In loving memory of my brother

Nels Anderson II

1

PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Vous pouvez nous écrire à :

Chambre d'information

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

**A Chemical and Isotopic Study of the Age, Petrogenesis and Magmatic Evolution
of the Mount Pleasant Caldera complex, New Brunswick**

by

H. Elizabeth Anderson, M.Sc.

**A thesis submitted to the Faculty of Graduate Studies and Research in partial
fulfillment of the requirements for the degree of
Doctor of Philosophy, Department of Earth Sciences**

Carleton University

Ottawa, Ontario

October, 1992

copyright

1992, H. Elizabeth Anderson

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file / Votre référence

Our file / Notre référence

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-315-84044 7

Canada

The undersigned hereby recommend to the Faculty of Graduate Studies and Research, acceptance of the thesis "A chemical and isotopic study of the age, petrogenesis and magmatic evolution of the Mount Pleasant caldera complex, New Brunswick", submitted by H. Elizabeth Anderson, M.Sc., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

.....

Chairman, Department of Earth Sciences

.....

Thesis supervisor

.....

Thesis co-supervisor

.....

External examiner

Carleton University
November 1992

ABSTRACT

The age, petrogenesis and magmatic evolution of the magma chamber of the Mount Pleasant Caldera complex are examined using a combined isotopic and geochemical approach. This epicontinental caldera complex, occurring in the Canadian Appalachians, contains a variety of mildly potassic igneous rocks ranging from tholeiitic basalts to calcalkaline andesites, monzogranites and rhyolites with felsic rocks predominant. These rocks were emplaced at the end of the Acadian Orogeny and at the onset of a period of crustal extension and thermal subsidence that formed the Maritimes Basin.

Combined Rb/Sr and O isotopic studies of volcanic and hypabyssal rocks of the Mount Pleasant caldera complex permit the recognition of a small data (6 samples) set that is unaffected by syn-magmatic crustal contamination and post-magmatic hydrothermal alteration. This has allowed Rb-Sr dating of the emplacement of the caldera complex at 368 ± 5 Ma ($^{87}\text{Sr}/^{86}\text{Sr}_i = 0.70611$; M.S.W.D = 2.8). The isochron samples comprise andesites to high-silica rhyolites of the intracaldera facies; basaltic rocks that are not isochronous have Sr initial ratios very close to this value.

The geological implications of the isochron are that a wide range of effusive and hypabyssal igneous rocks in the caldera are part of an isotopically closed system. Furthermore, stratigraphic relationships indicate that the entire range of magma compositions (andesite — high-silica rhyolite) coexisted in a single magma chamber. In order to test and constrain these conclusions the method of Pearce Element Ratio (PER) analysis was adapted to the complex felsic system of the Mount Pleasant Caldera. PER analysis was then used in combination with conventional trace element modelling to determine the chemical and physical processes that controlled magmatic evolution in the high-level andesite-rhyolite magma chamber. The results show that highly silicic magmas of the Mt. Pleasant Caldera were derived from an andesitic parental magma by a two-stage process of convective fractionation. In stage 1 fractionation of andesite produced a monzogranite differentiate (McDougall Brook Microgranite). In stage 2, fractionation of the monzogranite produced high-silica rhyolite tuffs of the Little Mount Pleasant and Seelys Formations. The calculated assemblages were different than those estimated from modal mineralogy. Both stages are characterized by multiple saturation with several major and accessory minerals. From this it is concluded that *in situ* crystallization accompanied by convective

fractionation was occurring simultaneously in two different parts of a vertically stratified magma chamber. The magma chamber apparently consisted of a chemically stratified, double-diffusive lower andesite layer, a homogeneous, monzogranitic middle layer, and a chemically stratified, double-diffusive, upper high-silica rhyolite layer. This inherently unstable configuration could have been maintained in a state of dynamic equilibrium by repeated injections of andesite into the base of the magma chamber.

Combined isotopic and trace element studies indicate that caldera magmas were partial melts of an asthenospheric source (OIB) that underwent extensive fractionation and hybridization through assimilation of crustal materials. Unaltered caldera volcanics are characterized by positive ϵ_{Nd} values (+3.3 - +0.5), mildly radiogenic Sr initial ratios (~.706) and radiogenic Pb isotopic ratios with high $^{207}Pb/^{204}Pb$ values (15.63 - 15.74). These data indicate that the mafic rocks (basalts and andesites) are derived from asthenospheric mantle that was contaminated with ancient lower crustal material (probable basement of Proterozoic Avalonian Terrane). Contamination presumably occurred by crustal underplating of the mantle derived magmas accompanied by assimilation and fractional crystallization. The felsic magmas were derived by closed-system, convective fractionation of a mid- to upper-crustal andesitic magma chamber that separated from the lower-crustal chambers. The high-level magma chamber experienced minor subsequent mixing and contamination effects; high-silica rhyolites derived from the shallow roof-zone of the andesite-rhyolite magma chamber and basalts erupted from a deeper magma chamber(s) show evidence of O, Pb, and Sr isotopic contamination by supracrustal rocks.

The predominance of an asthenospheric component in source materials of the caldera complex indicates involvement of a mantle upwelling and partial melting process in caldera petrogenesis. This raises the possibility that post-tectonic crustal extension was active rather than passive as has been previously believed. Lithospheric delamination following Acadian orogenesis could be the cause of the asthenospheric upwelling required by the active extension hypothesis. Voluminous, predominantly felsic, bimodal, late- to post-tectonic magmatism in the northern Appalachians is commonly viewed as the product of crustal melting produced by overthickening of the continental crust during the Acadian orogeny. This view should be critically re-examined in light of the findings reported here.

ACKNOWLEDGEMENTS

This thesis was completed under the co-supervision of R.P. Taylor and J. Blenkinsop; I am grateful to them for providing a learning/research environment that was both challenging and supportive. Grazyna Kurzynska was an able and patient teacher of the techniques of isotope dilution and ion exchange chromatography. S.R. McCutcheon and L.R. Fyffe of the New Brunswick Department of Natural Resources and Energy provided material and logistical assistance and were sounding boards (and constructive critics) for some of the interpretations made in this thesis. R. Parrish of the Geological Survey of Canada provided a mixed ^{233}U , ^{235}U - ^{206}Pb spike. I have benefitted as well from discussions with fellow students and colleagues at the Ottawa-Carleton Geoscience Centre; I would like to make particular mention of Richard Ernst, Tony Simonetti, Keith Bell and Jeff Card. My husband, R.T. Patterson, was computer drafting consultant and a constant source of moral support.

Funding for the project was provided by N.S.E.R.C. grants to Taylor and Blenkinsop. I gratefully acknowledge Ontario Graduate Scholarsips, Carleton University scholarships, a Geological Society of America research grant (1989) and travel funding from Carleton University and the Graduate Students Association.

METHOD OF PRESENTATION

This thesis is presented as a series of articles in order to facilitate their publication in scientific journals.

ORIGINAL CONTRIBUTION

During 1990 and 1991, I completed all of the radiogenic isotopic analyses reported in this thesis, including sample preparation, chemical separation, mass spectrometry and data handling. This work was done with samples donated by S.R. McCutcheon and samples that I collected in 1989. The oxygen isotopic analyses were collected by R.P. Taylor at Menlo Park. Whole rock geochemical analyses of samples used for isotopic studies were obtained by technical staff at the University of Ottawa and École Polytechnique.

The first chapter of this thesis has been extracted from a paper, in preparation, that was co-authored with S.R. McCutcheon for submission to Geological Magazine. This paper is based entirely on field and geochemical data from McCutcheon's thesis. My contribution consisted of rewriting material from the thesis in the present format, and re-interpreting the whole-rock geochemistry. The stratigraphy and eruptive history of the caldera are based entirely on McCutcheon's interpretations.

I am the sole contributor to chapters 2, 3 and 4 of this thesis and take full responsibility for the interpretations made therein.

TABLE OF CONTENTS

ACCEPTANCE SHEET	ii
ABSTRACT	iii
ACKNOWLEDGMENTS	v
METHOD OF PRESENTATION	vi
ORIGINAL CONTRIBUTION	vi
TABLE OF CONTENTS	v
LIST OF FIGURES	x
LIST OF TABLES	xi

CHAPTER 1: Petrology and eruptive history of the Late Devonian Mount Pleasant caldera complex, Canadian Appalachians. by S.R. McCutcheon and

H.E. Anderson	1
Abstract	1
Introduction	2
Regional geology and tectonic setting	3
Stratigraphy of the caldera complex	6
The exocaldera sequence	6
The intracaldera sequence	11
The late caldera-fill sequence	15
Petrography and mineral chemistry of the igneous rocks	18
Mineralogy and mineral chemistry	18
Mica	20
Amphibole	20
Pyroxene	22
Olivine	24
Accessory minerals	24
Feldspars	26
Quartz	29
Implications of phenocryst textures	29
Lithochemistry	31
Classification	31
Mafic rocks	33
Chemical variation	33
Tectonic discrimination and petrogenesis	35

Felsic rocks	35
Chemical variation	35
Tectonic discrimination and petrogenesis	37
Conclusions	43
Caldera recognition	43
Correlation of intracaldera and exocaldera stratigraphy	44
Magmatic evolution	45
Eruptive history	46
Tectonic implications	49
Acknowledgments	49
References	50
CHAPTER 2: Magmatic evolution of the epizonal magma chamber of the Mount Pleasant Caldera complex: Part 1. evidence from Rb/Sr geochronology, and O isotope and trace element geochemistry.	56
Abstract	56
Introduction	57
Tectonic setting and geology of the caldera complex	59
Analytical methods	64
Results	66
Oxygen isotopic variations	66
Rb-Sr geochronology	68
$^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios (Sr_i)	72
Modelling the magmatic evolution of the magma chamber(s)	73
Descriptive geochemistry and process identification	73
Discussion and Conclusions	78
Comparison with previous dating attempts	78
Geophysical setting of the magma chamber	82
Implications for felsic magmatism in the northern Appalachians	83
References	84
CHAPTER 3: Magmatic evolution of the epizonal magma chamber of the Mount Pleasant Caldera complex: Part 2. Evidence from Pearce Element Ratio analysis of chemical variation in the igneous rocks.	90
Abstract	90
Introduction	91
Geology of the caldera complex	94
Petrography of the intracaldera igneous rocks	96

	ix
Analytical Methods	99
Modelling the magmatic evolution of the magma chamber(s)	99
Introduction	99
Descriptive geochemistry	100
Pearce Element Ratio modelling of major element variation	106
Trace element modelling	112
Discussion	117
Fluid dynamics of magma chambers	118
Implications of the model for magmatic evolution of the Mount Pleasant Caldera	120
Implications for fluid dynamics of the magma chamber	122
Conclusions	125
References	127
CHAPTER 4: Evolution of mantle-derived magmatism in post-compressional lithosphere of the northern Appalachian Orogen: isotopic and trace element evidence from the Mount Pleasant Caldera complex, New Brunswick, Canada.	131
Abstract	131
Introduction	132
Geologic setting	133
Analytical methods	138
Results	139
O and Sr isotopic data	139
Pb isotopic data	141
Nd isotopic data	148
Trace element systematics	153
Discussion	157
Mantle reservoirs	159
Crustal reservoirs	160
Model of magmatic evolution of the Mount Pleasant caldera in the lithosphere	164
Tectonic implications	166
Conclusion	168
References	169

APPENDICES

Appendix A-1: Table of whole-rock geochemical analyses
A-1

LIST OF FIGURES

Figure 1-1. Tectonic lithofacies map of southwestern New Brunswick and location of Mount Pleasant Caldera complex (after Fyffe et al., 1991).	4
Figure 1-2. Geology of the Mount Pleasant Caldera complex.	7
Figure 1-3. Volcanic textures of the exocaldera sequence.	10
Figure 1-4. Field relations and rock textures of intracaldera rocks.	13
Figure 1-5. Field relations and rock textures of late caldera-fill rocks.	17
Figure 1-6. Composition of white micas.	21
Figure 1-7. Pyroxene compositions.	23
Figure 1-8. Plot of CeO_2 (wt %) vs. SiO_2 (wt %) of apatite.	25
Figure 1-9. Photomicrographs of feldspar and quartz phenocrysts and xenocrysts.	28
Figure 1-10. Classification of Piskahegan Group igneous rocks.	32
Figure 1-11. Chemical variation diagrams of selected major and trace elements from Piskahegan Group igneous rocks.	34
Figure 1-12. Primitive mantle normalized incompatible trace element plot of Piskahegan Group basalts and andesites.	36
Figure 1-13. Chondrite-normalized REE plots of felsic volcanic rocks.	39
Figure 1-14. Rb versus (Y + Nb) tectonic discriminant diagram for granitic rocks after Pearce et al. (1984) with samples from McDougall Brook Microgranite.	41
Figure 1-15. Enrichment-depletion diagram for a single cooling unit of the Rothea Formation.	42
Figure 1-16. Eruptive history of the Mount Pleasant Caldera.	47
Figure 2-1. Tectonic lithofacies map of southwestern New Brunswick.	58
Figure 2-2. Geology of the Mount Pleasant Caldera complex.	61
Figure 2-3. Variations of A. Sr, B. Rb and C. $^{87}\text{Rb}/^{86}\text{Sr}$ as functions of $\delta^{18}\text{O}$ variation.	67
Figure 2-4. Plots of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{87}\text{Rb}/^{86}\text{Sr}$.	69
Figure 2-5. Variations of A. $\delta^{18}\text{O}$, and B. Sr as functions of Sr_i variation.	71
Figure 2-6. Plot of Rb (ppm) versus Th (ppm).	76
Figure 2-7. Model curves for fractional crystallization and batch partial melting compared with variations of a highly compatible trace element (Sr) and a highly incompatible trace element (Rb) in the caldera volcanic rocks.	77
Figure 2-8. Plots of log of selected trace elements (ppm) versus log Th (ppm).	79

Figure 3-1. Geology of the Piskahegan Group comprising the Mount Pleasant Caldera and related outflow facies rocks.	95
Figure 3-2. Plots of log value of selected trace elements (ppm) versus log Th (ppm).	103
Figure 3-3. Simple-numerator PER variation diagrams with Th as the common denominator.	105
Figure 3-4. Complex-numerator "assemblage test " diagrams.	109
Figure 3-5. Comparison of model and actual trace element variations of Mt. Pleasant igneous rocks.	116
Figure 3-6. Fluid dynamic model of the Mount Pleasant magma chamber.	123
Figure 4-1. Location of Mount Pleasant caldera complex and tectonic lithofacies map of southwestern New Brunswick.	134
Figure 4-2. Geology of the Mount Pleasant caldera complex.	137
Figure 4-3. Variations of $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$ as functions of $\delta^{18}\text{O}$ variation.	140
Figure 4-4. Variations of $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$, ϵ_{ND} , and T_{DM} as a function of SiO_2 variation.	142
Figure 4-5. Variations in measured Pb isotopic ratios as a function of $\delta^{18}\text{O}$ variation.	145
Figure 4-6. Common Pb secondary isochron diagrams.	146
Figure 4-7. Sr-Nd anticorrelation diagram.	151
Figure 4-8. Ta/Yb versus Th/Yb diagram of Piskahegan Group basalts and andesites.	155
Figure 4-9. Normalized plots of trace element abundances in Mount Pleasant basalts and andesites.	156
Figure 4-10. Model of magmatic evolution of the Mount Pleasant Caldera complex in the lithosphere.	165
Figure 4-11. Model of gravitational subduction of mantle lithosphere in the post-tectonic northern Appalachians.	167

LIST OF TABLES

Table 1-1. Petrography of igneous rocks of the Mount Pleasant Caldera complex.	19
Table 2-1. Rb-Sr and oxygen isotopic data for Mount Pleasant igneous rocks.	65

Table 2-2. Phenocryst and groundmass mineralogy of selected igneous rocks of the Mount Pleasant caldera complex.	74
Table 2-3. Summary of geochronological data for the Mount Pleasant area.	81
Table 3-1. Phenocryst and groundmass mineralogy of selected igneous rocks of the Mount Pleasant caldera complex.	98
Table 3-2. Mineral composition matrix for igneous rocks of the Mount Pleasant Caldera.	107
Table 3-3. Regression slopes, intercepts and errors for complex-numerator PER diagrams of igneous rocks of the Mount Pleasant Caldera.	108
Table 3-4. Regression slopes, intercepts and errors for complex-numerator PER diagrams of igneous rocks of the Mount Pleasant Caldera.	111
Table 3-5. Mineral assemblage for stages 1 and 2 fractionation based on PER analysis and mineral/melt and bulk partition coefficients assigned to selected trace elements for use in trace element forward modelling.	113
Table 4-1. Pb isotopic data.	143
Table 4-2. Model Pb parameters for AFC curves in Fig. 4-5.	147
Table 4-3. Sm and Nd isotopic data for Mount Pleasant igneous rocks.	149
Table 4-4. Model Nd and Sr parameters for AFC curves in Fig. 4-7.	152

In loving memory of my brother

Nels Anderson II

CHAPTER 1. Petrology and eruptive history of the Late Devonian Mount Pleasant Caldera complex, Canadian Appalachians

ABSTRACT

Stratigraphic, petrographic, and geochemical evidence indicate that the volcano-sedimentary rocks of the Late Devonian Piskahagan Group, located in the northern Appalachians of southern New Brunswick, represent the eroded remnants of a large epicontinental caldera complex. This complex – the Mount Pleasant Caldera – is one of few recognizable pre-Cenozoic calderas. An intracaldera sequence that crops out in a triangular-shaped area consists of: thick ash flow tuffs; thick sedimentary breccias that dip inward, and; stocks of intermediate to felsic composition that intrude the volcanic pile or are localized along caldera-margin faults. The intracaldera sequence exhibits a gravity low suggesting that it is underlain by granitic plutons. An exocaldera sequence includes ash flow and air fall tuffs, mafic lavas, alluvial redbeds and porphyritic lava flows that comprise five formations. A late caldera-fill sequence contains rocks that are similar to those of the outflow facies and comprises three formations.

Geochemical and mineralogical data indicate that the basaltic rocks are mantle-derived, high-K tholeiites with intraplate chemical affinities. The andesites were probably derived from basaltic magma by fractional crystallization and assimilation of crustal material. The andesites and more felsic rocks form a high-K, apparently calcalkaline series with post-collision chemical affinities. They could be derived from mafic magma that differentiated at depth in the crust. Alternatively the felsic rocks could be unrelated to the andesites and represent partial melts of lower crustal rocks, and if so are not

differentiates of a calcalkaline series. The various felsic units are related by episodes of fractional crystallization in a high level zoned magma chamber. Fractionation was repeatedly interrupted by eruption of material from the roof zone such that seven stages of caldera development have been identified. The genesis of the caldera is related to a period of crustal thinning that followed the Acadian Orogeny in the northern Appalachians.

INTRODUCTION

Most of the known epicontinental caldera complexes in the world are of Cenozoic age, probably because older complexes are buried or have been modified by tectonic and/or erosional processes to such an extent that they can rarely be recognized. Some pre-Cenozoic examples have been described, including the Precambrian Butler Hill Caldera in Missouri (Sides *et al.*, 1984), the Silurian Springdale complex in Newfoundland (Coyle and Strong, 1987), the Permian cauldrons of the Oslo rift in Norway (Ofstedahl, 1978), and the famous Glen Coe complex in Britain (Clough *et al.*, 1909). The Mount Pleasant Caldera, located in southern New Brunswick, is one of only two known calderas in the northern Appalachians. Previous workers postulated that this volcanic complex had been erupted from a caldera but the stratigraphy was not documented and a specific intracaldera sequence was not recognized (McCutcheon, 1991). In this paper the stratigraphy, mineralogy and chemistry of the Mount Pleasant Caldera are examined in detail. From these lines of evidence the petrology and eruptive history of the complex are deduced.

"Epicontinental-type" calderas are underlain by continental crust and are formed by collapse of the roof of an epizonal magma chamber in response to voluminous eruptions of magma. They have large diameters (several kilometers) and are characterized by eruption volumes greater than 100 km^3 (Smith, 1979). Siliceous ash flow tuffs

dominate the eruptive products. Caldera complexes are directly related to high-level granite plutons of batholithic dimensions (Burnham, 1979; Lipman, 1984). The magmas in these plutons, at the time of emplacement, must have had high temperatures and been undersaturated with respect to an aqueous vapour phase – otherwise they would not have reached shallow crustal depths (c.f. Pitcher, 1979; Clemens, 1984) where caldera collapse can occur. According to Lipman (1984) calderas have the following physical features: 1) they are subsidence structures with steep boundary faults; 2) they generally have negative gravity expression; 3) they are characterized by different lithofacies at successive levels of erosion; 4) they have distinct intracaldera and caldera outflow facies and; 5) they have a generalized life cycle that includes precollapse, collapse, resurgence, and caldera-fill stages.

Many ash flow tuffs erupted from calderas exhibit mineralogical and chemical zonation reflecting gradients that existed in the magma chamber just prior to eruption (e.g., Lipman, et al. 1966; Baker and McBirney, 1985). The longer the repose time in the magma chamber between eruptions, the better this zonation is manifested in the eruptive products (Smith, 1979), which may include high-silica rhyolites.

REGIONAL GEOLOGY AND TECTONIC SETTING

Southwestern New Brunswick, excluding strata within the Maritimes Basin, consists of several northeast-trending fault blocks that contain rocks ranging in age from Precambrian to Late Devonian. These blocks comprise two terranes and a cover sequence (Fyffe et al., 1992) as shown in Figure 1-1. The configuration of the various fault blocks was largely established during the Acadian Orogeny (McCutcheon, 1981; Ruitenberg and McCutcheon, 1982; McCutcheon and Robinson, 1987). Deformation accompanying the Acadian Orogeny imparted a generally northeasterly-trending structural fabric to the rocks and produced numerous northeasterly- and northwesterly-trending faults, many of

Figure 1-1. Tectonic lithofacies map of southwestern New Brunswick (after Fyffe et al., 1992) with location of the Mount Pleasant Caldera complex.

which were re-activated during Devonian-Carboniferous time (Ruitenberg and McCutcheon, 1982).

A period of syn-Acadian magmatism is manifested by bimodal volcanism (van Waggoner and Fay, 1988) of the Upper Silurian to Lower Devonian Mascarene Cover Sequence (Fig. 1-1). These interbedded volcanic and sedimentary rocks are compressed into broad open folds and the sedimentary rocks have cleavage indicating that compressional tectonism was still active after the time of deposition. A period of granitoid "Acadian plutonism" overlapped with and followed this volcanism (Fyffe et al., 1981). Isotopic and field evidence from these granitoids indicates that Acadian polyphase deformation took place in Silurian to Middle Devonian time (Hubacher and Lux, 1987; Bevier, 1988; MacLellan and Taylor, 1989; McCutcheon and Bevier, 1990). The post-tectonic Mount Douglas Granite, comprising the youngest and highest-level phases of the Saint George Batholith, has a Late Devonian age (367 Ma) based on U/Pb (Bevier, 1988) and $^{40}\text{Ar}/^{39}\text{Ar}$ (McLeod et al., 1988) dates. The Mount Pleasant Caldera, with a 368 Ma Rb/Sr isochron age (see Chapter 2), is the same age as the Mount Douglas Granite and together they comprise the last major products of this protracted period of magmatism.

The late- to post-Acadian magmatism was followed closely by formation of the Maritimes Basin by tensional collapse and thermal subsidence that followed Acadian continental collision (McCutcheon and Robinson, 1987; Durling and Marillier, 1990). The Late Devonian and Carboniferous rocks of the Basin are the product of an aborted-rift environment as indicated by structural, magmatic and geophysical evidence of widespread crustal extension (McCutcheon and Robinson, 1987; Fyffe and Barr, 1986; Durling and Marillier, 1990). The Piskahegan rocks were deposited just before or during the initial rapid-subsidence stage of basin development, as were a number of other volcanic suites in Nova Scotia and Newfoundland (McCutcheon and Robinson, 1987).

STRATIGRAPHY OF THE CALDERA COMPLEX

The Mount Pleasant Caldera is a north-south trending, triangular feature with minimum dimensions of 13 by 34 km based on regional gravity and magnetic maps (Williams, 1978). Rocks of granitic composition are not confined to the caldera because the associated gravity low extends to the west. The northern half of the caldera is concealed by overlying Middle Mississippian and Pennsylvanian strata of the Maritimes Basin.

Rocks of the caldera complex comprise the Late Devonian Piskahegan Group (McGregor and McCutcheon, 1988) that is divisible into intracaldera, exocaldera, and late caldera-fill sequences (e.g. McCutcheon, 1991 and Fig. 1-2). Each is described briefly below.

The Exocaldera Sequence

The exocaldera sequence, in ascending stratigraphic order, consists of the Hoyt Station Basalt, Rothea Formation, South Oromocto Andesite, Carrow Formation, and Bailey Rock Rhyolite. The first and last units have the least areal extent.

The Hoyt Station Basalt contains at least two flow units with minor associated pebble- to cobble-conglomerate and lithic lapilli tuff. The basalt is characterized by zoned, sieve-textured plagioclase phenocrysts and quartz xenocrysts.

The Rothea Formation is divisible, in ascending order, into the Sophia, Juvenile and Image Brook members. The Sophia member is further divisible into two cooling units - a lower, unwelded but compacted, pumiceous lapilli-tuff (Fig. 1-3A) and an upper welded unit comprising two crystal tuffs. The upper unit invariably has around 1% altered biotite. The Juvenile Member grades from nearly aphyric tuff at the base to crystal tuff at the top. The Image Brook Member consists of a lower fine-grained redbed unit and an upper lithic tuff. The lithic clasts lack a penetrative fabric and, therefore, were derived from rocks that post-date the Acadian Orogeny. The absence of internal

Figure 1-2. Geology of the Piskahagan Group comprising the Mount Pleasant Caldera complex and related outflow facies rocks (after McCutcheon, 1991)

layering, presence of broken crystals, shard textures, eutaxitic foliation, and areal extent of the units indicate that the Rothea tuffs represent a sequence of ash flows.

The South Oromocto Andesite is composed of at least three lava flows with the basal flow being the most areally extensive and the only one exhibiting porphyritic texture. Calcite veins and hematite bands near the tops result from degassing of the flow interiors. In the Image Brook area, the andesite abuts the Image Brook Member and overlies the Sophia Member of the Rothea Formation.

The Carrow Formation is an alluvial fan deposit (McGregor and McCutcheon, 1988) dominated by a fining-upward redbed unit that grades from pebble- to cobble-conglomerate at the base to mudstone with intercalated calcrete at the top. Toward the southwest the conglomerate contains abundant clasts of the Seelys and Rothea Formations, but to the northeast, metasedimentary clasts predominate. In the lower part of this formation there is an unwelded but highly compacted, pumiceous lapilli tuff. Near the southwestern end of the Carrow outcrop belt, basalt and a basalt-clast mud flow deposit occur near the top of the formation. A spore locality from the upper part of the Carrow Formation has yielded a precise Late Famennian age (MacGregor and McCutcheon, 1988).

The Bailey Rock Rhyolite is a quartz- and feldspar-phyric lava flow. The groundmass is generally recrystallized but at one locality it is merely devitrified and textures such as flow-banding, perlitic cracks, and spherulites are well preserved (Fig. 1-3B). The contact between the Bailey Rock Rhyolite and Carrow Formation at one locality is inferred to be intrusive because phenocrysts in the rhyolite fine toward the contact. The distribution of the rhyolite around the periphery of the caldera margin suggests that it was extruded from the "ring fracture zone" of the caldera. It is unique in that it crosses the boundary between the exocaldera and intracaldera sequences (Fig. 1-2). A saprolite separates the Bailey Rock from the overlying late caldera-fill sequence (Kleef Formation).

Figure 1-3. Volcanic textures of the exocaldera sequence. A. Photomicrograph of shard texture in the lower member of the Rothea Formation. B. Photomicrograph of remnant spherulitic texture in the Bailey Rock Rhyolite. Plane light.

0.1 mm

A

1 mm

B

The Intracaldera Sequence

The intracaldera rocks comprise, in ascending stratigraphic order, the Scoullar Mountain Formation, Little Mount Pleasant Formation, Seelys Formation and McDougall Brook Porphyritic Microgranite. In addition, there are felsic dykes and one mafic dyke that intrude the Scoullar Mountain and Little Mount Pleasant Formations, respectively.

The Scoullar Mountain Formation is characterized by sedimentary breccia and interbedded andesitic lava flows but felsic pyroclastic rocks occur locally and one sandstone-conglomerate unit is present. The sedimentary breccia is dominated by angular, unsorted, pebble- to boulder-size, angular, metasedimentary fragments in a comminuted matrix of the same material (Fig. 1-4A). Minor clasts of undeformed crystal tuff containing about 1% altered biotite phenocrysts are also present. Internal layering and a water-worked matrix are rare. These breccias were probably formed from talus and/or other types of colluvium that were shed from the ring-fracture fault scarp of the caldera. A pumiceous lapilli tuff near the apparent top of the formation has about 1% amphibole and accessory apatite. Intraformational folding in another tuff is indicative of post-depositional flowage, suggesting that this tuff was deposited on a slope - probably the talus slope at the caldera margin. These tuffs are considered to be ash flow deposits because they are unbedded and contain well-developed eutaxitic foliation and pumice pseudomorphs. The Scoullar Mountain Formation is overlain by the Little Mount Pleasant Formation (Sinclair et al., 1988).

The Little Mount Pleasant Formation comprises a basal flow-banded rhyolite and two crystal tuff units. The tuff units are characterized by distinctive, unflattened to weakly flattened, microcrystalline, recrystallized pumice fragments (Fig. 1-4B) and chloritized amphibole with associated apatite, features that readily distinguish them from tuffs of the Seelys Formation. Phenocrysts inside these recrystallized pumice fragments are an order of magnitude larger than those outside, indicating significant mechanical

Figure 1-4. Field relations and rock textures of intracaldera rocks. A. Cut slab of sedimentary breccia with crystal tuff clast (white) at upper left. B. Cut slab of pumiceous crystal tuff from the Little Mount Pleasant Formation with unflattened pumice fragment in upper right. C. Cut slab of pumiceous crystal tuff from the Seelys Formation with well-developed eutaxitic foliation. D. Outcrop showing granitoid xenolith in McDougall Brook Porphyritic Microgranite. Small divisions on scale in A, B, and C are in millimetres.

breakage of phenocrysts during eruption. These tuffs are considered to be pyroclastic flow deposits. The Mount Pleasant Mine area is believed to be an eruptive centre for Little Mount Pleasant tuffs because these rocks have intrusive contacts with metasedimentary rocks at the Mount Pleasant Mine portal and at Little Mount Pleasant (Kooiman et al., 1986).

The Seelys Formation, in ascending stratigraphic order, consists of: lithic tuffs and pumice-bearing, lithic lapilli tuffs; banded, pumiceous crystal tuff and; densely welded crystal tuff. The Seelys tuffs are generally characterized by a well-developed eutaxitic foliation and broken phenocrysts (Fig. 1-4C) indicating that they are pyroclastic flow deposits. Quartz and feldspar phenocrysts increase in size and abundance from base to top in the upper unit, probably reflecting phenocryst gradients in the source magma chamber. Biotite is rarely observed and other ferromagnesian phenocrysts are absent. The basal unit contains clasts of metasedimentary rocks, Scoullar Mountain andesite, and Little Mount Pleasant rhyolite. The Seelys Formation is inferred to underlie the Bailey Rock Rhyolite because of the map distribution of these two units (Fig. 1-2) and because conglomerate of the Carrow Formation contains clasts of Seelys tuff.

The McDougall Brook Porphyritic Microgranite consists mostly of porphyritic, allotriomorphic granular to micrographic monzogranite with a marginal unit consisting of feldspar (+/- quartz) porphyry and minor equigranular to subporphyritic, fine-grained, quartz monzonite (IUGS classification; LeMaitre, 1989). The grain size of the groundmass of the porphyry and the size and abundance of feldspar phenocrysts both increase inward, away from the contacts. Chloritized amphibole with associated apatite is the main ferromagnesian phase in all three units. Mineralogical and textural variations in these rocks (i.e., from aphanitic rocks with quartz-feldspar phenocrysts at the contact to more ferromagnesian mineral-rich, fine-grained interior rocks with variable textures and phenocryst contents) may indicate that the original magma was compositionally zoned or that there was more than one injection of magma into the chamber. The McDougall

Brook Microgranite is observed to intrude the Seelys Formation to the northeast of Big Scott Mountain. Large roof pendants of Little Mount Pleasant Formation, and occasional xenoliths of granitic (Fig. 1-4D) and metasedimentary rock have been observed in the microgranite. Sinclair et al. (1988) infer that the McDougall Brook Microgranite is extrusive rather than intrusive in the Mount Pleasant Mine area.

The Late Caldera-Fill Sequence

The late caldera-fill rocks include the Mount Pleasant Porphyry and its associated breccias, unnamed rapakivi dykes, the Big Scott Mountain Formation and the Kleef Formation. The first two units are separated spatially, both from each other and from the other two formations. The late caldera-fill sequence is younger than both the exocaldera and intracaldera sequences. The ages of these rocks are most likely Late Devonian but could range into the Mississippian.

The Mount Pleasant Porphyry is restricted to the area of the Mount Pleasant Mine where it occurs as flow-banded dykes (Fig. 1-5A) and small, plug-like bodies. Crosscutting relationships between the dykes (and between equivalent microgranites and porphyries in drill holes and underground workings) indicate multiple stages of intrusion. Two types of magmatic-hydrothermal alteration are associated with these rocks: 1) an older and more voluminous quartz-topaz type associated with extensive brecciation and tungsten-molybdenum deposits, and; 2) a younger, chloritic type associated with tin deposits (Kooiman et al., 1986).

Rapakivi dykes are composite bodies with leucocratic, porphyritic centres and melanocratic, sparsely porphyritic margins. The rocks are characterized by large phenocrysts of quartz and feldspar (Fig. 1-5B). In one locality, a porphyritic rhyolite that is lithologically similar to these dyke rocks is considered to be their extrusive equivalent.

The Big Scott Mountain Formation consists of, in ascending order, porphyritic to nearly aphyric rhyolite, lithic to lithic-lapilli tuff and crystal tuff. The rhyolites are

Figure 1-5. Field relations and rock textures of late caldera-fill rocks. A. Outcrop of flow-banded dyke of the Mount Pleasant Porphyry with country rock xenolith. B. Cut slab from a rapakivi dyke with large rapakivi feldspar (top left) and a nearly aphyric mafic xenolith (bottom right). C. Bedded tuff of the Big Scott Mtn. Formation with a large boulder-size clast. Note compaction of bedding around the clast.

generally characterized by pseudomorphs after pyroxene, sparse pseudomorphs after biotite, and low quartz abundances, features indicative of high emplacement temperatures and low water contents of the magma(s). Primary layering is discernible in the crystal tuff (Fig. 1-5C) indicating that these tuffs are air fall deposits derived from a Plinian eruption. One of the rhyolite units appears to disconformably overlie McDougall Brook Microgranite. The lithic tuffs contain clasts that were derived from Seelys tuff and McDougall Brook Microgranite.

The Kleef Formation, from base to top, includes conglomeratic redbeds, porphyritic to glomeroporphyritic basalt and pumiceous, lithic tuff to lithic lapilli tuff. The redbeds are considered to be debris flows because they form thick layers, lack internal bedding, and are poorly sorted. Pebble- to cobble-conglomerates contain clasts of Scoullar Mountain and Seelys tuffs, and Bailey Rock and Big Scott Mountain rhyolites that were derived from the south. The basalt has diabasic to subophitic textures and large plagioclase phenocrysts (up to 2 cm) that become even coarser and glomeroporphyritic near the top of the unit. The lithic tuffs are characterized by a reddish-brown colour, abundant fossil pumice, angular quartz, and lack of internal layering indicating that they originated from a pyroclastic flow. The Kleef Formation is disconformably overlain by post-volcanic redbeds of the Shin Formation, which postdates the middle Mississippian (Visean) Windsor Group.

PETROGRAPHY AND MINERAL CHEMISTRY OF THE IGNEOUS ROCKS

Mineralogy and Mineral Chemistry

Although igneous textures are generally well-preserved in the Piskahegan Group rocks, the primary mineralogy is not well preserved. The petrographic features of the major igneous lithologies are summarized in Table 1-1. The principal phenocryst phases in the felsic rocks, in their most common order of abundance, are quartz, K-feldspar,

Table 1-1. Petrography of igneous rocks of the Mount Pleasant caldera complex. Lithologies are increasingly felsic from top to bottom of the table. An = anorthite content of Pl; Ap = apatite; Az = azurite; Bt = biotite; Chl = chlorite; Cpx = clinopyroxene; Hbl = hornblende; Kfs = K-feldspar; Mal = malachite; Ol = olivine; Or = orthoclase content of Kfs; Pl = plagioclase content of Kfs; Pl-mag = titanomagnetite; Qtz = quartz; Zrn = zircon.

Formation/ Lithodeme Unit	Quartz	K-feldspar	Plagioclase	Biotite	Amphibole	Pyroxene	Accessory Minerals	Mineralogy	Texture
Mount Pleasant Basalt			50%-45% An, locally abraded					Pl, Cpx, Ti-mag, Ap, Chl	diabasic to subdiabasic; amphibolized with Qtz, Chl, Horn, Hbl and Az near top
Mount Pleasant Basalt	microcrystic quartz		75%-31% An; some textured; sericitized; co-aligned cores					Pl, Cpx, Ti-mag, Chl	massive; diabasic; locally amphibolized
Mount Pleasant Basalt			rare; abraded					Pl, Chl	diabasic; amphibolized
Mount Pleasant Basalt			60%-47% An; rare slime texture			1 mm; some augite	Qtz(?) pseudomorphs	Pl, Cpx, Ti-mag	massive; crystal to micro-crystalline; upper basalt non-porphritic; top amphibolized
Mount Pleasant Basalt			tubid; variably sericitized; sericitized	Chl pseudomorphs		locally chloritized	Qtz(?) pseudomorphs; maritized Ti- mag; Ag	Pl, Chl, Ti-mag; local interstitial Kfs and Qtz	massive to amphibolized; plagioclase; microcrystalline or micro-pelitic
Mount Pleasant Basalt	apophanitic; re-entrants; abraded	irregular texture; < 3 cm; abraded; re-entrants; 80% Or; locally abraded	< 3 cm; abraded; locally developed slime texture				maritized Ti- mag; Ag		microcrystalline
Mount Pleasant Basalt	apophanitic re- entrants; abraded	coarse patch porphyritic	44%-20% An, locally abraded	partially chloritized		minor; some in some amorph phenocrysts	maritized Ti- mag; Ag; Zn	Kfs, Pl, Qtz, Hbl, Ti-mag, Ap; Bt locally	diabasic granular to microcrystalline; contact-pseudomorph locally crystalline
Mount Pleasant Basalt	apophanitic; re-entrants; abraded	67% Or; coarse patch porphyritic	abraded				maritized Ti- mag; Ag; Zn		crystalline or microcrystalline; micro-pelitic Qtz-Kfs intergrowths; locally sericitized; base-banded; porphyritic textures; glaucophane
Mount Pleasant Basalt	broken	broken; tubid; sericitized; locally porphyritic	commonly abraded; locally 23%-21% An; broken	chloritized			maritized Ti- mag; Ag; Zn		unabraded; large well-defined coarse porphyritic; contact relation body
Mount Pleasant Basalt	broken	broken; tubid; sericitized; locally abraded	broken	plagioclase abraded		possible pseudomorphs	Zn; Ti-mag		contact relation; spherulitic; pseudomorphous porphyritic fragments; chaotic; middle unit has apophanitic base grading to crystal-rich top
Mount Pleasant Basalt	broken	67% Or; broken	abraded; broken			possible pseudomorphs	maritized Ti- mag; Ag; Zn		contact relation
Mount Pleasant Basalt	broken	60% Or; broken; tubid; sericitized; locally microcrystalline	abraded; broken	rare; plagioclase			new Ti-mag; maritized Zn		contact relation; zoned with increasing phenocryst abundance from base to top
Mount Pleasant Basalt	subhedral to subhedral crystals; no re-entrants	CH + Zn + Pl alteration	minor; sericitized; inclusions in pseudomorphed Kfs	colored grain boundaries; partially chloritized			trace Zn		base banding
Mount Pleasant Basalt	broken	broken		pseudomorphs					massive; contact relation; weakly bedded (crystal sizes graded)
Mount Pleasant Basalt	minor; < 1 mm	minor; < 3.5 mm	abraded	pseudomorphs		minor; pseudomorphs			base layering

plagioclase, biotite, magnetite, zircon, and apatite. In a few units, pseudomorphs of pyroxene and/or amphibole are present instead of biotite. The main mineral phases in the mafic rocks are plagioclase, clinopyroxene, amphibole, and opaque oxides. The ferromagnesian mineral assemblage displays the classic calcalkaline trend pyroxene → amphibole → biotite going from mafic to felsic lithologies (Table 1-1).

