Magmatic evolution and subsolidus alteration of annite in nepheline syenites, Mont Saint-Hilaire, Québec

by

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Abstract

Nepheline syenite represents the highly differentiated product of fractional crystallization in the Poudrette quarry at Mont Saint-Hilaire, Quebec. It also records a significant subsolidus overprint due to circulation of post-magmatic fluids. Annite, the ferrous-irondominant member of the biotite series, represents up to 20% of the typical nepheline syenites.

Hand samples cover the complete range of freshness, from unaltered to hydrothermally modified rocks. Identification of minerals and estimation of their abundances and compositions were obtained with optical microscopy and electron-microprobe analysis. I also used a combined approach of X-ray diffraction and high-resolution transmission electron microscopy.

With respect to annite composition, Fe/(Fe + Mg) varies from 0.74 (porphyritic nepheline syenite) to 0.98 (poikilitic nepheline syenite). Concerning the habit of annite, the melt composition controls the order of crystallization, which then in turn controls whether the annite is bladed and skeletal or oikocrystic. The rock from the Poudrette dyke is a hypersolvus nepheline syenite in which the bladed annite was a liquidus phase; therefore, the order of crystallization was "normal" (mafic mineral first), whereas in poikilitic nepheline syenite, this order was reverse. The proportion of Ti decreases with Fe/(Fe + Mg), whereas that of Mn increases; F and Cl contents are very low in spite of their availability.

The application of *n*-alkylammonium cation exchange reveals the presence of planar structural defects as a result of dehydrogenation-type reactions. The annite records the results of oxidation during cooling, *i.e.*, open-system behavior in this degassing pluton.

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Sommaire

Les venues de syénite néphélinique représentent le produit le plus différencié de la cristallisation fractionnée dans la carrière Poudrette au mont Saint-Hilaire, Québec. Ces roches témoignent aussi de signes d'une altération subsolidus due à la circulation de fluides post-magmatiques. L'annite, membre de la série de la biotite à dominance de Fe²⁺, représente jusqu'à 20% de syénites néphéliniques typiques.

Les échantillons choisis sont représentatifs d'un éventail de roches, allant des plus saines jusqu'aux plus altérées. Une identification des minéraux et une estimation de leur proportion modale et de leur composition a été faite en utilisant le microscope optique et la microsconde électronique. J'ai aussi utilisé la diffraction X et la microscopie électronique par transmission à haute résolution.

Par rapport à la composition, Fe/(Fe + Mg) va de 0.74 (syénite néphélinique porphyrique) à 0.98 (syénite néphélinique poecilitique). La morphologie de l'annite serait régie par la composition du magma, qui détermine l'ordre de cristallisation; l'annite se manifeste soit en lamelles skelettiques, soit en texture oïkocristique. La syénite néphélinique du filon Poudrette possède une texture hypersolvus et renferme de l'annite en lamelles, dont la croissance était près du liquidus. C'est donc dire que l'ordre de cristallisation était "normal" (minéral mafique d'abord). En revanche, dans la syénite néphélinique poecilitique, cet ordre est inversé. La proportion du Ti diminue à mesure qu'augmente Fe/(Fe + Mg), tandis que la proportion de Mn augmente. Les teneurs en F et Cl sont très faibles malgré leur disponibilité.

L'application de l'échange des cations interfoliaires par *n*-alkylammonium révèle la présence de défauts structuraux planaires résultant des réactions accompagnant la perte de l'hydrogène. L'annite témoigne donc d'une oxydation au cours du refroidissement, c'est-à-dire, d'un comportement en système ouvert dans ce pluton au cours de son dégazage.

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I would like to extend my heartfelt thanks to Behdad, my nephew.

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"We see what we know"

Johann Wolfgang von Goethe (1749-1832), celebrated German poet and scientist, after whom the mineral goethite named.

Dedication

This study is dedicated to my parents, my dear sister Negin, my nephew Behdad Bayat, my niece Bahar Bayat, and in loving memory to my uncle Ahmad Shivaei for their love, patience, and encouragement all through my research work. I hope that it will be an appropriate tribute to them. "I need to put up with two or three caterpillars if I want to get to know the butterflies." ⁽¹⁾

⁽¹⁾ Excerpted from "The Little Prince" by Antoine de Saint-Exupéry (1900-1944). Copyright 1943 by Harcourt Brace & Company; Copyright renewed 1971 by Harcourt Brace & Company. All rights reserved.

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Chapter 1

Introduction

Nepheline syenite represents the most highly differentiated product of igneous activity at Mont Saint-Hilaire (MSH), the best known of the Monteregian complexes, in the Montreal area of southern Quebec (Adams 1903). This rock, which is dominant in the Poudrette quarry, on the northeastern side of the intrusive body, also records a significant subsolidus overprint owing to the circulation of postmagmatic fluids. Annite forms up to 20% of the nepheline syenite, and can be a sensitive monitor of magmatic phenomena and of postmagmatic alteration. Such post-magmatic phenomena may lead to oxidation, metasomatism, pseudomorphism and transformation into secondary phyllosilicates and other products.

