile program; Trace-element contents below 10 ppm are precise but the accuracy is questionable; - below detection limit.

Appendix 3.1h

Chemical composition of trioctahedral mica (XRF) with
chemical formulas calculated with minfile program.

Sample Type	116C 5	117E 5	118-2 5	119-1 5	119-2 5	120A 5	120B 5	120C 5	121B 5	121H 5
wt. %										
SiO ₂	37.3	35.6	39.9	38.8	36.3	38.5	36.8	36.4	39.1	38.9
TiO ₂	2.58	3.41	1.87	3.30	3.45	3.04	2.91	3.01	1.20	1.09
Al ₂ O ₃	14.30	15.86	14.07	15.04	14.53	15.17	15.72	15.28	12.53	12.17
FeOt	19.14	20.37	18.92	21.25	22.44	19.55	20.33	20.32	16.59	15.94
MnO	0.42	0.69	0.55	0.17	0.15	0.93	0.78	0.81	0.15	0.22
MgO	12.30	9.46	12.01	10.05	10.83	9.80	9.89	9.70	16.81	16.28
BaO	0.22	0.07	0.07	0.07	0.05	0.02	0.14	0.04	0.75	0.70
CaO	0.18	0.21	0.26	0.08	0.27	0.07	0.05	0.07	0.15	0.07
Na ₂ O	0.12	0.21	0.52	0.37	0.50	0.29	0.26	-	0.49	0.05
K ₂ O	9.04	8.86	9.27	8.82	7.92	8.75	9.58	9.50	9.15	9.61
Rb ₂ O	0.14	0.11	0.08	0.05	0.05	0.14	0.07	0.14	0.05	0.00
H ₂ O	3.44	3.39	3.43	3.40	3.43	3.40	3.38	3.38	3.52	0.59
Total	99.15	98.23	100.93	101.43	99.93	99.58	99.93	98.63	100.51	95.63
S wt. %	0.01	0.03	0.02	0.03	0.03	0.02	0.02	0.02	0.02	0.03
Ba ppm	1980	61	588	586	451	167	1289	360	6699	6240
Cr	57	38	31	30	21	15	78	25	36	66
Zr	5	-	3	3	-	-	-	3	8	-
Sr	12	-	-	7	14	6	-	-	63	32
Rb	1242	963	693	498	461	1247	617	1261	410	439
Y	27	13	29	13	15	41	11	19	24	5
Nb	137	82	257	40	43	188	126	131	-	2
Zn	401	849	409	139	150	538	601	605	138	210
Ni	85	-	-	-	-	41	69	33	-	12
V	92	35	53	212	197	231	239	226	129	136
#Si IV	6.55	6.41	6.91	6.75	6.36	6.82	6.54	6.55	6.64	6.75
#Al IV	1.45	1.59	1.09	1.25	1.64	1.18	1.46	1.45	1.36	1.25
T site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
#Al VI	1.51	1.78	1.78	1.83	1.36	1.98	1.83	1.79	1.14	1.24
#Ti VI	0.34	0.46	0.24	0.43	0.45	0.40	0.39	0.41	0.15	0.14
#Fe +2	2.81	3.07	2.74	3.09	3.29	2.89	3.02	3.06	2.35	2.31
#Mn +2	0.06	0.11	0.08	0.03	0.02	0.12	0.12	0.12	0.02	0.03
#Mg	3.22	2.54	3.10	2.60	2.83	2.58	2.62	2.60	4.25	4.21
O site	7.95	7.95	7.95	7.98	7.95	7.99	7.98	7.98	7.92	7.94
#Ba	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.05	0.05
#Ca	0.03	0.04	0.05	0.01	0.05	0.01	0.01	0.01	0.03	0.01
#Na	0.04	0.07	0.17	0.12	0.17	0.10	0.09	-	0.16	0.02
#K	2.03	2.04	2.05	1.96	1.77	1.98	2.17	2.18	1.98	2.13
#Rb	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.00	54.87
A site	2.13	2.17	2.28	2.11	2.00	2.10	2.29	2.21	2.22	57.08
#O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
#OH	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite, 7-gneiss; FeOt denotes total Fe expressed as FeO; H₂O calculated using minfile program; Trace-element contents below 10 ppm are precise but the accuracy is questionable; - below detection limit.

Appendix 3.1i

Chemical composition of trioctahedral mica (XRF) with chemical formulas calculated with minfile program.

Samples	121J	122A	122C	122F	124-4	124-5	124-7	124-8	1423-80
Type	5	5	5	5	5	5	5	5	7
wt. %									
SiO ₂	38.5	37.9	37.2	39.0	38.1	37.2	39.2	39.7	40.4
TiO ₂	1.10	2.25	2.56	2.34	2.39	2.35	1.80	1.65	1.21
Al ₂ O ₃	12.22	15.76	14.56	15.22	14.50	13.64	14.17	14.27	12.57
FeOt	16.11	23.49	22.51	23.46	18.91	20.72	18.46	18.00	1.57
MnO	0.20	0.82	1.18	1.04	1.25	1.32	1.15	1.22	0.02
MgO	16.11	3.11	3.58	3.00	9.27	9.40	10.68	10.79	27.47
BaO	0.78	0.01	0.01	0.01	0.03	0.02	0.05	0.04	0.11
CaO	0.09	0.66	1.10	0.18	0.07	0.37	0.05	0.10	1.31
Na ₂ O	0.24	-	-	0.46	0.12	0.24	0.14	0.14	0.46
K ₂ O	9.50	6.69	7.81	8.06	9.32	8.68	9.54	9.60	9.46
Rb ₂ O	0.05	0.49	0.49	0.47	0.69	0.65	0.49	0.48	0.01
H ₂ O	3.50	3.33	3.29	3.26	3.36	3.37	3.39	3.40	3.81
Total	98.4	94.5	94.3	96.5	98.0	97.9	99.1	99.4	98.4
S wt. %	0.04	0.03	0.04	0.02	0.03	0.03	0.03	0.03	0.06
Ba ppm	6990	130	110	50	290	140	410	380	1020
Cr	41	27	37	20	18	-	48	28	67
Zr	3	4	-	5	70	1391	-	3	93
Sr	34	13	13	9	17	28	14	12	44
Rb	448	4450	4451	4241	6198	5955	4476	4383	123
Y	9	85	41	137	50	161	37	38	8
Nb	2	1350	719	950	452	504	528	525	6
Zn	220	2032	1960	1358	794	809	742	799	121
Ni	6	71	63	41	133	43	107	108	-
V	134	-	-	-	32	57	41	37	44
#Si IV	6.71	7.23	7.20	7.44	6.94	6.77	6.99	7.05	6.48
#Al IV	1.29	0.77	0.80	0.56	1.06	1.23	1.01	0.95	1.52
T site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
#Al VI	1.22	2.77	2.52	2.86	2.06	1.69	1.97	2.04	0.85
#Ti VI	0.14	0.32	0.37	0.34	0.33	0.32	0.24	0.22	0.15
#Fe +2	2.35	3.75	3.65	3.74	2.88	3.16	2.76	2.68	0.21
#Mn +2	0.03	0.13	0.19	0.17	0.19	0.20	0.17	0.18	0.00
#Mg	4.18	0.89	1.03	0.85	2.52	2.55	2.84	2.86	6.56
O site	7.93	7.86	7.77	7.96	7.98	7.93	7.99	7.98	7.77
#Ba	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
#Ca	0.02	0.13	0.23	0.04	0.01	0.07	0.01	0.02	0.22
#Na	0.08	-	-	0.17	0.04	0.08	0.05	0.05	0.14
#K	2.11	1.63	1.93	1.96	2.17	2.02	2.17	2.18	1.93
#Rb	0.01	0.06	0.06	0.06	0.08	0.08	0.06	0.06	0.00
A site	2.27	1.83	2.22	2.23	2.31	2.25	2.29	2.30	2.31
#O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
#OH	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite, 7-gneiss; FeOt denotes total Fe expressed as FeO; H₂O calculated using minfile program; Trace-element contents below 10 ppm are precise but the accuracy is questionable; - below detection limit.

Appendix 3.2a

Chemical compositions of Ca pyroxene (XRF) and formulas
calculated using the minfile program

Sample Type	20B 2	26B 2	61C-1 2	62F 2	62D-1 2	9A 3	9E 3	20C 3	22B 3	22C 3
wt. %	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
SiO ₂	52.3	52.1	53.6	54.6	55.64	54.0	53.7	51.2	51.0	51.7
TiO ₂	0.09	0.10	0.04	0.03	0.05	0.07	0.02	0.04	0.03	0.03
Al ₂ O ₃	0.74	0.96	1.52	0.34	0.50	1.19	0.48	0.54	1.07	1.00
Fe ₂ O ₃ *	1.96	4.44	5.60	2.15	0.29	-	2.32	2.84	7.61	4.71
FeO	9.42	5.94	-3E+00	-6E-01	1.21	8.31	4.17	13.60	3.56	6.41
MnO	0.60	0.24	0.08	0.09	0.07	0.26	0.20	0.59	0.24	0.25
MgO	12.08	12.95	19.37	18.52	19.98	13.34	15.64	9.37	13.02	12.85
CaO	22.58	22.98	22.92	24.86	21.88	22.32	23.29	21.50	23.35	22.79
Na ₂ O	0.43	0.77	0.61	0.16	0.25	0.49	0.43	0.56	0.86	0.65
K ₂ O	0.03	0.02	0.25	0.05	0.15	0.02	0.03	0.06	0.03	0.04
Total	100.2	100.4	100.6	100.2	100.0	100.0	100.2	100.3	100.8	100.5
S wt. %	0.02	0.03	0.04	0.04	0.03	0.04	0.03	0.03	0.03	0.01
Ba ppm	39	73	111	64	89	89	72	63	138	125
Cr	34	62	3	12	12	213	49	9	199	183
Zr	442	129	10	3	2	35	13	50	7	10
Sr	41	55	159	83	86	46	37	43	79	82
Rb	23	-	3	-	-	-	-	-	-	-
Y	82	16	28	18	29	58	89	175	29	29
Nb	22	65	-	-	-	-	-	-	-	-
Zn	672	284	72	85	66	215	234	448	174	201
Ni	-	-	-	-	-	-	-	-	-	-
V	155	120	5	7	7	183	77	77	224	229
#Si IV	1.97	1.94	1.92	1.97	2.00	2.01	1.97	1.97	1.90	1.94
#Al IV	0.03	0.04	0.06	0.01	0.00	-	0.02	0.02	0.05	0.04
#Fe +3	-	0.02	0.02	0.02	-	-	0.01	0.01	0.05	0.02
T site	2.00	2.00	2.00	2.00	2.00	2.01	2.00	2.00	2.00	2.00
#Al VI	0.00	-	-	-	0.02	0.05	-	-	-	-
#Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
#Fe +3	0.06	0.10	0.13	0.04	0.01	-	0.05	0.07	0.16	0.11
#Fe +2	0.30	0.19	-1E-01	-2E-02	0.04	0.26	0.13	0.44	0.11	0.20
#Mn +2	0.02	0.01	0.00	0.00	0.00	0.01	0.01	0.02	0.01	0.01
#Mg	0.68	0.72	1.03	1.00	1.07	0.74	0.86	0.54	0.72	0.72
#Ca	0.91	0.92	0.88	0.96	0.84	0.89	0.92	0.89	0.93	0.91
#Na	0.03	0.06	0.04	0.01	0.02	0.04	0.03	0.04	0.06	0.05
#K	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00
M1,M2	2.00	2.00	2.00	2.00	2.00	1.99	2.00	2.00	2.00	2.00
#O	6.00	6.00	6.00	6.00	6.00	6.02	6.00	6.00	6.00	6.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite; Fe₂O₃* calculated by formula using minfile; Trace-element contents below 10 ppm are precise but the accuracy is questionable; - below detection limit.

Appendix 3.2b Chemical compositions of Ca pyroxene (XRF) and formulas calculated using the minfile program

Sample Type	26A 3	30C 3	30A 3	50C 3	50J 3	50D-1 3	62B 3	62C-1 3	65A 3	65B 3
wt. %										
SiO ₂	52.6	54.9	53.7	52.8	48.7	53.1	53.5	53.6	53.7	53.8
TiO ₂	0.04	0.06	0.06	0.15	0.32	0.14	0.05	0.04	0.03	0.02
Al ₂ O ₃	1.11	0.88	0.63	1.89	1.40	1.64	0.74	1.21	0.71	0.46
Fe ₂ O ₃ *	4.59	-	2.85	4.13	7.16	4.13	4.02	2.28	2.06	2.29
FeO	2.94	6.71	3.04	0.93	12.22	0.75	-8E-02	2.03	2.55	1.67
MnO	0.15	0.21	0.21	0.13	0.50	0.12	0.15	0.16	0.14	0.13
MgO	14.73	15.90	16.11	16.10	8.26	17.00	16.83	16.21	16.28	16.82
CaO	23.63	20.62	23.14	23.51	21.34	22.80	24.72	24.19	24.41	24.80
Na ₂ O	0.70	0.59	0.55	0.72	0.79	0.56	0.42	0.41	0.24	0.16
K ₂ O	0.01	0.14	0.02	0.03	0.02	0.20	0.09	0.06	0.06	0.03
Total	100.5	100.0	100.3	100.4	100.7	100.4	100.4	100.2	100.2	100.2
S wt. %	0.05	0.03	0.02	0.05	0.05	0.01	0.05	0.03	0.02	0.04
Ba ppm	75	101	65	116	65	173	78	114	75	85
Cr	50	73	34	27	42	40	17	10	24	19
Zr	13	53	39	28	80	20	3	21	4	-
Sr	72	39	41	59	55	69	111	441	36	27
Rb	-	-	-	-	-	11	-	88	-	-
Y	5	65	67	8	19	11	15	-	23	17
Nb	-	-	-	-	27	-	-	-	-	-
Zn	166	250	203	131	366	130	107	149	48	50
Ni	-	-	-	-	-	-	-	-	-	-
V	112	141	139	157	148	118	33	30	14	14
#Si IV	1.94	2.02	1.97	1.92	1.88	1.93	1.94	1.96	1.97	1.96
#Al IV	0.05	-	0.03	0.08	0.06	0.07	0.03	0.04	0.03	0.02
#Fe +3	0.02	-	0.01	-	0.05	-	0.02	-	-	0.02
T site	2.00	2.02	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
#Al VI	-	0.04	-	0.01	-	-	-	0.01	-	-
#Ti	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
#Fe +3	0.11	-	0.07	0.11	0.21	0.11	0.09	0.06	0.06	0.04
#Fe +2	0.09	0.21	0.09	0.03	0.40	0.02	-2E-03	0.06	0.08	0.05
#Mn +2	0.00	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00
#Mg	0.81	0.87	0.88	0.87	0.48	0.92	0.91	0.88	0.89	0.92
#Ca	0.93	0.81	0.91	0.92	0.88	0.89	0.96	0.95	0.96	0.97
#Na	0.05	0.04	0.04	0.05	0.06	0.04	0.03	0.03	0.02	0.01
#K	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
M1,M2	2.00	1.98	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
#O	6.00	6.01	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite; Fe₂O₃* calculated by formula using minfile; Trace-element contents below 10 ppm precise but the accuracy is questionable; - below detection.

Appendix 3.2c Chemical compositions of Ca pyroxene (XRF) and formulas calculated using the minfile program

Sample Type wt. %	66H 3	70N 3	70K 3	70M 3	70J 3	108-5 3	108-3 3	60D-1 4	60D 4	60A 4
SiO ₂	52.4	53.0	52.5	52.5	53.1	54.0	53.5	53.7	50.7	51.2
TiO ₂	0.02	0.02	0.02	0.05	0.05	0.08	0.06	0.05	0.31	0.03
Al ₂ O ₃	0.95	1.10	0.69	1.18	1.08	0.78	1.18	0.35	1.02	1.06
Fe ₂ O ₃ *	2.96	3.36	4.74	5.10	3.76	4.64	3.89	4.53	5.93	5.80
FeO	7.87	3.11	2.98	1.24	1.50	-6E-02	1.32	-3E+00	6.38	6.41
MnO	0.28	0.19	0.20	0.19	0.17	0.28	0.30	0.07	0.29	0.29
MgO	13.50	15.45	14.99	15.95	16.17	17.44	15.66	18.91	11.84	12.20
CaO	21.79	23.63	23.77	23.65	24.07	22.28	23.47	25.52	23.50	22.91
Na ₂ O	0.52	0.42	0.51	0.54	0.45	0.93	0.93	0.11	0.62	0.73
K ₂ O	0.03	0.10	0.03	0.07	0.04	0.14	0.04	0.06	0.04	0.01
Total	100.3	100.3	100.5	100.5	100.4	100.5	100.4	100.5	100.6	100.6
S wt. %	0.05	0.05	0.04	0.04	0.03	0.03	0.05	0.02	0.05	0.03
Ba ppm	88	161	116	151	94	82	85	56	89	93
Cr	37	23	39	36	24	9	49	-	53	65
Zr	8	3	3	8	11	49	52	-	47	16
Sr	90	88	94	76	269	144	110	164	103	95
Rb	-	-	-	-	-	-	-	-	-	-
Y	18	19	21	20	17	26	19	41	30	14
Nb	-	-	2	2	-	2	-	-	18	-
Zn	362	215	241	190	144	188	242	63	317	341
Ni	-	-	-	-	-	-	-	-	4	6
V	192	80	94	58	59	13	39	9	131	143
#Si IV	1.96	1.95	1.94	1.92	1.94	1.95	1.95	1.94	1.91	1.92
#Al IV	0.04	0.05	0.03	0.05	0.05	0.03	0.05	0.01	0.05	0.05
#Fe +3	-	0.01	0.03	0.03	0.01	0.01	-	0.05	0.05	0.03
T site	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
#Al VI	-	-	-	-	-	-	0.00	-	-	-
#Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
#Fe +3	0.08	0.08	0.10	0.14	0.09	0.13	0.11	0.07	0.12	0.13
#Fe +2	0.25	0.10	0.09	0.04	0.05	-2E-03	0.04	-9E-02	0.20	0.20
#Mn +2	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01
#Mg	0.75	0.85	0.82	0.87	0.88	0.94	0.85	1.02	0.66	0.68
#Ca	0.87	0.93	0.94	0.93	0.94	0.86	0.92	0.98	0.95	0.92
#Na	0.04	0.03	0.04	0.04	0.03	0.07	0.07	0.01	0.05	0.05
#K	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
M1,M2	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
#O	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite; Fe₂O₃* calculated by formula using minfile; Trace-element contents below 10 ppm precise but the accuracy is questionable; - below detection.

Appendix 3.2d Chemical compositions of Ca pyroxene (XRF) and formulas calculated using the minfile program

Sample	60	62A
Type	4	5
wt. %	-----	-----
SiO ₂	51.2	51.3
TiO ₂	0.18	0.16
Al ₂ O ₃	1.00	2.33
Fe ₂ O ₃ *	4.87	4.74
FeO	7.30	8.50
MnO	0.29	0.46
MgO	11.87	10.07
CaO	23.18	21.33
Na ₂ O	0.59	1.47
K ₂ O	0.05	0.12
Total	100.5	100.5
S wt. %	0.05	0.00
Ba ppm	88	86
Cr	46	44
Zr	14	30
Sr	114	52
Rb	-	-
Y	23	40
Nb	11	-
Zn	334	263
Ni	-	63
V	127	168
#Si IV	1.93	1.93
#Al IV	0.04	0.07
#Fe +3	0.03	-
T site	2.00	2.00
#Al VI	-	0.04
#Ti	0.01	0.00
#Fe +3	0.11	0.13
#Fe +2	0.23	0.27
#Mn +2	0.01	0.01
#Mg	0.67	0.57
#Ca	0.94	0.86
#Na	0.04	0.11
#K	0.00	0.01
M1,M2	2.00	2.00
#O	6.00	6.00

NOTES: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite; Fe₂O₃* calculated by formula using minfile; Trace-element contents below 10 ppm precise but the accuracy is questionable; - below detection.

Appendix 3.3 Chemical composition of amphibole (XRF) and mineral formula
Calculated using minfile

Sample Type	9F 3	19C 3	19D 3	50F 3	62E 3	64C 3	112B-3 3	14D 4	27C 4
wt. %									
SiO ₂	43.5	53.9	53.6	45.5	42.5	43.8	55.8	41.2	46.1
TiO ₂	0.16	0.26	0.13	0.24	0.06	0.27	0.09	0.89	0.92
Al ₂ O ₃	13.90	2.09	2.18	13.12	15.35	12.53	1.43	8.81	5.91
FeO	3.19	5.50	1.95	1.33	3.31	11.34	0.60	20.90	17.81
MnO	0.06	0.31	0.16	0.03	0.08	0.13	0.05	0.68	1.22
MgO	18.54	19.72	22.20	20.79	18.44	14.73	22.38	7.97	10.62
ZnO	0.02	0.05	0.02	0.01	0.01	0.01	0.01	0.11	0.05
CaO	12.55	7.02	9.64	12.12	12.73	11.71	11.88	9.98	5.84
Na ₂ O	3.03	5.59	4.25	2.83	2.45	2.19	2.33	3.12	6.06
K ₂ O	0.98	1.72	1.29	0.72	1.56	1.43	0.91	1.70	1.15
H ₂ O*	2.07	2.09	2.10	2.12	2.08	2.05	2.14	1.88	1.94
Total	98.0	98.3	97.5	98.9	98.6	100.2	97.7	97.2	97.6
S wt. %	0.04	0.05	0.03	0.02	0.05	0.02	0.04	0.02	0.05
Ba ppm	100	80	70	210	270	130	100	80	60
Cr	36	34	35	38	-	24	39	52	151
Zr	131	202	22	79	85	41	10	207	547
Sr	61	147	105	80	534	34	50	86	32
Rb	-	18	7	-	14	12	19	52	-
Y	79	8	13	15	86	46	6	95	57
Nb	10	28	18	7	15	26	-	110	65
Zn	156	433	175	117	133	109	87	1036	502
Ni	17	-	-	-	-	-	-	-	-
V	60	54	29	79	14	530	12	97	289
#Si IV	6.28	7.74	7.64	6.43	6.13	6.40	7.84	6.57	7.13
#Al IV	1.72	0.26	0.36	1.57	1.87	1.60	0.16	1.43	0.87
T site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
#Al VI	0.65	0.09	0.00	0.61	0.73	0.56	0.08	0.23	0.21
#Ti	0.02	0.03	0.01	0.03	0.01	0.03	0.01	0.11	0.11
#Mg	4.00	4.22	4.72	4.37	3.96	3.21	4.68	1.90	2.45
#Fe +2	0.34	0.66	0.23	-	0.30	1.20	0.07	2.77	2.24
#Zn	-	0.00	0.00	-	-	-	0.00	-	-
#Mn	-	-	0.02	-	-	-	0.01	-	-
#Ca	-	-	0.01	-	-	-	0.15	-	-
M1,2,3	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
#Mg	-	-	-	0.01	-	-	-	-	-
#Fe +2	0.05	-	-	0.16	0.10	0.19	-	0.02	0.07
#Zn	0.00	0.00	-	0.00	0.00	0.00	-	0.01	0.01
#Mn	0.01	0.04	-	0.00	0.01	0.02	-	0.09	0.16
#Ca	1.94	1.08	1.47	1.83	1.89	1.79	1.79	1.71	0.97
#Na	-	0.88	0.53	-	-	-	0.21	0.16	0.80
M4 site	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
#Ca	0.00	-	-1E-02	0.00	0.08	0.04	-2E-01	-	-
#Na	0.85	0.68	0.65	0.77	0.68	0.62	0.42	0.80	1.02
#K	0.18	0.31	0.23	0.13	0.29	0.27	0.16	0.35	0.23
A site	1.03	0.99	0.87	0.91	1.05	0.93	0.43	1.15	1.25
#O	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00	22.00
#OH	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00

Notes: Type of host; 1-marble, 2-silicated marble, 3-skarn, 4-vein selvage, 5-pegmatite; Fe₂O₃ calculated by formula using minfile was removed because it remained less than 0.005 wt.%; H₂O* was calculated using minfile. Trace-element contents below 10 ppm precise but the accuracy is questionable; - below detection.

Appendix 3.4 Carbonate compositions and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope compositions

Sample		CaO wt. %	MgO wt. %	MnO wt. %	FeO wt. %	Zn ppm	Sr ppm	Na ppm	Y ppm	Ba ppm	180	13C
Faraday	PEG	55.04	0.32	0.520	1.276	0	2013	363	479	161	11.92	-2.3
26H	PEG	57.85	0.04	0.139	0.298	3	770	165	309	147	12.26	-2.13
26G	PEG	57.18	0.07	0.115	0.356	0	1144	121	136	273	12.44	-1.61
26F	PEG	57.61	0.04	0.150	0.321	0	693	132	334	17	12.01	-2.25
121J	PEG	59.66	0.24	0.292	1.151	3	4400	110	77	107	11.36	-3.04
121I	PEG	51.16	0.32	0.390	1.638	0	7150	77	94	152	11.35	-2.72
121H	PEG	57.87	0.22	0.321	1.186	1	1320	77	74	1133	11.53	-2.92
126	PEG	56.3	0	0.03	0.02	80	168	500	0	43	15.08	-3.38
127	PEG	54.14	0.41	0.42	0.7	32	2190	1000	210	80	13.46	-2.21
128	PEG	51.5	0.56	0.85	0.95	0	158	3600	80	40	8.34	-5.15
9J-1	SKARN	58.06	0.27	0.174	0.715	5	1221	143	338	19	15.51	-1.77
9J	SKARN	38.31	0.16	0.123	0.814	0	1155	33	141	178	22.58	1.53
9F	SKARN	57.62	0.59	0.057	0.249	0	572	132	201	4	22.11	1.74
9E	SKARN	58.83	0.44	0.085	0.404	1	715	121	169	23	19.71	1.17
70H	SKARN	58.30	0.29	0.110	0.361	16	1738	77	131	17	12.61	-3.2
70K	SKARN	55.23	0.23	0.116	0.476	0	1848	88	180	278	12.43	-2.53
70I	SKARN	58.72	0.32	0.120	0.502	8	2002	132	184	18	12.44	-2.42
70H	SKARN	61.23	0.26	0.115	0.320	5	1694	99	145	12	12.54	-2.2
70G	SKARN	56.83	0.37	0.121	0.591	0	2167	198	183	44	12.12	-2.41
70D	SKARN	59.52	0.04	0.135	0.649	6	2090	99	179	17	11.65	-2.8
6A	SKARN	48.17	0.87	0.142	0.312	0	2057	88	374	79	18.89	-2.08

66H	SKARN	59.02	0.24	0.262	0.739	3	1980	88	94	18	11.82	-4.25
66E	SKARN	49.55	0.45	0.195	0.819	0	3190	66	186	78	13.54	-2.71
66D	SKARN	47.40	18.71	0.040	0.520	31	88	66	4	4	14.83	-4.06
66c-2	SKARN	55.77	1.16	0.031	0.502	5	704	110	13	21	20.61	1.58
66C	SKARN	69.44	1.02	0.081	0.813	6	1012	143	30	53	18.33	0.69
65A	SKARN	59.75	0.67	0.148	0.555	4	803	143	150	24	15.24	-0.75
62F-1	SKARN	56.34	0.81	0.095	0.292	4	2398	33	74	17	15.77	-1.3
62E	SKARN	57.56	0.51	0.071	0.208	1	2156	66	76	10	16.42	-1.18
62B	SKARN	55.93	0.30	0.110	0.279	0	2343	44	129	22	13.73	-3.66
61A	SKARN	57.37	0.68	0.059	0.066	4	2420	55	117	7	17.58	-0.8
50R-1	SKARN	60.56	1.29	0.123	0.476	8	1936	110	65	29	16.34	-1.42
50Q	SKARN	49.76	3.67	0.120	0.433	8	1452	121	63	12	16.72	-1.24
500	SKARN	57.34	1.88	0.135	0.263	3	2420	209	74	65	16.25	-1.3
50N	SKARN	39.99	2.33	0.032	0.000	1	1320	22	28	16	19.33	-0.28
50M	SKARN	56.31	1.24	0.146	0.519	5	1859	44	94	28	16.09	-2.06
50F	SKARN	52.65	1.65	0.050	0.154	1	1375	66	55	12	18.25	-0.43
50E	SKARN	50.88	2.57	0.498	0.098	0	693	44	36	17	21.04	0.68
50D-1	SKARN	48.65	0.93	0.112	0.529	0	1870	55	160	47	16.26	-2.22
50C	SKARN	57.54	0.81	0.101	0.414	10	1903	132	93	104	14.8	-2.02
50B	SKARN	51.86	1.53	0.023	0.264	0	649	33	39	200	19.35	-0.14
30E	SKARN	52.90	0.26	0.263	0.983	0	1419	77	393	65	16.6	0.69
30C	SKARN	58.75	0.47	0.144	0.591	4	1397	242	381	180	16.57	0.76
30B	SKARN	55.82	0.43	0.143	0.677	4	1375	242	389	168	16.84	0.23
30A	SKARN	51.99	0.42	0.192	0.737	5	1375	132	362	92	16.94	0.3

28C-1	SKARN	54.24	0.79	0.200	1.082	6	1551	110	327	56	13.3	-3.18
26A	SKARN	58.81	0.28	0.092	0.435	5	1529	209	65	32	12.81	-1.47
20C	SKARN	56.91	0.17	0.192	0.924	7	1364	66	201	11	13.82	-2.25
19D	SKARN	50.20	0.61	0.215	0.258	5	4345	429	265	168	16.45	-1.59
19C-3	SKARN	49.33	1.32	0.170	0.459	8	3905	341	413	235	16.86	-0.32
19C-2	SKARN	57.88	1.27	0.212	0.221	8	3201	363	206	97	17.16	-0.3
19A	SKARN	49.88	0.33	0.270	0.312	8	4576	407	210	759	14.11	-3.44
113-6	SKARN	54.02	0.80	0.213	0.860	8	2090	77	76	56	15.55	-3.07
113-5	SKARN	47.11	6.95	0.089	0.390	9	363	143	14	12	20.94	0.75
113-4	SKARN	56.87	0.35	0.151	0.846	8	2970	165	155	171	14	-3.04
113-3	SKARN	57.52	0.59	0.032	0.298	1	1430	143	37	130	17.96	-0.22
112c	SKARN	52.68	3.11	0.036	0	8	1155	121	7	118	24.16	-3.46
112B-3	SKARN	55.48	0.63	0.066	0.045	3	1683	121	56	341	20.41	-1.53
10C	SKARN	52.71	0.49	0.196	0.279	0	3960	209	287	151	17.19	-3.5
108-5	SKARN	55.80	0.43	0.178	0.366	0	4158	242	165	254	18.26	-0.18
108-3	SKARN	65.20	0.27	0.154	0.152	3	3278	132	81	47	15.06	-4.32
108-2	SKARN	59.30	0.37	0.261	0.390	3	3850	209	195	101		
108-1	SKARN	55.24	0.47	0.210	0.498	4	3839	132	191	213	13.88	-4.4
9L	VEIN	48.26	0.38	0.163	0.890	4	1628	77	362	61	15.19	-2.8
9J'	VEIN	54.36	0.21	0.160	0.733	1	1617	110	349	104	14.83	-2.95
9H	VEIN	59.27	0.06	0.350	0.735	10	1661	176	436	70	9.26	-3.96
64D	VEIN	51.89	0.62	0.147	0.662	0	803	66	276	24	15.81	-1.33
60D	VEIN	51.55	0.39	0.119	0.831	4	2277	33	105	36	12.29	-2.96
60B	VEIN	52.95	0.20	0.079	0.673	0	2200	77	103	78	12.29	-3.02

60A	VEIN	60.82	0.28	0.138	0.676	5	2255	56	77	37	12.62	-2.8
60 Matte	VEIN	57.74	0.38	0.135	0.795	0	2321	44	119	39	12.53	-2.98
57B	VEI.	51.15	0.08	0.294	0.637	0	880	77	78	28	15.57	-5.43
27C	VEIN	55.09	0.32	0.111	1.458	5	1650	451	1144	309	14	-3.47
27B	VEIN	49.37	1.54	0.144	1.425	12	1958	528	1011	162	14.1	-4.18
21B	VEIN	51.92	0.16	0.402	1.051	6	1606	253	464	214	10.91	-4.13
21A	VEIN	53.88	0.18	0.410	1.179	6	1419	132	607	87	10.88	-4.19
14D	VEIN	50.10	0.32	0.611	1.322	10	1716	132	345	71		
14B	VEIN	49.12	0.28	0.557	1.607	9	1859	99	426	53	8.92	-4.14
14A	VEIN	49.58	0.19	0.520	0.864	4	1760	132	880	90	8.74	-4.03
10B	VEIN	40.37	0.35	0.351	1.184	6	5280	198	207	53	13.54	-3.93
GT1-5	SILMAR	51.20	1.55	0.023	0.581	6	968	44	9	71	23.26	3.17
62D-1	SILMAR	55.97	1.45	0.090	0.561	7	2365	77	88	79	16.36	-0.92
61D-1	SILMAR	58.11	1.40	0.080	0.246	5	2354	66	104	18	16.03	-0.99
61C-1	SILMAR	48.90	0.64	0.074	0.163	0	2453	44	160	12	17.2	-0.86
50L	SILMAR	47.07	2.72	0.121	0.604	3	1771	165	66	42	14.73	-1.99
26B	SILMAR	59.01	1.07	0.066	0.804	1	583	143	1023	34	12.34	-1.84
20B	SILMAR	54.51	1.18	0.237	1.263	0	1694	275	777	495	14.46	-1.94
114-2	SILMAR	47.55	0.38	0.174	0.851	2	7755	143	103	65	11.33	-2.94
114-1	CARB	60.00	0.22	0.126	0.362	4	8030	154	59	77	9.37	-2.88
9H	MARBLE	47.07	2.12	0.049	0.479	0	220	55	16	38	24.35	2.68
9K-1	MARBLE	49.01	2.51	0.036	0.332	2	297	33	27	4	24.21	2
9C	MARBLE	57.80	0.53	0.059	0.319	0	539	132	183	10	21.55	1.47
50P	MARBLE	45.08	10.17	0.015	0.320	5	352	44	36	8	19.94	0.74

50A	MARBLE	51.06	1.37	0.004	0.221	0	3355	11	55	212	18.95	-0.14
1423A-80	MARBLE	60.75	1.88	0.027	0.315	5	484	77	10	43	23.88	2.01
1374-3	MARBLE	54.43	1.69	0.023	0.624	12	132	77	14	58	23.32	2.13

Appendix 3.5 Apatite compositions

Sample Type	28C-1 3	108-1 3	113-6 3	113-4 3	9J 4	10B 4	14A 4	14B 4
SiO ₂	1.69	0.20	0.97	0.77	1.34	0.28	0.68	0.82
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.00
Al ₂ O ₃	0.04	0.01	0.03	0.02	0.10	0.03	0.02	0.07
Fe ₂ O ₃	0.21	0.45	0.21	0.31	0.11	0.48	0.13	0.16
MgO	0.00	0.19	0.23	0.21	0.20	0.23	0.11	0.24
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	50.3	54.7	53.5	52.9	50.1	52.4	53.5	52.5
Na ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P ₂ O ₅	37.5	41.1	39.0	45.1	40.62	45.4	39.4	38.6
S	0.35	0.80	1.48	0.38	0.10	0.33	0.10	0.13
Total	90.4	97.4	95.4	99.7	92.6	99.1	94.0	92.5
ppm								
Ba	87	102	116	90	94	102	122	75
Cr	0	0	0	0	0	0	0	0
Zr	16	69	32	48	14	80	15	20
Sr	1178	4377	1758	2318	971	3857	1123	1317
Rb	0	0	0	0	0	0	0	0
Y	1062	431	807	709	4609	536	3130	3498
Nb	0	0	0	0	0	0	0	0
Zn	62	0	0	0	0	0	0	0
Ni	83	20	60	62	482	30	308	355
V	0	0	0	0	0	0	0	0

Sample Type	21A 4	57B 4	60B 4	60D 4	60 4	121I 5	114-2 6
SiO ₂	1.06	1.28	1.10	1.21	1.14	0.43	0.81
TiO ₂	0.00	0.00	0.00	0.01	0.02	0.00	0.00
Al ₂ O ₃	0.02	0.07	0.05	0.10	0.06	0.03	0.00
Fe ₂ O ₃	0.08	0.40	0.24	0.23	0.26	0.45	1.00
MgO	0.23	0.29	0.22	0.15	0.30	0.12	0.17
MnO	0.00	0.00	0.00	0.00	0.00	0.01	0.00
CaO	54.0	52.8	51.6	51.8	51.9	54.4	54.0
Na ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.00	0.01	0.01	0.00	0.00	0.00	0.00
P ₂ O ₅	39.5	37.0	37.2	37.8	38.1	39.6	41.8
S	0.25	0.15	1.66	0.95	0.95	0.23	1.2
Total	95.2	92.0	92.2	92.3	92.8	95.2	99.0
ppm							
Ba	89	91	113	133	133	200	97
Cr	0	0	0	0	0	0	0
Zr	10	69	34	33	33	83	152
Sr	899	2507	1585	1744	1770	5821	9333
Rb	0	0	0	0	0	0	3
Y	4335	876	985	1407	1173	411	954
Nb	0	0	0	0	0	0	0
Zn	0	48	0	0	0	43	0
Ni	457	56	86	137	115	0	80
V	0	0	0	0	0	10	0

Appendix 3.6a Calculated average chemical compositions of selected granitic pegmatites from the Grenville Province

Sample No.	SG-2	SG-6	SG-9	SG-18	GEN	AF3	GC	BIC	TG	CK	CD	LEG	AF1
Ref.	1	1	1	1	1	2	2	2	2	2	2	2	2
wt. %	73.2	73.2	73.2	74.2	70.3	73.6	71.6	74.5	73.7	73.1	72.3	70.9	69.0
SiO ₂	0.10	0.13	0.31	0.10	0.32	0.04	0.29	0.03	0.12	0.01	0.15	0.29	0.05
TiO ₂	14.45	14.35	12.90	13.85	14.47	13.67	13.68	12.30	13.60	13.10	12.85	14.20	14.00
Al ₂ O ₃	0.09	0.15	0.24	0.17	2.23	0.60	0.53	0.00	0.50	-	-	1.40	-
FeO	0.88	0.72	1.74	0.51	1.67	0.59	1.74	1.30	0.25	0.55	0.70	1.0	7.70
MnO	0.02	0.02	0.02	0.02	0.04	0.10	0.03	0.02	0.02	0.01	0.02	0.03	0.00
MgO	0.29	0.34	0.69	0.23	1.04	0.12	0.29	0.20	0.30	0.10	0.20	0.60	0.40
CaO	1.25	1.13	0.56	1.04	1.56	0.97	1.11	0.80	0.15	0.10	0.60	0.80	0.50
Na ₂ O	3.53	2.92	2.16	2.96	3.42	2.53	2.89	4.10	2.20	2.15	2.45	2.95	3.50
K ₂ O	5.09	6.21	6.61	6.00	4.52	6.20	5.63	4.60	7.80	8.65	8.05	5.85	4.80
P ₂ O ₅	0.03	0.08	0.09	0.03	0.15	0.01	0.04	0.01	0.05	0.02	0.03	0.09	0.05
H ₂ O	0.33	0.33	0.35	0.48	0.36	-	-	-	-	-	-	-	-
Total 99.3	99.6	98.8	99.6	100.1	98.5	97.8	97.9	97.9	98.6	97.7	97.3	98.1	100.0
ppm													
Cl	264	200	270	250	158	-	-	-	-	-	-	-	-
F	157	204	400	169	405	-	-	-	-	-	-	-	-
S	-	500	2600	600	800	-	-	-	-	-	-	-	-
Ba	276	372	446	394	446	-	-	-	-	-	-	-	-
Rb	127	139	178	122	127	-	-	-	-	-	-	-	-
Sr	234	220	206	209	219	-	-	-	-	-	-	-	-
Zn	41	64	55	31	37	-	-	-	-	-	-	-	-
Zr	50	48	18	69	599	-	-	-	-	-	-	-	-
U	139	274	969	82	675	-	-	-	-	-	-	-	-
Th	17	29	123	34	222	-	-	-	-	-	-	-	-
q	29.53	29.34	32.21	31.22	28.35	32.66	29.52	31.64	30.40	27.17	26.34	28.91	28.99
c	0.93	0.96	1.39	0.67	1.48	1.06	0.91	-	1.39	0.07	-	1.78	2.28
or	30.06	36.68	39.04	35.44	26.70	36.62	33.25	27.20	46.07	51.12	47.54	34.55	28.57
ab	29.86	24.70	18.27	25.04	28.94	21.40	24.45	34.73	18.61	18.20	20.72	24.96	29.84
an	6.00	5.08	2.19	4.96	6.76	4.75	5.24	1.57	0.42	0.31	0.29	3.38	2.17
hy	2.14	1.87	4.24	1.24	3.35	1.01	3.06	-	0.74	0.25	-	1.75	1.00
di	-	-	-	-	-	-	-	1.08	-	-	1.08	-	-
wo	-	-	-	-	-	-	-	0.39	-	-	0.28	-	-
mt	0.13	0.22	0.35	0.25	3.24	0.87	0.77	-	0.53	0.00	-	2.03	-
il	0.19	0.25	0.59	0.19	0.61	0.08	0.55	0.04	0.23	0.02	0.04	0.55	-
hm	-	-	-	-	-	-	-	1.17	0.14	-	0.63	-	7.70
ru	-	-	-	-	-	-	-	-	-	-	-	-	0.95
tn	-	-	-	-	-	-	-	0.02	-	-	0.31	-	-
ap	0.07	0.18	0.20	0.07	0.33	0.02	0.09	0.02	0.11	0.04	0.07	0.20	0.11

Appendix 3.6b Calculated average chemical compositions of selected granitic pegmatites from the Grenville Province

Smpl No.	I90	RDC	JMV	RPL6	RPL7	RPL8	RPL9	GI2	GI4	BP11	BQ13	FG4	FG5
Ref.	1	2	1	1	1	1	1	1	1	1	1	1	1
wt.%	2		3	3	3	3	3	3	3	3	3	3	3
SiO ₂	73.4	73.6	73.0	63.0	61.2	74.0	85.6	72.5	75.5	77.4	75.4	68.9	74.7
TiO ₂	0.06	0.14	0.20	0.50	0.40	0.20	0.00	0.10	0.10	0.00	0.00	0.20	0.90
Al ₂ O ₃	13.20	14.70	14.30	18.20	18.80	13.50	8.90	15.50	13.40	14.50	14.90	15.00	4.60
Fe ₂ O ₃	-	-	0.10	1.30	0.40	0.20	0.00	0.10	0.30	0.20	0.40	0.90	9.00
FeO	1.30	1.50	1.00	2.40	2.40	1.80	0.20	0.90	0.60	0.10	0.40	0.40	3.40
MnO	0.02	0.00	0.10	0.10	0.10	0.10	0.10	0.20	0.10	0.00	0.40	0.10	0.10
MgO	0.10	0.30	0.20	1.30	1.10	0.50	0.00	0.00	0.20	0.30	0.10	0.20	0.20
CaO	0.80	0.70	0.70	1.60	1.60	1.30	1.50	0.90	1.00	0.60	0.60	1.30	0.60
Na ₂ O	2.20	3.60	2.90	2.70	2.70	3.10	3.00	6.40	5.40	3.00	5.40	4.80	1.40
K ₂ O	6.90	5.40	6.30	8.50	8.60	4.20	0.20	2.10	1.70	7.00	1.90	5.90	1.40
P ₂ O ₅	0.01	0.03	0.04	0.63	0.54	0.07	0.00	0.03	0.03	0.03	0.11	0.05	0.05
H ₂ O	-	-	0.60	0.70	0.50	0.40	0.00	0.30	0.20	0.30	0.30	0.30	0.60
Total	98.0	100.0	99.4	100.9	98.34	99.37	99.5	99.0	98.5	100.3	99.9	98.1	97.0
ppm													
Cl	-	-	-	-	400	200	-	300	0	200	200	300	200
F	-	-	-	700	700	500	-	100	100	100	200	600	300
S	-	-	0	200	100	1300	-	0	200	300	100	0	0
Ba	-	-	1000	1500	1500	500	100	0	0	400	0	600	200
Rb	-	-	300	300	300	200	0	300	100	300	200	300	0
Sr	-	-	300	500	500	200	0	100	100	100	0	200	100
Zn	-	-	0	100	0	0	0	100	100	0	0	100	100
Zr	-	-	300	300	100	2000	100	200	0	100	0	100	12200
U	-	-	5	4	3	1380	20	45	23	18	5	3	167
Th	-	-	0	0	0	219	0	23	16	18	1	0	0
q	32.43	30.20	29.63	9.97	7.41	35.23	64.19	24.60	34.86	28.43	35.10	16.37	59.88
c	0.68	1.74	1.53	3.16	3.44	1.66	1.02	1.13	0.93	0.97	3.14		
or	40.81	31.94	37.21	50.25	50.84	24.80	1.18	12.40	10.04	41.35	11.22	34.85	8.26
ab	18.64	30.50	24.53	22.86	22.86	26.22	25.37	54.14	45.68	25.38	45.68	40.61	11.83
an	3.91	3.28	3.21	3.82	4.41	5.99	7.44	4.27	4.76	2.78	2.26	1.96	2.13
hy	0.25	0.75	2.11	5.93	6.34	4.24	0.04	1.78	1.37	0.76	1.40	-	0.31
di	-	-	-	-	-	-	-	-	-	-	-	1.08	0.40
wo	-	-	-	-	-	-	-	-	-	-	-	1.16	-
mt	-	-	0.15	1.89	0.58	0.29	0.26	0.15	0.44	0.29	0.58	1.04	8.69
il	0.04	-	0.38	0.95	0.76	0.38	-	0.19	0.19	-	-	0.38	1.71
hm	1.17	1.36	-	-	-	-	-	-	-	-	-	0.19	3.02
ru	0.04	0.14	-	-	-	-	-	-	-	-	-	-	-
tn	-	-	-	-	-	-	-	-	-	-	-	-	-
ap	0.02	0.18	0.09	1.39	1.19	0.15	-	0.07	0.07	0.07	0.24	0.11	0.11

Appendix 3.6c Calculated average chemical compositions of selected granitic pegmatites from the Grenville Province