Commonly, the only pristine phenocryst phases are quartz, zircon, and apatite. Rare magnetite microphenocrysts trapped in quartz are well preserved but most magnetite grains exhibit evidence of oxidation and exsolution. The textures and mineralogies of these rocks record a variety of magmatic and post-magmatic processes that have affected the volcanic rocks of the Mount Pleasant Caldera.

Mica

Biotite phenocrysts or their pseudomorphs only occur in felsic caldera rocks (see Table 1-1). Biotite is best preserved in the Rothea Formation (exocaldera sequence), where it may retain its original brown to reddish-brown pleochroism, with opaque oxide inclusions along cleavage planes. Biotite is commonly partially to completely pseudomorphed by either chlorite or by muscovite with trains of opaque inclusions defining original cleavage planes, particularly in the intracaldera rocks. This secondary white mica has low titanium and high iron contents (Fig. 1-6A) indicating a deuteric origin. Such an origin is also suggested by compositions between ideal muscovite and ideal phengite, with points scattered about the muscovite-phengite join (Fig. 1-6B). This is in marked contrast to typical metamorphic micas that plot to the left of this line, more toward the ferriphengite endmember (cf. Guidotti, 1984; his Fig. 1-6).

Amphibole

Amphibole occurs mainly in intracaldera igneous rocks with intermediate silica content (see Table 1-1). The least altered grains generally are dark brownish-green,

Figure 1-6. Compositions of white micas. A. $\text{Fe}_2\text{O}_3 - \text{TiO}_2^{\text{T}} - \text{MgO}$ plot after Monier et al. (1984). B. $\text{Al}_{(\text{iv})} - \text{Al}_{(\text{vi})} - (\text{Mg} + \text{Fe})$ plot after Guidotti (1984). Circled dots are samples with fewer than 3.25 atoms per formula unit.

anhedral to subhedral crystals that occur most commonly in glomeroporphyritic clusters with plagioclase, opaque oxides, and apatite. Remnant clinopyroxene cores indicate that amphibole crystallized after pyroxene and inclusion relationships show that most amphibole crystallized together with plagioclase, magnetite, and apatite. The McDougall Brook Microgranite contains a second population of younger, bluish-green amphibole occurring as subhedral overgrowths on the phenocrysts or as separate interstitial crystals intergrown with K-feldspar and quartz in the groundmass. Amphibole occurs as inclusions in quartz in the Juvenile Member of the Rothea Formation. In addition, pseudomorphs after pyroxene and/or amphibole occur in other units (see Table 1-1).

Amphibole is commonly partially to completely altered to assemblages of chlorite, epidote $\pm$ titanite $\pm$ calcite so that its original composition can seldom be determined. However, the McDougall Brook Porphyritic Microgranite contains fresh calcic amphiboles ($\text{Ca} + \text{Na}_{\text{ap}} \geq 1.34$ and $\text{Na}_{\text{ap}} < 0.67$) classified as hornblende using the scheme of Hawthorne (1981) or as edenite according to Giret et al. (1980). According to Giret et al., amphiboles with this composition belong to the "interstitial texture type" that formed in the "late magmatic to subsolidus stage of crystallization" and began to crystallize from magmas that were not yet saturated with respect to water.

Pyroxene

Pyroxene occurs in all of the mafic rocks of the caldera complex as subhedral phenocrysts, in anhedral ophitic intergrowths in the groundmass, or as inclusions in plagioclase. In some pyroxene phenocrysts, cores and rims have different colour and optical extinction angles. Microprobe analyses indicate that the pyroxene is augite (Fig. 1-7A); neither pigeonite nor orthopyroxene have been observed and are presumed not to have crystallized. All of the augites are more calcic than the early part of the Skaergaard augite trend (Wager and Brown, 1968), which is consistent with the interpretation that they crystallized on a single-pyroxene surface of the liquidus. In general, the augites are

Figure 1-7. Pyroxene compositions. **A.** Pyroxene quadrilateral (after Deer et al., 1966) with microprobe analyses plotting in the augite field. **B.** Ca + Na vs. Ti plot Piskahegan Group data plotting in the subalkaline field. **C.** Ca vs. (Ti + Cr) plot with Piskahegan Group data plotting mainly in the anorogenic field. **B.** and **C.** after Leterrier et al. (1982). Arrows connect core to rim compositions in the Hoyt Station basalt and separate populations in the rapakivi dykes.

restricted in composition (Fig. 1-7) although in the Kleef basalts, they contain relatively high Ti contents, and in the Hoyt Station basalt high-Ti and -Ca phenocryst cores are zoned to low-Ti and -Ca rims, with high Mg and Fe contents comparable to groundmass grains. On the tectonic discrimination diagrams of Leterrier et al. (1982) the pyroxene compositions plot in the "tholeiitic + calcalkalic" field (Fig. 1-7B) and predominantly in the "non-orogenic" field (Fig. 1-7C).

Pyroxene is less common in the felsic rocks. Clinopyroxene occurs in the mafic margins of the rapakivi dykes and a few remnant clinopyroxenes are found in the cores of amphiboles in the McDougall Brook Porphyritic Microgranite.

Olivine

Pseudomorphs, inferred to be after olivine, have been found locally in Scoullar Mountain andesites. The pseudomorphs are subcircular to prismatic, with serpentine and/or chlorite interiors that are rimmed and cross-cut by opaque oxides. Locally they are partially enclosed in unaltered pyroxene. They more commonly occur in the groundmass and have chloritic reaction rims indicating that they were out of equilibrium with the magma at the time of groundmass crystallization.

Accessory Minerals

Apatite microphenocrysts occur in a variety of felsic to intermediate caldera rocks (see Table 1-1). In felsic rocks the apatites are generally euhedral, unaltered and zoned, with higher CeO_2 and SiO_2 contents in rims than in cores (Fig. 1-8). Apatites in the Scoullar Mountain andesites, locally making up as much as 1% of the rock, are unzoned with lower CeO_2 and SiO_2 than those from the felsic volcanic rocks.

Titanic magnetite microphenocrysts and groundmass grains occur in the Scoullar Mountain andesites but are more commonly confined to the groundmass in the other mafic rocks. They typically contain fine exsolution lamellae of hematite (martitization).

Figure 1-8. Plot of CeO_2 (wt. %) vs. SiO_2 (wt. %) of apatite. Arrows connect core to rim compositions.

The microphenocrysts occur both in the groundmass and as inclusions in the ferromagnesian minerals. They may in turn contain inclusions of apatite and zircon.

Subhedral to euhedral zircon is generally pristine except in the lower part of the Seelys Formation where it is metamict. The zircon may be zoned, with rare xenocrystic cores. Zircon commonly contains acicular apatite inclusions and occurs as inclusions in all minerals except apatite.

Feldspars

The felsic volcanic rocks of the caldera complex contain highly altered feldspars. K-feldspar is invariably turbid and contains highly variable amounts of coarse perthite. In the intracaldera rocks, K-feldspar may also be saussuritized locally. Harris (1964) reported finding remnant sanidine within microperthite of the Little Mount Pleasant tuff. Plagioclase phenocrysts are partially altered to sericite, which obscures or obliterates twinning and gives the crystals a speckled appearance. Microprobe analyses from different rock units indicate that most of the plagioclase has been albitized. Only one sample from the Little Mount Pleasant tuff contains remnant oligoclase.

All of the mafic caldera rocks contain plagioclase, in the groundmass as well as phenocrysts. Plagioclase is somewhat better preserved in mafic rocks compared to the felsic rocks and is rarely albitized. Plagioclase compositions in the South Oromocto Andesite, Scoullar Mountain andesite, and Kleef Basalt are in the range An_{68-47} . In the Hoyt Station Basalt, plagioclase compositions range from An_{31-39} in rims to An_{45-75} in cores.

Some plagioclase phenocrysts from the Hoyt Station basalt consist of large dendrites (i.e., an array of faceted, optically continuous crystals; Fig. 1-9A). Many of the phenocrysts contain zones of sieve textured material in otherwise faceted crystals (Fig. 1-9B). In the basalts, the inclusions in the sieve textured material comprise chlorite, pyroxene or opaque oxides.

Figure 1-9. Photomicrographs of feldspar and quartz phenocrysts and xenocrysts. A. Optically continuous plagioclase dendrite in Hoyt Station Basalt. B. Sieve-textured plagioclase in Hoyt Station Basalt. C. K-feldspar phenocryst in Bailey Rock Rhyolite with deep re-entrants and vermicular groundmass inclusions. D. Euhedral quartz phenocryst in Rothea tuff with re-entrant. E. Quartz phenocryst in Bailey Rock Rhyolite with cellular rim. F. Clinopyroxene-mantled quartz xenocryst with glass inclusion in Hoyt Station Basalt.

0.5mm

A

0.5mm

D

0.5mm

B

0.5mm

E

0.5mm

C

0.5mm

F

Quartz

Quartz is virtually unstrained in all of the volcanic rocks and commonly contains undevitrified glass inclusions, indicating that it was unaffected by compressional tectonism.

A variety of quartz morphologies are observed (Fig. 1-9D, E). For example, quartz phenocrysts in the McDougall Brook Microgranite are anhedral to subhedral with some re-entrants in crystal boundaries. Many crystals are rimmed by groundmass quartz that is in optical continuity with its host phenocryst. The rapakivi dykes contain quartz similar to that in the microgranite except that skeletal to dendritic crystals are more commonly developed. In the Bailey Rock Rhyolite, quartz phenocrysts have a variety of crystal shapes including: 1) euhedral dipyrmidal forms with characteristic square to diamond-shaped cross-sections; 2) dipyrmidal forms with deep re-entrants, and; 3) skeletal or cellular forms in which lobes of quartz protrude from a single crystal, growing around channels of groundmass material (Fig. 1-9E). In the tuffaceous rocks the crystals are commonly broken, indicating that they predated eruption.

Implications of Quartz and Feldspar Phenocryst Textures

Re-entrants in quartz phenocrysts have generally been considered to be the result of resorption. However, resorption should be accompanied by degradation of crystal faceting. The occurrence of faceted quartz crystals with re-entrants in rocks with a quartz-bearing groundmass requires an alternative explanation. Recent experimental studies (MacLellan and Trembath, 1991) indicate that all of the quartz textures described above can be produced by crystallization under different (but relatively rapid) cooling rate conditions of the magma. For example, euhedral to anhedral quartz with re-entrants (Fig. 1-9D) may form during relatively slow cooling. As the cooling rate increases, euhedral and skeletal crystals (Fig. 1-9E) become progressively more common relative to anhedral

crystals. These observations indicate that cooling rates were relatively slow in the McDougall Brook Microgranite, becoming progressively faster in the rapakivi dikes and Bailey Rock Rhyolite, an interpretation supported by the field relations.

Sieve-textured and dendritic plagioclase (Figs. 1-9D, E) and K-feldspar phenocrysts with vermicular re-entrants/inclusions (Fig. 1-9F) may also have crystallized under conditions of relatively rapid cooling. Sieve-textured plagioclase has been attributed to: 1) 'internal melting' accompanying resorption (Tsucheyama and Takahashi, 1983), or; 2) mixing of basaltic and rhyolitic magmas (Eichelberger, 1978). Plagioclase dendrites have been crystallized experimentally at temperatures well below the solidus without mixing (Lofgren, 1974). Partial infilling of dendritic crystals that formed during rapid cooling of the magma could also produce sieve-textured plagioclase. The sieve textured plagioclase of the Mount Pleasant Caldera was probably not produced by internal melting because the mafic inclusions commonly found in these crystals are unlikely products of plagioclase melting. Magma mixing and magma extrusion can both create conditions of rapid cooling and the textures of quartz coexisting with the sieve-textured feldspar may indicate which process is the most probable. The coexistence of sieve textured plagioclase and quartz xenocrysts (Fig. 1-9F) in the Hoyt Station Basalt, is most readily explained by mixing of a small amount of felsic magma with the basalt (cf. Stimac and Pearce, 1992). The coexistence of sieve-textured plagioclase and skeletal quartz in the Bailey Rock Rhyolite and marginal phases of the McDougall Brook Porphyritic Microgranite suggest that both textures have a similar origin - crystallization induced by rapid cooling in response to ascent and/or emplacement/eruption of the magma.

The original feldspar mineralogy of the felsic igneous rocks consisted of sanidine and oligoclase. The present character of the feldspars (microperthite and albite) has resulted from post-eruptive, subsolidus modification of their structure and chemistry, probably through Na and K exchange between the feldspar phenocrysts and the

groundmass during devitrification. The sodium was probably largely derived from devitrification of the felsic glass because sodium is liberated from, and potassium is added to the groundmass during devitrification (e.g., Lipman, 1965; Noble, 1970; Stewart, 1979). Albitization of plagioclase in the mafic rocks may have been hampered by reduced amounts of glassy groundmass or absence of sea water. The alteration/devitrification process was probably deuteric as indicated by the white mica compositions.

LITHOCHEMISTRY

Whole-rock chemical analyses for 91 samples that represent the least altered igneous rocks were selected for petrochemical evaluation from a suite of 128 samples from McCutcheon (1991). Details of the analytical methods and tables of data are presented in McCutcheon (1991).

Classification

The silica vs. alkalis diagram (LeMaitre, 1989; Fig. 1-10A) and AFM diagram (Irvine and Baragar, 1971; Fig. 1-10B) enable classification of the Piskahegan Group igneous rocks using major element chemistry. The basalts classify as high-K tholeiites in Fig. 1-10A and as Fe-rich tholeiites in Fig. 1-10B, which is consistent with their pyroxene compositions. There is, however some ambiguity in the classification of the more felsic rocks; these show a calcalkaline trend in Fig. 1-10B but overlap the basalt-rhyolite series and the high-K ($\text{Na}_2\text{O} - 2.0 \leq \text{K}_2\text{O}$) trachybasalt - shoshonite - latite - trachydacite (normative quartz > 20%) - rhyolite series in Fig. 1-10A. The potassic character of these rocks is considered to be primary because: 1) the microgranites, which are holocrystalline, are potassic, and; 2) analyses of glass inclusions in quartz from some of the felsic rocks also plot in or above the high-K (tholeiitic) rhyolite field

Figure 1-10. Classification of Piskahagan Group igneous rocks. A. Silica versus alkalis chemical classification scheme after LeMaitre (1989). B. AFM discrimination diagram for tholeiitic and calcalkaline igneous rocks after Irvine and Baragar (1971).

(McCutcheon, 1991). However, they are not viewed as alkaline since the rapakivi dykes and McDougall Brook Microgranites have pyroxenes with subalkaline affinities (see Fig. 1-7B). The felsic rocks are therefore considered to be a potassic calcalkaline suite.

Harker variation diagrams (Fig. 1-11) show clearly that there is no "silica gap" between mafic and felsic members of the Piskahegan Group igneous rocks. Neither are there simple trends that can be attributed to a single liquid line of descent. The mafic rocks are volumetrically insignificant and exhibit different chemical behaviour compared to the felsic ones. The two groups of rocks are possibly unrelated and are therefore considered separately.

Mafic rocks (Kleef Basalt, Hoyt Station Basalt, South Oromocto Andesite, Scoullar Mountain andesites and diorites).

Chemical Variation.

The Kleef and Hoyt Station basalts contain higher MgO, CaO, Na₂O, P₂O₅, Sr, and lower K₂O, Rb, and Th contents than the andesites (Fig. 1-11). The observed trends in Figure 1-11 are generally consistent with fractional crystallization of pyroxene, plagioclase, Fe-Ti oxides, and apatite but there is no simple relationship between the stratigraphic position of a unit and its position along the inferred fractionation trends. Furthermore, plots of MgO, Al₂O₃, P₂O₅, Zr, and Cr show considerable scatter. Because these elements are generally immobile during alteration (Winchester and Floyd, 1977) this scatter probably results from primary magmatic processes. This suggests the presence of multiple magma reservoirs and/or a complex process of magma recharge, fractionation, contamination, and magma mixing within a single mafic reservoir.

Figure 1-11. Chemical variation diagrams of selected major and trace elements from Piskagehan Group igneous rocks. Symbols as in Fig. 1-10.

Tectonic Discrimination and Petrogenesis

The basalts are characterized by high Zr contents and Zr/Y, Th/Yb, and La/Yb ratios that are characteristic of intraplate basalts (Pearce and Norry, 1979; Pearce, 1983; Sun and McDonough, 1989). Compared to the basalts, the andesites have higher Th/Yb ratios which could be due to a "subduction component" in the source region or to crustal contamination (Pearce, 1983); the latter interpretation is preferred since there is no evidence of subduction beneath the New Brunswick Appalachians after the Ordovician (Fyffe and Swinden, 1991). Crustally-contaminated andesites could be produced by combined assimilation and fractional crystallization of basaltic magmas. Comparison of the primitive mantle-normalized trace element patterns of the basalts and andesites (Fig. 1-12) lends support to this interpretation. The basalts have a fairly smooth pattern that is moderately enriched in highly incompatible trace elements, which is typical of intraplate basalts (Sun and McDonough, 1989). This pattern has small peaks in Ba, Th, LREE and a large peak at Li, which are indicative of minor contamination by crustal material and/or post-depositional alteration. In contrast the andesites are more enriched in all of the incompatible trace elements, particularly Rb, K, Ba, U, and Th. These features combined with depletions in Nb, Ti, Sr and P indicate that the andesites are the products of crustal contamination combined with fractional crystallization of titanomagnetite, plagioclase, and apatite from a basaltic magma.

Felsic Rocks (McDougall Brook Microgranite, Bailey Rock Rhyolite, Rapakivi Dykes, Mount Pleasant Porphyry, and Rothea, Scoullar Mountain, Little Mount Pleasant, Seelys, and Big Scott Mountain tuffs).

Chemical Variation

The McDougall Brook Microgranite and rapakivi dykes (intracaldera and late caldera-fill, respectively) contain the lowest SiO₂, K₂O, Rb, Ba, Th, Ce and the highest

Figure 1-12. Primitive mantle normalized incompatible trace element plot of Piskahagan Group basalts and andesites. Normalization factors from Sun and McDonough (1989).

Al_2O_3 , MgO , CaO , TiO_2 , P_2O_5 , Sr, Zr, and Sc of the felsic rocks (Fig. 1-11). Felsic rocks with $> 70\%$ SiO_2 exhibit similar compositional trends and overlap in compositional space indicating a common control on their evolution. This is not apparent in Figure 1-11 because individual units cannot be shown at this scale but is readily apparent if these rocks are plotted in more detail (McCutcheon, 1991). These trends are consistent with fractional crystallization of the observed phenocryst assemblage. The Mount Pleasant Porphyry is the most highly fractionated with lower MgO , TiO_2 and P_2O_5 and higher Th and Rb than most other felsic caldera rocks.

Chondrite-normalized REE patterns for selected samples are shown in Figure 1-13. Rocks with intermediate compositions (McDougall Brook Microgranite and rapakivi dykes) have LREE-enriched patterns with small negative Eu anomalies (Fig. 1-13A). The more siliceous ash flow tuffs and lava flows tend to be zoned; early-erupted tuffs are more siliceous than late-erupted ones. As silica content increases, the negative Eu anomaly becomes more pronounced, a trend that occurs both within individual units (Fig. 1-13B) and within entire formations (Fig. 1-13C; also Seelys Formation, Bailey Rock Rhyolite). However, extremely fractionated rocks such as the Mount Pleasant Porphyry (Fig. 1-13D) and the upper unit of the Little Mount Pleasant tuff (Fig. 1-13C) show a pattern characterized by HREE enrichment, with or without LREE depletion. These features suggest that felsic magma evolution was controlled by a common process.

Tectonic Discrimination & Petrogenesis

Based on concentrations of Rb, Y and Nb (Figure 1-14), the Piskahagan felsic igneous rocks have characteristics transitional between those of within-plate granites (WPG), volcanic arc granites (VAG), and syn-collisional granites (syn-COLG) although most samples plot just within the WPG field. Such transitional characteristics are typical of post-collision granites according to Pearce et al. (1984). This would be consistent

Figure 1-13. Chondrite-normalized REE plots of felsic volcanic rocks. A. McDougall Brook Microgranites, B. single cooling unit of the Rothea Formation, C. Little Mount Pleasant tuffs, and D. Mount Pleasant Porphyry. Normalization factors from Sun and McDonough (1989).

with the post-collisional, pre-extensional environment that probably existed in the northern Appalachians at the time of formation of the Mount Pleasant Caldera.

The intra- and inter-unit chemical variations of the felsic igneous rocks could be explained by mechanical sorting of crystals and vitric components *during* eruption, and/or fractionation to produce a zoned magma chamber *prior* to eruption. Fisher and Schmincke (1984) have discussed the effects of mechanical sorting and concluded that: a) mechanical sorting preferentially enriches the basal part of a pyroclastic flow with crystals; b) fine-grained fallout deposits have lower crystal/vitric ratios than their cogenetic pyroclastic flows, and; c) the chemical composition of a pyroclastic flow may depart dramatically from its associated pumice fragments (i.e., the pre-eruptive magma). On the other hand, large-volume ash flow tuffs commonly show evidence of magma fractionation prior to eruption in the form of upward increases in crystal size and abundance, upward appearance of new mineral phases and upward increases in the abundance of compatible elements and corresponding decreases of incompatible elements.

The REE patterns provide evidence that the felsic igneous rocks are related to each other by fractional crystallization. Feldspars are the only minerals that effectively remove Eu from a magma and the Eu contents of K-feldspars are typically higher than those in plagioclase (Hildreth, 1979). The REE patterns suggest that fractionation of K-feldspar was relatively unimportant in the evolution of the McDougall Brook Microgranite and rapakivi dykes but was very important in the evolution of the more felsic rocks.

Excellent stratigraphic control in the Rothea Formation permits examination of chemical variations within single pyroclastic cooling units. An upward reduction in magnitude of the Eu anomaly within these cooling units (Fig. 1-13B) suggests that the magma chamber was compositionally zoned and that feldspar crystallization was important to the development of this zonation. These cooling units exhibit upward increases in the size and abundance of phenocrysts. In general the sense of chemical

Figure 1-14. Rb - (Y + Nb) tectonic discriminant diagram for granitic rocks after Pearce et al. (1984) with samples of McDougall Brook Microgranite. COLG = syn-collision granites; WPG = within plate granites; ORG = orogenic granites; VAG = volcanic arc granites.

Figure 1-15. Enrichment-depletion diagram for a single cooling unit of the Rothea Formation. Diagram constructed by dividing ppm values of elements from the base of the unit by those from the top.

zonation is from most-evolved to least-evolved from base to top of each unit. The bases of the units are enriched in incompatible elements Li, Rb, Y, Nb, heavy REE, Th and U, base metals and As (Fig. 1-15) and depleted in elements that are incorporated in essential and accessory phases, including feldspars (Al, Ca, Na, K, Sr), zircon (Zr), iron-titanium oxides (Fe, Ti), and apatite (P). On the other hand, the enrichment of Mg in the base of the flow may indicate that ferromagnesian phenocrysts were mechanically sorted during eruption.

The LREE's exhibit compatible chemical behaviour in the felsic units but there is no single mineral phase in the rocks that can account for this behaviour. The LREE's can be partitioned from a felsic magma by minerals such as titanite, allanite, and monazite (Miller and Mittlefehldt, 1982) but none of these minerals have been identified in the rocks; furthermore the strong incompatibility of Th (Fig. 1-11) precludes fractionation of monazite (which tends to be fine-grained and easily overlooked). However, it is also possible that the LREE's are concentrated in other phases. For example, Hildreth (1979) found that biotite, pyroxenes, magnetite, and apatite all concentrated LREE's in the Bishop Tuff. The Ce-rich rims of apatites found in the Piskahegan Group tuffs indicate that a similar phenomenon occurs in the highly evolved tuffs. Mass balance calculations indicate that removal of nearly 1% of apatite containing 2 wt.% Ce would be required to account for the Ce lost from the upper unit of the Little Mount Pleasant Formation. There is insufficient P_2O_5 in these tuffs for this much apatite to crystallize, so other minerals besides apatite must have been involved in LREE removal.

CONCLUSIONS

Caldera Recognition

The Piskahegan Group comprises an epicontinental caldera complex and related outflow facies because it overlies Acadian-thickened continental crust and the triangular

area in Figure 1-2 (about 110 km²) exhibits many of the characteristic features of caldera complexes described by Lipman (1984). For example: (a) The area is underlain by thick ash flow tuffs – the Little Mount Pleasant and Seelys Formations – that do not occur in the exocaldera sequence; (b) The Scoullar Mountain sedimentary breccias lie near the apparent base of the sequence and dip into the triangular area (Fig. 1-2). These breccias are equivalent to Lipman's (1984) mesobreccia; (c) There are a number of small intrusions along the east and west sides of the triangular area – including parts of the Bailey Rock and Little Mount Pleasant Formations – that are considered to be 'ring-fracture' intrusions but the main intrusive mass is within the center of the triangle, and; (d) The triangular area has negative gravity and positive magnetic expressions not exhibited by the rest of the group, common features of calderas because they are underlain by felsic plutons.

Correlation of Intracaldera and Exocaldera Stratigraphy

The relative stratigraphic position of units in the exocaldera and intracaldera sequences is based on the following observations: (a) biotite pseudomorphs are found only in parts of the Rothea Formation (exocaldera sequence) and volcanic clasts within sedimentary and pyroclastic breccias near the apparent base of the Scoullar Mountain Formation (intracaldera sequence). From this relationship it is inferred that eruption of the Rothea tuffs preceded or coincided with caldera collapse and may have been the cause of the collapse; (b) andesitic rocks occur only in the South Oromocto Andesite (exocaldera sequence) and the Scoullar Mountain Formation (intracaldera sequence), which are inferred to be time equivalents; (c) the Carrow Formation (exocaldera sequence) contains clasts from the Seelys Formation (intracaldera sequence), and; (d) the Bailey Rock Rhyolite, which occurs in both sequences, intrudes and/or overlies the Carrow Formation but is intruded by, or grades into, the McDougall Brook Microgranite (intracaldera sequence). This microgranite was emplaced within, rather than beneath, the

volcanic pile. Phenocryst textures indicate that moderately rapid crystallization occurred during or after emplacement of the microgranite and that the volcanic pile had cooled significantly before emplacement. The level of emplacement, stratigraphic position, and location within the central part of the caldera suggest that its intrusion accompanied resurgent doming of the caldera floor.

Extensive erosion of intracaldera and exocaldera rocks prior to deposition of the late caldera-fill sequence is indicated by deposition of the late caldera-fill rocks disconformably on the McDougall Brook Microgranite, and the presence of a saprolite between the Bailey Rock Formation and the late caldera fill-rocks. The late caldera-fill sequence is therefore not part of the Mount Pleasant caldera-forming cycle. However there is no evidence to suggest a separate volcanic source for the late caldera-fill rocks

Magmatic Evolution

The phenocryst textures and mineralogy of both mafic and felsic rocks are indicative of rapid, low pressure crystallization and probably do not provide reliable information about the mineralogy of deep-seated source regions.

The Piskahegan volcanic suite include high-K, tholeiitic, intraplate basalts and a high-K calcalkaline suite ranging from andesite to rhyolite. The lack of regular compositional variations among mafic units with time or silica content, and textural features suggest that the mafic magmas evolved by some combination of fractional crystallization, assimilation, and magma mixing. Comparison of abundances of incompatible trace elements in the calcalkaline andesites and tholeiitic basalts suggest that the former are derived by combined assimilation and fractional crystallization of the latter.

The precise relationship between the mafic and felsic rocks cannot be determined from the data presented here. The felsic rocks could be derived by extensive hybridization and fractionation of basaltic magma (e.g., Musselwhite et al., 1989);

conversely they could represent partial melts of lower crustal protoliths (e.g., Huppert and Sparks, 1988) after intrusion of basaltic magma. Density contrasts and temperature differences between basaltic and rhyolitic liquids tend to impede mafic magmas from reaching the surface (Hildreth, 1981). This probably explains why there are so few basalts in the Piskahegan Group.

Most of the ash flow tuffs are silica-rich (greater than 71% SiO_2) and several exhibit textural, mineralogical and chemical zonation from base to top. This zonation apparently reflects gradients that existed in the original magma chamber prior to eruption, with mechanical sorting of crystals during eruption being of minor importance. The compositional zonation in felsic volcanic units and overlap in compositional space among the units can be explained by a zoned magma chamber that repeatedly underwent differentiation between eruptions.

Eruptive History

Seven stages of caldera development are envisioned (Fig. 1-16), assuming that there were separate mantle-derived mafic magmas and crust-derived felsic magmas:

Stage 1: Pre-caldera volcanism was limited to the Hoyt Station Basalt and minor crystal-poor rhyolite (occurring as clasts in conglomerate associated with the basalt).

Stage 2: Caldera collapse occurred with eruption of the lowest tuff unit of the Rothea Formation. A pyroclastic unit near the apparent base of the Scoullar Mountain Formation is a possible intracaldera facies of the Rothea Formation.

Stage 3: After collapse, debris was shed from the caldera walls, including clasts of Rothea tuff. Andesitic lavas were erupted from the ring-fracture zone because of disruption of the magma chamber stratification either directly, by collapse of the cauldron block, or indirectly, by sinking of stoped blocks. Simultaneous eruption of ash-flow tuffs resulted in a sequence of interbedded tuffs, sedimentary breccias and andesitic

Figure 1-16. Eruptive history of the Mount Pleasant Caldera complex. See text for details

lavas. Some of the tuffs had outflow facies (upper members of the Rothea Fm.) and an andesitic lava (South Oromocto Andesite) was deposited on top of them.

Stage 4: An eruption hiatus permitted the re-establishment of magma chamber stratification. Then highly differentiated, crystal-poor rhyolite of the Little Mount Pleasant Formation (4a) was erupted from the ring- fracture zone. Shortly thereafter, the Little Mount Pleasant tuffs (4b) were erupted. The absence of coeval outflow tuffs or caldera-margin sedimentary breccias indicates that eruption of these tuffs maintained the level of the caldera floor and volume was not lost to an outflow facies.

Stage 5: Another hiatus permitted zonation to develop in the magma chamber prior to eruption of the Seelys ash-flow tuffs. As with the Little Mount Pleasant tuff, there is no sedimentary breccia facies at the caldera margin, but Seelys clasts occur in conglomerate of the outflow sequence (Carrow Formation). Basalt is also present in the outflow facies. Input of basaltic magma at the base of the chamber may have triggered this eruption.

Stage 6: After zonation was re-established, compositionally inhomogeneous, coarsely porphyritic Bailey Rock Rhyolite was extruded from the ring-fracture zone. Shortly thereafter McDougall Brook Microgranite was intruded into the volcanic pile. This was accompanied by stoping of the chamber roof and resurgent doming of the caldera floor. Rapakivi dykes may have been emplaced at this time. The whole caldera complex cooled.

Stage 7: A new (or weakly resurgent) volcanic cycle began some time later. A rhyolitic magma chamber was re-established beneath Mount Pleasant; it became highly differentiated and fed the crystal-poor Mount Pleasant Porphyry dykes (but not pyroclastic deposits). The composite dykes, breccias and associated tungsten-molybdenum and tin deposits were generated by progressive, inward cooling and degassing of the magma chamber. This igneous activity was focused on the southwest margin of the dormant caldera. The source area for the Kleef basalt and Big Scott Mountain lavas has not been identified.

Tectonic Implications

The Mount Pleasant Caldera has chemical characteristics that could result in ambiguous or incorrect tectonic discrimination if the entire rock suite was not considered as a whole. For example the basalts could be inferred to have intraplate characteristics, the andesites to be subduction-related, and the microgranites to have had a post-collision origin. Unfortunately such incomplete, tectonized and/or altered volcanic sequences are often all that are available for analysis in the northern Appalachian-Caledonian Orogen; not surprisingly, all three of the above mentioned tectonic settings have been proposed for one suite or another and such interpretations are often in conflict with each other or other kinds of geological evidence. The epicontinental, post-collisional, early- to syn-extensional tectonic setting of the caldera complex may apply to some or all of these other igneous suites.

The Mount Pleasant Caldera is spatially, temporally, and genetically related to both the voluminous late- to post-compressional plutonism and volcanism of the Acadian Orogeny and to the Maritimes Basin. Although it is debatable whether caldera emplacement preceded or followed the onset of the extensional tectonics that produced the basin, it is clear that most of the plutonic activity and some earlier volcanic activity preceded it. Input of mantle-derived basaltic magmas into the base of the continental crust was certainly involved in both caldera formation and basin formation, and by inference, in the preceding plutonism. This raises the possibility that basaltic underplating, and hence mantle upwelling, preceded Late Devonian to Carboniferous crustal extension in the northern Appalachians and was the driving force rather than the result of extension.

Acknowledgements. Funding for this work was provided under the Canada-New Brunswick Mineral Development Agreement (1985-1990) and by Natural Sciences and Engineering Research Grants to P.T. Robinson and R.P. Taylor. Critical reviews by

R.P. Taylor and A.D. Fowler, which led to improvements in the manuscript, are gratefully acknowledged.

References

- Baker, B.H. & McBirney, A.R. 1985. Liquid fractionation. Part III. Geochemistry of zoned magmas and the compositional effects of liquid fractionation. *Journal of Volcanology and Geothermal Research* 24, 55-81.
- Bevier, M.L. 1988. Timing of Paleozoic plutonism in the Miramichi terrane, New Brunswick. *Geological Society of America Program with Abstracts*, 20(1), 7.
- Burnham, W.C. 1979. Magmas and hydrothermal fluids. In: Barnes, H.L. (ed.) *Geochemistry of hydrothermal ore deposits*. John Wiley and Sons, New York, 71-136.
- Christiansen, E.H., Sheridan, M.F. & Burt, D.M. 1986. The geology and geochemistry of Cenozoic topaz rhyolites from the western United States. *Geological Society of America, Special Paper* 205, 74 pp.
- Clemens J.D. 1984. Water contents of silicic to intermediate magmas. *Lithos* 17, 273-287.
- Clough, C.T., Maufe, H.B. & Bailey, E.B. 1909. The cauldron subsidence of Glen Coe, and the associated igneous phenomena. *Quarterly Journal of the Geological Society of London* 65, 611-676.
- Coyle, M. & Strong, D.F. 1987. Geology of the Springdale Group: A newly recognized Silurian epicontinental-type caldera in Newfoundland. *Canadian Journal of Earth Sciences* 24, 1135-1148.
- Deer, W.A., Howie, R.A. & Zussman, J. 1966. *An introduction to the rock-forming minerals*. London: Longmans, Green and Co. Ltd., 528 pp.

- Durling, P.W. & Marillier, F.J.Y. 1990. Structural trends and basement rock subdivisions in the western Gulf of St. Lawrence, northern Appalachians. *Atlantic Geology* 26, 79-95.
- Eichelberger, J.C. 1978. Andesitic volcanism and crustal evolution. *Nature* 275, 21-27.
- Fisher, R.V. & Schmincke, H.U. 1984. *Pyroclastic rocks*. New York: Springer-Verlag, 472 pp.
- Fyffe, L.R. & Barr, S.M. 1986. Petrochemistry and tectonic significance of Carboniferous volcanic rocks in New Brunswick. *Canadian Journal of Earth Sciences* 23, 1243-1256.
- Fyffe, L.R., McLeod, M.J. & Ruitenburg, A.A. 1992. A geotraverse across the St. Croix - Avalon terrane boundary, southern New Brunswick. Geological Association of Canada, Mineralogical Association of Canada, Joint Annual Meeting, Wolfville '92; Field Trip A1, Guidebook, 44 pp.
- Fyffe, L.R., Pajari, G.E., Jr. & Cherry, M.E. 1981. The Acadian plutonic rocks of New Brunswick. *Maritime Sediments and Atlantic Geology* 17, 23-36.
- Fyffe, L.R. & Swinden, H.S. 1991. Paleotectonic setting of Cambrio-Ordovician volcanic rocks in the Canadian Appalachians. *Geoscience Canada* 18, 145-157.
- Giret, A., Bonin, B. & Leger, J.M. 1980. Amphibole compositional trends in oversaturated and undersaturated alkaline plutonic ring complexes. *Canadian Mineralogist* 18, 481-495.
- Guidotti, G.V. 1984. Micas in metamorphic rocks. *Mineralogical Society of America, Reviews in Mineralogy* 13, 357-467.
- Harris, F.R. 1964. Volcanic rocks of the Sunday Lake area, New Brunswick. Unpublished M.Sc. thesis, University of New Brunswick, Fredericton, N.B., 141 pp.
- Hawthorne, F.C. 1981. Crystal chemistry of the amphiboles. *Mineralogical Society of America, Reviews in Mineralogy* 9A, 1-102.