The objective of this thesis is to document the textural development of the annite, its composition, the range of ionic substitutions, its textural relation to other primary minerals, the importance of postmagmatic changes, and the local environments of crystallization. I intend to characterize the annite by means of optical microscopy, electron-microprobe analysis, X-ray diffraction (powder method), and transmission electron microscopy. Although the focus is on one mineral, such a combined analytical approach is likely to provide new insight into the final stage of crystallization of the best known of the Monteregian complexes.

Why is Mont Saint-Hilaire the best known of the Monteregian complexes?

As at other Monteregian intrusive centers, rocks of the Mont Saint-Hilaire complex have an alkaline tendency. Extensive fractionation of a mafic alkaline parental magma led to a silica-undersaturated syenitic magma of peralkaline character, highly enriched in incompatible elements such as Nb, Ti, Zr, the rare-earth elements (REE), and Li. Crystallization of such a nepheline-bearing syenitic magma produced an alkaline fluid phase. The host rocks, in large part limestone and shale of the Richmond Group, were very reactive in the presence of such a peralkaline fluid, and were transformed into marble and hornfels, locally alkali-metasomatized. Decarbonation and dehydration reactions in the host rocks are responsible for the production of CO_2 and H_2O . The formation of various geochemically specialized "micro-environments" (Piilonen *et al.* 1998), even on the scale of the Poudrette quarry, accounts for the great diversity of minerals.

Mont Saint-Hilaire contains exceptional examples of sérandite, catapleiite, sodalite, leifite, carletonite, to name but a few. In all, 328 mineral species have been identified there (Horváth and Pfenninger-Horváth 2000). Of these 328 minerals, 56 are carbonates, which indicates the importance of the carbonate-bearing wallrocks in providing the necessary carbonate in solution. The formation of carbonate complexes in a peralkaline aqueous fluid allowed the rare-earth and high-field-strength elements be mobilized in this environment (Wood 1990a, b). It is one of the aims of this investigation to document the results of the interaction of the annite with such a peralkaline aqueous fluid during cooling.

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Chapter 2

The Mont Saint-Hilaire intrusive complex

Geological setting

Mont Saint-Hilaire (Fig. 1) forms part of the Monteregian alkaline SiO₂-undersaturated igneous province, first grouped and described by Hunt (1859). Adams (1903) recognized the Monteregian intrusive bodies as a distinct petrographic province, extending eastward from the Montreal area in southern Quebec. The Monteregian Hills (O'Neil 1914) lie along a curvilinear belt that extends from Oka, 35 km west of Montreal, to Megantic, 190 km to the east (Fig. 2). The ten major intrusive bodies making up that petrographic province were emplaced in Paleozoic rocks of the St. Lawrence Lowlands during the Cretaceous period. Dresser and Denis (1944, p. 460) concluded that the Monteregian magmas, upon arriving at preferred horizons in the Paleozoic host-rocks, may well have spread laterally to form laccoliths. Feininger and Goodacre (1995) modeled the shape of the eight out of ten major intrusive bodies at depth through the quantitative interpretation of the Bouguer gravity anomalies. In their gravity study, they made use of density measured on unweathered hand-specimens. They documented the presence of about 200 km³ of mafic and ultramafic rocks at depth.



Fig. 1. Location map (modified after Horváth and Gault, 1990)



Fig. 2. Intrusive bodies that constitute the Monteregian igneous province (map modified after Horváth and Gault, 1990). To some, the Megantic complex should not be included.

This volume is only 57% of the whole, in their opinion; the remainder is made up of lower-density felsic rocks generally on top of the mafic rocks, and not easily detectable by the gravity method. Most of these laccoliths formed from magma emplaced along the buried Precambrian-Paleozoic unconformity (Fig. 3). From their data, the lower surface of the Mont Saint-Hilaire laccolith is inferred to lie 1.6 km above this unconformity (Fig. 3). Steep or vertical structures in parts of the Mont Saint-Hilaire complex (Currie 1989) imply that this intrusion may have a pipe-like form similar to that mapped at Mont Saint-Grégoire (Philpotts 1968; intrusive center number 6 on Fig. 2).

Doig and Barton (1968) distinguished four main periods of alkaline igneous activity associated with the St. Lawrence rift system by K-Ar dating. The Monteregian activity was the most recent episode of rifting, associated with the St. Lawrence and Ottawa grabens (Gold 1967). Dykes with ages similar to those of the Monteregian intrusions can be found extending along the Champlain Valley and throughout New England (Zartman *et al.* 1967), and the rocks of the White Mountain magma series of New Hampshire are only slightly older. An ⁴⁰Ar/³⁹Ar analysis of biotite from nepheline diorite, nepheline syenite and amphibole gabbro at Mont Saint-Hilaire, provided by Gilbert and Foland (1985), indicates an age of 124.4 \pm 1.2 Ma, the standard deviation implying to them a geologically short interval of intrusion. These authors did not provide bulk-composition data on biotite in their isotopic study.