Smpl No.	HM12	T-#	H-#	C-8	P-#	H-50	HLA	ML	UA	MA	UU	MB	CR8
Ref.	4	5	5	5	5	5	6	7	8	8	8	8	9
wt. %													
SiO ₂	80.6	78.25	82.9	73.9	70.3	74.9	72.6	73.4	73.08	73.0	68.3	76.3	73.7
TiO ₂	0.10	0.20	0.35	0.27	0.39	0.21	0.10	0.06	0.07	0.30	1.22	0.08	0.13
Al ₂ O ₃	11.10	11.89	10.00	13.87	14.59	12.54	14.98	13.47	13.90	10.53	11.51	12.57	14.01
Fe ₂ O ₃	0.30	1.16	0.23	2.48	3.21	1.20	1.49	0.74	1.28	7.39	4.33	0.98	1.12
MnO	0.00	0.02	0.00	0.03	0.05	0.01	0.01	0.03	0.01	0.03	0.11	0.00	0.02
MgO	0.10	0.44	0.30	0.36	0.69	0.52	0.05	0.30	0.04	0.04	1.24	0.10	0.40
CaO	0.90	1.23	0.94	0.87	1.68	0.43	1.93	0.51	0.39	0.45	4.87	0.48	0.95
Na ₂ O	3.30	2.44	1.71	5.66	3.38	1.70	4.02	3.47	3.85	2.71	3.75	3.25	2.93
K ₂ O	2.40	4.11	4.83	2.76	4.92	7.95	4.26	6.86	6.42	4.99	4.40	3.90	6.22
P ₂ O ₅	0.01	-	-	-	-	-	-	0.01	0.00	0.01	0.14	0.00	0.00
H ₂ O	0.40	-	-	-	-	-	-	-	-	-	-	-	-
Total 99.2	99.7	101.6	100.2	99.2	99.5	99.4	99.9	99.9	99.0	99.4	99.9	97.6	99.5
ppm													
Cl	100	-	-	-	-	-	-	-	-	-	-	-	-
F	0	-	-	-	-	-	-	-	-	-	-	-	-
S	10000	-	-	-	-	-	100	100	0	0	100	500	100
Ba	400	-	-	-	-	-	368	463	333	307	317	379	579
Rb	100	-	-	-	-	-	274	220	306	250	241	193	157
Sr	300	-	-	-	-	-	350	157	119	95	144	156	176
Zn	0	-	-	-	-	-	-	-	2	33	913	20	20
Zr	100	-	-	-	-	-	166	-	111	840	104	680	16
U	3	-	-	-	-	519	-	-	-	-	-	-	-
Th	7	-	-	-	-	1186	-	-	-	-	-	-	-
q	50.20	45.07	52.04	28.04	27.15	32.95	28.70	25.86	25.33	37.22	23.12	41.28	30.22
c	1.46	1.19	0.25	-	0.65	0.36	0.25	-	-	-	2.13	0.73	-
or	14.17	24.27	28.52	16.30	29.06	46.96	25.16	40.51	37.90	29.46	25.77	23.03	36.74
ab	27.91	20.64	14.46	47.88	28.59	14.38	34.01	29.35	32.56	22.92	31.46	27.49	24.79
an	4.40	6.10	4.66	4.29	8.33	2.13	9.57	0.92	1.68	1.83	1.56	2.38	4.71
hy	0.25	1.09	0.74	0.89	1.71	1.29	0.12	0.22	0.08	0.10	-	0.25	0.99
dl	-	-	-	-	-	-	-	1.14	0.04	-	6.63	-	-
vo	-	-	-	-	-	-	-	-	-	-	3.84	-	-
mt	-	-	-	-	-	-	-	-	-	-	-	-	-
ll	-	0.04	-	0.06	0.11	0.02	0.02	0.06	0.02	0.06	0.23	-	0.04
hm	0.30	1.16	0.23	2.49	3.22	1.20	1.49	0.74	1.28	7.41	4.30	0.98	1.12
ru	-	0.18	0.35	0.23	0.33	0.20	0.09	-	-	0.17	-	0.08	0.11
tn	-	-	-	0.02	-	-	-	0.06	0.14	0.24	2.67	-	-
ap	0.02	-	-	-	-	-	-	0.02	-	0.02	0.31	-	-

Appendix 3.6d Calculated average chemical compositions of selected granitic pegmatites from the Grenville Province

Smpl No.	G-1	P-1	P-2	P-3	P-4	L26	L107	L3	L118	L116	L4B	L13B
Ref.	10	10	10	10	10	11	11	11	11	11	11	11
wt. %	71.3	68.7	63.49	73.5	73.8	75.7	73.8	72.7	71.1	72.0	74.5	73.7
SiO ₂	0.33	0.12	0.61	0.09	0.03	0.07	0.06	0.01	0.02	0.02	0.04	0.68
Al ₂ O ₃	14.90	16.00	17.05	15.60	15.60	12.80	13.13	13.90	14.55	15.43	13.39	12.65
Fe ₂ O ₃	1.22	1.00	1.43	0.13	0.07	0.24	0.55	0.21	0.44	0.45	0.60	0.74
FeO	0.84	0.78	1.17	0.23	0.14	-	-	-	-	-	-	-
MnO	0.03	0.04	0.07	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.07	0.68	0.80	0.25	0.21	0.15	0.17	0.08	0.18	0.26	0.25	0.36
CaO	2.25	0.18	2.96	1.20	0.07	0.59	0.99	0.34	0.19	2.34	0.82	2.30
Na ₂ O	4.19	3.73	4.85	2.89	4.08	3.32	4.27	3.02	2.07	5.78	2.63	5.53
K ₂ O	4.34	7.48	6.76	6.40	6.42	6.20	4.58	7.68	10.17	1.48	6.82	1.06
F ₂ O ₃	0.09	0.00	0.13	0.00	0.00	0.01	0.02	0.01	0.02	0.01	0.01	0.02
H ₂ O	0.22	0.32	0.25	0.11	0.19	-	-	-	-	-	-	-
Total 99.8	99.7	99.6	100.4	100.6	99.05	97.6	97.6	97.92	98.7	97.8	99.1	97.08
ppm												
S	-	-	-	-	-	400	500	400	300	500	500	500
Ba	-	-	-	-	-	736	504	1470	607	514	843	114
Rb	-	-	-	-	-	261	233	354	343	48	196	51
Sr	-	-	-	-	-	430	159	551	153	1101	278	231
Zn	-	-	-	-	-	75	92	89	59	56	51	61
Zr	-	-	-	-	-	24	73	414	6	40	18	190
q	25.97	15.40	4.16	29.20	24.99	31.47	29.50	24.91	19.59	27.38	31.02	33.47
c	1.05	-	1.74	1.81	-	-	0.02	-	-	0.09	0.21	-
or	25.63	46.31	39.94	37.80	37.92	36.60	27.04	45.37	60.08	48.89	40.28	6.24
ab	35.45	31.56	41.04	24.45	34.52	28.07	36.11	25.55	17.51	11.54	22.25	46.53
an	9.03	0.89	4.79	5.95	0.35	1.71	3.13	1.62	0.37	-	4.00	6.53
hy	-	2.17	-	0.79	0.67	0.03	-	0.20	0.30	0.65	0.62	0.03
dl	0.46	-	4.48	-	-	0.74	0.92	-	0.32	-	-	1.85
wo	0.40	-	1.39	-	-	-	0.13	-	-	-	-	-
mt	1.77	1.45	2.08	0.19	0.10	-	-	-	-	-	-	-
ll	0.63	0.23	1.16	0.17	0.06	0.02	0.02	0.02	0.02	0.02	0.02	0.02
hm	-	-	-	-	-	0.24	0.55	0.21	0.44	0.45	0.60	0.74
ru	-	-	-	-	-	-	-	-	-	-	0.03	-
tn	-	-	-	-	-	-	-	-	-	0.01	-	1.63
ap	0.20	-	0.29	-	-	0.02	0.04	0.02	0.04	0.02	0.02	0.04

References (Ref): 1, Ford (1983); 2, Fowler (1980); 3, Rimsalte (1983, 1985); 4, Rimsalte (1984); 5, Tremblay (1974); 6, Hervert (1979); 7, Cousineau (1986); 8, Habib (1982); 9, Bottomley (1988); 10, Armstrong and Gittins (1969); 11, this study. Smpl = sample number; No. = number of samples.

APPENDIX 4A In situ gamma-ray spectrometry data

Loc	Sample	Type	XK	eUppm	eThppm	log XK	log eU	log eTh
1.0	1	A	2.9	57	438	0.46	1.76	2.64
1.0	9	A	4.0	1	4	0.60	0.00	0.60
1.0	2	N	1.7	1	1	0.23	0.00	0.00
1.0	10	A	5.0	115	87	0.70	2.06	1.94
1.0	3	J	2.8	16	99	0.45	1.20	2.00
1.0	11	A	4.4	11	33	0.64	1.04	1.52
1.0	4	A	2.7	26	127	0.43	1.41	2.10
1.0	12	J	0.2	2	2	-0.70	0.30	0.30
1.0	5	N	1.2	1	4	0.08	0.00	0.60
1.0	13	A	3.0	6	32	0.48	0.78	1.51
1.0	6	F	10.3	218	67	1.01	2.34	1.83
1.0	7	M	0.8	2	2	-0.10	0.30	0.30
1.0	8	A	5.3	18	135	0.72	1.26	2.13
2.0	1	M	2.7	2.0	3.0	0.43	0.30	0.48
2.0	10	A	6.2	296.0	1727.0	0.79	2.47	3.24
2.0	2	B	6.5	9.0	11.0	0.81	0.95	1.04
2.0	3	G	1.5	5.0	6.0	0.18	0.70	0.78
2.0	4	A	6.7	5.0	6.0	0.83	0.70	0.78
2.0	5	A	5.5	9.0	8.0	0.74	0.95	0.90
2.0	6	A	5.6	12.0	18.0	0.75	1.08	1.26
2.0	7	A	8.3	16.0	11.0	0.92	1.20	1.04
2.0	8	K	7.5	7.0	10.0	0.88	0.85	1.00
2.0	9	A	1.6	296.0	807.0	0.20	2.47	2.91
7.0	1	A	7.3	19.0	61.0	0.86	1.28	1.79
7.0	10	H	28.7	3728.0	2097.0	1.46	3.57	3.32
7.0	2	A	5.7	4.0	12.0	ERR	0.60	1.08
7.0	3	N	2.1	3.0	9.0	0.32	0.48	0.95
7.0	4	N	3.1	2.0	4.0	0.49	0.30	0.60
7.0	5	K	4.3	59.0	175.0	0.63	1.77	2.24
7.0	6	K	3.6	12.0	30.0	0.56	1.08	1.48
7.0	7	K	6.0	12.0	41.0	0.78	1.08	1.61
7.0	8	K	2.1	444.0	1594.0	0.32	2.65	3.20
7.0	9	D	2.2	6.0	15.0	0.34	0.78	1.18
8.0	1	L	0.9	2.0	8.0	-0.05	0.30	0.90
8.0	2	F	3.2	2.0	4.0	0.51	0.30	0.60
8.0	3	K	4.2	7.0	21.0	0.62	0.85	1.32
8.0	4	F	3.6	1.0	3.0	0.56	0.00	0.48
8.0	5	C	5.2	3.0	7.0	0.72	0.48	0.85
8.0	6	F	3.3	2.0	4.0	0.52	0.30	0.60
8.0	7	C	5.4	1.0	3.0	0.73	0.00	0.48
8.0	8	F	2.9	5.0	23.0	0.46	0.70	1.36
8.0	9	N	5.1	5.0	10.0	0.71	0.70	1.00
9.0	1	I	2.5	178	81	0.40	2.25	1.91
9.0	10	H	0.5	17	13	-0.30	1.23	1.11
9.0	11	L	0.4	8	9	-0.40	0.90	0.95
9.0	12	L	0.3	9	10	-0.52	0.95	1.00
9.0	13	T	5.8	239	191	0.76	2.38	2.28
9.0	14	K	3.4	11	17	0.53	1.04	1.23
9.0	15	N	2.2	9	11	0.34	0.95	1.04
9.0	16	K	2.4	8	11	0.38	0.90	1.04
9.0	17	K	2.6	8	21	0.41	0.90	1.32
9.0	18	K	3.4	11	26	0.53	1.04	1.41
9.0	19	K	1.5	15	44	0.18	1.18	1.64
9.0	2	D	3.7	46	42	0.57	1.66	1.62
9.0	20	K	3.2	17	52	0.51	1.23	1.72
9.0	21	K	1.4	13	43	0.15	1.11	1.63
9.0	3	J	0.3	250	3388	-0.52	2.40	3.53
9.0	4	D	4.2	18	61	0.62	1.26	1.79
9.0	5	A	3.9	17	43	0.59	1.23	1.63
9.0	6	A	5.3	17	99	0.72	1.23	2.00
9.0	7	H	2.4	20	32	0.38	1.30	1.51
9.0	8	J	1.7	39	46	0.23	1.59	1.66
9.0	9	H	4.3	206	130	0.63	2.31	2.11
14.0	1	N	3.1	8	13	0.49	0.90	1.11

Loc	Sample	Type	XK	eUppm	eThppm	log K	log eU	log eTh
14.0	2	K	2.0	171	92	0.30	2.23	1.96
14.0	3	K	3.6	71	44	0.56	1.85	1.64
14.0	4	K	3.8	2711	817	0.58	3.43	2.91
14.0	5	K	3.9	45	29	0.59	1.65	1.46
14.0	6	K	2.7	17	38	0.43	1.23	1.58
15.0	1	D	5.2	88	780	0.72	1.94	2.89
15.0	2	H	2.4	34	361	0.38	1.53	2.56
15.0	3	L	1.4	1	15	0.15	0.00	1.18
15.0	4	I	2.1	173	2033	0.32	2.24	3.31
16.0	1	A	3.6	14	12	0.56	1.15	1.08
16.0	2	A	4.0	18	24	0.60	1.26	1.38
16.0	3	A	1.9	125	203	0.28	2.10	2.31
16.0	4	A	0.9	45	54	-0.05	1.65	1.73
16.0	5	B	8.0	585	457	0.90	2.77	2.66
16.0	6	M	0.8	2	4	-0.10	0.30	0.60
17.0	1	B	5.6	69	194	0.75	1.84	2.29
17.0	2	A	4.0	41	98	0.60	1.61	1.99
17.0	3	A	5.9	347	415	0.77	2.54	2.62
17.0	4	A	5.1	136	193	0.71	2.13	2.29
17.0	5	E	2.4	246	202	0.38	2.39	2.31
18.0	1	I	1.3	16	14	0.11	1.20	1.15
18.0	2	L	0.7	2	6	-0.15	0.30	0.78
18.0	3	K	4.7	7	189	0.67	0.85	2.28
18.0	4	A	4.5	4	4	0.65	0.60	0.60
19.0	1	H	4.0	105	278	0.60	2.02	2.44
19.0	2	A	3.1	6	33	0.49	0.78	1.52
19.0	3	K	1.5	3	9	0.18	0.48	0.95
19.0	4	J	0.4	5	15	-0.40	0.70	1.18
19.0	5	L	0.2	2	5	-0.70	0.30	0.70
19.0	6	K	0.4	2	12	-0.40	0.30	1.08
19.0	7	K	6.1	10	24	0.79	1.00	1.38
19.0	8	I	3.0	114	110	0.48	2.06	2.04
19.0	9	B	2.1	3	14	0.32	0.48	1.15
20.0	1	L	1.3	12.0	22.0	0.11	1.08	1.34
20.0	2	H	3.7	427.0	389.0	0.57	2.63	2.59
20.0	3	H	2.3	15.0	30.0	0.36	1.18	1.48
20.0	4	D	2.8	18.0	45.0	0.45	1.26	1.65
20.0	5	H	1.9	16.0	26.0	0.28	1.20	1.41
20.0	6	D	3.9	10.0	11.0	0.59	1.00	1.04
20.0	7	H	6.0	1250.0	459.0	0.78	3.10	2.66
21.0	1	K	72.6	1630	1029	1.86	3.21	3.01
21.0	2	N	0.8	7	13	-0.10	0.85	1.11
21.0	3	K	5.5	187	183	0.74	2.27	2.26
21.0	4	K	41.7	672	381	1.62	2.83	2.58
22.0	1	A	5.5	2	12	0.74	0.30	1.08
22.0	2	C	2.3	7	24	0.36	0.85	1.38
22.0	3	A	5.5	3	14	0.74	0.48	1.15
22.0	4	A	5.6	2	18	0.75	0.30	1.26
22.0	5	C	2.2	14	43	0.34	1.15	1.63
22.0	6	C	3.8	9	44	0.58	0.95	1.64
22.0	7	A	4.0	5	40	0.60	0.70	1.60
22.0	8	F	0.7	7	44	-0.15	0.85	1.64
23.0	1	K	9.2	76	1582	0.96	1.88	3.20
23.0	2	K	6.4	51	1581	0.81	1.71	3.20
23.0	3	K	1.1	5	33	0.04	0.70	1.52
23.0	4	I	0.9	8	71	-0.05	0.90	1.85
24.0	1	L	0.5	4	17	-0.30	0.60	1.23
24.0	2	A	3.2	302	345	0.51	2.48	2.54
24.0	3	A	3.0	70	149	0.48	1.85	2.17
24.0	4	I	0.1	2	3	-1.00	0.30	0.48
24.0	5	H	1.5	66	34	0.18	1.82	1.53
24.0	6	H	1.8	178	450	0.26	2.25	2.65
24.0	7	H	0.7	18	34	-0.15	1.26	1.53
25.0	1	H	0.3	4	11	-0.52	0.60	1.04
25.0	2	H	1.1	77	138	0.04	1.89	2.14
25.0	3	H	0.1	587	138	-1.00	2.77	2.14

Loc	Sample	Type	KX	eUppm	eThppm	log KX	log eU	log eTh
25.0	4	L	0.4	1	2	-0.40	0.00	0.30
25.0	5	I	4.9	243	1215	0.69	2.39	3.08
26.0	1	K	2.6	12	37	0.41	1.08	1.57
26.0	2	J	0.2	2	6	-0.70	0.30	0.78
26.0	3	J	1.0	4	8	0.00	0.60	0.90
26.0	4	J	2.3	127	31	0.36	2.10	1.49
26.0	5	K	2.3	63	31	0.36	1.80	1.49
26.0	6	J	0.3	96	27	-0.52	1.98	1.43
26.0	7	J	14.9	1438	263	1.17	3.16	2.42
29.0	1	L	0.7	2	4	-0.15	0.30	0.60
29.0	10	J	3.0	125	110	0.48	2.10	2.04
29.0	11	A	4.8	4	17	0.68	0.60	1.23
29.0	2	D	4.6	9	31	0.66	0.95	1.49
29.0	3	H	2.4	143	159	0.38	2.16	2.20
29.0	4	K	2.2	20	31	0.34	1.30	1.49
29.0	5	F	3.5	34	60	0.54	1.53	1.78
29.0	6	H	19.8	1560	1819	1.30	3.19	3.26
29.0	7	C	4.3	21	37	0.63	1.32	1.57
29.0	8	H	6.8	1439	1436	0.83	3.16	3.16
29.0	9	H	5.0	1028	1061	0.70	3.01	3.03
30.0	1	H	1.0	14	36	0.00	1.15	1.56
30.0	10	A	1.3	26	119	0.11	1.41	2.08
30.0	11	H	1.6	78	196	0.20	1.89	2.29
30.0	12	I	6.0	246	133	0.78	2.39	2.12
30.0	13	H	25.9	2159	905	1.41	3.33	2.96
30.0	14	H	2.3	68	119	0.36	1.83	2.08
30.0	15	H	173.0	13349	11311	2.24	4.13	4.05
30.0	2	H	1.8	22	90	0.26	1.34	1.95
30.0	3	H	2.7	43	197	0.43	1.63	2.29
30.0	4	D	2.0	9	46	0.30	0.95	1.66
30.0	5	H	0.9	13	82	-0.05	1.11	1.91
30.0	6	H	0.6	7	39	-0.22	0.85	1.59
30.0	7	K	8.0	119	4857	0.90	2.08	3.69
30.0	8	D	2.7	25	36	0.43	1.40	1.56
30.0	9	D	2.7	99	76	0.43	2.00	1.88
31.0	1	M	1.6	4	54	0.20	0.60	1.73
31.0	10	B	4.7	36	56	0.67	1.56	1.75
31.0	11	B	5.3	43	42	0.72	1.63	1.62
31.0	12	B	6.8	259	1535	0.83	2.41	3.19
31.0	13	B	12.9	301	262	1.11	2.48	2.42
31.0	2	M	3.6	5	17	0.56	0.70	1.23
31.0	3	L	2.1	4	5	0.32	0.60	0.70
31.0	5	K	3.6	59	138	0.56	1.77	2.14
31.0	6	K	4.4	79	138	0.64	1.90	2.14
31.0	7	K	2.4	26	88	0.38	1.41	1.94
31.0	8	K	5.4	47	136	0.73	1.67	2.13
31.0	9	B	11.2	273	553	1.05	2.44	2.74
32.0	1	N	3.8	5	27	0.58	0.70	1.43
32.0	2	H	2.3	27	150	0.36	1.43	2.18
32.0	3	H	3.2	50	103	0.51	1.70	2.01
32.0	4	H	2.8	58	128	0.45	1.76	2.11
32.0	5	H	1.9	87	139	0.28	1.94	2.14
32.0	6	H	92.4	2464	5124	1.97	3.39	3.71
32.0	7	A	4.7	2	13	0.67	0.30	1.11
33.0	1	K	1.8	69	112	0.26	1.84	2.05
33.0	2	K	2.2	83	129	0.34	1.92	2.11
33.0	3	B	3.3	36	750	0.52	1.56	2.88
34.0	1	A	5.6	20	56	0.75	1.30	1.75
34.0	2	B	6.3	31	96	0.80	1.49	1.98
34.0	3	B	6.0	30	86	0.78	1.48	1.93
34.0	4	A	5.8	10	28	0.76	1.00	1.45
34.0	5	L	0.7	2	4	-0.15	0.30	0.60
35.0	1	E	3.4	4	765	0.53	0.60	2.88
35.0	2	E	-5.4	-81	13021	ERR	ERR	4.11
35.0	3	A	3.5	1	56	0.54	0.00	1.75
36.0	1	H	1.4	9	23	0.15	0.95	1.36

Loc	Sample	Type	XK	eUppm	eThppm	log XK	log eU	log eTh
36.0	2	L	1.1	5	10	0.04	0.70	1.00
36.0	3	J	4.5	9	16	0.65	0.95	1.20
36.0	4	J	1.4	1	8	0.15	0.00	0.90
36.0	5	J	0.7	2	4	-0.15	0.30	0.60
36.0	6	H	0.5	3	4	-0.30	0.48	0.60
36.0	7	K	4.0	5	7	0.60	0.70	0.85
36.0	8	K	1.4	6	9	0.15	0.78	0.95
37.0	1	K	3.3	6	10	0.52	0.78	1.00
37.0	10	A	6.7	1	10	0.83	0.00	1.00
37.0	2	H	3.5	6	5	0.54	0.78	0.70
37.0	3	J	2.4	27	12	0.38	1.43	1.08
37.0	4	K	1.6	15	13	0.20	1.18	1.11
37.0	5	J	1.6	9	7	0.20	0.95	0.85
37.0	6	J	1.6	13	11	0.20	1.11	1.04
37.0	7	J	1.4	2	7	0.15	0.30	0.85
37.0	8	J	2.1	4	8	0.32	0.60	0.90
37.0	9	A	6.9	2	16	0.84	0.30	1.20
38.0	1	A	6.7	0	7	0.83	ERR	0.85
38.0	2	A	1.6	0	3	0.20	ERR	0.48
38.0	3	A	5.7	1	4	0.76	0.00	0.60
38.0	4	K	4.0	2	9	0.60	0.30	0.95
38.0	5	K	3.0	2	7	0.48	0.30	0.85
38.0	6	A	2.9	1	3	0.46	0.00	0.48
38.0	7	K	1.8	2	13	0.26	0.30	1.11
38.0	8	K	2.0	6	36	0.30	0.78	1.56
38.0	9	B	4.2	3	23	0.62	0.48	1.36
39.0	1	K	3.2	4	19	0.51	0.60	1.28
39.0	2	K	2.5	4	16	0.40	0.60	1.20
39.0	3	K	1.7	4	18	0.23	0.60	1.26
39.0	4	K	2.7	4	24	0.43	0.60	1.38
39.0	5	K	4.2	7	55	0.62	0.85	1.74
40.0	1	K	0.1	1	3	-1.00	0.00	0.48
40.0	2	H	1.2	2	11	0.08	0.30	1.04
41.0	1	K	1.1	5	12	0.04	0.70	1.08
41.0	2	K	3.3	16	24	0.52	1.20	1.38
41.0	3	K	2.6	5	10	0.41	0.70	1.00
41.0	4	K	1.1	8	15	0.04	0.90	1.18
41.0	5	N	4.5	5	11	0.65	0.70	1.04
41.0	6	K	4.5	5	15	0.65	0.70	1.18
42.0	1	J	1.4	8	62	0.15	0.90	1.79
42.0	10	J	1.4	9	92	0.15	0.95	1.96
42.0	11	J	0.8	4	42	-0.10	0.60	1.62
42.0	12	J	1.3	5	25	0.11	0.70	1.40
42.0	13	K	0.2	8	83	-0.70	0.90	1.92
42.0	2	K	1.6	6	41	0.20	0.78	1.61
42.0	3	K	2.3	8	41	0.36	0.90	1.61
42.0	4	B	6.4	5	56	0.81	0.70	1.75
42.0	5	K	2.7	5	35	0.43	0.70	1.54
42.0	6	K	4.6	5	35	0.66	0.70	1.54
42.0	7	K	2.3	8	69	0.36	0.90	1.84
42.0	8	K	1.7	8	65	0.23	0.90	1.81
42.0	9	K	1.4	3	39	0.15	0.48	1.59
43.0	1	L	0.8	2	8	-0.10	0.30	0.90
43.0	10	K	8.5	187	111	0.93	2.27	2.05
43.0	2	A	1.7	11	36	0.23	1.04	1.56
43.0	3	H	1.2	7	21	0.08	0.85	1.32
43.0	4	H	8.0	75	77	0.90	1.88	1.89
43.0	5	A	4.5	3	7	0.65	0.48	0.85
43.0	6	A	3.0	10	45	0.48	1.00	1.65
43.0	7	B	8.8	131	96	0.94	2.12	1.98
43.0	8	A	5.1	36	52	0.71	1.56	1.72
43.0	9	K	6.3	264	110	0.80	2.42	2.04
44.0	1	N	1.7	0	5	0.23	ERR	0.70
44.0	2	A	5.3	7	66	0.72	0.85	1.82
44.0	3	B	5.1	32	394	0.71	1.51	2.60
44.0	4	B	5.3	14	210	0.72	1.15	2.32

Loc	Sample	Type	IK	eUppm	eThppm	log IK	log eU	log eTh
44.0	5	A	5.2	4	39	0.72	0.60	1.59
44.0	6	A	4.4	2	13	0.64	0.30	1.11
44.0	7	A	3.4	7	35	0.53	0.85	1.54
44.0	8	A	5.5	7	35	0.74	0.85	1.54
44.0	9	A	6.2	11	45	0.79	1.04	1.65
45.0	1	L	0.4	3	5	-0.40	0.48	0.70
45.0	2	A	4.9	3	7	0.69	0.48	0.85
45.0	3	H	1.2	13	24	0.08	1.11	1.38
45.0	4	A	2.6	15	34	0.41	1.18	1.53
45.0	5	A	4.6	3	12	0.66	0.48	1.08
45.0	6	A	1.9	10	25	0.28	1.00	1.40
46.0	1	A	3.9	6	48	0.59	0.78	1.68
46.0	2	D	22.3	694	1993	1.35	2.84	3.30
46.0	3	D	5.5	26	52	0.74	1.41	1.72
46.0	4	L	2.4	3	5	0.38	0.48	0.70
46.0	5	A	4.2	45	73	0.62	1.65	1.86
47.0	1	B	4.7	8	61	0.67	0.90	1.79
47.0	10	A	2.0	52	38	0.30	1.72	1.58
47.0	11	A	3.3	6	6	0.52	0.78	0.78
47.0	12	A	2.2	42	31	0.34	1.62	1.49
47.0	13	K	34.3	916	2769	1.54	2.96	3.44
47.0	14	A	6.9	6	5	0.84	0.78	0.70
47.0	2	M	2.6	3	7	0.41	0.48	0.85
47.0	3	L	1.1	2	3	0.04	0.30	0.48
47.0	4	I	1.4	2	5	0.15	0.30	0.70
47.0	5	L	0.6	1	2	-0.22	0.00	0.30
47.0	6	E	9.8	261	179	0.99	2.42	2.25
47.0	7	E	5.4	193	120	0.73	2.29	2.08
47.0	8	N	3.1	1	3	0.49	0.00	0.48
47.0	9	K	5.6	113	191	0.75	2.05	2.28
48.0	1	D	3.5	2	8	0.54	0.30	0.90
48.0	2	O	0.8	1	19	-0.10	0.00	1.28
49.0	1	B	4.5	15	191	0.65	1.18	2.28
49.0	2	B	1.8	53	534	0.26	1.72	2.73
49.0	3	B	2.5	112	1101	0.40	2.05	3.04
49.0	4	A	4.7	7	107	0.67	0.85	2.03
49.0	5	A	6.1	3	48	0.79	0.48	1.68
49.0	6	K	4.5	2	12	0.65	0.30	1.08
50.0	1	B	4.7	73	313	0.67	1.86	2.50
50.0	10	A	3.7	4	71	0.57	0.60	1.85
50.0	2	N	2.5	3	16	0.40	0.48	1.20
50.0	3	D	3.1	52	309	0.49	1.72	2.49
50.0	4	A	3.5	2	26	0.54	0.30	1.41
50.0	5	A	4.9	2	61	0.69	0.30	1.79
50.0	6	B	5.8	15	247	0.76	1.18	2.39
50.0	7	G	0.6	2	9	-0.22	0.30	0.95
50.0	8	A	2.4	31	802	0.38	1.49	2.90
50.0	9	H	0.3	6	53	-0.52	0.78	1.72
52.0	1	C	5.6	7	26	0.75	0.85	1.41
52.0	2	F	2.8	3	11	0.45	0.48	1.04
52.0	3	O	0.4	2	7	-0.40	0.30	0.85
52.0	4	F	1.7	3	14	0.23	0.48	1.15
52.0	5	L	1.0	2	7	0.00	0.30	0.85
52.0	6	A	5.2	1	3	0.72	0.00	0.48
52.0	7	F	1.1	2	13	0.04	0.30	1.11
53.0	1	B	5.3	4	19	0.72	0.60	1.28
53.0	2	B	4.7	3	16	0.67	0.48	1.20
53.0	3	K	5.2	59	872	0.72	1.77	2.94
53.0	4	K	1.7	146	1446	0.23	2.16	3.16
53.0	5	N	5.4	5	42	0.73	0.70	1.62
53.0	6	K	3.4	56	442	0.53	1.75	2.65
53.0	7	K	2.6	11	180	0.41	1.04	2.26
53.0	8	K	2.9	96	1244	0.46	1.98	3.09
54.0	1	A	4.5	8	15	0.65	0.90	1.18
54.0	2	N	3.5	2	18	0.54	0.30	1.26
54.0	3	K	1.7	2	12	0.23	0.30	1.08

Loc	Sample	Type	IX	eUppm	eThppm	log IX	log eU	log eTh
54.0	4	K	2.2	3	20	0.34	0.48	1.30
54.0	5	N	4.5	3	9	0.65	0.48	0.95
54.0	6	K	3.4	8	34	0.53	0.90	1.53
54.0	7	B	3.4	7	31	0.53	0.85	1.49
54.0	8	N	3.0	3	18	0.48	0.48	1.26
55.0	1	E	2.6	14	283	0.41	1.15	2.45
55.0	10	E	1.1	3	33	0.04	0.48	1.52
55.0	11	D	5.6	8	9	0.75	0.90	0.95
55.0	2	A	1.5	6	33	0.18	0.78	1.52
55.0	3	N	1.3	3	6	0.11	0.48	0.78
55.0	4	K	7.0	24	92	0.85	1.38	1.96
55.0	5	N	1.9	6	21	0.28	0.78	1.32
55.0	6	E	5.1	26	67	0.71	1.41	1.83
55.0	7	E	2.0	4	78	0.30	0.60	1.89
55.0	8	N	1.4	1	7	0.15	0.00	0.85
55.0	9	A	3.9	3	72	0.59	0.48	1.86
56.0	1	A	2.3	1	11	0.36	0.00	1.04
56.0	2	A	2.6	100	1283	0.41	2.00	3.11
56.0	3	E	3.0	51	1109	0.48	1.71	3.04
56.0	4	N	4.5	8	30	0.65	0.90	1.48
56.0	5	N	4.8	2	8	0.68	0.30	0.90
56.0	6	H	0.7	3	11	-0.15	0.48	1.04
56.0	7	A	4.9	44	507	0.69	1.64	2.71
56.0	8	A	5.5	1	7	0.74	0.00	0.85
56.0	9	A	3.2	2	17	0.51	0.30	1.23
57.0	1	N	2.6	9	32	0.41	0.95	1.51
57.0	2	M	1.6	0	6	0.20	ERR	0.78
57.0	3	K	3.7	9	65	0.57	0.95	1.81
57.0	4	N	3.5	5	45	0.54	0.70	1.65
57.0	5	A	2.5	9	11	0.40	0.95	1.04
57.0	6	K	1.6	9	44	0.20	0.95	1.64
57.0	7	K	2.0	5	44	0.30	0.70	1.64
57.0	8	K	2.7	92	783	0.43	1.96	2.89
57.0	9	K	4.1	42	317	0.61	1.62	2.50
58.0	1	K	1.7	3	13	0.23	0.48	1.11
58.0	2	K	2.8	4	14	0.45	0.60	1.15
58.0	3	N	3.7	5	20	0.57	0.70	1.30
58.0	4	K	3.6	4	14	0.56	0.60	1.15
58.0	5	B	3.3	5	28	0.52	0.70	1.45
58.0	6	K	0.7	1	7	-0.15	0.00	0.85
59.0	1	N	2.0	2	5	0.30	0.30	0.70
59.0	2	B	3.7	2	8	0.57	0.30	0.90
59.0	3	A	4.3	3	11	0.63	0.48	1.04
59.0	4	A	4.8	9	86	0.68	0.95	1.93
59.0	5	K	4.9	19	28	0.69	1.28	1.45
59.0	6	E	3.9	4	7	0.59	0.60	0.85
60.0	1	N	4.2	5	19	0.62	0.70	1.28
60.0	10	J	2.1	357	3475	0.32	2.55	3.54
60.0	11	C	3.9	10	423	0.59	1.00	2.63
60.0	12	N	4.8	4	17	0.68	0.60	1.23
60.0	13	N	6.3	3	10	0.80	0.48	1.00
60.0	14	E	6.6	3	48	0.82	0.48	1.68
60.0	15	E	6.0	0	61	0.78	ERR	1.79
60.0	2	F	1.4	17	90	0.15	1.23	1.95
60.0	3	F	2.3	20	135	0.36	1.30	2.13
60.0	4	G	1.5	17	61	0.18	1.23	1.79
60.0	5	F	4.1	4	24	0.61	0.60	1.38
60.0	6	J	1.5	9	121	0.18	0.95	2.08
60.0	7	J	3.7	25	265	0.57	1.40	2.42
60.0	8	J	6.6	604	5999	0.82	2.78	3.78
60.0	9	J	2.2	204	1752	0.34	2.31	3.24
61.0	1	D	5.4	45	83	0.73	1.65	1.92
61.0	2	I	52.2	884	2539	1.72	2.95	3.40
61.0	3	I	104.7	1759	4885	2.02	3.25	3.69
62.0	1	F	0.8	2	7	-0.10	0.30	0.85
62.0	2	F	3.0	2	16	0.48	0.30	1.20

Loc	Sample	Type	IX	eUppa	eThppa	log IX	log eU	log eTh
62.0	3	F	2.7	1	6	0.43	0.00	0.78
62.0	4	J	1.6	1	3	0.20	0.00	0.48
62.0	5	C	6.2	8	31	0.79	0.90	1.49
62.0	6	C	4.1	58	729	0.61	1.75	2.86
62.0	7	C	1.1	80	823	0.04	1.90	2.92
62.0	8	I	18.6	424	1970	1.27	2.63	3.29
62.0	9	H	2.4	42	167	0.38	1.62	2.22
63.0	1	M	0.3	2	3	-0.52	0.30	0.48
63.0	2	A	3.5	35	57	0.54	1.54	1.76
63.0	3	A	5.1	44	76	0.71	1.64	1.88
63.0	4	A	3.9	25	41	0.59	1.40	1.61
63.0	5	M	0.8	1	4	-0.10	0.00	0.60
63.0	6	A	8.2	104	187	0.91	2.02	2.27
63.0	7	A	7.7	106	199	0.89	2.03	2.30
63.0	8	A	4.7	45	74	0.67	1.65	1.87
64.0	1	B	2.1	41	321	0.32	1.61	2.51
64.0	2	B	2.6	21	73	0.41	1.32	1.86
64.0	3	B	3.8	241	1470	0.58	2.38	3.17
64.0	4	M	2.0	3	9	0.30	0.48	0.95
64.0	5	G	2.2	113	313	0.34	2.05	2.50
64.0	6	A	0.7	21	20	-0.15	1.32	1.30
64.0	7	C	10.5	331	1275	1.02	2.52	3.11
65.0	1	B	1.3	38	41	0.11	1.58	1.61
65.0	12	L	0.1	1	1	-1.00	0.00	0.00
65.0	2	B	1.5	28	45	0.18	1.45	1.65
65.0	3	M	0.3	7	5	-0.52	0.85	0.70
65.0	4	L	0.0	1	1	ERR	0.00	0.00
65.0	5	H	4.5	52	49	0.65	1.72	1.69
65.0	6	A	0.9	17	20	-0.05	1.23	1.30
65.0	7	H	118.7	1350	1568	2.07	3.13	3.20
66.0	1	H	6.9	652	5300	0.84	2.81	3.80
66.0	10	A	1.0	2	11	0.00	0.30	1.04
66.0	11	H	18.2	404	833	1.26	2.61	2.92
66.0	13	E	5.2	44	251	0.72	1.64	2.40
66.0	14	F	4.0	161	994	0.60	2.21	3.00
66.0	15	N	5.3	8	65	0.72	0.90	1.81
66.0	16	E	3.7	8	332	0.57	0.90	2.52
66.0	17	K	2.0	186	1127	0.30	2.27	3.05
66.0	18	L	0.4	1	4	-0.40	0.00	0.60
66.0	19	D	1.8	74	321	0.26	1.87	2.51
66.0	2	D	1.8	66	623	0.26	1.82	2.79
66.0	20	D	5.0	12	27	0.70	1.08	1.43
66.0	3	L	0.2	0	5	-0.70	ERR	0.70
66.0	4	N	2.7	3	18	0.43	0.48	1.26
66.0	5	A	2.9	4	35	0.46	0.60	1.54
66.0	6	H	0.6	4	19	-0.22	0.60	1.28
66.0	7	D	4.9	4	16	0.69	0.60	1.20
66.0	8	H	1.1	34	106	0.04	1.53	2.03
66.0	9	B	1.3	3	10	0.11	0.48	1.00
67.0	1	J	0.7	3	21	-0.15	0.48	1.32
67.0	2	D	0.2	37	678	-0.70	1.57	2.83
67.0	3	D	3.7	22	89	0.57	1.34	1.95
68.0	1	N	5.8	6	22	0.76	0.78	1.34
68.0	2	F	1.8	15	13	0.26	1.18	1.11
68.0	3	B	5.4	9	23	0.73	0.95	1.36
68.0	4	D	6.2	8	10	0.79	0.90	1.00
68.0	5	F	0.8	6	6	-0.10	0.78	0.78
68.0	6	F	1.0	3	3	0.00	0.48	0.48
69.0	1	A	6.6	3	13	0.82	0.48	1.11
69.0	10	J	13.0	564	180	1.11	2.75	2.26
69.0	11	J	0.3	48	13	-0.52	1.68	1.11
69.0	12	N	2.2	15	9	0.34	1.18	0.95
69.0	2	A	3.9	4	44	0.59	0.60	1.64
69.0	3	N	4.1	5	17	0.61	0.70	1.23
69.0	4	M	1.3	4	6	0.11	0.60	0.78
69.0	5	B	2.2	69	405	0.34	1.84	2.61

Loc	Sample	Type	ZK	eUppm	eThppm	log ZK	log eU	log eTh
69.0	6	J	4.9	56	66	0.69	1.75	1.82
69.0	7	N	4.7	19	72	0.67	1.28	1.86
69.0	8	K	16.5	481	168	1.22	2.68	2.23
69.0	9	B	5.4	18	28	0.73	1.26	1.45
70.0	1	O	0.4	2	4	-0.40	0.30	0.60
70.0	10	J	1.7	3	6	0.23	0.48	0.78
70.0	11	J	0.6	6	8	-0.22	0.78	0.90
70.0	12	J	2.0	1	5	0.30	0.30	0.70
70.0	13	F	2.3	25	54	0.36	1.40	1.73
70.0	14	O	1.5	1	3	0.18	0.00	0.48
70.0	15	C	4.1	5	134	0.61	0.70	2.13
70.0	16	A	4.5	5	51	0.65	0.70	1.71
70.0	17	F	1.7	35	285	0.23	1.54	2.45
70.0	2	F	1.5	4	24	0.18	0.60	1.38
70.0	3	F	1.6	4	7	0.20	0.60	0.85
70.0	4	F	2.2	3	9	0.34	0.48	0.95
70.0	5	F	1.6	8	11	0.20	0.90	1.04
70.0	6	C	1.3	9	25	0.11	0.95	1.40
70.0	7	F	3.6	2	6	0.56	0.30	0.78
70.0	8	F	1.7	2	9	0.23	0.30	0.95
70.0	9	F	2.7	3	8	0.43	0.48	0.90
71.0	1	N	3.3	3	15	0.52	0.48	1.18
71.0	2	F	2.4	49	50	0.38	1.69	1.70
71.0	3	F	11.4	599	218	1.06	2.78	2.34
72.0	1	M	1.2	3	9	0.08	0.48	0.95
72.0	2	B	5.0	5	83	0.70	0.70	1.92
72.0	3	B	4.8	4	175	0.68	0.60	2.24
72.0	4	B	1.5	9	647	0.18	0.95	2.81
72.0	5	J	5.8	139	62	0.76	2.14	1.79
73.0	1	A	4.6	11	38	0.66	1.04	1.58
73.0	2	A	6.4	12	39	0.81	1.08	1.59
73.0	3	N	3.7	9	22	0.57	0.95	1.34
73.0	4	A	5.7	13	35	0.76	1.11	1.54
73.0	5	E	2.3	25	66	0.36	1.40	1.82
73.0	6	A	6.9	9	22	0.84	0.95	1.34
73.0	7	E	3.6	31	66	0.56	1.49	1.82
73.0	8	A	3.1	10	65	0.49	1.00	1.81
74.0	1	A	2.7	0	2	0.43	ERR	0.30
74.0	10	D	4.6	2	6	0.66	0.30	0.78
74.0	11	J	1.4	7	67	0.15	0.85	1.83
74.0	12	J	4.0	3	19	0.60	0.48	1.28
74.0	13	C	5.3	3	17	0.72	0.48	1.23
74.0	14	F	3.7	2	13	0.57	0.30	1.11
74.0	15	C	2.0	0	5	0.30	ERR	0.70
74.0	2	O	1.3	1	2	0.11	0.00	0.30
74.0	3	C	6.2	2	14	0.79	0.30	1.15
74.0	4	F	1.0	0	4	0.00	ERR	0.60
74.0	5	D	5.1	1	4	0.71	0.00	0.60
74.0	6	F	2.4	3	10	0.38	0.48	1.00
74.0	7	A	2.5	1	2	0.40	0.00	0.30
74.0	8	N	1.5	1	6	0.18	0.00	0.78
74.0	9	C	4.5	3	8	0.65	0.48	0.90
75.0	1	O	2.8	1	12	0.45	0.00	1.08
75.0	2	F	2.8	3	16	0.45	0.48	1.20
75.0	3	C	1.6	1	8	0.20	0.00	0.90
75.0	4	J	3.3	2	8	0.52	0.30	0.90
75.0	5	A	3.0	4	6	0.48	0.60	0.78
75.0	6	J	0.6	1	7	-0.22	0.00	0.85
75.0	7	F	1.3	1	8	0.11	0.00	0.90
76.0	1	A	3.5	5	17	0.54	0.70	1.23
76.0	2	O	0.5	0	4	-0.30	ERR	0.60
76.0	3	J	1.0	1	12	0.00	0.00	1.08
76.0	4	C	6.4	1	19	0.81	0.00	1.28
76.0	5	C	7.0	2	22	0.85	0.30	1.34
76.0	6	C	9.0	7	99	0.95	0.85	2.00
76.0	7	A	3.1	2	3	0.49	0.30	0.48

Loc	Sample	Type	IK	eUppm	eThppm	log IK	log eU	log eTh
77.0	1	F	4.1	1	6	0.61	0.00	0.78
77.0	2	F	8.4	1	6	0.92	0.00	0.78
77.0	3	C	8.5	1	5	0.93	0.00	0.70
77.0	4	C	8.1	1	24	0.91	0.00	1.38
77.0	5	J	3.3	2	22	0.52	0.30	1.34
77.0	6	F	3.9	2	21	0.59	0.30	1.32
77.0	7	J	3.7	4	40	0.57	0.60	1.60
78.0	1	F	1.2	9	65	0.08	0.95	1.81
78.0	10	J	43.1	543	314	1.63	2.73	2.50
78.0	11	J	12.3	269	128	1.09	2.43	2.11
78.0	2	F	1.3	2	7	0.11	0.30	0.85
78.0	3	C	5.7	19	57	0.76	1.28	1.76
78.0	4	K	6.0	18	107	0.78	1.26	2.03
78.0	5	F	0.8	3	12	-0.10	0.48	1.08
78.0	6	A	6.1	3	20	0.79	0.48	1.30
78.0	7	A	1.1	26	51	0.04	1.41	1.71
78.0	8	C	3.9	5	16	0.59	0.70	1.20
78.0	9	K	3.7	43	304	0.57	1.63	2.48
79.0	1	O	1.2	5	8	0.08	0.70	0.90
79.0	2	J	0.8	3	18	-0.10	0.48	1.26
79.0	3	J	1.2	4	13	0.08	0.60	1.11
80.0	1	N	4.3	2	6	0.63	0.30	0.78
80.0	10	J	1.1	6	96	0.04	0.78	1.98
80.0	2	N	5.8	2	10	0.76	0.30	1.00
80.0	3	N	1.3	0	1	0.11	ERR	0.00
80.0	4	B	1.9	1	4	0.28	0.00	0.60
80.0	5	C	5.7	1	2	0.76	0.00	0.30
80.0	6	F	0.6	3	34	-0.22	0.48	1.53
80.0	7	D	7.3	2	17	0.86	0.30	1.23
80.0	8	I	0.7	2	21	-0.15	0.30	1.32
80.0	9	J	0.5	11	110	-0.30	1.04	2.04
81.0	1	M	1.5	4	14	0.18	0.60	1.15
81.0	10	L	0.2	2	3	-0.70	0.30	0.48
81.0	11	D	3.9	8	20	0.59	0.90	1.30
81.0	12	L	0.4	1	2	-0.40	0.00	0.30
81.0	13	H	2.8	1	6	0.45	0.00	0.78
81.0	14	D	5.7	2	8	0.76	0.30	0.90
81.0	15	I	1.6	1	5	0.20	0.00	0.70
81.0	16	L	1.4	2	10	0.15	0.30	1.00
81.0	2	N	0.9	2	4	-0.05	0.30	0.60
81.0	3	A	4.0	4	9	0.60	0.60	0.95
81.0	4	B	1.5	80	132	0.18	1.90	2.12
81.0	5	E	1.5	101	333	0.18	2.00	2.52
81.0	6	N	0.6	1	0	-0.22	0.00	ERR
81.0	7	K	0.5	1	0	-0.22	0.00	ERR
81.0	8	B	0.5	353	1123	0.87	2.55	3.05
81.0	9	B	2.1	194	450	0.32	2.29	2.65
82.0	1	D	4.4	17	48	0.64	1.23	1.68
82.0	2	B	3.9	24	67	0.59	1.38	1.83
82.0	3	L	1.1	1	5	0.04	0.00	0.70
82.0	4	O	1.0	3	4	0.00	0.48	0.60
82.0	5	A	6.4	5	59	0.81	0.70	1.77
82.0	6	A	4.1	1	2	0.61	0.00	0.30
82.0	7	L	0.5	1	1	-0.30	0.00	0.00
83.0	1	L	0.4	1	2	-0.40	0.00	0.30
83.0	2	D	3.3	5	16	0.52	0.70	1.20
83.0	3	D	1.5	19	80	0.18	1.28	1.50
83.0	4	D	3.0	34	36	0.48	1.53	1.56
83.0	5	H	4.9	4	7	0.69	0.60	0.85
83.0	6	D	3.3	92	164	0.52	1.96	2.21
83.0	7	D	1.0	129	518	0.00	2.11	2.71
84.0	1	L	0.8	2	8	-0.10	0.30	0.90
84.0	2	D	7.0	6	41	0.85	0.78	1.61
84.0	3	H	1.9	21	32	0.28	1.32	1.51
84.0	4	D	6.8	13	105	0.83	1.11	2.02
85.0	1	J	1.7	12	21	0.23	1.08	1.32