- Hildreth, E.W. 1981. Gradients in silicic magma chambers: implications for lithospheric magmatism. *Journal of Geophysical Research* 86, 10153-10192.
- Hildreth, E.W. 1979. The Bishop Tuff: evidence for the origin of compositional zonation in silicic magma chambers. *Geological Society of America Special Paper* 180, 43-75.
- Hubacher, F.A. & Lux, D.R. 1987. Timing of the Acadian deformation in northeastern Maine. *Geology* 15, 80-83.
- Huppert, H.E. & Sparks, R.S.J. 1988. The generation of granitic magmas by intrusion of basalt into continental crust. *Journal of Petrology* 29, 599-624.
- Irvine, T.N. & Baragar, W.R.A. 1971. Guide to the chemical classification of the common volcanic rocks. *Canadian Journal of Earth Sciences* 8, 523-548.
- Kooiman, G.J.A., McLeod, M.J. & Sinclair, W.D. 1986. Porphyry tungsten-molybdenum ore bodies, polymetallic veins and replacement bodies, and tin-bearing zones in the Fire Tower Zone, Mount Pleasant, New Brunswick. *Economic Geology* 81, 1356-1373.
- LeMaitre, R.W. 1989. *A Classification of Igneous Rocks and Glossary of Terms*. Oxford: Blackwell Scientific Publications, 193 pp.
- Leterrier, J., Maury, R.C., Thonon, P., Girard, D. & Marchal, M. 1982. Clinopyroxene composition as a method of identification of the magmatic affinities of paleo-volcanic series. *Earth and Planetary Science Letters* 59, 139-154.
- Lipman, P.W. 1965. Chemical comparison of glassy and crystalline volcanic rocks. *United States Geological Survey, Bulletin* 1201-D, D1-24.
- Lipman, P.W. 1984. The roots of ash flow calderas in western North America: windows into the tops of granitic batholiths. *Journal of Geophysical Research* 89, 8801-8841.
- Lipman, P.W., Christiansen, R.L. & O'Conner, J.T. 1966. A compositionally zoned ash-flow sheet in southern Nevada. *United States Geological Survey, Professional Paper* 524-F, 45 pp.

- Lofgren, G. 1974. An experimental study of plagioclase crystal morphology: isothermal crystallization. *American Journal of Science* 274, 243-273.
- MacLellan, H.E. and Taylor, R.P. 1989. Geology and geochemistry of the Burnthill granite and its related W-Sm-Mo-F mineral deposits, central New Brunswick. *Canadian Journal of Earth Sciences* 26, 499-514.
- MacLellan, H.E. & Trembath, L.T. 1991. The role of quartz crystallization in the development and preservation of granitic texture: experimental evidence at 1 kbar. *American Mineralogist* 76, 1291-1305.
- McCutcheon, S.R. 1991. The Late Devonian Mount Pleasant Caldera complex: stratigraphy, mineralogy, geochemistry and geologic setting of a Sn-W deposit in southwestern New Brunswick. unpublished Ph.D. thesis, Dalhousie University, Halifax, Nova Scotia, 609 pp.
- McCutcheon S.R. 1981. Revised stratigraphy of the Long Reach area, southern New Brunswick: evidence for major northwestward-directed Acadian thrusting. *Canadian Journal of Earth Sciences* 18, 646-656.
- McCutcheon, S.R. & Bevier, M.L. 1990. Implications of field relations and U-Pb geochronology for the age of gold mineralization and timing of Acadian deformation in northern New Brunswick. *Atlantic Geology* 26, 237-246.
- McCutcheon S.R. & Robinson, P.T. 1987. Geological constraints on the genesis of the Maritimes Basin, Atlantic Canada. *Canadian Society of Petroleum Geologists, Memoir* 12, 287-297.
- McGregor, D.C. & McCutcheon, S.R. 1988. Implications of spore evidence for Late Devonian age of the Piskahegan Group, southwestern New Brunswick. *Canadian Journal of Earth Sciences* 25, 1349-1364.
- McLeod M J., Taylor, R.P. & Lux, D.R. 1988. Geology, $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology and Sn-W-bearing sheeted veins of the Mount Douglas Granite, southwestern New Brunswick. *Canadian Institute of Mining and Metallurgy Bulletin* 81, 70-77.

- Miller, C.F. & Mittlefehldt, D.W. 1982. Light rare earth element depletion in felsic magmas. *Geology* 10, 129-133.
- Monier, G., Mergoil-Daniel, J. & Labernardiere, H. 1984. Generations successives de muscovites et feldspaths potassiques dans les leucogranites du massif de Millevaches (Massif Central français). *Bulletin Mineralogique* 107, 55-68.
- Musselwhite, D.S., DePaolo, D.J. & McCurry, M. 1989. The evolution of a silicic magma system: isotopic and chemical evidence from the Woods Mountain volcanic center, eastern California. *Contributions to Mineralogy and Petrology* 101, 19-29.
- Noble, D.C. 1970. Loss of sodium from crystallized comendite welded tuffs of the Miocene Grouse Canyon Member of the Belted Range Tuff, Nevada. *Geological Society of America Bulletin* 81, 2677-2688.
- Oftedahl, C. 1978. Cauldrons of the Permian Oslo rift. *Journal of Volcanology and Geothermal Research* 3, 343-371.
- Pearce, J.A. 1983. Role of sub-continental lithosphere in magma genesis at active continental margins. In *Continental Basalts and Mantle Xenoliths* (eds C.J. Hawkesworth and M.J. Norry), *Shiva Geology Series*, 230-249.
- Pearce, J.A., Harris B.W. & Tindle, A.G. 1984. Trace element discrimination diagrams for the tectonic interpretation of granitic rocks. *Journal of Petrology* 25, 956-983.
- Pearce, J.A. & Norry, M.J. 1979. Petrogenetic implications of Ti, Zr, Y, and Nb variations in volcanic rocks. *Contributions to Mineralogy and Petrology* 69, 33-47.
- Pitcher, W.S. 1979. The nature, ascent and emplacement of granitic magmas. *Journal of the Geological Society of London* 136, 627-662.
- Ruitenberg, A.A. & McCutcheon, S.R. 1982. Acadian and Hercynian structural evolution of southern New Brunswick. *Geological Association of Canada, Special Paper* 24, 131-148.
- Sides, J.R., Bickford, M.E., Shuster, R.D. & Nusbaum, R.L. 1984. Calderas in the St. Francois Mountains, south eastern Missouri. *Journal of Geophysical Research* 86, 10349-10364.

- Sinclair, W.D., Kooiman, G.J.A. & Martin, D.A. 1988. Geological setting of granites and related tin deposits in the North Zone, Mount Pleasant, New Brunswick. *Current Research, Part B, Geological Survey of Canada, Paper 88-1B*, 201-208.
- Smith, R.L. 1979. Ash-flow magmatism. *Geological Society of America, Special Paper 180*, 5-27.
- Stewart, D.B. 1979. The formation of siliceous potassic glassy rocks. In *The evolution of the igneous rocks: fiftieth anniversary perspectives* (ed H.S. Yoder Jr.) Princeton: Princeton University Press, 339-350.
- Stimac, J.A. & Pearce, T.H. 1992. Textural evidence of mafic-felsic magma interaction in dacite lavas, Clear Lake, California. *American Mineralogist* 77, 795-809.
- Sun, S.-s. & McDonough, W.F. 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geological Society Special Publication No. 42*, 313-345.
- Tschiyama, A. & Takahashi, E. 1983. Melting kinetics of a plagioclase feldspar. *Contributions to Mineralogy and Petrology* 84, 345-354.
- van Waggoner, N.A. & Fay, V.K. 1988. Stratigraphy and volcanology of a portion of the Lower Devonian volcanic rocks of southwestern New Brunswick. *Geological Survey of Canada, Paper 88-1B*, 69-78.
- Wager, L.R. & Brown, G.M. 1968. *Layered Igneous Rocks*. London: Oliver and Boyd, Ltd., 588 pp.
- Williams, D.A. 1978. Compilation Bouger gravity map of New Brunswick, Scale 1:250,000, Woodstock (21J). New Brunswick Department of Natural Resources, Mineral Resources Division, Plate 78-42e.
- Winchester, J.A. & Floyd, P.A. 1977. Geochemical discrimination of different magma series and their differentiation products using immobile elements. *Chemical Geology* 20: 325-343.

CHAPTER 2. Magmatic evolution of the epizonal magma chamber of the Mount Pleasant Caldera complex: Part 1. Evidence from Rb/Sr geochronology, and O isotope and trace element geochemistry.

ABSTRACT

The age and magmatic evolution of the magma chamber of the Mount Pleasant Caldera complex is examined using a combined isotopic and geochemical approach. Rb-Sr and O isotope studies of volcanic and hypabyssal rocks of the complex permit the recognition of a small data set (6 samples) that is unaffected by syn-magmatic crustal contamination and post-magmatic alteration. This has allowed Rb-Sr dating of the emplacement of the caldera complex at 368 ± 5 Ma ($^{87}\text{Sr}/^{86}\text{Sr}_i = 0.70611$; M.S.W.D = 2.8), with the isochron samples comprising andesites to high-silica rhyolites of the intracaldera sequence. Basaltic rocks of the outflow and late caldera-fill sequences that are not isochronous have initial Sr isotope ratios very close to this value. Systematic variations of trace element chemistry of the intracaldera volcanic and plutonic rocks support the interpretation that the intracaldera felsic rocks were derived from an andesitic parent by closed-system fractional crystallization. The andesites are high temperature magmas that are unlikely to be produced by partial melting of a lower crustal protolith. It is inferred therefore that they are crustally-contaminated mantle melts. The Mount Pleasant Caldera complex is genetically related to voluminous post-tectonic Devonian granitic plutonism in the Canadian Appalachians. This plutonism has generally been assumed to be produced by partial melting of lower crustal protoliths. This assumption should be re-examined in light of the present study.

INTRODUCTION

The Mount Pleasant Caldera complex, located in the northern Appalachians (Fig. 2-1) is a rare example of a pre-Cenozoic epicontinental caldera (Chapter 1). An understanding of the geochronology and petrogenesis of the caldera complex is important because: 1) it is one of the last magmatic events in a period of syn- to post-compressional magmatism of the Acadian Orogeny; 2) it was emplaced at or near the onset of a period of crustal extension and thermal collapse that resulted in the formation of a large aborted rift (Maritimes Basin); 3) it contains a broad range of igneous rock types that have potentially preserved evidence of the complex array of processes that could have been involved in its petrogenesis; 4) its stratigraphy is well-known and the volcanic rocks are clearly genetically related, and; 5) the caldera is undeformed and less altered than many other volcanic complexes in the northern Appalachians (e.g., Coyle and Strong, 1987; Dostal et al., 1983; Blanchard et al., 1984). Therefore, a detailed petrochemical study of the caldera complex has the potential to provide insights into the magmatic evolution of the caldera complex, the petrogenesis of the related syn- to post-compressional Acadian magmatism, and the tectonic processes involved in magma genesis and evolution.

Stratigraphic, petrographic and whole rock geochemical data indicate the presence of a high-level magma chamber beneath the Mount Pleasant Caldera complex that underwent repeated episodes of fractional crystallization punctuated by episodic eruptions (McCutcheon, 1991; Chapter 1). In the present study the range of magma compositions existing within the magma chamber is extended to include more mafic end-members (andesite). It is further demonstrated that this magma chamber can be viewed as a closed system and that the more felsic rocks were produced by fractional crystallization of the andesites. The range of magmatic compositions exhibiting closed system behaviour is identified from a Rb/Sr isochron of six samples. Reverse modelling of the

Figure 2-1. Tectonic lithofacies map of southwestern New Brunswick (after Fyffe et al., 1992) with location of the Mount Pleasant Caldera complex.

trace element geochemistry lends further support to the interpretation of closed system behaviour.

The isotopic age of the caldera complex and the relative ages of caldera volcanism and late plutonism associated with economic Sn-W-Mo mineralization, located along the southwest margin of the caldera, have been problematic. In the past the caldera complex has been inferred to be of Early Carboniferous age because of its stratigraphic position (van de Poll, 1967). It unconformably overlies rocks that were deformed during the Acadian Orogeny (which culminated in the Middle Devonian) and is in turn overlain unconformably by Middle Mississippian strata of the Maritimes Basin. However, McGregor and McCutcheon (1988) have identified Late Fammenian spores in sediments in the exocaldera sequence. On the other hand, Kooiman et al. (1986) reported whole rock K/Ar dates and a Rb/Sr errorchron indicating an age of 330-340 Ma for granitic intrusion and mineralization at the Mount Pleasant Mine, raising the possibility that this mineralization was not related to caldera magmatism. Evidence presented here indicates that all of the magmatic activity occurred during the Late Devonian and that the younger apparent ages are produced by post-magmatic modification of the isotopic compositions of these rocks.

TECTONIC SETTING AND GEOLOGY OF THE CALDERA COMPLEX

Southwestern New Brunswick consists of several northeast-trending fault blocks that contain rocks ranging in age from Precambrian to Late Devonian. These blocks comprise two terranes and two cover sequences (St. Peter and Fyffe, 1991; Fyffe et al., 1992) as shown in Figure 2-1. The configuration of the various fault blocks was largely established during the Acadian Orogeny (McCutcheon, 1981; Ruitenberg and McCutcheon, 1982; McCutcheon and Robinson, 1987).

A period of late-Acadian volcanism occurred in the Late Silurian to Lower Devonian, and crops out as bimodal volcanic rocks (Fig. 2-1) forming part of the Mascarene Cover Sequence (van Waggoner and Fay, 1988). A period of mainly granitoid "Acadian plutonism" overlapped with and followed this volcanism (Fyffe et al., 1981). Isotopic and field evidence from these granitoids indicate that Acadian polyphase deformation took place in Silurian to Middle Devonian time (e.g., Hubacher and Lux, 1987; Bevier, 1989; MacLellan and Taylor, 1989; McCutcheon and Bevier, 1990). The post-tectonic Mount Douglas Granite, comprising the youngest and highest-level phases of the Saint George Batholith, has a Late Devonian age (367 Ma) based on U/Pb (Bevier, 1989) and $^{40}\text{Ar}/^{39}\text{Ar}$ (McLeod et al., 1988) dates. Data presented in this study indicate that the Mount Pleasant Caldera and the closely associated Pomeroy Intrusive Suite are the same age (McGregor and McCutcheon, 1988) as the Mount Douglas Granite. These igneous bodies comprise the last major products of this protracted period of magmatism.

The late- to post-Acadian magmatism was followed closely by formation of the Maritimes Basin, which resulted from tensional collapse and thermal subsidence that followed Acadian continental collision (McCutcheon and Robinson, 1987; Durling and Marillier, 1990). The Late Devonian and Carboniferous rocks of the Basin are the product of an aborted-rift environment as indicated by structural, magmatic, and geophysical evidence of widespread crustal extension (McCutcheon and Robinson, 1987; Fyffe and Barr, 1986; Durling and Marillier, 1990). The Mount Pleasant Caldera was emplaced just before or during the initial rapid-subsidence stage of basin development, as were a number of other volcanic suites in Nova Scotia and Newfoundland (McCutcheon and Robinson, 1987).

The Mount Pleasant Caldera complex comprises three lithofacies (intracaldera, exocaldera and late caldera-fill sequences in Fig. 2-2) that form the Piskahegan Group. The intracaldera sequence comprises a triangular area that includes: thick ash flow tuffs

Figure 2-2. Geology of the Piskahegan Group comprising the Mount Pleasant Caldera complex and related outflow facies rocks (after McCutcheon, 1991)

that do not occur outside; thick sedimentary breccias that dip inward; and stocks and dykes of intermediate to felsic composition that intrude the volcanic pile or are localized along caldera-margin faults (McCutcheon, 1991; Fig. 2-2). This triangular area is a gravity low indicating that it is underlain by felsic plutons. The intracaldera sequence contrasts with those of the exocaldera and late caldera-fill sequences, which include relatively thin ash flow and air fall tuffs, mafic lavas, alluvial redbeds and porphyritic lava flows.

The volcanic and sedimentary rocks of the intracaldera sequence form the caldera *sensu stricto* and their stratigraphic relationships indicate that the Mount Pleasant volcanics were emplaced in a typical caldera-forming cycle. The oldest exposed rocks in this sequence are mesobreccias and intercalated andesitic lava flows and rhyolitic ash flow tuffs (intruded by small dioritic stocks and dykes) of the Scoullar Mountain Formation (Fig. 2-2). These rocks were emplaced around the margins of the caldera following cauldron collapse. The andesites in this formation are stratigraphically correlated with the South Oromocto Andesite in the exocaldera sequence. No other andesites occur in the caldera sequence. Subsequently, chemically and mineralogically zoned rhyolitic ash flow tuffs of the Little Mount Pleasant Formation were erupted from the ring fracture zone. The absence of younger margin-breccias and correlative exocaldera tuffs indicate that eruption of the tuff maintained the level of the caldera floor and that volume was not lost to an outflow facies. A second major eruption produced another zoned, rhyolitic ash flow tuff sequence — the Seelys Formation (Fig. 2-2). This eruption was accompanied by deposition of alluvial fan sediments (containing clasts of Seelys tuff) and eruption of basaltic flows in the exocaldera sequence. It has been postulated that input of basaltic magma into the base of the chamber triggered eruption of the Seelys tuffs (Chapter 1). The last major event consisted of extrusion of rhyolitic lava flows from the ring fracture into the exocaldera sequence, followed by resurgent doming of the caldera floor, stoping of the magma chamber roof, and intrusion of the McDougall

Brook Microgranite into the volcanic pile (Fig. 2-2). Intrusion of the Mount Pleasant Porphyry was a later event that is volumetrically unimportant but of interest due to associated economic Sn-W-Mo deposits. It has been a matter of debate whether this activity occurred during the waning stages of the caldera forming cycle or represents a much younger igneous/hydrothermal event (Kooiman et al., 1986; Sinclair et al., 1988; McCutcheon, 1991).

The geochemistry of the Mount Pleasant Caldera volcanics indicates that the basaltic rocks are mantle-derived, high-K tholeiites and that the associated high-K, calcalkaline andesites could have been derived from the basalts by fractional crystallization and assimilation of crustal material. The more felsic rocks form a high-K calcalkaline series and are probably related to each other by episodes of fractional crystallization of a high level zoned magma chamber whose evolution was repeatedly interrupted by eruption of material from the roof zone (Chapter 1). The felsic rocks could have been derived either from a mafic, mantle-derived magma by fractional crystallization, or from a crustal protolith by partial melting, but the latter process has generally been assumed for the Mount Pleasant Caldera as well as the bulk of the voluminous late- to post-Acadian felsic magmatism in the northern Appalachians (e.g., Fyffe et al., 1981; Chapter 1).

Three postmagmatic processes have been identified that affected the mineralogy and chemistry of the Mount Pleasant Caldera complex (McCutcheon, 1991). The first process is devitrification (and commonly recrystallization as well) of felsic flows and tuffs; this process has resulted in mobility of alkalis, loss of Na from the system and albitization of oligoclase. The second process is deuteric alteration; this has affected many of the rocks, both mafic and felsic, and resulted in sericitization and chloritization of feldspars, amphibole, biotite, and locally, clinopyroxene. The third process is hydrothermal alteration associated with cooling of the volcanic pile and associated intrusions; this process is localized along faults and fractures and is easily recognized

and avoided during the sampling process. The only unaltered minerals are quartz, apatite, zircon, and locally, clinopyroxene.

ANALYTICAL METHODS

Oxygen isotope analyses of 17 samples were performed at the U.S.G.S. stable isotope facility at Menlo park using standard procedures. Oxygen was extracted with BrF_5 (Clayton and Mayeda, 1963) and ClF_3 (Borthwick and Harmon, 1982) and subsequently converted to CO_2 for analysis. The data are reported in permil (‰) values, relative to the Standard Mean Ocean Water reference standard (O'Neil, 1986). During the course of this study, the National Bureau of Standards sample NBS 28 yielded $\delta^{18}\text{O} = 9.6\text{‰}$.

Rubidium and Sr were separated from 23 samples using conventional ion exchange chromatography techniques. Sr isotope analyses were made on a multi-collector Finnigan-MAT 261 solid-source mass spectrometer, operating in the static mode. Rb and Sr were run as chlorides on Re double filaments. With the exception of sample MC-314a (see Table 2-1), Sr isotopic ratios were measured on unspiked sample splits and concentrations were determined from spiked splits. Sr ratios are normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. A typical isotopic analysis of Sr consisting of averaged values of 100 measurements had a 2σ error of about 0.002%. The reproducibility of the isotopic ratios, estimated on the basis of replicate analyses of chemical standards, is about 0.002% (2σ); the NBS-987 standard gives a value for $^{87}\text{Sr}/^{86}\text{Sr} = 0.71025 \pm 0.00002$. Rb/Sr ratios determined for National Bureau of Standards samples NBS-278 and NBS-688 were 2.004 (accepted value = 2.008) and 0.00128 (accepted value = 0.00129) respectively. The error on Rb/Sr ratios of Mount Pleasant Caldera samples is estimated to be 0.8%. Blank determinations during the course of this work averaged 1 ng. for Sr and 1.5 ng. for Rb. Since the minimum concentrations of Sr and Rb measured in samples

Table 2-1. Rb-Sr and Oxygen isotopic data for Mount Pleasant igneous rocks. Calculations made with decay constant from Steiger and Jäger (1977). *isochronous samples. **measured Sr isotopic ratio calculated from spiked sample.

Sample	Formation/Unit	$(^{87}\text{Sr}/^{86}\text{Sr})_m$	$1/\text{Sr}$	$(^{87}\text{Sr}/^{86}\text{Sr})_i$	Rb (ppm)	Sr (ppm)	$\delta^{18}\text{O}$	Model Age (Ma)
MC-314a**	Mount Pleasant Porphyry	3.985	0.002	0.6822	548	3.32		365
MC-013	Rothea tuff	0.72354	0.319	0.70710	232	214.2	14.57	390
MC-196	Bailey Rock Rhyolite	0.90234	0.023	0.67514	346	23.55	9.75	318
MC-101d	Bailey Rock Rhyolite	0.73696	0.165	0.70522	205	98.02	13.06	358
MC-074b*	McDougall Bk. Microgranite	0.74846	0.122	0.70545	298	105.5	6.59	362
MC-082c*	McDougall Bk. Microgranite	0.73618	0.173	0.70582	246	116.6	6.92	365
MC-306a*	Little Mt. Pleasant Fm.	0.76270	0.094	0.70684	275	75.01	6.95	373
82-19*	Little Mt. Pleasant Fm.	0.78922	0.015	0.70707	361	67.08	7.02	372
82-14	Little Mt. Pleasant Fm.	0.97736	0.047	0.68779	366	21.30	8.79	345
MC-229a	Seelys Fm.	0.89332	0.029	0.71134	308	26.09	8.85	379
MC-158b	Seelys Fm.	0.78749	0.074	0.71665	260	55.99	7.82	423
MC-123a	Rapakivi Dykes	0.71666	0.575	0.70755	224	372.9	9.97	426
LM-14	Rapakivi Dykes	0.73611	0.178	0.70669	159	82.34		375
MC-065a	Big Scott Mtn. rhyolite	0.71813	0.778	0.71140	156	350.8	14.61	656
LM-6*	Scoullar Mtn. andesite	0.71315	0.738	0.70605	114	242.5		365
MC-159c	Scoullar Mtn. andesite	0.71234	0.966	0.70592	141	395.8	7.78	423
LM-15*	Scoullar Mtn. diorite	0.71019	1.292	0.70613	118	442.2		370
MC-014	South Oromocto Andesite	0.70879	3.145	0.70712	58.0	524.8	11.04	591
LM-9	South Oromocto Andesite	0.70733	5.051	0.70629	55.7	815.9		433
MC-008a	Hoyt Station basalt	0.70893	71.429	0.70886	1.98	398.3	9.87	12900
MC-024	Kleef basalt	0.70863	4.132	0.70736	52.9	630.8	8.58	730
LM-17a	Kleef basalt	0.70698	1.920	0.70631	20.5	462.6		477
MC-020a1	Carrow basalt	0.70971	4.831	0.70863	12.0	169.7	7.82	1210

were 3.3 and 1.9 ppm respectively and sample sizes were not restricted (> 50 milligrams), blank corrections were deemed unnecessary.

27 whole-rock samples representing the major caldera igneous lithologies have been analyzed for major and trace elements. Major elements and Ba, Rb, Sr, Ni, Cr, V, Zr, Nb, Y, and Zn were analyzed using duplicate glass disks at the University of Ottawa using standard X-Ray fluorescence techniques. Sc, Sb, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th and U were analyzed by INAA at Ecole Polytechnique in Montreal. The averaged values of duplicate analyses are provided in Appendix 1; further details of the methods are provided in Taylor (1992). For the modelling, additional data from previous studies (McCutcheon, 1991; see Chapter 1) have also been used. A limited number of duplicate analyses from this and McCutcheon's study indicate that interlaboratory agreement is good for the INAA results and for the X-Ray fluorescence analyses with the exception of Y, Nb, Cr and Ni (see for example MC-074b, MC-082c and MC-158b in Appendix 1); these elements were not used in the modelling.

RESULTS

Oxygen Isotopic Variations

Oxygen isotope data for the igneous rocks of the Mount Pleasant Caldera complex are presented in Table 2-1. There is a large range of values from 6.6‰ to 14.6‰. There is no obvious correlation between oxygen isotopic content and indices of differentiation such as SiO₂ content. Neither is there any correlation between oxygen isotopic content and stratigraphic position of mafic samples, felsic samples or the volcanic system as a whole.

Plots of $\delta^{18}\text{O}$ versus Rb, Sr and Rb/Sr (Fig. 2-3) demonstrate that the igneous rocks can be subdivided into four groups on the basis of their chemical and oxygen isotopic compositions. Unaltered samples (set 1 in Fig. 2-3) are characterized by a

Figure 2-3. Variations of A. Sr, B. Rb, and C. $^{87}\text{Rb}/^{86}\text{Sr}$ as functions of $\delta^{18}\text{O}$ variation. Numbered fields are described in the text.

restricted range of $\delta^{18}\text{O}$ compositions and Sr contents, and moderate variations of Rb content and Rb/Sr ratio. The remaining samples have variations that define trends moving away from the unaltered samples. The first trend (sample sets 2 & 3 in Fig. 2-3) is characterized by a decrease in Rb/Sr ratio and Rb content, notable increase in Sr content and dramatic increase in $\delta^{18}\text{O}$, indicating variable degrees of interaction with fluids that have equilibrated with a ^{18}O -rich source (or low temperature hydrothermal fluid that was strongly fractionating ^{18}O), and which has removed Rb and or introduced Sr to the volcanic rocks — herewith referred to as the geothermal trend. The second trend (set 4 in Fig. 2-3) is characterized by moderate increases in $\delta^{18}\text{O}$ values and dramatic increases in Rb/Sr ratios produced by decreasing Sr and increasing Rb contents. Since this trend is defined by some of the felsic ash flow tuffs it is most easily interpreted to be the result of fractionation (to produce a zoned magma chamber with progressively greater Rb/Sr ratios near the top) accompanied by a small amount of contamination to produce an increase in $\delta^{18}\text{O}$ values (approximately 3 ‰) that is in excess of that which would be expected due to fractionation alone (approximately 1.5 ‰ over the temperature range 800 - 730 °C; Matsuhisa et al., 1979). This interpretation is supported by the observation of variably digested lithic lapilli in the felsic tuffs of the Seelys Formation that affected by this second trend — referred to as the assimilation fractional crystallization (AFC) trend.

Rb-Sr Geochronology

The complete Rb and Sr data set for igneous rocks of the Mount Pleasant Caldera complex are listed in Table 2-1 and represented graphically in Figure 2-4a. These data produce a scattered array. However, a subset of the data (set 1 in Fig. 2-3) defines a six-point isochron as shown in Figure 2-4b. The isochron samples include an andesite and diorite from the Scoullar Mountain Formation, two samples of McDougall Brook Microgranite and two ash flow tuffs from the Little Mount Pleasant Formation (see Table

Figure 2-4. Plots of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{87}\text{Rb}/^{86}\text{Sr}$. A. An errorochron comprised of all data. B. A six-point isochron comprised of unaltered data from field 1 of Fig. 2-3. The isochron was regressed using the method of York (1969).

2-1). The only major intracaldera lithology not represented on the isochron diagram is the Seelys Formation. The Seelys tuffs plot on the assimilation fractional crystallization trend in Fig. 2-3 and locally contain small lithic lapilli in various stages of digestion (McCutcheon, 1991). Clearly this has modified the Rb-Sr systematics of the Seelys tuffs.

Indicators that the isochron is not a mixing line include: 1) the small M.S.W.D., which would be unlikely to result from mixing phenomena involving such a large range of sample compositions; 2) a narrow range of oxygen isotopic contents of these samples (6.6 - 7.0 per mil) which could represent magmatic values, and from which it is inferred that these samples have suffered minimal post-magmatic alteration, and; 3) a date of 368 Ma and initial ratio of 0.70611 that are geologically reasonable. This isotopic date is within analytical uncertainty of a biostratigraphic age (Late Fammenian) previously determined for miospores collected from a sedimentary horizon of the exocaldera sequence (McGregor and McCutcheon, 1988). The age of the Upper and Lower Fammenian boundaries are estimated at 360 +/- 10 Ma and 367 +/- 12 Ma respectively (Palmer, 1983). It is noteworthy that both the oxygen isotopic values and initial Sr isotopic ratio of the isochron samples are consistent with mantle-derived magmas that have experienced some crustal contamination.

The samples from the errorchron, while exhibiting scatter, nonetheless yield a date similar to that of the isochron; regression of all the data in Table 2-1 yields a date of 370 ± 60 Ma with M.S.W.D. = 1614. This indicates that: 1) the geological events producing the scatter were generally not significantly younger than the age of the caldera and; 2) most samples exchanged very little Sr with alteration fluids and/or the country rocks. This indicates that geothermal alteration probably occurred during cooling of the volcanic pile. Two Rb-rich samples, MC-196 and 82-14, plotting well below the reference isochron in Fig. 2-4a are notable exceptions to these generalizations. These samples have either gained Rb or lost radiogenic Sr some time after caldera emplacement.

Figure 2-5. Variations of A. $\delta^{18}\text{O}$, and B. Sr as functions of initial Sr ratio. Symbols as in Fig. 2-3. Patterned bar indicates isochron value of $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$. Errors are smaller than sample size except for $\delta^{18}\text{O}$, which is shown in the upper left corner of B.

These samples have most probably lost radiogenic Sr because: their Rb-rich compositions are attributable to fractionation; they are highly siliceous; radiogenic Sr is readily removed from the feldspar and mica structures that host Rb in them, and; they yield young model ages (see below).

$^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios (Sr_i) and Model ages

Two types of model calculations are included in Table 2-1: values of Sr_i , calculated for individual samples based on the isochron age of 368 Ma; and model ages, calculated assuming an initial ratio of 0.70611.

Strontium and $\delta^{18}\text{O}$ are plotted as functions of Sr_i in Figure 2-5. From Fig. 2-5a it can be seen that Sr_i does not vary systematically as a function of Sr content or other indices of magmatic differentiation such as SiO_2 . However there are differences between the mafic and felsic rocks, the mafic rocks exhibiting less scatter than the felsic rocks. Mafic rocks exhibit no correlation between Sr content and Sr_i . However $\delta^{18}\text{O}$ and Sr_i are correlated (Fig. 2-5b); within the basalts and within the andesites, Sr_i increases slightly as $\delta^{18}\text{O}$ increases, indicating that these variations are due to geothermal alteration. Mafic rocks with large Sr_i values also have model ages that are older than the rocks themselves, mainly because the isochron value of the initial ratio assumed in the calculation is too low, indicating that radiogenic Sr was introduced into the mafic rocks by the geothermal alteration process.

Felsic samples that have Sr_i values greater than the isochron value also have older model ages and large $\delta^{18}\text{O}$ values (Table 2-1); both are attributed to contamination of the igneous rocks with radiogenic Sr from the supracrustal country rocks by AFC and geothermal alteration processes as discussed above. Two Rb-rich samples, MC-196 and 82-14, with low (and geologically unreasonable) Sr_i values have lost radiogenic Sr at some time after caldera emplacement; the model ages for these samples, 318 and 345 Ma, respectively, may provide an approximation of the time of radiogenic Sr loss. Another

Rb-rich sample from the Mount Pleasant Porphyry, MC-314a, also has a low calculated Sr_i value. However the model age of this sample, 365 Ma, is very close to the isochron value. The Rb/Sr ratio of this sample is so high (see Table 2-1) that the model age calculation is insensitive to relatively large errors in the measured and initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios. Because of this insensitivity the model age of this sample is probably geologically meaningful suggesting that the age of the Mount Pleasant Porphyry is close to that of the intracaldera rocks determined by the Rb/Sr isochron. It also appears that the entire igneous suite of the caldera complex, when uncontaminated by supracrustal Sr, had an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of approximately 0.7061.

MODELLING THE MAGMATIC EVOLUTION OF THE MAGMA CHAMBER(S)

An assumption implicit in the Rb-Sr isochron method is that isochronous samples have Sr isotopic compositions that have evolved in a closed system. If this assumption is true for the Mount Pleasant Caldera then the intracaldera rocks ranging from andesite to rhyolite evolved as a closed magmatic system. This range of magma compositions are probably not the products of partial melting of a crustal protolith because the andesites have liquidus temperatures in excess of 1000 °C that would be difficult or impossible to achieve in the continental crust. This would indicate that the predominantly felsic rocks of the caldera are the products of mantle derived magmatism. On the other hand, it seems surprising that such a large range of igneous rocks types that evolved in thick continental crust remained an isotopically closed system throughout their evolution. Thus it seems prudent to test the closed system fractional crystallization model for the andesite through rhyolite intracaldera igneous rocks further.

Table 2-2. Phenocryst and groundmass mineralogy of selected igneous rocks of the Mount Pleasant caldera complex. Lithologies increases in silica content from top to bottom of table. An = anorthite content of Pl; Ap = apatite; Bt = biotite; Chl = chlorite; Cpx = clinopyroxene; Hbl = hornblende; Kfs = K-feldspar; Ol = olivine; Pl = plagioclase; Ti-mag = titanomagnetite; Qtz = quartz; Zrn = zircon. § occurs rarely. *xenocrystic. Abbreviations after Kretz (1983).

Formation/	P H E N O C R Y S T S	Pl	Cpx	Hbl	Bt	Kfs	Qtz	Accessory Minerals	G R O U N D M A S S	Mineralogy
Kleef Formation		x								Pl, Cpx, Ti-mag, Ap, Chl
Hoyt Station Basalt		x					.			Pl, Cpx, Ti-mag, Chl
South Oromocto Andesite		x	x					Ol(?) pseudomorphs		Pl, Cpx, Ti-mag
Scouler Mtn. andesite		x	x	x				Ol(?) pseudomorphs; martitized Ti-mag; Ap		Pl, Chl, Ti-mag; local interstitial Kfs and Qtz
McDougall Brook Microgranite		x	§	x	x	x	x	martitized Ti-mag; Ap; Zrn		Kfs, Pl, Qtz, Hbl, Ti-mag, Ap; Bt locally
Little Mt. Pleasant Fm.		x		x	x	x	x	martitized Ti-mag; Ap; Zrn		
Seelys Fm.		x			x	x	x	rare Ti-mag; metamict Zrn		
Mt. Pleasant Porphyry		x			x	x	x	trace Zrn		

Descriptive Geochemistry and Process Identification

Reverse modelling of the trace element geochemistry of a suite of cogenetic igneous rocks requires identification of at least one highly incompatible trace element. Given the mineralogy listed in Table 2-2 and the range of elements analyzed (Appendix 1), only a few trace elements are likely candidates — Th, U, Rb and Ta (e.g., Henderson, 1981). Uranium and Ta are not ideal because of their very low concentrations and variability in these rocks. In contrast, Rb and Th have higher abundances, greater variability, and can be measured with greater precision. A plot of Rb content versus Th content (Fig. 2-6) allows comparison of these two elements, which covary and are positively correlated, indicating that both are incompatible. However, in contrast to Th, Rb shows a considerable range of variation within units as well as between units. This indicates that the distribution of Rb may have been affected by other processes in addition to fractional crystallization. In contrast, Th is known to be one of the least sensitive elements to exogenous processes. Therefore Th is considered to be the best choice of an incompatible element for modelling purposes.

A test of the hypothesis that the andesitic through rhyolitic volcanic rocks of the Mount Pleasant Caldera complex are related through fractional crystallization is shown graphically in Figure 2-7. For a trace element T that is being affected by batch partial melting or Rayleigh fractional crystallization, if $D \ll 1$, then $F = T_0/T_L$ where D = bulk distribution coefficient, F = fraction of liquid during fractional crystallization or partial melting, T_0 = weight fraction of T in the parent, and T_L = weight fraction of T in the fractionated liquid (e.g., Hanson, 1978). Using this relationship, theoretical curves for batch partial melting and Rayleigh fractionation can be compared with trends of the Mount Pleasant Caldera data. Curves for fractional partial melting would be similar to those for batch melting and are not shown. Most of the data and particularly the isochronous samples conform to variations in Th and Sr content expected for closed system fractionation of an andesitic magma chamber with bulk distribution coefficients

Figure 2-6. Plot of Rb (ppm) versus Th (ppm) in igneous rocks of the Mount Pleasant Caldera. The data define two trends as indicated by the arrows. The main trend is defined by a positive, linear covariation of Rb and Th. The second trend is toward increasing Rb contents within particular rock types. Symbols as in Fig. 2-3.

Figure 2-7. Model curves for fractional crystallization and batch partial melting compared with variations of a highly compatible trace element (Sr) and a highly incompatible trace element (Rb) in the caldera rocks. F = fraction of melt; Sr_L = Sr content of fractionating magma; Th_L = Th content of fractionating magma; Th_O = Th content of parental magma. D = bulk distribution coefficient.

for Sr of between 3 and 4. Similar results are obtained using Rb instead of Th (not shown). The data clearly do not conform to the model partial melting curves.

If the rocks were produced by fractional crystallization then the nature of the bulk distribution coefficients of trace elements can be evaluated from log-log trace element variation diagrams with a highly incompatible element on the abscissa (Allègre et al., 1977). Log-log plots of Th versus selected trace elements are shown in Fig. 2-8. The Kleef basalts (indicated by arrows in Fig. 2-8) have trace element contents that do not follow trends defined by the rest of the data, particularly with respect to Sr and REE. Kleef basalts may therefore not be related to the rest of the suite through simple crystal fractionation. U, Ta, and Rb show consistent incompatible behaviour. The other elements show more complex behaviour. Lu (and other heavy REE) is incompatible, with an increase in slope in felsic compositions indicating that it becomes even more so. Sr is highly compatible and the increasing slope of the trend indicates that its compatibility increases during differentiation. Sc and Zr are moderately compatible and incompatible, respectively, except in intermediate compositions where they are both strongly compatible. K, Ba and Eu are incompatible in mafic rocks but compatible in felsic rocks. La (and other light REE) are generally incompatible except in the Seelys tuffs where it becomes highly compatible. These relationships indicate complex and changing crystallization patterns in an evolving magma chamber.

DISCUSSION AND CONCLUSIONS

Comparison with Previous Dating Attempts

Previous dating attempts have been directed primarily at determining the age of the "late intrusive phases" of the Mount Pleasant Caldera complex, the closely associated Pomeroy Intrusive Suite (represented by the Beech Hill and Pleasant Ridge granites in Table 2-3), and deposits of Sn-W-Mo deposits that are associated with them. These data

Figure 2-8. Plots of log of selected trace elements(ppm) versus log Th (ppm). A. compatible elements. B. incompatible elements. C. incompatible elements that show compatibility changes in felsic compositions.

are summarized in Table 2-3. Most of these data are derived from the use of the K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ methods and indicate ages in the range 358 Ma -367 Ma, which are indistinguishable from the Rb/Sr isochron age for the intracaldera igneous rocks and the model age of the Mount Pleasant Porphyry reported here. However, two Rb/Sr whole rock dates and two K/Ar dates reported by Kooiman et al. (1986) and Fyffe et al. (1981) indicate an age of approximately 340 Ma. This is probably not the true age of the intrusive rocks at the mine because: 1) K/Ar dates of their contact aureole and $^{40}\text{Ar}/^{39}\text{Ar}$ dates from biotites in similar rocks yield older ages (Table 2-3), and; 2) the samples used had extremely high Rb/Sr ratios which would make them susceptible to loss of radiogenic Sr and this has occurred in at least some Rb-rich felsic caldera rocks as described above. Furthermore, the isochron date reported here and the Kooiman et al. errorchron shared a common sample (82-19), which was the most Rb-poor sample of the previous study but the most Rb-rich sample in the present one. Kontak et. al. (1991) have concluded that anomalously young whole-rock Rb/Sr dates of granitic intrusions and related mineral deposits in Nova Scotia are the product of isotopic resetting produced by a tectonothermal event at circa. 330-340 Ma that was unrelated to the magmatism and mineralization. This later event probably involved rejuvenation of faults that had been the loci for mineralization. A similar tectonothermal event occurring in the time range 320-345 Ma (as indicated by the model ages) has probably affected the Mount Pleasant Caldera. The two samples from this study with anomalously low Sr_i values were collected from widely spaced localities but both were situated close to the caldera ring fracture system; these faults could have been reactivated or served as channels for movement of hydrothermal fluids at some time after caldera emplacement. Therefore, the magmatism and mineralization at the Mount Pleasant Mine are not younger than about 360 Ma. and were probably formed during the waning stages of the caldera cycle. Detailed modelling in Chapter 3 does in fact indicate that the Mount Pleasant Porphyry, and by association, the granitic rocks beneath the Mount Pleasant Mine could be derived

Table 2-3. Summary of geochronological data for the Mount Pleasant area. All ages are quoted. Abbreviations are: (P) = ^{40}Ar - ^{39}Ar plateau age; (T) = ^{40}Ar - ^{39}Ar total gas age; (I) = Rb-Sr isochron age; (E) = Rb-Sr errorchron age. References are: 1, McLeod et al. (1988); 2, McLeod (pers. comm., 1992); 3, sample GSC 89-113 in Hunt and Roddick (1990); 4, Billiton Canada internal report (1986); 5, McGregor & McCutcheon (1988); 6, Butt (1976); 7, Fyffe et al. (1981); 8, Kooiman et al. (1986).

Age (Ma)	Method	Material	Host lithology/setting	Reference
367 $\pm$ 2	^{40}Ar - ^{39}Ar (P)	Biotite	Mount Douglas Granite; youngest intrusive unit of Saint George Batholith.	1
367 $\pm$ 7	^{40}Ar - ^{39}Ar (P)	Biotite		
366 $\pm$ 1	U-Pb	Monazite	Mount Douglas Granite; youngest intrusive unit of Saint George Batholith.	2
361 $\pm$ 9	K-Ar	Whole rock	Biotite hornfels in sedimentary breccia unit intercalated with felsic ash-flow tuff of the	3
360 $\pm$ 1	^{40}Ar - ^{39}Ar (P)	Lithium mica	Pleasant Ridge granite pluton located 13 km southwest of the caldera margin.	4
ca. 360	----	Miospores	Carrow Formation, an alluvial fan deposit in the exocaldera sequence.	5
ca. 359	^{40}Ar - ^{39}Ar (T)	Biotite	Granitic intrusives, Fire Tower Zone, Mount Pleasant Mine area,	4
ca. 358	^{40}Ar - ^{39}Ar (T)	Biotite	hydrothermally altered	
349 $\pm$ 11	Rb-Sr(I)	Whole rocks	Beech Hill granite pluton, located 6 km southwest of the caldera margin.	6
337 $\pm$ 15	Rb-Sr(I)	Whole rocks	Beech Hill granite pluton.	7
339 $\pm$ 10	K-Ar	Whole rock	Granite porphyry, Fire Tower Zone, Mount Pleasant Mine area,	8
334 $\pm$ 7	K-Ar		hydrothermally altered.	
328 $\pm$ 4	Rb-Sr(E)	Whole rocks	Granitic intrusives, Fire Tower Zone, hydrothermally altered.	8

by extreme fractional crystallization (90-98%) of a monzogranitic magma that formed the McDougall Brook Microgranite.

Geophysical Setting of the Magma Chamber

Acceptance of the conclusion that there was a closed system andesitic to rhyolitic magma chamber beneath the caldera leads to several questions. There is no doubt that there was a large body of felsic magma beneath the caldera complex, as indicated by the coincidence of the intracaldera sequence with a gravity low (Williams, 1978). Detailed gravity modelling of the Saint George Batholith and associated plutons (Thomas and Willis, 1989) indicates that the felsic magma chamber associated with the Mount Pleasant Caldera could have been 4-5 km thick. If these felsic rocks were indeed derived by magmatic fractionation of an andesitic parent, then the geochemical model requires an original andesitic magma chamber 2-3 times this size. Such a chamber would represent half the present thickness of the crust in this area (Durling and Marillier, 1991). What are the physical and chemical conditions that would allow such a large, initially mafic magma chamber to undergo fractionation with such minimal interaction with its wall rocks? Intuitively it can be reasoned that magmas with low liquidus temperatures, intruded into cold country rocks, would assimilate the least amount of their country rocks. Country rocks are heated the least when the rates of magma injection and magmatic evolution are high (Shaw, 1980). Metamorphic country rocks with low water contents and permeability might also inhibit assimilation of and/or exchange of material with the country rocks, particularly that involving fluid movements. If the country rocks were cold enough at a depth of 15 km to have minimal interaction with andesitic magmas, then it seems likely that either geothermal gradients were low or the crust was thick (effectively accomplishing the same thing). The widespread magmatic activity occurring throughout the area during the Devonian would tend to indicate that the crust was thick because such extensive magmatism should be an effective mechanism for increasing

2

PM-1 3 1/2" x 4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

geothermal gradients in thin crust (e.g., Gans, 1987). This would tend to suggest that the Mount Pleasant Caldera was formed by rapid rates of injection and evolution of andesitic magmas into cold country rocks in relatively thick crust and that crustal extension was still in the early stages or had not yet begun, at least within the upper crust where the magma chamber resided.

Implications for Felsic Magmatism in the Northern Appalachians

The northern Appalachians experienced widespread granitoid magmatism that was broadly late- to post-tectonic in character, and occurred in the Late Silurian to Late Devonian in the Canadian Appalachians. This magmatism, even when accompanied by coeval mafic activity has been viewed by most researchers as a product of partial melting of crustal protoliths (e.g., Fyffe et al., 1981; McCutcheon, 1991). The rationale for this is the relatively small volumes of mafic rocks compared to felsic rocks. The mechanisms most commonly invoked are heating of lower crust that was thickened during orogenesis, or less commonly, post-tectonic rifting. If any genetic role is accorded to the mafic materials it is generally limited to providing an additional heat source for the melting of the crust. Petrogenetic research has thus focused on the nature of the lower crustal source regions (e.g., Ayuso and Bevier, 1991). There are in fact, many syn- to late-tectonic granitoids that were derived from wet, low temperature magmas that could have been partial melts of crustal protoliths— these granitoids are highly peraluminous (containing muscovite, garnet, andalusite, etc.), with restite xenoliths, and are generally emplaced at relatively deep crustal levels due to adiabatic cooling caused by their high volatile contents. Magmas like these could have low liquidus temperatures ($< 750^{\circ}\text{C}$). In contrast, many of the late- to post-tectonic granitoids are biotite and/or hornblende-bearing, relatively anhydrous (with the exception of late-stage fractionates), emplaced at high crustal levels, and therefore must have had high liquidus temperatures ($800\text{--}900^{\circ}\text{C}$). These temperatures are difficult to achieve in the crust; if the possibility is allowed

that these magmas are derived from more mafic magmas, as in the case of the Mount Pleasant Caldera magma chamber, a crustal protolith becomes an impossibility (e.g. Morse, 1991).

The results of this study require a re-examination of several of these assumptions. Firstly, a predominance of felsic over mafic rocks does not necessarily require that mafic magmas played a minor role in the petrogenesis of the felsic magmas. Throughgoing crustal fractures formed in an extensional environment may be required to tap dense mantle-derived magmas from the base of the crust to the earth's surface (e.g., Spera, 1980; Shaw, 1980). Basaltic magmas intruded into crust that is not fractured and extending will tend to be ponded at deep levels where they can undergo extensive hybridization and fractionation. In the Mount Pleasant Caldera the felsic rocks are clearly fractionates of andesitic parents. Trace element chemistry further suggests that the andesites are hybridized fractionates of mantle-derived basalts (Chapter 1). This is potentially the case for all of the post-tectonic granitoid magmatism in southern New Brunswick. Therefore the mechanism for magma production must include upwelling and emplacement in the crust of large amounts of mantle-derived basalts. In the case of the Mount Pleasant Caldera it could be assumed that such an upwelling was caused by the period of crustal extension that produced the Maritimes Basin. However, the early plutons of the Saint George Batholith were certainly emplaced in a pre-extensional environment. Therefore, it is possible that mantle upwelling was the cause of late- to post compressional granitoid magmatism and subsequent crustal extension in the Canadian Appalachians.

REFERENCES

- Allègre CJ, Treuil M, Minster JF, Minster B, Albarede F (1977) Systematic use of trace element in Igneous Processes. *Contrib Mineral Petrol* 60: 57-75

- Ayuso RA, Bevier ML (1991) Regional differences in Pb isotopic compositions of feldspars in plutonic rocks of the northern Appalachian Mountains, U.S.A. and Canada: a geochemical method of terrane correlation. *Tectonics* 10, 191-212.
- Bevier ML (1989) U-Pb geochronological studies of igneous rocks in New Brunswick. In: Abbott SA (ed.) *Thirteenth Annual Review of Activities, project resumes, 1988*. New Brunswick Department of Natural Resources & Energy, Mineral Resources & Energy Division, Information Circular 88-2, 134-140
- Blanchard M-C, Jamieson RA, More EB (1984) Late Devonian — Early Carboniferous volcanism on western Cape Breton Island, Nova Scotia. *Canadian Journal of Earth Sciences* 21: 762-774
- Borthwick J, Harmon RS (1982) A note regarding ClF_3 as an alternative to BrF_5 for oxygen isotope analysis. *Geochim Cosmochim Acta* 46: 1665-1668
- Butt (1976) Genesis of granitic stocks in southwestern New Brunswick. unpublished Ph.D. thesis, University of New Brunswick, Fredericton, New Brunswick, 234 pp.
- Clayton RN, Mayeda TK (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim Cosmochim Acta* 27: 43-52
- Dostal J, Keppie JD, Dupuy C (1983) Petrology and geochemistry of Devonian-Carboniferous volcanic rocks in Nova Scotia. *Maritime Sediments and Atlantic Geology* 19: 59-71
- Durling PW, Marillier FJY (1990) Structural trends and basement rock subdivisions in the western Gulf of St. Lawrence, northern Appalachians. *Atlantic Geology* 26: 79-95
- Fyffe LR, Barr SM (1986) Petrochemistry and tectonic significance of Carboniferous volcanic rocks in New Brunswick. *Canadian Journal of Earth Sciences* 23: 1243-1256

- Fyffe LR, McLeod MJ, Ruitenburg AA (1992) A geotraverse across the St. Croix - Avalon terrane boundary, southern New Brunswick. Geological Association of Canada, Mineralogical Association of Canada, Joint Annual Meeting, Wolfville '92; Field Trip A1, Guidebook, 44 pp.
- Fyffe LR, Pajari GE Jr., Cherry ME (1981) The Acadian plutonic rocks of New Brunswick. *Maritime Sediments and Atlantic Geology* 17: 23-36
- Gans PB (1987) An open-system, two-layer crustal stretching model for the eastern Great Basin. *Tectonics* 6: 1-12
- Hanson GN (1978) The application of trace elements to the petrogenesis of igneous rocks of granitic composition. *Earth and Planetary Science Letters* 38: 26-43.
- Henderson P (1981) *Inorganic geochemistry*. Pergamon Press, New York, 353 pp.
- Hubacher FA, Lux DR (1987) Timing of the Acadian deformation in northeastern Maine. *Geology* 15: 80-83
- Hunt PA, Roddick JC (1990) A compilation of K-Ar ages, Report 20. In: *Radiogenic Age and Isotopic Studies: Report 3*, Geological Survey of Canada, Paper 89-2, 153-190
- Kontak DJ, Cormier RF (1991) Geochronological evidence for multiple tectonothermal overprinting events in the East Kemptville muscovite-topaz leucogranite, Yarmouth County, Nova Scotia, Canada. *Canadian Journal of Earth Sciences* 28: 209-224
- Kooiman GJA, McLeod MJ, Sinclair WD (1986) Porphyry tungsten-molybdenum ore bodies, polymetallic veins and replacement bodies, and tin-bearing zones in the Fire Tower Zone, Mount Pleasant, New Brunswick. *Economic Geology* 81: 1356-1373
- Kretz R (1983) Symbols for rock-forming minerals. *Am Mineral* 68: 277-279
- MacLellan HE, Taylor RP (1989) Geology and geochemistry of the Burnthill granite and its related W-Sm-Mo-F mineral deposits, central New Brunswick. *Canadian Journal of Earth Sciences* 26: 499-514

- McCutcheon SR (1991) The Late Devonian Mount Pleasant Caldera complex: stratigraphy, mineralogy, geochemistry and geologic setting of a Sn-W deposit in southwestern New Brunswick. unpublished Ph.D. thesis, Dalhousie University, Halifax, Nova Scotia, 609 pp**
- McCutcheon SR, Bevier ML (1990) Implications of field relations and U-Pb geochronology for the age of gold mineralization and timing of Acadian deformation in northern New Brunswick. *Atlantic Geology* 26: 237-246**
- McCutcheon SR, Robinson PT (1987) Geological constraints on the genesis of the Maritimes Basin, Atlantic Canada. *Canadian Society of Petroleum Geologists, Memoir* 12: 287-297**
- McGregor DC, McCutcheon SR (1988) Implications of spore evidence for Late Devonian age of the Piskahegan Group, southwestern New Brunswick. *Canadian Journal of Earth Sciences* 25: 1349-1364**
- McLeod M J, Taylor RP, Lux DR (1988) Geology, $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology and Sn-W-bearing sheeted veins of the Mount Douglas Granite, southwestern New Brunswick. *Canadian Institute of Mining and Metallurgy Bulletin* 81: 70-77**
- Matsuhisa Y, Goldsmith JR, Clayton RN (1979) Oxygen isotope fractionation in the system quartz - albite - anorthite - water. *Geochimica et Cosmochimica Acta* 43: 1131-1140**
- Morse SA (1991) Basaltic magma from the crust is not a free option. *EOS* 72(14): 161**
- O'Neil JR (1986) Theoretical and experimental aspects of isotopic fractionation. In: Valley JW, Taylor HP Jr., O'Neil JR (eds.) *Stable isotopes in high temperature geological processes*, Mineralogical Society of America, *Reviews in Mineralogy* 16: 1-40**
- Palmer AR (1983) The Decade of North American Geologic 1983 Time Scale. *Geology* 11: 503-504**

- Ruitenburg AA, McCutcheon SR (1982) Acadian and Hercynian structural evolution of southern New Brunswick. Geological Association of Canada, Special Paper 24: 131-148
- St. Peter CJ, Fyffe LR (1990) Structural trends and basement rock subdivisions in the western Gulf of St. Lawrence: Discussion. *Atlantic Geology* 26: 277-279
- Shaw HR (1980) The fracture mechanisms of magma transport from the mantle to the surface. In: Hargraves RB (ed.) *Physics of Magmatic processes*, Princeton University Press, Princeton, New Jersey, 201-264
- Sinclair WD, Kooiman GJA, Martin DA (1988) Geological setting of granites and related tin deposits in the North Zone, Mount Pleasant, New Brunswick. Current Research, Part B, Geological Survey of Canada, Paper 88-1B: 201-208
- Spera FJ (1980) Aspects of magma transport. In: Hargraves RB (ed.) *Physics of Magmatic processes*, Princeton University Press, Princeton, New Jersey, 265-323
- Steiger RH, Jäger E (1977) Subcommittee on geochronology: convention on the use of decay constants in geo- and cosmochemistry. *Earth Planet Sci Lett* 36: 359-362
- Sun S.-s., McDonough WF (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. Geological Society Special Publication No. 42: 313-345
- Taylor RP (1992) Petrological and geochemical characteristics of the Pleasant Ridge zinnwaldite — topaz granite, southern New Brunswick, and comparisons with other topaz-bearing felsic rocks. *Canadian Mineralogist* 30:895-921
- Thomas MD, Willis C (1989) Gravity modelling of the Saint George Batholith and adjacent terrane within the Appalachian Orogen, southern New Brunswick. *Canadian Journal of Earth Sciences* 26: 561-576
- van de Poll HW (1967) Carboniferous volcanic and sedimentary rocks of the Mount Pleasant area, New Brunswick. New Brunswick Department of Natural Resources, Mineral Resources Branch, Report of Investigation, 52 pp.

van Waggoner NA, Fay VK (1988) Stratigraphy and volcanology of a portion of the Lower Devonian volcanic rocks of southwestern New Brunswick. Geological Survey of Canada, Paper 88-1B: 69-78

Williams DA (1978) Compilation Bouger gravity map of New Brunswick, Scale 1:250,000, Woodstock (21J). New Brunswick Department of Natural Resources, Mineral Resources Division, Plate 78-42e.

York D (1969) Least-squares fitting of a straight line with correlated errors. Earth Planet. Sci. Lett. 5: 320-324.

**CHAPTER 3. Magmatic evolution of the epizonal magma chamber of the
Mount Pleasant Caldera complex: Part 2. Evidence from Pearce
Element Ratio analysis of chemical variation in the igneous rocks**

ABSTRACT

Detailed Pearce Element Ratio analysis, in combination with conventional trace element modelling, demonstrate that highly silicic magmas of the Mount Pleasant Caldera were derived from an andesitic parental magma by a two-stage process of convective fractionation. In Chapter 2, it was shown that a wide range of effusive and hypabyssal igneous rocks in the caldera are part of an isotopically closed system, and stratigraphic relationships indicate that the entire range of magma compositions (andesite — high-silica rhyolite) coexisted in the magma chamber. By adapting the method of Pearce Element Ratio graphical analysis to the complex felsic system of the Mount Pleasant Caldera it is possible to identify two stages of fractionation and to quantify the mineral assemblage involved in fractionation at each stage. In stage 1, fractionation of andesite produced a monzogranitic differentiate (McDougall Brook Microgranite). In stage 2, fractionation of the monzogranite produced high-silica rhyolite. The calculated assemblages are different than the modal mineralogy. Both stages are characterized by multiple saturation with several essential and accessory minerals. From this it is concluded that *in situ* crystallization accompanied by convective fractionation was occurring simultaneously in two different parts of a vertically stratified magma chamber. The magma chamber apparently consisted of a stratified, double-diffusive lower andesite layer (layer a) a relatively homogeneous, monzogranitic middle layer (layer b), and a

stratified, double-diffusive, upper high-silica rhyolite layer (layer c). This inherently unstable configuration could have been maintained in a state of dynamic equilibrium by repeated injections of andesitic magma into the base of the chamber.

INTRODUCTION

The Mount Pleasant Caldera complex, located in the northern Appalachians, is a rare example of a pre-Cenozoic epicontinental caldera complex (Chapter 1). An understanding of age and petrogenesis of the Mount Pleasant Caldera complex are important because: 1) it is one of the last magmatic events in a period of syn- to post-tectonic magmatism of the Acadian Orogeny; 2) it was emplaced at or near the onset of a period of crustal extension and thermal collapse that resulted in the formation of a large aborted rift (Maritimes Basin); 3) it contains a broad range of igneous rock types that have potentially preserved evidence of the complex array of processes that were involved in its petrogenesis; 4) its stratigraphy is well-known and the volcanic rocks are clearly related genetically, and; 5) it is undeformed and less altered than many other volcanic complexes in the northern Appalachians (e.g., Coyle and Strong, 1987; Blanchard et al., 1984; Dostal et al., 1983). The Mount Pleasant Caldera thus affords a rare opportunity to study the petrogenesis of post-tectonic magmatism in the northern Appalachians.

Stratigraphic, petrographic, and whole rock geochemical data indicate the presence of a high-level felsic magma chamber beneath the Mount Pleasant Caldera complex that underwent repeated episodes of fractional crystallization punctuated by episodic eruptions (Chapters 1 and 2). In Chapter 2 the range of magma compositions that coexisted within the magma chamber was determined to vary from high-silica rhyolite to andesite, on the basis of Sr and O isotope, and trace element data. It was further demonstrated that this magma chamber could be viewed as a closed system and that the more felsic rocks were probably produced by fractional crystallization of the

andesites, on the basis of reverse modelling of trace element chemical variation. However, this interpretation presented a contradiction because on the basis of forward modelling of trace element variation, McCutcheon (1991) concluded that the felsic rocks could not be derived from the andesites by fractional crystallization of the modal phenocryst assemblage present in the andesites. This situation, where isotopic and trace element modelling seem to require different interpretations of the petrogenesis of a single igneous system, is not uncommon in igneous petrology and is often rationalized by hypothesizing that the geochemical behaviour of the isotopes and trace elements are somehow "decoupled".

In this study the apparent contradiction is resolved for the case of the Mount Pleasant Caldera by demonstrating that the fractionating mineral assemblage of the andesitic parent was different from the modal mineralogy of erupted andesites. It is further shown that fractionation of the magma chamber involved a two-stage process of convective fractionation (in combination with *in situ* crystallization) that occurred in different parts of the magma chamber and involved different magma compositions.

In order to perform this analysis it was necessary to devise a method, other than point counting of thin sections, of estimating proportions of fractionating minerals. This has been accomplished by adapting the method of Pearce Element Ratio (PER) analysis, most commonly applied to basaltic systems, to the analysis of the multiply saturated, more felsic suite of the Mount Pleasant Caldera. PER diagrams can be used to reverse model major element geochemical variations. These diagrams were developed by Pearce (1968) to overcome the closure problem that generally prevents graphical modelling of petrogenetic trends using Harker variation diagrams. A thorough treatment of the method is provided in Russell and Stanley (1990) and in references cited therein.

The denominator of a PER is a conserved element — one whose mass does not change during the process being investigated — in this case an element that is incompatible in minerals crystallizing from the magma. The result of this normalization

procedure is that data distribution is due entirely to the relative variations of the numerator components. The method can tolerate a small degree of compatibility of the denominator element — errors are insignificant as long as its bulk distribution coefficient (D) < 0.01 (Ernst, 1990). For the case where $0.01 < D < 1$, the slopes of PER diagrams can be corrected for incomplete conservation of the denominator element (Ernst, *ibid.*). Spurious correlations produced by choice of a denominator that is not conserved can be recognized because the resulting induced correlation constrains the data to intercept the origin (Pearce, 1987).

The numerator of a PER is chosen to be another element, or an equation designed to represent the stoichiometry of minerals crystallizing from the system. PER diagrams can be interpreted quantitatively in terms of mineral losses (or gains) during fractional crystallization. In systems that have not suffered post-magmatic alteration, where the denominator is a major element whose concentration has been measured with high precision, rigorous analysis of competing genetic hypotheses is possible, using statistical criteria. Such rigorous analysis is not possible in the case of the rocks of the Mount Pleasant Caldera where several types of postmagmatic alteration have been identified (particularly affecting the felsic rocks) and only trace elements (whose concentrations are difficult to measure with great precision) are conserved throughout the process of magmatic evolution. To overcome this problem, PER analysis has been used in conjunction with isotopic analysis and conventional trace element modelling in order to test and constrain two assumptions that are fundamental to the PER method: 1) that the system was closed, and; 2) that the denominator element was conserved. Used in this way, PER analysis can provide vital information about the evolution of complex magmatic systems that cannot be obtained by any other means.

GEOLOGY OF THE CALDERA COMPLEX

The regional and tectonic environment and geochronology of the Mount Pleasant Caldera complex have been discussed in detail in Chapter 2. The Mount Pleasant Caldera complex comprises three lithofacies (intracaldera, exocaldera and late caldera-fill sequences in Fig. 3-1) that form the Piskahegan Group. Attention is focused here on the intracaldera sequence, which contains all of the igneous rocks that belong to the isotopically closed system identified in Chapter 2.

The intracaldera sequence of the rocks of the caldera complex was emplaced in a typical caldera-forming cycle (McCutcheon, 1991; Chapter 1). The oldest exposed rocks in this sequence (Fig. 3-1) are mesobreccias and intercalated andesitic lava flows and rhyolitic ash flow tuffs (intruded by small dioritic stocks and dykes) of the Scoullar Mountain Formation. These rocks were emplaced around the margins of the caldera following cauldron collapse. The Scoullar Mountain andesites are stratigraphically correlated with the South Oromocto Andesite of the exocaldera sequence. No other andesites occur in the caldera complex. Subsequently, chemically and mineralogically zoned rhyolitic ash flow tuffs of the Little Mount Pleasant Formation were erupted. The absence of younger margin-breccias in the intracaldera sequence, and correlative ash flow tuffs in the exocaldera sequence, indicates that eruption of the tuff maintained the level of the caldera floor and that volume was not lost to an outflow facies. A second major eruption produced another zoned, rhyolitic ash flow tuff sequence — the Seelys Formation. This eruption was accompanied by deposition of alluvial fan sediments (containing Seelys tuff clasts) and eruption of basaltic lava flows in the exocaldera sequence. McCutcheon (1991) has postulated that input of basaltic magma into the base of the chamber triggered eruption of the Seelys ash flow tuffs. The last major event consisted of extrusion of rhyolitic lava flows from the ring fracture zone into the exocaldera sequence, followed by resurgent doming of the caldera floor, stopping of the

Figure 3-1. Geology of the Piskahegan Group comprising the Mount Pleasant Caldera and related outflow facies rocks (after McCutcheon, 1991).

magma chamber roof, and intrusion of the McDougall Brook Microgranite into the intracaldera volcanic pile. Intrusion of the highly evolved Mount Pleasant Porphyry was a later event that is volumetrically unimportant but of interest due to associated economic Sn-W-Mo deposits. It has been a matter of debate whether this later intrusive activity occurred during the waning stages of the caldera forming cycle or represents a much younger igneous/hydrothermal event (e.g., Kooiman et al, 1986; McCutcheon, 1991; Chapter 1).

The geochemistry of the Mount Pleasant Caldera volcanics (Chapter 1) indicates that the basaltic rocks are mantle-derived, high-K tholeiites and that the associated high-K, calcalkaline andesites could have been derived from the basalts by fractional crystallization and assimilation of crustal material. The more felsic rocks form a high-K calcalkaline series and are probably related by episodes of fractional crystallization of a high level zoned magma chamber whose evolution was repeatedly interrupted by eruption of material from the roof zone. The felsic rocks were apparently derived from closed-system fractional crystallization of an andesitic magma (Chapter 2).

PETROGRAPHY OF THE INTRACALDERA IGNEOUS ROCKS

The petrography and mineral chemistry of the caldera complex has been described in detail in Chapter 1 and is briefly summarized in Table 3-1. The mineralogy is complex and changes substantially from the mafic to felsic units. The only minerals that are typically unaltered are quartz, apatite, zircon, and locally, clinopyroxene. The phenocryst mineralogy of the mafic rocks is predominantly plagioclase and augite. Plagioclase is commonly sericitized and/or saussuritized although zoning and zone compositions may still be recognized in many samples. Chlorite-oxide pseudomorphs after olivine occur locally in the Scoullar Mountain andesite and are often partially enclosed in other phenocrysts. These pseudomorphs have been referred to as xenocrysts

(McCutcheon, 1991) but the model presented below suggests that they could in fact be phenocrysts of their host magma. In addition to these minerals, partially to completely chloritized hornblende (edenite according to the classification scheme of Giret et al., 1980) occurs in andesites and diorites of the Scoullar Mountain Formation and McDougall Brook Microgranite, and altered biotite in the latter. In the most mafic rocks, apatite and Fe-Ti oxides occur in the groundmass but appear as microphenocrysts in some of the Scoullar Mountain andesites and more felsic rocks. The oxides have experienced substantial subsolidus modification in the form of exsolution and oxidation, which obscures their original mineralogy and composition.

In the felsic ash flow tuffs and lava flows the phenocryst mineralogy is significantly different. The phenocryst mineralogy, in the most common order of decreasing abundance, is quartz, K-feldspar, plagioclase, biotite, Fe-Ti oxide, apatite, and zircon. Inclusion relationships indicate that the crystallization sequence is the reverse of the abundances (McCutcheon, 1991). There is however some variability in modal phenocryst proportions and locally, K-feldspar is more abundant than quartz. Clinopyroxene phenocrysts occur sporadically in minor amounts. Chloritized amphibole is locally more abundant than biotite. All of the aluminosilicate minerals are strongly altered. Ferromagnesian minerals are partially to completely sericitized or chloritized. The feldspars are commonly sericitized and/or saussaritized and may be totally replaced by secondary minerals in some localities. K-feldspar invariably exhibits coarse patch perthite in variable proportions to the host. Plagioclase is frequently albitized but is believed to have been oligoclase originally (Harris, 1964).

Three postmagmatic processes affecting the mineralogy and chemistry of the Mount Pleasant Caldera have been identified (McCutcheon, 1991). The first process is devitrification (and commonly recrystallization as well) of felsic lava flows and ash flow tuffs. This process has resulted in mobility of alkalis, loss of Na from the system and albitization of oligoclase. The second process is deuteric alteration; this has affected

Table 3-1. Phenocryst and groundmass mineralogy of selected igneous rocks of the Mount Pleasant caldera complex. Lithologies increases in silica content from top to bottom of table. An = anorthite content of Pl; Ap = apatite; Bt = biotite; Chl = chlorite; Cpx = clinopyroxene; Hbl = hornblende; Kfs = K-feldspar; Ol = olivine; Pl = plagioclase; Ti-mag = titanomagnetite; Qtz = quartz; Zrn = zircon. § occurs rarely. *xenocrystic. Abbreviations after Kretz (1983).

Formation/		Pl	Cpx	Hbl	Bt	Kfs	Qtz	Accessory Minerals		Mineralogy
Kleef Formation	P H E N O C R Y S T S	x							G R O U N D M A S S	Pl, Cpx, Ti-mag, Ap, Chl
Hoyt Station Basalt		x					.			Pl, Cpx, Ti-mag, Chl
South Oromocto Andesite		x	x					Ol(?) pseudomorphs		Pl, Cpx, Ti-mag
Scouller Mtn. andesite		x	x	x				Ol(?) pseudomorphs; martitized Ti-mag; Ap		Pl, Chl, Ti-mag; local interstitial Kfs and Qtz
McDougall Brook Microgranite		x	§	x	x	x	x	martitized Ti-mag; Ap; Zrn		Kfs, Pl, Qtz, Hbl, Ti-mag, Ap; Bt locally
Little Mt. Pleasant Fm.		x		x	x	x	x	martitized Ti-mag; Ap; Zrn		
Seelys Fm.		x			x	x	x	rare Ti-mag; metamict Zrn		
Mt. Pleasant Porphyry		x			x	x	x	trace Zrn		

many of the rocks, both mafic and felsic, and resulted in sericitization and chloritization of feldspars, amphibole, biotite, and locally, clinopyroxene. The third process is hydrothermal alteration associated with degassing of the volcanic pile and associated intrusions. This process is localized along faults and fractures and can generally be recognized and avoided during the sampling process.

ANALYTICAL METHODS

27 whole-rock samples representing the major caldera igneous lithologies have been analyzed for major and trace elements. Major elements and Ba, Rb, Sr, Ni, Cr, V, Zr, Nb, Y, and Zn were analyzed using duplicate glass disks at the University of Ottawa using standard X-Ray fluorescence techniques. Sc, Sb, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th and U were analyzed by INAA at Ecole Polytechnique in Montreal. The averaged values of duplicate analyses are provided in Appendix 1; further details of the methods are provided in Taylor (1992). For the modelling, additional data from previous studies (McCutcheon, 1991; see Chapter 1; Appendix 1) have also been used. A limited number of duplicate analyses from this and McCutcheon's study indicate that interlaboratory agreement is good for the INAA results and for the X-Ray Fluorescence analyses with the exception of Y, Nb, Cr and Ni (see for example MC-074b, MC-082c and MC-158b in Appendix 1); these elements were not used in the modelling.

MODELLING THE MAGMATIC EVOLUTION OF THE MAGMA CHAMBER(S)

Introduction

Forward modelling of the magmatic evolution of the Mount Pleasant intracaldera volcanic rocks presents considerable challenges for the following reasons: 1) modal phenocryst proportions within the various units are variable making it difficult to estimate model mineral proportions from the rock modes; 2) phenocryst mineralogy changes as

rock types become more felsic, as shown in Table 3-1, making it impossible to assume constant modal mineralogy ; 3) it cannot be assumed that mineral/melt or bulk distribution coefficients are constant because of the large compositional range of magmas in combination with the first two reasons. Furthermore, fractional crystallization in both felsic and mafic magma chambers can be limited to certain portions of the magma chamber, usually the sides and/or floors (e.g., Sparks et al., 1984; McBirney et al., 1985; Turner and Campbell, 1986; Langmuir, 1989) raising the possibility that the modal mineralogy of the rock samples that are representative of the bulk magma(s) are unrepresentative of the fractionating mineral assemblage that is causing the chemical variation in the sample suite. Therefore an alternative modelling approach is required. The approach adopted here involves calculation of the fractionating mineral assemblage from PER analysis of major element variations as described above. This assemblage is then used for forward modelling. The results of the forward modelling can be used to test the assumption of conservation of the denominator element used in the PER analysis. If this assumption is not substantially correct a correction can be applied to the slopes of the PER diagrams, to account for errors in slopes caused by partial compatibility of the denominator element, as long as the bulk distribution coefficient of the element (D) remains less than one (if no element has a value of D less than one the method will not work). The process is then repeated iteratively and the results reassessed. In the present study, correction of the model for the mafic rocks proved unnecessary, and the first iteration of the modelled variation of the felsic rocks was sufficient to produce a solution that successfully modelled both the major and trace element variations.

Descriptive Geochemistry

The modelling approach requires that at least one element can be identified as being highly incompatible in a cogenetic suite of rocks. Given the mineralogy listed in Table 3-1 and the range of elements analyzed (Appendix 1), only a few trace elements are

likely candidates — Th, U, Rb and Ta (e.g., Henderson, 1981). Uranium and Ta are not ideal because of their very low concentrations and limited variability in the caldera rocks. In contrast to U and Ta, Rb and Th have higher abundances, greater variability, and can be measured with greater precision. In Chapter 2 it was shown that Rb and Th covary and are positively correlated indicating that both are incompatible; but, in contrast to Th, Rb shows a considerable range of variation within units as well as between units. This indicates that Rb contents are governed by more than one process. Perhaps Rb is partitioned preferentially into a magmatic fluid phase and is therefore partially decoupled from expected magmatic variations. In contrast, Th is known to be one of the least sensitive elements to exogenous processes. Therefore Th is considered to be the best choice of incompatible element for modelling purposes.

If the caldera rocks were produced by fractional crystallization then the D values of trace elements can be evaluated from log-log trace element variation diagrams with a highly incompatible element on the abscissa (Allègre et al., 1977). Log-log plots of Th vs. selected trace elements are shown in Fig. 3-2. The Kleef basalts have trace element contents that do not follow trends defined by the rest of the data, particularly with respect to Sr and REE. The Kleef basalts may therefore not be related to the rest of the suite by closed system fractional crystallization and are excluded from further discussion. U and Rb show consistent incompatible behaviour and their D values can be calculated from the slopes of the lines in these diagrams. The other elements show more complex behavior. Sr is highly compatible and the increasing slope of the trend indicates that its compatibility increases during differentiation. Lu (along with other heavy REE) is incompatible and its degree of incompatibility becomes even greater in felsic compositions. Sc and Zn are slightly compatible except in intermediate compositions where they are strongly compatible. Ba and Eu are incompatible in mafic rocks but compatible in felsic rocks. La (along with other light REE) is generally incompatible except in the Seelys ash flow tuffs where it becomes highly compatible. These

relationships indicate complex and changing crystallization patterns in an evolving magma chamber. However they also indicate that D values can reasonably be assumed to remain constant over restricted intervals of magma compositions.

A series of simple numerator type PER diagrams for major elements are plotted on Figure 3-3 along with vectors showing trends that would result from fractional crystallization of minerals that could influence the trends. In the mafic to intermediate rocks — South Oromocto Andesite, Scoullar Mountain andesites and diorites and McDougall Brook Microgranite — the most highly correlated trends are for diagrams containing Al, Mg, Ca Na and P, indicating that pyroxene (+/- olivine +/- hornblende), plagioclase, and apatite were the fractionating minerals. Scatter in Ti and Fe is probably due to variable magmatic crystallization histories of Fe-Ti oxides in these rocks; in particular, a group of three andesites (including sample LM-6 in Fig. 3-3) plot off the main trends on plots of Ti/Th, Fe/Th and P/Th versus Si/Th in Figure 3-3. These three samples contain microphenocrysts of apatite and Fe-Ti oxides; the geochemical trends suggest that these phenocrysts have accumulated in these samples; they have therefore been omitted from the calculations that follow. Extreme scatter of K and Zr indicate that fractionation of a silicate mineral cannot account for the observed variations of these elements and could also be indicative of some open-system behaviour of these elements in the andesites. In the felsic rocks, Si, Al, K and Na and to a lesser extent, Zr, dominate the variation in all diagrams, which indicates that fractionation of quartz, alkali feldspar, and zircon are responsible for the changing chemistry of these rocks; Fe and Si are well correlated also indicating that an Fe-rich ferromagnesian mineral (biotite and/or hornblende) is still fractionating from the felsic rocks. The mafic and felsic rocks have clearly crystallized a different mineral assemblage so the two are analyzed separately below.

Figure 3-2. Plots of log value of selected trace elements (ppm) versus log Th (ppm).