Loc	Sample	Type	XX	eUppm	eThppm	log XX	log eU	log eTh
85.0	10	D	4.3	4	5	0.63	0.60	0.70
85.0	2	J	12.9	285	117	1.11	2.45	2.07
85.0	3	D	5.1	6	5	0.71	0.78	0.70
85.0	4	L	1.4	3	5	0.15	0.48	0.70
85.0	5	M	2.5	3	8	0.40	0.48	0.90
85.0	6	O	2.0	3	3	0.30	0.48	0.48
85.0	7	D	3.9	22	52	0.59	1.34	1.72
85.0	8	N	2.7	7	14	0.43	0.85	1.15
85.0	9	K	2.2	8	7	0.34	0.90	0.85
86.0	1	A	3.0	14	165	0.48	1.15	2.22
86.0	2	C	4.4	23	120	0.64	1.36	2.08
86.0	3	F	2.1	6	8	0.32	0.78	0.90
86.0	4	C	3.4	15	314	0.53	1.18	2.50
86.0	5	F	30.7	744	666	1.49	2.87	2.82
86.0	6	K	4.9	84	334	0.69	1.92	2.52
86.0	7	O	2.9	8	12	0.46	0.90	1.08
86.0	8	C	2.4	28	370	0.38	1.45	2.57
87.0	1	D	6.6	1	4	0.82	0.00	0.60
87.0	2	C	11.0	4	26	1.04	0.60	1.41
87.0	3	F	3.3	2	24	0.52	0.30	1.38
87.0	4	F	6.2	2	18	0.79	0.30	1.26
87.0	5	F	6.2	2	18	0.79	0.30	1.26
87.0	6	C	6.6	2	14	0.82	0.30	1.15
87.0	7	A	10.3	3	30	1.01	0.48	1.48
87.0	8	J	4.6	3	24	0.66	0.48	1.38
88.0	1	A	5.9	1	2	0.77	0.00	0.30
88.0	2	A	6.1	1	2	0.79	0.00	0.30
88.0	3	C	3.0	1	7	0.48	0.00	0.85
88.0	4	O	0.9	1	3	-0.05	0.00	0.48
88.0	5	C	4.9	2	8	0.69	0.30	0.90
88.0	6	B	4.5	1	2	0.65	0.00	0.30
89.0	1	J	3.8	6	40	0.58	0.78	1.60
89.0	2	A	4.9	1	5	0.69	0.00	0.70
89.0	3	B	5.0	1	5	0.70	0.00	0.70
89.0	4	N	4.0	1	7	0.60	0.00	0.85
89.0	5	C	8.5	2	16	0.93	0.30	1.20
89.0	6	A	7.7	3	16	0.89	0.48	1.20
89.0	7	B	2.0	1	3	0.30	0.00	0.48
89.0	8	A	3.9	2	7	0.59	0.30	0.85
90.0	1	O	0.2	0	2	-0.70	ERR	0.30
90.0	2	C	5.3	0	11	0.72	ERR	1.04
90.0	3	O	2.8	1	8	0.45	0.00	0.90
90.0	4	O	0.7	1	2	-0.15	0.00	0.30
90.0	5	N	0.8	0	1	-0.10	ERR	0.00
91.0	1	B	7.0	1	5	0.85	0.00	0.70
91.0	2	L	0.4	1	1	-0.40	0.00	0.00
91.0	3	A	5.2	4	9	0.72	0.60	0.95
91.0	4	L	0.4	0	4	-0.40	ERR	0.60
91.0	5	K	1.1	3	14	0.04	0.48	1.15
91.0	6	K	1.3	3	19	0.11	0.48	1.28
91.0	7	K	5.7	6	41	0.76	0.78	1.61
92.0	1	L	1.0	1	2	0.00	0.00	0.30
92.0	2	D	2.2	2	49	0.34	0.30	1.69
92.0	3	D	6.8	0	4	0.83	ERR	0.60
92.0	4	D	3.7	3	16	0.57	0.48	1.20
92.0	5	D	3.3	5	22	0.52	0.70	1.34
92.0	6	A	2.4	10	74	0.38	1.00	1.87
93.0	1	C	4.4	1	5	0.64	0.00	0.70
93.0	2	K	4.0	1	4	0.60	0.00	0.60
93.0	3	O	0.1	0	1	-1.00	ERR	0.00
93.0	4	J	0.1	2	17	-1.00	0.30	1.23
93.0	5	J	0.3	1	13	-0.52	0.00	1.11
93.0	6	J	0.4	1	7	-0.40	0.00	0.85
94.0	1	A	1.4	2	6	0.15	0.30	0.78
94.0	2	A	2.9	12	20	0.46	1.08	1.30
94.0	3	C	2.2	4	9	0.34	0.60	0.95

Loc	Sample	Type	XK	eUppm	eThppm	log XK	log eU	log eTh
95.0	1	H	1.8	27	23	0.26	1.43	1.36
95.0	2	L	0.7	4	4	-0.15	0.60	0.60
95.0	3	D	0.7	5	4	-0.15	0.70	0.60
95.0	4	D	3.7	26	27	0.57	1.41	1.43
95.0	5	D	4.4	44	39	0.64	1.64	1.59
95.0	6	L	0.2	3	1	-0.70	0.48	0.00
96.0	1	M	1.5	1	3	0.18	0.00	0.48
96.0	2	N	3.1	1	6	0.49	0.00	0.78
96.0	3	F	1.7	1	2	0.23	0.00	0.30
97.0	1	L	0.3	0	0	-0.52	ERR	ERR
97.0	2	N	3.3	1	1	0.52	0.00	0.00
97.0	3	E	5.1	6	21	0.71	0.78	1.32
97.0	4	K	5.5	4	10	0.74	0.60	1.00
97.0	5	N	5.3	3	6	0.72	0.48	0.78
97.0	6	K	4.1	4	17	0.61	0.60	1.23
97.0	7	C	4.2	9	42	0.62	0.95	1.62
98.0	1	L	0.3	0	1	-0.52	ERR	0.00
98.0	10	F	1.0	15	41	0.00	1.18	1.61
98.0	11	N	3.8	1	5	0.58	0.00	0.70
98.0	2	I	0.2	0	2	-0.70	ERR	0.30
98.0	3	H	0.5	0	2	-0.30	ERR	0.30
98.0	4	F	0.6	2	0	-0.22	0.30	ERR
98.0	5	F	2.3	9	4	0.36	0.95	0.60
98.0	6	H	0.5	1	2	-0.30	0.00	0.30
98.0	7	F	0.3	1	2	-0.52	0.00	0.30
98.0	8	K	3.7	21	13	0.57	1.32	1.11
98.0	9	J	0.4	2	7	-0.40	0.30	0.85
102.0	1	A	1.6	0	5	0.20	ERR	0.70
102.0	2	A	1.5	1	3	0.18	0.00	0.48
102.0	3	A	8.4	0	1	0.92	ERR	0.00
102.0	4	B	3.0	3	6	0.48	0.48	0.78
102.0	5	B	3.8	11	15	0.58	1.04	1.18
103.0	1	B	4.1	3	19	0.61	0.48	1.28
103.0	1	B	0.9	210	147	-0.05	2.32	2.17
103.0	10	C	3.8	5	33	0.58	0.70	1.52
103.0	11	B	2.4	4	16	0.38	0.60	1.20
103.0	2	B	5.6	2	22	0.75	0.30	1.34
103.0	2	B	5.6	99	76	0.75	2.00	1.88
103.0	3	A	3.6	53	47	0.56	1.72	1.67
103.0	3	A	8.3	2	7	0.92	0.30	0.85
103.0	4	M	0.9	15	12	-0.05	1.18	1.08
103.0	4	B	4.0	4	13	0.60	0.60	1.11
103.0	5	A	4.7	1078	783	0.67	3.03	2.89
103.0	5	E	5.9	21	82	0.77	1.32	1.91
103.0	6	M	0.7	2	0	-0.15	0.30	ERR
103.0	6	E	2.6	8	17	0.41	0.90	1.23
103.0	7	B	2.4	52	43	0.38	1.72	1.63
103.0	7	E	4.0	5	16	0.60	0.70	1.20
103.0	8	A	4.8	15	39	0.68	1.18	1.59
103.0	8	A	4.2	19	19	0.62	1.28	1.28
103.0	9	A	3.6	20	203	0.56	1.30	2.31
104.0	1	E	8.6	467	416	0.93	2.67	2.62
104.0	10	B	4.5	72	428	0.65	1.86	2.63
104.0	11	B	3.8	94	245	0.58	1.97	2.39
104.0	12	N	2.8	7	12	0.45	0.85	1.08
104.0	2	A	3.9	80	110	0.59	1.90	2.04
104.0	3	S	5.4	172	290	0.73	2.24	2.46
104.0	4	B	0.0	325	400	ERR	2.51	2.60
104.0	5	B	4.7	128	541	0.67	2.11	2.73
104.0	6	B	4.6	32	117	0.66	1.51	2.07
104.0	7	B	2.6	73	703	0.41	1.86	2.85
104.0	8	B	3.5	145	744	0.54	2.16	2.87
104.0	9	B	8.8	336	1201	0.94	2.53	3.08
105.0	1	A	5.8	0	2	0.76	ERR	0.30
105.0	2	A	6.3	2	12	0.80	0.30	1.08
105.0	3	A	7.7	2	6	0.89	0.30	0.78

Loc	Sample	Type	XK	eUppm	eThppm	log XK	log eU	log eTh
105.0	4	A	4.9	5	11	0.69	0.70	1.04
106.0	1	L	2.5	11	19	0.40	1.04	1.28
106.0	2	L	2.6	9	19	0.41	0.95	1.28
106.0	3	J	1.9	9	15	0.28	0.95	1.18
107.0	1	N	2.7	8	49	0.43	0.90	1.69
107.0	2	N	2.2	6	13	0.34	0.78	1.11
107.0	3	E	3.3	50	89	0.52	1.70	1.95
107.0	4	E	2.6	179	203	0.41	2.25	2.31
107.0	5	E	2.4	195	248	0.38	2.29	2.39
107.0	6	N	3.1	4	7	0.49	0.60	0.85
108.0	1	J	4.0	8.0	14.0	0.60	0.90	1.15
108.0	10	H	2.2	8.0	45.0	0.34	0.90	1.65
108.0	11	H	1.7	5.0	26.0	0.23	0.70	1.41
108.0	12	F	0.9	2.0	8.0	-0.05	0.30	0.90
108.0	13	F	3.5	7.0	16.0	0.54	0.85	1.20
108.0	14	J	2.8	7.0	14.0	0.45	0.85	1.15
108.0	2	O	2.4	13.0	27.0	0.38	1.11	1.43
108.0	3	J	1.9	7.0	28.0	0.28	0.85	1.45
108.0	4	L	1.8	11.0	20.0	0.26	1.04	1.30
108.0	5	E	4.2	1.0	12.0	0.62	0.00	1.08
108.0	6	A	4.3	13.0	281.0	0.63	1.11	2.45
108.0	7	C	2.8	17.0	409.0	0.45	1.23	2.61
108.0	8	A	4.8	1.0	7.0	0.68	0.00	0.85
108.0	9	A	5.0	3.0	68.0	0.70	0.48	1.83
109.0	1	B	7.0	6.0	27.0	0.85	0.78	1.43
109.0	2	B	5.6	6.0	19.0	0.75	0.78	1.28
109.0	3	M	6.5	4.0	10.0	0.81	0.60	1.00
109.0	4	A	7.6	5.0	13.0	0.88	0.70	1.11
109.0	5	A	5.0	3.0	13.0	0.70	0.48	1.11
109.0	6	A	6.2	5.0	54.0	0.79	0.70	1.73
109.0	7	M	5.7	5.0	17.0	0.76	0.70	1.23
109.0	8	B	6.7	97.0	143.0	0.83	1.99	2.16
110.0	1	L	1.3	2.0	5.0	0.11	0.30	0.70
110.0	2	L	0.6	0.0	2.0	-0.22	ERR	0.30
110.0	3	H	1.3	5.0	21.0	0.11	0.70	1.32
111.0	1	L	1.1	1.0	10.0	0.04	0.00	1.00
111.0	2	D	6.3	10.0	375.0	0.80	1.00	2.57
111.0	3	D	5.1	4.0	87.0	0.71	0.60	1.94
111.0	4	D	6.1	26.0	1017.0	0.79	1.41	3.01
111.0	5	H	3.0	11.0	690.0	0.48	1.04	2.84
111.0	6	H	2.8	9.0	80.0	0.45	0.95	1.90
111.0	7	D	3.6	20.0	50.0	0.56	1.30	1.70
112.0	1	H	2.4	5.0	30.0	0.38	0.70	1.48
112.0	10	O	2.5	4.0	6.0	0.40	0.60	0.78
112.0	11	L	1.4	2.0	4.0	0.15	0.30	0.60
112.0	12	D	6.2	15.0	64.0	0.79	1.20	1.81
112.0	13	K	2.2	32.0	31.0	0.34	1.51	1.49
112.0	14	D	4.7	29.0	94.0	0.67	1.46	1.97
112.0	15	H	5.5	186.0	990.0	0.74	2.27	3.00
112.0	16	I	2.1	2.0	7.0	0.32	0.30	0.85
112.0	17	I	4.0	177.0	732.0	0.60	2.25	2.86
112.0	18	H	4.6	119.0	585.0	0.66	2.08	2.77
112.0	2	D	3.3	14.0	55.0	0.52	1.15	1.74
112.0	3	D	3.8	8.0	40.0	0.58	0.90	1.60
112.0	4	H	3.5	11.0	48.0	0.54	1.04	1.68
112.0	5	D	5.7	562.0	1254.0	0.76	2.75	3.10
112.0	6	H	3.2	12.0	45.0	0.51	1.08	1.65
112.0	7	K	4.3	35.0	208.0	0.63	1.54	2.32
112.0	8	I	1.8	5.0	19.0	0.26	0.70	1.28
112.0	9	L	1.2	4.0	9.0	0.08	0.60	0.95
113.0	1	D	5.7	2.0	22.0	0.76	0.30	1.34
113.0	10	B	2.0	7.0	24.0	0.30	0.85	1.38
113.0	2	D	7.6	16.0	32.0	0.88	1.20	1.51
113.0	3	J	0.8	5.0	16.0	-0.10	0.70	1.20
113.0	4	I	1.4	6.0	20.0	0.15	0.78	1.30
113.0	5	I	1.2	4.0	17.0	0.08	0.60	1.23

Loc	Sample	Type	XX	eUppa	eThppa	log XX	log eU	log eTh
113.0	6	J	2.0	6.0	29.0	0.30	0.78	1.46
113.0	7	J	2.6	12.0	60.0	0.41	1.08	1.78
113.0	8	J	4.7	8.0	39.0	0.67	0.90	1.59
113.0	9	H	3.0	443.0	1150.0	0.48	2.65	3.06
114.0	1	A	5.9	3.0	9.0	0.77	0.48	0.95
114.0	2	B	6.5	6.0	15.0	0.81	0.78	1.18
114.0	3	B	7.2	5.0	23.0	0.86	0.70	1.36
114.0	4	K	1.4	2.0	12.0	0.15	0.30	1.08
114.0	5	K	5.8	5.0	22.0	0.76	0.70	1.34
114.0	6	L	1.2	2.0	19.0	0.08	0.30	1.28
114.0	7	M	1.5	2.0	11.0	0.18	0.30	1.04
115.0	1	B	4.7	42.0	69.0	0.67	1.62	1.84
115.0	2	B	3.8	53.0	44.0	0.58	1.72	1.64
115.0	3	B	4.3	119.0	91.0	0.63	2.08	1.96
116.0	1	A	3.7	4.0	5.0	0.57	0.60	0.70
116.0	10	A	4.9	1.0	1.0	0.69	0.00	0.00
116.0	11	M	4.8	2.0	3.0	0.68	0.30	0.48
116.0	12	B	5.5	3.0	3.0	0.74	0.48	0.48
116.0	13	M	2.9	3.0	4.0	0.46	0.48	0.60
116.0	2	A	6.1	0.0	3.0	0.79	ERR	0.48
116.0	3	A	1.6	2.0	3.0	0.20	0.30	0.48
116.0	4	A	2.4	25.0	17.0	0.38	1.40	1.23
116.0	5	B	2.8	16.0	10.0	0.45	1.20	1.00
116.0	6	A	7.4	296.0	152.0	0.87	2.47	2.18
116.0	7	A	1.6	501.0	213.0	0.20	2.70	2.33
116.0	8	A	9.1	1.0	2.0	0.96	0.00	0.30
116.0	9	A	2.1	99.0	28.0	0.32	2.00	1.45
117.0	1	M	1.0	0.0	2.0	0.00	ERR	0.30
117.0	2	A	4.4	1.0	1.0	0.64	0.00	0.00
117.0	3	A	3.8	2.0	3.0	0.58	0.30	0.48
117.0	4	B	3.4	2.0	3.0	0.54	0.30	0.48
117.0	5	M	2.5	1.0	2.0	0.40	0.00	0.30
117.0	6	B	1.4	1.0	2.0	0.15	0.00	0.30
117.0	7	B	1.7	41.0	13.0	0.23	1.61	1.11
117.0	8	A	2.6	0.0	1.0	0.41	ERR	0.00
117.0	9	B	3.1	1.0	2.0	0.49	0.00	0.30
118.0	1	A	1.5	1.0	5.0	0.18	0.00	0.70
118.0	2	A	1.5	1.0	8.0	0.18	0.00	0.90
118.0	3	B	4.6	2.0	5.0	0.66	0.30	0.70
118.0	4	C	5.1	1.0	11.0	0.71	0.00	1.04
118.0	5	A	4.8	1.0	8.0	0.68	0.00	0.90
118.0	6	A	2.9	1.0	7.0	0.46	0.00	0.85
118.0	7	N	4.7	1.0	7.0	0.67	0.00	0.85
118.0	8	B	2.8	3.0	4.0	0.45	0.48	0.60
120.0	1	A	0.5	1.0	2.0	-0.30	0.00	0.30
120.0	2	A	3.3	32.0	17.0	0.52	1.51	1.23
120.0	3	A	0.5	1.0	2.0	-0.30	0.00	0.30
120.0	4	A	1.8	4.0	17.0	0.25	0.60	1.23
120.0	5	B	42.2	463.0	274.0	1.63	2.67	2.44
120.0	6	C	2.4	16.0	160.0	0.38	1.20	2.20
120.0	7	A	3.4	10.0	15.0	0.53	1.00	1.18
120.0	8	B	2.6	7.0	26.0	0.41	0.85	1.41
121.0	1	B	3.8	2.0	3.0	0.58	0.30	0.48
121.0	2	B	3.6	3.0	5.0	0.56	0.48	0.70
121.0	3	B	7.8	7.0	5.0	0.89	0.85	0.70
121.0	4	B	4.2	5.0	5.0	0.62	0.70	0.70
121.0	5	B	5.4	81.0	30.0	0.73	1.91	1.48
121.0	6	M	4.0	2.0	4.0	0.60	0.30	0.60
122.0	1	B	3.8	38.0	32.0	0.58	1.58	1.51
122.0	2	B	4.8	134.0	86.0	0.68	2.13	1.93
122.0	3	B	1.6	61.0	57.0	0.20	1.79	1.76
122.0	4	B	2.2	48.0	44.0	0.34	1.68	1.64
122.0	5	B	3.5	40.0	37.0	0.54	1.60	1.57
122.0	6	B	3.6	34.0	46.0	0.56	1.53	1.66
122.0	7	A	8.0	12.0	17.0	0.90	1.08	1.23

APPENDIX 4B SUMMARY OF DATA

		%K	eUppm	eThppm	eU/eTh	log K	log eU	log eTh	U/Th
PYROXENITE	(O)	1.36	2.61	7.06	0.38	-0.02	0.32	0.69	0.25
S.D.	n = 17	0.94	3.20	6.60	0.29	0.41	0.36	0.37	0.05
GNEISS	(N)	3.22	4.22	15.07	0.34	0.45	0.52	1.01	0.27
S.D.	n = 54	1.44	3.60	14.87	0.28	0.24	0.35	0.42	0.04
AMPHIBOLITE	(M)	2.14	3.15	8.42	0.47	0.21	0.44	0.78	0.23
S.D.	n = 25	1.60	2.84	10.18	0.35	0.34	0.27	0.34	0.04
MARBLE	(L)	0.87	2.85	6.68	0.51	-0.16	0.36	0.68	0.22
S.D.	n = 46	0.63	3.00	5.77	0.47	0.33	0.33	0.39	0.04
GNEISS VEIN	(K)	4.70	93.73	241.59	0.49	0.47	1.19	1.72	0.24
S.D.	n = 106	8.40	322.49	624.00	0.60	0.37	0.73	0.69	0.08
PXTE VEIN	(J)	3.27	82.53	266.36	0.75	0.22	1.03	1.51	0.21
S.D.	n = 65	5.82	215.03	940.13	1.11	0.49	0.82	0.71	0.03
MARBLE VEIN	(I)	11.40	379.71	760.90	0.57	0.43	1.57	1.91	0.14
S.D.	n = 21	24.42	411.08	1239.83	0.58	0.69	1.03	1.06	0.01
MARBLE SKARN	(H)	9.31	490.85	608.46	0.65	0.41	1.65	1.98	0.20
S.D.	n = 59	27.18	1715.38	1675.86	0.70	0.57	0.93	0.83	0.03
AMPHTE SKARN	(G)	1.45	34.25	97.25	0.42	0.12	1.07	1.50	0.20
S.D.	n = 4	0.57	45.81	126.47	0.24	0.21	0.66	0.69	0.05
PXTE SKARN	(F)	3.24	37.55	58.67	0.48	0.34	0.72	1.22	0.20
S.D.	n = 54	4.33	129.01	161.02	0.62	0.35	0.67	0.58	0.03
GNEISS PEG	(E)	3.74	69.22	671.30	0.43	0.56	1.37	2.07	0.16
S.D.	n = 26	2.70	114.12	2434.05	0.46	0.22	0.74	0.67	0.01
MARBLE PEG	(D)	4.53	43.67	167.95	0.41	0.58	1.14	1.65	0.15
S.D.	n = 57	2.90	114.37	350.65	0.34	0.28	0.61	0.67	ERR
PXTE PEG	(C)	4.84	17.19	127.33	0.19	0.63	0.73	1.50	0.24
S.D.	n = 42	2.33	49.55	250.62	0.17	0.23	0.58	0.68	0.08
AMPHTE PEG	(B)	4.71	65.95	192.46	0.57	0.60	1.28	1.72	0.30
S.D.	n = 96	4.39	105.64	316.33	0.55	0.25	0.75	0.76	0.11
PEGMATITE	(A)	4.30	33.79	80.17	0.45	0.58	0.89	1.35	0.23
S.D.	n = 163	1.93	105.64	203.73	0.48	0.24	0.68	0.66	0.04

APPENDIX 4C SUMMARY OF INDIVIDUAL DEPOSITS

DEPOSIT	PEG U/Th	SKARN U/Th	VEIN U/Th	PEG Log eU	SKARN Log eU	VEIN Log eU	PEG Log eTh	SKARN Log eTh	VEIN log eTh
1	0.37	3.25	0.58	1.19	2.34	0.75	1.78	1.83	1.15
2	0.78	0.83	0.7	1.4	0.7	0.85	1.6	0.78	1
7	0.35	1.78	0.33	0.89	3.57	1.65	1.35	3.32	2.13
8	0.38	0.39	0.33	0.24	0.33	0.85	0.67	0.76	1.32
9	0.49	1.17	0.63	1.35	1.61	1.36	1.76	1.58	1.71
14			1.75			2.08			1.91
15	0.11	0.09	0.1	1.94	1.53	2.21	2.89	2.56	3.31
16	0.93			1.79			1.83		
17	0.88			2.1			2.3		
18	1		0.55	0.6		1.03	0.6		1.72
19	0.19	0.38	0.45	0.63	2.02	0.91	1.34	2.44	1.33
20	0.66	1.24		1.13	2.03		1.35	2.04	
21			1.45			2.77			2.62
22	0.21	0.16		0.68	0.85		1.39	1.64	
23			0.08			1.3			2.44
24	0.67	1.18	0.67	2.17	1.79	0.3	2.36	1.9	0.48
25		1.72	0.2		1.75	2.39		1.77	3.08
26			2.33			1.57			1.44
29	0.37	0.86	0.9	0.96	2.61	1.7	1.43	2.69	1.77
30	0.55	0.64	0.94	1.44	1.92	2.24	1.8	2.3	2.91
31	0.69		0.4	2.1		2.24	2.34		2.08
32	0.15	0.45		0.3	2.04		1.11	2.43	
33	0.05		0.6	1.56		1.88	2.88		2.08
34	0.35			1.32			1.78		
35	0.02			0.3			2.91		
36		0.57	0.51		0.72	0.55		0.98	0.9
37	0.12	1.2	1.05	0.15	0.78	0.91	1.1	0.7	0.98
38	0.14		0.21	0.1		0.42	0.75		2.06
39			0.2			0.65			1.37
40		0.18	0.33		0.3	0		1.04	0.48
41			0.49			0.84			1.16
42	0.09		0.2	0.7		0.78	1.75		1.69
43	0.54	0.65	1.99	1.24	1.37	2.35	1.55	1.61	2.04
44	0.14			0.89			1.77		
45	0.38	0.54		0.79	1.11		1.22	1.38	
46	0.4			1.67			2.14		
47	1.16		0.44	1.37		2.23	1.52		2.14
48	0.25			0.3			0.9		
49	0.08		0.17	1.26		0.3	2.35		1.08
50	0.1	0.17		1.06	0.54		2.19	1.34	
52	0.3	0.21		0.43	0.42		0.95	1.1	
53	0.2		0.1	0.54		1.74	1.24		2.82
54	0.38		0.19	0.88		0.56	1.34		1.3
55	0.24		0.26	0.83		1.38	1.72		1.96
56	0.1	0.27		0.94	0.48		2	1.04	
57	0.82		0.16	0.95		1.23	1.04		2.1
58	0.18		0.23	0.7		0.42	1.45		1.07
59	0.3		0.68	0.58		1.28	1.18		1.45
60	0.03	0.2	0.1	0.49	1.09	1.99	2.03	1.81	3.01
61	0.54		0.35	1.65		3.1	1.92		3.55
62	0.15	0.21	0.28	1.52	0.56	1.32	2.42	1.26	1.89
63	0.58			1.71			1.95		
64	0.38	0.36		1.83	2.05		2.39	2.5	
65	0.87	0.96		1.42	2.43		1.52	2.45	
66	0.23	0.25	0.17	1.03	2.44	2.27	1.83	2.61	3.05
67	0.15		0.14	1.45		0.48	2.39		1.32
68	0.6	1.05		0.93	0.81		1.18	0.79	
69	0.28		2.63	1.05		2.22	1.7		1.86
70	0.17	0.37	0.48	0.78	0.73	0.42	1.75	1.23	0.79

DEPOSIT	PEG U/Th	SKARN U/Th	VEIN U/Th	PEG Log eU	SKARN Log eU	VEIN Log eU	PEG Log eTh	SKARN Log eTh	VEIN log eTh
71		1.86			2.24			2.02	
72	0.03		2.2	0.75		2.14	2.32		1.79
73	0.34			1.15			1.64		
74	0.22	0.15	0.13	0.2	0.26	0.67	0.75	0.9	1.56
75	0.4	0.16	0.2	0.3	0.24	0.15	0.84	1.05	0.88
76	0.27		0.08	0.43		0	1.27		1.08
77	0.12	0.15	0.1	0	0.08	0.45	1.04	0.96	1.47
78	0.32	0.23	1.04	0.97	0.58	2.22	1.49	1.24	2.28
79			0.24			0.54			1.19
80	0.29	0.09	0.09	0.1	0.48	0.71	0.71	1.53	1.78
81	0.39	0.17	0.1	1.55	0	0	1.93	0.78	0.35
82	0.32			0.83			1.4		
83	0.46	0.57		1.52	0.62		1.92	0.85	
84	0.14	0.66		0.92	1.32		1.82	1.51	
85	0.81		1.65	0.91		0.47	1.04		1.41
86	0.1	0.94	0.25	1.28	1.83	1.92	2.34	1.86	2.52
87	0.16	0.1	0.13	0.35	0.3	0.48	1.16	1.3	1.38
88	0.38			0.08			0.53		
89	0.22		0.2	0.18		0.78	0.86		1.6
91	0.32		0.17	0.3		0.58	0.83		1.35
92	0.12			0.5			1.34		
93	0.2		0.15	0		0.08	0.7		0.95
94	0.46			1.01			1.01		
95	1.13	1.17		1.25	1.43		1.21	1.36	
96		0.5			0			0.3	
97	0.25		0.3	0.87		0.6	1.47		1.12
98		0.6	0.63		0.41	0.54		0.52	0.75
102	0.31			0.3			0.63		
103	0.6			1.2			1.59		
104	0.44			2.12			2.58		
105	0.24			0.43			0.8		
106			0.6			0.95			1.18
107	0.74			2.08			2.22		
108	0.07	0.27	0.44	0.56	0.69	0.87	1.76	1.29	1.25
109	0.32			0.91			1.47		
110		0.24			0.7			1.32	
111	0.13	0.07		1.08	1		2.31	2.37	
112	0.29	0.21	0.4	1.49	1.43	1.26	2.04	2.12	1.76
113	0.29	0.39	0.24	0.78	2.65	0.81	1.41	3.06	1.43
115	1.04			1.81			1.81		
116	1.35			1.01			0.97		
117	0.93			0.37			0.38		
118	0.26			0.11			0.81		
120	0.73			0.9			1.29		
121	1.27			0.85			0.81		
122	1.06			1.63			1.43		

A dynamic growth model of quartz-feldspar graphic
intergrowths from granitic pegmatites in the southwestern
Grenville Province

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ABSTRACT

During the formation of Grenville Province U-, Th-, Mo-, REE-, and Nb-bearing granitic pegmatites, crystallization conditions were such that widespread graphic quartz-feldspar intergrowths were formed. The alkali feldspar-quartz intergrowth is characterized by angular rods of quartz which have an irregular inner interface and a planar outer interface with alkali feldspar. This is interpreted as quartz that nucleated epitaxially on rough edges and corners of alkali feldspar crystals. Rapid growth, at or near volatile-saturated conditions resulted in quartz saturation along the irregular melt-feldspar interface. Slow diffusion of Si and Al species (network formers) at the interface was likely the rate-controlling step for the metastable quartz saturation. Quartz saturation occurred along corners and edges where the feldspar grew most rapidly. Diffusion-limited growth resulted in SiO_2 buildup at the interface producing oscillations from quartz oversaturated to undersaturated conditions and thus the rhythmic quartz-feldspar intergrowths. The transition from planar, to edge, to cellular growth, and changes in the lobate inner feldspar-quartz boundary occurred in response to changes caused by crystallization which affect Si/Al diffusion rates. Evidence of volatile phase saturation in these pegmatite indicates that water was a catalyst for feldspar growth and that lower water activities in the melt decrease Si diffusivity at the interface.

Keywords: graphic, granophyric, growth kinetics, diffusion, pegmatite

INTRODUCTION

Graphic texture is a regular (cuneiform) intergrowth of two mineral phases; typically quartz and alkali feldspar. The granophyric texture is the irregular finer-grained counterpart of graphic texture. Detailed textural, petrographic, and chemical examination of twenty five graphic granite pegmatites from ten localities in the southwestern Grenville Province has provided insight into their formation.

Numerous hypotheses have been proposed for the formation of graphic texture, but simultaneous growth of quartz and feldspar near the thermal minimum, originally proposed by Vogt (1931), is considered to be the controlling mechanism (e.g., Barker 1970, Černý 1971, Hughes 1971). Replacement of feldspar by quartz-saturated solutions (Wahlstrom 1939, Drescher-Kaden 1948, Augustithis 1962, Seclaman & Constantinescu 1972) and vapour-phase crystallization (Simpson 1962) have also been proposed. Schloemer (1964) produced the texture by hydrothermal coprecipitation of quartz and feldspar. Lofgren (1971) also observed the texture in rhyolitic glass devitrification experimental charges. Maaløe (1974), Smith (1974), Walker (1976), Carstens (1983), Fenn (1986), and London et al. (1989) have proposed that the textures are formed near the cotectic or eutectic for the system but are not necessarily an equilibrium phenomenon. Fenn (1986) and London et al. (1989) experimentally produced the texture from granitic bulk compositions within the K-feldspar primary field and concluded the texture is related to the interplay of diffusion and growth kinetics.

Graphic and granophyric textures have been interpreted to result from rapid crystallization at volatile-saturated conditions (Mehnert 1968, Barker 1970, Smith 1974, Hibbard 1980, Martin 1982, Shannon et al. 1982, Černý & Meintzer 1988, Kirkham & Sinclair 1988). Both these textures occur within marginal facies of pegmatite, pegmatite pods, miarolitic cavities, aplites and are also associated with hydrothermal

mineralization.

This paper identifies morphological and compositional features of the intergrowths which support the diffusion-controlled growth model. However, the growth dynamics differ from those proposed by Carstens (1983) and Fenn (1986) for granophyre and graphic texture. Their mechanism involved short range continuous diffusion of quartz- and feldspar-forming components to a crystallizing surface containing both minerals. Observation and interpretation of the lobate feldspar to quartz growth boundaries suggests that quartz nucleated on feldspar growth surfaces. The effect of a dissolved and free volatile phase is examined because there is an empirical relationship between the development of graphic texture and evidence of volatile saturation in these pegmatites.

GEOLOGICAL SETTING

The U, Th, Mo, REE and Nb-bearing granitic pegmatites in the southwestern Grenville Province have abundant examples of well developed graphic texture. In general, granitic pegmatites form both concordant and discordant dykes in the gneisses, marbles, and amphibolites. They can attain widths of tens of metres to hundreds metres and have lengths up to several kilometers. Some of the larger pegmatites are associated with mineral deposits, for example the Faraday uranium pegmatite in Bancroft, Ontario. Figure 1 illustrates the distribution of sample localities within the Central Metasedimentary Belt of the Grenville Province. Several of the graphic granite pegmatites samples studied are hosted in mixed marbles, calc-silicate rocks, and paragneisses (samples 26, 43, 49, 52, 108, & 122) as this study forms part of a larger study on pegmatite-related skarns. The remaining samples (57, 105, 109, & 118) are pegmatites discordantly hosted in biotite-bearing quartzofeldspathic gneisses. The local geology and setting of eight of these occurrences may be found in Lentz (1991b) and a brief description of the

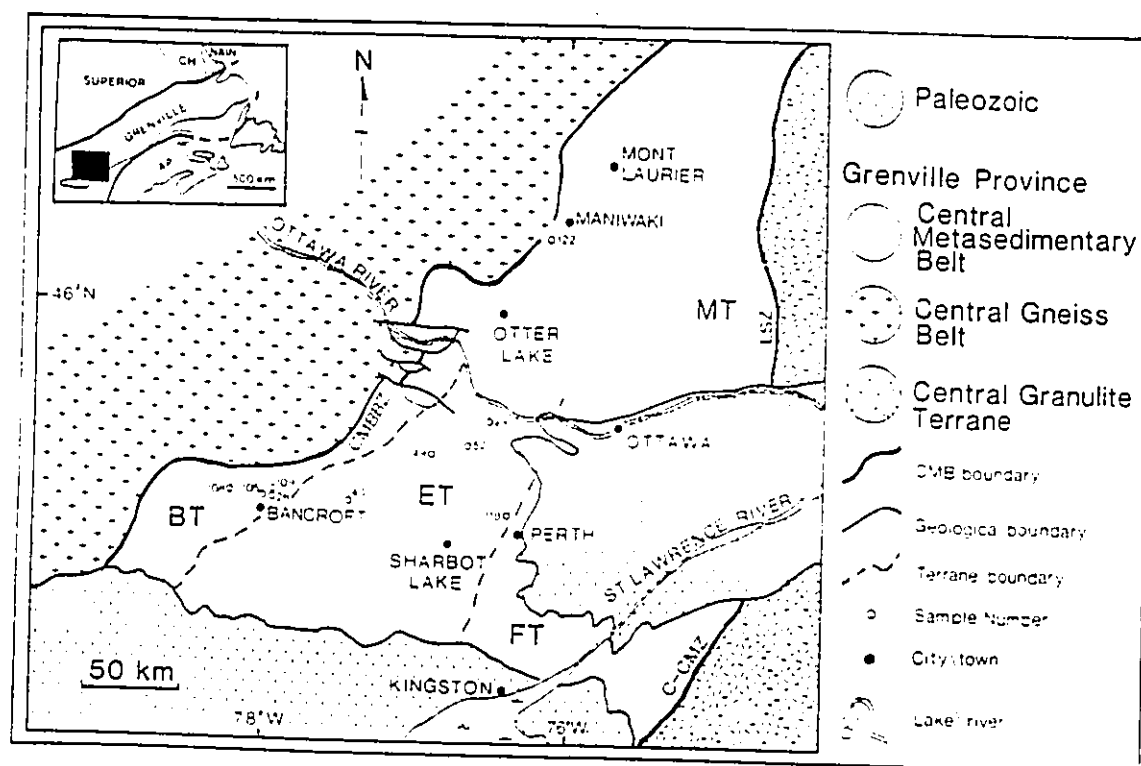


Fig. 1 Sample localities for graphic texture located within the Central Metasedimentary Belt (CMB) of the southwestern Grenville Province (after Davidson 1986). BT - Bancroft terrane, ET - Elzevier terrane, FT - Frontenac terrane, MT - Mont Laurier terrane, CMBBZ - Central Metasedimentary Belt Boundary Zone, C-CMZ - Colton-Carthage Mylonite Zone, LSZ - Labelle Shear Zone. Sample Numbers and names; 26 - MacDonald U-REE-Mo pegmatite, 43 - Liedke Mo pegmatite, 49 - Legris U-REE pegmatite, 52 - Belanger's Corner granite, 57 - Goshen "B" U-REE U pegmatite, 105 - McCormack U pegmatite, 108 - Armac Mo pegmatite, 109 - Genesee U pegmatite, 118 - Perth U pegmatite, and 122 - Blue Sea Lake amazonite pegmatite. Within the inset, the black square outlines the map, CH - Churchill Province, AP - Appalachians.

mineralogy and geology of the Blue Sea Lake pegmatite (122) and the Perth Quarry (118) may be found in Sabina (1987).

The granitic pegmatites under consideration are late tectonic (1020 to 1060 Ma, U-Pb zircon; Rimsaite 1982, Easton 1986) with respect to the Grenville Orogeny (ca. 1090 Ma; Easton 1986) and were emplaced into the Grenville rocks at pressures and temperatures less than peak metamorphic conditions (Lentz 1991b), compatible with their generally undeformed nature (Fowler and Doig 1983a). $^{40}\text{Ar}/^{39}\text{Ar}$ cooling curves for the Bancroft terrane of the Central Metasedimentary Belt (CMB) suggest that the pegmatites intruded while temperatures remained between 500°C and 550°C (Berger & York 1981) consistent with the development of exogranitic pegmatite skarn mineral assemblages (Lentz 1989, 1991b). Pressures have been estimated to be between 300 and 500 MPa based on fluid inclusion studies on the MacDonald zoned pegmatite (Peach 1951), and are consistent with the pressure-temperature-time paths presented by Martignole (1986). These conditions differ from the peak metamorphic conditions inferred (upper amphibolite facies; 650°C and 600 to 700 MPa) for the host rocks (Davidson 1986).

GRANITIC PEGMATITES

Introduction

The granitic pegmatites are composed essentially of quartz, microcline, and plagioclase, with lesser amounts of biotite, amphibole, calcic pyroxene, titanite, magnetite, zircon, allanite, calcite, and fluorite. Field evidence suggests that some of the ferromagnesian phases, locally concentrated along the contact zone, originated by a complex process of hybridization or skarnification (Satterly 1956, Shaw 1958, Masson & Gordon 1981, Haynes 1986, Lentz 1991a, b). Partial melting of rocks in the Central Gneiss Belt during post-tectonic uplift produced H_2O -undersaturated, anatectic melts deeper within the crust (Lentz 1991b) although lower crustal

or mantle origins for these melts have also been proposed based on radiogenic isotope evidence (Fowler and Doig 1983a). Fractional crystallization of anhydrous silicates (quartz and feldspar) during their ascent within the crust caused the enrichment in rare metal and volatile components, to the point of saturation (Lentz 1991b). In addition to H₂O, HF (< 1 wt.%), HCl, and alkali chlorides were constituents of the melt and vapour phase based on the presence of micas, fluorite, and scapolite in and around the pegmatites (Lentz 1991b). Goad (1990) found that many of these pegmatites had feldspar trace-element abundance characteristics of rare-metal bearing pegmatites. The pegmatitic feldspars crystallized at temperatures above 600° to 650°C based on two feldspar geothermometry (Sempels 1971, Pride 1974) and trace-element (Rb) partitioning between biotite and K-feldspar (Lentz & Kretz 1989). This temperature is consistent with that of the thermal minima in the haplogranite system and the phase relations are quite comparable to the Spruce Pine pegmatite at a pressure of 500 MPa (Fenn 1986; Strong 1988) although biotite is more prevalent than muscovite in the samples studied.

Pegmatite Textures

Numerous textural variations occur within Grenville pegmatites, indicative of the variable conditions of crystallization. The pegmatites occur as both zoned and unzoned types (Hewitt 1967). Most bodies are unzoned and contain fine-grained aplitic (<1 mm) to coarse-grained pegmatitic (ten's of cm); however, the average grain-size is 1 to 3 cm. The crystals are dominantly subhedral and equigranular. In the zoned granite pegmatites, grain size varies from medium-grained to very coarse-grained (3 cm to >1 m). Ferromagnesian silicates are euhedral, whereas quartz and the feldspar are subhedral to anhedral, except in the core zone. Perthitic microcline is ubiquitous. Feldspar

exsolution postdated the formation of the graphic texture, as the traces of exsolution lamellae transect quartz intergrowths.

Description of graphic granite pegmatites

Storey & Vos (1981) have described the occurrence of the graphic texture in 40 of the 50 pegmatite-deposits examined in the Bancroft-Renfrew area of Ontario. deSchmid (1916) and Spence (1932) noted that the mining of feldspar and quartz from many zoned pegmatites ceased after coarse- to fine-grained graphic granite pegmatite was encountered at depth. The graphic texture is extremely variable even on outcrop scale; grain sizes range from 2 mm to greater than 10 cm (Spence 1932, Hewitt 1967, Storey & Vos 1981). The reported grain size of the graphic texture is the average distance between adjacent quartz domains and varies from fine (0.25 to 1 mm), to coarse (greater than 10 mm).

The quartz forms discontinuous plates, triangular rods, and angular corners (blebs) which impart the characteristic cuneiform texture in two dimensions (2D) (Fig. 2 & 3). The graphic quartz has an anhedral (irregular) inner boundary whereas the outer boundary is euhedral (planar). This observation indicates that quartz nucleated on the anhedral boundaries of the feldspar and grew to a more euhedral form (Fig. 3). The cusped protuberances are particularly obvious in the coarser-grained varieties of graphic texture (Fig. 3b). In the finer-grained samples, quartz has a saw-tooth-shaped inner surface (Fig. 3e).

Surprisingly, the irregular nature of the inner surface of the rod quartz has not been documented. This may be in part due to the lack of preservation of the irregular interface (e.g., Smith 1974). This relationship indicates that quartz nucleated onto an irregular feldspar interface and grew to more regular (prismatic) outer surface. The formation of feldspar protuberances into the melt are a result of a change from planar (equilibrium) to cellular growth (non equilibrium;

Fig. 2 Coarse-grained graphic granite pegmatite (unknown
Grenville locality; 35 cm wide; GSC photo # 204994).