Figure 3-3. Simple-numerator PER variation diagrams with Th as the common denominator. Andesite samples referred to in the modelling are circled and labelled. Mineral abbreviations as in Table 3-1. Vectors show direction of variation caused by fractional crystallization of the minerals indicated. Vectors do not indicate magnitude of variation or absolute values of particular ratios.

• Mount Pleasant Porphyry • Little Mount Pleasant Formation
 • McDougall Brook Microgranite • Scoullar Mountain andesites/diorites
 • Seelys Formation • South Ormoco Andesite

PER modelling of major element variation

Assemblage test diagrams are a type of PER diagram designed with a simple numerator (element present in all of the mineral phases of interest — commonly Si or Al) on the abscissa, and a complex numerator (representing the mineral assemblage hypothesized to cause all of the variation of the abscissa numerator) on the ordinate. These diagrams allow determination of the mineral assemblage responsible for observed chemical variation in a rock suite. The correct assemblage produces a line through the trend of the data with a slope of one. The method and computer programs used to generate these diagrams were developed and described by Stanley and Russell (1989a). The mineral composition matrix used in the calculations is given in Table 3-2; entries in the table correspond to moles of an element in a mole of the mineral in question.

For both the mafic and felsic rocks, several phase assemblage test diagrams were constructed to test rival hypotheses concerning the fractionating mineral assemblage. All "possible" assemblages were tested with at least one diagram and as many diagrams as possible were constructed for each assemblage. The results are tabulated in Table 3-3 and the 'best-fit' assemblages are shown in Figure 3-4. The problem, particularly in the case of the data for mafic caldera rocks, was to determine which ferromagnesian silicate mineral(s) were being fractionated. For the mafic rocks, augite + plagioclase, augite + hornblende + plagioclase, and augite + orthopyroxene + plagioclase could be rejected on the basis of the slopes of the data trends. There were two different assemblages that could not be rejected — olivine + augite (+ plagioclase + magnetite + apatite) and olivine + augite + hornblende (+ plagioclase + magnetite + apatite); for the sake of simplicity, only the former is considered further. However, it is important to remember that amphibole has not been eliminated as a possible fractionating mineral. Similarly for the felsic rocks the silicate assemblage was determined to consist of quartz + K-feldspar + plagioclase + biotite (+/- hornblende + apatite + zircon).

Table 3-2. Mineral composition matrix for igneous rocks of the Mount Pleasant Caldera. Il = ilmenite; Mt = magnetite; other abbreviations as in Table 3-1. Values for Qtz, Zrn and Ap based on idealized mineral stoichiometry. Values for Aug, Hbl and Bt based on microprobe analyses of these minerals taken from McCutcheon (1991). Pl, Kfs, Ti-mag and Ol expressed as endmembers Ab, Or, An, Il, Mt, Fo and Fa due to subsolidus modification of these minerals in the rocks, which precluded accurate mineral analysis. Value for Ol calculated assuming Mg#s of clinopyroxene and olivine were the same.

[illegible]

Table 3-3. Regression slopes, intercepts and errors for complex-numerator PER diagrams of igneous rocks of the Mount Pleasant Caldera. S.E. = standard error; R = correlation coefficient.

Assemblage	PER Ratio	Slope	+1 S.E.	-1 S.E.	Y-Intercept	+1 S.E.	-1 S.E.	R
Stage 1: Andesites and Microgranites								
Pl + Cpx	(Al + 2.61Mg + 2Na)/Si	1.251	1.335	1.172	-1311984	-1158718	-1475556	0.90
Pl + Cpx	(0.49Mg + 2Ca + 3Na - 0.667Py)/Si	1.035	1.128	0.95	-1192371	-1026699	-1372902	0.84
Pl + Cpx	(3Al + 6.84Mg - 4Ca + 1.33Py)/Si	1.733	1.85	1.624	-1661331	-1448479	-1888531	0.90
Pl + Cpx + Opx	(0.577Al + Fe - Ti + Mg + 0.849Ca + 2.42Na - 0.283Py)/Si	1.243	1.339	1.154	-1331831	-1158570	-1518470	0.87
Pl + Cpx + Hbl	(0.692Al + 1.958Mg - 0.617Ca + 2.31Na - 0.206Py)/Si	1.181	1.266	1.102	-1268256	-1114840	-1432652	0.89
Pl + Cpx + Hbl	(0.178Ti + Al - 0.178Fe + 2.73Mg + 2Na)/Si	1.237	1.32	1.158	-1300915	-1148813	-1463285	0.90
Pl + Cpx + Hbl	(1.33Ti + 3Al - 1.33Fe + 7.79Mg - 4Ca + 1.33Py)/Si	1.656	1.789	1.533	-1633665	-1397285	-1895261	0.87
Pl + Cpx + Ol	(0.17Al + 0.5Fe - 0.5Ti + 0.5Mg + 1.66Ca - 0.553P + 2.83Na)/Si	1.116	1.211	1.027	-1250323	-1078882	-1436480	0.85
Pl + Cpx + Ol + Hbl	(0.17Al + 0.5Fe - 0.5Ti + 0.5Mg + 1.66Ca + 2.83Na - 10.55Py)/Si	1.144	1.274	1.028	-1625438	-1399534	-1876870	0.77
Stage 2: Felsic Rocks								
Ab + Or	(Na+K)/Al	0.7714	0.8029	0.7411	15508	22135	8609	0.95
An + Ab + Or	(2Ca+Na+K)/Al	0.8703	0.9036	0.8383	7459	14466	184	0.96
Bt + An + Ab + Or	(2Mg+2Ca+Na+K)/Al	0.9556	0.9926	0.92	2258	10049	-5835	0.95
Hbl + Bt + An + Ab + Or	(0.72Mg+2Ca+Na+K)/Al	0.9004	0.9341	0.8678	5768	12893	-1625	0.96

Figure 3-4. Complex-numerator "assemblage test" diagrams. A. Diagram to test for Si variation due to fractionation of olivine + augite + plagioclase in mafic to intermediate caldera igneous rocks. B. Diagram to test for Al variation due to fractionation of K-feldspar + plagioclase + biotite + hornblende in felsic caldera igneous rocks. Vectors show both direction and magnitude of variation caused by removal of equimolar amounts of the indicated minerals. Symbols as in Figure 3-3. Abbreviations as in Table 3-1. Reference dashed lines have slopes = 1. Actual slopes shown with solid line. Note that neither diagram provides a good discrimination of the presence or absence of hornblende crystallization.

The simple PER diagrams (Fig. 3-3) were used to determine the bulk composition of the fractionating mineral assemblages. The slopes of each leg in each diagram were calculated with PEARCE.PLOT, a PER plotting and data handling program (Stanley and Russell, 1989b) using the "reduced major axis" method of York (1966). The slope is equal to the ratio of the numerator elements in units of moles. Following the method of Ernst et al. (1988), this slope can be expressed as an equation that is the sum of mineral phases that contribute to the variation. For example, for the mafic to intermediate rocks

$$\Delta(\text{Al/Si}) = \Delta(0.1 \text{ Aug} + 2\text{An} + \text{Ab})/\text{Si}. \quad (1)$$

Similar expressions are easily derived for $\Delta(\text{Fe/Si})$, $\Delta(\text{Mg/Si})$, $\Delta(\text{Ca/Si})$, $\Delta(\text{Na/Si})$, $\Delta(\text{P/Si})$ and $\Delta(\text{Ti/Si})$ using Table 3-2. The equations are then solved using the slopes given in Table 3-4. The total fractionating mineral assemblage is given by

$$\Delta(\text{Total/Si}) = \Delta(\text{Fo} + \text{Fa} + \text{Aug} + \text{An} + \text{Ab} + \text{Ap} + \text{Il} + \text{Mag})/\text{Si} \quad (2)$$

This is a system of seven equations with 8 unknowns requiring a simplifying assumption in order to yield a solution. The simplification is accomplished by assuming that the Mg#s of augite and olivine are the same (0.58) thereby reducing $\Delta(\text{Fo/Si}) + \Delta(\text{Fa/Si})$ to $\Delta(\text{Ol/Si})$ in equation (2).

A similar procedure is followed for the felsic rocks. In this case the amount of quartz fractionating from the system is calculated from the following relationships

$$\Delta(\text{Si/Si}) = 1 = \Delta(\text{Qtz} + \text{Or} + \text{Ab} + \text{An} + \text{Bt} \pm \text{Hbl} + \text{Zrn})/\text{Si} \quad (3)$$

$$\Delta(\text{Total/Si}) = \Delta(\text{Si/Si}) + \Delta(\text{Ap} + \text{Mag} + \text{Il})/\text{Si} \quad (4)$$

For the felsic system there are 9 equations to describe 10 unknowns and a another simplification is necessary. In this case biotite + hornblende are modelled as biotite. This is done because biotite provides a better fit than hornblende in the phase assemblage test diagrams and because D values for hornblende in silica oversaturated felsic rocks are very poorly known. Unfortunately this simplification will affect the trace element

Table 3-4. Regression slopes, intercepts and errors for simple-numerator P/R diagrams of igneous rocks of the Mount Pleasant Caldera. S.E. = standard error; R = correlation coefficient.

Ratio	slope	+1 S.E.	- 1 S.E.	Y-intercept	+1 S.E.	-1 S.E.	R
Stage 1: Andesites and Microgranites							
Ti/Si	0.13911	0.04155	0.03681	-55082	-50597	-59846	0.92
Al/Si	0.43871	0.4585	0.41977	-318256	-281428	-356746	0.95
Fe/Si	0.26872	0.28545	0.25297	-369782	-339027	-402452	0.92
Mn/Si	0.0039	0.00448	0.0034	-5070	-4091	-6194	0.70
Mg/Si	0.20801	0.22502	0.19228	-327773	-297194	-360852	0.86
Ca/Si	0.25822	0.27916	0.23886	-397129	-359475	-437836	0.86
Na/Si	0.1577	0.18197	0.13667	-113912	-73010	-161109	0.66
K/Si	-	-	-	-	-	-	-
P/Si	0.01465	0.01545	0.01389	-21545	-20067	-23104	0.93
Zr/Si	-	-	-	-	-	-	-
Stage 2: Felsic Rocks							
Ti/Si	0.0048	0.0052	0.0045	-3352	-3003	-3727	0.87
Al/Si	0.2239	0.2303	0.2177	-29662	-22753	-36768	0.97
Fe/Si	0.0277	0.03	0.0255	-11770	-9420	-14315	0.83
Mn/Si	0.0008	0.0011	0.0006	-475	-256	-766	0.28
Mg/Si	0.0133	0.016	0.0111	-8068	-5600	-11030	0.48
Ca/Si	0.0184	0.0229	0.0148	-13654	-9666	-18608	0.40
Na/Si	0.0706	0.0841	0.0593	3172	15714	-11758	0.50
K/Si	0.1224	0.1287	0.1164	-33092	-26460	-40063	0.92
P/Si	0.001	0.0012	0.0009	-693	-565	-838	0.68
Zr/Si	0.00003	0.00003	0.00003	-17.8	-15.8	-19.8	0.90

modelling, particularly with respect to partitioning behaviour of Rb and Sc, which have different partitioning behaviours in hornblende compared to biotite. The solutions to equations 1 through 4 are given in Table 3-5. Assuming that the assumptions (described above) required in the method are correct, then this represents the total mineral assemblage involved in the fractional crystallization history of the zoned andesite to high silica rhyolite magma chamber of the Mount Pleasant Caldera. Rb-Sr isotopic data (Chapter 2) provide independent corroboration that the closed system assumption is valid. Two uncertainties remain after the PER modelling: 1) the assumption of conservation of Th has not been clearly demonstrated, and; 2) the phase assemblage test diagrams could not constrain the mineral assemblages involved with a high degree of statistical certainty.

Trace Element Modelling

In order to increase the level of confidence that the calculated mineral assemblages provide a reasonable estimate of the actual assemblages, the calculated assemblages given in Table 3-5 are used for forward modelling of the trace element variation of the Mount Pleasant Caldera. The model assumes perfect Rayleigh fractionation in a two-stage process: 1) fractionation of andesite to produce the McDougall Brook Microgranite, and; 2) fractionation of the microgranite to produce the high-silica rocks. The mineral-melt partition coefficients chosen for these two stages are given in Table 3-5.

The coefficients for minerals in stage 1 were determined using a computer program that calculates coefficients for mafic mineral assemblages, taking into account both their compositional and temperature dependence (Nielson, in press). The composition chosen was a mafic andesite (LM-9; Appendix 1) and the liquidus temperature input to the program was 1100 °C. The results of the modelling are compared with actual trace element variations using chondrite-normalized trace element

Table 3-5. Mineral assemblage for stages 1 and 2 fractionation based on PER analysis, and mineral/melt and bulk partition coefficients assigned to selected trace elements for use in trace element forward modelling.

Mineral	wt. %	Mineral-melt partition coefficients														
		U	Th	Rb	K	Ba	La	Ce	Nd	Sm	Eu	Dy	Yb	Lu	Sr	Sc
Stage 1: Mafic rocks																
olivine	10.03	0.000	0.001	0.001	0.000	0.008	0.000	0.000	0.000	0.002	0.003	0.005	0.063	0.108	0.001	0.313
augite	22.77	0.022	0.060	0.013	0.015	0.060	0.242	0.337	0.638	0.867	1.093	2.249	2.621	2.660	0.560	8.018
anorthite	24.42	0.012	0.006	0.129	0.150	0.564	0.134	0.076	0.079	0.042	0.044	0.034	0.028	0.027	2.750	0.073
albite	27.58	0.012	0.008	0.129	0.150	0.564	0.134	0.076	0.079	0.042	0.044	0.034	0.028	0.027	2.750	0.073
apatite	1.64	0.650	2.769	0.000	0.000	0.000	9.379	13.715	21.509	29.919	32.410	22.612	9.959	8.966	1.690	0.054
magnetite	9.60	0.053	0.038	0.000	0.000	0.000	0.003	0.003	0.002	0.003	0.004	0.007	0.020	0.023	0.040	1.951
ilmenite	3.96	0.022	0.060	0.000	0.000	0.000	0.007	0.008	0.008	0.009	0.009	0.009	0.024	0.029	0.000	1.951
Bulk Partition Coefficients		0.028	0.069	0.070	0.081	0.307	0.280	0.342	0.540	0.712	0.806	0.903	0.784	0.781	1.589	2.160
Stage 2: Felsic rocks																
quartz	13.65	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
orthoclase	32.42	0.027	0.016	0.740	1.490	6.730	0.104	0.045	0.054	0.028	3.500	0.047	0.024	0.050	26.000	0.040
albite	23.99	0.018	0.013	0.204	0.263	1.130	0.170	0.082	0.085	0.043	4.200	0.037	0.031	0.031	14.950	0.114
anorthite	9.19	0.018	0.013	0.204	0.263	1.130	0.170	0.082	0.085	0.043	4.200	0.037	0.031	0.031	14.950	0.114
biotite	18.66	0.190	1.740	5.300	5.630	7.000	3.550	3.490	2.700	1.760	1.000	1.050	0.690	0.800	0.360	15.500
apatite	0.33	1.020	4.350	0.000	0.000	0.000	15.000	31.000	50.000	54.000	27.000	42.000	21.000	17.000	2.660	0.065
zircon	0.02	298.000	62.400	0.000	0.000	0.000	26.600	23.500	22.100	17.700	12.000	95.000	490.000	635.000	0.000	60.300
ilmenite	1.00	0.740	0.094	0.000	0.000	0.000	32.000	26.000	18.000	12.500	7.200	2.400	1.340	1.400	0.000	12.400
Bulk Partition Coefficients		0.422	0.678	1.368	1.477	2.072	1.418	1.369	1.205	0.973	2.103	0.710	0.620	0.650	5.621	3.368

diagrams in Figure 3-5a. The biggest problem with the model is the behaviour of the trace alkali and alkaline earth elements Rb, Ba, and Sr (not shown in Fig. 3-5a). The model underestimates the variations caused by the incompatibility of Rb and compatibility of Sr by almost an order of magnitude and overestimates the variation caused by Ba incompatibility by a factor of 2. Because the poor fit is restricted to these elements the likely cause of the bad fit is incorrect D values. This could be due to poorly known partition coefficients for the feldspars in mafic rocks and/or incorrect assumptions involved in the calculation method of Nielson (in press). For example the two-lattice model used by Nielson may adequately explain REE behaviour but not the behaviour of Rb, Ba and Sr. However, because a 'perfect -fit' assemblage could not be obtained for the mafic rocks with the phase assemblage test diagrams, it is also possible that there is some error in the calculated fractionating mineral assemblage.

Most of the partition coefficients for the stage 2 fractionation were taken from Henderson (1981) and Mahood et al. (1983). Maximum values were assigned because partition coefficients of a broad range of trace elements are known to increase markedly in high-silica systems (Mahood and Hildreth, 1983). Partition coefficients for plagioclase were obtained from the Nielson (in press) program, inputting whole rock chemistry for sample (MC-082c; Appendix 1) and a liquidus temperature of 950 °C (calculated from phosphorous concentrations according to Watson and Harrison, 1984). These data were then forward modelled. The result compared poorly with actual trace element variations in the felsic rocks. In particular, the model predicted incompatibility of LREE whereas they actually behave compatibly in the felsic rocks. When approximately 0.3 wt. % allanite was arbitrarily added to the model mineralogy, a better fit was obtained. In doing so it was observed that D_{Th} increased substantially — to 0.6. This made it apparent that the problem with the model stemmed from the relatively weak conservation of Th in the felsic system. In order to correct the problem, correction factors for the slopes of trend 2 on the simple PER diagrams were calculated using the method of Ernst (1990; equation

Figure 3-6. Comparison of model and actual trace element variations of Mt. Pleasant igneous rocks. A. Stage 1: variations in the andesite — monzogranite fractionation stage. B. Stage 2: variations in the monzogranite — high-silica rhyolite — Mt. Pleasant Porphyry fractionation stage. Solid curves indicate actual trace element signatures of selected samples. Dashed curves indicate model trace element variations for Rayleigh fractionation; numbers indicate percent crystallization by weight.

10a), and assuming $D_{Th} = 0.6$. Using these corrected slopes, the mineral assemblage was recalculated and the trace element variations remodelled. This second iteration of the model is illustrated and compared with actual trace element variations in Figure 3-5b.

DISCUSSION

The results of both the major and trace element modelling indicate that magmatic evolution of the Mount Pleasant Caldera occurred by a two-stage fractionation process. In stage 1, the monzogranitic magma that crystallized to produce McDougall Brook Microgranite was formed by 40-60% fractional crystallization of an andesitic 'parent'. In stage 2, as much as 60%, 80% and 98% fractionation of the monzogranitic magma was required to produce the high silica rocks of the Little Mount Pleasant Formation, the Seelys Formation, and the Mount Pleasant Porphyry, respectively. The andesitic 'parent' was probably not a single, homogeneous, magma. Nielson (1990) has shown that even minor amounts of assimilation and mixing can produce significant scatter in trends of PER diagrams constructed with incompatible elements in the numerator whereas diagrams using compatible-element numerators are relatively insensitive to such effects. Therefore the scatter in the andesites and basalts on simple PER diagrams with Zr/Th and K/Th are good indicators that open-system processes have affected the mafic rocks to a small degree, and this may in turn have introduced errors into the PER analysis of the mineral assemblage fractionating from the mafic magmas. Even though the Mount Pleasant Caldera magma chamber was a closed system with respect to Sr isotopes (Chapter 2), it must have been large. It probably grew to its pre-eruption size over a period of time (10^5 - 10^6 a) by tapping of magmas at depth. The chamber erupted repeatedly and presumably underwent periodic recharge as well. Therefore, it is not surprising that a single, homogenous "parental" magma for the sampled rock suite cannot be identified. Since the evidence for open system behaviour is restricted to the mafic

endmembers and the Sr systematics of the andesite-rhyolite suite indicate a closed system, it is concluded that the open system behaviour occurred prior to entry into the high-level magma chamber. However, it seems clear that whatever distillation process produced the parental andesitic magma(s) must have homogenized Sr isotopic compositions and potentially the major and trace element chemistry as well.

Fluid Dynamics of Magma Chambers

The ramifications of this two-stage fractionation model can best be understood if they are discussed in the context of recent experimental and theoretical studies of the fluid dynamics of magma chambers. The two processes that control the fluid dynamics and crystallization behaviour of magma chambers are thermal and compositional convection. Turner and Campbell (1986) predict that thermal convection in mafic magma chambers with vertical dimensions $> 1\text{ km}$ will be energetic immediately after the chamber is filled or refilled. However, thermal convection will become less important as crystallization proceeds due to the combined effects of increasing viscosity, decreasing temperature, and decreasing chamber size. The walls (+/- bottom and roof) are the sites where crystallization and fractionation occur (Sparks et al., 1984). This is referred to as *in situ* fractional crystallization (e.g., Langmuir, 1989). During *in situ* crystallization the density of adjacent magma will become different from that of the main magma chamber causing these magmas to convect away from the crystals. This process is referred to as convective fractionation by Sparks et al. (1984) and liquid fractionation by McBirney et al. (1985). Compositional convection may dominate over thermal convection in many cases. Convective fractionation is capable of generating highly differentiated liquids at an early stage in the evolution of a magma chamber without requiring large amounts of crystallization of the whole system — if the evolved magmas formed along the walls of the magma chamber are not remixed with the convecting magma.

Sparks et al. (1984) and Turner and Campbell (1986) consider that magmas in high-level magma chambers are likely to be vertically stratified in terms of their density, composition, and temperature. Gradients in these properties can be created during filling and replenishment of the chamber, or by various fractionation mechanisms. Continuous gradients are unstable due to convection so that these bodies break down into a series of well-mixed horizontal layers of contrasting density and chemical composition that convect independently and are separated by thin diffusive interfaces. Heat is transferred more readily across these interfaces than chemical constituents, a factor which tends to stabilize double-diffusive systems. Density and viscosity differences between double-diffusive layers inhibit mixing (Campbell and Turner, 1986). Conversely, crystallization may act in the opposite direction if it occurs most rapidly in the deeper, denser layers, by reducing density and viscosity contrasts and thereby promoting mixing between double diffusive layers.

The manner in which convective fractionation proceeds depends both on the physicochemical properties of the magma and on the shape of the magma chamber. In calcalkaline systems like the Mount Pleasant Caldera, fractionation always produces residual liquids of progressively lower density. If fractionation occurs on the bottom of the magma chamber, buoyant fluids will rise into the overlying magma promoting vigorous convection, mixing, and destruction of magma chamber stratification (Campbell and Turner, 1986). However, if fractionation is limited to the sides of a magma chamber, a different situation arises. McBirney et al. (1985) have examined the case where an initially homogenous magma in a deep magma chamber with vertical walls undergoes crystallization along the walls. The fractionated liquid next to the wall can form a buoyant compositional boundary layer that flows up the wall and accumulates as a separate zone in the upper levels of the reservoir. The rising magma is not compositionally homogeneous and different 'batches' of magma rise to different levels according to their individual density and viscosity. Such a process can explain the marked zonation

characteristic of epizonal silicic magma chambers (Sparks et al., 1984; McBirney et al., 1985). Thermal convection in the main body of the magma chamber may be laminar (i.e., the magma convects upward in the center and counterflow occurs downward along the relatively cold margins) as described by McBirney et al. (1985) or it may be turbulent as described by Campbell et al. (1986). Mixing between the thermally convecting main magma and the buoyant boundary layer will occur to an extent that depends on specific conditions in the magma chamber.

Implications for magmatic evolution of the Mount Pleasant Caldera

In situ crystallization combined with convective fractionation are hypothetical geological processes that have been modelled experimentally as described above, and simulated analytically and numerically (Langmuir, 1989; Nielson and de Long, in press), but have not been previously identified geochemically in silicic magmatic systems. However, the potential of PER analysis for recognizing these processes in natural systems has been recognized (e.g., Nielson and de Long, 1992). Two outstanding characteristics of these processes are well developed in the Mount Pleasant rocks: 1) modal mineralogy that does not explain chemical variation, and; 2) chemical variation that requires multiple saturation of the system with liquidus and subliquidus mineral phases. PER analysis has allowed not only recognition, but quantification of these processes.

Focusing on stage 1, it is evident that the modelled mineral assemblage, while being different from the mode, is consistent with the conclusion of Gill (1981) that fractional crystallization of plagioclase + orthopyroxene/olivine + augite + magnetite is the most viable explanation of the geological, chemical and mineralogical characteristics of most orogenic andesites. Furthermore, the model indicates that the fractionating magma was multiply saturated, rather than following a liquid line of descent. Phase equilibria - based simulations of *in situ* crystallization accompanied by convective

fractionation (Langmuir, 1989; Nielson and de Long, in press) indicate that multiple saturation is a characteristic of this type of fractionation.

The mineralogy of the model fractionating assemblage for stage 1 (Table 3-5) contains olivine, which is generally absent from the mode, and also contains significantly larger-than-modal abundances of Fe-Ti oxides. These discrepancies explain why the method used here provides a reasonable trace element model while an earlier attempt based on modal mineralogy (McCutcheon, 1991) failed. It is only with hindsight that fractionation of these phases becomes an obvious requirement. How else could the dramatic depletions in Fe and Ti in this system be achieved? No silicate minerals could be responsible for such variations under conditions suitable to the genesis of the Mount Pleasant Caldera (i.e., amphibole, which could remove these elements requires pressures > 8 kb., H₂O contents > 10 wt.%, and temperatures < 1000 °C to stabilize amphibole on the liquidus). Although crystallization of hornblende is not precluded by the model, it would still be expected to crystallize later than Fe-Ti oxide in the liquid line of descent. Therefore, hornblende could contribute to, but could not be the sole cause of, the Fe and Ti variations observed. Furthermore, this result leads to the conclusion that the phenocryst assemblage of the erupted magmas is not representative of the mineral assemblage involved in the magmatic evolution of the Mount Pleasant Caldera. Therefore, fractionation was not occurring everywhere at once but must have been restricted to certain locations that were not tapped by the eruptions. The same conclusion is reached for stage 2 fractionation using a similar line of reasoning. These observations lead again to the conclusion that *in situ* crystallization coupled with convective fractionation were the controlling processes in both stages of magmatic evolution of the Mount Pleasant Caldera.

Implications for fluid dynamics of the magma chamber

The simplest way to interpret the geochemical variations apparent from the PER analysis is that a parental andesite evolved into a felsic magma with the chemical composition of the McDougall Brook Microgranite by a process of convective fractionation of stage 1 mineral assemblage, *followed* by fractionation of the stage 2 mineral assemblage in the microgranite to produce the high-silica ash flow tuffs and lava flows and the Mount Pleasant Porphyry. However, stratigraphic relationships indicate that the andesites and high-silica rhyolites *coexisted* in the magma chamber (Chapter 1). If this is, in fact, the case then the Mount Pleasant magmatic system contained at least three compositional zones as shown in Figure 3-6c: a) a chemically stratified lower andesite that produced the variations observed in stage 1 fractionation; b) a middle homogeneous monzogranitic magma that produced little or no variation on PER diagrams and produces the inflection between stages 1 and 2, and; c) an upper, chemically stratified high-silica magma, which produced the variation observed in stage 2 fractionation. The upper and lower zones are interpreted to be multiply-layered, double-diffusive systems rather than continuously zoned layers, in accordance with fluid dynamic theory.

Stage 1 fractionation occurred in layer a. The most buoyant fractionate of this process must have been the McDougall Brook Microgranite. If this were not the case, the products of stage 2 fractionation should show the effects of mixing with the products of stage 1 fractionation. This would have eliminated the inflection on PER diagrams marking the change from one process to the other, resulting in a more gradual change. The coexistence in time of stages 1 and 2 fractionation requires the existence of two discreet sites for crystallization. The floor of the magma chamber was probably not a site for stage 1 crystallization because this would be expected to result in vigorous convection and mixing of layers a and b of the magma chamber as described by Turner and Campbell (1986). It is therefore supposed that crystallization of stage 1 occurred on

Figure 3-6. Fluid dynamic model of the Mount Pleasant magma chamber. A. Early double diffusive stage produced by periodic replenishment of layer a and sidewall crystallization to produce layer b. B. Hiatus in andesite replenishment causes fractionation of layer a, homogenization of layer b and development of layer c. C. Resumption of magma chamber replenishment allows layer c to be re-established. See text for further explanations. Dark areas represent zones of crystallization. Heavy lines with arrows denote double-diffusive convection patterns. Dashed lines with arrows denote convective fractionation flow patterns. Thin horizontal lines denote double-diffusive density/viscosity/compositional interfaces.

the walls of layer **a** allowing a buoyant boundary layer to rise by laminar flow into layer **b** without disrupting compositional gradients produced by double-diffusive layering of layer **a**. Periodic replenishment of the chamber with new batches of andesite seem to be required to: 1) prevent crystallization on the floor of the magma chamber (due to regular inputs of heat); 2) create and maintain double diffusive density stratification in layer **a**, and; 3) sustain stage 1 fractionation without allowing it to evolve into stage 2 fractionation.

Two processes are envisaged that could result in the development of stage 2 fractionation. In both cases, the system initially had the configuration shown in Fig. 3-6a, with a stratified, double diffusive layer **a** being maintained by repeated injections of andesite into the base of the chamber. This layer fed a growing, stratified layer **b** by sidewall crystallization and convective fractionation. In one scenario, stage 2 fractionation began once layer **b** reached a certain thickness and fractionates of stage 1 no longer ascended to the top of layer **b**, which then become the site of new crystallization involving only layer **b**. This explanation seems somewhat unsatisfactory in that it does not explain how homogenization of layer **b** occurred. An alternate explanation would require a hiatus in replenishment of andesite from deep-seated sources. This hiatus would result in the following according to fluid dynamic theory: 1) gradual evolution of the bulk composition of layer **a** toward the composition of layer **b**; 2) reduction of density and viscosity contrasts within layer **a** and between layers **a** and **b**, which would promote mixing and homogenization, and 3) crystallization on the chamber floor which would further enhance the tendency of the system to mix and homogenize. At some point in this process, layers **a** and **b** would evolve into layer **b** and stage 2 fractionation could begin in the homogenized layer **b** to produce stratified layer **c** in the manner suggested by McBirney et al. (1985) and illustrated in Figure 3-6b. If this was followed by renewed, periodic replenishment of the chamber, layer **a** could be re-established and stage 1 fractionation could resume. Stage 1 fractionation in the renewed layer **a** could

then maintain the size of layer b during continued stage 2 fractionation. Periodic episodes of voluminous high-silica ash flow eruption would continue as long as this dynamic, double-diffusive system was maintained in a steady state through regular injections of new magma into the base of the magma chamber as shown in Figure 3-6c. This model provides an internally consistent explanation for all of the available evidence but probably is not a unique solution because it is not known what the actual shape of the magma chamber was. If this information could be obtained by independent means then a unique fluid dynamic model of the caldera magma chamber might be possible.

The resurgent doming of the McDougall Brook Microgranite certainly marked the waning of the caldera-forming cycle. From this point onward, the magma chamber was unable to generate sufficient buoyant forces and/or hydrostatic pressures to rupture its lid. At this stage, layer c was no longer being generated on a large scale, because crystallization was beginning to occur in the cooler, convecting main magma. When the system cooled sufficiently for crystallization to occur throughout the magma, double-diffusive systems began to break down as a result of decreasing density contrasts and increasing compositional convection (McBirney et al., 1985). However, convective fractionation during this waning stage still produced small cupolas of static, highly fractionated, fluid- and metal-charged granitic magmas such as the Mount Pleasant Porphyry. Because such late-stage fractionation was occurring on a smaller scale, it was not interrupted by eruption and was able to progress to extreme degrees of fractionation. Economic mineralization at Mount Pleasant was a by-product of this extreme fractionation.

CONCLUSIONS

The method of Pearce element ratio analysis has been adapted to the problems of multiply saturated felsic magmatic systems. The application has been demonstrated using

the geochemistry of the igneous rocks of the Mount Pleasant Caldera. This method can be applied to any magmatic system for which there is at least one incompatible major or trace element, and can work even when this element is weakly conserved, by applying the error correction procedure of Ernst (1990). However, under these circumstances errors are amplified and spurious correlations become more probable. It is therefore essential that PER analysis be performed in conjunction with other methods such as conventional trace element reverse and forward modelling that can be used to test and verify the PER results.

Using the method described above it has been demonstrated that highly silicic magmas of the Mount Pleasant Caldera were derived from an andesitic parental magma by a two-stage process of convective fractionation. In Chapter 2 it was shown that a wide range of effusive and hypabyssal igneous rocks in the caldera are part of an isotopically closed system, and stratigraphic relationships indicate that the entire range of magma compositions (andesite — high-silica rhyolite) coexisted in the magma chamber. In stage 1, fractionation of andesite produced a monzogranitic differentiate (McDougall Brook Microgranite). In stage 2, fractionation of the monzogranitic magma produced high-silica rhyolite. The calculated assemblages were different than those estimated from modal mineralogy. Both stages are characterized by multiple saturation with several essential and accessory minerals. From this it is concluded that *in situ* crystallization accompanied by convective fractionation was occurring simultaneously in two different parts of a vertically stratified magma chamber. The magma chamber apparently consisted of a stratified, double-diffusive lower andesite layer (layer a) a relatively homogeneous, monzogranitic middle layer (layer b), and an upper, stratified, double-diffusive high-silica rhyolite layer (layer c). This inherently unstable configuration was maintained in a state of dynamic equilibrium by repeated injections of andesitic magma into the base of the chamber.

The PER method of geochemical analysis must involve simplifying assumptions, as described above, when applied to detailed petrogenetic modelling of such complex systems as the Mount Pleasant Caldera. However, these assumptions are preferable to the alternative, which is forward modelling of trace element variation based on the potentially *erroneous* assumption that the modal mineralogy is representative of the fractionating mineral assemblage. This is the probable cause of a well-known paradox in petrology, where isotopic studies indicate that a magmatic system is closed but forward modelling of trace element variation indicates that the evolved rocks could not be derived by fractional crystallization of the modal mineral assemblage of the least evolved rocks. In the past this contradiction has often been rationalized by suggesting that the trace element variations are somehow "decoupled" from the major element and isotopic variations. PER analysis has resolved this apparent contradiction in the case of the Mount Pleasant Caldera by demonstrating that the conventional modelling was based on a false assumption. The effort involved in PER analysis is further justified by the fact that it offers the only means of identifying and quantifying processes of *in situ* crystallization and convective fractionation *in natural systems*, which is crucial to a rigorous understanding of magmatic evolution of all igneous systems.

References

- Allègre CJ, Treuil M, Minster JF, Minster B, Albarede F (1977) Systematic use of trace element in Igneous Process. *Contrib Mineral Petrol* 60: 57-75
- Blanchard M-C, Jamieson RA, More EB (1984) Late Devonian — Early Carboniferous volcanism on western Cape Breton Island, Nova Scotia. *Canadian Journal of Earth Sciences* 21: 762-774.

- Coyle M, Strong DF (1987) Geology of the Springdale Group: A newly recognized Silurian epicontinental-type caldera in Newfoundland. *Can J Earth Sci* 24: 1135-1148
- Dostal J, Keppie JD, Dupuy C (1983) Petrology and geochemistry of Devonian-Carboniferous volcanic rocks in Nova Scotia. *Maritime Sediments and Atlantic Geology* 19: 59-71
- Durling PW, Marillier FJY (1990) Structural trends and basement rock subdivisions in the western Gulf of St. Lawrence, northern Appalachians. *Atlantic Geology* 26: 79-95
- Ernst RE (1990) Sensitivity of Pearce element ratio analysis to nonconserved behaviour of the denominator element. In: Russell JK, Stanley CR (eds) *Theory and application of Pearce element ratios to geochemical data analysis*. Geological Association of Canada Short Course Volume #8: 217-234
- Ernst RE, Fowler AD, Pearce TH (1988) Modelling of igneous fractionation and other processes using Pearce diagrams. *Contrib Mineral Petrol* 100: 12-18.
- Gill JB (1981) *Orogenic Andesites and Plate Tectonics*. Springer-Verlag, New York, 390 pp.
- Giret A, Bonin B, Leger JM (1980) Amphibole compositional trends in oversaturated and undersaturated alkaline plutonic ring complexes. *Can Mineral* 18: 481-495
- Harris FR (1964) Volcanic rocks of the Sunday Lake area, New Brunswick. Unpublished M.Sc. thesis, University of New Brunswick, Fredericton, New Brunswick, 141 pp.
- Henderson P (1981) *Inorganic geochemistry*. Pergamon Press, New York, 353 pp.
- Kooiman GJA, McLeod MJ, Sinclair WD (1986) Porphyry tungsten-molybdenum ore bodies, polymetallic veins and replacement bodies, and tin-bearing zones in the Fire Tower Zone, Mount Pleasant, New Brunswick. *Economic Geology* 81: 1356-1373
- Kretz R (1983) Symbols for rock-forming minerals. *Am Mineral* 68: 277-279

- Langmuir CH (1989) Geochemical consequences of in situ crystallization. *Nature* 340: 199-205
- Mahood G, Hildreth W (1983) Large partition coefficients for trace elements in high-silica rhyolites. *Geochim Cosmochim Acta* 47: 11-30
- McBirney AR, Baker BH, Nilson RH (1985) Liquid fractionation. Part I: basic principles and experimental simulations. *J Volcanology Geothermal Research* 24: 1-24
- McCutcheon SR (1991) The Late Devonian Mount Pleasant Caldera complex: stratigraphy, mineralogy, geochemistry and geologic setting of a Sn-W deposit in southwestern New Brunswick. Ph.D. thesis, Dalhousie University, Halifax, Nova Scotia, 609 pp.
- Nielson RL (in press) BIGD.FOR: a FORTRAN program to calculate trace element partition coefficients of natural mafic and intermediate composition magmas. *Computers and Geosciences*
- Nielson RL (1990) The use of simulated data sets for the evaluation of the sensitivity of Pearce element ratio analysis. In: Russell JK, Stanley CR (eds) *Theory and application of Pearce element ratios to geochemical data analysis*. Geological Association of Canada Short Course Volume 8: 157-178
- Nielson RL, de Long SE (1992) A numerical approach to boundary layer fractionation: application to differentiation in natural magma systems. *Contrib Mineral Petrol*: in press
- Pearce TH (1968) A contribution to the theory of variation diagrams. *Contrib Mineral Petrol* 19: 142-157
- Pearce TH (1987) The identification and assessment of spurious trends in Pearce-type ratio variation diagrams: a discussion of some statistical arguments. *Contrib Mineral Petrol* 97: 529-534

- Russell JK, Stanley CR (1990) Theory and application of Pearce element ratios to geochemical data analysis. Geological Association of Canada Short Course Volume 8: 315 pp.
- Sparks RSJ, Huppert HE, Turner JS (1984) The fluid dynamics of evolving magma chambers. Phil Trans Roy Soc Lond A310:511-534
- Stanley CR, Russell JK (1989a) Petrologic hypothesis testing with Pearce element ratio diagrams: derivation of diagram axes. Contrib Mineral Petrol 103: 78-89
- Stanley CR, Russell JK (1989b) PEARCE.PLOT: a turbo-pascal program for the analysis of rock compositions with Pearce element ratio diagrams. Computers & Geosciences 15:905-926
- Taylor RP (1992) Petrological and geochemical characteristics of the Pleasant Ridge zinnwaldite — topaz granite, southern New Brunswick, and comparisons with other topaz-bearing felsic rocks. Canadian Mineralogist 30:895-921
- Turner JS, Campbell IH (1986) Convection and mixing in magma chambers. Earth Sci Reviews 23: 255-352
- Watson EB, Harrison TM (1984) Accessory minerals and the geochemical evolution of crustal magmatic systems: a summary and prospectus of experimental approaches. Physics of the Earth and Planetary Interiors 35: 19-30.
- York D (1966) Least-squares fitting of a straight line. Canadian Journal of Physics 44: 1079-1086

CHAPTER 4. Evolution of mantle-derived magmatism in post-compressional lithosphere of the northern Appalachian Orogen: isotopic and trace element evidence from the Mount Pleasant Caldera complex, New Brunswick, Canada

ABSTRACT

The post-tectonic, epicontinental, Mount Pleasant Caldera complex, occurring in the Canadian Appalachians contains a variety of mildly potassic igneous rocks ranging from tholeiitic basalts to calcalkaline andesites, monzogranites, and rhyolites with felsic rocks predominant. These rocks were emplaced at the end of the Acadian Orogeny and at the onset of a period of crustal extension and thermal subsidence that formed the Maritimes Basin. Combined isotopic and trace element studies indicate that these magmas are partial melts of an asthenospheric source (OIB) that has undergone extensive fractionation and hybridization through assimilation of crustal materials.

Unaltered caldera volcanic rocks are characterized by positive ϵ_{Nd} values (+3.3 - +0.5), mildly radiogenic Sr initial ratios (~ 0.706), and radiogenic Pb isotopic ratios with crustal $^{207}\text{Pb}/^{204}\text{Pb}$ values (15.63 - 15.74). Modelling of these data, and trace element variations, indicates that the mafic rocks (basalts and andesites) were derived from asthenospheric mantle that was contaminated with older lower crustal material (probable basement of Proterozoic Avalonian Terrane). Contamination presumably occurred by crustal underplating of the mantle derived magmas accompanied by assimilation and fractional crystallization. The Sr and O isotopic data and trace element variations indicate that the felsic magmas were derived by closed-system, Rayleigh

Fractionation of a mid- to upper-crustal andesitic magma chamber that separated from the lower-crustal chambers. The high-level magma chamber experienced minor subsequent mixing and contamination effects; high-silica rhyolites derived from the shallow roof-zone of the andesite-rhyolite magma chamber and basalts erupted from a deeper magma chamber(s) show evidence of O, Sr, and Pb isotopic contamination by supracrustal rocks.

The predominance of an asthenospheric component in source materials of the caldera complex indicates involvement of a mantle upwelling and partial melting process in caldera petrogenesis. Such an episode of upwelling could also have been the driving force for the period of crustal extension manifested by the Maritimes Basin. Lithospheric delamination following Acadian orogenesis could be the cause of the asthenospheric upwelling required by the active extension hypothesis. Voluminous, predominantly felsic, bimodal, late- to post-tectonic magmatism in the northern Appalachians is commonly viewed as the product of crustal melting produced by overthickening of the continental crust during the Acadian orogeny. This view should be critically re-examined in light of the findings reported here.

INTRODUCTION

Voluminous, Late Paleozoic, post-tectonic magmatism in the northern Appalachians occurs in the form of granitoid and bimodal plutons and batholithic suites, and their volcanic equivalents. The Mount Pleasant Caldera complex represents one of the last major magmatic events in this period of 'Acadian' magmatism. This magmatism is commonly viewed as the product of crustal melting produced by: 1) overthickening of the continental crust during the Acadian orogeny (e.g., McCutcheon and Robinson, 1987; McLeod, 1990; Bevier and Whalen, 1990), and/or, 2) localized rifting (e.g., Hogan and Sinha, 1991; Van Waggoner and Fay, 1988; Gates and

Moench, 1981). The Mount Pleasant Caldera offers a rare opportunity to test these views because: 1) it contains a broad range of igneous rock types that have potentially preserved evidence of the complex array of processes that could have been involved in its petrogenesis; 2) its stratigraphic relations are well-known and the igneous rocks are clearly cogenetic (Chapters 1, 2, and 3), and; 3) it is undeformed and less altered than many other volcanic complexes in the northern Appalachians (e.g., Coyle and Strong, 1987; Blanchard et al., 1984; Dostal et al., 1983).

The caldera complex was emplaced near the onset of a period of crustal extension and thermal collapse that resulted in the formation of the Maritimes Basin, a large aborted rift (McCutcheon and Robinson, 1987). The pivotal position of the caldera complex at the end of magmatism and at the onset of basin formation raises the possibility that the magmatism and extension are related. In this study radiogenic (Sr, Nd, Pb) and stable (O) isotope studies and major and trace element geochemistry are used to examine, in detail, the petrogenesis of the magmas of the caldera complex. The insights gained are then used to explore the relationship between the 'Acadian' magmatism and subsequent crustal extension. It will be shown that development of a better and more rigorous understanding of the petrogenesis of the 'Acadian' magmatism is essential to development of viable tectonic models for the post-compressional evolution of the Appalachian Orogen.

GEOLOGIC SETTING

Southwestern New Brunswick contains two terranes and two cover sequences ranging in age from Precambrian to Carboniferous (St. Peter and Fyffe, 1991; Fyffe et al., 1992) as shown in Figure 4-1. The configuration of the various fault blocks was largely established during the Acadian Orogeny (McCutcheon, 1981; Ruitenberg and McCutcheon, 1982; McCutcheon and Robinson, 1987). Deformation accompanying

Figure 4-1. Tectonic lithofacies map of southwestern New Brunswick (after Fyffe et al., 1992) with location of the Mount Pleasant Caldera complex.

the Acadian Orogeny imparted a generally northeasterly-trending structural fabric to the rocks and produced numerous northeasterly- and northwesterly-trending faults, many of which were re-activated during Devonian-Carboniferous time (Ruitenberg and McCutcheon, 1982).

A period of late- to post-Acadian magmatism commenced in the Late Silurian to Lower Devonian Mascarene Cover Sequence (Fig. 4-1) with bimodal volcanism in southern New Brunswick and eastern Maine (Gates and Moench, 1981; van Waggoner and Fay, 1988). The petrogenesis of these volcanic rocks is debatable and, in a co-authored paper, Gates and Moench (1981) wrote dissenting opinions of their petrogenesis; the volcanics were considered by Moench to be the products of a mantle plume, but they have intraplate geochemical affinities which led Gates (and van Waggoner and Fay, 1988) to propose that they were rift-related. However, these volcanic and interbedded sedimentary rocks are compressed into broad open folds and the sediments are cleaved indicating that compressional tectonism had not yet ceased. Furthermore, the interbedded sediments form a regressive sequence indicating that the land was emerging during this period of deposition. This and other lines of evidence mentioned below indicate that the Late Silurian- Early Devonian was a time of ongoing Acadian compression.

A period of granitoid "Acadian plutonism" overlapped with and followed this volcanism (Fyffe et al., 1981). Isotopic and field evidence from these granitoids indicate that Acadian polyphase deformation took place in Silurian to Middle Devonian time (e.g., Hubacher and Lux, 1987; Bevier and Whalen, 1990; MacLellan and Taylor, 1989; McCutcheon and Bevier, 1990). The Saint George Batholith consists of gabbroic and granitoid plutons that were emplaced over a time interval spanning the Late Silurian to the Late Devonian. The post-tectonic Mount Douglas Granite, comprising the youngest and highest-level phases of the Saint George Batholith, has a Late Devonian age (367 Ma) using both the U/Pb (Bevier, 1989) and $^{40}\text{Ar}/^{39}\text{Ar}$ methods

(McLeod et al., 1988). The Mount Pleasant Caldera, with a Rb/Sr isochron age of 368 Ma (Chapter 2), is the same age as Mount Douglas Granite and together they comprise the last major products of this protracted period of magmatism.

The late- to post-tectonic magmatism was followed closely by formation of the Maritimes Basin by tensional collapse and thermal subsidence in the Late Devonian (McCutcheon and Robinson, 1987; Durling and Marillier, 1990). The Late Devonian and Carboniferous rocks of the Basin are the product of an aborted-rift environment as indicated by structural, magmatic, and geophysical evidence of widespread crustal extension (McCutcheon and Robinson, 1987; Fyffe and Barr, 1986; Durling and Marillier, 1990). The Mount Pleasant Caldera was emplaced just before, or during, the initial rapid-subsidence stage of basin development, as were a number of other volcanic suites in Nova Scotia and Newfoundland (McCutcheon and Robinson, 1987). The felsic rocks of the caldera complex were derived by closed-system convective fractionation of an andesitic magma chamber (Chapters 2 and 3). The andesites are inferred to have been derived by combined assimilation/fractional crystallization (AFC) of basaltic precursors (Chapter 1).

The stratigraphy of the caldera complex is shown in Figure 4-2. The complex is comprised of three sequences — the exocaldera, intracaldera and late caldera-fill sequences. The lithologies are dominated by felsic ash flow tuffs and lava flows. However, in the waning stages, felsic intrusions (McDougall Brook Microgranite, Mount Pleasant Porphyry, rapakivi dykes) become more common. Minor basaltic lava flows occur in the exocaldera and late caldera- fill sequences. Andesitic lava flows and associated diorite stocks occur only in association with caldera margin collapse breccias of the Scoullar Mountain Formation (intracaldera sequence) and in the stratigraphically correlated South Oromocto Andesite (exocaldera sequence).

Figure 4-2. Geology of the Piskahagan Group comprising the Mount Pleasant Caldera complex and related outflow facies rocks (after McCutcheon, 1991)

ANALYTICAL METHODS

Oxygen and strontium data used here have been presented in Chapter 2 to which the reader is referred for a description of the methods of O and Sr analysis. All radiogenic isotope analyses were made at Carleton University on a multi-collector Finnigan-MAT 261 solid-source mass spectrometer, operating in the static mode.

Nd and Sm were separated using reverse phase chromatography (Richard et al., 1976). Concentrations were determined by isotope dilution mass spectrometry using ^{145}Nd and ^{149}Sm spikes. Nd isotopic ratios were determined from unspiked Nd separates; the data are corrected to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ (O'Nions et al., 1977). A typical isotopic analysis consisting of averaged values of 100 measurements has a 2σ error of about 0.002%. The reproducibility of the isotopic ratios, estimated on the basis of replicate analyses of chemical standards and samples, is about 0.003% (2σ) and the precision of Sm/Nd ratios is estimated to be approximately 0.5%. Initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are reported as ϵ_{Nd} values relative to the chondritic uniform reservoir (CHUR) at 368 Ma (the time of caldera formation determined in Chapter 2 using the Rb/Sr isochron dating technique). The present-day $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of CHUR is taken to be 0.512638 (Wasserburg et al., 1981) and the present-day $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of CHUR is taken to be 0.1967 (Jacobsen and Wasserburg, 1980).

Lead was separated using HBr and HCl on anion-exchange columns using conventional methods. Samples were loaded in the mass spectrometer in a mixture of phosphoric acid and silica gel and run at temperatures between 1250-1300 °C. A fractionation correction of 0.1% per mass unit difference in the measured isotopic ratio was applied to the data based on the difference between the accepted value of standard NBS-982 and replicate analyses of this standard performed during the course of the investigation. Based on replicate analyses of standards and samples, the precision of

$^{207}\text{Pb}/^{204}\text{Pb}$ isotopic analyses is estimated to be $\pm 0.1\%$ (2σ). Total procedural blanks ranged from 0.2 ng Pb to 1.2 ng Pb and averaged 0.6 ng Pb. Pb concentrations of ten samples were measured by isotope dilution using a mixed ^{206}Pb — ^{233}U , ^{235}U spike. U and Th analyses were obtained by instrumental neutron activation analysis at École Polytechnique in Montreal.

RESULTS

O and Sr isotopic data

Oxygen and strontium results that are pertinent to the present study are summarized below. A plot of $\delta^{18}\text{O}$ vs. Rb/Sr (Fig. 4-3a) illustrates the different processes affecting the oxygen isotopic compositions of the caldera igneous rocks. The data show 3 distinct patterns of geochemical variation. Unaltered samples (set 1 in Fig. 4-3a) are characterized by a restricted range of $\delta^{18}\text{O}$ compositions and moderate variation of Rb/Sr ratios. Another group (set 2 in Fig. 4-3a) is characterized by a trend of decreasing Rb/Sr ratios and dramatically increasing $\delta^{18}\text{O}$ values. These variations have been interpreted in Chapter 2 to be the result of variable degrees of interaction with fluids that have equilibrated with a ^{18}O -rich source (or low temperature hydrothermal fluid that was strongly fractionating ^{18}O). A third group (set 3 in Fig. 4-3a) is characterized by moderate increases in $\delta^{18}\text{O}$ values and dramatic increases in Rb/Sr ratios. This trend is defined by felsic tuffs and is the result of fractionation (to produce the progressively greater Rb/Sr ratios) accompanied by minor contamination to produce an increase in $\delta^{18}\text{O}$ values (≈ 3 per mil) that is in excess of that which would be expected due to fractionation alone (≈ 1 per mil; Matsuhisa et al., 1978). This interpretation is supported by the observation of variably digested lithic lapilli in the rock types represented in sample set 3 (Seelys ash flow tuffs mainly).

Figure 4-3. Variations of A. $^{87}\text{Rb}/^{86}\text{Sr}_{\text{measured}}$ and B. $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$ as functions of $\delta^{18}\text{O}$ variation. Numbered fields are described in the text. Patterned bar represents isochron value of the initial ratio. Sample with arrow plots off the diagram in direction indicated.

Values of Sr_i are calculated for individual samples based on the Rb/Sr isochron age of the caldera complex of 368 Ma (Chapter 2). There is no systematic variation of Sr_i as a function of Sr content (not shown), indicating that fractionation was not accompanied systematically by assimilation. On a plot of Sr_i versus SiO_2 (Fig. 4-4a), the most felsic and most mafic rocks show the greatest deviation from the isochronous initial ratio of 0.70611, both tending to higher values. This is an indication that these endmember magma compositions may have been preferentially affected by contamination and alteration. These relationships are further clarified with a plot of $\delta^{18}O$ versus Sr_i in Figure 4-3b. The felsic rocks exhibit more scatter than the mafic rocks. Some felsic rocks have Sr_i values above that of the isochron, which is attributed to contamination with the supracrustal country rocks by AFC and geothermal alteration processes as discussed above. Two samples have low Sr_i values and young model ages and have probably lost radiogenic Sr at approximately 320-345 Ma (as indicated by the model ages; see Chapter 2). Mafic rocks show more limited Sr_i variation; there is no correlation between Sr content and Sr_i , but $\delta^{18}O$ and Sr_i may be weakly correlated. Within the basalts and within the andesites, Sr_i increases slightly as $\delta^{18}O$ increases, indicating that these variations are due to country rock contamination.

Pb isotopic data

Lead isotopic data are presented in Table 4-1. There is no systematic change of measured Pb isotopic values as a function of SiO_2 content (not shown). However, there are small but systematic variations in all three Pb isotopic ratios as a function of $\delta^{18}O$ (Fig. 4-5). The correlation between $(^{208}Pb/^{204}Pb)_m$ and $\delta^{18}O$ suggests that these variations are caused by geothermal alteration and/or assimilation as described above. Furthermore, common Pb was introduced by these processes rather than Th, since Th is extremely immobile in hydrothermal fluids (see Taylor and McLennan, 1985) and thus

Figure 4-4. Variations of A. $^{87}\text{Sr}/^{86}\text{Sr}_{\text{initial}}$, B. ϵ_{Nd} and, C. T_{DM} as functions of SiO_2 variation. Patterned bar as in Fig. 4-3. Errors in A and C are less than symbol size. Errors in B are shown on the diagram.

Table 4-1. Pb isotopic data. All Pb ratios are corrected for fractionation of 0.1% per mass unit.

Sample	Rock type	$^{206}\text{Pb}/^{204}\text{Pb}_m$	$^{207}\text{Pb}/^{204}\text{Pb}_m$	$^{208}\text{Pb}/^{204}\text{Pb}_m$	U (ppm)	Th (ppm)	Pb (ppm)	μ	$^{206}\text{Pb}/^{204}\text{Pb}_i$	$^{207}\text{Pb}/^{204}\text{Pb}_i$	$^{208}\text{Pb}/^{204}\text{Pb}_i$
MC-013	Rothea Fm. tuff	18.95	15.65	39.65	2.9	29.5					
MC-196	Bailey Rock Rhyolite	19.84	15.69	40.17	4.2	25.2					
MC-101d	Bailey Rock Rhyolite	19.16	15.71	39.17	5.0	22.2	33.16	9.8	18.59	15.71	38.35
MC-074b	McDougall Bk. Microgranite	18.88	15.64	38.89	2.4	14.7	21.66	7.1	18.46	15.64	38.06
MC-082c	McDougall Bk. Microgranite	19.15	15.69	39.34	3.3	17.1					
LM-5	McDougall Bk. Microgranite	19.03	15.65	38.82	3.8	11.1	18.96	12.9	18.27	15.65	38.11
MC-306a	Little Mt. Pleasant Fm. tuff	18.47	15.63	38.32							
MC-120b	Little Mt. Pleasant Fm. tuff	19.05	15.66	39.06	3.9	21.2	26.02	9.7	18.48	15.66	38.06
82-19	Little Mt. Pleasant Fm. tuff	18.97	15.64	38.83	1.0	22					
MC-229a	Seelys Fm. tuff	19.43	15.69	39.15							
MC-158b	Seelys Fm. tuff	19.06	15.65	39.16	5.6	29.7					
MC-123a	Rapakivi dyke	19.44	15.71	39.30	5.2	17.8					
LM-14	Rapakivi dyke	20.68	15.74	40.42	5.4	23.1	10.47	34.7	18.64	15.74	37.60
MC-065a	Big Scott Mtn. Fm. rhyolite	19.45	15.70	39.49	5.6	30.6					
MC-159c	Scoullar Mtn. Fm. andesite	19.14	15.67	38.98	3.5	11.7					
LM-6	Scoullar Mtn. Fm. andesite	18.93	15.64	38.82	3.0	11.6	20.43	9.4	18.38	15.64	38.13
LM-15	Scoullar Mtn. Fm. diorite	19.12	15.67	38.99	2.5	9.2	10.26	15.8	18.19	15.67	37.89
MC-014	South Oromocio Andesite	19.27	15.67	38.72	3.1	6.8	8.17	24.3	17.84	15.67	37.71
MC-024	Kleef Fm. basalt	18.85	15.64	38.75	0.8	4.2					

would not be expected to contribute to the observed variability of $(^{208}\text{Pb}/^{204}\text{Pb})_m$. Values of $(^{206}\text{Pb}/^{204}\text{Pb})_m$ increase with increasing $\delta^{18}\text{O}$ indicating that the contaminant was radiogenic, but there is little or no variation of $(^{207}\text{Pb}/^{204}\text{Pb})_m$ with $\delta^{18}\text{O}$ variation indicating that this radiogenic source was not ancient. These observations indicate that measured Pb isotopic ratios have been affected by supracrustal contamination and alteration in much the same way that Sr has.

Measured values of Pb isotopic ratios are plotted on $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ secondary isochron diagrams in Figure 4-6. The measured ratios define trends that are probably mixing lines rather than isochrons for the reasons stated above. A lead-in-feldspar sample (taken from a felsic caldera intrusion) from Ayuso and Bevier (1991) is also plotted for comparison. The data in Figure 4-6a plot along the trend of the Stacey and Kramers (1975) model curve and to the right of the geochron indicating that they were derived from a source with time-integrated U/Pb ratios that are larger than bulk Earth; these radiogenic Pb isotopic compositions are typical of the upper crust. The high $(^{207}\text{Pb}/^{204}\text{Pb})_m$ ratios further record an ancient fractionation event. OIB-source mantle and continental crust could both generate the large observed $(^{206}\text{Pb}/^{204}\text{Pb})_m$ ratios but the large $(^{207}\text{Pb}/^{204}\text{Pb})_m$ ratios implicate old crustal materials in the petrogenesis of these rocks. The 'good fit' of the data from this study and the Pb-isotopic field of Avalon terrane rocks defined by Ayuso and Bevier (1991), indicate that the late Proterozoic Avalon terrane is the most probable source of the crustal contamination.

Figure 4-6 also shows values of 8 initial Pb ratios calculated using INAA data for U and Th concentrations. Initial ratios of the felsic rocks plot close to the Pb in feldspar value obtained from the McDougall Brook Microgranite. Mafic samples plot further to the left with less radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ initial ratios — $(^{206}\text{Pb}/^{204}\text{Pb})_i$. If these samples also had less radiogenic values of $(^{207}\text{Pb}/^{204}\text{Pb})_i$ and $(^{208}\text{Pb}/^{204}\text{Pb})_i$ they would plot on a mixing trend between Devonian mantle and Avalon Terrane (see

Figure 4-5. Variations in measured Pb isotopic ratios as a function of $\delta^{18}\text{O}$ variation. Error bars at lower right of each diagram.

Figure 4-6. Common Pb secondary isochron diagrams. A. $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and B. $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$. S&K = second stage Pb growth curve after Stacey and Kramer (1975). NHRL = northern hemisphere (mantle) reference line defined by Hart (1984). The Pb fields of Avalon Terrane defined by Ayuso and Bevier (1991). AFC curve calculated from model parameters in Table 4-2. Errors in measured ratios are approximately symbol size; errors in initial ratios are shown in the diagrams and discussed in the text.

Table 4-2. Model Pb parameters for AFC curves in Fig. 4-5 (equations from DePaolo, 1981). r = ratio of assimilation rate to fractionation rate; D = bulk distribution coefficient; $C(L)_0$ = concentration of element in original magma; C^* = concentration of element in contaminant; $\epsilon(L)_0$ = isotopic ratio in original magma; ϵ^* = isotopic ratio in derivative magma; F = fraction of melt; $C(L)$ = concentration of element in remaining magma; $\epsilon(L)$ = isotopic ratio in remaining magma.

$^{206}\text{Pb}/^{204}\text{Pb}$:	$r=$	0.5	$^{207}\text{Pb}/^{204}\text{Pb}$:	$r=$	0.5
	$D=$	0.01		$D=$	0.01
	$C(L)_0=$	1		$C(L)_0=$	1
	$C^*=$	15		$C^*=$	15
	$\epsilon(L)_0=$	17.80		$\epsilon(L)_0=$	15.45
	$\epsilon^*=$	18.50		$\epsilon^*=$	15.65
	$r/(r-1+D)$	-1.02		$r/(r-1+D)$	-1.02

F	$C(L)$	$\epsilon(L)$	F	$C(L)$	$\epsilon(L)$
0.9	2.8	18.22	0.9	3	15.57
0.8	5.0	18.33	0.8	5	15.60
0.7	7.8	18.37	0.7	8	15.61
0.6	11.6	18.40	0.6	12	15.62
0.5	16.9	18.42	0.5	17	15.63
0.4	24.7	18.43	0.4	25	15.63
0.3	37.8	18.44	0.3	38	15.63
0.2	63.6	18.45	0.2	64	15.63
0.1	140.4	18.45	0.1	140	15.64

Fig. 4-6a) but this is not the case. There seems to be no geological reason for the observed trends so an analytical reason is likely. Specifically, the INAA analyses of U lack precision, with errors in the range 5-10%, and may be overestimating the U concentrations (probably due to underestimation of the background), particularly in the mafic rocks, which have the lowest concentrations of this element. This analytical problem would affect $(^{206}\text{Pb}/^{204}\text{Pb})_i$ to a much greater extent than the other initial ratios because: 1) the age correction factor for $(^{207}\text{Pb}/^{204}\text{Pb})_i = 0.00$ (within analytical error for these samples), and; 2) systematic errors in the Th analysis are less likely (than for U) because the concentrations are higher and can therefore be measured more precisely, and the error in the estimation of $(^{208}\text{Pb}/^{204}\text{Pb})_i$ is small (see Fig. 4-6b). Therefore, the trends in the Pb initial ratios in Figure 4-6 are probably an artifact of systematic errors in the measurement of U concentrations and are probably not preserving any evidence of mantle-crust mixing. Isotope dilution determinations of U would help in this regard! However, the AFC calculations demonstrate (see Table 4-2 and Fig. 4-6a) that only 10% AFC is required to shift the isotopic composition of a mantle-derived magma approximately 90% toward the isotopic composition of the crustal contaminant because there is much more Pb in the contaminant than in the original magma. The caldera volcanic rocks have almost certainly seen greater degrees of AFC than this so that little or no evidence of mantle-crust mixing is expected to be preserved in mafic caldera rocks and none in the felsic rocks.

Nd isotopic data

Nd isotopic data are provided in Table 4-3. The Nd isotopic compositions are age corrected using the Rb-Sr isochron age (368 Ma) of the caldera complex (Chapter 2). The initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, expressed as $\epsilon^{(368)}$, have a restricted range of values between +3.3 and +0.1. There is no correlation between ϵ_{Nd} -values and $\delta^{18}\text{O}$ -values indicating that the isotopic composition of Nd has not been significantly affected by

Table 4-3. Sm and Nd isotopic data for Mount Pleasant igneous rocks. T_{DM} = depleted model ages calculated using present day depleted mantle values from Michard et al.(1985). * concentrations and isotopic ratios determined from different digestions. ** spike contamination.

Sample	Formation/Unit	$(^{143}\text{Nd}/^{144}\text{Nd})_i$	$(^{147}\text{Sm}/^{144}\text{Nd})_m$	Nd (ppm)	Sm (ppm)	$(^{143}\text{Nd}/^{144}\text{Nd})_i$	ϵ_{Nd}	T_{DM}
MC-196	Bailey Rock Rhyolite	0.51247	0.1156	37.13	7.10	0.512190	0.54	924E+06
MC-074b	McDougall Brook Microgranite	0.51245	0.1022	56.54	9.55	0.512190	0.70	851E+05
MC-306a*	McDougall Brook Microgranite	0.51242	0.0943	55.08	8.59	0.512188	0.48	835E+06
MC-158b	Seelys Formation tuff	0.51247	0.1257	53.30	11.08	0.512166	0.06	1021E+06
MC-123a	Rapakivi dyke	0.51254	0.1214	46.98	9.44	0.512245	1.61	873E+06
LM-14	Rapakivi dyke	0.51250	0.1158	60.42	11.57	0.512223	1.17	878E+06
MC-065a	Big Scott Mtn. Formation rhyolite	0.51252	0.1251	28.64	5.92	0.512222	1.14	930E+06
MC-314a	Mt. Pleasant Porphyry	0.51254	0.1460	28.19	6.81	0.512188	0.49	1150E+06
MC-159c	Scoullar Mtn. Formation andesite	0.51247	0.1166	48.29	9.32	0.512186	0.45	936E+06
LM-6*	Scoullar Mtn. Formation andesite	0.51254	0.1258	71.82	14.95	0.512238	1.46	908E+06
LM-15	Scoullar Mtn. Formation diorite	0.51248	0.1178	41.31	8.06	0.512194	0.61	931E+06
LM-9	South Oromocto Andesite	0.51255	0.1201	45.24	8.98	0.512260	1.89	845E+06
MC-009a*	Hoyt Station Basalt	0.51264	0.1326	34.74	7.62	0.512321	3.09	807E+06
MC-024	Kleef Formation basalt	0.51263	0.1378	63.16	14.40	0.512294	2.56	884E+06
LM-17a**	Kleef Formation basalt	0.51253	0.1361	56.28	12.67	0.512198	0.69	1043E+06

supracrustal contamination and post-magmatic alteration of the caldera complex igneous rocks. Despite their limited range it is clear that the Nd isotopic values of the igneous rocks of the caldera complex represent a mixture of two endmembers. This can be seen in the variation of ϵ_{Nd} -values and Nd model ages as functions of SiO_2 content (Fig. 4-4 b, c). Mafic samples have larger ϵ_{Nd} values and slightly younger model ages than felsic samples. From this it can be inferred that there are at least two sources involved in the production of the caldera magmas. The positive ϵ_{Nd} -values indicate that one source has a time-integrated depletion in LREE. The old model ages could implicate either ancient lower crust or ancient, lithospheric mantle as the second source.

When the Sr and Nd data are plotted together on an anticorrelation plot (Fig. 4-7), the data fall into two groups. One group consists of the unaltered samples, including isochronous andesite to rhyolite samples (determined from Rb/Sr geochronology in Chapter 2), and a basaltic andesite and a basalt sample that are non-isochronous but also apparently unaffected by post-magmatic alteration. Variation of these data is dominated by decreasing ϵ_{Nd} -values in quadrant 1. Therefore the mixing of the two inferred sources is dominated by variation of ϵ_{Nd} -values. One source has the characteristics of depleted mantle. The second source, with relatively unradiogenic Nd and mildly radiogenic Sr and Proterozoic model ages is inferred to be in the lower crust and is correlated with the 'Avalon terrane' source indicated by the Pb data. A second group of samples consists of mafic to felsic rocks that are known to have been affected by supracrustal contamination and/or post-magmatic alteration (based on $\delta^{18}O$ -values). The result of either of these processes is to shift the data toward higher Sr_i values (discussed above and in Chapter 2) and the trend of these data in Figure 4-7 demonstrate that this shift occurs without obviously affecting ϵ_{Nd} -values. The Paleozoic flyschoid sediments that form the country rocks to the caldera might be expected to have the requisite isotopic characteristics for this inferred supracrustal

★ Depleted mantle @ 368 Ma ✚ Lower crustal contaminant ✖ Upper crustal contaminant

Figure 4-7. Sr-Nd anticorrelation diagram. Bold filled symbols are Mount Pleasant data. Dotted field and x's are St George Batholith data: Nd data from J.B. Whalen (personal communication) and Sr initial ratios are from Rb/Sr isochrons (L.R. Fyffe, personal communication; the highest ϵ_{Nd} value is from the Bocabec Gabbro; two other data points are from the Magaguadavic and Utopia granitoid plutons. Three model AFC curves are shown. The lower crustal curve was calculated using the following parameters: depleted mantle having isotopic characteristics estimated by Bell and Blenkinsop (1987) as $\text{Nd}_i = 0.51240$ and $\text{Sr}_i = 0.70315$ at $T = 368$ Ma. Lower crustal and upper crustal contaminant compositions are inferred from the isotopic variations of the caldera volcanics. Other model parameters are given in Tables 4a and b. Error bars at lower right of diagram.

Table 4-4. Model Nd and Sr parameters for AFC curves in Fig. 4-7 (equations from DePaolo, 1981). r = ratio of assimilation rate to fractionation rate; D = bulk distribution coefficient; $C(L)_0$ = concentration of element in original magma; C^* = concentration of element in contaminant; $\epsilon(L)_0$ = isotopic ratio in original magma; ϵ^* = isotopic ratio in derivative magma; F = fraction of melt.

Lower crust					
Nd:	$r=$	0.5	Sr:	$r=$	0.5
	$D=$	0.2		$D=$	2.5
	$C(L)_0=$	25		$C(L)_0=$	400
	$C^*=$	40		$C^*=$	300
	$\epsilon(L)_0=$	5.6		$\epsilon(L)_0=$	0.70315
	$\epsilon^*=$	-4.00		$\epsilon^*=$	0.707
F	C(L)	$\epsilon(L)$	F	C(L)	$\epsilon(L)$
0.9	30.98	4.25	0.9	288.2	0.70349
0.8	38.13	3.20	0.8	208.1	0.70397
0.7	46.87	2.34	0.7	153.0	0.70458
0.6	57.88	1.63	0.6	117.1	0.70530
0.5	72.27	1.03	0.5	95.3	0.70599
0.4	92.18	0.51	0.4	83.3	0.70653
Upper crust leg A					
Nd:	$r=$	0.3	Sr:	$r=$	0.3
	$D=$	0.2		$D=$	3
	$C(L)_0=$	25		$C(L)_0=$	400
	$C^*=$	30		$C^*=$	400
	$\epsilon(L)_0=$	5.6		$\epsilon(L)_0=$	0.70315
	$\epsilon^*=$	0.00		$\epsilon^*=$	0.712
F	C(L)	$\epsilon(L)$	F	C(L)	$\epsilon(L)$
0.9	28.36	5.32	0.9	298.2	0.70360
0.8	32.43	5.06	0.8	219.3	0.70424
0.7	37.48	4.82	0.7	159.9	0.70514
0.6	43.93	4.59	0.6	117.1	0.70636
0.5	52.55	4.37	0.5	87.8	0.70787
0.4	64.74	4.16	0.4	69.3	0.70948
Upper crust leg B					
Nd:	$r=$	0.3	Sr:	$r=$	0.3
	$D=$	0.2		$D=$	3
	$C(L)_0=$	46.9		$C(L)_0=$	208
	$C^*=$	30		$C^*=$	400
	$\epsilon(L)_0=$	2.34		$\epsilon(L)_0=$	0.70397
	$\epsilon^*=$	0.00		$\epsilon^*=$	0.71
F	C(L)	$\epsilon(L)$	F	C(L)	$\epsilon(L)$
0.9	51.97	2.28	0.9	162.4	0.70472
0.8	58.11	2.21	0.8	127.0	0.70568
0.7	65.73	2.15	0.7	100.4	0.70685
0.6	75.48	2.09	0.6	81.3	0.70816
0.5	88.48	2.04	0.5	68.2	0.70949
0.4	106.88	1.98	0.4	59.8	0.71063

contaminant — those of being radiogenic with respect to Sr and having ϵ_{Nd} -values near zero, possibly reflecting a mixed juvenile and ancient provenance — and are tentatively identified as the source of the supracrustal contamination and/or post-magmatic alteration of the Mount Pleasant Caldera.

All of the caldera samples analyzed have been affected by the lower crustal contaminant to some extent and the supracrustal contamination, where observed, is superimposed on the pre-existing lower crustal contamination. These relationships are modelled with DePaolo's (1981) AFC equations (Fig. 4-7). Details of the model parameters are given in Table 4-4. Limited data available from the Saint George Batholith (Fig. 4-7) have Sr-Nd signatures similar to those of the Mount Pleasant samples. This is a further indication that the two systems were generated by the same processes involving the same source materials.

Trace element systematics

The geochemistry of the caldera complex has been described in Chapters 1 and 2. The igneous rocks are all mildly potassic with tholeiitic basalts and calcalkaline andesites through rhyolites. Detailed major- and trace-element modelling presented in Chapter 3 has demonstrated that the high-level magma chamber of the caldera complex was zoned from an andesitic base to a high-silica rhyolite roof-zone and evolved by a complex process of convective fractionation. In its first-order geochemical and isotopic behaviour, this high-level magma chamber can be regarded as a closed system, although minor contamination effects can be detected. This interpretation is consistent with the data presented above and is discussed further in Chapter 3. The concern of the present study is the ultimate origin of the associated basaltic magmas and their relationship to the andesites that were parental to the felsic magmas. It is taken as a fact that the basalts are partial melts of mantle source materials (e.g., Morse, 1991) and this is corroborated by the isotopic data for basalts of the Mount Pleasant Caldera. These

basalts are characterized by high Zr contents, and Zr/Y and Th/Yb ratios (Chapter 1) that are characteristic of intraplate basalts (Pearce and Norry, 1979; Pearce, 1983). Also, based on their Th/Yb and Ta/Yb ratios (Fig. 4-8) it would seem that the caldera basalts have suffered relatively little crustal contamination.

The primitive mantle normalized trace element patterns of basalts and andesites from the caldera complex and tholeiitic basalts from Hawaii are compared in Figure 4-9a. The caldera basalts have a fairly smooth pattern that is moderately enriched in highly incompatible trace elements. Oceanic intraplate basalts have very similar trace element patterns (Sun and McDonough, 1989) as exemplified by the Hawaiian basalt pattern. Average Ce/Yb and Sm/Yb ratios of the caldera basalts are 20.6 and 2.3 respectively which are similar to the tholeiitic Hawaiian basalt values of 18.2 and 3.0 respectively (BASALTIC VOLCANISM STUDY PROJECT, 1981). However, compared to tholeiitic Hawaiian basalts the caldera basalts are enriched in all incompatible elements by factors ranging from 2 to 5. Assuming that the Hawaiian and Mount Pleasant basalts were derived from similar upper mantle sources, the relative enrichment of incompatible elements in the caldera basalts could be due to smaller degrees of partial melting and/or greater degrees of fractional crystallization in the mantle.

Based on trends on major and trace element variation diagrams (Chapter 1) it has been inferred that fractional crystallization of pyroxene, plagioclase, Fe-Ti oxides and apatite were involved in the evolution of the basaltic magmas into andesitic magmas. However, plots of MgO, Al₂O₃, P₂O₅, Zr and Cr and show considerable scatter; since these elements generally remain immobile during alteration this scatter is probably due to petrogenetic processes acting on the magmas. This indicates the presence of multiple reservoirs and/or a complex process of magma recharge, fractionation, contamination and magma mixing within a single mafic reservoir. Compared to the basalts, the andesites have higher Th/Yb ratios which could be due to a "subduction component" in the source region or to crustal contamination (Fig. 4-8);

Figure 4-8. Ta/Yb versus Th/Yb diagram of Piskahagan Group basalts and andesites after Pearce (1983). Sh = shoshonitic; Ca = calcalkaline; Th = tholeiitic; A = alteration; S = subduction; C = crustal contamination; W = within-plate enrichment; F = fractional crystallization.

Figure 4-9. Normalized plots of trace element abundances in Mt. Pleasant basalts and andesites. A. Primitive mantle-normalized incompatible trace element abundances of Mt. Pleasant rocks and Hawaiian basalts. Normalization factors from Sun and McDonough (1989). B. Model fractionation curves for Hawaiian basalts compared to Hawaiian basalt-normalized trace element abundances of caldera basalts. Hawaiian basalt composition is the average of 10 analyses from Mt. Kilauea tholeiitic basalts (BASALTIC VOLCANISM STUDY PROJECT, 1981).

the latter interpretation is preferred since there is no evidence of subduction beneath the New Brunswick Appalachians after the Ordovician (Fyffe and Swinden, 1991). The andesites are generally more enriched in all of the incompatible trace elements but particularly in the highly incompatible trace elements Rb, K, Ba, U, and Th (Fig. 4-9a) giving the trace element pattern a steeper slope; this combined with troughs at Nb, Ti, Sr, and P are indicators of crustal contamination combined with fractional crystallization of Fe-Ti oxides, plagioclase and apatite. Therefore the trace element patterns support the conclusion, based on the isotope systematics, that the andesites are derived from the basalts through AFC.