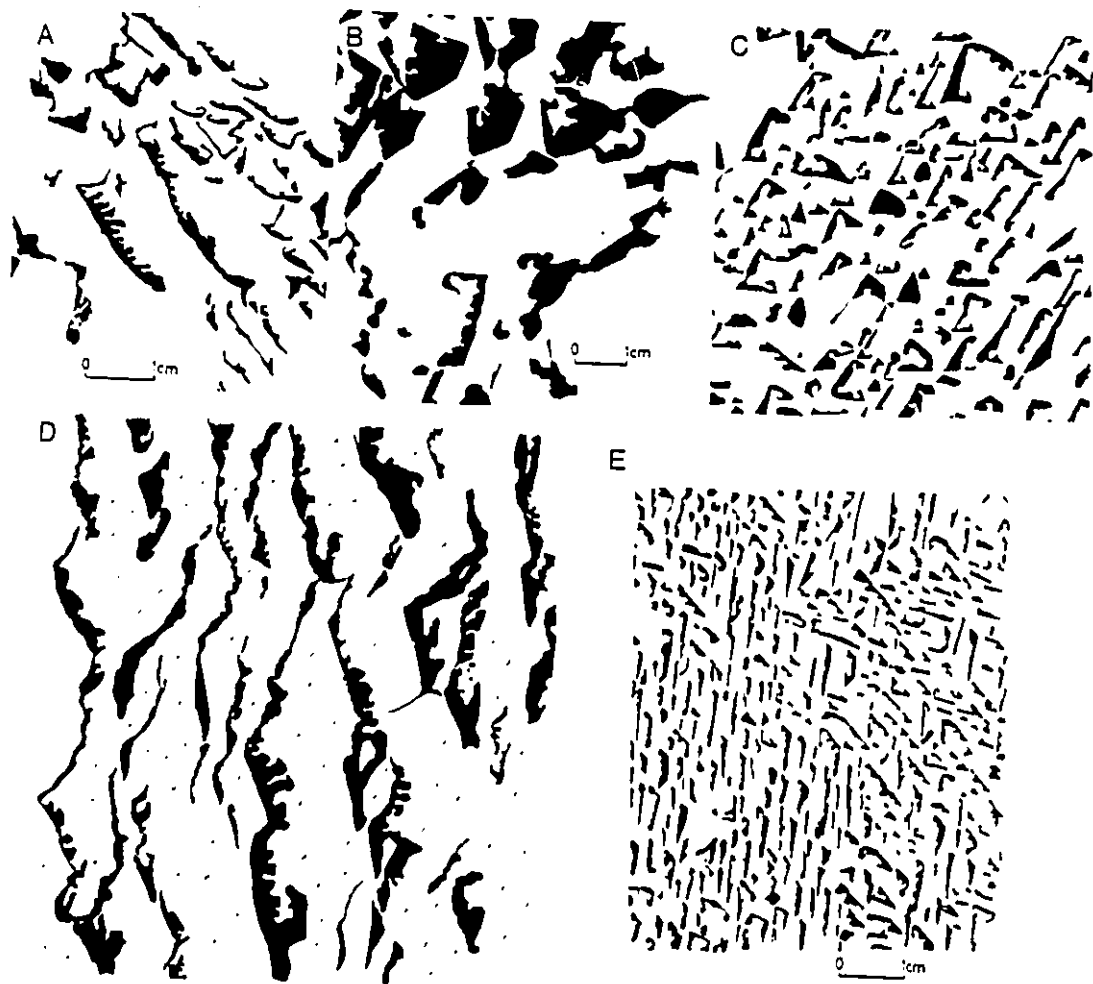


Fig. 3 A. Tracings of coarse-grained graphic texture with irregular lobate quartz-feldspar interface (parallel to edge) (Sample # 105-1) B. Sketch of coarse-grained graphic texture with faceted quartz-feldspar outer interface and irregular interface (perpendicular to edge or at corner) (Sample # 57F). C. Sketch of coarse-grained graphic granite pegmatite from Hybla pegmatite field near Bancroft, Ontario (perpendicular to edge; Figure 10.81, Hurlbut & Klein 1977) D. Sketch of coarse-grained lobate-textured graphic granite pegmatite from Topsham, Maine (no scale) (Appalachian) (after deSchmid 1916) E. Sketch of medium-grained graphic granite pegmatite with sawtooth and barbed shaped inner quartz/feldspar margin (after deSchmid 1916).

e.g., Fenn 1986). The hook-shaped protuberances at the feldspar-melt interface (irregular inner Qtz-Kfs surface) have the appearance of screw-dislocation growth in side view. Quartz saturation did not occur until the outermost portion of the feldspar protuberances crystallized. The bulbous-shaped tips of the protuberances suggest that either 1) quartz nucleated in the embayments and overgrew the protuberances, or 2) the feldspar protuberances extended beyond the silica enriched zone but were overgrown upon quartz saturation.

Composition of graphic granitic pegmatites

A comprehensive compilation of the chemical compositions of Grenville pegmatites and aplites indicates an average composition near the volatile-saturated minimum or eutectic in the haplogranite system at approximately 400 MPa (Lentz & Kretz 1989). Results of twenty-five chemical analyses of graphic granitic pegmatite from 10 localities (Table 1) are presented in Figure 4a. Representative samples consisting of single feldspar crystals and their contained quartz intergrowths were analysed. The sample varied from 2 to 5 kg depending on the grain size. The samples contain less than 1 vol. % of additional phases. This was confirmed by the normative mineralogy (> 99 wt.% quartz, orthoclase, albite, and anorthite in the norm; Table 1). The low abundance of anorthite (0 to 1.7 wt.%) in the norm is an artefact of the analysis of perthitic microcline. Therefore a separate plagioclase phase was not incorporated into the graphic texture. The system quartz-albite-orthoclase-H₂O (Fig. 4b) is used to illustrate the phase relations because of the considerable experimental work on the haplogranite equilibria. The quartz-K-feldspar intergrowths consistently fall on the feldspar side of the cotectic. This would also include the two samples of quartz-plagioclase intergrowths that are located in the quartz-saturated field if the calcic component of plagioclase was considered. There is no obvious relationship

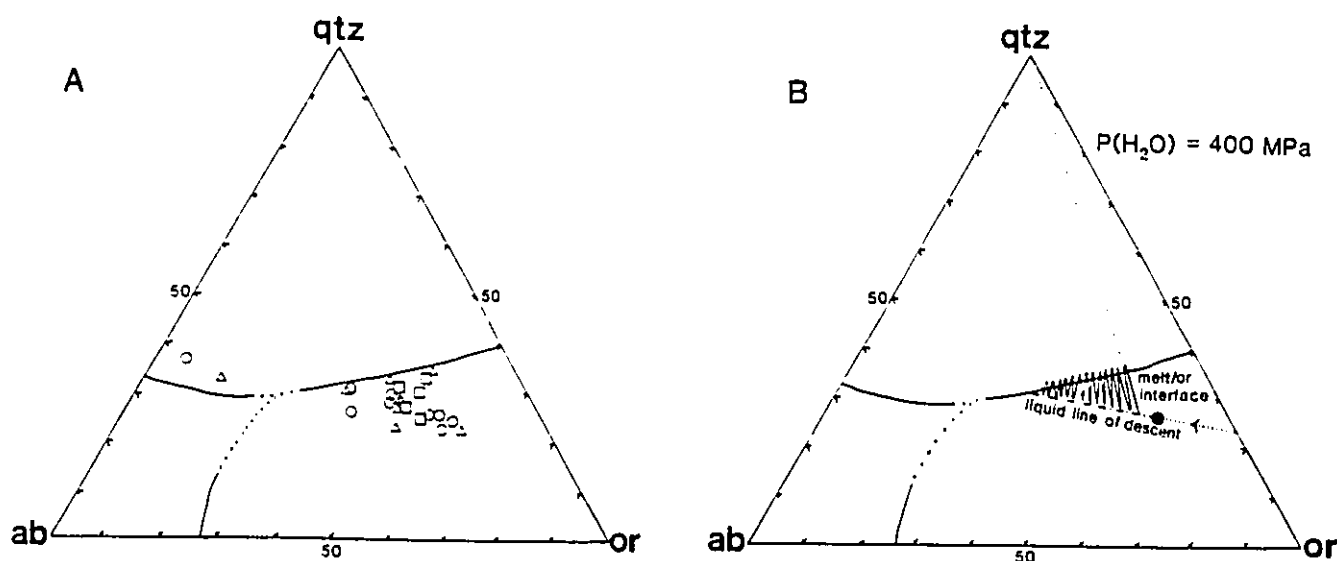


Fig. 4 A. The pseudoternary system quartz (Qtz) - albite (Ab) - K-feldspar (Or) with normative mineralogy of 23 graphic granite pegmatites (this study). The squares are coarse-grained, circles are medium-grained, and triangles are fine-grained samples. B. The estimated pseudoternary quartz (Qtz) - albite (Ab) - K-feldspar (Or) diagram with the phase boundaries for the haplogranite system at 400 MPa $P(H_2O)$. The dot represents the approximate melt composition; The dashed-dotted line indicates the integrated liquid evolution over the course of the graphic texture crystallization. The jagged line represents the melt composition at the feldspar-melt interface which is responsible for the atypical liquid line of descent. intergrowths have an average quartz content of 27.0 ± 1.5 wt.% ($n = 23$).

TABLE 1 Whole-rock chemical composition of graphic granite pegmatites in the southwestern Grenville Province

Sample	52-1	52-2	26C	43E	49-1	49-2	49-3	49-4	49-5	49-6	49-7	57F	105-1
Texture	mg	mg	mg	fg	cg	fg	mg	cg	mg	mg	mg	cg	mg
SiO ₂ wt. %	73.3	72.6	76.1	74.3	74.2	75.2	75.5	73.7	75.7	74.5	74.4	75.5	71.5
TiO ₂	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00
Al ₂ O ₃	14.28	14.38	14.46	13.75	14.00	13.48	13.59	14.46	13.38	13.33	13.67	12.78	14.10
Fe ₂ O ₃	0.07	0.10	0.17	0.12	0.18	0.20	0.14	0.15	0.14	0.19	0.21	0.23	0.40
MgO	0.24	0.21	0.1	0.14	0.00	0.01	0.12	0.07	0.06	0.08	0.21	0.14	0.28
CaO	0.17	0.09	1.64	0.19	0.11	0.10	0.07	0.09	0.09	0.09	0.07	0.66	0.11
Na ₂ O	2.24	1.79	6.23	2.86	2.72	2.73	3.01	3.24	2.89	2.81	2.94	2.71	2.50
K ₂ O	9.60	10.28	0.85	8.11	7.88	7.61	7.71	8.31	7.61	7.57	7.92	7.11	8.82
MnO	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.01	0.01
P ₂ O ₅	0.00	0.01	0.00	0.01	0.02	0.02	0.01	0.00	0.01	0.03	0.00	0.00	0.01
Total	100.0	99.5	99.7	99.5	99.1	99.3	100.1	100.0	99.9	98.7	99.6	99.1	98.0
Ba ppm	70	80	90	480	490	430	440	460	460	440	330	1380	1050
Sr	17	61	234	177	383	319	344	383	351	373	350	848	491
Rb	567	501	33	296	614	508	517	573	497	509	538	361	612
g wt. %													
Or	22.83	22.30	33.54	26.24	28.28	30.19	28.04	22.74	29.51	28.94	26.52	31.21	22.58
ab	56.73	60.75	5.08	48.16	47.04	45.27	45.56	49.11	44.97	44.74	46.81	42.02	52.12
an	18.95	15.15	52.21	24.29	23.27	23.27	25.47	27.42	24.45	23.78	24.88	22.93	21.15
	0.56	0.45	8.12	0.76	0.42	0.37	0.28	0.37	0.38	0.25	0.35	1.71	0.48

Sample	105-2	108-1	108-2	108-3	108-4	109-1	109-2	118-1	118-2	122-1	122-2	122-3
Texture	fg	mg	cg	cg	mg	cg	cg	mg	cg	cg	cg	mg
SiO ₂ wt. %	74.5	75.1	75.8	74.8	73.9	77.0	74.7	72.8	72.3	75.7	72.8	73.3
TiO ₂	0.00	0.01	0.01	0.00	0.01	0.00	0.03	0.01	0.00	0.00	0.00	0.00
Al ₂ O ₃	13.70	13.26	13.16	13.74	14.00	12.48	14.13	13.90	14.51	12.80	14.33	14.10
Fe ₂ O ₃	0.19	0.17	0.20	0.15	0.24	0.16	0.32	0.18	0.12	0.11	0.12	0.08
MgO	0.00	0.16	0.18	0.13	0.12	0.05	0.21	0.06	0.11	0.00	0.00	0.00
CaO	0.21	0.42	0.12	0.11	0.19	0.08	1.17	0.15	0.26	0.09	0.06	0.18
Na ₂ O	2.25	3.60	3.76	4.13	3.93	1.84	5.74	1.89	2.00	1.94	1.97	2.08
K ₂ O	8.36	6.27	6.21	6.49	6.65	8.31	2.09	9.83	10.30	8.30	9.55	9.39
MnO	0.01	0.01	0.00	0.00	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01
P ₂ O ₅	0.02	0.02	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.02
Total	99.2	99.1	99.5	99.5	99.1	99.9	98.4	98.8	99.6	98.9	98.8	99.0
Ba ppm	490	710	710	760	690	370	180	590	580	140	120	110
Sr	298	506	480	495	396	177	159	136	145	30	37	32
Rb	955	221	221	219	237	405	144	306	318	1247	1533	1618
g wt. %												
Or	29.67	29.51	29.86	25.85	25.28	34.26	31.02	24.12	20.44	33.05	24.50	25.19
ab	49.41	37.41	36.88	38.47	39.65	49.17	12.53	58.80	61.34	49.58	57.80	56.02
an	19.04	30.72	31.99	34.69	33.59	15.57	49.33	16.16	17.31	16.25	16.84	17.77
	0.91	3.55	0.53	0.00	0.88	0.40	5.90	0.43	0.00	0.45	0.30	0.76

* Notes: fg - fine grained, mg - medium grained and cg - coarse grained graphic texture. X-ray fluorescence (Philips PW 1410) analyses of major- and trace elements were performed on fused disks at the University of Ottawa. GA and SY-2 were used as internal standards for determining accuracy and several duplicates for determining precision. Estimates of precision for major elements are less than 2%, except for Na₂O (3%), and for trace elements is less than 5%.

between the grain size of graphic texture and composition with respect to the eutectic.

Phase-equilibria considerations

The evolution of a granitic melt saturated in quartz and feldspar to a feldspar-saturated melt is problematic. In order for the graphic texture to grow it is necessary that equilibrium quartz saturation not occur throughout the melt, therefore appropriate granite phase equilibria must be considered.

At the approximate pressures and temperatures corresponding to pegmatite crystallization (H_2O -saturated), the quartz and alkali feldspar cotectic at 500 MPa (Luth et al. 1964) is located at Qtz = 28% (eutectic) ($650^{\circ}C$) to Qtz = 36% (Qtz-Or pseudobinary eutectic) ($735^{\circ}C$). At 300 MPa, the cotectic lies between Qtz = 33% (eutectic) ($665^{\circ}C$) to Qtz = 42% (Qtz-Or pseudobinary eutectic) ($745^{\circ}C$) (Tuttle & Bowen 1958). By interpolation, an alkali feldspar composition of Or₇₀ at 400 MPa corresponds to 35% quartz along the cotectic. The minor fluorine present, based mainly on fluorite in associated skarn and fluorine-rich biotites from the pegmatites, would reduce the liquidus and solidus temperatures in the Qtz-Or-Ab system and expand the quartz field. At a pressure of 275 MPa, Wyllie & Tuttle (1961) noted a decrease in the volatile-saturated thermal minimum from $675^{\circ}C$ to $595^{\circ}C$ with the addition of 4 wt.% fluorine. Manning (1981) noted a substantial shift to higher proportions of feldspar with the addition of fluorine at 100 MPa (volatile saturated). These observations suggest that similar shifts in the quartz-feldspar equilibria would occur at 400 MPa pressure with addition of fluorine. The inferred concentration of fluorine in the granitic melts that led to the Grenville pegmatites is variable but is estimated to be less than 1 wt.%. The maximum effect on the solidus is, by analogy, on the order of $30^{\circ}C$ yielding a $600^{\circ}C$ eutectic temperature, thus enhancing the stability field of quartz

mainly at the expense of albite. In contrast, a decrease in the confining pressure can displace the quartz-orthoclase cotectic enhancing the feldspar crystallization field with respect to quartz. The occurrence of only large alkali feldspar phenocrysts do not preclude quartz saturation elsewhere in the pegmatitic melt, however the phase equilibria indicate that crystallization in the feldspar field is possible under specific conditions.

A DYNAMIC CRYSTALLIZATION MODEL FOR GRAPHIC INTERGROWTHS

The observation of lobate inner boundaries on feldspar-hosted quartz is critical (Figs. 2 & 3). Rough boundaries arise during conditions of high supercooling (Woodruff 1973) when the supply of growth atoms is restricted by low diffusivities or depletion of crystallizing constituents in the boundary layer. This results in non-equilibrium growth. Protuberances on the crystal face become stabilized and grow (e.g. Nittmann and Stanley 1986). We interpret the lobate inner boundary as the onset of diffusion-limited conditions during feldspar growth. Feldspar-hosted quartz in graphic intergrowths has the characteristic prism, arrow, and rod morphologies. Fenn (1977) found that the growth morphology of feldspar changes from equilibrium planar to skeletal growth as a function of the degree of undercooling. Corners and edges subtend more solid angle in the melt than planar crystal faces and preferentially grow because they access a greater volume of melt. The striking patterns of graphic texture are the result of consistent angular relationships between the quartz intergrowths and the host feldspar crystal imposed during growth. We interpret them to be due to preferential quartz nucleation and growth along corners, edges and, to a lesser extent, faces of alkali-feldspar. The observed narrow quartz arrows and prisms are 2D sections of quartz growth along edges of feldspar, whereas rods represent 2D slices of edge or surface growth of quartz on the host feldspar. Figure 5 is a schematic three dimensional (3D) image of graphic

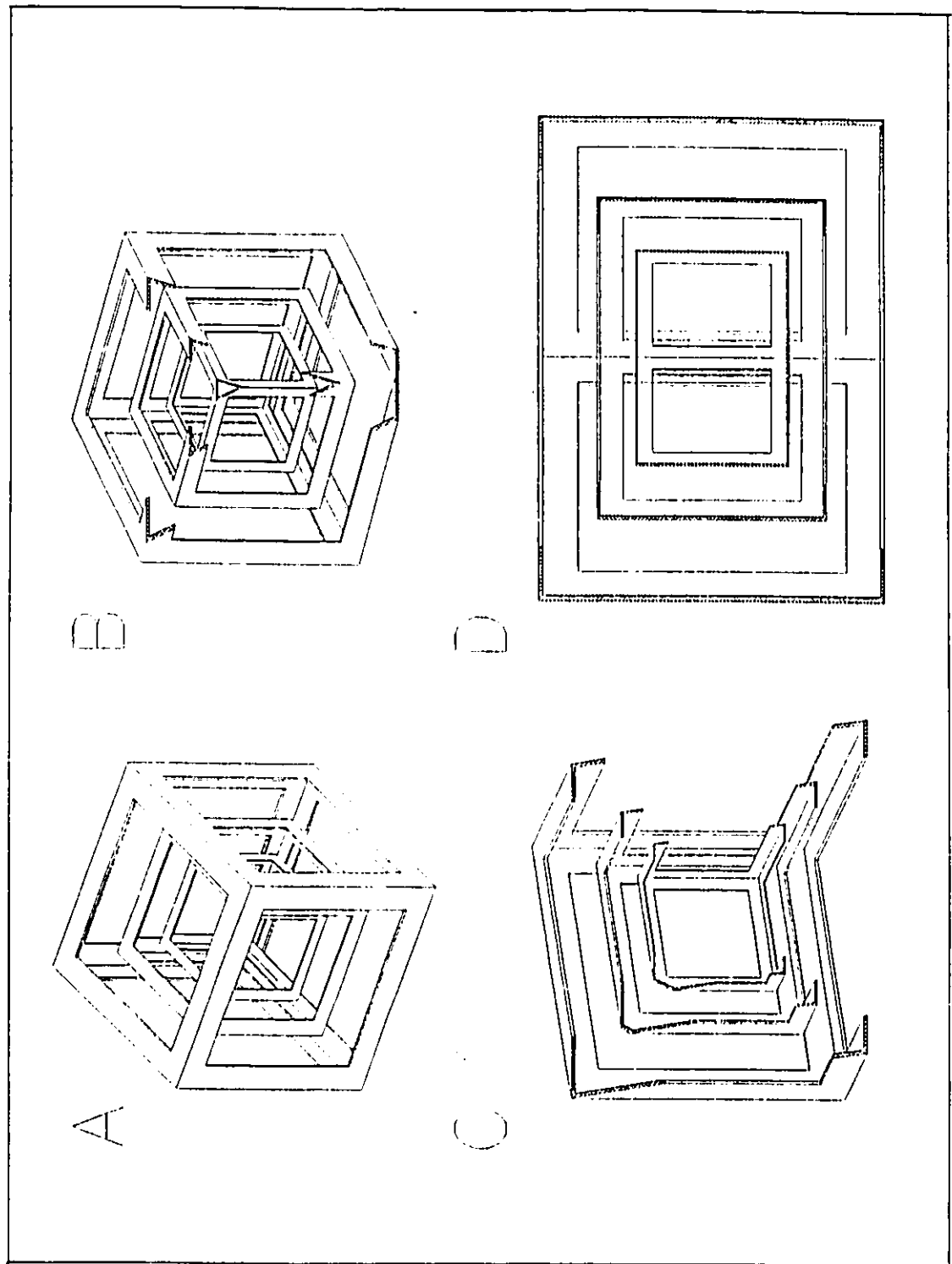


Fig. 5 Schematic three dimensional (3D) drawings of three quartz (angles)-feldspar (space) intergrowths illustrating possible 2D morphologies graphic texture (cross hatched) A. Simple 3D view of quartz (angles) inside feldspar (space) B. and C. Oblique sections through quartz/feldspar intergrowth with 2D view (cross hatched) D. 2D view (110) view of A with 2D section (cross hatched).

quartz-feldspar intergrowth that illustrates the geometric aspects of the growth. For simplicity of design we used a cubic rather than monoclinic feldspar host. Note that quartz (hachured) occurs along corners and edges of the feldspar and illustrates a few of the possible geometries of quartz in feldspar. The spacing between the three sequential episodes of quartz growth is exaggerated in order to exemplify the 3D nature of the texture; it portrays only the large-scale morphologies and leaves out details on the irregular (inner) and regular (outer) surfaces.

As shown previously, the growth for the graphic texture in Grenville Province pegmatite occurred at an approximate pressure of 400 MPa and a minimum melt temperature near 600°C close to H₂O-saturated conditions. Figure 4b illustrates the dynamics of the growth. Alkali feldspar was the first mineral on the liquidus. Growth of the feldspar in this melt required the rejection of H₂O and excess silica. An increase in dissolved volatiles alone should slightly increase the diffusivities of all feldspar components by decreasing melt polymerization (Dingwell 1986; Scarfe 1986). This has the effect of increasing growth rates. In fact, Fenn (1986) proposed that increased growth occurred in response to the increasing water activity at the melt interface. Thus the net effect of the rejected H₂O is to catalyze feldspar growth in the immediate vicinity of the crystal. Initially this process is self-propagating because growth will cause rejection of H₂O which increases the rate of growth and so on. Depletion of Al species in the boundary layer (Si enrichment) results from more rapid feldspar growth and slow diffusion of Al species from the bulk melt into the boundary layer. Therefore, diffusion-limited growth of feldspar arises (Fig. 6). Thus edges and corners become sites of preferred growth and the feldspar faces become rough. Eventually SiO₂ builds up to saturation at these sites and quartz is epitaxially nucleated

and grown on the feldspar structure. The quartz growth depletes the boundary layer in Si relative to Al resulting in renewed alkali feldspar crystallization.

DISCUSSION

The shape of quartz in graphic quartz-feldspar intergrowths is a function of orientation of the feldspar (Fersmann 1928, Simpson 1962, Smith 1974), as is observed here. The detailed work by Heritsch & Holler (1960) and Simpson (1962) shows that quartz rods change shape along their length. Consistent orientations have also been observed by Fersmann (1928) Simpson (1962) and Smith (1974). The detailed work by Heritsch & Holler (1960) and Simpson (1962) shows that quartz rods change shape along their length. Surprisingly, the irregular nature of the inner surface of the rod quartz has not been documented. This may be in part due to the lack of preservation of the irregular interface (e.g., Smith 1974). Fersman (1928) found a 42° angle between the C axes of quartz and feldspar. Using X-ray and optical techniques Wahlstrom (1939) found no particular orientation. However, Heritsch (1953 a,b), Heritsch & Holler (1960), Heritsch et al. (1962), Choudrury et al. (1965) and Bakumenko (1966 a,b) using both X-ray and optical techniques confirmed several angular relationships.

We found consistent proportions of quartz to feldspar (28 wt.% normative quartz) in graphic pegmatites from southwestern Grenville Province (Table 1). Similarly, Erdmansdorffer (1942) found an average of 27 vol.% quartz and a range of 10 to 65 vol.% quartz in quartz-microcline intergrowths. Twenty five vol.% quartz was observed by Vogt (1931), whereas deSchmid (1916) determined an average 28.9 wt.% quartz for the Lower St. Lawrence pegmatites. Cerny (1971) found similar proportions of quartz to feldspar in a study of Czechoslovak graphic pegmatites. Mehnert (1968) argued that a quartz to feldspar ratio of 27:73 was not compatible with the quartz-feldspar cotectic melt. Within each data set, the

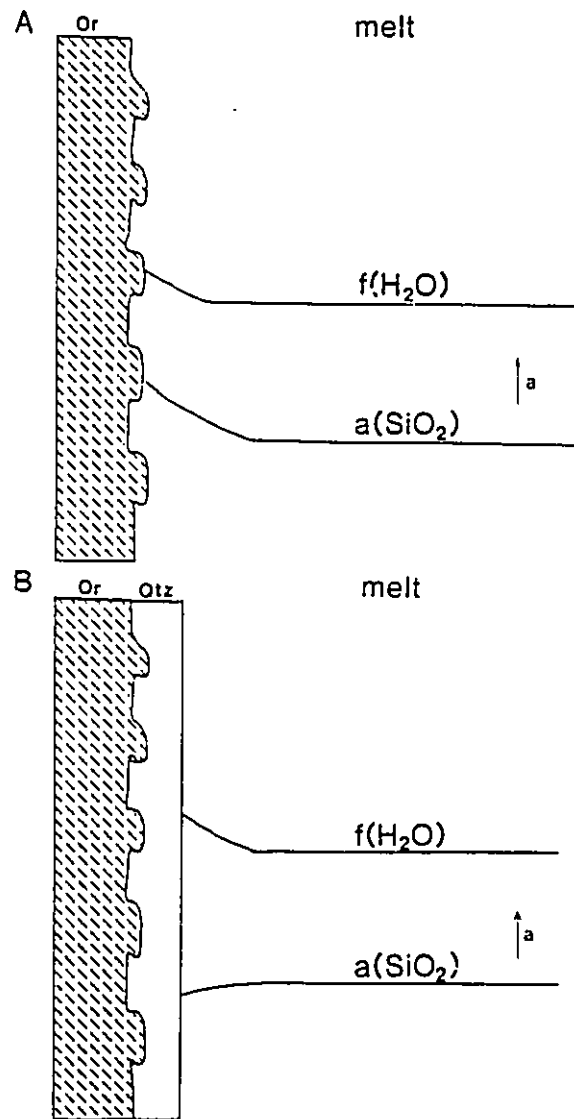


Fig. 6 A. Schematic representation of compositional variations at the feldspar-melt interface preceding quartz nucleation B. Schematic representation of compositional profiles at quartz/melt interface after quartz nucleation. The relative fugacity of water ($f(\text{H}_2\text{O})$) and activity of quartz ($a(\text{SiO}_2)$) at the mineral interface.

volume proportion of quartz is approximately constant indicative of a recurrent process.

The diffusivity of Si and Al species are very low in low-temperature granitic systems (Hofmann 1980, Dunn 1986); however, the depolymerization of the melt by network modifiers (H_2O and HF) will reduce viscosity and increase diffusion in volatile-rich granitic melts (Scarfe 1986). The diffusivity of H_2O in obsidian and granitic melt is between 10^{-8} and 10^{-9} cm^2/s at temperatures between 600°C and 800°C (Shaw 1974; Arzi 1978; Karsten et al. 1982). The effect of depolymerization of the Si(Al)-O tetrahedra coordinated with OH⁻ could considerably reduce the diffusivity of OH⁻ in the melt and increase the diffusivity of Si and Al because of their coherent behavior. The nucleation and growth of either quartz or feldspar at the interface may be too rapid for the rejected H_2O to diffuse into the volatile-undersaturated melt, and may create locally volatile-saturated conditions at the interface. Evidence of volatile saturation was found by Fenn & Luth (1973) who reported the presence of fluid inclusions in experiments at H_2O -undersaturated conditions. The limiting factor in diffusion-controlled crystal growth is most likely the diffusion of Si away from the feldspar and diffusion of Al toward the feldspar interface since the diffusivities of potassium and sodium are considerably greater (Hofmann 1980, Dunn 1986).

Perhaps the most unusual feature of the proposed model is the oscillatory nature. Therefore, the liquid line of descent is distinctly different to the familiar equilibrium case (Fig. 4b). Under diffusion-limited conditions the liquid immediately adjacent to the feldspar becomes enriched in SiO_2 , driving the interface melt composition towards quartz until quartz saturation is achieved (Fig. 4b). After quartz saturation, boundary layer melt compositions are driven back towards bulk melt compositions into the field of feldspar

saturation. This cycle is repeated resulting in a modified liquid line of descent for the bulk melt (Fig. 4b) . The graphic intergrowths are a non-equilibrium phenomenon. If the crystallization were equilibrium (i.e. was well mixed) one would observe a granitic texture produced by the crystallization of alkali feldspar and crystallization of discrete quartz crystals. It is now known that systems driven far from equilibrium may have an oscillatory behaviour (e.g. Nicolis and Prigogine 1989). These oscillators also produce striking spatial or temporal patterns that according to Gray and Scott (1990) are due to an interaction of autocatalytic or thermal feedback with the diffusive transport properties of the molecules in the system. The proposed model for graphic intergrowths identifies H₂O as the catalyst that changes the diffusion properties of the melt with crystallization. The corner and edge habit, and inner lobate boundaries of quartz indicates that the feldspar growth was diffusion limited. Conversely, the euhedral outer boundaries of the quartz with feldspar is indicative of a return to an equilibrium style of growth (Fenn 1977). Oscillation in far from equilibrium growth are often characterized by a transition from stable to unstable growth of one phase followed by an abrupt and stable growth of a different phase (e.g. Gray and Scott 1990).

The formation of epitactic quartz on feldspar may be indicative of a relatively low density of nuclei for quartz, which is expected at very low undercoolings.

Swanson (1977), Fenn (1977) and Dowty (1980) have shown that feldspar nucleation and growth curves shift toward the liquidus at higher volatile contents in the melt and noted a decrease in the amount of growth and nucleation. This results in a low crystal surface area to melt volume ratio. Therefore, on average, species must diffuse further to the interface than the case where the crystal surface area to melt volume ratio is high. As a consequence, diffusivity is the limiting factor in the rate of crystal growth. Heterogeneous

nucleation in pegmatites, particularly along the walls, will initiate crystal growth at low degrees of supercooling. This is substantiated by Fenn (1986) and London et al. (1989), who found the graphic texture along the walls of their reaction vessels. Fenn (1986) suggested that increased growth occurred in response to the increasing water activity at the melt interface, which increased growth rate owing to smaller undercoolings.

The common association of graphic and granophyric textures in granites and pegmatites indicates that understanding the nature of the magmatic-hydrothermal transition is key to the formation of these textures. There is an increasing body of experimental information on the phase relations in volatile (H_2O)-bearing granitic magmas (melt+crystal+vapour) (Luth & Tuttle 1969, Maaløe & Wyllie 1975, Whitney 1975, Whitney 1977, Naney 1983, Huang & Wyllie 1986, London et al. 1989). The crystallization history of granitic magmas may be significantly affected by the original volatile contents (amount and species).

Figure 7 illustrates in a qualitative manner the nature of the vapour-saturation surface in terms of pressure, temperature, wt.% H_2O for a melt of granitic composition. The crystallization of anhydrous silicates in the melt enriches the remainder of the melt in that component by volatile diffusion away from the crystallizing interface (Jahns and Burnham 1969, Fenn 1977; Fig. 7 curve A), to the point of achieving saturation in the volatile phase. H_2O -saturated conditions at the interface enhance feldspar growth and result in progressively decreasing water activities in the melt away from feldspar melt interface. This produces decreasing cation diffusivities away from the crystal. Therefore, factors affecting volatile phase saturation and separation in the melt are important, in particular geostatic pressure changes arising from emplacement of the pegmatite and hydrofracturing associated with volatile phase separation (Fig. 7, curve B).

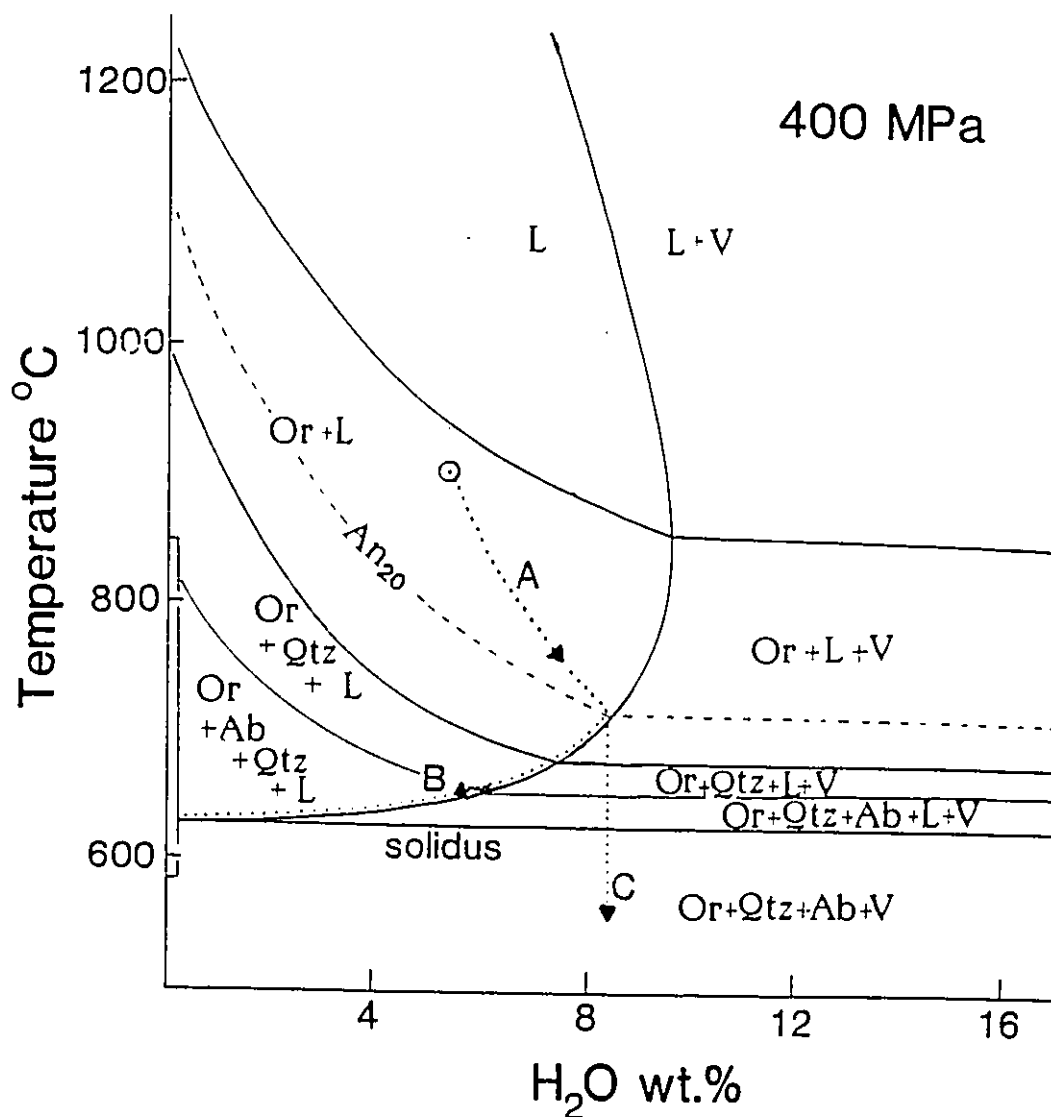


Fig. 7 Schematic representation of crystallization of a granitic melt and conditions of saturation in the haplogranite system at 400 MPa similar to the experimentally-derived granite equilibria (Fenn 1986) although the sequence of crystallization has been modified so that orthoclase appears on the liquidus before quartz as explained in the text. Curve A is the liquid line of descent at volatile-undersaturated conditions due to orthoclase crystallization and intermittent metastable quartz saturation, curve B is the path of crystallization at volatile-saturated conditions with separation of the vapour phase, and curve C is the path of volatile saturated crystallization for a fluid partially retained in the pegmatite into subsolidus conditions. Within the pegmatite plagioclase compositions in the system are variable between albite and oligoclase. The absence of plagioclase in the graphic texture is probably due to crystallization kinetics and diffusion of Na away from the crystallizing interface.

If the fluid is retained within the pegmatite because the competency of the rocks is not exceeded (Fig. 7, curve C), internal replacement of primary minerals and textures would occur (London et al. 1989).

The development of coarse- to fine-grained graphic and granophyric textures in zoned and unzoned Grenville pegmatites indicates that volatile-phase saturation is a key phenomena which may be related to partitioning of U, Th, Mo, REE, and Nb into the volatile phase (Flynn and Burnham 1978, Fowler and Doig 1983b, Candela and Holland 1984, Keppler and Wyllie 1990). Partitioning of U, Th, Mo, REE, and Nb into the volatile phase during second boiling of the granitic pegmatite melt is partly responsible for subeconomic concentrations of these elements in pegmatites and related deposits (Lentz 1991a & b).

CONCLUSIONS

The physical conditions within the Grenville U, Mo, REE, and Nb-bearing granitic pegmatites were responsible for the formation of graphic quartz feldspar intergrowths. The spatial distribution of graphic texture in these pegmatites near the host rock contact suggests that the saturation of a volatile phase during crystallization is important to understanding their formation. The available whole-rock geochemical data, the volume proportions of quartz to K-feldspar, and phase-equilibrium data in the fluorine-bearing haplogranite system favour nearly-simultaneous crystallization of quartz and K-feldspar from a melt approaching the cotectic (quartz saturation). Close observation of the textures, reveals an irregular quartz-K-feldspar boundary and indicates that quartz preferentially grew on the corners and edges of the feldspar. During feldspar growth, the area immediately surrounding alkali feldspar crystals became depleted in Al and enriched in Si. The polymerizing effect of Si build up in the melt is counteracted by the depolymerizing effect of rejected H₂O in the boundary layer. This results in enhanced growth in

the vicinity of the boundary layer but diffusion of Al into and Si away from the crystal face result in a decrease in feldspar growth as the melt boundary layer widens. This resulted in growth being concentrated at crystal edges and corners and the production of rough crystal faces (feldspar protuberances). The build up rejected silica resulted in quartz saturation and epitaxial nucleation. Growth of quartz depleted the silica concentration in the boundary layer melt and restored feldspar-saturated growth. This process repeated and resulted in the oscillation of the melt composition at the interface from quartz oversaturated to undersaturated conditions producing rhythmic quartz-feldspar intergrowths. The saturation of a volatile phase (H_2O) at the feldspar-melt interface may increase undercooling and further reduce diffusion of silica away from the feldspar.

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PETROGENESIS AND GEOCHEMICAL COMPOSITION OF BIOTITES
IN RARE-ELEMENT GRANITIC PEGMATITES
IN THE SOUTHWESTERN GRENVILLE PROVINCE, CANADA

by

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ABSTRACT

Field and mineralogical observations with chemical analyses of biotite from late-tectonic Grenville pegmatites are used to characterize and evaluate the petrogenesis of rare-element (U, Th, Mo, Nb, REE) pegmatites in part of the southwestern Grenville Province. These pegmatites occur within middle to upper amphibolite facies rocks along and adjacent to shear zones and have hybridized margins because of interaction with their host rocks. Endomorphic and exomorphic biotite forms by the mechanical incorporation or hydrothermal replacement of pre-existing biotite, hornblende, Ca pyroxene and/or feldspar. This is accompanied by chemical re-equilibration and an increase in grain size of the biotite comparable to feldspars, and inherit the chemical characteristics of the pegmatite. The chemical compositions of biotite from unzoned, partially-zoned, and zoned pegmatites indicate a trend of increasing chemical fractionation based on LIL enrichment. Volatile enrichment and vapor-phase saturation is probably responsible for the development of partially-zoned and zoned pegmatites although internal melt fractionation cannot be ruled out.

There is considerable overlap in calculated $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})$ (3.2 to 4.7) and $\log(f_{\text{H}_2\text{O}}/f_{\text{HCl}})$ (1.3 to 2.8) for biotites (@ 600°C) among different pegmatites. In general, the Fe/(Fe+Mg) ratio ranges between (0.22 and 0.86). The most highly fractionated biotites have high Fe/(Fe+Mg), Al, Mn, Rb, Nb, and Zn and low Ba. Commonly, magnetite and microcline coexist with biotites having an Fe/(Fe+Mg) ratio between 0.54 to 0.65. The diffusive loss of H_2 gas near or at H_2O vapor saturation at high $\text{H}_2\text{O}/\text{Fe}^{2+}$ may be responsible for the oxidized nature of pegmatites. Rare-element enrichment due to pegmatite fractionation combined with partitioning of rare-elements from the pegmatite melt into the volatile phase and subsequent interaction with the host rocks is key to the formation of these rare-element mineral deposits.

INTRODUCTION

The late-tectonic granitic pegmatites intruded a complex sequence of supracrustal and mafic to felsic plutonic rocks of the Central Metasedimentary Belt (CMB) of the Grenville Province (Figure 1). Early- to late-tectonic granitic pegmatites occur throughout the Central Metasedimentary Belt of the Grenville Province with the exception of the greenschist-grade metamorphic low near Madoc, Ontario. However, the late-tectonic granitic pegmatites are the largest of the Grenville pegmatites and are associated with enrichments of U, Th, Mo, REE, Nb, and Be. It has been proposed that these pegmatitic melts originated from in situ partial melting because there is evidence of local partial melting. However, the discordant nature of these pegmatites, enrichment of LIL and HFSE elements, and the disproportionate amount of "melanosome" to pegmatite "leucosome" does not support this hypothesis. Alternatively the pegmatites may represent fractionates from late-tectonic, weakly-alkaline granitoid rocks (Fowler and Doig 1983a; Černý 1990) or mid-crustal partial melts associated with crustal thickening and rebound (Lentz 1991b, 1992). The absence of cogenetic plutons associated with these pegmatites, their moderately fractionated nature, and primitive Sr isotopic signature (Fowler and Doig 1983a; Lentz et al. 1991) lends support to the latter hypothesis.

Biotite has been used successfully as a marker of chemical fractionation in granites (Ragland et al. 1968; Barrière and Cotten 1979; Hawthorne and Černý 1982; Speer 1984). Biotite is the most common ferromagnesian phase in these granitic pegmatites. This regional examination of late-tectonic granitic pegmatites was conducted to determine relationships between the pegmatites and the host rock and examine the mineralogical, textural, and geochemical variations within pegmatitic biotites as it pertains to rare element enrichment. This study examines the major- and trace-element compositions

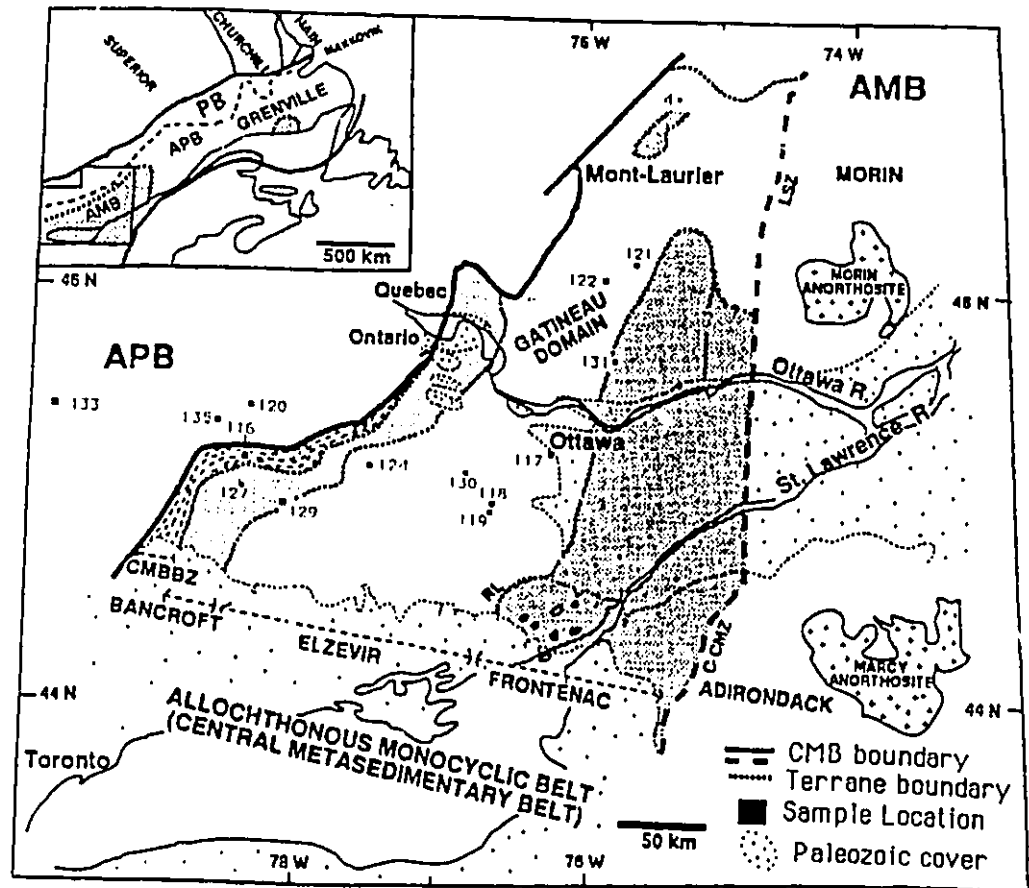


Figure 1 Tectonic subdivisions of the southwestern Grenville Province (inset) (modified from Corriveau et al. 1990). PB, Paraautochthonous Belt; APB, Allochthonous Polycyclic Belt; AMB, Allochthonous Monocyclic Belt (Central Metasedimentary Belt (CMB) is part of the AMB); CMBBZ, Central Metasedimentary Belt Boundary Zone; RL, Rideau Lake fault, C-CMZ, Colton-Carthage Mylonite Zone; LSZ, Labelle Shear Zone. Biotite samples: 4, Michinamecus U pegmatite; 116 Maynooth barren pegmatite; 117, South March feldspar pegmatite; 118, Perth feldspar pegmatite; 119, Kirkham feldspar pegmatite; 120, Comet quartz-U pegmatite; 121, ACME Mo-U pegmatite; 122, Blue Sea amazonite pegmatite; 124, Wall Gem Be, U, REE pegmatite; 127, New Armstrong pegmatite; 129, Goulding-Keene nepheline pegmatite; 130, Whytock quartz-U-REE pegmatite; 131, Evans-Lou U, REE feldspar pegmatite; 133, McQuire U pegmatite; 134, Pieds des Monts; 135, Lake St. Peter euxenite-bearing pegmatite.

Table 1 General descriptions of biotite-bearing granitic pegmatites sampled in this study

No.	Name	Type	Field	Rare elements	Comments
4	Mitchinamecus	unzoned	Mont Laurier	U, Th	pegmatite margin with bi-amp gneiss
116	Maynooth	unzoned	Bancroft	-	biotite occurs throughout pegmatite
117	South March	unzoned	Ottawa	-	pegmatite margins in amphibolite
118	Perth	unzoned	Perth	U, Th	pegmatite margin with amphibolite
119	Kirkham	unzoned	Perth	U, Th, Mo	pegmatite margin with amphibolite
120	Comet	part-zoned	Madawaska	U, Th	pegmatite margin/core in bi gneiss
121	ACME	unzoned	Maniwaki	Mo	pegmatite margin in bi gneiss
122	Blue Sea	part-zoned	Maniwaki	U, Th, REE, Mo	biotite occurs throughout pegmatite
124	Wall Gem	zoned	Quadeville	Be, REE, Nb, Th	pegmatite margin/core in bi gneiss
127	Kenmac-Chiboug.	part-zoned	Bancroft	U, Th, Mo	GSC sample 65744
129	Goulding Keene	unzoned	Bancroft	U, Th, REE, fl	nepheline-biotite throughout pegmatite
130	Whytock	zoned	Perth	U, Th, REE, Nb?	pegmatite margins with bi gneiss
131	Evans Lou	zoned	Wakefield	U, Th, REE, Nb	pegmatite margins with bi gneiss
133	McQuire	part-zoned	Conger	U, Th, ?	Ellsworth GSC sample 24
134	Pleds des Monts	part-zoned	St. Lawrence	U, Th, REE, ?	Ellsworth GSC sample 269
135	Lake St. Peter	part-zoned	Madawaska	U, Th, Mo, REE	Ellsworth GSC sample 85

of 27 biotites from 15 pegmatite bodies (Tables 1 and 2) and compares them to previous biotite analyses from Grenville pegmatites (Lentz 1992).

DESCRIPTION OF GRANITIC PEGMATITES

INTRODUCTION

The granitic pegmatites of the southwestern Grenville Province have been examined by Hewitt (1967), Tremblay (1974), Masson and Gordon (1981), Storey and Vos (1981), Haynes (1986), Goad (1990) and Lentz (1991a,b, 1992), hence only a brief discussion is necessary. Granitic pegmatite occur both as sills and dikes with respect to the predominant fabric developed within the host rock. They range in size from small (1 metre wide) to very large (> 50 metres wide), for example, the Faraday pegmatite swarm near Bancroft, Ontario. The granitic pegmatites intruded rocks of the Grenville Province (ca. 1020-1060 Ma) after the culmination of the Grenville orogenic event (i.e. Ottawan orogeny at ca. 1090-1100 Ma; Easton 1986). It is estimated that the pegmatites crystallized at approximately 630°C and 400 MPa P(H₂O) based on geological and thermochronological constraints (Lentz 1991b, 1992). The dikes were evidently granitic melts intruded along structurally weak zones, particularly normal faults (reactivated thrust zones) and late-crustal shears bounding large competent domains resulting in a preferred orientation of many of the pegmatites within individual districts. The margins of some granite pegmatites were affected by syn- to post-emplacement shearing (mylonitization) compatible with emplacement in structurally active zones, which has been attributed to the further enrichment of U (ie. Faraday; Habib 1982).

MINERALOGY AND PETROGRAPHY

Quartz is present in the granitic pegmatites as milky to smoky quartz. Plagioclase, of albite to oligoclase composition, is present in the simple pegmatites as fine-grained albite to oligoclase. Perthitic microcline is usually

the most abundant phase in the granite pegmatites and occurs in various shades of pink to red reflecting the degree of secondary earthy hematization.

In general, ferromagnesian phases comprise less than 5 percent of the pegmatites and are usually concentrated in the outer parts of the body. Biotite, the most common ferromagnesian phase in the granitic pegmatites, has recorded many of the physio-chemical processes occurring within the pegmatite, which are key to it's chemical evolution. Fine- to coarse-grained hornblende is also common in granitic pegmatites with increased grain size coincident with it's decreasing abundance. Hornblende is mainly a hybrid product in the pegmatites, that is to say it occurs in pegmatites hosted by hornblende gneisses, amphibolites and/or carbonate-bearing gneisses (eg. Richardson pegmatite). Although not common, Ca pyroxene occurs mainly in the hybrid and skarn margins of granite pegmatites hosted in carbonate-bearing lithologies. Ca pyroxene-bearing endoskarn most commonly occurs with K-feldspar, plagioclase (or scapolite), and titanite. Muscovite is common in some Grenville pegmatites but in this study was only present in the Whytock zoned pegmatite. Magnetite occurs as small (< 1cm) equant, euhedral crystals disseminated in the radioactive pegmatites with or without other ferromagnesian phases. The magnetite is commonly associated with intense secondary hematization of the feldspars and when present is found in the contact zones of the pegmatite. Euhedral titanite is a common accessory phase particularly along margins of the pegmatite.

PEGMATITE-HOST ROCK INTERACTION

The margins of the granite pegmatites with the host rock gneisses may have sharp to diffuse contacts. The diffuse pegmatite contact zones represent hybridized pegmatite which is mineralogically heterogeneous (biotite, hornblende, aegirine-augite, magnetite, allanite, titanite, zircon, and more rarely euxenite, allanite, cyrtolite, and yttrian

andradite, uraninite, uranothorite, and molybdenite (Lentz 1991a,b)). The hybrid portions of zoned pegmatites occur along the wall and border zones and to a lesser extent in the intermediate zones. Generally, the concordant pegmatites have reacted more completely with the host rocks than the discordant pegmatites (Hewitt 1967; Lentz 1991a). These reaction zones may be endoskarns produced in response to the interaction of the pegmatite and the host rock by the hydrothermal fluids at both hypersolidus or subsolidus conditions. Hybridization is most evident in gneisses with a high mafic mineral content, particularly amphibolites and biotite gneisses.

PEGMATITE ZONATION

The granitic pegmatites occur as unzoned, partially-zoned, and zoned types. Unzoned granitic pegmatites range in width from 1 to 50 m and may exceed 1 km in length. The grain size varies from very fine-grained aplite (< 1mm) to medium-grained (3 to 10 cm) pegmatite. The granite pegmatites are dominantly fine-grained pegmatitic with average grain sizes of 1 to 3 cm with an equigranular texture (pegmatite nomenclature). The partially-zoned pegmatites, have much in common with the unzoned pegmatites but have a central coarse-grained quartz and/or feldspar core with lesser proportions of feldspar and biotite. Zoned pegmatites occur more rarely, for example the Wall Gem beryllium pegmatite (East zone) near Quadeville, Ontario (Figure 2). The grain size ranges from medium- to very coarse-grained pegmatitic (3 cm to < 1m). They contain quartz, amazonitic microcline, plagioclase, biotite, hornblende, garnet, titanite, molybdenite, allanite, uranothorite, zircon, and more rarely euxenite, fluorite, uranothorite, tourmaline, and clevelandite (Figure 2).

Graphic and granophyric quartz and K-feldspar intergrowths are commonly present in the cupolas of the unzoned granite pegmatites and wall zones of zoned pegmatites. Graphic and granophyric pegmatite is commonly found near the zone between

mineralized pegmatite/skarn and barren granite pegmatite as well as the transition between unzoned and zoned pegmatite (Lentz and Fowler 1992).

METHODS

Major-elements, F and Cl were determined using a Camebax microprobe (Geological Survey of Canada) on biotite flakes mounted on a glass slide using an operating current of 9.5 nanoamps operating. Three microprobe analyses were averaged per sample. The mineral separates were prepared by careful separation of coarse-grained (> 1 to 20 cm diameter) micas by optical examination and removal of inclusions (> 99.5 vol. % pure). Trace-element (Ba, Cr, Sr, Rb, Y, Nb, Zn, Ni, and V) analyses were determined on fused disks of very pure mica separates (1.3 g) and analysed on a Philips Biotite-bearing zones were sampled for study. PW1410 XRF unit in the University of Ottawa Geochemistry Laboratory. It is possible that some trace-elements (Cr, Y, REE and possibly Nb) are anomalous due to inclusions, however, the consistency of the trace elements obtained between duplicate analyses and several biotites within a single pegmatite body do not suggest significant contamination. The ferrous iron content of biotite was determined using the modified Wilson method (Whipple 1974). Duplicate biotite (122C) were used to estimate the precision of the XRF analyses; the precision, expressed as maximum relative standard deviation, is: Ba = 16 %, Cr = 14 %, Sr = 13 %, Rb = 0.74%, Y = 31 %, Nb = 0.28 %, Zn = 0.26 %, Ni = 16 %, V = 100 %. However, Ba, Y, Ni, and V abundances are low and relative deviation should be on the order of a few percent. SY-3, DR-N, and BR (Abbey 1983) were run as internal standards for both XRF and titration analyses. The rare-earth element data were determined by instrumental neutron activation at the Institut de génie énergétique, École Polytechnique, Université de Montréal, Montréal, Quebec and were corrected for U and Th interferences according to Kennedy and Fowler (1983).

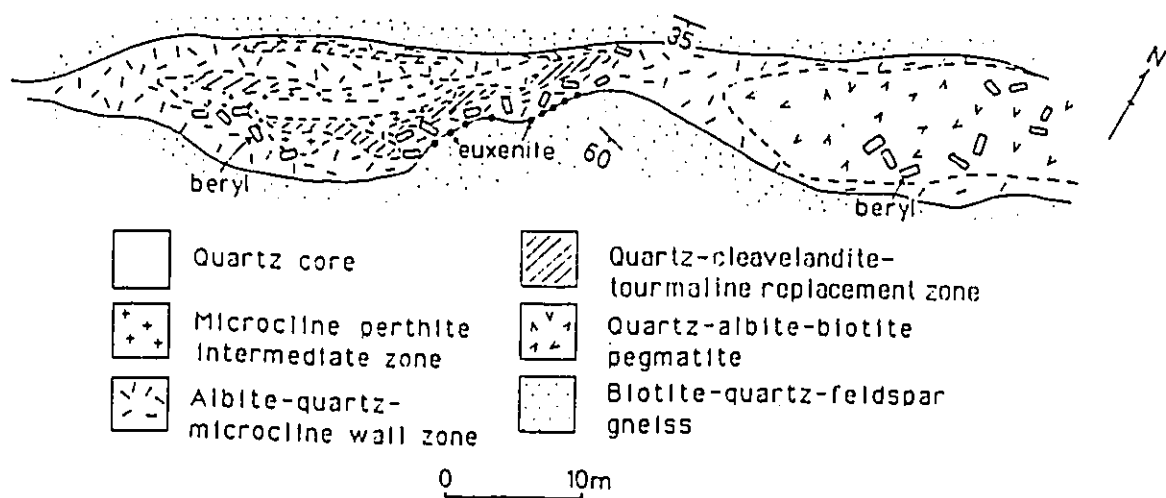


Figure 2 Wall Gem zoned granitic pegmatite (East Quarry), Quadeville, Ontario (modified after Storey and Vos 1981).

BIOTITE SYSTEMATICS

DESCRIPTION OF SAMPLED PEGMATITES

Biotite may comprise up to 5 volume percent of the granitic pegmatite except along the margins. Grain size varies from fine- to coarse-grained (pegmatitic) and there is, in general, an increase in size toward the central portion of the bodies. Most of the localities examined have been located by Sabina (1986, 1987; Figure 1; Table 1).

Several biotites from a radioactive unzoned pegmatite north of Mont Laurier (# 4) occur as clusters within fine- to medium-grained granite pegmatite near the contacts with amphibolites and biotite-quartz-feldspar gneisses. A weakly radioactive unzoned pegmatite (# 116) west of Maynooth, Ontario is hosted within the Central Metasedimentary Belt Boundary Zone biotite-quartz-feldspar gneisses and forms irregular -shaped aggregates within the medium-grained pegmatite. The South March biotite-bearing pegmatite (# 117) has a sharp discordant contact with amphibolite. The Perth pegmatite (# 118) is amphibolite- and gneiss hosted, texturally heterogeneous and complexly hybridized with xenocrystic hornblende being replaced by biotite. The Kirkham molybdenite-bearing, unzoned pegmatite (# 119) is hosted in amphibolite. The Comet quartz pegmatite is hosted within biotite-rich quartz-feldspar gneisses in the Central Gneiss Belt just north of Madawaska, Ontario (Storey and Vos 1981). The ACME molybdenite-bearing pegmatite (# 121) is discordantly hosted in amphibolites and biotite-quartz-feldspar gneiss. The hybrid biotite pegmatite margins are transitional into metasomatically altered gneisses. The Blue Sea feldspar quarry (# 122) is a poorly exposed, partially-zoned pegmatite hosted in amphibolites and marbles. Biotite is characteristic of all textural varieties and coexists with amazonite, tourmaline, and fluorite. The zoned Wall Gem Be pegmatite (sample 124) is concordantly hosted in biotite-bearing quartz-feldspar gneiss and minor intercalated amphibolite. Biotite

Table 2 Chemical composition of biotite from granitic pegmatites in the southwestern Grenville Province

Type	4B	4C	116A	116B	116C	117E	118-2	119-1	119-2	120A	120B	120C	121B	121H	121J	122A	122C	124-4	124-5	124-7	124-8	127	130-18	131	133	134	135
SiO ₂	56.8	56.8	56.8	56.8	56.8	56.2	56.2	56.4	56.4	56.3	56.3	56.0	56.3	56.4	56.4	56.4	56.4	56.4	56.4	56.4	56.4	56.4	56.4	56.4	56.4	56.4	56.4
TiO ₂	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	
Al ₂ O ₃	14.70	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	14.55	
Fe ₂ O ₃	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	4.56	
MnO	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	16.46	
MgO	10.17	10.28	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	11.66	
BaO	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	
CaO	0.02	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Na ₂ O	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	
K ₂ O	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	9.55	
PbO	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	
H ₂ O ⁺	3.74	3.61	2.82	3.61	2.82	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	3.61	
F	0.33	0.49	0.20	0.35	0.20	0.35	0.20	0.35	0.20	0.35	0.20	0.35	0.20	0.35	0.20	0.35	0.20	0.35	0.20	0.35	0.20	0.35	0.20	0.35	0.20	0.35	
Cl	0.18	0.17	0.20	0.43	0.26	0.07	0.18	0.32	0.30	0.06	0.06	0.04	0.18	0.25	0.27	0.10	0.13	0.07	0.03	0.02	0.05	0.18	0.17	0.35	0.06	0.10	
O-F	0.14	0.21	0.93	0.15	0.87	0.59	0.17	0.18	0.16	0.27	0.23	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	
O-Cl	0.04	0.04	0.05	0.10	0.06	0.02	0.04	0.07	0.07	0.01	0.01	0.01	0.04	0.06	0.06	0.02	0.03	0.02	0.01	0.00	0.01	0.04	0.04	0.04	0.04	0.04	
Total	100.2	99.2	100.3	99.8	100.7	99.4	101.6	100.1	99.1	99.6	100.6	98.4	98.5	100.5	99.8	97.8	96.4	99.9	99.9	98.4	100.2	101.9	100.7	100.7	100.7	101.0	
Cr ppm	20	19	64	46	57	38	31	30	21	15	78	25	36	66	41	27	37	18	0	48	35	44	35	37	44	43	
Sr	7	4	14	14	12	1	1	7	14	5	1	1	63	32	34	13	13	17	28	14	16	17	5	16	0	8	
Y	19	26	36	50	27	13	29	13	15	41	11	19	24	5	9	85	41	50	161	37	44	0	70	16	0	7	
Nb	141	364	106	231	137	82	257	40	43	165	126	131	0	2	2	2332	719	452	504	528	521	65	574	632	613	473	
Zn	269	274	438	312	401	849	499	139	150	538	601	605	138	210	220	2032	1660	784	809	742	801	517	592	428	437	677	
Fe	19	17	89	74	65	0	0	0	0	41	69	33	0	12	6	71	63	133	43	107	106	33	37	79	73	54	
V	110	120	112	106	92	35	53	212	187	231	239	225	129	136	134	0	0	32	57	41	40	158	293	0	0	0	
Fe/(Fe+Mg)	0.53	0.53	0.47	0.55	0.48	0.58	0.47	0.55	0.56	0.56	0.55	0.56	0.56	0.57	0.56	0.66	0.56	0.55	0.52	0.51	0.49	0.2	0.57	0.60	0.63	0.54	
#Si	5.58	5.65	5.67	5.79	5.62	5.91	5.73	5.65	5.67	5.67	5.58	5.59	5.90	5.92	5.97	5.91	5.77	5.88	5.91	5.93	6.05	6.19	5.61	6.05	5.98	5.69	
#Al	2.42	2.35	2.11	2.33	2.21	2.38	2.08	2.27	2.35	2.32	2.41	2.10	2.10	2.06	2.03	2.09	2.23	2.12	2.09	2.07	1.95	1.74	2.39	1.95	2.62	2.31	
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
#Fe	0.21	0.30	0.27	0.35	0.16	0.40	0.37	0.26	0.29	0.34	0.21	0.28	0.33	0.13	0.13	0.30	0.31	0.26	0.29	0.21	0.19	0.10	0.34	0.39	0.32	0.36	
#Mn	0.52	0.35	0.23	0.32	0.25	0.39	0.21	0.39	0.40	0.36	0.32	0.33	0.13	0.13	0.13	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	
#Fe + 3	2.09	2.66	2.42	2.71	2.13	2.74	2.35	2.70	2.78	2.63	2.18	2.04	1.83	2.03	2.00	2.90	2.48	1.85	2.47	1.72	2.32	0.96	1.90	2.35	2.34	2.24	
#Mn + 2	0.07	0.06	0.06	0.06	0.05	0.10	0.07	0.02	0.02	0.06	0.10	0.09	0.01	0.03	0.02	0.15	0.07	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	
#Mg	2.30	2.37	2.68	2.25	2.70	1.95	2.65	2.25	2.18	2.15	2.18	2.10	3.68	3.46	3.84	3.58	1.98	2.02	2.30	2.35	2.41	4.28	2.01	1.58	1.63	2.24	
#Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
#Ca	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
#Na	0.03	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	
#K	1.85	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	1.83	
#Pb	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
#Sr	1.89	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	1.88	
#O	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	
#OH	3.80	3.72	2.86	3.72	2.86	3.72	3.71	3.74	3.67	3.72	3.62	3.72	3.62	3.72	3.62	3.72	3.62	3.72	3.62	3.72	3.62	3.72	3.62	3.72	3.62	3.72	
#F	0.16	0.24	1.06	0.17	0.99	0.69	0.19	0.21	0.18	0.32	0.25	0.37	0.25	0.20	0.20	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	
#Cl	0.05	0.04	0.05	0.11	0.07	0.02	0.05	0.02	0.05	0.01	0.02	0.01	0.05	0.06	0.07	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	
X _{Si}	0.42	0.41	0.47	0.40	0.48	0.55	0.40	0.50</																			

NOTES: O - unzoned, O - partially zoned, ● - zoned pegmatite; * H₂O was calculated. Pb is possibly an additional element in biotites from sample 122 and 124 as they coexist with amazonite. X_{Si}, X_{Al}, and X_{Mn} were calculated according to Gunow et al. (1950). log(H₂O)/HF and log(H₂O)/HCl were calculated from intercept values calculated according to Munoz (1984) for a T = 600°C. Mineral formula were calculated using Minitale created by A. Alfi and E. Essene at the University of Michigan, Ann Arbor, Michigan.

is concentrated in the border zone of the pegmatite whereas sample 124-5 is biotitized gneiss at the contact. The Kenmac-Chibougama U pegmatite (#127; GSC No. 65744) is a poorly zoned pegmatite. The Whytock zoned pegmatite has abundant muscovite and K-feldspar in the border zone and rare biotite. Biotite is very rare in the Evans-Lou zoned rare-element pegmatite (# 131). The McQuire uraninite-bearing pegmatite, Conger township (# 133; GSC Ellsworth 24; not visited) is a probably a partially-zoned pegmatite. The Pieds des Monts biotite pegmatite (#134; GSC Ellsworth 269; not visited) is located on Murray Bay along the North shore of the St. Lawrence river. The Lake St. Peter partially-zoned, euxenite-bearing biotite pegmatite (# 135; GSC Ellsworth 85; not visited). Samples 127, 133, 134, and 135 were obtained courtesy of Gary Ansell (Geological Survey of Canada) hence the character of these pegmatites remains poorly documented.

MAJOR- AND TRACE-ELEMENT COMPOSITION

The chemical composition of biotite illustrates the combined effects of differentiation, hybridization, and volatile phase separation in these pegmatite as the biotites are particularly sensitive indicators of changing physio-chemical conditions within the melt (Figures 3 and 4). Generally, the $Fe/(Fe+Mg)$ ratio of biotites is not a reliable indicator of pegmatite fractionation because the Fe-enrichment trend of some biotites is interrupted by the stability field magnetite-sanidine-gas (see Redox considerations).

The major- and trace-element compositions of biotite are very uniform within most portions of the pegmatite except possibly at the host rock contacts (Table 2). There is an increase in siderophyllite component and a general increase in Al_{IV} and Al_{VI} with increasing $Fe/(Fe+Mg)$ ratio in most micas (Figures 3 and 4). There is also a slight inverse relationship between Al^{IV} and Al_{VI} . The aluminum in both octahedral and tetrahedral sites, in part, reflects the peraluminosity of the pegmatite.

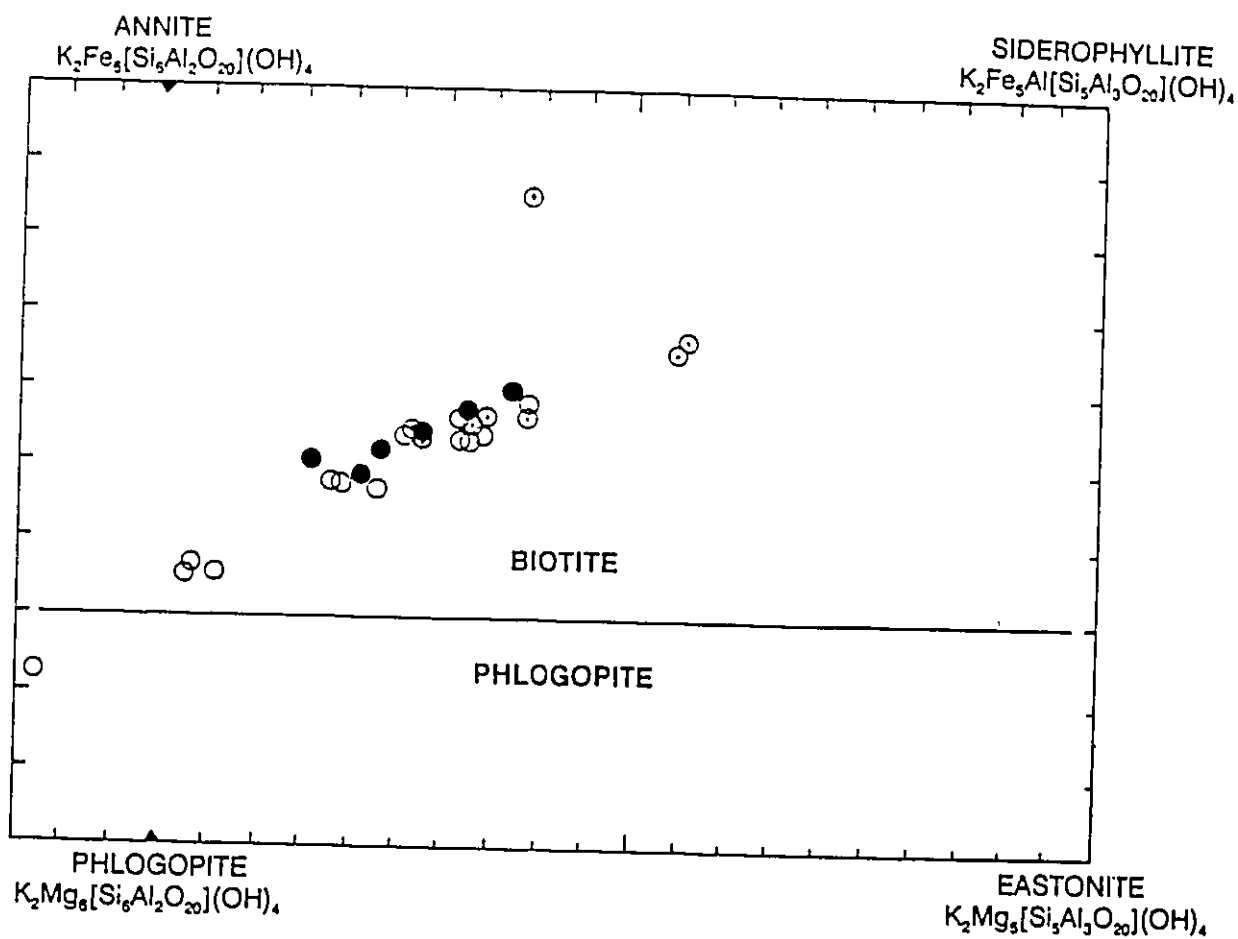


Figure 3 Trioctohedral mica component diagram with phlogopite-biotite fields for zoned pegmatites (●), partially zoned (⊙), and unzoned pegmatites (○) (Table 2).

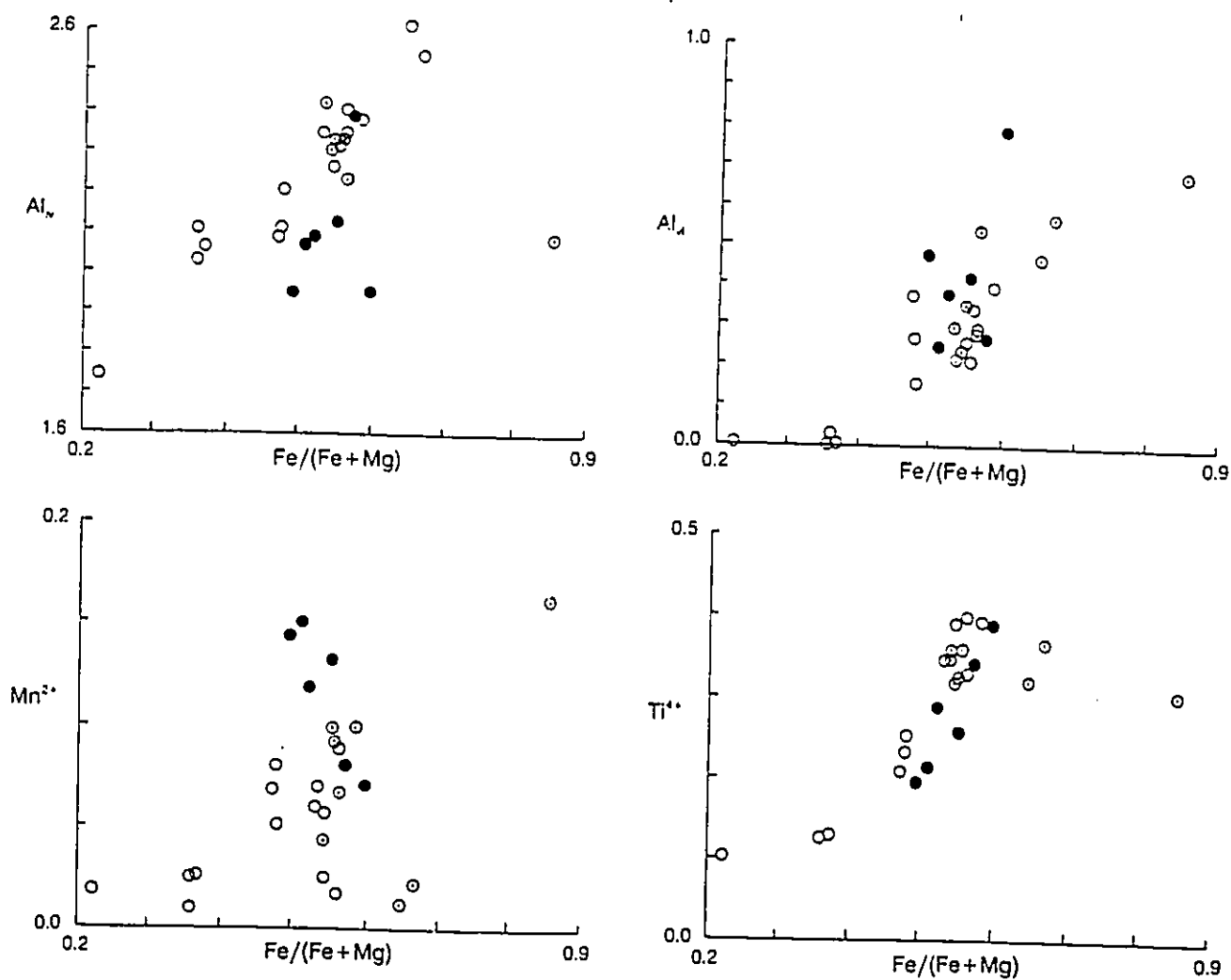


Figure 4 Structural components of biotite, Al_{iv} vs $Fe/(Fe+Mg)$, Al_{vi} vs $Fe/(Fe+Mg)$, Mn^{2+} vs $Fe/(Fe+Mg)$ and Ti^{4+} vs $Fe/(Fe+Mg)$ ratios for zoned pegmatites (●), partially zoned (⊙), and unzoned pegmatites (○) (Table 2).

The tetrahedral positions are filled with Si^{4+} , Al^{3+} and Fe^{3+} in these biotites; however, the octahedral positions range from 5.2 to 5.9 (Table 2) illustrating their partial dioctahedral character. The normal abundance of K and Na in A site is variable from 1.88 to 2.05. The Na^+ is variable from 0 to 0.15 in the A site. There were no systematic variations observed in the behaviour of A-site major cations. Manganese and titanium increase with increasing $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio (Figure 4). A network of very fine-grained rutile intergrowths in some biotites are suspected to be a subsolidus exsolution phenomena or cogenetic intergrowth (Rimsaite 1967). With exception of the zoned pegmatites, there is a weak enrichment of Rb, Zn, and Nb and a corresponding decrease in Ba with increasing $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio, Al, Mn, and Ti content. Niobium contents are consistently high and regular within biotites within a single pegmatite and may be associated with the titanium in titaniferous biotite. It is possible that Y, V, and Cr are related to microinclusions in the biotites. In general, the biotites most closely associated with the host rocks and the margins of the pegmatites have lower $\text{Fe}/(\text{Fe}+\text{Mg})$, Al, Ba and Sr contents (samples 121 and 116 in Table 2 and Figure 5). These contents are similar to biotites from Grenville gneisses (Lentz 1992). The zoned pegmatites (samples 124, 130, 131) have higher average contents of $\text{Fe}/(\text{Fe}+\text{Mg})$, Mn^{2+} , Zn and Rb and lower Ba and Sr in comparison to unzoned and partially-zoned pegmatites (Figures 4 and 5). Rimsaite (1985) reported 4 biotite analyses from the Mont Laurier area with very similar compositions to samples 4B and 4C (Table 2) from the same area.

The rare-earth-element contents of selected biotites were analyzed. Results indicate that the normal abundances are below 10 times chondrite with variations due to the possible presence of microinclusions of allanite and zircon (Table 3; Figure 6). The positive Eu anomaly in sample 124-7 may result from contamination by fluorite because the remaining samples

with a small or no negative Eu anomaly. The low REE, U, and Th abundances reflect the low biotite/melt K_D (0.5 to 0.8) for the REE, U and Th in low temperature, chemically-evolved granitic pegmatite systems (Congdon and Nash 1991).

HYDROXY COMPOSITION

The systematics of the hydroxyl sites (F, Cl, and OH) are potentially useful for qualitatively characterizing the relative HF, HCl, and H₂O activities in the pegmatite. However, the hydroxyl sites are particularly susceptible to secondary chloritization resulting in a decrease in F by exchange with an OH anion. Mica dehydroxylation may occur during initial mica decomposition (Rimsaite 1970). These phenomena are suspected to be responsible for the marked variation in hydroxyl elements within individual pegmatite bodies. However, high X(F) contents are considered primary. The presence of interstitial fluorite in the Blue Sea (122) and Wall Gem (124) pegmatite may affect the X(F) of biotite. The consistently high X(F) in the ACME (samples 121) and the Kenmac-Chibougamau (# 127) pegmatites may be attributed to the lower Fe/(Fe+Mg) ratio of biotite (Fe-F avoidance; Munoz 1984). In order to correct for the effects of Fe-F avoidance, $\log (f_{H_2O}/f_{HF})$ and $\log (f_{H_2O}/f_{HCl})$ ratios were calculated for the micas according to the method of Munoz (1984) at an inferred temperature of 600°C (Figure 7). There is considerable overlap between the f_{H_2O}/f_{HF} ratios for various pegmatite types which, in part, may be related to the ratio calculation at a fixed temperature (600°C). In general, the biotites from partially-zoned and zoned pegmatite bodies have higher f_{H_2O}/f_{HCl} compared to biotites from unzoned pegmatites.

REDOX CONSIDERATIONS

Previous analyses of biotite from Grenville pegmatites have an average Fe^{3+}/Fe^{2+} ratio of 0.44 ± 0.20 ($n = 8$) (Lentz 1992). The biotites in this study have an average Fe^{3+}/Fe^{2+} ratio of 0.29 ± 0.09 ($n = 12$) from granitic pegmatites. Figure 8

Table 3 Rare-earth element composition of selected biotites from Grenville pegmatites.

Sample	4B	116C	120B	122A	124-7
Type	○	○	⊙	⊙	●
La	20.1	1.6	2.0	4.1	25.4
Ce	26.5	5.7	<3	11.3	6.1
Nd	12.7	5.6	<4	13.1	5.7
Sm	2.3	2.4	0.42	5.9	0.42
Eu	0.30	0.60	<0.4	0.63	0.38
Tb	0.10	0.34	<0.2	2.6	<0.2
Dy	<2	2.6	<2	19.6	<2
Yb	0.5	1.8	<0.3	31.4	<0.3
Lu	0.21	0.29	<0.2	5.1	<0.2
Th	12.5	0.43	0.39	27.6	0.59
U	46	2.0	0.71	62	0.33

NOTES: See Figure 3 for pegmatite type. Sample 120B not plotted on figure 6.

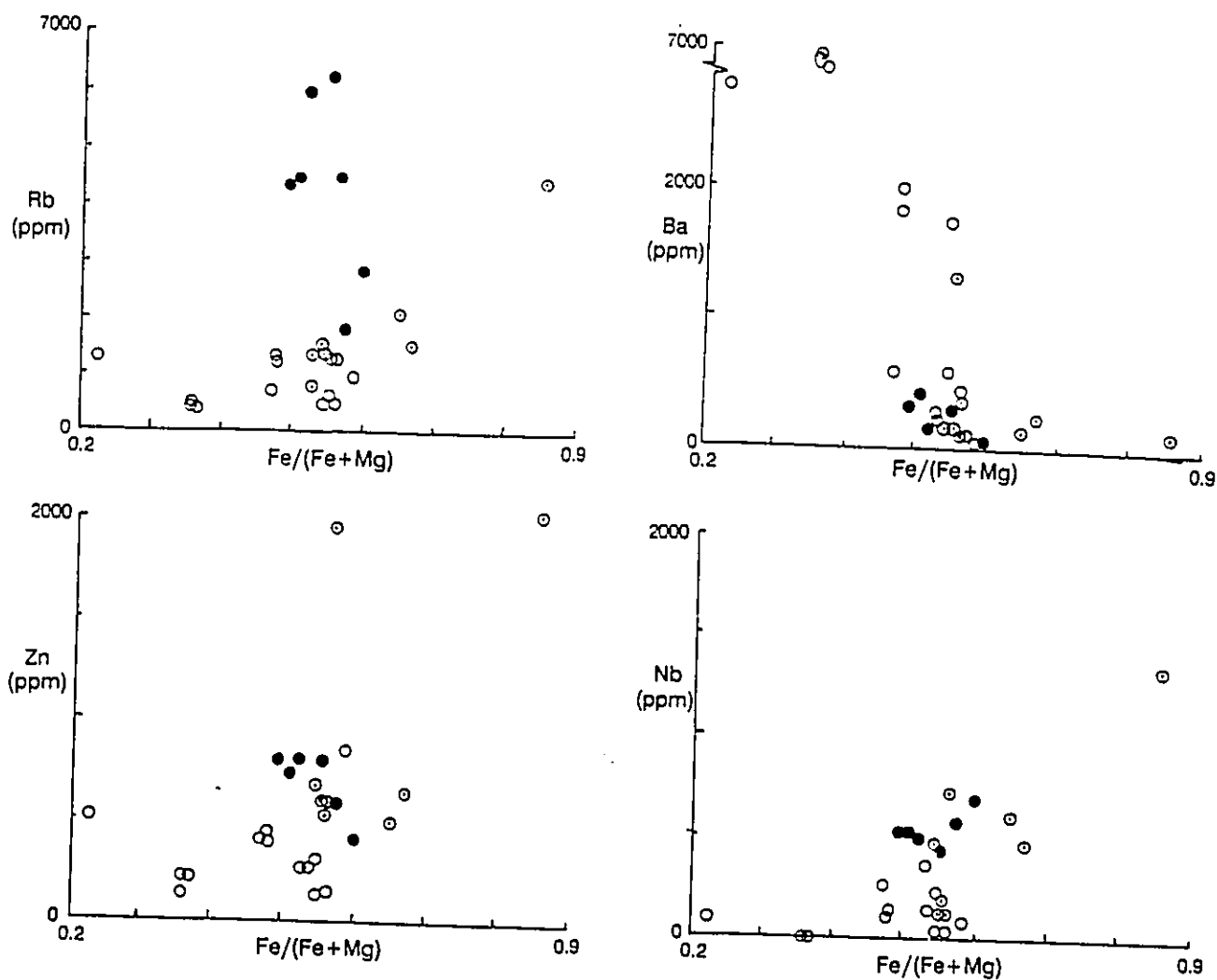


Figure 5 Biotite trace-element compositions versus Fe/(Fe+Mg) ratio (Table 2) for zoned pegmatites (●), partially zoned (⊙), and unzoned pegmatites (○) (Table 2).

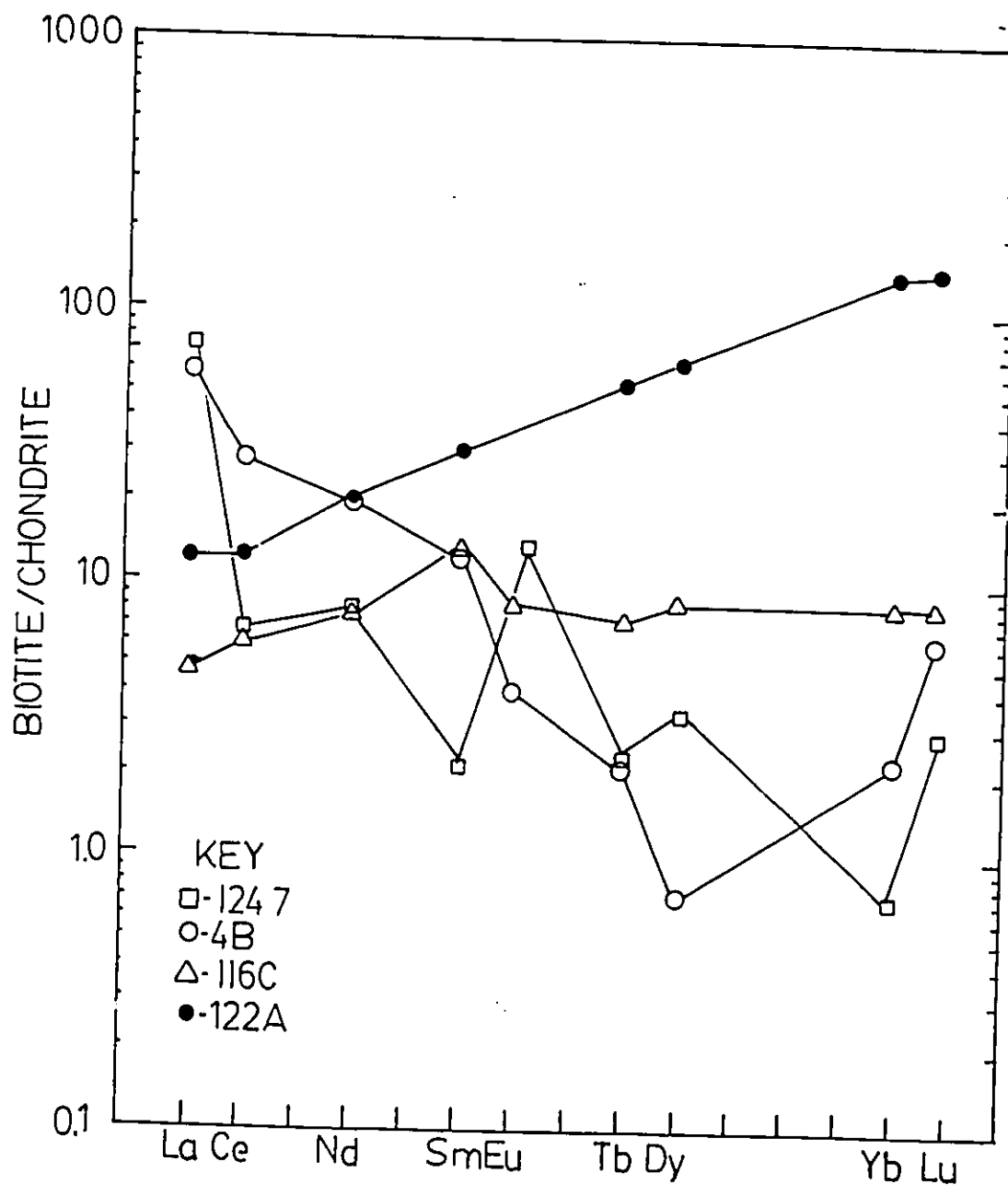


Figure 6 Rare-earth element compositions from four selected biotites from Grenville pegmatites normalized to the average chondrite of Andrews and Ebihara (1982). Sample 120B is not plotted because most of the data is below detection limit. The samples were analysed by INAA at the École Polytechnique and corrected for U and Th interferences according to Kennedy and Fowler (1983).

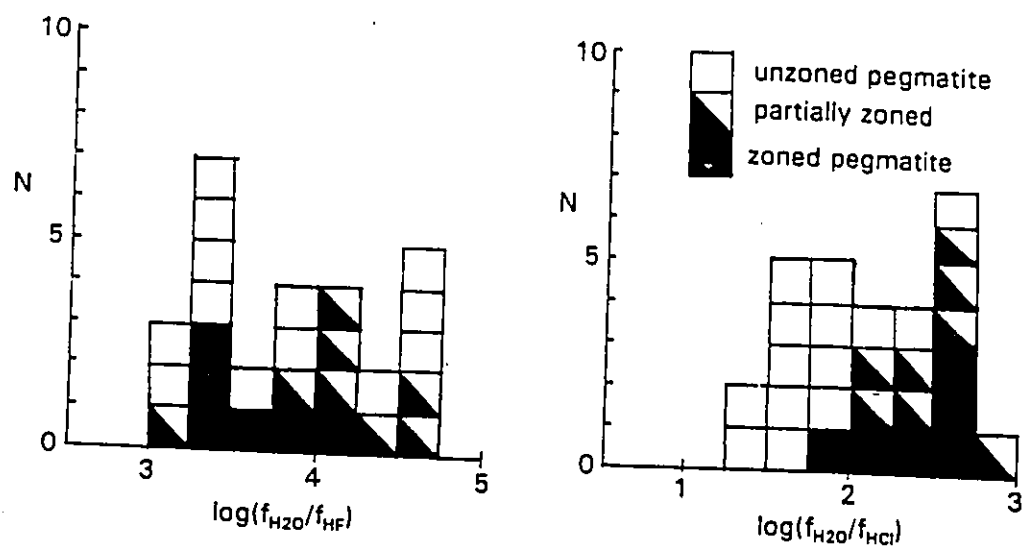


Figure 7 Calculated log(f_{H_2O}/f_{HF}) and log(f_{H_2O}/f_{HCl}) ratios for biotites from unzoned, partially-zoned, and zoned pegmatites according to the method described by Munoz (1984).

illustrates the range in $\text{Fe}^{3+} - \text{Fe}^{2+} - \text{Mg}^{2+}$ contents of biotites in the study. With the exception of biotites from the Goulding-Keene nepheline-bearing pegmatite, the biotite from the zoned Wall Gem beryllium granitic pegmatite has the highest $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. Several of these pegmatites have coarse magnetite present. The lowest ratio is in an unoxidized, white to blue, partially zoned pegmatite (Blue Sea) that crystallized biotite early and is hosted in marble. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio for some biotites indicate a range of oxidation independent of the total Fe content of the biotite but dependant on hybridization (reducing trend) and/or vapor phase separation (oxidizing trend). The presence of magnetite and K-feldspar $\pm$ biotite in many mineralized pegmatites indicates that more oxidizing conditions prevailed. At a temperature of 600°C the transition from magnetite-bearing pegmatite to biotite-bearing pegmatite occurs at approximately $\log f(\text{O}_2) = -15$ to -16 at 70 mole % annite (Figure 9) in biotite (Reaction 1) which is very close to the magnetite-hematite transition at $\log f(\text{O}_2) = -14$ (Wones and Eugster 1965). However,

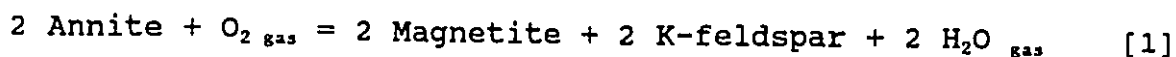


Figure 9 is reproduced at 207 MPa (2070 bars) as was originally presented by Wones and Eugster (1965). This diagram serves only to illustrate the steep oxidation-crystallization trend for these granitic pegmatites and the intersection of the magnetite - hematite boundary at a $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio of biotite between 0.55 and 0.65 coexisting with sanidine and magnetite. The proximity to the hematite-magnetite boundary may explain the intense earthy hematization commonly associated with the magnetite-bearing pegmatites. Higher Al, Mg and F contents of biotite can increase the stability of biotite with respect to the assemblage magnetite - sanidine (Rutherford 1969). These factors may explain the coexistence of 40 mole % annite - magnetite - 80

mole % K-feldspar at the molybdenite-bearing ACME pegmatite.

Dehydroxylation of biotite may be responsible for some oxidation of Fe^{2+} to Fe^{3+} during subsolidus alteration similar to processes described by Rimsaite (1970). This could possibly account for some of the range in $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios observed in the biotites under consideration although caution was used in selecting samples in this study.

DISCUSSION

Exomorphic biotite may be formed up to 10 meters from the pegmatite contact by either pervasive or vein replacement of the host rocks as well as replacement of pre-existing metamorphic biotite. Two processes may be operative; pegmatite-derived hydrothermal iron reacts with feldspar in gneiss resulting in biotitization, and/or hydrothermal potassium reacts with pre-existing ferromagnesian phases, in particular hornblende, to stabilize biotite similar to the mechanism of Brimall *et al.* (1985). Hydrothermal alteration of amphibolites to biotite-rich assemblages is common in the vicinity of granitic pegmatites (Hawthorne and Černý 1982; Shearer *et al.* (1987); Morgan and London 1987). Numerous exomorphic phlogopite-rich skarns are associated with granitic pegmatites with marble and clinopyroxenite host rocks (Lentz 1991a,b, 1992). The biotites that represent replacements after hornblende and pyroxene may inherit some of the chemical characteristics of the phase. Morgan and London (1987) found that the $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio of the exomorphic biotite was similar to that of the hornblende being replaced. Although a hydrothermal mechanism is proposed by Brimhall *et al.* (1985) for the biotitization of hornblende, within the pegmatite re-equilibration and recrystallization in the presence of a hydrous pegmatitic magma could explain the conversion of hornblende to biotite.