DISCUSSION

Potential source regions and contributors to the chemical and isotopic character of continental rock suites include the lower mantle, asthenosphere, lithospheric mantle, and the crust. Menzies and Kyle (1990) have pointed out that there are generally two schools of thought on the derivation of continental volcanic rocks as follows:

"...the debate to date has concentrated on continental rocks being derived from: (1) the asthenosphere with a dominant crustal contamination overprint, or; (2) the asthenosphere and the mantle section of the lithosphere with a minor crustal overprint. Any attempt to resolve this issue has been partly confused by the overwhelming and uncritical embrace of the evidence of enriched mantle."

Isotopic and chemical studies of mantle xenoliths in continental igneous rocks (e.g., Menzies and Hawkesworth, 1987) have shown that metasomatic introduction of minerals such as amphibole, phlogopite, apatite, sphene, perovskite, and carbonate are common in some regions. This has led to the recognition that isotopically and chemically depleted lithosphere, produced during ancient crust-forming events, could be subsequently re-enriched; this re-enrichment could produce a fertile source for

intracontinental plate alkaline magmatism. The evidence of enriched mantle usually comes in the form of rock suites characterized by isotopic signatures indicative of a depleted mantle source combined with trace element signatures characterized by enrichment in highly incompatible elements, including: (1) high-field strength elements (HFSE) like Ti, Zr, and Hf and; (2) large-ion lithophile elements (LILE) like Rb, Th, U, and light REE. This is taken to be an indication of enrichment (invariably within 100 Ma of eruption) of a depleted source material with these incompatible elements through metasomatism of a rigid non-convecting (*ergo* lithospheric) mantle with small volume fluids and/or melts derived from the asthenosphere. The source is then concluded to be lithospheric. However, this is not the only manner in which these chemical and isotopic characteristics can arise. For example, recent studies (e.g., McKenzie and O'Nions, 1991; Ellam, 1992) demonstrate, on theoretical grounds, that incompatible trace element enrichment of partial melts of depleted source materials can result from the dynamics of the partial melting process itself. The isotopic composition of the melt is derived from the depleted parent. However the chemical composition, including patterns of trace element 'depletion' or 'enrichment' are complex functions of the length of the magma column over which melting occurs, mineralogy of the parent, depth of final magma separation, percentage of partial melting, and the length of time over which the process continues. Since combined isotopic depletion and trace element enrichment allow, but do not require, a metasomatic enrichment process, such a conclusion is not warranted without additional evidence. In the case of Hawaiian tholeiitic basalts McKenzie and O'Nions (1991) modelled their isotopic and trace element characteristics in terms of small degrees of partial melting in a column of upwelling mantle asthenosphere in the garnet-spinel transition zone.

Mantle reservoirs

In the Mount Pleasant Caldera complex the depleted Nd isotopic signatures, combined with incompatible trace element enrichment, are interpreted to indicate that these magmas were derived in the asthenosphere from source materials similar to that of oceanic island basalts (OIB). Trace element enriched lithosphere has only been unambiguously identified from Archean cratons (Menzies, 1990) and there is no evidence for the occurrence of Archean basement anywhere in the Appalachian mobile belt. Furthermore, Bell and Blenkinsop (1987) identified LILE depleted, rather than enriched, mantle in the Archean craton to the west of the Appalachians. Foland et al. (1988) also have inferred involvement of an OIB-type mantle source in the petrogenesis of alkaline Mesozoic plutonism in the Appalachians of New England and Quebec.

The chemical and isotopic signatures of the caldera complex can be derived by fractional crystallization of a basalt (with the characteristics of Hawaiian tholeiite) in combination with contamination by crustal materials. The light REE enriched trace element patterns of Hawaiian tholeiitic basalts (Fig. 4-9a) are considered to be the product of partial melting at pressures of the spinel-garnet transition zone (depths of 60-80 km; McKenzie and O'Nions, 1991; Ellam, 1992). The similarity of the slopes of the Hawaiian and caldera trace element patterns suggests that the caldera basalts could have been derived by a similar process. However, the caldera basalts are clearly fractionated; they have low Mg numbers (< 50), and Ni (28-40 ppm), and Cr (10-70) contents (Appendix 1). These data indicate low pressure crystallization of olivine and chromian spinel from a more mafic precursor — olivine occurs on the liquidus at pressures < 12 kb (BASALTIC VOLCANISM STUDY PROJECT, 1981). In Figure 4-9b, fractional crystallization of Hawaiian tholeiite is modelled using an assemblage 80% olivine, 10% orthopyroxene and 10% chrome spinel. Partition coefficients were calculated using the method and computer program of Nielson (in press). Although the

choice of assemblage was not constrained by phase equilibria, the calculations are relatively insensitive to changes in mineral proportions (in the absence of plagioclase crystallization) because all of the elements except Ni, Cr, and Sc are highly incompatible in olivine, pyroxene and spinel. The results show that the enrichment of incompatible trace elements in basalts of the Mount Pleasant Caldera is only partially explained by fractional crystallization of a preexisting magma like the Hawaiian basalts. At most 20-30% fractional crystallization is allowed by the abundances of the compatible elements Ni and Cr. The abundances of certain of the incompatible elements — middle REE (Sm, Eu, Tb) and Sr — could be produced by 20-30% fractional crystallization of a Hawaiian-type parent. There is no indication of plagioclase fractionation (unless crystallization is being balanced by assimilation of a similar plagioclase component). The negative Ti anomaly probably indicates fractionation of an Fe-Ti oxide. The marked enrichment of all other elements is attributed to crustal rather than lithospheric mantle contamination because: (1) Pb-isotopic signatures are crustal, and; (2) the subcontinental mantle, even when metasomatized, is depleted in incompatible elements relative to the materials being considered here (e.g., McDonough, 1990; McDonough and Frey, 1989).

Crustal reservoirs

Based on the Sr-Nd isotope systematics of the caldera complex igneous rocks, two distinct crustal reservoirs are inferred — an upper crustal reservoir and a lower crustal reservoir. The supracrustal reservoir has contaminated the high-silica rhyolites, basalts, and basaltic andesites of the caldera complex with radiogenic Sr and Pb and ^{18}O through some combination of assimilation, fractional crystallization, and post-magmatic alteration; intermediate-composition magmas were the least affected. The contamination of the felsic and mafic rocks are probably caused by different processes. Silicic magmas formed near the roof zone of the magma chamber were generally the

most strongly affected by supracrustal AFC; these rocks could potentially have had long-term exposure to the roof zone country rocks where the bulk of the magma chamber heat is lost. These magmas are the most volatile enriched which would: (1) facilitate exchange with their country rocks at the magmatic stage, and; (2) tend to generate explosive eruptions which would promote mechanical assimilation. The basalts and basaltic andesites also show the affects of supracrustal contamination. This can be seen in Figure 4-7 where the mafic rocks are displaced further to the right of the mantle array and the lower crustal AFC model curve than are more felsic, isochronous caldera lithologies. This variation is modelled by an AFC process in Figure 4-7, and is probably also applicable to the isotopic composition of gabbroic rocks of the St. George Batholith. However, supracrustal contamination of the mafic caldera volcanic rocks probably has an origin other than AFC. A clue to the nature of the process involved is provided by the high Li concentrations (as much as 100 ppm; Chapter 1) in the caldera basalts and andesites. Such high concentrations of Li could only be produced by some form of alteration or assimilation. However, large quantities of country rock assimilation would be required to produce such high Li concentrations but the most mafic compositions seem to have the highest concentrations. On the other hand, caldera formation waters associated with the felsic volcanic pile and magmatic/hydrothermal fluids derived from the roof of the felsic magma chamber might:(1) contain large abundances of these elements, and; (2) be highly soluble in the hot, dry mafic magmas. Therefore, the contamination of the mafic rocks probably occurred through absorption of these caldera formation waters or magmatic/hydrothermal fluids (that were contaminated with ^{18}O and radiogenic Sr and Pb from the country rocks waters) during or after eruption. Devitrification products of the glassy groundmass of the mafic rocks would contain Fe-rich clays that are capable of partitioning, and thus retaining Li in these rocks.

The radiogenic isotope data indicate that the caldera igneous rocks have been contaminated and hybridized by an ancient crustal contaminant. The andesites were derived by AFC of mantle-derived basaltic magmas in this crustal source region. This source has isotopic characteristics similar to Avalon Terrane, which does not outcrop in the study area but which has been inferred to form the basement of the study area based on isotopic (Ayuso and Bevier, 1991), geological (Currie and Hunt, 1991), and geophysical (Thomas and Willis, 1989) evidence. Gravity modelling by Thomas and Willis (*ibid.*) identified the presence of Avalon-type basement rocks at depths greater than 9 km, which would place it in the middle or lower crust. The lower crust is the assumed location because these Fe-rich, high density basalts would be expected to pond in the lower crust (e.g., Hildreth, 1981). Simple AFC modelling (see Figs. 4-5 and 4-7 and Tables 4-2 and 4-4) indicates that the andesites would be derived by approximately 50% fractional crystallization of a basaltic precursor, assuming a ratio (r) of assimilation rate to crystallization rate of 0.5. At this r -value, only 10-20% AFC is required for the fractionates to take on the Pb-isotopic characteristics of the assimilate. This model thus reproduces the mixed Nd and Sr isotopic values and crustal Pb values observed in the caldera complex

Some indications of the mineralogy of this lower crustal contaminant can be made based on the trace element patterns in Figures 4-9a and 4-9b. It is assumed that contamination occurred by preferential dissolution or partial melting of certain minerals in the contaminant. The basalts show enrichments in P, Zr, K, and Ba (Figs. 4-9a and 4-9b) that indicate apatite, zircon, and K-feldspar are being assimilated. This trend may continue during evolution of the andesites but is complicated by the onset of fractional crystallization of plagioclase, Fe-Ti oxides and apatite (Fig. 4-9a). The enrichment of light and heavy REE relative to middle REE in caldera basalts in Figure 4-9b may indicate that there is a residual mineral in the crustal protolith that concentrates heavy REE. Two metamorphic minerals that partition middle REE in

preference to light and heavy REE are clinopyroxene and hornblende (Grauch, 1989). However, the convex up REE pattern of clinopyroxene occurs in two-pyroxene granulites and is balanced by a concave up REE pattern in coexisting orthopyroxene. Assimilation of a two-pyroxene granulite would not produce a middle REE depleted magma composition unless orthopyroxene was assimilated but clinopyroxene was not, which seems unlikely. Therefore, the middle-REE depleted pattern of caldera rocks observed in Figure 4-9b probably indicates assimilation of an amphibole-bearing protolith that retained amphibole in the residue. In southern New Brunswick, amphibolitic gneisses are common in Avalon Terrane rocks older than 780 Ma (Currie, 1988).

As noted by Ayuso and Bevier (1991) the caldera igneous rocks have radiogenic Pb-isotopic compositions that are generally associated with the middle and upper crust. The lower crust is generally considered to be mafic, granulitic, U-depleted and therefore unradiogenic with respect to Pb. However, Ben Othman et al., 1984 observed that model ages of granulites are generally much older than their geological (i.e., age of granulite grade metamorphism) age and that their geological age is inevitably the same as a major orogenic event, and concluded that "... granulite-facies metamorphism seems always to be linked to major orogeny. It does not reflect a continuous reequilibration process at depth stopped by the upwelling of a piece of lower crust to the surface during some event not related to any large orogenesis. If such re-equilibration at depth followed by 'upwelling' occurs, this event is related to a major orogenesis". From this it is inferred that supracrustal Avalon Terrane rocks were tectonically emplaced in the lower crust during the Acadian Orogeny and had either undergone granulite metamorphism during the Acadian Orogeny or were possibly becoming granulitized by the same processes involved in caldera formation.

Model of magmatic evolution of the Mount Pleasant Caldera in the lithosphere

The results and discussion allow construction of a dynamic model of evolution of the Mount Pleasant Caldera complex in the post-compressional lithosphere of the northern Appalachians. This model is illustrated schematically in Figure 4-10. The similarity of the caldera basalts to OIB indicates that they have a similar origin — small degrees of partial melting in a zone of upwelling mantle at pressures equivalent to the garnet transition zone. Some of the basalts are fractionated with little evidence of crustal contamination suggesting that they might have undergone fractionation en route to the base of the crust, where their density prevented further ascent. The underplated basalts underwent substantial AFC during which they evolved into andesitic compositions. The lower density of the hybrid andesites allowed continued ascent of magma into a middle or upper crustal magma chamber. The andesites were cooler than the basalts and were emplaced in cooler country rocks. As a result, assimilation ceased to be of major importance in further evolution of the caldera-forming magmatic system. Further magmatic evolution of this magma chamber occurred by a two-stage process of convective fractionation as detailed in Chapter 3. The magma chamber became vertically stratified with an andesitic base that was being periodically replenished and a rapidly growing felsic roof zone. Eventually, the magma chamber lid failed and the caldera-forming volcanism began. The initial failure apparently disrupted the magma chamber stratigraphy at this time and allowed extrusion of andesites from the base of the high-level stratified chamber — andesites and diorites of the Scoullar Mountain Formation and the South Oromocto Andesite were emplaced. This was the only time that andesites were extruded. The remainder of the caldera-forming cycle was characterized by repeated eruptions of rhyolitic ash flow tuffs and lavas. The waning stages saw eruptions replaced by resurgent intrusions of the McDougall Brook Microgranite and the Mount Pleasant Porphyry. Three times during this activity,

Figure 4-10. Model of magmatic evolution of the Mount Pleasant Caldera complex in the lithosphere. See text for description.

thoroughgoing fractures must have developed allowing eruptions of dense basalt into the exocaldera and late caldera-fill sequence.

Tectonic Implications

The recognition that post-tectonic felsic magmatism of the Mount Pleasant Caldera is the fractionated and hybridized product of mantle-derived partial melts of an OIB-type source has important implications for post-compressional evolution of the orogen. The Maritimes Basin has been regarded as a passive rift (McCutcheon and Robinson, 1987). The implication of this interpretation is that mantle partial melts would occur in response to shallow, adiabatic, mantle upwelling and melting caused by lithospheric extension. These mantle partial melts would be expected to have MORB rather than OIB characteristics (McKenzie and Bickle, 1988). Furthermore, the limited data available suggest that the Saint George Batholith has isotopic and geochemical characteristics like the caldera complex and could have been formed by the same process. The earliest phases of the Saint George Batholith were being emplaced in the Late Silurian, well before the end of Acadian compression. This raises the possibility that mantle upwelling began while compression was ongoing. If this is the case and if it was sustained until the Late Devonian, then mantle upwelling was probably the cause rather than the result of lithospheric extension.

There are two possible mechanisms that are theoretically capable of producing a period of mantle upwelling: (1) a hot spot or plume, or; (2) gravitational subduction of tectonically thickened lithosphere. Gravitational subduction of the lithosphere is an attractive hypothesis because its fundamental cause can be related to orogeny and it has consequences that can be predicted, and therefore tested. In this hypothesis, continent-continent collision pushes cold crust downward into the mantle which thickens the mechanical boundary layer as shown in Figure 4-11. This layer is denser than the mantle underneath it and is inherently unstable. It could be expected to detach and sink

Figure 4-11 Model of gravitational subduction of mantle lithosphere in the post tectonic northern Appalachians. See text for description

into the mantle in much the same way that oceanic lithosphere is returned to the mantle. In response, hot asthenosphere could ascend and undergo partial melting. If this process was initiated before compression had ceased, the mantle partial melts would tend to produce plutonism rather than volcanism, possibly excepting the initial stages. If upwelling continued after the cessation of compression it could be the driving force behind a period of crustal extension. There is sufficient evidence for the occurrence of such a process in the northern Appalachians that the possibility should be critically evaluated as an alternative to existing models.

CONCLUSION

The most important conclusion to arise from this study is that the predominantly felsic magmatism of the Mount Pleasant Caldera is the result of extensive hybridization of mantle-derived basalts in the continental crust. A similar origin is proposed for the Saint George Batholith. The mantle source for this magmatism is similar to OIB and seems to require active mantle upwelling and partial melting over a period of time ranging from the Late Silurian to the Late Devonian and possibly longer. It is proposed that this episode of upwelling was caused by gravitational subduction of the subcontinental lithosphere near the end of the Acadian Orogeny. The result was an initial transient episode of volcanism (Mascarene volcanic rocks), followed by a more extended period of voluminous plutonism (Acadian magmatism), caldera development (Mount Pleasant Caldera), and finally by thermal collapse and crustal extension (Maritimes Basin formation). This hypothesis is not adequately constrained by available data but constitutes a testable hypothesis that can be more rigorously evaluated by further studies.

REFERENCES

- Ayuso RA, Bevier ML (1991) Regional differences in Pb isotopic compositions of feldspars in plutonic rocks of the northern Appalachian Mountains, U.S.A. and Canada: a geochemical method of terrane correlation. *Tectonics* 10: 191-212
- BASALTIC VOLCANISM STUDY PROJECT (1981) Basaltic volcanism on the terrestrial planets. Pergamon Press Inc., New York, 1286 p.
- Bell K, Blenkinsop J (1987) Archean depleted mantle: evidence from Nd and Sr initial isotopic ratios of carbonatites. *Geochimica et Cosmochimica Acta* 51: 291-298
- Ben Othman D, Polvé M, Allègre CJ (1984) Nd-Sr isotopic composition of granulites and constraints on the evolution of the lower continental crust. *Nature* 307: 510-515
- Bevier ML (1989) U-Pb geochronological studies of igneous rocks in New Brunswick. In: Abbott SA (ed.) Thirteenth Annual Review of Activities, project resumes, 1988. New Brunswick Department of Natural Resources & Energy, Mineral Resources & Energy Division, Information Circular 88-2, 134-140
- Bevier ML, Whalen, JB (1990) Tectonic significance of Silurian magmatism in the Canadian Appalachians. *Geology* 18: 411-414.
- Blanchard M-C, Jamieson RA, More, EB (1984) Late Devonian — Early Carboniferous volcanism in western Cape Breton Island, Nova Scotia. *Canadian Journal of Earth Sciences* 21: 762-774
- Coyle M, Strong DF (1987) Geology of the Springdale Group: A newly recognized Silurian epicontinental-type caldera in Newfoundland. *Canadian Journal of Earth Sciences* 24: 1135-1148
- Currie KL (1988) The western end of the Avalon zone in southern New Brunswick. *Maritime Sediments and Atlantic Geology* 24: 339-352

- Currie KL, Hunt PA (1991) Latest Precambrian igneous activity near Saint John, New Brunswick. In: Radiogenic age and isotopic studies, Report 4, Geological Survey of Canada Paper 90-2, 11-17
- DePaolo DJ (1981) Trace element and isotopic effects of combined wallrock assimilation and fractional crystallization. *Earth and Planetary Science Letters* 53: 189-202
- Doe BR, Delevaux M, Albers JP (1985) The Plumbotectonics of the West Shasta mining district, Eastern Klamath Mountains, California. *Economic Geology* 80: 2136-2148.
- Dostal J, Dupuy C, Keppie JD (1983) Petrology and geochemistry of Devonian-Carboniferous volcanic rocks in Nova Scotia. *Maritime Sediments and Atlantic Geology* 19: 59-71
- Durling PW, Marillier FJY (1990) Structural trends and basement rock subdivisions in the western Gulf of St. Lawrence, northern Appalachians. *Atlantic Geology* 26: 79-95
- Ellam, RM (1992) Lithospheric thickness as a control on basalt geochemistry. *Geology* 20: 153-156
- Foland KA, Chen J-f, Gilbert LA (1988) Nd and Sr isotopic signatures of Mesozoic plutons in northeast North America. *Geology* 16: 684-687
- Fyffe LR, Barr SM (1986) Petrochemistry and tectonic significance of Carboniferous volcanic rocks in New Brunswick. *Canadian Journal of Earth Sciences* 23: 1243-1256
- Fyffe LR, McLeod MJ, Ruitenburg AA (1992) A geotraverse across the St. Croix - Avalon terrane boundary, southern New Brunswick. Geological Association of Canada, Mineralogical Association of Canada, Joint Annual Meeting, Wolfville '92; Field Trip A1, Guidebook, 44 pp.

- Fyffe LR, Pajari GE, Jr, Cherry ME (1981) The Acadian plutonic rocks of New Brunswick. *Maritime Sediments and Atlantic Geology* 17: 23-36
- Fyffe LR, Swinburn HS (1991) Paleotectonic setting of Cambro-Ordovician volcanic rocks in the Canadian Appalachians. *Geoscience Canada* 18: 145-157
- Gates O, Moench RH (1981) Bimodal Silurian and Lower Devonian volcanic rock assemblages in the Machias-Eastport area, Maine. United States Geological Survey Professional Paper 1184, 32 pp.
- Grauch RI (1989) Rare earth elements in metamorphic rocks. In: Lipin BR, McKay GA (eds) *Reviews in Mineralogy 21: Geochemistry and mineralogy of rare earth elements*, Mineralogical Society of America, 147-168
- Hart SR (1984) The DUPAL anomaly: a large-scale isotopic anomaly in the southern hemisphere. *Nature* 309: 753-756
- Hildreth W (1981) Gradients in silicic magma chambers: implications for lithospheric magmatism. *Journal of Geophysical Research* 86: 10153-10192
- Hogan JP, Sinha AK (1989) Compositional variation of plutonism in the Coastal Maine Magmatic Province: mode of origin and tectonic setting. In: Tucker RD, Marvinney RG (eds) *Studies in Maine Geology volume 4: Igneous and Metamorphic Geology*, Maine Geological Survey, 1-35
- Hubacher FA, Lux DR (1987) Timing of the Acadian deformation in northeastern Maine. *Geology* 15: 80-83
- Jacobsen SB, Wasserburg GJ (1980) Sm-Nd isotopic evolution of chondrites. *Earth and Planetary Science Letters* 50: 139-155
- Latin D, Waters FG (1991) Generating melt during rifting in the North Sea. *Nature* 351: 559-562
- MacLellan HE, Taylor RP (1989) Geology and geochemistry of the Burnhill granite and its related W-Sm-Mo-F mineral deposits, central New Brunswick. *Canadian Journal of Earth Sciences* 26: 499-514

- Matsuhisa Y, Goldsmith JR, Clayton RN (1979) Oxygen isotope fractionation in the system quartz - albite - anorthite - water. *Geochimica et Cosmochimica Acta* 43: 1131-1140
- McCutcheon SR (1981) Revised stratigraphy of the Long Reach area, southern New Brunswick: evidence for major northwestward-directed Acadian thrusting. *Canadian Journal of Earth Sciences* 18: 646-656
- McCutcheon SR (1991) The Late Devonian Mount Pleasant Caldera complex: stratigraphy, mineralogy, geochemistry and geologic setting of a Sn-W deposit in southwestern New Brunswick. unpublished Ph.D. thesis, Dalhousie University, Halifax, Nova Scotia, 609 pp.
- McCutcheon SR, Bevier ML (1990) Implications of field relations and U-Pb geochronology for the age of gold mineralization and timing of Acadian deformation in northern New Brunswick. *Atlantic Geology* 26: 237-246
- McCutcheon SR, Robinson PT (1987) Geological constraints on the genesis of the Maritimes Basin, Atlantic Canada. *Canadian Society of Petroleum Geologists, Memoir* 12, 287-297
- McDonough WF (1990) Constraints on the composition of the continental lithospheric mantle. *Earth and Planetary Science Letters* 101: 1-18
- McDonough WF, Frey FA (1989) Rare earth elements in upper mantle rocks. In: Lipin BR, McKay GA (eds) *Reviews in Mineralogy* 21: Geochemistry and mineralogy of rare earth elements, Mineralogical Society of America, 99-146
- McGregor DC, McCutcheon SR (1988) Implications of spore evidence for Late Devonian age of the Piskahegan Group, southwestern New Brunswick. *Canadian Journal of Earth Sciences* 25, 1349-1364
- McLeod MJ (1990) Geology, geochemistry, and related mineral deposits of the Saint George Batholith; Charlotte, Queens and Kings Counties, New Brunswick. New

- Brunswick Natural Resources & Energy, Mineral Resources Division, Mineral Resources Report 5, 169 pp.
- McLeod M J, Taylor RP, Lux DR (1988) Geology, $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology and Sn-W-bearing sheeted veins of the Mount Douglas Granite, southwestern New Brunswick. Canadian Institute of Mining and Metallurgy Bulletin 81: 70-77
- McKenzie D, Bickle MJ (1988) The volume and composition of melt generated by extension of the lithosphere. *Journal of Petrology* 29: 625-679
- McKenzie D, O'Nions RK (1991) Partial melt distributions from inversion of rare earth element concentrations. *Journal of Petrology* 32: 1021-1091
- Menzies MA (1990) Archean, Proterozoic and Phanerozoic lithospheres. In: Menzies, M.A. (ed.) *Continental mantle*, Clarendon Press, Oxford, 69-86
- Menzies MA, Hawkesworth JC (1987) Upper mantle processes and composition. In: Nixon PH (ed.) *Mantle xenoliths*, Wiley, Chichester, 725-738.
- Menzies MA, Kyle PR (1990) Continental volcanism: a crust-mantle probe. In: M.A. Menzies (ed.), *Continental Mantle*, Clarendon Press, Oxford, ??? pp.
- Michard A, Gurriet P, Soudant M, Albarede F (1985) Nd isotopes in French Proterozoic shales: external vs. internal aspects of crustal evolution. *Geochimica et Cosmochimica Acta* 49: 601-610
- Morse SA (1991) Basaltic magma from the crust is not a free option. *EOS* 72(14): 161
- Nielson RL (in press) BIGD.FOR: a FORTRAN program to calculate trace element partition coefficients for natural mafic and intermediate composition magmas. *Computers and Geosciences*
- O'Nions RK, Hamilton PJ, Evensen (1977) Variations in $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in oceanic basalts. *Earth and Planetary Science Letters* 34: 13-22
- Pearce JA (1983) Role of sub-continental lithosphere in magma genesis at active continental margins. In: Hawkesworth CJ, Norry MJ (eds.) *Continental Basalts and Mantle Xenoliths*, Shiva Geology Series, 230-249.

- Pearce JA, Norry MJ (1979) Petrogenetic implications of Ti, Zr, Y, and Nb variations in volcanic rocks. *Contributions to Mineralogy and Petrology* 69: 33-47
- Richard P, Shimizu N, Allègre CJ (1976) $^{143}\text{Nd}/^{146}\text{Nd}$, a natural tracer: application to oceanic basalts. *Earth and Planetary Science Letters* 31: 269-278
- Ruitenburg AA, McCutcheon SR (1982) Acadian and Hercynian structural evolution of southern New Brunswick. *Geological Association of Canada, Special Paper* 24: 131-148
- St. Peter CJ, Fyffe LR (1990) Structural trends and basement rock subdivisions in the western Gulf of St. Lawrence: Discussion. *Atlantic Geology* 26: 277-279
- Stacey JS, Kramers JD (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth and Planetary Science Letters* 26: 207-221
- Sun S-s, McDonough WF (1989) Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geological Society Special Publication No. 42*: 313-345
- Taylor SR, McLennan SM (1985) *The Continental Crust: its Composition and Evolution*. Blackwell Scientific Publications, 312 pp.
- Thomas MD, Willis C (1989) Gravity modelling of the Saint George Batholith and adjacent terrane within the Appalachian Orogen, southern New Brunswick. *Canadian Journal of Earth Science* 26: 561-576
- van Wageningen NA, Fay VK (1988) Stratigraphy and volcanology of a portion of the Lower Devonian volcanic rocks of southwestern New Brunswick. *Geological Survey of Canada, Paper* 88-1B: 69-78
- Wasserburg GJ, Jacobsen SB, DePaolo DJ, McCulloch MT, Wen T (1981) Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. *Geochimica et Cosmochimica Acta* 45: 2311-2332

Appendix Table A-1. Geochemical analyses of igneous rocks of the Mount Pleasant Caldera. Samples without a letter prefix are from McCutcheon (1991). Samples in bold type are from this study. Samples from this study that are prefixed LM were collected in the field by the author. Samples from this study that are prefixed MC were donated by S.R. McCutcheon. Sample 82-19 was donated by D.Sinclair. *indicates average of duplicate analyses (XRF data only). HSB = Hoyt Station Basalt; SMFA = Scoullar Mountain Formation andesite; SMFD = Scoullar Mountain Formation diorite; SOA = South Oromocto Andesite; KF = Kleef Formation basalt; RF = Rothea Formation ash flow tuff; LMPPF = Little Mount Pleasant Formation ash flow tuff; SF = Seelys Formation ash flow tuff; BRR = Bailey Rock Rhyolite; BSMF = Big Scott Mountain Formation rhyolite; MBM = McDougall Brook Microgranite; MPP = Mount Pleasant Porphyry; THG = True Hill Granite; RD = rapakivi dyke.

Appendix Table A-1 (continued)

A-2

Sample	3c	9b-1	MC-9	131a	131b-3	LM-6*	159b-1	159c	MC-159c
Group	HSB	HSB	HSB	SMFA	SMFA	SMFA	SMFA	SMFA	SMFA
Chapter	1,2,3,4	1,2,3,4	2,3,4	1,2,3,4	1,2,3,4	2,3,4	1,2,3,4	1	2,3,4
SiO ₂	50.6	51.9	45.73	58.3	59.8	59.51	61.9	60.1	61
TiO ₂	2.21	2.26	2.46	1.46	1.49	1.59	1.19	1.23	1.27
Al ₂ O ₃	15.8	15.3	13.76	13.8	14	13.96	14	15	14.98
Fe ₂ O ₃ (T)			11.98			10.76			7.03
Fe ₂ O ₃	3.28	3.59		3.99	5.64		5.4	3.31	
FeO	6.4	5.1		5.4	3.9		1.6	3.2	
MnO	0.16	0.22	0.38	0.17	0.18	0.18	0.1	0.13	0.14
MgO	4.46	4.8	6.09	1.57	1.69	1.71	1.25	2.2	2.36
CaO	7.35	6.37	7.41	3.7	3.4	4.02	5.21	3.38	3.34
Na ₂ O	3.4	3.88	5	3.92	3.28	4.38	2.76	3.61	3.49
K ₂ O	1.01	1.09	0.08	3.54	3.95	3.12	2.89	3.92	3.96
P ₂ O ₅	0.48	0.5	0.43	0.54	0.58	0.66	0.31	0.31	0.31
*H ₂ O	2.4	2.5		1.6	1.6		1.7	1.8	
LOI	2.77	2.85		1.39	1.85		2.39	2.62	
Total	97.55	97.51	93.52	98.04	99.51	100.11	98.31	98.19	98.1
Mg#	0.35	0.42		0.18	0.25		0.38	0.35	
Q	5.2	5.9		11.2	14.5		22.5	13.5	
Ab	6	6.4		20.9	23.3		17.1	23.2	
Or	28.8	32.8		33.2	27.8		23.4	30.6	
An	24.9	21.1		9.6	11.8		17.3	13.2	
C	0	0		0	0		0	0	
Di	6.9	5.8		4.1	1.1		5.4	1.3	
H _y	13.5	12.3		8.9	10.6		3.8	7.6	
Mt	4.8	5.2		4.3	4.3		3.9	4	
Il	4.2	4.3		2.8	2.8		2.3	2.3	
Hem	0	0		0	0		0	0	
Ap	1.1	1.2		1.4	1.3		0.7	0.7	
Ru	0	0		0	0		0	0	
Li	74	100		44	43		40	51	
Sc	31	32	18.2	23	26	22.9	21	20	19.73
V	0	0	289	0	70	0	0	0	136
Cr	70	70	74	10	19	96.5	20	20	25
Ni	35	35	0	8	12	27.5	15	12	0
Rb	50	40	0	130	150	109	90	150	136
Sr	540	860	394	280	210	242.5	280	440	370
Y	40	20	289	60	60	81	30	50	49
Zr	210	220	202	590	560	535	310	330	309
Nb	20	5	8	30	40	32	30	30	12
Zn	130	140	138	170	160	139	94	110	92
Ba	580	690	137	740	740	757	580	780	662
Hf			4.8			12.2			7.7
Ta			0.74			2.06			1.4
Th	6	6	3.4	12	13	11.6	14	13	11.7
U	2	2	1.7	3	4	3	4	4	3.5
La	32	30	27	64	74	66	65	53	50.4
Ce	86	71	59	131	158	144	120	104	113.7
Nd	37	29	34	58	71	72	0	43	52.2
Sm	7.4	7	7.6	13.7	15.3	14.4	11	9.1	9.28
Eu	2.2	2.1	2.32	3.08	3.53	3.77	0	1.86	2.02
Tb	1.1	1	1.21	2.1	2.2	2.14	0	1.2	1.35
Yb	3.56	3.11	3.2	6.88	7.52	6.8	0	4.42	3.8
Lu	0.56	0.49	0.5	1.03	1.12	1.07	0.8	0.66	0.63

Appendix Table A-1 (continued)

A-3

Sample	257a2	259c	LM-15*	11	12	14-2	MC-14	LM-9*	422a
Group	SMFD	SMFD	SMFD	SOA	SOA	SOA	SOA	SOA	SOA
Chapter	1,2,3,4	1,2,3,4	2,3,4	1,2,3,4	1,2,3,4	1	2	2,3,4	1,2,3,4
SiO ₂	61.4	62.9	57.76	55.4	53.3	56.2	57.24	55.98	51.3
TiO ₂	1.21	1.12	1.28	1.58	1.4	1.36	1.4	0.52	1.32
Al ₂ O ₃	15	14.3	15.14	16.1	15.5	15.6	15.77	15.93	15.9
			8.07				7.16	8.51	
FeO ₂	3.9	2.57		4.68	4.39	4.56			2.36
FeO	2.3	3.9		3.2	3.3	2.2			5.3
MnO	0.09	0.15	0.14	0.07	0.12	0.08	0.08	0.151	0.13
MgO	1.56	1.99	3.35	4.07	3.6	4.08	4.28	3.56	5.94
CaO	3.8	3.65	6.08	6.25	6.74	4.68	4.13	5.93	7.14
Na ₂ O	2.95	2.74	2.82	3.42	2.79	2.82	2.85	3.44	3.2
K ₂ O	5.08	3.16	2.89	2.16	2.77	3.33	3.41	2.74	1.58
P ₂ O ₅	0.42	0.4	0.29	0.49	0.45	0.43	0.48	0.52	0.38
H ₂ O	0.8	1.7		1.7	1.8	2.3			2.1
LOI	1.62	2.47		2.39	2.16	3.31			3
Total	98.51	98.58	98.03	99.12	96.16	97.64	97.12	98.55	96.65
Mg#	0.34	0.28		0.5	0.46	0.59			0.47
Q	15.3	23.6		8.8	8	11.1			2.8
Ab	30	18.7		12.8	16.4	19.7			9.3
Or	25	23.2		28.9	23.6	23.9			27.1
An	12.7			22.2	21.6	20.1			24.4
C	0	0.7		0	0	0			0
Di	2.8	0		4.5	7.2	0.3			6.9
Hy	4.7	8.4		11.5	9.5	12.4			17.3
Mt	3.9	3.7		4.5	4.2	4.2			3.4
Il	2.3	2.1		3	2.7	2.6			2.5
Hem	0	0		0	0	0			0
Ap	1	0.9		1.1	1	1			0.9
Ru	0	0		0	0	0			0
Li	42	91		43	42	83			60
Sc	18	18	21.6	24	20	21	19.6	18.2	25
V	100	100	110	190	0	0	130	70	200
Cr	19	22	69.5	66	60	60	76	40	150
Ni	9	9	28	38	47	49	32	26	110
Rb	200	180	114.5	60	70	60	55	52.5	50
Sr	360	230	443	480	690	610	526	830	560
Y	50	30	39	30	30	40	41	43	10
Zr	480	470	239	320	320	320	308	320	200
Nb	30	30	11.5	30	10	5	14	18	20
Zn	100	120	82	96	120		91	90	110
Ba	1060	910	620.5	580	820	1540	1359	731	570
Hf			6				7.3	7.5	
Ta			1.37				0.98	1.43	
Th	10	10	9.2	8	7	7	6.8	7	5
U	3	4	2.5	2	2	5	3.1	1.72	1
La	64	57	42	50	44	45	43	45	35
Ce	116	111	86	104	90	92	87	92	72
Nd	35	33	41	54	0	0	42	45	30
Sm	8.66	8.14	7.4	9.65	8.5	8.5	7.3	8.4	6.86
Eu	2.73	3.16	2.04	2.47	0	0	2.34	2.43	1.82
Tb	1.3	1.7	1.06	1.2	0	0	1.04	1.09	0.9
Yb	3.95	3.95	3.3	3.83	0	0	3	3.5	2.82
Lu	0.71	0.74	0.5	0.58	0.58	0.51	0.46	0.53	0.42

Appendix Table A-1 (continued)

A-4

Sample	24	MC-24	LM-17a*	35-1	421a	13-3	MC-13	250	254
Group	KF	KF	KF	KF	RF	RF	RF	LMPF	LMPF
Chapter	1	2,3,4	2,3,4	1,2,3,4	1	1	2	1,2,3	1,2,3
SiO ₂	47.6	43.01	48.65	50.6	74	72.9	73.91	77.2	76
TiO ₂	2.69	2.5	3.2	2.94	0.28	0.29		0.04	0.07
Al ₂ O ₃	16	14.69	14.99	15.2	13.3	13.1	13.03	12.8	13.1
		11.28	13.96				2.42		
FeO ₂	933			8.29	0.99	2.21		0.82	0.87
FeO	2.4			3.6	0.6	0.05		0.05	0.05
MnO	0.26	0.24	0.19	0.19	0.05	0.02	0.02	0.05	0.07
MgO	3.98	3.84	3.96	3.16	0.47	0.61	0.65	0.03	0.08
CaO	6.63	6.07	8.75	7.65	0.81	0.32	0.31	0.28	0.17
Na ₂ O	3.59	3.3	2.99	3.07	4.66	2.66	2.51	3.29	3.76
K ₂ O	1.46	1.29	1.1	1.1	3.36	5.66	5.7	4.98	4.89
P ₂ O ₅	1.05	1.05	1.09	0.88	0.05	0.06	0.03	0.01	0.03
H ₂ O	2.3			1.7	1.1	1		0.4	0.4
LOI	2.85			2.16	1.39	1.7		0.77	0.85
Total	97.29	97.63	99.07	98.38	99.67	98.88	99.02	99.95	99.49
Mg#	0.56			0.41	0.38	0.9		0.32	0.55
Q	2.1			94	31.7	337		38.4	35
Ab	8.6			6.5	19.9	335		29.4	28.9
Or	30.4			26	394	22.5		27.8	31.3
An	23.2			24.5	3.7	1.2		1.3	0.7
C	0			0	0.6	2.2		1.5	1.4
Di	2.3			6.3	0	0		0	0
H ₂	14.3			9.6	1.2	3		0.1	0.2
Mt	6.1			6.4	1.3	1.1		0.2	0.2
Il	5.1			5.6	0.5	0.6		0.1	0.1
Hem	0			0	0.1	0		0.7	0.7
Ap	2.4			2	0.1	0.1		0	0.1
Ru	0			0	0	0		0	0
La	210			140	24	12		48	34
Sc	25	24.5	28.2	27	6	5	4.45	7	7
V	0	146	64.5	0	14	18	3	4	6
Cr	10	16	52	30	10	0	0	20	10
Ni	28	7	29	40	4	6	1	2	1
Rb	40	38	15	30	160	250	241	620	590
Sr	550	520	460	390	90	260	216	5	10
Y	50	56	62.5	50	30	70	72	110	120
Zr	490	406	413	430	240	330	335	100	80
Nb	40	27	35	30	10	20	23	60	60
Zn	200	149	148	170	43	44	68	42	57
Ba	550	465	429	460	400	390	277	110	80
Hf		10.2	9.5				9.7		
Ta		2.27	2.24				2.3		
Th	3	4.2	3.4	4	19	31	29.5	39	39
U	1	0.75	0.77	1	5	4	2.9	9	5
La	47	46	44	42	73	118	98.6	7	7
Ce	114	103	94	93	150	203	184	29	32
Nd	47	60	55	58	55	76	75.3	15	15
Sm	12.9	13.1	11.3	11.4	8.26	14	12.66	6.92	7.61
Eu	3.35	4.03	3.96	3.16	1.17	0.77	0.66	0.12	0.22
Tb	1.9	1.99	1.74	1.7	0.8	1.9	1.95	2.4	2.1
Yb	5.46	5	5.1	4.84	3.52	6.69	5.6	9.71	10.9
Lu	0.8	0.81	0.76	0.71	0.61	0.95	0.87	1.61	1.77