The covariance of Fe, Al, Ti, and Mn may be controlled by crystal chemical factors. However, the trace elements are not as tightly constrained by these factors because of their trace

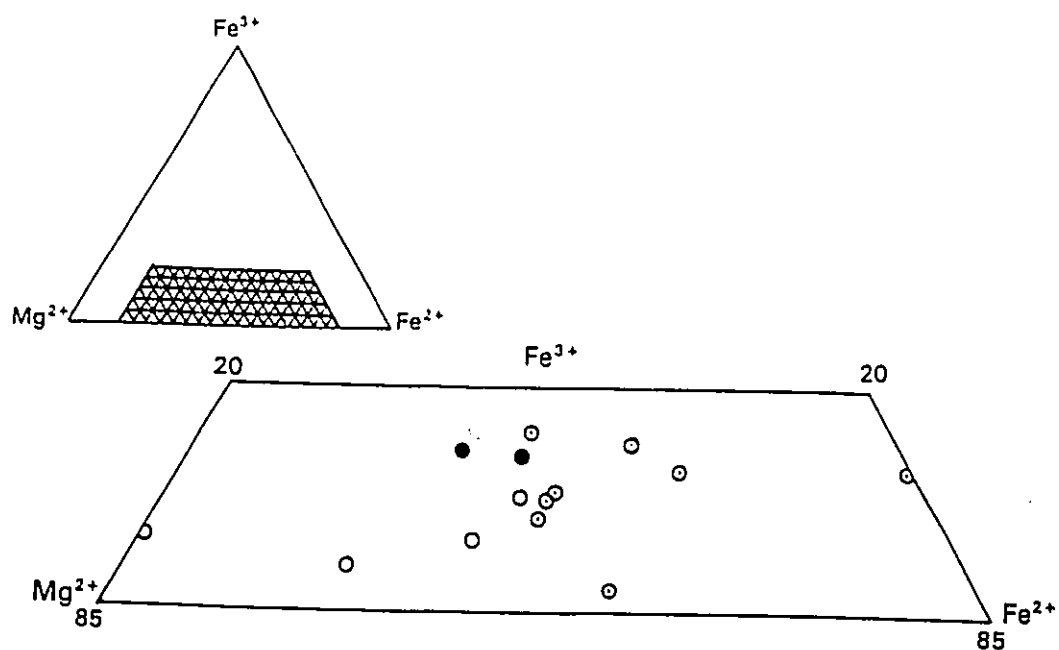


Figure 8 Distribution of Fe^{3+} - Fe^{2+} - Mg^{2+} in biotites for zoned pegmatites (●), partially zoned pegmatites (⊙), and unzoned pegmatites (○) (Table 2).

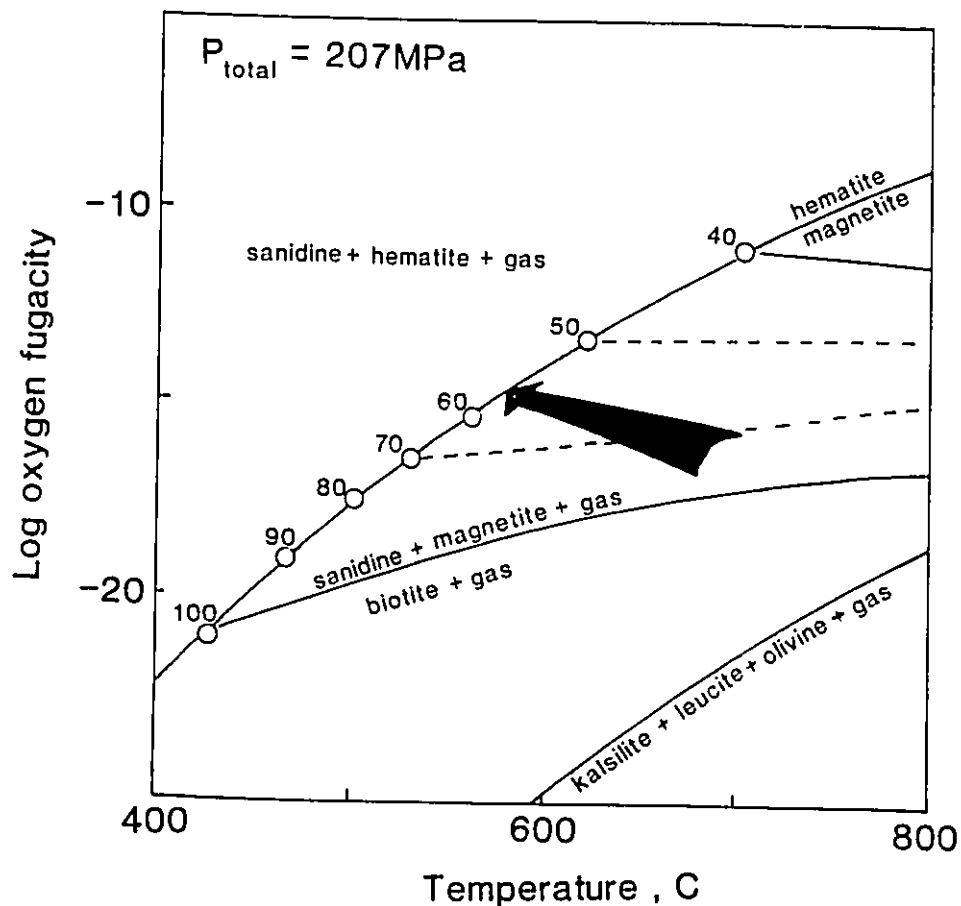


Figure 9 Log $f(\text{O}_2)$ versus temperature (T) mineral stability diagram showing the range of stabilities of the biotite-phlogopite solid solution series and gas coexisting with sanidine-magnetite-gas (modified from Wones and Eugster 1965). The black arrow represents the range of conditions experienced only by granitic pegmatites with coexisting magnetite and K-feldspar. The limitations of the diagram are discussed in the text.

abundances. The covariance of the major elements with the trace elements, particularly Rb, Ba, Zn, and Nb indicates that biotite compositional variation reflects chemical fractionation of the pegmatites. The strong variation of trace elements, compared to major elements within biotites, is particularly useful as an index to chemical fractionation.

These late-tectonic granitic pegmatites probably originated as H₂O-undersaturated fractional partial melts originating from deeper crustal levels, possibly generated by the introduction of fluids into volatile-undersaturated gneissic rocks (Lentz 1991b). These low temperature melts would begin crystallizing during their ascent to higher crustal levels. Melt/crystal distribution coefficients for pegmatite compositions (Congdon and Nash 1991) indicate that these elements are enriched during fractional crystallization. London (1987) has suggested that internal zoning is a result of continued fractionation to lower solidus temperatures. The moderate $f(\text{H}_2\text{O})/f(\text{HF})$ for most of these pegmatites including the zoned variety translate to low HF concentrations in the melt ($< 0.2\%$) thus having negligible effect on the melt solidi and liquidi. However, Černý *et al.* (1985) have suggested that some extreme rare-element enrichments are associated with volatile phase saturation.

Experimental investigations by Naney (1983) on crystallization of ferromagnesian phases in granitic melt suggest that the early stability of biotite is indicative of high $f(\text{H}_2\text{O})$ in the melt. The presence of fluorine would increase biotite stability and possibly lower solidus temperature of the melt. However, the overlap in $f_{\text{H}_2\text{O}}/f_{\text{HF}}$ ratios probably results from several factors; the effect of fluorine on enhancement of biotite stability at high temperature of crystallization, the preferential loss of H₂O compared to HF during vapor phase separation, and the secondary alteration of biotite which readily involves

hydroxyl exchange. The $f_{\text{H}_2\text{O}}/f_{\text{HF}}$ and $f_{\text{H}_2\text{O}}/f_{\text{HCl}}$ ratios are consistent with studies of phlogopite in associated skarns and veins in the Grenville (Lentz 1992) and micas spatially associated with highly fractionated pegmatites (Morgan & London 1987, Shrearer *et al.* 1986; Congdon and Nash 1991). The $f_{\text{H}_2\text{O}}/f_{\text{HF}}$ ratios calculated from the F intercept value (Munoz 1984) are moderate relative to other chemically-evolved granitic rocks. For instance, the $\text{IV}(\text{F})_{\text{bl}}$ for these pegmatites (2.2-0.9) lie between those of the Santa Rita porphyry Cu deposit (2.2-1.9), Pike Peak granite (1.5), and the Henderson Mo deposit (0.7) (Munoz 1984). These $f_{\text{H}_2\text{O}}/f_{\text{2HF}}$ ratios equate to less than 0.1 wt.% HF content of the pegmatite melts which do not support significant depression of pegmatite solidi and liquidus. Alternatively, granitic melt near vapor saturation is generally at lowest temperature and, as a result, is the most fractionated. It is possible that element partitioning into the vapor phase and re-equilibration at structurally high levels within a zoned pegmatite may enhance the chemical fractionation of zoned pegmatites.

The coexistence of biotite ($\text{Fe}/(\text{Fe}+\text{Mg}) = 0.60$), microcline, and magnetite closely associated with intense earthy hematization implies evolution of the pegmatite to oxidized conditions near the hematite-magnetite buffer curve. The presence of yttrian andradite as an endoskarn mineral in some pegmatites including the MacDonald U-, Mo-, and REE-bearing partially zoned pegmatite supports this observation (Lentz 1991b). The coincidence of the oxidation trend and increasing chemical fractionation would imply the role of volatile phase saturation of the pegmatite. It has been shown experimentally that the $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio of biotite is not appreciably affected by water-saturated or undersaturated conditions (Puziewicz and Johannes 1990). However, it is hypothesized that the diffusive loss of hydrogen gas (H_2) during and preceding H_2O saturation is responsible for the increase in

the oxygen fugacity. Candela (1986) has proposed that the susceptibility of a silicate melt to magmatic-oxidation was a function of the H_2O/Fe^{2+} ratio. It has been shown isotopically that diffusive loss of H_2 gas occurs relative to H_2O occurs in volcanic environments (Taylor 1988), although this has not been demonstrated in deeper crustal environments. In this case, the high proportion of H_2O to Fe^{2+} would make these pegmatites particularly susceptible to magmatic-oxidation during volatile phase saturation.

The coincidence of U, Th, Mo, REE, and Nb enrichment within the exocontact metasomatic replacement zones, and possibly the endocontact zones as well, imply the existence of a deuteric hydrothermal phase responsible for element partitioning, complexing, and deposition. Keppler and Wyllie (1990) and Flynn and Burnham (1978) experimentally determined that fluid-melt partition coefficients ($K_D^{fluid/melt}$) for U, Th, and REE were most strongly increased by HF and to a lesser extent by HCl but were low in pure H_2O experiments. Candela and Holland (1984) showed that hydroxide concentration was responsible for partitioning Mo into vapor coexisting with melt. These partition coefficients will increase to positive values as the remaining melt fractionates during crystallization. Analogously, the H_2O/HF ratio will decrease during vapor-saturated crystallization due to the lower solubility of H_2O in the melt, thus increasing the K_D value. In addition, molecular (alkali-(U, Th, REE)-OH,F,Cl) complexes may be effective at these high temperatures and pressures. Slight decreases in temperature and/or pressure accompanied by competing complexes in the endocontact and exocontact environment may have resulted in the saturation of rare-element minerals (Fowler and Doig 1983b).

CONCLUSIONS

Field, mineralogical and chemical analyses of biotite from late-tectonic U-, Th-, Mo-, REE-, and Nb-bearing Grenville

granitic pegmatites are used to examine the petrogenesis of rare-element pegmatites in the southwestern Grenville Province. The most abundant pegmatites were emplaced into middle to upper amphibolite facies rocks dominantly along and adjacent to shear zones.

The mineralogy and composition of the hybrid pegmatites is strongly affected by hybridization with the host rocks and is key to rare-element enrichment in the pegmatite. Endomorphic and exomorphic biotite forms by the mechanical incorporation or hydrothermal replacement of hornblende, Ca pyroxene and/or feldspar. Chemical re-equilibration and growth of the hybrid biotite is responsible for inheriting the chemical characteristics of the pegmatite. In general, there is an increase in the $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio and Al contents in the most fractionated biotites which is coincident with higher Mn, Rb, Nb, and Zn and lower Ba contents. This trend crudely coincides with development of zoning in these pegmatites. There is considerable overlap in the $f_{\text{H}_2\text{O}}/f_{\text{HF}}$ ratio of unzoned to zoned pegmatites. However, the zoned and partially zoned varieties have higher $f_{\text{H}_2\text{O}}/f_{\text{HCl}}$ ratios. For several of the pegmatites, the Fe-enrichment trend in biotite is interrupted by the stability field of sanidine - magnetite - gas and/or sanidine - hematite - gas at an $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio between 0.55 and 0.65 for most of the granitic pegmatites. It is possible that the evolution of H_2 gas at high $\text{H}_2\text{O}/\text{Fe}$ ratios is responsible for the higher Fe^{3+} content of biotites and the appearance of magnetite.

Rare-element partitioning into an evolving hydrothermal fluid is possibly responsible for U, Th, Mo, REE, and Nb enrichment in the endo and exocontact zones of the pegmatites.

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Radioelement distribution in U, Th, Mo, and rare-earth-element pegmatites, skarns, and veins in a portion of the Grenville Province, Ontario and Quebec

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Gamma-ray spectrometer measurements were obtained at and in the vicinity of 104 of the 124 U, Th, Mo, and rare-earth-element (REE) occurrences examined in the Central Metasedimentary Belt of the Grenville Province. Spatial, temporal, mineralogical, and geochemical relationships among granitic pegmatites, phlogopite – scapolite – Ca pyroxene skarns, and fluorite – apatite – calcite veins hosting U, Th, Mo, and REE minerals indicate a common magmatic–hydrothermal origin. Quartz–feldspar gneisses in the Central Metasedimentary Belt ($n = 54$) have low abundances of uranium (1–7 ppm) and thorium (4–27 ppm) suggesting that partial melting, fractional crystallization, and volatile phase separation were responsible for the enrichment of uranium (2–37 ppm) and thorium (5–102 ppm) in uncontaminated granitic pegmatites ($n = 163$) derived during ultrametamorphism. The U/Th ratio is probably inherited from the source quartz–feldspar gneiss protolith and enhanced during fractionation.

Average U and Th concentrations and U/Th ratios at numerous localities show significant positive correlations among pegmatites, skarns, and veins, providing further evidence for a related origin. The interaction of the pegmatite-derived hydrothermal fluids with host rocks produced a spectrum of types and styles of alteration, which include (i) hybridization and (or) endoskarnification along pegmatite margins; (ii) marble- and clinopyroxenite-hosted exoskarn; and (iii) fluorite–apatite–calcite veins. The deposition of U, Th, Mo, and REE from the evolving hydrothermal fluid is responsible for the heterogeneous distribution of U, Th, and REE minerals and molybdenite within pegmatites, skarns, and veins at each locality. Secondary enrichment of uranium in association with hematitized sheared pegmatites and veins may be responsible for the observed large variation in U/Th ratios at some sites.

Des mesures par spectrométrie de rayonnement gamma ont été effectuées sur, et au voisinage, de 104 des 124 indices d'U, de Th, de Mo et de terres rares trouvés dans la zone métasédimentaire centrale de la province de Grenville. Les relations spatiales, géochronologiques, minéralogiques et géochimiques des pegmatites granitiques, des skarns à phlogopite – scapolite – pyroxène calcique et des veines de fluorite–apatite–calcite incorporant des minéraux d'U, de Th, de Mo et de terres rares indiquent pour tous ces matériaux une origine magmatique–hydrothermale commune. Les faibles teneurs en uranium (1–7 ppm) et thorium (4–27 ppm) des gneiss quartzo-feldspathiques dans la zone métasédimentaire centrale ($n = 54$) suggèrent que la fusion partielle, la cristallisation fractionnée et la séparation des substances volatiles sont les facteurs de l'enrichissement en uranium (2–37 ppm) et en thorium (5–102 ppm) des pegmatites granitiques non contaminées ($n = 163$) dérivées durant l'ultramétamorphisme. Le rapport U/Th est probablement hérité du protolite, le gneiss quartzo-feldspathique, et il a été rehaussé durant le fractionnement.

Les teneurs moyennes en U et Th et les rapports U/Th de plusieurs localités qui présentent des corrélations positives parmi les pegmatites, les skarns, et les veines apportent de nouveaux arguments qui appuient une origine commune. L'interaction des fluides hydrothermaux qui ont dérivé des pegmatites avec les roches encaissantes a créé divers types et styles d'altération, incluant (i) une hybridation et (ou) une endoskarnification des bordures des pegmatites; (ii) un exoskarn contenant marbre et clinopyroxénite; et (iii) des veines de fluorite–apatite–calcite. La minéralisation en U, Th, Mo et terres rares à partir de venues de fluide hydrothermal est responsable de la distribution hétérogène des minéraux d'U, de Th, de terres rares et de la molybdénite dans les pegmatites, skarns et veines de chaque site étudié. La grande variation dans les rapports U/Th observée à certains sites résulte probablement de l'enrichissement secondaire en uranium lié aux pegmatites et veines cisailées et hématisées.

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Introduction

Numerous radioactive granitic pegmatites, phlogopite–scapolite – Ca pyroxene skarns, and fluorite–apatite–calcite veins with U, Th, Mo, and rare-earth-element (REE) minerals occur in rocks of the Central Metasedimentary Belt (CMB) of the Grenville Province (Figs. 1, 2). Satterly (1956), Shaw (1958), Shaw *et al.* (1963), Hewitt (1967), and others have studied these rocks and suggested that they are genetically related.

Many of the radioactive deposits have been mined for apatite (late 1880's), molybdenum (late 1910's), phlogopite (early 1920's), muscovite and feldspar (1930's), fluorite (late 1940's) and most recently uranium (late 1950's and late 1970's to early 1980's). Petrogenetic models for the origin of these deposits have evolved as more data have become available on the structure, metamorphism, and geochronology of the Grenville Province.

The present study involves a radiometric examination of the deposits on a local and a regional scale to establish a chemical relationship among the pegmatites, skarns, and veins. Gamma-

ray spectrometric analyses ($n = 856$) were made on outcrops at or in the vicinity of 104 occurrences of U, Th, Mo, and REE pegmatites, skarns, and veins in the southwest part of the Grenville Province (Fig. 3).

Analytical methods

Gamma-ray spectrometric measurements were made on outcrop surfaces with a four-channel, portable gamma-ray spectrometer (McPhar Spectra 44) equipped with a 7.5×7.5 cm, thallium-activated, sodium iodide (NaI) crystal. A total-count scintillometer was used to characterize the radioactivity before measurements were made. The conversion factors for calculating element abundances were obtained by calibrating the spectrometer at the calibration pads located at the Canada Centre for Mineral and Energy Technology facility in Nepean, Ontario. The instrument was recalibrated at least twice daily with a ^{137}Cs source to correct for drift. The counting time was 2 min. The abundances of K, U, and Th were determined from the intensities of ^{40}K (1.46 MeV), ^{214}Bi (1.76 MeV), and ^{208}Tl

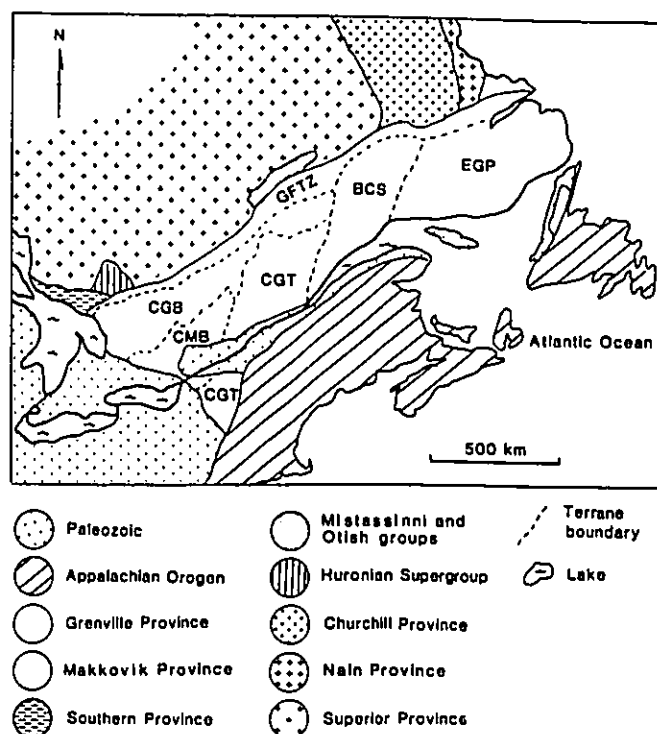


FIG. 1. Sketch map of the Grenville Province and bordering areas. Subdivisions: EGP, Eastern Grenville Province; BCS, Baie Comeau segment; CGB, Central Gneiss Belt; GFTZ, Grenville Front tectonic zone; CGT, Central Granulite Terrane; CMB, Central Metasedimentary Belt (modified from Moore 1986, Fig. 1).

(2.61 MeV), respectively, and U and Th are expressed as equivalent units (eU ppm and eTh ppm). These abundances of K, U, and Th are proportional to the abundances of the daughter elements when in a state of radiometric equilibrium, allowing for background correction (Killeen and Cameron 1977). Precision is estimated to be the square root of the value based on counting statistics and on numerous replicate analyses. Accuracy is estimated to be well within the limits of precision for the method (Ford 1983).

Geological setting

The U-, Th-, Mo-, and REE-bearing deposits occur within the Central Metasedimentary Belt (CMB) of the Grenville Province, with the exception of those along the north shore of the St. Lawrence River. The CMB consists of marbles, gneisses, and metavolcanic rocks that have been intruded by mafic to felsic igneous rocks. Intrusion occurred before, during, and after the Grenville orogeny, which culminated in the Ottawa orogeny ca. 1090 Ma (Easton 1986). The CMB forms the southwestern portion of the Grenville Province and is bounded to the north by the Central Gneiss Belt (CGB) and to the southeast by the Central Granulite Terrane (CGT) (Figs. 1, 2). The boundary between the CMB and the underlying CGB is the Central Metasedimentary Belt boundary zone, which strikes northeast-southwest and dips southeast at a low angle (Fig. 2) (Davidson 1986). The rocks in the Bancroft Terrane (Fig. 2) within the CMB are middle to upper amphibolite facies (approximately 650°C), whereas those along the northwestern and southeastern margins of the belt are upper amphibolite to granulite facies. Thermal denudation studies using the $^{40}\text{Ar}/^{39}\text{Ar}$ method (Berger and York 1981) and numerous K-Ar age determina-

TABLE 1. Uranium deposits in the Grenville Province (after Satterly 1956)

1. Deposits in granite pegmatite
A. Zoned pegmatite
B. Unzoned pegmatite
1. Red pegmatite
2. White pegmatite
2. Metasomatic skarn deposits
A. Marble-hosted skarns
1. Dolomitic marbles
2. Calcitic marbles
B. Metamorphic pyroxenite-hosted skarns
3. Hydrothermal fluorite-apatite-calcite veins
A. Gneiss-hosted veins
B. Amphibolite-hosted veins
C. Marble-hosted veins
D. Metamorphic pyroxenite-hosted veins

tions suggest that the Bancroft Terrane remained above 500°C between 1100 and 980 Ma. The granitic pegmatites formed during this period (ca. 1020–1050 Ma; Rimsaite 1982; Easton 1986; Heaman *et al.* 1987) when host-rock temperatures were approximately 550°C. They are associated with skarns and veins that are mineralogically similar to regional metamorphic assemblages.

Field and petrological considerations

Satterly (1956) subdivided the uranium deposits in the Bancroft area into three main types: pegmatites, skarns, and veins (Table 1).

Radioactive granitic pegmatites

Pegmatite dikes occur throughout the CMB and cut all rock types except late diabase dikes. Radioactive dikes are relatively large (from several metres up to 100 m across) and consist of quartz, K-feldspar, oligoclase, and minor biotite; small amounts of Ca pyroxene, hornblende, magnetite, allanite, pyrite, and other minerals are present locally. The pegmatites include zoned and unzoned granite pegmatites of both mineralogically simple and complex types (Masson and Gordon 1981; Storey and Vos 1981). The simple types consist dominantly of quartz, K-feldspar, and plagioclase, whereas the complex varieties have interacted with the host rocks more extensively and contain variable amounts of biotite, Ca pyroxene, hornblende, magnetite, pyrite, and numerous rare minerals. The complex pegmatites also commonly host U, Th, Mo, and REE mineralization.

Hematization (oxidation) of some of the pegmatites has redistributed radioactive components after the magmatic stage. Pegmatites that have been extensively hematized have red feldspars. This contrasts with white pegmatites commonly occurring in marble sequences (Tremblay 1974). Charbonneau and Jonasson (1976) and Fowler and Doig (1983a, 1983b) found that white pegmatites (high U/Th) were marble hosted, whereas red pegmatites (low U/Th) were amphibolite and gneiss hosted.

Several large uraniferous granitic pegmatites (Faraday, Bicroft, Greyhawk, Dyno, and Halo) were brought into production in the mid- to late 1950's and closed shortly thereafter, having produced a total of 5500 t U at an average grade of 1600 ppm U and 200–2000 ppm Th. The Faraday mine was brought back into production as the Madawaska mine in the late 1970's and closed again in 1982. This deposit averages 1900 ppm U and contains a few million tonnes of estimated ore reserves

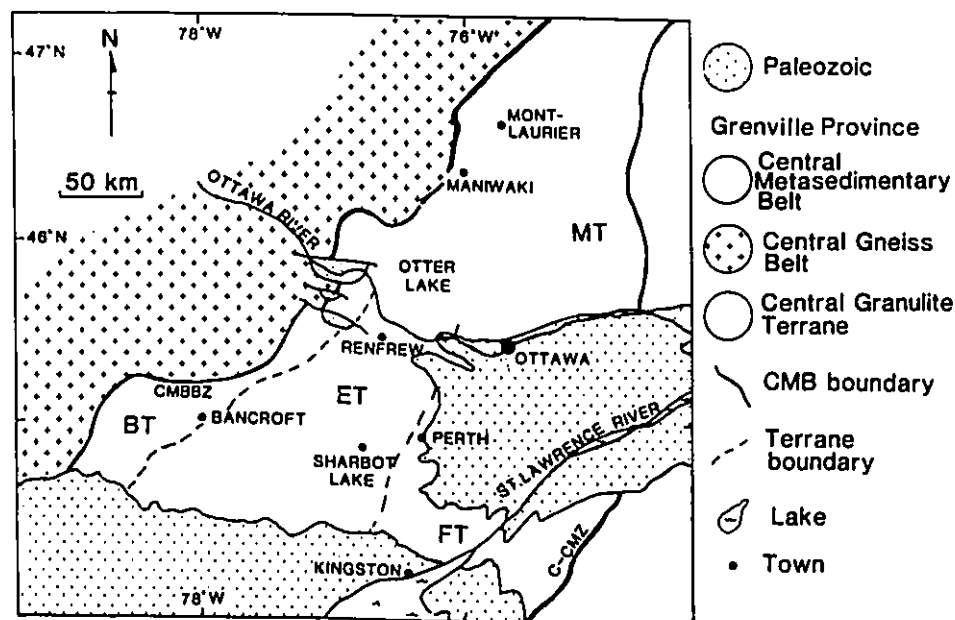


FIG. 2. Distribution of terranes in the southwestern Grenville Province (modified from Davidson 1986, Fig. 1). CMBBZ, Central Metasedimentary Belt boundary zone; C-CMZ, Colton-Carhage mylonite zone; BT, Bancroft Terrane; FT, Frontenac Terrane; ET, Elzevier Terrane; MT, Mont-Laurier Terrane.

TABLE 2. Uranium and thorium concentrations (ppm) in Grenville pegmatites

	n	U	Th	U/Th	Method ^a
Mont-Laurier area					
Charbonneau (1973)	1	77	50	2.4	R
Tremblay (1974)	30	862 (1 234)	1 541 (2 507)	3.4 (4.3)	C
Rimsaite (1982)	6	882 (904)	1 135 (1 230)	2.0 (2.4)	C
Baie-Johan-Betz					
Rimsaite (1981 ^b)	11	1 270 (1 437)	331 (289)	4.5 (2.8)	C
Rimsaite (1982)	5	1 807 (1 968)	489 (327)	3.5 (3.0)	C
Western Quebec					
Shaw (1958)	6	3 730 (3 152)	6 540 (4 861)	1.1 (1.5)	C
Renfrew					
Masson and Gordon (1981)	14	1 324 (3 942)	905 (2 069)	0.9 (0.8)	C
Renfrew-Amprior area					
Masson and Gordon (1981)	7	611 (1 169)	3 027 (4 907)	0.1 (0.1)	C
Dacre area					
Masson and Gordon (1981)	8	983 (1 392)	12 057 (11 233)		C
Themistocleous (1981 ^a)	22	1 203 (1 707)	47 920 (49 192)		C
Themistocleous (1981 ^b)	65	43 (120)	1 510 (6 417)		C
Sharbot Lake					
Ford (1982)	183	25	26	1.6	R
Bancroft					
Satterly (1957)	2	7 000	4 600	1.5	C
Masson and Gordon (1981)	14	651 (816)	2 671 (3 124)	0.5 (0.7)	C
Rimsaite (1982)	6	8 967 (13 414)	4 282 (4 134)	2.3 (3.0)	C
Rimsaite (1983 ^b)	9	3 125 (3 461)	1 596 (2 795)	3.1 (4.5)	C

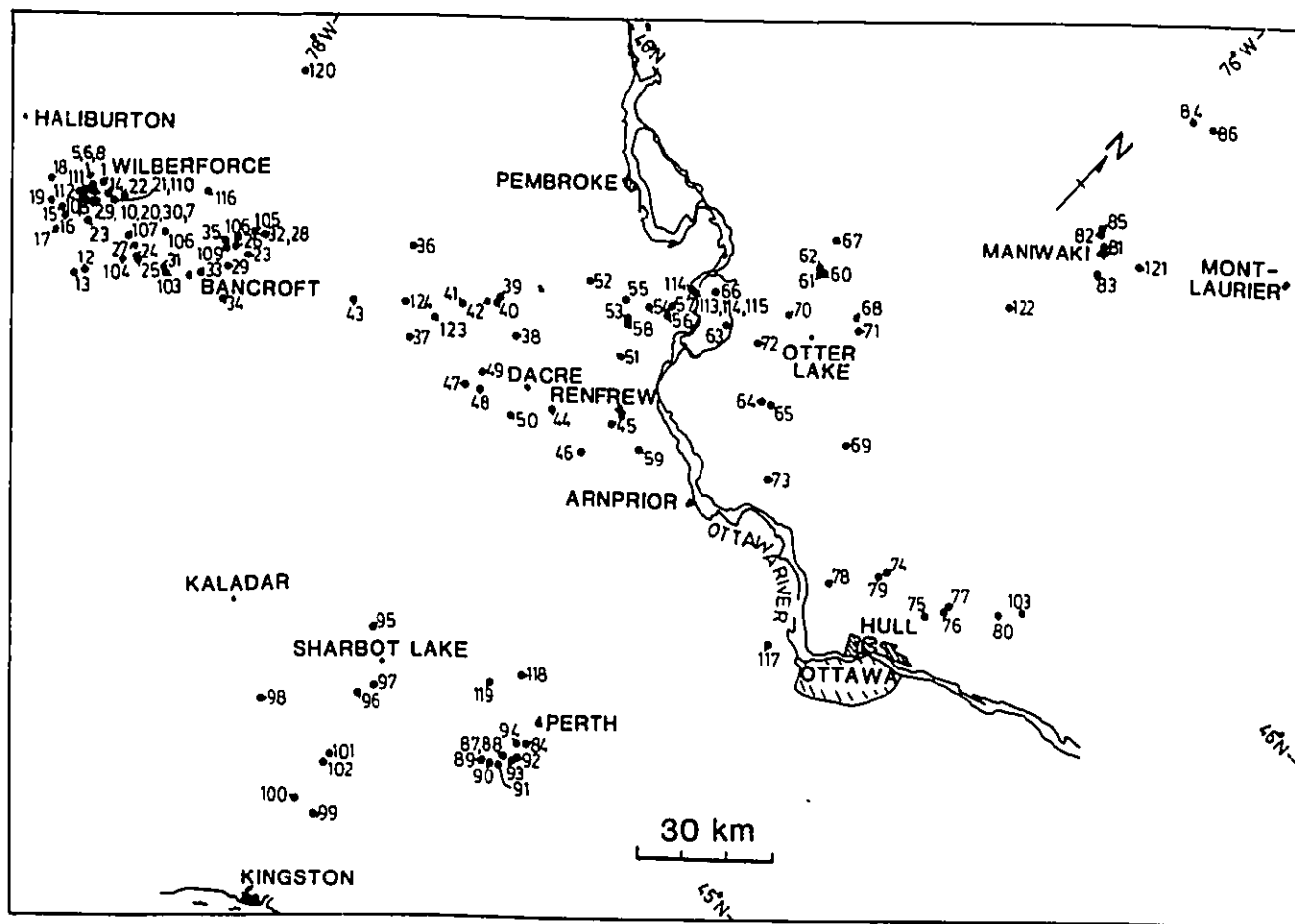
NOTES: U/Th is the average of individual U/Th ratios. Values in parentheses represent one standard deviation about the mean. n, number of measurements.

^aR, radiometric; C, chemical.

(Robertson 1981). Table 2 summarizes published analytical data on the U and Th concentrations and U/Th ratios for pegmatites from several areas in the Grenville Province.

In situ gamma-ray spectrometric measurements were made primarily on late-tectonic mineralized pegmatites. "Contamin-

ated" pegmatites (hybridized-skarnified by interaction with host rocks) were subdivided on the basis of host-rock type in an attempt to distinguish radioelement differences among them. Results presented in Table 3 indicate that all pegmatites are substantially more radioactive than their host rocks and tend to



1. Harcourt Mo skarn
2. Halo U-Mo pegmatite/skarn
3. Field trip
4. Mont-Laurier field trip
5. Desmond Mo-U skarn
6. Wilberforce Mo skarn
7. Joiner Mo-U skarn/vein
8. American Molybdenites Mo skarn
9. Cardiff South U skarn/vein
10. Cardiff West U occurrence
11. Tory Hill field trip
12. Dyno Turn road cut pegmatite
13. Elmridge Mines skarn
14. Richardson (Fission) U vein
15. Saranac zircon pegmatite/skarn
16. Saranac East pegmatite
17. Rare-Earth U pegmatite
18. G. Padwell Mo skarn
19. Millar's apatite skarn/vein
20. Cardiff A zone skarn/vein
21. Tripp & Montgomery U vein
22. Clark fluorite pegmatite/skarn
23. Kemp Th, U skarn
24. Howard-Kerr U pegmatite/skarn
25. Lockwood U skarn
26. McDonald feldspar pegmatite
27. Silver Crater skarn/vein
28. Quirk U pegmatite/skarn
29. South State U skarn
30. Cardiff North Zone skarn vein
31. Madawaska U pegmatite
32. Normingo U skarn
33. Eagles Nest vein
34. Urban Quebec U pegmatite/skarn
35. Hybla skarn
36. Rockingham U pegmatite/skarn
37. Jamieson Mo skarn/vein
38. Grattan Twp. U pegmatite/skarn
39. Meany apatite vein
40. Smart apatite skarn/vein
41. Opeongo U pegmatite/skarn
42. Turner's Island apatite vein
43. Liedke Mo skarn/vein
44. Dugeon U pegmatite
45. Belanger's Corner skarn
46. Mountain Chute U pegmatite/skarn
47. Spain Mo-U pegmatite/skarn
48. Sunset Mo skarn
49. H.A. Legris U pegmatite
50. Hunt Mo pegmatite/skarn
51. Field trip
52. Cole Mo skarn
53. Woermke No. 4 vein
54. Ross apatite vein
55. Rose Mo pegmatite
56. Elliot's apatite vein
57. Vaughan U pegmatite/vein
58. Cobden apatite vein
59. Dempsey's U vein
60. Matte apatite-U vein
61. Camp U pegmatite/skarn/vein
62. Thorianite skarn
63. Dunraven U pegmatite
64. Kirkham Mo pegmatite/skarn/vein
65. Quebec Metals U pegmatite/skarn
66. Calumet U skarn/vein
67. Squaw Lake Mo skarn/vein
68. Brady Mo skarn
69. Bain Mo-U pegmatite/skarn/vein
70. Litchfield Mo skarn/vein
71. Clapham Mo skarn
72. Lawless Lake U skarn/vein
73. Moss Mo pegmatite
74. Dacey apatite skarn/vein
75. Phosphate Queen apatite skarn/vein
76. Jackson-Rae apatite vein
77. Blackburn apatite vein
78. Chaput-Payne Mo skarn/vein
79. Vavesour apatite skarn/vein
80. Emerald apatite skarn/vein
81. McSherry U pegmatite
82. Cilgen U skarn
83. Opicawa U pegmatite
84. Highway skarn
85. Maniwaki Mo skarn/vein
86. Duvex U pegmatite
87. Otty Lake apatite vein
88. Old Anthony mica skarn
89. Star Hill apatite skarn/vein
90. Mica skarn
91. Silver Queen apatite skarn/vein
92. Perthite pegmatite
93. Roger's apatite skarn/vein
94. McLaren apatite skarn/vein
95. Avery Mo skarn
96. Eagle Lake apatite skarn/vein
97. St. George apatite vein
98. Chilsom Mo skarn
99. Lacey mica skarn
100. Freeborn mica skarn
101. Kingston-Beresford mica skarn
102. Richardson feldspar pegmatite
103. Greyhawk U pegmatite
104. Bicraft U pegmatite
105. Genesee No. 2 pegmatite
106. Baptiste Lake skarn
107. Croft U pegmatite
108. Armac Mo pegmatite/skarn/vein
109. McCormack feldspar pegmatite
110. Road outcrop
111. Cockle Lake U skarn
112. Essonville-Wilberforce U skarn
113. Barrage Rocher-Fendu U skarn/vein
114. Sullivan Island carbonatite
115. Calumat Contact U skarn/vein
116. Maynooth pegmatite
117. South March feldspar pegmatite
118. Perth feldspar pegmatite
119. Kirkham Mo-U pegmatite
120. Comet quartz pegmatite
121. Acme Mo pegmatite
122. Blue Sea feldspar pegmatite
123. Road outcrop
124. Wall Gem Be pegmatite

FIG. 3. Pegmatites, skarns, and veins examined within the southwestern Grenville Province. Numbers denoted as field trips are not located on map.

TABLE 3. Mean gamma-ray spectrometric analyses from the southwest Grenville Province

Rock type	n	%K	eU (ppm)	eTh (ppm)
Clinopyroxenite	17	1.0 ^{+1.5} _{-0.6}	2 ⁺³ ₋₁	5 ⁺⁶ ₋₃
Gneiss	54	2.8 ^{+2.1} _{-1.2}	3 ⁺⁴ ₋₂	10 ⁺¹⁷ ₋₆
Amphibolite	25	1.6 ^{+1.9} _{-0.9}	3 ⁺² ₋₁	6 ⁺⁷ ₋₃
Marbles	46	0.7 ^{+0.8} _{-0.4}	2 ⁺³ ₋₁	5 ⁺⁷ ₋₃
Gneiss-hosted veins	106	3.0 ^{+2.9} _{-1.7}	15 ⁺⁶⁸ ₋₁₂	52 ⁺²⁰⁵ ₋₄₁
Clinopyroxenite-hosted veins	65	1.7 ^{+3.4} _{-1.2}	11 ⁺⁶⁰ ₋₉	32 ⁺¹³⁴ ₋₂₆
Marble-hosted veins	21	2.7 ^{+10.5} _{-2.2}	37 ⁺³⁶¹ ₋₃₄	81 ⁺⁸⁵² ₋₇₂
Marble-hosted skarn	59	2.6 ^{+6.9} _{-1.9}	47 ⁺³³³ ₋₄₂	95 ⁺⁵⁵⁰ ₋₈₁
Amphibolite-hosted skarn	4	1.3 ^{+1.1} _{-0.5}	12 ⁺⁴² ₋₉	32 ⁺¹²³ ₋₂₆
Clinopyroxenite-hosted skarn	54	2.2 ^{+2.7} _{-1.2}	5 ⁺²⁰ ₋₄	17 ⁺⁴⁶ ₋₁₃
Hybrid pegmatite (gneiss)	26	3.6 ^{+4.4} _{-1.4}	23 ⁺¹⁰⁶ ₋₁₉	117 ⁺⁴³³ ₋₉₂
Hybrid pegmatite (marble)	57	3.8 ^{+3.4} _{-1.8}	14 ⁺⁴² ₋₁₁	45 ⁺²⁰⁹ ₋₃₅
Hybrid pegmatite (clinopyroxenite)	42	4.3 ^{+2.9} _{-1.8}	5 ⁺¹⁵ ₋₃	32 ⁺¹¹⁹ ₋₂₅
Hybrid pegmatite (amphibolite)	96	4.2 ^{+3.2} _{-2.3}	19 ⁺⁸⁸ ₋₁₆	52 ⁺²⁵⁰ ₋₄₃
Pegmatite	163	3.8 ^{+2.8} _{-1.6}	8 ⁺²⁹ ₋₆	22 ⁺⁸⁰ ₋₁₇

NOTES: Values in the table are means and standard deviations (1 σ) from the log distribution. n, number of measurements

have higher U/Th ratios. Average U/Th ratios of hybrid pegmatites differ according to the host rock: marble (highest); amphibolite and clinopyroxenite (intermediate); quartz-feldspar (lowest). Total uranium tends to be highest in pegmatites hosted by gneiss and amphibolite. The unhybridized pegmatites have U/Th ratios similar to those of the contaminated pegmatites but are lower in uranium and thorium.

Radioactive skarns

Radioactive skarns are hosted in marbles, clinopyroxenite, and amphibolite. They occur as tabular, lens-shaped, and irregular bodies in marginal zones of granite pegmatites, veins, and replacement zones (mantos). The skarns consist dominantly of Ca pyroxene, phlogopite, and calcite and may contain pyrite and (or) pyrrhotite. They differ from the marbles in that they are radioactive (Table 3), generally lack fabric because of recrystallization, and are coarse grained. Silicated marbles evidently are metasomatically altered dolomitic to calcitic marbles with interstitial calcite (grey, yellow, orange, or pink), diopside, tremolite, phlogopite, and sulfides.

Clinopyroxenite-hosted skarns are replacement zones (veins or mantos) and consist dominantly of coarse-grained Ca pyroxene, feldspar (plagioclase or K-feldspar), scapolite, phlogopite, and minor calcite. The coarse grain size and the presence of apatite, fluorite, pyrite, pyrrhotite, molybdenite, and (or) radioactive minerals distinguish these skarns from "metamorphic pyroxenites" (clinopyroxenites).

Satterly (1956) described numerous occurrences of silicated marble (Bicroft Mine, South State deposit), and Shaw (1958) described several similar deposits in the Quebec townships of Grand Calumet (Calumet uranium mines) and Huddersfield (Yates). The Calumet uranium mines deposit had an estimated 550 000 t of ore with an average grade of 470 ppm U and 1300 ppm Th (Shaw 1958). The Halo U pegmatite-skarn near Wilberforce, Ontario, and the Bain and Kirkham Mo pegmatite-skarn southwest of Otter Lake, Quebec, are examples of Mo-bearing radioactive "metamorphic pyroxenite"-hosted skarns.

Radioactive fluorite-apatite-calcite veins

The radioactive fluorite-apatite-calcite veins are up to a few hundred metres long and a few metres wide. They occur as

discordant to concordant veins that pinch and swell along dip and strike. The veins formed in shear zones and along contacts between lithologic units. Heterogeneously distributed fine- to coarse-grained Ca pyroxene, amphibole, biotite, feldspar, titanite, and radioactive minerals commonly occur along the margins of the veins and decrease in size into the wall rock. The alteration assemblages are partially determined by wall-rock composition. Marble-hosted veins resemble silicated marbles but seem to have been formed by discordant fracture filling rather than replacement (e.g., Cardiff uranium-fluorite occurrence). "Metamorphic pyroxenite"-hosted veins (clinopyroxenite) are similar to skarns but have less feldspar (plagioclase - K-feldspar) and scapolite. Abundant fine- to coarse-grained Ca pyroxene, tremolite, and phlogopite form selvages of the veins with traces of molybdenite, pyrite, and pyrrhotite. Gneiss-hosted fluorite-apatite-calcite veins occur throughout the CMB and, in many cases, are associated with marginal coarse-grained K-feldspar, Ca pyroxene, amphibole, biotite, pyrite, and (or) magnetite (e.g., Richardson U-fluorite deposit). Hornblende and biotite are the dominant components of vein selvages in amphibolites: these selvages also contain minor scapolite, plagioclase, or K-feldspar. In general, quartz-feldspar gneiss-hosted veins have less ferromagnesian minerals than do veins in other rock types (i.e., Matte zone, Yates deposit; Shaw 1958; Lafontaine 1980). The veins have similar average radioelement abundances irrespective of the host rock in which they were formed (Table 3). The average radioelement abundance of the veins is within the range of the skarns and pegmatites (Table 3).

Radioactive minerals

The predominant radioactive minerals are allanite, cyrtolite (REE, U, Th zircon), titanite, uraninite, uranothorite, thorite, pyrochlore minerals (pyrochlore, betafite, microlite), fergusonite, formantite, euxenite, and polycrase (Satterly 1956; Shaw 1958; Hewitt 1967). Abundances of uranium and thorium in selected radioactive minerals in Grenville radioactive deposits are summarized in Table 4. Lafontaine (1980) found high REE oxide abundances in uraninites, thorianites, and allanites from the Yates area. Robinson and Abbey (1957) noted that urano-

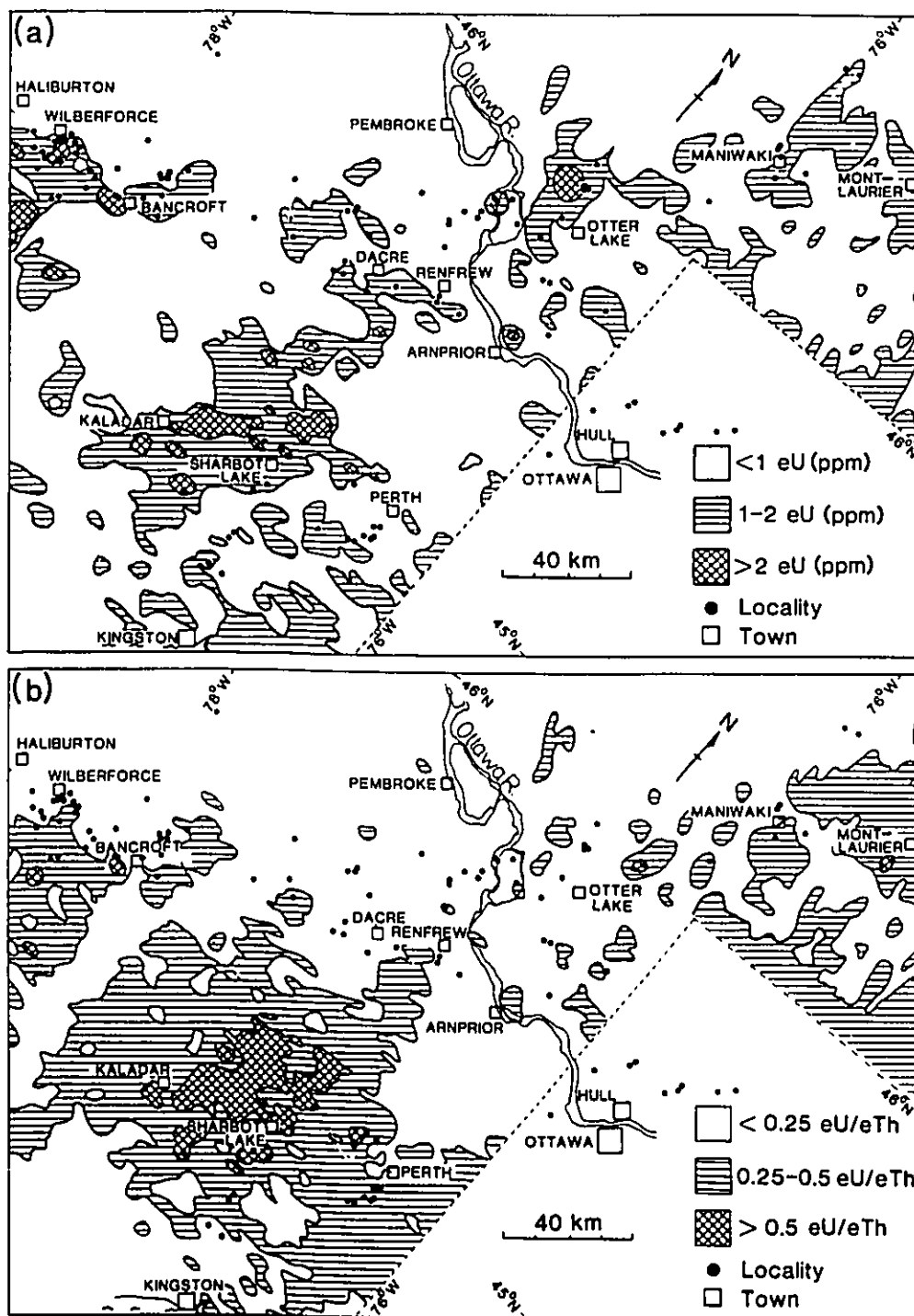


FIG. 4. Regional airborne gamma-ray spectrometry compilation at 5 km line spacing. (a) Equivalent uranium (eU ppm) and (b) U/Th contours of the southwestern Grenville Province. The contours represent averages of several square kilometres of ground concentrations. Sources of information: Geological Survey of Canada (1976, 1977, 1978a–1978c, 1983).

thorites from pegmatites are lower in rare earths than those from skarns because of the presence of REE-rich minerals in the skarns. Hurley and Fairbairn (1957), Tremblay (1974), Rimsaite (1980), and Habib (1982) found high U (0.3–0.5 wt.%) and Th (0.1–0.2 wt.%) in zircons. Uranium concentrations in monazite from three Cardiff pegmatites average 2840 ppm ($1\sigma = 290$ ppm) (Habib 1982). Allanites have low uranium (average = 1236 ppm; $1\sigma = 456$ ppm) (Habib 1982) and high but variable ThO_2 (Table 4). Titanites in Cardiff pegmatites have higher uranium concentrations (eU = 680 ppm; $1\sigma = 220$ ppm) than

those in the host rocks (eU = 260 ppm; $1\sigma = 60$ ppm). The abundance and stability of these minor phases are responsible for the observed radioelement distribution in these deposits.

Gamma-ray spectrometry

Airborne U and U/Th distribution

Airborne gamma-ray spectrometry data represent average surface concentrations over a large area (several square kilometres at a 5 km line spacing). Charbonneau *et al.* (1976) found that airborne concentrations are proportional to, but less than,

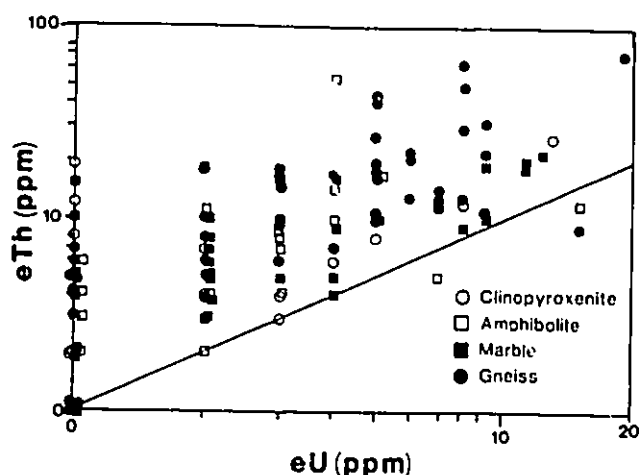


FIG. 5. Concentrations of equivalent uranium (eU) and equivalent thorium (eTh) in the four dominant host-rock types.

rock exposure concentrations, mainly because of the effect of overburden. Airborne gamma-ray spectrometry data from the Grenville Province (Fig. 4) clearly show the general distribution of uranium occurrences. Most of the known occurrences are inside the >1 ppm eU ppm contour interval (Fig. 4a); the largest ones are inside the >2 ppm eU contour interval.

It has been shown that airborne uranium and thorium anomalies coincide with radioactive pegmatites throughout the southern Grenville Province (Charbonneau 1973; Ford and Charbonneau 1979; Ford 1982, 1983). The Sharbot Lake area has high uranium and low thorium, the Otter Lake area has high thorium and moderate uranium, and the Bancroft area has high uranium and high thorium, indicating regional variations in uranium and thorium abundances.

In situ gamma-ray spectrometry

A total of 856 gamma-ray spectrometric ground measurements were made during the present study. The results are grouped under "host rocks," "pegmatites," "skarns," and "veins" in Table 3 and are plotted in Figs. 5-8.

Host rocks

U and Th values for the four main types of host rocks (gneisses, amphibolites, clinopyroxenites, and marbles) are plotted in Figure 5. Gneisses are rich in quartz-feldspar and have variable mafic content; amphibolites contain abundant amphibole, with lesser amounts of biotite, Ca pyroxene, and plagioclase; clinopyroxenites have greater than 50% (by volume) Mg-rich Ca pyroxene and lesser plagioclase, scapolite, and phlogopite.

All host rocks have low U and Th abundances. Averages for the various groups, expressed as eU and eTh, are as follows: gneisses, 3 and 10; amphibolite, 3 and 6; clinopyroxenites, 2 and 5; and marbles, 2 and 5 (Table 3). These data indicate that all host rocks are similar in uranium and thorium, with the exception of the gneisses, which have substantially higher thorium.

The results compare well with those of Charbonneau (1973; host rocks in the Mont Laurier area: 2 ppm eU and 4 ppm eTh), Rimsaite (1981a; gneisses in the Bancroft area: 4 ppm U), and Ford (1982; host rocks in the Sharbot Lake area: 3-5 ppm eU and 3-11 ppm eTh).

Radioelement relationship among pegmatites, skarns, and veins

The *in situ* radioelement data for pegmatites, skarns, and

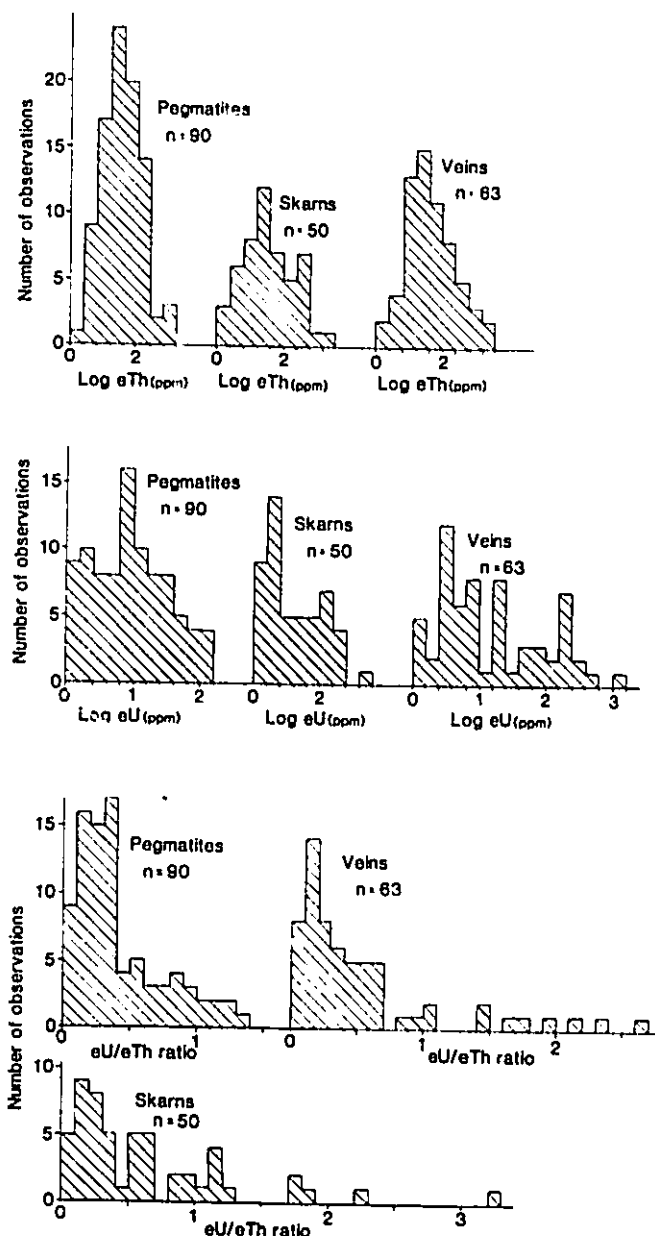


FIG. 6. Frequency distribution of log eTh, log eU, and eU/eTh in pegmatites, skarns, and veins. Plotted data are averages of several values from each locality. Of the 124 localities visited, 104 were examined for radioelement contents; 90 have pegmatites, 50 have skarns, and 63 have veins.

veins have log-normal distributions (Fig. 6) and show that U and Th concentrations and U/Th ratios are similar in the three types of deposits.

To further illustrate the similarity among the three types of deposits, average values of log eU, log eTh, and eU/eTh were computed for pegmatites, skarns, and veins from each of the 104 localities. Of the 104 localities, 45 have both pegmatites and skarns, 51 have pegmatites and veins, and 32 have skarns and veins. Figure 7 displays three plots (pegmatites vs. skarns, pegmatites vs. veins, and skarns vs. veins) for each set of data. The correlation coefficients for the data in Fig. 7 indicate that there is a statistically significant geochemical relationship at a deposit scale. Confidence levels for five of the nine graphs exceed 90%; for four of them the level is $>95\%$.

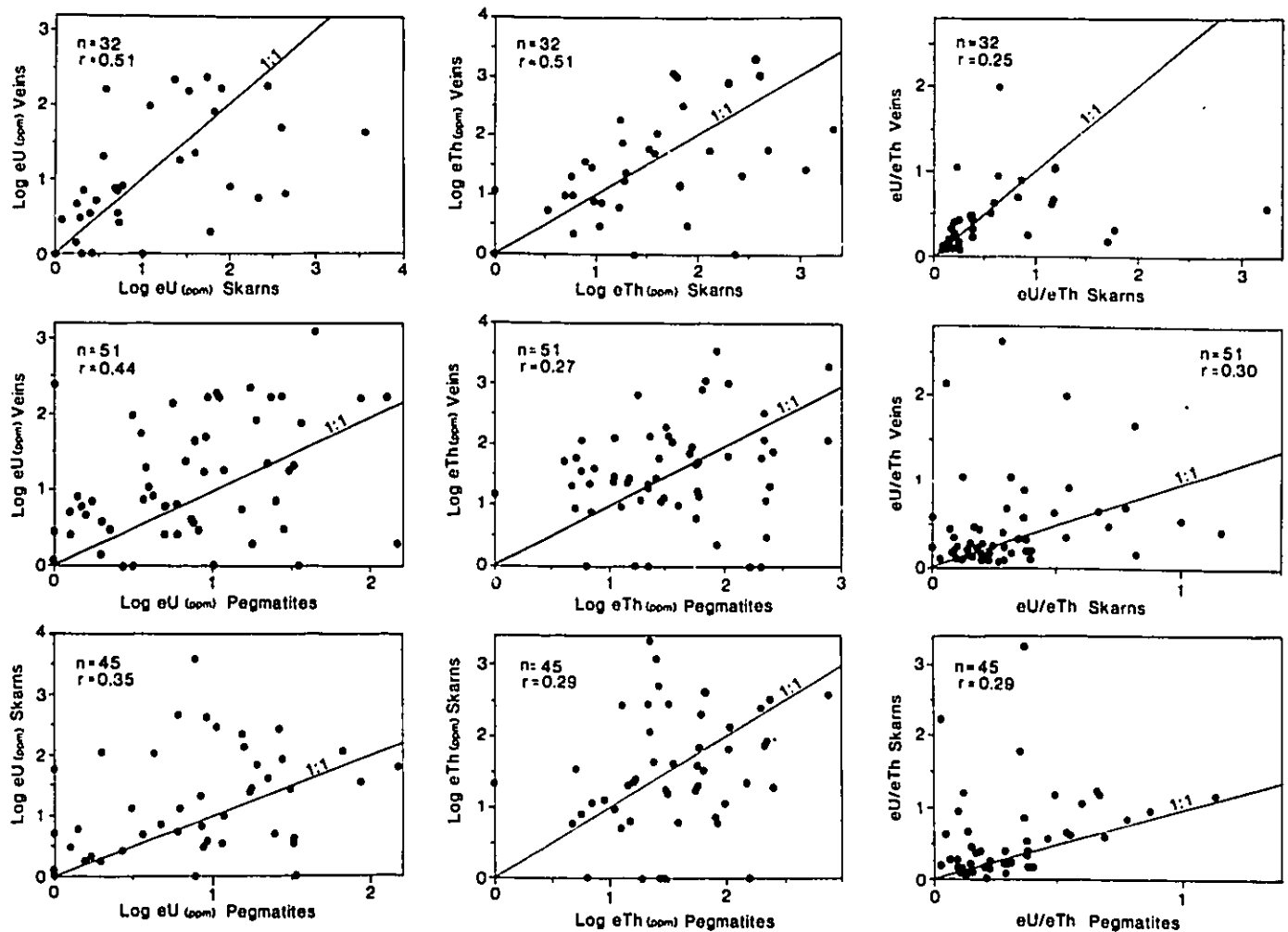


FIG. 7. Radioclement (log eU, log eTh, and eU/eTh) distribution: skarns vs. veins; pegmatites vs. veins; and pegmatites vs. skarns.

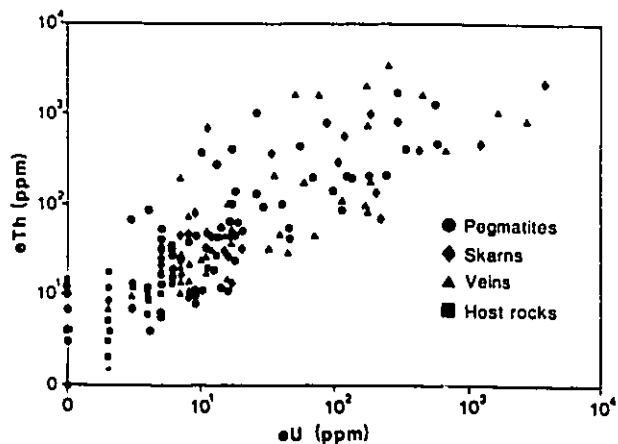


FIG. 8. Distribution of uranium and thorium in pegmatites, skarns, veins, and host rocks in the Wilberforce area of the Grenville Province.

Wilberforce area

In the vicinity of Wilberforce, U-, Th-, Mo-, and REE-bearing pegmatites, skarns, and fluorite-apatite-calcite veins are especially numerous. The Halo U-Mo pegmatite, the Cardiff U-fluorite skarns and veins, the Richardson U-fluorite apatite-calcite veins, and the Joiner Mo-U calcite veins are just

a few of the better known deposits. *In situ* gamma-ray spectrometry analyses ($n = 171$) from 22 occurrences in this area illustrate that radioclement abundances covary among the three main deposit types (pegmatites, skarns, and veins) and host rocks (Fig. 8).

Discussion

Within the pegmatites there is a close correlation between the abundance of ferromagnesian phases and uranium content (Tremblay 1974; Haynes 1986). Stratabound (concordant) pegmatites were generally hybridized to a greater degree than discordant pegmatites. Their mafic-rich selvages are products of the hybridization-skarnification process (Rimsaite 1983b, 1984, 1985, 1986; Lentz and Kretz 1989; Lentz, in preparation), although many researchers refer to them as melanosomes and migmatites (Allen 1971; Tremblay 1974; Rimsaite 1980, 1982; Masson and Gordon 1981; Ford 1982, 1983; Henderson 1982). These hybrid zones indicate that pegmatites were contaminated during emplacement into overlying host rocks. Variations in U, Th, and U/Th on a regional scale may indicate both differential fractionation into minerals and crustal heterogeneities in the source protolith of the pegmatites during ultrametamorphism at depth. Fowler and Doig (1983b) have shown that U, Th, and REE were differentially mobilized during the hydrothermal stage of pegmatite crystallization.

TABLE 4. Uranium- and thorium-bearing minerals from the Grenville Province

	UO ₂ (wt.%)	ThO ₂ (wt.%)	n	Host	Reference
Uraninite					
i		<10		Pegmatite	Robinson and Sabina (1955)
ii		<10		Pegmatite	Tremblay (1974)
iii		3.9		Pegmatite	Rimsaite (1986)
iv		10-18		Skarn	Robinson and Sabina (1955)
v		>20		Skarn	Robinson and Sabina (1955)
vi		36.9	9	Skarn	Lafontaine (1980)
vii		3.9		Secondary	Rimsaite (1986)
Thorianite					
i	35.4	40.1	1	Skarn	Robinson and Sabina (1955)
ii	30.5	52.3	17	Skarn	Lafontaine (1980)
Uranothorite					
i	11.3 (2.2)	47.4 (5.6)	5	Pegmatite	Robinson and Abbey (1957)
ii	15.2 (8.1)	52.8 (5.9)	14	Pegmatite	Habib (1982)
iii	10.1 (3.3)	50.4 (4.8)	4	Skarn	Robinson and Abbey (1957)
iv	5.7	59.3	6	Skarn	Lafontaine (1980)
v	8.4	58.7	12	Vein	Lafontaine (1980)
Zircons					
i	0.53 (0.74)	0.11 (0.13)		Pegmatite-skarn	Hurley and Fairbairn (1957)
ii	0.2-0.5			Pegmatite	Tremblay (1974)
iii	0.69, 0.65		2	Pegmatite	Rimsaite (1980)
iv	0.45±0.10		27	Pegmatite	Habib (1982)
Allanite					
i		0.41	1	Pegmatite	Fronde! (1964)
ii	0.12 (0.05)		27	Pegmatite	Habib (1982)
iii		0.74 (0.82)	27	Pegmatite	MacFarlane (1987)
iv		1.2	1	Skarn	Lafontaine (1980)
v		0.49 (0.43)	9	Veins	MacFarlane (1987)

NOTES: Values in parentheses are one standard deviation about the mean. n, number of analyses.

Satterly (1956), Shaw (1958), Shaw *et al.* (1963), Hewitt (1967), and Masson and Gordon (1981) have noted the close spatial relationship among Grenville pegmatites, skarns, and veins. Masson and Gordon (1981) and Haynes (1986) suggested that some radioactive mineralization may be syngenetic or have a metamorphic-hydrothermal origin (South State north deposit). Lentz (1989), however, favours a magmatic-metasomatic origin for some humite minerals in radioactive marbles because of their close association with pegmatites. A genetic association between pegmatites and Mo-bearing skarns was questioned by Vokes (1963) and refuted by Karvinen (1973), who proposed a metamorphic-hydrothermal origin for molybdenite-bearing skarns with fluids derived by regional metamorphic dehydration reactions. This, however, is inconsistent with their late-tectonic origin.

The spatial and temporal relationships among the pegmatites, skarns, and veins indicate that the fluids related to the pegmatites were responsible for the formation of the skarns and veins. Figure 9 is a schematic representation illustrating spatial relationships among the three deposit types. This hypothesis is supported by Nishimori *et al.* (1977), Masson and Gordon (1981), and Lentz (1989, in preparation).

The U-, Th-, Mo-, and REE-bearing fluorite-apatite-calcite veins have a controversial origin. Satterly (1956) noted that the large Silver Crater biotite-hornblende-apatite-calcite vein was mineralogically similar to carbonatites. Other apatite-calcite veins have also been interpreted as carbonatites (Robertson 1981; Mungall 1989; S. Lumbers, personal communication, 1988) because their mineralogy is similar to carbonatites

and in a few areas the veins are apparently not associated with pegmatites and skarns. Masson and Gordon (1981) and Storey and Vos (1981) have described the "fenite-like," pyroxene alteration mantling these veins, which have been interpreted as fenites (Mungall 1989). However, Masson and Gordon (1981), Storey and Vos (1981), and Lentz (1989, in preparation) suggested that the fluorite-apatite-calcite veins are hydrothermal and that Ca pyroxene formed as a result of Ca and Mg metasomatism from a chemically modified skarn hydrothermal fluid derived from the granitic pegmatites. The relative abundances of fluorite, apatite, and calcite are variable due to changing H₂CO₃, HF, and H₃PO₄ fugacities of the hydrothermal fluid (Lentz 1989).

Conclusions

This study presents *in situ* gamma-ray spectrometry data on the distribution of uranium and thorium in U-Th-Mo-REE pegmatites, skarns, and veins of the Central Metasedimentary Belt of the Grenville Province. The following conclusions and inferences can be drawn from this data and from previously published work:

(1) Spatial, temporal, and mineralogical relationships indicate that the phlogopite - scapolite - Ca pyroxene skarns and fluorite-apatite-calcite veins are related to vapour-phase saturation of granitic pegmatites.

(2) The low abundance of uranium (1-4 ppm; 1σ range) and thorium (4-17 ppm) in the host gneisses (n = 54) suggests that fractional crystallization and volatile-phase saturation, in addition to partial melting at depth, may have been responsible for

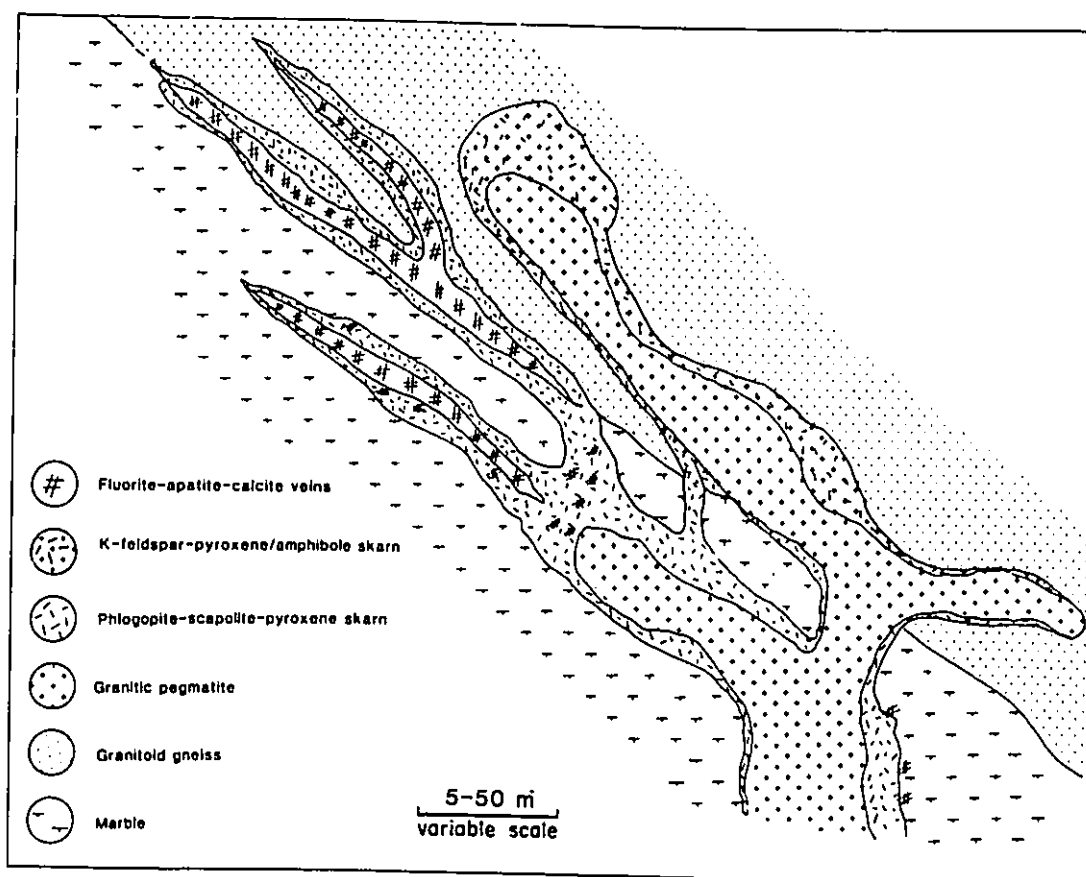


FIG. 9. Schematic representation of petrogenetic relationships among U-, Th-, Mo-, and REE-bearing granitic pegmatites, skarns, and fluorite-apatite-calcite veins in the Central Metasedimentary Belt of the Grenville Province.

enrichment of uranium (2–37 ppm) and thorium (5–102 ppm), molybdenum, and REE in the granitic pegmatite melts. Hybridization–skarnification along pegmatite margins seems to be key to initial U, Th, and rare-element deposition.

(3) Airborne radiometric data indicate that certain regions have characteristic abundances of uranium and thorium contents, in the mineralization of the three deposit types. This would seem to favour an inherent radioelement crustal signature in the pegmatite's source protolith.

(4) Average U and Th concentrations and U/Th ratios for numerous localities show significant positive correlations between pegmatites and skarns ($r = 0.35, 0.29, 0.29$, respectively; $n = 45$), pegmatites and veins ($r = 0.44, 0.27, 0.31$; $n = 51$), and skarns and veins ($r = 0.51, 0.51, 0.25$; $n = 32$) (>90% confidence level), providing further evidence for a related origin. The distribution of uranium and thorium in these deposits is consistent with a pegmatite-related, magmatic–hydrothermal origin for the radioactive skarns and fluorite-apatite-calcite veins.

(5) Secondary mobilization of uranium, coincident with hematization along shear zones, is partly responsible for variations in uranium abundance and U/Th ratios in the deposits.

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Curriculum Vitae

David Lentz

Education

University of New Brunswick, Fredericton, N.B. 1983-1986

Diploma: M.Sc. Geology (1986)

Thesis: Geology and Depositional Conditions of Tin
Lodes at True Hill, N.B.

University of New Brunswick, Fredericton, N.B. 1979-1983

Diploma: B.Sc. (Honours) Geology (1983)

Publications

Lentz, D.R., 1992. Episode of brecciation at the True Hill Bi-Sn-Mo deposit, southwestern New Brunswick. Geological Association of Canada Field Trip, WOLFVILLE'92, in press.

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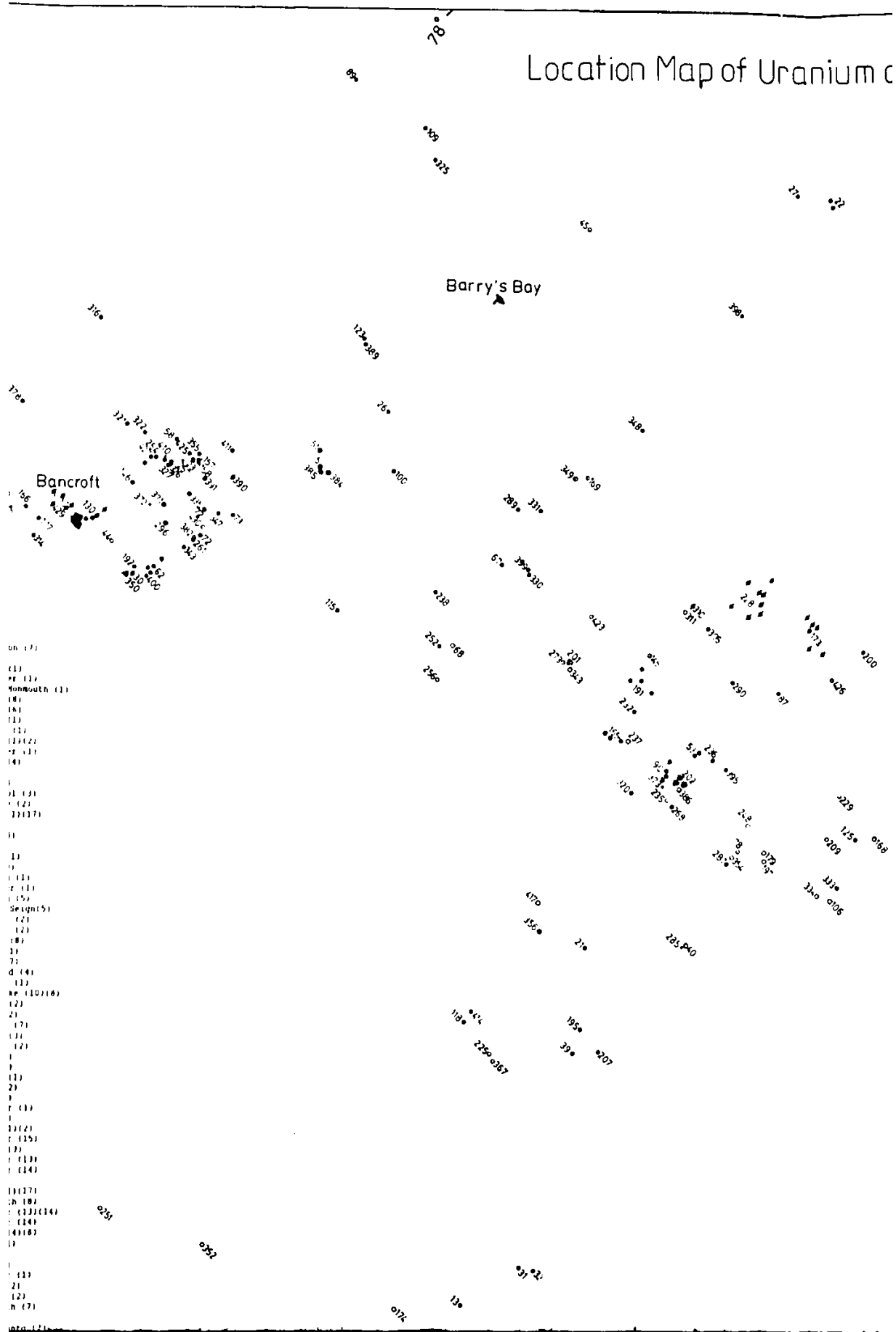
Scholarships

NSERC Post-graduate scholarship (Univ. of Ottawa) (1986-1989)
Entrance scholarship (Univ. of Ottawa) (1986-1989)
Research grant for isotopic studies (Univ. of Ottawa)
Travel Scholarship (Univ. of Ottawa) (1990)

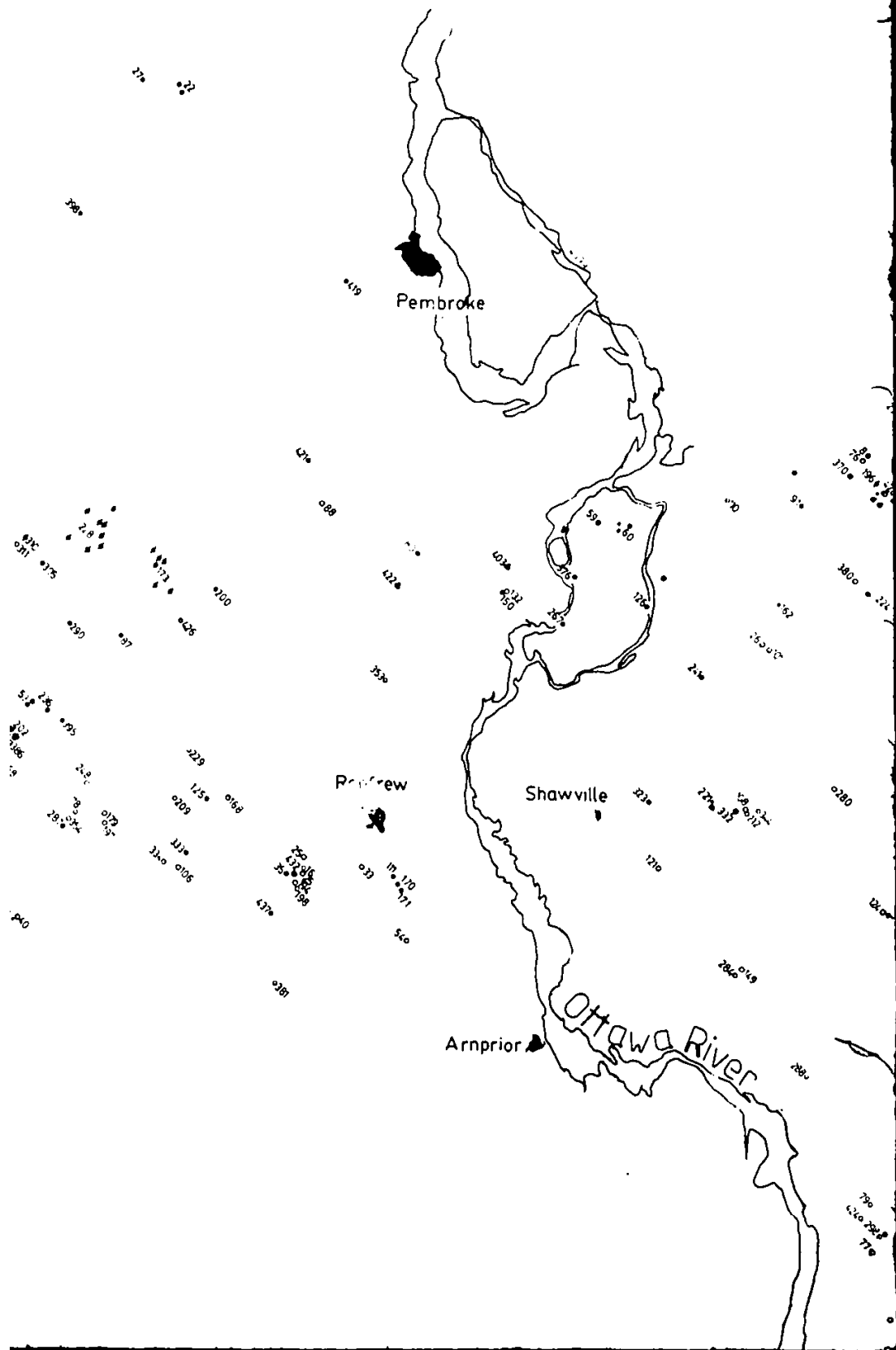
Haliburton

1. Acadia Mining Corporation (S,D) U
2. Adanichia Prop. (D) U
3. Aldfield Mining (D) U
4. Alta and Weard Mines (D) U
5. Ambis Occurrence (D) U
6. American Molybdenites Deposit (S, Mo)
7. Anstruther Rare Metals Company (D) U
8. Arthor Sulfur Mining (S,D) U
9. Atlin-Puller (B.C. LTD.) (D) U
10. Aubelle Mines Ltd. (D) U
11. Augustus Exploration (D) U
12. Aumacho River Mines Ltd. (D) U
13. Avery Occurrence (S,D) U-Mo
14. Avilabona Mines Ltd. (D) U
15. Back (Wallingford) Mine (D) U
16. Bagot Molybdenite Deposit (D) Mo
17. Bain Deposit (Indian Lake) (S,D) Mo-U
18. Bancroft Uranium Mines (D) U
19. Bancroft Uranium Mines Ltd. (D) U
20. Barret Mines Ltd. (D) U
21. Barret Occurrence (D) U
22. Barr Feldspar Quarry (D) U
23. Bartlett Mine Occurrence (D) U
24. Baskatong Occurrence (S,D) Mo
25. Belanger's Corners (S,D) Mo
26. Bennett Lake (D) U
27. Betz Occurrence (D) U
28. Bibis Yukon Mines Ltd. (D) U
29. Bicroft Uranium Mines Ltd. (S,D) U-Mo
30. Big Well Mines (D) U-Mo
31. Black Creek C zone (D) U
32. Black Creek S zone (D) U
33. Blackies Mountain Deposit (S,D) Mo
34. V. Blott (D) U
35. Boicey Occurrence (D) U-Mo
36. Bolan Prop. (S) Mo
37. Bonaventure Uranium Mines (S,D) U
38. Bonville Gold Mines Ltd. (D) U
39. Borden Occurrence (D) U
40. Box Deposit (S,D) Mo
41. Brady Prop. (D) U-Mo
42. Branson Occurrence (S,D) U
43. Briar Court Mines Prop. (D) U
44. Bronson Deposit (D) Mo
45. Broton Deposit (D) Mo
46. Brough Lake (D) Mo
47. Brouillard Prop. (D) U
48. Brunton Deposit (S) Mo
49. Brunsman Mines Ltd. (D) U
50. Buchhorn Deposit (S,D) Mo
51. Burgess Occurrence (D) U
52. Burns Occurrence (D) Mo
53. Burns Long Lake (D) U
54. Burnstown Deposit (D) U
55. Bunker Hill Extension Mines Ltd. (D) U
56. Burns Shore Mines Ltd. (S,D) U
57. L. Cadsky (D)
58. Cairns Occurrence (D) U
59. Calumet Contact Uranium Mines (S,D) U-Mo
60. Calumet Uranium Mines Ltd. (V,S,D) U-Mo
61. Calvert Occurrence (S) Mo
62. Cam-Lower Dunganon Occurrence (D) U
63. Cameron Mine (D) U
64. Cameron Black Mine (D) U
65. Canada All Metals Kk. (V,S,D) U-Mo
66. Canada Radium Corporation (D) U
67. Canada
68. Monmouth (S)
69. Clapham (S)
70. Aldfield (S)
71. Sicotte (S)
72. Carlow (S)
73. Monmouth (S)
74. Anstruther (S)
75. Huddersfield (S)
76. Anstruther (S)
77. Burleigh (S)
78. Cardiff (S)
79. Olden (S)
80. Anstruther (S)
81. Derry (S)
82. Ragot (S)
83. Masham (S)
84. Cardiff (S)
85. Glamorgan (S)
86. Bresham (S)
87. Hatawatthan (S)
88. Fraser (S)
89. Montegale (S)
90. Baskatong (S)
91. Ragot (S)
92. Bangor (S)
93. Richard (S)
94. Burleigh (S)
95. Cardiff (S)
96. Harvey (S)
97. Palmerston (S)
98. Palmerston (S)
99. Bagot (S)
100. Galwey (S)
101. Bagot (S)
102. Litchfield (S)
103. Huddersfield (S)
104. Paraday (S)
105. South Canonto (S)
106. Brougham (S)
107. Clapham (S)
108. Faraday (S)
109. Anstruther (S)
110. Dunganon (S)
111. Burns (S)
112. Cardiff (S)
113. Lillies (S)
114. Lyndoch (S)
115. Anstruther (S)
116. Bagot (S)
117. Carlow (S)
118. Sheffield (S)
119. Grand Calumet (S)
120. Grand Calumet (S)
121. Dunganon (S)
122. Murchison (S)
123. Murchison (S)
124. Monmouth (S)
125. Cardiff (S)
126. J. Eastman (D) U
127. Elliot Deposit (S) Mo
128. Kinridge Mines Ltd. (S,D) U-Mo
129. El Sol Gold Mines Ltd. (D) U
130. Empire Oil and Minerals (D) U
131. Evans O'Brien, Treasur Hill (S,D) U-Mo
132. Evans Lou Mine (D) U-Mo
133. Fab Metal Mines (D) U
134. Fairley Red Lake Gold Mines Ltd. (D) U
135. Faraday Uranium Mines Ltd. (V,S,D) U-Mo
136. Farcroft Mines Ltd. (D) U
137. Farrell Prospect (D) Mo
138. Farm Pt. (S,D) Mo
139. Feldspar Quarry (D) U
140. Feinhaber Deposit (D) Mo
141. Ferrill Occurrence (D) U
142. Fission Mines Ltd. (V) U-Mo
143. Flynn Mine (D) Mo
144. Foley Prop. (S,D) Mo
145. Forester Falls Occurrence (D) U
146. U.K. Foster (D) U
147. Galwood Mines (D) U
148. Ganyade Uranium Mines (D) U
149. Garland Mining and Development (D) U
150. Gatiueau Uranium Mines Ltd. (S,D) U
151. Gaudy Prop. (D) U
152. Genesee No2 Mine (D) U
153. Genesee No2 (South) (D) U
154. Gibson Occurrence (S,D) Mo
155. J. Gilbert (D) U
156. C. Giles (D) U
157. Giroux Prop. (Beat Lake) (V,S,D) Mo
158. A. Godfrey (D) U
159. Godfrey (D) Mo
160. Godin Lake (D) U
161. Goldhawk Occurrence (D) U
162. Gole Mine (D) U
163. Gorman Deposit (S,D) Mo
164. Gorman Lake Occurrence (D) U
165. Goshen A Occurrence (D) U
166. Goshen B Occurrence (D) U
167. B. Gould (S) U
168. Grattan Twp. Occurrences (V,D) U
169. Gray Occurrence (S) Mo
170. Grey Wolf Ex. (Stoney Creek) (D) U
171. Grey Wolf Ex. (Nogies Creek) (D) U
172. Greyhawk Uranium mines (D) U
173. Guernette Granite (D) U
174. Guisey Deposit (S,D) Mo
175. Gull Minerals A (D) U
176. Gull Minerals K (D) U
177. Hagerty Property (D) U
178. Halo Uranium Mines (S,D) U-Mo
179. Hamilton Molybdenum Alloys Ltd (D) Mo
180. Hanson Zone (D) U
181. Hanson Lake west (D) U
182. Harcourt Deposit (S,D) Mo
183. Hazeur Chibougamau Mines (D) U
184. Henley Prop. (D) U
185. Henley Prop. (D) Mo
186. Higgins Uranium Mining Co. (D) U
187. Highland Lake Area (D) U
188. Highway 500 Occurrence (D) U
189. E.T. Hogan (D) U
190. Hond Lake (S,D) Mo
191. Honsberger Occurrence (D) U
192. J. Eastman (D) U
193. Kinridge Mines Ltd. (S,D) U-Mo
194. El Sol Gold Mines Ltd. (D) U
195. Empire Oil and Minerals (D) U
196. Evans O'Brien, Treasur Hill (S,D) U-Mo
197. Evans Lou Mine (D) U-Mo
198. Fab Metal Mines (D) U
199. Fairley Red Lake Gold Mines Ltd. (D) U
200. Faraday Uranium Mines Ltd. (V,S,D) U-Mo
201. Farcroft Mines Ltd. (D) U
202. Farrell Prospect (D) Mo
203. Farm Pt. (S,D) Mo
204. Feldspar Quarry (D) U
205. Feinhaber Deposit (D) Mo
206. Ferrill Occurrence (D) U
207. Fission Mines Ltd. (V) U-Mo
208. Flynn Mine (D) Mo
209. Foley Prop. (S,D) Mo
210. Forester Falls Occurrence (D) U
211. U.K. Foster (D) U
212. Galwood Mines (D) U
213. Ganyade Uranium Mines (D) U
214. Garland Mining and Development (D) U
215. Gatiueau Uranium Mines Ltd. (S,D) U
216. Gaudy Prop. (D) U
217. Genesee No2 Mine (D) U
218. Genesee No2 (South) (D) U
219. Gibson Occurrence (S,D) Mo
220. J. Gilbert (D) U
221. C. Giles (D) U
222. Giroux Prop. (Beat Lake) (V,S,D) Mo
223. A. Godfrey (D) U
224. Godfrey (D) Mo
225. Godin Lake (D) U
226. Goldhawk Occurrence (D) U
227. Gole Mine (D) U
228. Gorman Deposit (S,D) Mo
229. Gorman Lake Occurrence (D) U
230. Goshen A Occurrence (D) U
231. Goshen B Occurrence (D) U
232. B. Gould (S) U
233. Grattan Twp. Occurrences (V,D) U
234. Gray Occurrence (S) Mo
235. Grey Wolf Ex. (Stoney Creek) (D) U
236. Grey Wolf Ex. (Nogies Creek) (D) U
237. Greyhawk Uranium mines (D) U
238. Guernette Granite (D) U
239. Guisey Deposit (S,D) Mo
240. Gull Minerals A (D) U
241. Gull Minerals K (D) U
242. Hagerty Property (D) U
243. Halo Uranium Mines (S,D) U-Mo
244. Hamilton Molybdenum Alloys Ltd (D) Mo
245. Hanson Zone (D) U
246. Hanson Lake west (D) U
247. Harcourt Deposit (S,D) Mo
248. Hazeur Chibougamau Mines (D) U
249. Henley Prop. (D) U
250. Henley Prop. (D) Mo
251. Higgins Uranium Mining Co. (D) U
252. Highland Lake Area (D) U
253. Highway 500 Occurrence (D) U
254. E.T. Hogan (D) U
255. Hond Lake (S,D) Mo
256. Honsberger Occurrence (D) U
257. J. Eastman (D) U
258. Kinridge Mines Ltd. (S,D) U-Mo
259. El Sol Gold Mines Ltd. (D) U
260. Empire Oil and Minerals (D) U
261. Evans O'Brien, Treasur Hill (S,D) U-Mo
262. Evans Lou Mine (D) U-Mo
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264. Fairley Red Lake Gold Mines Ltd. (D) U
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267. Farrell Prospect (D) Mo
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270. Feinhaber Deposit (D) Mo
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274. Foley Prop. (S,D) Mo
275. Forester Falls Occurrence (D) U
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306. Gull Minerals K (D) U
307. Hagerty Property (D) U
308. Halo Uranium Mines (S,D) U-Mo
309. Hamilton Molybdenum Alloys Ltd (D) Mo
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311. Hanson Lake west (D) U
312. Harcourt Deposit (S,D) Mo
313. Hazeur Chibougamau Mines (D) U
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315. Henley Prop. (D) Mo
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321. Honsberger Occurrence (D) U
322. J. Eastman (D) U
323. Kinridge Mines Ltd. (S,D) U-Mo
324. El Sol Gold Mines Ltd. (D) U
325. Empire Oil and Minerals (D) U
326. Evans O'Brien, Treasur Hill (S,D) U-Mo
327. Evans Lou Mine (D) U-Mo
328. Fab Metal Mines (D) U
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330. Faraday Uranium Mines Ltd. (V,S,D) U-Mo
331. Farcroft Mines Ltd. (D) U
332. Farrell Prospect (D) Mo
333. Farm Pt. (S,D) Mo
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335. Feinhaber Deposit (D) Mo
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338. Flynn Mine (D) Mo
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340. Forester Falls Occurrence (D) U
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342. Galwood Mines (D) U
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344. Garland Mining and Development (D) U
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348. Genesee No2 (South) (D) U
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351. C. Giles (D) U
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354. Godfrey (D) Mo
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378. Hazeur Chibougamau Mines (D) U
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393. Fab Metal Mines (D) U
394. Fairley Red Lake Gold Mines Ltd. (D) U
395. Faraday Uranium Mines Ltd. (V,S,D) U-Mo
396. Farcroft Mines Ltd. (D) U
397. Farrell Prospect (D) Mo
398. Farm Pt. (S,D) Mo
399. Feldspar Quarry (D) U
400. Feinhaber Deposit (D) Mo
401. Ferrill Occurrence (D) U
402. Fission Mines Ltd. (V) U-Mo
403. Flynn Mine (D) Mo
404. Foley Prop. (S,D) Mo
405. Forester Falls Occurrence (D) U
406. U.K. Foster (D) U
407. Galwood Mines (D) U
408. Ganyade Uranium Mines (D) U
409. Garland Mining and Development (D) U
410. Gatiueau Uranium Mines Ltd. (S,D) U
411. Gaudy Prop. (D) U
412. Genesee No2 Mine (D) U
413. Genesee No2 (South) (D) U
414. Gibson Occurrence (S,D) Mo
415. J. Gilbert (D) U
416. C. Giles (D) U
417. Giroux Prop. (Beat Lake) (V,S,D) Mo
418. A. Godfrey (D) U
419. Godfrey (D) Mo
420. Godin Lake (D) U
421. Goldhawk Occurrence (D) U
422. Gole Mine (D) U
423. Gorman Deposit (S,D) Mo
424. Gorman Lake Occurrence (D) U
425. Goshen A Occurrence (D) U
426. Goshen B Occurrence (D) U
427. B. Gould (S) U
428. Grattan Twp. Occurrences (V,D) U
429. Gray Occurrence (S) Mo
430. Grey Wolf Ex. (Stoney Creek) (D) U
431. Grey Wolf Ex. (Nogies Creek) (D) U
432. Greyhawk Uranium mines (D) U
433. Guernette Granite (D) U
434. Guisey Deposit (S,D) Mo
435. Gull Minerals A (D) U
436. Gull Minerals K (D) U
437. Hagerty Property (D) U
438. Halo Uranium Mines (S,D) U-Mo
439. Hamilton Molybdenum Alloys Ltd (D) Mo
440. Hanson Zone (D) U
441. Hanson Lake west (D) U
442. Harcourt Deposit (S,D) Mo
443. Hazeur Chibougamau Mines (D) U
444. Henley Prop. (D) U
445. Henley Prop. (D) Mo
446. Higgins Uranium Mining Co. (D) U
447. Highland Lake Area (D) U
448. Highway 500 Occurrence (D) U
449. E.T. Hogan (D) U
450. Hond Lake (S,D) Mo
451. Honsberger Occurrence (D) U
452. J. Eastman (D) U
453. Kinridge Mines Ltd. (S,D) U-Mo
454. El Sol Gold Mines Ltd. (D) U
455. Empire Oil and Minerals (D) U
456. Evans O'Brien, Treasur Hill (S,D) U-Mo
457. Evans Lou Mine (D) U-Mo
458. Fab Metal Mines (D) U
459. Fairley Red Lake Gold Mines Ltd. (D) U
460. Faraday Uranium Mines Ltd. (V,S,D) U-Mo
461. Farcroft Mines Ltd. (D) U
462. Farrell Prospect (D) Mo
463. Farm Pt. (S,D) Mo
464. Feldspar Quarry (D) U
465. Feinhaber Deposit (D) Mo
466. Ferrill Occurrence (D) U
467. Fission Mines Ltd. (V) U-Mo
468. Flynn Mine (D) Mo
469. Foley Prop. (S,D) Mo
470. Forester Falls Occurrence (D) U
471. U.K. Foster (D) U
472. Galwood Mines (D) U
473. Ganyade Uranium Mines (D) U
474. Garland Mining and Development (D) U
475. Gatiueau Uranium Mines Ltd. (S,D) U
476. Gaudy Prop. (D) U
477. Genesee No2 Mine (D) U
478. Genesee No2 (South) (D) U
479. Gibson Occurrence (S,D) Mo
480. J. Gilbert (D) U
481. C. Giles (D) U
482. Giroux Prop. (Beat Lake) (V,S,D) Mo
483. A. Godfrey (D) U
484. Godfrey (D) Mo
485. Godin Lake (D) U
486. Goldhawk Occurrence (D) U
487. Gole Mine (D) U
488. Gorman Deposit (S,D) Mo
489. Gorman Lake Occurrence (D) U
490. Goshen A Occurrence (D) U
491. Goshen B Occurrence (D) U
492. B. Gould (S) U
493. Grattan Twp. Occurrences (V,D) U
494. Gray Occurrence (S) Mo
495. Grey Wolf Ex. (Stoney Creek) (D) U
496. Grey Wolf Ex. (Nogies Creek) (D) U
497. Greyhawk Uranium mines (D) U
498. Guernette Granite (D) U
499. Guisey Deposit (S,D) Mo
500. Gull Minerals A (D) U
501. Gull Minerals K (D) U
502. Hagerty Property (D) U
503. Halo Uranium Mines (S,D) U-Mo
504. Hamilton Molybdenum Alloys Ltd (D) Mo
505. Hanson Zone (D) U
506. Hanson Lake west (D) U
507. Harcourt Deposit (S,D) Mo
508. Hazeur Chibougamau Mines (D) U
509. Henley Prop. (D) U
510. Henley Prop. (D) Mo
511. Higgins Uranium Mining Co. (D) U
512. Highland Lake Area (D) U
513. Highway 500 Occurrence (D) U
514. E.T. Hogan (D) U
515. Hond Lake (S,D) Mo
516. Honsberger Occurrence (D) U
517. J. Eastman (D) U
518. Kinridge Mines Ltd. (S,D) U-Mo
519. El Sol Gold Mines Ltd. (D) U
520. Empire Oil and Minerals (D) U
521. Evans O'Brien, Treasur Hill (S,D) U-Mo
522. Evans Lou Mine (D) U-Mo
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524. Fairley Red Lake Gold Mines Ltd. (D) U
525. Faraday Uranium Mines Ltd. (V,S,D) U-Mo
526. Farcroft Mines Ltd. (D) U
527. Farrell Prospect (D) Mo
528. Farm Pt. (S,D) Mo
529. Feldspar Quarry (D) U
530. Feinhaber Deposit (D) Mo
531. Ferrill Occurrence (D) U
532. Fission Mines Ltd. (V) U-Mo
533. Flynn Mine (D) Mo
534. Foley Prop. (S,D) Mo
535. Forester Falls Occurrence (D) U
536. U.K. Foster (D) U
537. Galwood Mines (D) U
538. Ganyade Uranium Mines (D) U
539. Garland Mining and Development (D) U
540. Gatiueau Uranium Mines Ltd. (S,D) U
541. Gaudy Prop. (D) U
542. Genesee No2 Mine (D) U
543. Genesee No2 (South) (D) U
544. Gibson Occurrence (S,D) Mo
545. J. Gilbert (D) U
546. C. Giles (D) U
547. Giroux Prop. (Beat Lake) (V,S,D) Mo
548. A. Godfrey (D) U
549. Godfrey (D) Mo
550. Godin Lake (D) U
551. Goldhawk Occurrence (D) U
552. Gole Mine (D) U
553. Gorman Deposit (S,D) Mo
554. Gorman Lake Occurrence (D) U
555. Goshen A Occurrence (D) U
556. Goshen B Occurrence (D) U
557. B. Gould (S) U
558. Grattan Twp. Occurrences (V,D) U
559. Gray Occurrence (S) Mo
560. Grey Wolf Ex. (Stoney Creek) (D) U
561. Grey Wolf Ex. (Nogies Creek) (D) U
562. Greyhawk Uranium mines (D) U
563. Guernette Granite (D) U
564. Guisey Deposit (S,D) Mo
565. Gull Minerals A (D) U
566. Gull Minerals K (D) U
567. Hagerty Property (D) U
568. Halo Uranium Mines (S,D) U-Mo
569. Hamilton Molybdenum Alloys Ltd (D) Mo
570. Hanson Zone (D) U
571. Hanson Lake west (D) U
572. Harcourt Deposit (S,D) Mo
573. Hazeur Chibougamau Mines (D) U
574. Henley Prop. (D) U
575. Henley Prop. (D) Mo
576. Higgins Uranium Mining Co. (D) U
577. Highland Lake Area (D) U
578. Highway 500 Occurrence (D) U
579. E.T. Hogan (D) U
580. Hond Lake (S,D) Mo
581. Honsberger Occurrence (D) U
582. J. Eastman (D) U
583. Kinridge Mines Ltd. (S,D) U-Mo
584. El Sol Gold Mines Ltd. (D) U
585. Empire Oil and Minerals (D) U
586. Evans O'Brien, Treasur Hill (S,D) U-Mo
587. Evans Lou Mine (D) U-Mo
588. Fab Metal Mines (D) U
589. Fairley Red Lake Gold Mines Ltd. (D) U
590. Faraday Uranium Mines Ltd. (V,S,D) U-Mo
591. Farcroft Mines Ltd. (D) U
592. Farrell Prospect (D) Mo
593. Farm Pt. (S,D) Mo
594. Feldspar Quarry (D) U
595. Feinhaber Deposit (D) Mo
596. Ferrill Occurrence (D) U
597. Fission Mines Ltd. (V) U-Mo
598. Flynn Mine (D) Mo
599. Foley Prop. (S,D) Mo
600. Forester Falls Occurrence (D) U
601. U.K. Foster (D) U
602. Galwood Mines (D) U
603. Ganyade Uranium Mines (D) U
604. Garland Mining and Development (D) U
605. Gatiueau Uranium Mines Ltd. (S,D) U
606. Gaudy Prop. (D) U
607. Genesee No2 Mine (D) U
608. Genesee No2 (South) (D) U
609. Gibson Occurrence (S,D) Mo
610. J. Gilbert (D) U
611. C. Giles (D) U
612. Giroux Prop. (Beat Lake) (V,S,D) Mo
613. A. Godfrey (D) U
614. Godfrey (D) Mo
615. Godin Lake (D) U
616. Goldhawk Occurrence (D) U
617. Gole Mine (D) U
618. Gorman Deposit (S,D) Mo
619. Gorman Lake Occurrence (D) U
620. Goshen A Occurrence (D) U
621. Goshen B Occurrence (D) U
622. B. Gould (S) U
623. Grattan Twp. Occurrences (V,D) U
624. Gray Occurrence (S) Mo
625. Grey Wolf Ex. (Stoney Creek) (D) U
626. Grey Wolf Ex. (Nogies Creek) (D) U
627. Greyhawk Uranium mines (D) U
628. Guernette Granite (D) U
629. Guisey Deposit (S,D) Mo
630. Gull Minerals A (D) U
631. Gull Minerals K (D) U
632. Hagerty Property (D) U
633. Halo Uranium Mines (S,D) U-Mo
634. Hamilton Molybdenum Alloys Ltd (D) Mo
635. Hanson Zone (D) U
636. Hanson Lake west (D) U
637. Harcourt Deposit (S,D) Mo
638. Hazeur Chibougamau Mines (D) U
639. Henley Prop. (D) U
640. Henley Prop. (D) Mo
641. Higgins Uranium Mining Co. (D) U
642. Highland Lake Area (D) U
643. Highway 500 Occurrence (D) U
644. E.T. Hogan (D) U
645. Hond Lake (S,D) Mo
646. Honsberger Occurrence (D) U
647. J. Eastman (D) U
648. Kinridge Mines Ltd. (S,D) U-Mo
649. El Sol Gold Mines Ltd. (D) U
650. Empire Oil and Minerals (D) U
651. Evans O'Brien, Treasur Hill (S,D) U-Mo
652. Evans Lou Mine (D) U-Mo
653. Fab Metal Mines (D) U
654. Fairley Red Lake Gold Mines Ltd. (D) U
655. Faraday Uranium Mines Ltd. (V,S,D) U-Mo
656. Farcroft Mines Ltd. (D) U
657. Farrell Prospect (D) Mo
658. Farm Pt. (S,D) Mo
659. Feldspar Quarry (D) U
660. Feinhaber Deposit (D) Mo
661. Ferrill Occurrence (D) U
662. Fission Mines Ltd. (V) U-Mo
663. Flynn Mine (D) Mo
664. Foley Prop