Appendix Table A-1 (continued)

A-5

Sample	272a2-1	77a1	77a2	120b	MC-120b*	125b	128a1	140a1	MC-140a1
Group	LMPF	LMPF	LMPF	LMPF	LMPF	LMPF	LMPF	LMPF	LMPF
Chapter	1,2,3	1,2,3	1,2,3	1	2,3	1,2,3	1,2,3	1	2,3
SiO2	71.1	74.6	74.7	73.2	74.32	72.5	75.2	74.1	74.97
TiO2	0.35	0.24	0.24	0.25	0.26	0.3	0.22	0.27	0.27
Al2O3	14.2	12.9	12.6	13	13.01	13.6	12.8	13.2	13.23
					1.7				1.69
Fe2O3	1.85	0.6	1.28	1.26		0.52	0.77	1.68	
FeO	0.3	0.7	0.1	0.2		0.7	0.6	0.05	
MnO	0.05	0.03	0.02	0.02	0.04	0.04	0.03	0.03	0.03
MgO	0.35	0.26	0.2	0.21	0.3	0.31	0.23	0.49	0.39
CaO	1.53	0.16	0.38	0.38	0.42	0.44	0.56	0.52	0.17
Na2O	3.55	2.83	3	2.93	2.81	2.83	3.12	2.45	1.98
K2O	5.23	5.68	5.55	5.72	5.79	6.24	5.08	6.4	6.39
P2O5	0.37	0.04	0.04	0.05	0.04	0.06	0.04	0.06	0.04
H2O	0.6	0.8	0.8	0.6		1	0.7	0.7	
LOI	0.85	1.08	1	1.16		0.93	1.08	0.93	
Total	99.18	99.04	99.11	97.82	98.77	98.54	99.35	99.95	99.55
Mg#	0.48	0.22	0.61	0.45		0.26	0.23	0.88	
Q	26.2	35.8	35	33.3		30.7	36.1	33.7	
Ab	30.9	33.6	32.8	33.8		36.9	30	37.8	
Or	30	24	25.4	24.8		24	26.4	20.7	
An	7.1	0.5	1.6	1.6		1.8	2.5	2.2	
C	0.1	1.9	1.3	1.4		1.5	1.3	1.4	
Di	0	0	0	0		0	0	0	
Hy	2.2	1.1	0.5	0.5		1.2	0.7	1.2	
Mt	1.1	0.9	0	0		0.8	1.1	0	
Il	0.7	0.5	0.3	0.5		0.6	0.4	0.2	
Hem	0	0	1.3	1.3		0	0	1.7	
Ap	0.2	0.1	0.1	0.1		0.1	0.1	0.1	
Ru	0	0	0.1	0		0	0	0.2	
Li	18	32	33	27		32	24	19	
Sc	8	6	6	6	5.8	6	6	6	5.25
V	0	10	12	14	0	18	0	0	14
Cr	10	6	0	4	96.5	7	10	10	5
Ni	7	3	2	4	16	2	8	5	0
Rb	200	320	230	220	213	230	210	230	217
Sr	140	80	70	50	68.5	140	50	70	76
Y	40	40	40	10	43.5	30	50	40	49
Zr	330	180	180	210	211	240	170	240	233
Nb	10	20	20	20	14	10	20	10	11
Zn	74	49	46	43	41.5	74	63	45	44
Ba	680	300	310	410	291.5	610	260	470	399
Hf					6.5				6.6
Ta					1.35				1.4
Th	19	22	22	21	21.2	20	21	22	19.2
U	4	5	5	5	3.9	5	5	5	4
La	85	80	90	82	87	80	83	91	75.6
Ce	160	167	167	152	151	152	170	180	161.8
Nd	0	55	65	62	67	60	0	0	64.9
Sm	11	9.93	10.9	10.5	10.5	9.48	10.4	11.7	10.33
Eu	0	0.86	0.7	0.87	1.16	1.1	0	0	1.2
Tb	0	1	1.2	1.2	1.27	0.9	0	0	1.3
Yb	0	3.97	3.65	4.12	3.7	3.62	0	0	3.4
Lu	1	0.58	0.63	0.63	0.54	0.56	0.61	0.7	0.56

3

OF/DE

3

PM-1 3 1/2" x 4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

Appendix Table A-1 (continued)

Sample	140a2-1	140a3	140b	140d	288-1	299	300a2	MC-300a	A-6
Group	LMPF	LMPF	LMPF	LMPF	LMPF	LMPF	LMPF	LMPF	LMPF
Chapter	1,2,3	1,2,3	1,2,3	1,2,3	1,2,3	1,2,3	1	2,3	1,2,3
SiO2	74.9	74.4	74.8	74.7	72.6	74.7	74.8	75.72	74.7
TiO2	0.25	0.24	0.25	0.24	0.28	0.22	0.24	0.23	0.21
Al2O3	12.8	13.2	12.7	12.8	13	12.9	12.8	12.75	12.7
Fe2O3(T)								1.51	
Fe2O3	1.61	1.18	1.4	1.44	1.21	0.64	0.58		0.85
FeO	0.1	0.2	0.2	0.2	1.8	0.3	0.7		0.4
MnO	0.03	0.02	0.03	0.03	0.08	0.04	0.04	0.05	0.02
MgO	0.29	0.36	0.5	0.46	0.59	0.44	0.29	0.37	0.43
CaO	0.48	0.65	0.96	0.74	0.57	0.39	0.15	0.17	0.41
Na2O	2.62	2.65	2.32	2.16	2.36	3.47	2.37	2.3	3.03
K2O	5.43	5.36	5.14	5.99	5.47	5.28	6.21	6.21	5.74
P2O5	0.05	0.05	0.05	0.06	0.05	0.05	0.04	0.03	0.04
H2O	0.7	0.9	1	0.8	1.1	0.6	0.7		0.6
LOI	0.93	1.08	1.47	1.23	1.08	0.85	0.93		1.08
Total	99.26	99.21	99.35	99.6	99.11	99.53	98.92	99.49	99.13
Mg#	0.69	0.58	0.66	0.64	0.2	0.3	0.24		0.45
Q	37.6	36.7	39	37.2	35.1	32.7	36.4		33.7
Ab	32.1	31.7	30.4	35.4	32.3	31.2	36.7		33.9
Or	22.2	22.4	19.6	18.3	20	29.4	20		25.6
An	2.1	2.9	4.4	3.2	2.5	1.6	0.5		1.8
C	1.9	2	1.7	1.6	2.3	0.9	2		0.9
Di	0	0	0	0	0		0		0
Hy	0.7	0.9	1.3	1.2	3.5	1.8	1.2		1.1
Mt	0	0	0	0.1	1.8	0.9	0.8		0.8
Il	0.3	0.5	0.5	0.5	0.5	0.4	0.5		0.4
Hem	1.6	1.2	1.4	1.4	0	0	0		0.3
Ap	0.1	0.1	0.1	0.1	0.1	0.1	0.1		0.1
Ru	0.1	0	0	0	0	0	0		0
Li	18	23	23	21	24	29	27		26
Sc	4	6	6	6	9	7	6		6
V	0	0	0	0	0	0	12	4	0
Cr	10	10	10	10	20	10	3	0	10
Ni	4	4	4	4	6	4	4	0	4
Rb	220	200	200	220	280	220	280	282	240
Sr	60	70	70	80	90	70	80	70	90
Y	30	40	30	50	50	20	40	42	10
Zr	210	230	240	200	200	200	170	196	180
Nb	10	10	10	5	20	20	30	9	20
Zn	43	46	36	30	260	57	160	214	47
Ba	440	400	490	450	370	240	320	349	316
Hf									
Ta									
Th	19	22	22	22	23	23	24		23
U	5	4	7	5	7	4	6		4
La	78	82	91	80	82	87	81		77
Ce	153	159	190	170	168	170	155		150
Nd	0	0	0	0	0	0	56		0
Sm	9.1	10.1	11	10	10.4	10.8	9.36		8.6
Eu	0	0	0	0	0	0	0.73		0
Tb	0	0	0	0	0	0	1		0
Yb	0	0	0	0	0	0	3.43		0
Lu	0.52	0.63	0.6	0.7	0.77	0.7	0.61		0.5

Appendix Table A-1 (continued)

Sample	306d1	82-19	158b3	MC-158b	233a	233b	233c	3061	A-7
Group	I.MPF	I.MPF	SF	SF	SF	SF	SF	SF	SF
Chapter	1,2,3		1	2,3	1,2,3	1,2,3	1,2,3	1,2,3	1,2,3
SiO ₂	74.6	75.44	77.1	76.26	76.4	76.2	77.1	75.8	75.8
TiO ₂	0.21	0.2	0.13	0.1	0.1	0.1	0.09	0.18	0.13
Al ₂ O ₃	12.8	12.47	12.2	11.96	12.1	11.8	12	12.1	12.2
Fe ₂ O ₃ (T)		1.39		1.18					
Fe ₂ O ₃	0.72		0.82		0.82	0.79	0.74	0.48	1.03
FeO	0.5		0.3		0.3	0.4	0.3	0.5	0.3
MnO	0.02	0.06	0.03	0.04	0.02	0.03	0.1	0.02	0.03
MgO	0.45	0.5	0.23	0.3	0.33	0.37	0.34	0.17	0.18
CaO	0.3	0.4	0.34	0.33	0.23	0.93	0.15	0.48	0.43
Na ₂ O	3.15	1.79	2.71	2.45	2.99	3.57	3.02	2.27	3.17
K ₂ O	5.6	6.43	5.82	5.66	5.54	4.49	5.19	6.11	5.1
P ₂ O ₅	0.04	0.01	0.02	0	0.02	0.02	0.02	0.03	0.03
H ₂ O	0.7		0.6		0.6	0.6	0.5	0.09	0.7
LOI	0.85		0.77		0.93	1.31	0.85	0.93	0.7
Total	99.09	98.82	100.3	98.37	99.45	99.3	99.47	98.23	99.1
Mg#	0.41		0.37		0.46	0.42	0.47	0.21	0.32
Q	33.6		38.1		36.9	36.1	38.9	37.9	36.7
Ab	33.1		34.4		32.7	26.5	30.7	36.1	30.1
Or	26.7		22.9		25.3	30.2	25.6	19.2	26.8
An	1.2		1.6		1	2.9	0.6	2.2	1.9
C	1.1		0.9		0.8	0	1.2	1	0.8
Di	0		0		0	1.2	0	0	0
H ₂	1.1		0.6		0.8	0.4	0.9	0.7	0.5
M ₂	1		0.7		0.7	1.1	0.8	0.7	0.7
Il	0.4		0.3		0.2	0.2	0.2	0.3	0.3
Hem	0		0.4		0.3	0	0.2	0	0.6
Ap	0.1		0.1		0.1	0.1	0.1	0.1	0.1
Ru	0		0		0	0	0	0	0
Li	26		17		12	13	10	29	20
Sc	6	5.1	4	4.2	5	5	4	5	5
V	0	0	6	0	0	0	0	6	0
Cr	10	0	3	0	10	10	10	8	10
Ni	3	1	7	0	3	3	3	2	4
Rb	240	374	280	260	260	210	240	220	250
Sr	70	61	50	46	5	20	10	40	30
Y	40	64	30	0	40	70	50	30	60
Zr	180	179	110	125	120	140	100	210	150
Nb	10	11	30	14	30	30	10	20	10
Zn	62	62	30	37	42	43	39	46	62
Ba	290	265	60	65	30	60	50	230	90
Hf		5.4		5					
Ta		1.2		1.9					
Th	24	23	33	29.7	34	31	34	22	26
U	5	4.6	7	5.6	4	5	5	4	5
La	87	100	64	54.4	65	74	22	76	66
Ce	170		128	131.7	150	160	65	152	143
Nd	0		47	49.8	0	0	0	34	0
Sm	10.3		10.4	9.67	10.9	12	4.5	9.1	10.7
Eu	0	<1	0.24	0.07	0	0	0	0.36	0
Tb	0	2.4	1.1	1.4	0	0	0	0.9	0
Yb	0	9.2	4.88	4.5	0	0	0	3.45	0
Lu	0.6	1.2	0.79	0.69	0.7	0.9	0.6	0.57	0.82

Appendix Table A-1 (continued)

Sample	109	158c	158d1	175-1	204	218c	229a2	229b	A-8
Group	SF	SF	SF	SF	SF	SF	SF	SF	SF
Center	1,2,3	1,2,3	1,2,3	1,2,3	1,2,3	1,2,3	1,2,3	1,2,3	1,2,3
SiO ₂	75.2	76.1	76.8	75.3	75.1	76.3	77.6	76.3	75.7
TiO ₂	0.15	0.11	0.11	0.14	0.16	0.09	0.12	0.09	0.11
Al ₂ O ₃	12.8	12	12.2	12.5	12.2	12.4	12.4	11.6	11.9
Fe ₂ O ₃ (T)	1.15	0.94	1.05	1.22	0.91	1.04	1.05	0.81	0.88
Fe ₂ O ₃	0.5	0.2	0.1	0.6	0.7	0.1	0.1	0.2	0.3
MnO	0.03	0.01	0.03	0.06	0.06	0.01	0.03	0.02	0.02
MgO	0.22	0.36	0.17	0.36	0.32	0.13	0.2	0.29	0.34
CaO	0.3	0.2	0.17	0.79	1	0.24	0.32	0.28	0.47
Na ₂ O	3.19	2.94	3.09	3.31	2.77	3.6	2.8	2.94	3.15
K ₂ O	5.24	5.27	5.02	4.64	5.17	4.89	5.1	5.51	5.31
P ₂ O ₅	0.03	0.03	0.02	0.03	0.03	0.02	0.02	0.02	0.02
H ₂ O	0.8	0.7	0.7	0.9	0.7	0.5	0.7	0.6	0.6
LOI	1.08	1.08	0.93	0.93	0.93	0.93	1	0.93	0.7
Total	99.61	98.86	99.46	99.85	99.12	99.32	100.44	98.66	98.8
Mg#	0.25	0.58	0.57	0.32	0.26	0.5	0.61	0.53	0.47
Q	35.7	38	39.1	36.1	36.5	36	40.9	37.1	35.6
Ab	31	31.1	29.7	27.4	30.6	28.9	30.1	32.6	31.4
Or	27	24.9	26.2	28	23.4	30.5	23.7	24.9	26.7
An	1.3	0.8	0.7	3.7	4.8	1.1	1.5	1.3	2.2
C	1.4	1.2	1.4	0.7	0.3	0.8	1.7	0.3	0.2
Di	0	0	0	0	0	0	0	0	0
Hy	0.6	0.9	0.4	0.9	1.2	0.3	0.5	0.7	0.9
Mt	1.3	0.4	0.1	1.7	1.3	0.1	0.1	0.5	0.7
Il	0.3	0.2	0.2	0.3	0.3	0.2	0.2	0.2	0.2
Hem	0.3	0.7	1	0	0	1	1	0.5	0.4
Ap	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ru	0	0	0	0	0	0	0	0	0
Li	18	19	15	29	38	26	14	18	21
Sc	6	7	6	8	6	6	6	6	5
V	0	0	0	0	0	0	0	0	0
Cr	10	10	10	10	10	10	0	10	10
Ni	7	4	3	7	6	3	3	4	3
Rb	180	320	280	290	180	390	430	320	240
Sr	40	20	40	30	20	10	30	10	5
Y	60	50	60	100	50	60	70	40	40
Zr	230	140	150	160	190	130	140	120	130
Nb	20	30	20	40	40	20	40	40	30
Zn	64	35	45	74	62	24	35	44	44
Ba	200	80	110	120	190	100	110	30	20
Hf									
Ta									
Th	24	35	32	31	22	40	33	35	28
U	4	8	8	6	4	6	8	5	5
La	109	23	34	116	95	38	33	49	67
Ce	192	55	90	162	180	84	85	100	126
Nd	0	0	0	0	0	0	26	0	48
Sm	14.8	5.8	6.7	20.7	12.3	8.1	6.1	7.9	9.7
Eu	0	0	0	0	0	0	0.3	0	0.16
Tb	0	0	0	0	0	0	1.4	0	1.3
Yb	0	0	0	0	0	0	5.9	0	4.87
Lu	0.76	0.9	0.86	1.3	0.8	0.87	1.1	0.8	0.76

Appendix Table A-1 (continued)

A-9

Sample	249a	256	21a1	28a	101d	MC-101d	MC-196	102	187
Group	SF	SF	BRR	BRR	BRR	BRR	BRR	BRR	BRR
Chapter	1,2,3	1,2,3	1	1	1,2	Chapter	2	1	1
SiO ₂	75.7	75.6	75.7	72.8	71.9	70.9	76.26	73.5	75.3
TiO ₂	0.11	0.13	0.32	0.39	0.4	0.4	0.12	0.26	0.17
Al ₂ O ₃	12.3	12.3	12	13.3	13.3	13.1	11.64	13.2	12.7
Fe ₂ O ₃ (T)						2.73	1.59		
Fe ₂ O ₃	1.02	0.88	1.45	2.49	1.79			1.9	1.19
FeO	0.3	0.5	0.05	0.1	0.8			0.05	0.4
MnO	0.03	0.03	0.01	0.02	0.04	0.04	0.02	0.04	0.04
MgO	0.28	0.16	0.35	0.29	0.42	0.29	0.24	0.27	0.22
CaO	0.26	0.22	0.32	0.29	0.38	0.32	0.04	0.26	0.2
Na ₂ O	3.19	3.33	3.35	3.06	3.11	2.82	0.16	2.83	2.62
K ₂ O	4.98	5.22	4.6	5.37	6	5.92	8.84	6.17	5.78
P ₂ O ₅	0.03	0.04	0.08	0.09	0.1	0.1	0	0.06	0.03
H ₂ O	0.7	0.4	0.8	0.9	1			0.9	0.8
LOI	1.16	0.62	1.16	1.39	1.23			1.08	1
Total	98.9	98.81	99.03	99.1	99.24	96.79	99.01	99.44	99.45
Mg#	0.42	0.2	0.84	0.69	0.29			0.81	0.3
Q	37.2	35.6	37.6		29.7			32.1	37.3
Ab	29.4	30.9	27.2	31.7	35.5			36.5	34.2
Or	27	28.2	28.4	25.9	26.3			24	22.2
An	1.1	0.8	1.1	0.9	1.2			0.9	0.8
C	1.3	0.9	1.1	2.1	1.2			1.5	1.8
Di	0	0	0	0	0			0	0
H _y	0.7	0.4	0.9	2.3	1.1			1.9	0.6
Mt	0.8	1.3	0	1.3	1.6			0.9	0.9
Il	0.2	0.3	0.1	0.7	0.8			0.5	0.3
Hem	0.5	0	1.5	0	0.7			0	0.6
Ap	0.1	0.1	0.2	0.2	0.2			0.1	0.1
Ru	0	0	0.3	0	0			0	0
Li	27	32	34	18	57			21	11
Sc	6	5	4	6	6	6.61	5.44	4	5
V	0	0	0	0	0	0	63	0	0
Cr	10	10	20	10	10	3	3	5	5
Ni	4	3	7	3	5	0	0	3	3
Rb	300	220	150	240	260	252	350	300	190
Sr	20	70	300	190	220	176	21	100	60
Y	50	20	60	60	30	45	0	40	60
Zr	140	140	300	360	350	341	187	280	280
Nb	20	20	20	30	30	19	18	5	20
Zn	50	56	23	75	70	52	26	60	67
Ba	100	90	620	590	650	551	139	410	190
Hf						9.4	6.3		
Ta						1.9	1.9		
Th	33	28	24	25	24	22.2	25.2	30	21
U	4	4	14	4	6	5	4.2	9	3
La	44	64	103	31	54	48.6	47.6	80	113
Ce	94	156	120	123	110	116.5	97.1	156	184
Nd	0	0	0	0	0	43.7	45	0	0
Sm	7.5	9.2	12.6	4.6	7.6	7.7	7.51	8.8	14.2
Eu	0	0	0	0	0	0.98	0.36	0	0
Tb	0	0	0	0	0	1.15	1.2	0	0
Yb	0	0	0	0	0	3.8	4.8	0	0
Lu	0.83	0.75	1.1	0.94	0.7	0.6	0.77	0.68	0.92

Appendix Table A-1 (continued)

A-10

Sample Group	198 BRR	129c BSMF	51-3 BSMF	52 BSMF	64a1 BSMF	64a2-1 BSMF	65a BSMF	MC-065a BSMF	49a1 BSMF
	1	1	1	1	1	1	1	2	1
SiO2	74.7	75.7	77.2	74.1	76.4	73.8	77.6	78.76	80
TiO2	0.15	0.23	0.25	0.25	0.09	0.25	0.14	0.12	0.18
Al2O3	12.2	12.7	11.6	12.2	11.6	12.7	10.8	10.66	11
Fe2O3(T)								1.68	
Fe2O3	0.71	0.84	1.38	2.38	1.53	2.35	1.58		0.93
FeO	0.9	0.3	0.05	0.1	0.1	0.1	0.1		0.05
MnO	0.05	0.04	0.02	0.06	0.02	0.02	0.02	0.02	0.03
MgO	0.42	0.21	0.44	0.59	0.53	0.44	0.23	0.27	0.32
CaO	0.32	0.61	0.35	0.26	0.14	0.22	0.39	0.22	0.52
Na2O	2.45	3.4	3.26	2.21	2.56	2.28	2.94	2.59	6.32
K2O	5.84	5.21	3.6	5.9	5.16	6.02	4.57	4.66	0.38
P2O5	0.03	0.04	0.05	0.05	0.02	0.04	0.04	0	0.03
H2O	0.9	0.4	0.9	1.1	0.9	1.1	0.6		0.3
LOI	1.23	0.93	1.47	1.47	1.16	1.54	1		0.54
Total	98.67	99.68	99.1	99.2	99.05	99.32	99.01	99.12	100.06
Mg#	0.27	0.35	0.87	0.82	0.8	0.77	0.64		0.83
Q	36.5	34.5	43.2	36.6	40.7	35.7	41.9		40.7
Ab	34.5	30.8	21.3	34.9	30.5	35.6	27		2.3
Or	20.7	28.8	27.6	18.7	21.7	19.3	24.9		53.5
An	1.4	2.8	1.4	1	0.6	0.8	1.7		0.5
C	1.3	0.5	1.8	1.8	1.6	2.1	0.4		0
Di	0	0	0	0	0	0	0		1.2
Hy	2	0.5	1.1	3.2	1.3	2.8	0.6		0.2
Mt	1	0.4	0	1.2	0.1	1.2	0		0
Il	0.3	0.4	0.2	0.5	0.2	0.5	0.3		0.2
Hem	0	0.5	1.4	0	1.4	0	1.6		0.9
Ap	0.1	0.1	0.1	0.1	0.1	0.1	0.1		0.1
Ru	0	0	0.2	0	0	0	0		0
Li	20	22	22	34	51	11	11		20
Sc	6	5	4	4	2	4	4	3.47	5
V	0	8	24	0	0	0	0	7	0
Cr	10	5	7	10	20	10	10	0	20
Ni	3	2	9	4	4	4	4	0	4
Rb	220	260	150	210	300	240	170	149	20
Sr	20	20	480	160	100	100	380	289	230
Y	60	40	70	40	70	10	50	56	80
Zr	260	180	280	300	170	310	220	217	280
Nb	10	20	30	30	40	30	40	23	20
Zn	86	49	40	65	67	84	56	96	26
Ba	170	280	1280	930	130	450	440	316	120
Hf								7.4	
Ta								2.8	
Th	21	23	31	23	39	27	33	30.6	20
U	3	5	12	8	5	4	8	5.6	8
La	128	83	91	49	19	57	45	39.4	63
Ce	200	162	168	77	33	85	118	110.5	150
Nd	0	66	66	0	0	0	0	26.1	0
Sm	15.8	9.98	13.3	5.9	3.9	5.8	5.7	5.01	10.9
Eu	0	0.37	0.85	0	0	0	0	0.2	0
Tb	0	1.3	2	0	0	0	0	1.1	0
Yb	0	4.06	6.88	0	0	0	0	5.5	0
Lu	0.9	0.67	1.15	0.8	1.2	0.75	1.03	0.89	1.1

Appendix Table A-1 (continued)

A-11

sample	65c	MC-065c	50-2	33a2	82c-3	MC-82c	121a	121c	193b
Group	BSMF	BSMF	BSMF	MBM	MBM	MBM	MBM	MBM	MBM
Chapter	1	2	1	1,2,3	1,2,3	2,3	1,2,3	1,2,3	1,2,3
SiO ₂	72.4	72.83	79.7	74.4	68.7	69.41	69.9	68	66.4
TiO ₂	0.15	0.16	0.11	0.23	0.53	0.51	0.43	0.54	0.77
Al ₂ O ₃	13.6	13.35	11.1	12.9	15.9	14.2	14	14.7	13.8
Fe ₂ O ₃ (T)		2.21				2.79			
Fe ₂ O ₃	2.12		1.07	1.5	2.61		1.52	1.6	2.57
FeO	0.1		0.1	0.05	0.05		0.8	1.3	2.3
MnO	0.05	0.05	0.02	0.02	0.02	0.08	0.07	0.06	0.14
MgO	0.58	0.67	0.38	0.26	0.59	0.63	0.64	0.92	0.86
CaO	0.22	0.19	0.27	0.19	0.69	0.69	1.59	55	0.84
Na ₂ O	2.05	1.81	2.23	2.6	3.05	2.86	3.63	3.78	1.44
K ₂ O	6.39	6.38	3.45	5.97	5.81	5.75	4.98	5.82	7.56
P ₂ O ₅	0.03	0	0.02	0.03	0.13	0.1	0.11	0.15	0.24
H ₂ O	1.3		1.2	0.8	1.3		0.8	1.2	1.5
LOI	1.7		1.7	1.31	1.85		1.31	1.62	2
Total	98.99	97.81	99.65	98.95	99.38	98.91	98.47	98.62	98.42
Mg#	0.82		0.75	0.8	0.9		0.38	0.35	0.22
Q	34		52.4	35.7	26.1		25.7	21.5	25.2
Ab	37.8		20.4	35.3	34.3		29.4	34.4	44.7
Or	17.4		18.9	22	25.8		30.7	32	12.2
An	0.9		1.2	0.8	2.6		7.2	1.8	2.6
C	3		3.3	1.9	3.7		0	1.5	2.3
Di	0		0	0	0		0	0	0
Hly	3.1		1	0.7	2.8		1.6	2.6	5.4
Mt	1.1		0.1	0	1.3		1.6	2.3	2.5
Il	0.3		0.2	0.2	1		0.8	1	1.5
Hem	0		1	1.5	0		0.4	0	0
Ap	0.1		0.1	0.1	0.3		0.3	0.4	0.6
Ru	0		0	0.2	0		0	0	0
La	22		24	0	17		29	35	30
Sc	4		3	6	9	8.37	7	9	16
V	0	0	8	12	20	16	0	0	30
Cr	10	1	0	4	3	7	10	10	0
Ni	4	0	4	2	4	0	7	7	4
Rb	290	280	200	230	280	254	150	220	290
Sr	220	171	290	50	130	116	190	140	50
Y	30	66	130	10	60	59	10	50	40
Zr	280	289	120	350	480	464	390	460	550
Nb	30	24	50	30	20	12	10	10	20
Zn	94	81	45	44	39	59	55	73	96
Ba	460	368	480	460	1040	897	1120	1210	910
Hf						11.6			
Ta						1.5			
Th	38		32	18	17	17	15	17	14
U	6		5	2	4	3.3	4	4	4
La	73		61	44	106	91.8	55	62	83
Ce	163		93	108	144	137.3	94	120	128
Nd	0		54	28	59	63.1	0	0	70
Sm	5.9		12.8	5.45	10.5	9.73	7	8.1	12.8
Eu	0		0.14	0.6	1.85	1.85	0	0	2.51
Tb	0		2.4	0.6	1.2	1.31	0	0	1.8
Yb	0		9.5	2.69	4.5	3.9	0	0	5.62
Lu	1.1		1.39	0.45	0.69	0.62	0.6	0.7	0.85

Appendix Table A-1 (continued)

Sample	MC-193a	246b	270	289	301	29a2	MC-74b*	62a	A-12 74a2
Group	MBM	MBM	MBM	MBM	MBM	MBM	MBM	MBM	MBM
Chapter	2,3	1,2,3	1,2,3	1,2,3	1,2,3	1,2,3	2,3	1,2,3	1
SiO2	77.3	69.7	68.6	67.8	66.7	64.6	67.31	67.4	69.5
TiO2	0.16	0.51	0.46	0.51	0.67	0.78	0.57	0.71	0.47
Al2O3	11.64	15.5	14.7	14.6	15.6	14.1	14.2	14	14
Fe2O3(T)	1.48						3.41		
Fe2O3		1.41	1.9	1.33	1.95	2.08		2.57	1.58
FeO		0.1	0.7	1.9	1.8	3.4		2.1	1.1
MnO	0.02	0.01	0.06	0.19	0.11	0.11	0.08	0.11	0.06
MgO	0.31	0.14	0.67	0.85	0.73	0.95	0.76	0.65	0.72
CaO	0.08	0.34	2.23	0.72	1.35	2.73	1.71	1.74	0.92
Na2O	0.58	3.86	3.79	2.5	4.08	3.39	2.47	2.96	3.14
K2O	4.41	5.3	5.3	6.84	5.06	4.17	6.18	4.93	5.82
P2O5	0.02	0.11	0.12	0.13	0.19	0.26	0.16	0.21	0.12
H2O		1.1	0.8	1.3	1.1	1.4		1.8	1
LOI		1.7	1.08	1.54	1.39	2.31		2.39	1.39
Total	100.12	98.08	99.33	98.67	99.34	97.97	97.04	99.18	98.43
Mg#		0.52	0.43	0.26	0.24	0.18		0.19	0.34
Q		26.3	21.4	23.8	19.8	21		25.8	26.2
Ab		31.3	31.3	40.4	29.9	24.6		29.1	34.4
Or		32.7	32.1	21.2	34.5	28.7		25.1	26.6
An		1	7.5	2.7	5.5	10.9		7.3	3.8
C		3.1	0	2.1	1.4	0		1.1	1.2
Di		0	2.2	0	0	0.8		0	0
Hy		0.4	0.7	4	2.6	5.4		4.7	1.8
Mt		0	1.1	1.9	2.8	3		2.4	2.3
Il		0.2	0.9	1	1.3	1.5		1.4	0.9
Hem		1.4	1.1	0	0	0		0	0
Ap		0.3	0.3	0.3	0.4	0.6		0.5	0.3
Ru		0.4	0	0	0	0		0	0
Li		19	25	49	39	110		57	62
Sc		9	9	9	11	16		14	8
V	2	34	0	0	0	0	0	0	0
Cr	9	4	10	10	10	10	27	10	10
Ni	0	3	5	5	6	6	16.5	11	7
Rb	286	150	170	320	170	140	318	140	240
Sr	19	180	250	160	220	200	106.5	190	100
Y	39	50	30	50	40	80	42.5	70	50
Zr	232	460	480	520	500	520	38.5	540	340
Nb	14	40	30	5	5	30	14.5	20	30
Zn	42	54	66	260	110	120	53	130	69
Ba	278	1400	1210	1680	1330	780	829.5	970	820
Hf							9.5		
Ta							1.21		
Th		16	16	16	16	13	14.7	13	16
U		7	4	4	4	4	2.4	4	5
La		37	69	58	76	69	70	75	73
Ce		77	140	130	144	140	126	130	130
Nd		33	0	0	0	0	55	0	0
Sm		6.58	9.8	8.4	10.7	12.5	9	11	8.7
Eu		1.52	0	0	0	0	2.18	0	0
Tb		0.8	0	0	0	0	1.09	0	0
Yb		3.54	0	0	0	0	3.6	0	0
Lu		0.64	0.6	0.6	0.68	0.86	0.55	1	0.8

Appendix Table A-1 (continued)

A-13

Sample	MC-74a2	110a1-3	110a2-1	430-1	MC-314a*	316	500	123a	MC-123a*
Group	MBM	MBM	MBM	MBM	MPP	MPP	THG	RD	RD
Chapter	2,3	1,2,3	1,2,3	1,2,3	2,3	1,2,3	1	1	2
SiO2	71.02	65.8	67.2	66.1	75.67	74.7	75.3	63.8	64.03
TiO2	0.49	0.8	0.63	0.6	0.03	0.02	0.1	1.01	1.02
Al2O3	14.26	14.3	13.9	14.8	12.76	12	12.5	14.3	14.06
Fe2O3(T)	2.88				5.78				5.64
Fe2O3		2.68	2.46	1.76		0.7	1.07	3.31	
FeO		2.8	2	1.4		1.8	0.2	2.1	
MnO	0.07	0.09	0.09	0.07	0.19	0.14	0.03	0.1	0.1
MgO	0.66	0.76	0.89	0.78	0.16	0.44	0.1	1.65	1.76
CaO	0.87	2.48	1.8	1.94	0.21	0.65	0.45	2.44	2.37
Na2O	2.82	3.78	3.82	3.8	0	1.99	3.11	3.58	3.51
K2O	5.73	4.62	4.5	5.06	3.18	5.29	5.14	4.88	4.95
P2O5	0.13	0.24	0.17	0.16	0	0.01	0.02	0.24	0.25
H2O		0.9	1.1	1.2		1.2	0.7	1.6	
LOI		1.16	1.31	2		1.54	1.16	1.54	
Total	99.1	99.25	98.56	97.67	98.23	98.94	98.72	99.01	97.88
Mg#		0.17	0.26	0.3		0.16	0.28	0.38	
Q		19.6	21.8	19.7		39.5	36.5	17	
Ab		27.3	26.6	29.9		31.3	30.4	28.8	
Or		32	32.3	32.2		16.8	26.3	30.3	
An		8.4	7.5	8.4		3.2	2.1	8.5	
C		0	0	0		1.8	1.1	0	
Di		2	0.3	0.2		0	0	1.6	
Hf		3.6	5.1	2.1		4.1	0.3	5	
Mt		3.3	2.3	2.6		1	0.5	3.6	
Il		1.5	1.2	1.1		0	0.2	1.9	
Hem		0	0	0		0	0.8	0	
Ap		0.6	0.4	0.4		0	0.1	0.6	
Ru		0	0	0		0	0	0	
Li		38	29	32		58	14	56	
Sc		17	13	9	3.8	3	4	13	14.99
V	12	40	0	48	0	0	4	0	73
Cr	3	8	10	10	23.5	10	20	20	29
Ni	0	2	10	7	19.5	3	4	15	1.5
Rb	238	150	130	190	592	650	410	210	213.5
Sr	85	210	180	200	0	5	10	380	321
Y	49	40	70	60	83	190	110	60	55
Zr	348	580	500	410	134	120	150	270	276
Nb	11	30	20	30	99	90	70	20	10.5
Zn	73	100	97	95	1127	160	75	97	86.5
Ba	712	800	680	1100	80.5	120	190	710	561
Hf	8.6				10				
Ta	1.5				11.2				
Th	16	13	16	15	59.7	54	62	17	
U	4.1	3	3	5	12.9	30	24	5	
La	65.8	72	67	70	27	45	47	53	
Ce	145.8	136	120	138	59	120	76	101	
Nd	59.7	42	0	56	27	0	28	0	
Sm	9.44	9.38	9.2	9.88	6.8	14.3	6.6	9	
Eu	1.75	3.11	0	2.21	0.02	0	0.18	0	
Tb	1.18	1.8	0	1.1	1.69	0	2.5	0	
Yb	3.7	4.85	0	3.8	18.2	0	10.6	0	
Lu	0.59	0.87	0.7	0.59	2.7	3.1	1.92	0.7	

Appendix Table A-1 (continued)

Sample	123b	146a	LM-14*
Group	RD	RD	RD
Chapter	1	1	2
SiO ₂	58.7	68.9	71.5
TiO ₂	1.62	0.64	0.53
Al ₂ O ₃	14.2	13.6	13.48
Fe ₂ O ₃ (T)			3.43
Fe ₂ O ₃	2.38	2.7	
FeO	5.4	1	
MnO	0.2	0.06	0.07
MgO	3.54	0.8	0.84
CaO	4.5	1.09	0.79
Na ₂ O	2.72	3.44	4.32
K ₂ O	3.45	4.6	3.97
P ₂ O ₅	0.32	0.17	0.15
H ₂ O	2	1.7	
LOI	2.31	1.77	
Total	99.03	98.7	98.87
Mg#	0.34	0.38	
Q	13.9	27.2	
Ab	20.4	27.2	
Or	23	29.1	
An	16.4	4.3	
C	0	1.4	
Di	3.2	0	
Hy	12.9	4.2	
Mt	3.5	1.8	
Il	3.1	1.2	
Hem	0	0	
Ap	0.7	0.4	
Ru	0	0	
Li	160	49	
Sc	25	10	7
V	200	0	0
Cr	48	10	86.5
Ni	20	7	18
Rb	210	210	129.5
Sr	290	330	64
Y	30	40	58.5
Zr	290	340	271.5
Nb	20	10	15.5
Zn	74	69	50
Ba	600	570	363
Hf			7.1
Ta			1.52
Th	13	27	23.1
U	5	7	5.4
La	44	65	59
Ce	99	139	107
Nd	44	0	47
Sm	9.39	10	9
Eu	2.17	0	1.4
Tb	1.5	0	1.35
Yb	5.03	0	4.4
Lu	0.76	0.88	0.66

END

14-12-93

FIN