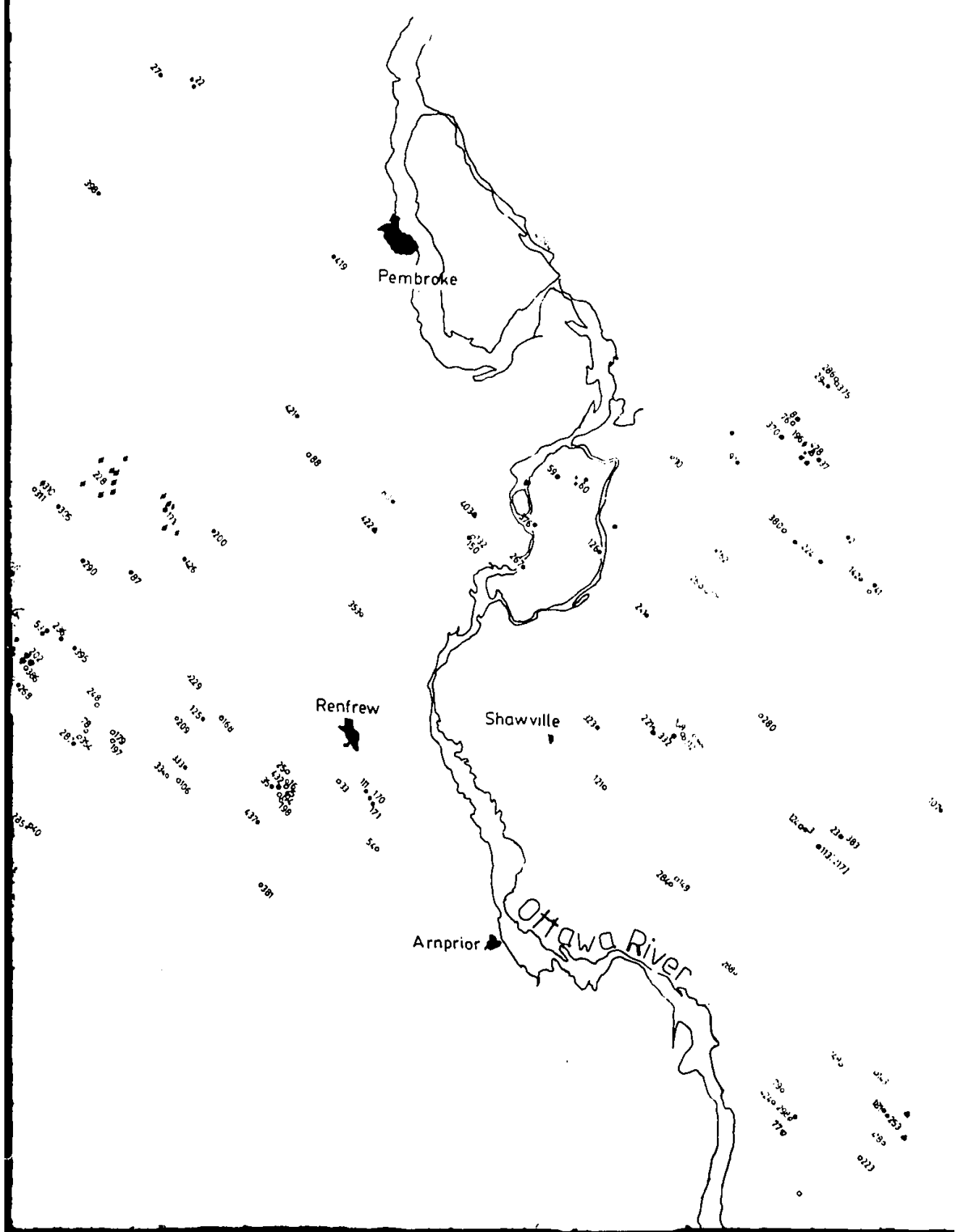
Location Map of Uranium

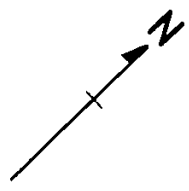


ap of Uranium and Molybdenum Pegmatite, Skarn, and



Map of Uranium and Molybdenum Pegmatite, Skarn, and Vein Deposits





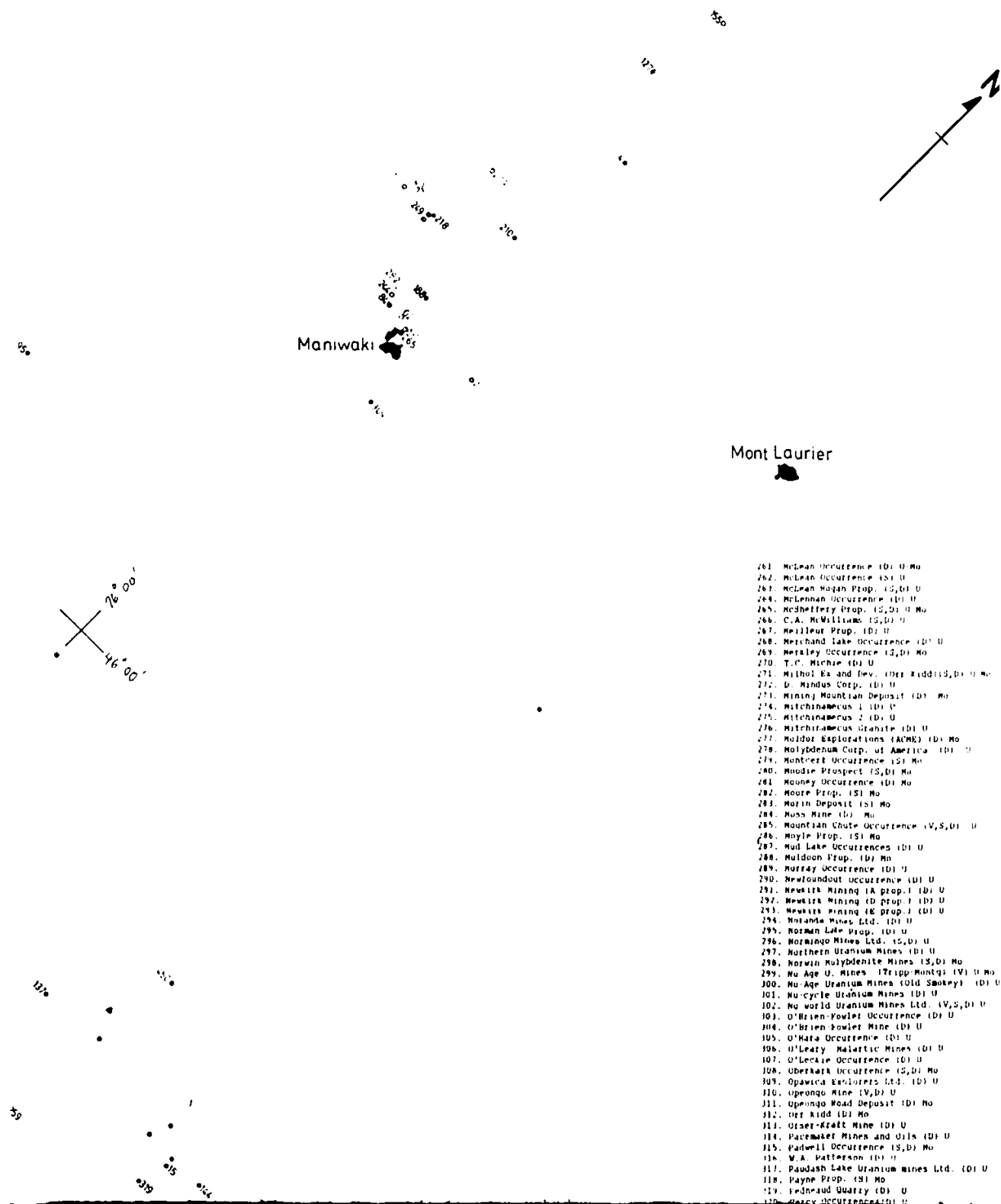
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2. Masson, S.L., and Gordon, J
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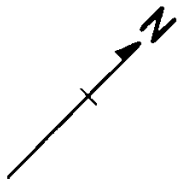
A detailed map of the Ottawa River area, showing the river's course, Shawville, and numerous depth soundings. A compass rose indicates a bearing of 76° 00' and a distance of 46' 00'. The map is labeled with various numbers and names, including 'Ottawa River', 'Shawville', and 'Man'.

~~76° 00'~~
~~46° 00'~~

f the southwest Grenville Province



47° 76°



Mont Laurier

261. McLean Occurrence (D) U-Mo	Dunham (1)	494. Tomlinson-Mullerite (Avon) (S,D) U-Mo	Cardiff (1)
262. McLean Occurrence (S) U	Hartcourt (1)	495. Toxey's Lake Occurrence (D) U	Brougham (1)
263. McLean Nugan Prop. (S,D) U	Cardiff (1)	496. Toppan Fluorite Mines (V,D) U	Cardiff (1)
264. McLennan Occurrence (D) U	Peck (1)	497. Triton Uranium Mines (S,D) U	Cardiff (1)
265. McShelley Prop. (S,D) U-Mo	Egan (1)	498. Turpins Bay Occurrence (D) U	Hagarty (2)
266. C.A. McWilliams (S,D) U	Egan (1)	499. Universal Light Metals Occurrence (D) U	Lyndoch (2)
267. Melville Prop. (D) U	Galloway (1)	500. Urban Quebec Occurrence (S,D) U	Dunham (2)
268. Mesland Lake Occurrence (D) U	Grande Salomet (1)	501. Urotoxic Mines (D) U	Monmouth (1)
269. Mesley Occurrence (S,D) Mo	Brougham (2)	502. Varlette Ag Occurrence (D) Mo	Glen (1)
270. T.C. Michie (D) U	North Crosby (1)	503. Vaughan Occurrence (V) U	Moss (2)
271. Mithei Ex and Dev. (Other Kidd) (S,D) U-Mo	Cardiff (1)	504. Villeneuve Prop. (S) Mo	Egan (1)
272. D. Mindus Corp. (D) U	Cardiff (1)	505. Villeneuve Mine (D) U	Downham (1)
273. Mining Mountain Deposit (D) Mo	Lyndoch (1)	506. Vadasa Gold Mines (S,D) U	Monmouth (1)
274. Mitchamers (D) U	MT. Laurier (1)	507. Vager Occurrence (S) Mo	Sheffield (1)
275. Mitchamers 2 (D) U	MT. Laurier (1)	508. Wakefield Quarry (O'Leary Malartic) (D) U	Wakefield (1)
276. Mitchamers Granite (D) U	MT. Laurier (1)	509. Waltham Feldspar (D) Mo	Thorne (1)
277. Molder Explorations (ACME) (D) Mo	Pennington (1)	510. Watson Feldspar Mine (D) U	Monteagle (2)
278. Molybdenum Corp. of America (D) U	Cardiff (1)	511. Welsh Kate Occurrence (D) U	Monteagle (1)
279. Montreal Occurrence (S) Mo	Egan (1)	512. Welsh No. 2 Prop. (D) Mo	Thorne (1)
280. Mudie Prospect (S,D) Mo	Aldfield (4)	513. West Lake Mining (V,D) U	Cardiff (1)
281. Mooney Occurrence (D) Mo	Cardiff (1)	514. Whyton Occurrence (D) U	Miller (2)
282. Moore Prop. (S) Mo	Egan (1)	515. Wilberforce Molybdenite (V,S) Mo U	Monmouth (1)
283. Morin Deposit (S) Mo	Major (1)	516. Wilkie Prop. (D) U	Low (1)
284. Moss Mine (D) Mo	Unslow (1)	517. Wilson Deposit (S,D) Mo	Malawatchan (1)
285. Mountain Chute Occurrence (V,S,D) U	North Canons (2)	518. Winning Church Mine (D) Mo	Hall (1)
286. Moyle Prop. (S) Mo	Huddersfield (1)	519. Wornake No. 1A (D) U	Alice (2)
287. Mud Lake Occurrences (D) U	Cardiff (1)	520. Wornake No. 2 (D) U	Alice (2)
288. Muldoon Prop. (D) Mo	Cardiff (1)	521. Wornake No. 2 (D) U	Bromley (2)
289. Murray Occurrence (D) U	Studenell (2)	522. Wornake No. 3 (V) U	Moss (2)
290. Newfoundland Occurrence (D) U	Grafton (2)	523. Wolf Fire Tower Deposit (D) Mo	Lyndoch (1)
291. Newell Mining (A prop.) (D) U	Anstruther (1)	524. Wood-Ormand (D) Mo	Bardley (4)
292. Newell Mining (D prop.) (D) U	Burlingame (1)	525. Woodcock Prop. (D) U	Monteagle (1)
293. Newell Mining (E prop.) (D) U	Burlingame (1)	526. Wren Deposit (D) Mo	Grafton (1)
294. Niandana Mines Ltd. (D) U	Huddersfield (1)	527. Wright Occurrence (D) U	Monteagle (1)
295. Norman Lake Prop. (D) U	MT. Laurier (1)	528. Yates Uranium Mines (V,S,D) U-Mo	Huddersfield (1)
296. Northington Mines Ltd. (S,D) U	Dunham (1)	529. York River Occurrences (V,D) U	Faraday (2)
297. Northern Uranium Mines (D) U	Cardiff (1)	530. York River Occurrences (D) Mo	Monteagle (1)
298. Norwin Molybdenite Mines (S,D) Mo	Bardley (1)	531. Zavitski No. 2 (D) U	Baqot (2)
299. Nu Age U. Mines (Tripp-Montg.) (V) U-Mo	Cardiff (1)	532. Zenith Deposit (S,D) Mo-U	Baqot (2)
300. Nu Age Uranium Mines (Old Spoke) (D) U	Monmouth (1)	533. Zennac Metal Mines (D) U	Anstruther (1)
301. Nu-Cycle Uranium Mines (D) U	Glen (1)		
302. Nu World Uranium Mines Ltd. (V,S,D) U	Glen (1)		
303. O'Brien-Powder Occurrence (D) U	Match (2)		
304. O'Brien-Powder Mine (D) U	Mattawan (1)		
305. O'Hara Occurrence (D) U	Sebastopol (2)		
306. O'Leary Malartic Mines (D) U	Wakefield (1)		
307. O'Leary Occurrence (D) U	Peck (1)		
308. Obermark Occurrence (S,D) Mo	Sheffield (1)		
309. Opawica Refractory (S) (D) U	Pennington (1)		
310. Opengong Mine (V,D) U	Sebastopol (2)		
311. Opengong Road Deposit (D) Mo	Sebastopol (1)		
312. Orr Kidd (D) Mo	Cardiff (1)		
313. Orser-Kraft Mine (D) U	Sherbrooke (1)		
314. Pacemaker Mines and Oils (D) U	Faraday (1)		
315. Padwell Occurrence (S,D) Mo	Monmouth (1)		
316. W.A. Patterson (D) U	Wernschel (1)		
317. Padash Lake Uranium Mines Ltd. (D) U	Cardiff (1)		
318. Payne Prop. (S) Mo	Hall (1)		
319. Peabody Quarry (D) U	Buckingham (1)		
320. Pease Occurrence (D) U	Griffith (1)		

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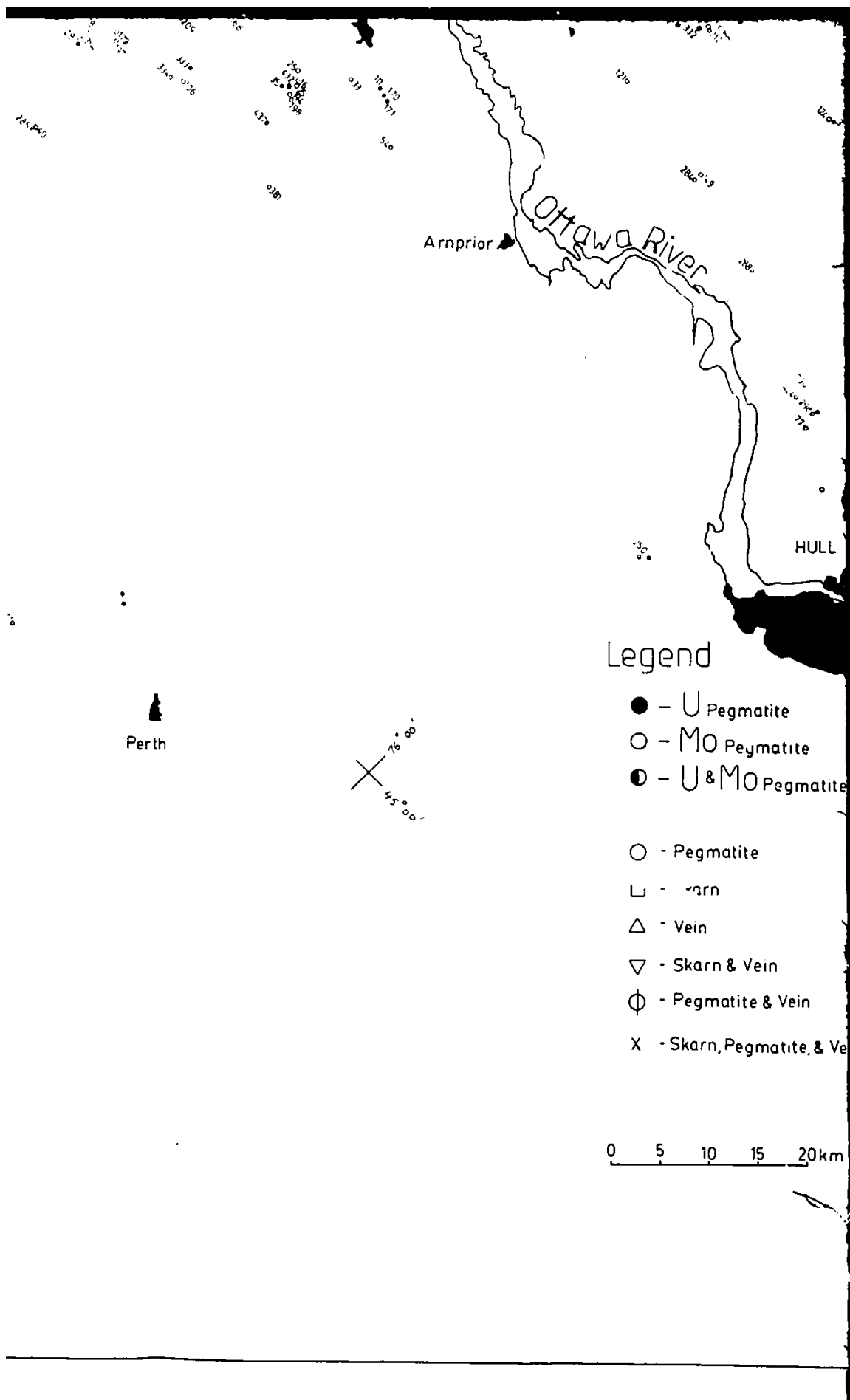
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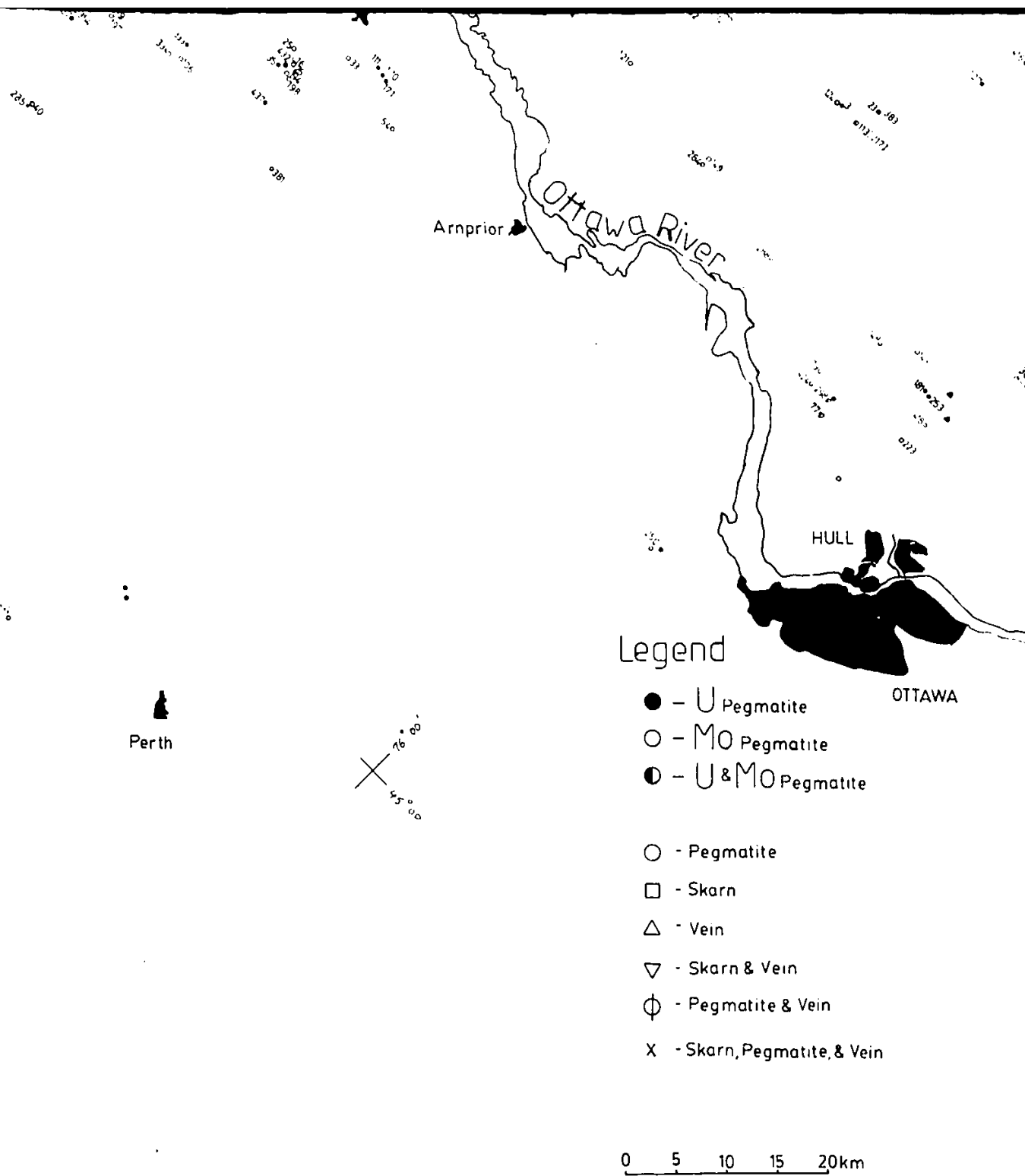
21. Barnett Occurrence (D) U
22. Barr Feldspar Quarry (D) U
23. Bartlett Mine Occurrence (D) U
24. Baskatong Occurrence (S,D) Mo
25. Belanger's Corners (S,D) Mo
26. Bennett Lake (D) U
27. Betz Occurrence (D) U
28. Bibis Tuton Mines Ltd. (D) U
29. Bickford Uranium Mines Ltd. (S,D) U-Mo
30. Big Hill Mines (D) (Kennedy) U
31. Black Creek 2 zone (D) U
32. Black Creek 3 zone (D) U
33. Blackies Mountain Deposit (S,D) Mo
34. W. Blott (D) U
35. Boicey Occurrence (D) U-Mo
36. Nolan Prop. (S) Mo
37. Bonaventure Uranium Mines (S,D) U
38. Bonville Gold Mines Ltd. (D) U
39. Boldon Occurrence (D) U
40. Bos Deposit (S,D) Mo
41. Brady Prop. (D) U-Mo
42. Brascan Occurrence (S,D) U
43. Briar Court Mines Prop. (D) U
44. Bronson Deposit (D) Mo
45. Broton Deposit (D) Mo
46. Brough Lake (D) U
47. Bruceton Deposit (S) Mo
48. Brunsum Mines Ltd. (D) U
49. Brunsum Mines Ltd. (D) U
50. Buckhorn Deposit (S,D) Mo
51. Burgess Occurrence (D) U
52. Burns Occurrence (D) U
53. Burns Long Lake (D) U
54. Burnston Deposit (D) U
55. Bunker Hill Extension Mines Ltd. (D) U
56. Burma Shore Mines Ltd. (S,D) U
57. L. Cadbury (D)
58. Cairns Occurrence (D) U
59. Calumet Contact Uranium Mines (S,D) U-Mo
60. Calumet Uranium Mines Ltd. (V,S,D) U-Mo
61. Calvert Occurrence (S) Mo
62. Cam-Lover Duganion Occurrence (D) U
63. Cameron Mine (D) U
64. Cameron-Alex Mine (D) U
65. Canada All Metals Ex. (V,S,D) U-Mo
66. Canada Radius Corporation (D) U
67. Canadian Beryllium Mines Occurrence (D) U
68. Canadian Dymo Mines Ltd. (D) U
69. Canadian John-Mansville Co. (D) U-Mo
70. Card Occurrence (V,D) U
71. Cardiff Uranium Mines Ltd. (V,S,D) U-Mo
72. Carr-Quicke-McFlish Prop. (S,D) U
73. Carr-Quicke-McFlish Prop. (S,D) U
74. Cassiar-Rainbow Gold Mines (V,U) U
75. Cavendish Uranium Mines Ltd. (D) U
76. Chabot Mine (S,D) Mo
77. Chaput-Payne Mine (V,S) U-Mo
78. Charlton Deposit (D) Mo
79. Chateaux Prop. (D) Mo
80. Chevrier Occurrence (D) U
81. Christie Lake Mines (D) U
82. Chisholm No. 1 Mine (S) Mo
83. Clark Deposit (V,S,D) (Topasari) U
84. Cliggen Prop. (S,D) Mo
85. Climax Molybdenum Comp. (D) U
86. Clow Occurrence (D) Mo
87. Colauet Feldspar Occurrence (D) U
88. Cole Deposit (S,D) Mo
89. Cumt Quartz Occurrence (D) U
90. Conrad Uranium Mines (D) U
91. Consolidated Halliwell (D) U
92. Consolidated Thor Mines Ltd. (S,D) U
93. Consolidated Tungsten M.C.C. Ltd. (D) U
94. Consolidated Uranium Corp. (D) U
95. Copper-Uranium Ltd. (D) U
96. Coral Occurrence (D) Mo
97. Cordell Gold Mines Ltd. (S,D) U
98. J.C. Cottrill (D) U
99. Cousinthe Occurrence (D) U
100. Craigmont Corundum Mines (D) U-Mo
101. Crawford Prop. (S) Mo
102. Creagh Prop. (S) Mo
103. Crowell Uranium and Dev. (D) U
104. Crystal Lake Occurrence (D) U
105. T. Cudney (S,D) U
106. Culhane Deposit (S) Mo
107. D'Alton Gold Mines (D) U
108. Dary Prop. (S) Mo
109. Davis Mica Occurrence (D) U
110. Davis Prop. (S) Mo
111. Deagry Hay Occurrence (D) U
112. G.H. Denfield (D) U
113. Desjardins Prop. (Kert Mo) (S) U-Mo
114. Desmond Mining Corp. (S,D) U-Mo
115. Dodd Occurrence (D) U
116. Dominion Mine (S) Mo
117. Donnie Prop. (S) Mo
118. Doran Occurrence (D) U
119. R.W. Doubt (D) U
120. Bradar Occurrence (D) Mo
121. Dragg Prop. (D) Mo
122. Drude Uranium Mines Ltd. (S,D) U
123. Dublestein Occurrence (D) U
124. Duclos Prop. (S) Mo
125. Dudgeon Occurrence (D) U
126. Dun Haven Mines Ltd. (D) U
127. Duva Oils And Mines (V,D) U-Mo
128. Dwyer Occurrence (S,D) Mo
129. Dwyer Occurrence (S) Mo
130. Eagers West Occurrence (V,D) U
131. Eagers West Occurrence (V,D) U
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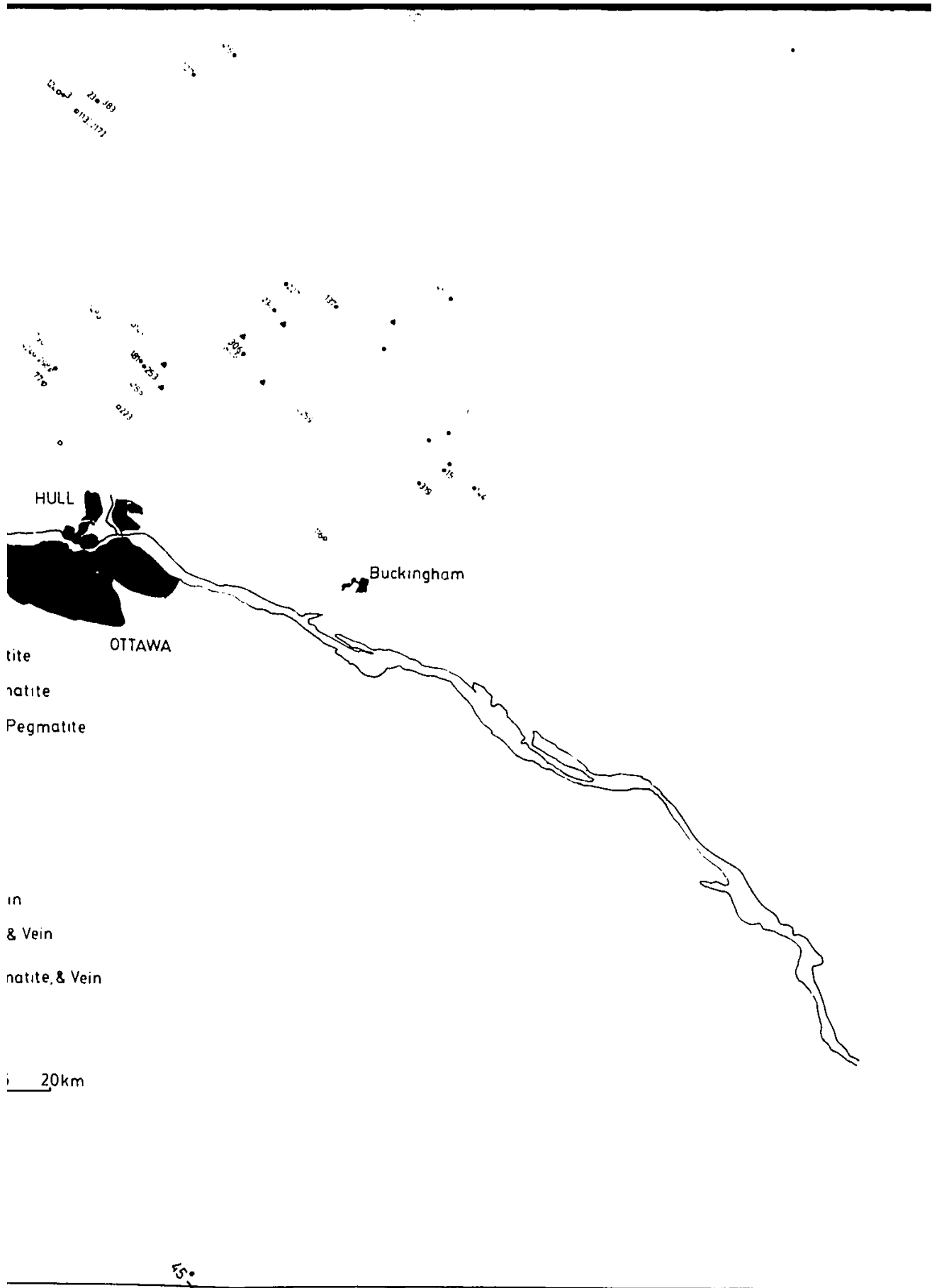


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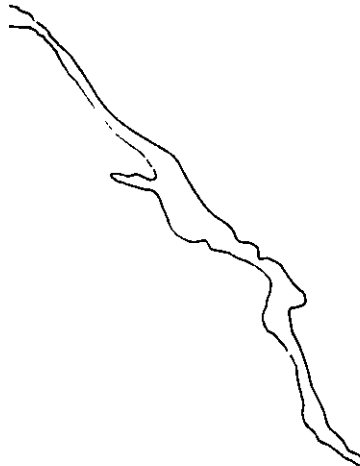
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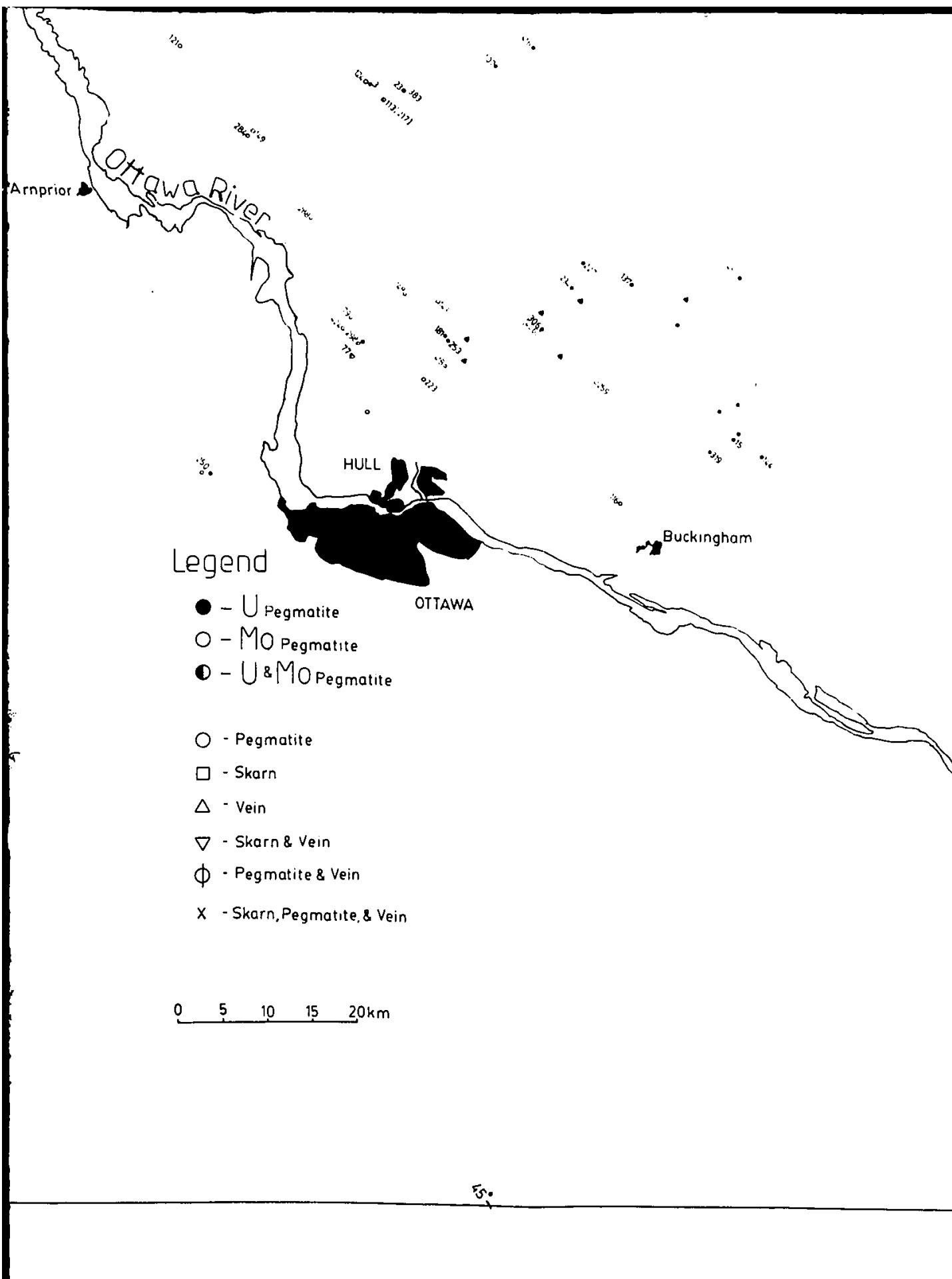
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404. Villeneuve Mine
405. Wadada Gold Mine
406. Wager Occurrence
408. Wakefield Quartz
410. Waltham Feldspar
411. Waltham Feldspar
411. Welsh Pass 1000
411. Welsh No. 1 Prop.
411. West Lake Mining
414. Whytock Occurrence
415. Whitehorn Mine
416. White Island 100
417. Wilson Deposit 10
417. Winning Church
417. Worsnax No. 1A 10
420. Worsnax No. 1B 10
421. Worsnax No. 1C 10
421. Worsnax No. 1D 10
421. Wolf Fire Tower
424. Wood Island 100
425. Woodson Prop. 10
426. Wren Deposit 100
427. Wright Occurrence
428. Yates Uranium Mine
429. York River Occurrence
430. York River Occurrence
431. Zavitza No. 100
432. Zenith Deposit 10
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