The Mont Saint-Hilaire pluton, about 10 km^2 in diameter, was subdivided by Currie (1983) into three suites (Fig. 4). The oldest, the Sunrise suite, consists of amphibolepyroxene gabbros, which commonly lack olivine, K-feldspar, and nepheline. That suite is truncated to the east and southeast by an intricate maze of breccias of the East Hill suite (Currie 1983, although not reflected in the simplified map used here as Fig. 4), and elsewhere by the younger ring intrusion of the Pain de Sucre suite. The most mafic unit of the Sunrise suite, titanaugite melagabbro, forms a continuous fringe around the Sunrise suite and occurs as large inclusions in the East Hill suite.

Dykes of similar rocks cut the hornfels collar west of the pluton. The Pain de Sucre suite consists of trachygabbro, nepheline diorite to nepheline syenite, locally intrudes (and encircles) the Sunrise suite, and forms a high-standing outer ring around the western part of the mountain. No dykes of this suite have been found in the hornfels collar.



Fig. 3. Schematic sequential cross-section illustrating the likely depth of emplacement of Mont Saint-Hilaire, Mont Saint-Bruno plutons, and the Ile Saint-Hélène breccia, and the inferred laccolithic shapes of those bodies at depth. Small arrows depict the descent of the body of magma following emplacement (modified after Feininger and Goodacre, 1995).



Fig. 4. Geology of the Mont Saint-Hilaire intrusive complex (modified after Horváth and Gault, 1990)

The youngest, the East Hill suite of nepheline syenite and sodalite syenite, is well exposed in the Poudrette quarry, where the samples were collected for this project (Fig. 4). In the East Hill suite, the evolved magma was emplaced along the outer contact of the complex, presumably late in its evolution. Other rock types exposed in the quarry include nepheline syenite pegmatite, marble xenoliths, hornfels and igneous breccias (Currie *et al.* 1983, 1986). Crystallization thus has taken place in a "contaminated" environment. Beginning a few hundred meters from the intrusive contact (Pouliot 1969), the host rock shows evidence of having tilted inward toward the intrusion, at progressively steeper angles as one nears the contact, to reach dips in excess of 45°, as noted schematically in Figure 3.

Marble and hornfels at Mont Saint-Hilaire developed at the expense of calcareous siltstone and shale of the Richmond and Lorraine groups, Upper Ordovician in age.

Magma types represented in the Poudrette quarry

Nepheline syenites exposed in the Poudrette quarry represent the late stages of magmatic evolution at Mont Saint-Hilaire. These silica-undersaturated rocks are peralkaline (presence of modal aegirine and annite) and cluster near the silica-undersaturated minimum in the system NaAlSiO₄–KAlSiO₄–SiO₂-H₂O (Hamilton and MacKenzie 1960). In a peralkaline [(Na + K) > Al] silica-undersaturated system, the very evolved magmas are not in the above system in the strict sense, but also contain Fe, Mn, and an array of incompatible elements like Zr, Nb, Ti, and Li. Such evolved melts are said to be agpaitic (Sørensen 1997). They are still expected to crystallize nepheline and alkali feldspar as dominant near-liquidus felsic minerals. Both are anhydrous phases; the corollary is that the residual melt becomes progressively enriched in mafic constituents (Fe, Mn), high-field-strength and then incompatible elements, as well as H₂O, F, and Cl. Exotic zirconosilicates, titanosilicates, and niobosilicates thus eventually will form near the solidus, as well as a fluid phase. Mont Saint-Hilaire thus offers a striking example of agpaitic crystallization (Sørensen 1997), in which the mafic minerals commonly appear after the crystallization of the felsic minerals.

The generation of a granitic melt occurs along the contacts between nepheline syenitic magma and hornfels, and leads to the formation of banded rocks in which anatexis has taken place. The transition from silica-undersaturated to silica-oversaturated compositions can occur on the scale of ten cm in the Poudrette quarry, and may serve as a small-scale equivalent for mechanisms of contamination of evolved silica-undersaturated magmas affecting other Monteregian complexes.

Major rock-types in the Poudrette quarry

In the Poudrette quarry, there are distinct geological environments, each with its own unique mineral assemblages. The features of the most important environments, or modes of occurrence, are as follows:

Porphyritic nepheline syenite

This is the main igneous body in the Poudrette quarry (Fig. 5); it is mostly exposed near the hornfelsic unit. It is dark grey in color, with the main constituent being whitish to greenish sodic plagioclase (40%) along with K-feldspar (20%), nepheline (30%) and mafic minerals such as annite (10%) in a fine-grained groundmass. Although porphyritic nepheline syenites are generally petrographically very homogeneous, the amount of sodic plagioclase increases (to 50-55%) toward the contact with poikilitic nepheline syenite bodies.

Porphyritic nepheline syenite is dark grey-colored, and contains phenocrysts of whitish to greenish plagioclase enclosed in a medium- to fine-grained matrix of feldspar, nepheline and a mafic mineral, mostly aegirine-augite and with some annite. Well-formed trapezohedra and clusters of analcime are found in cavities suggesting a hydrothermal origin of this mineral.

Currie (1983) stated that this rock contains a small but significant amount of trachytic matrix of feldspar, nepheline, as well as sodalite phenocrysts and xenocrysts.

Fig. 5. Geological map of the Poudrette quarry, Mont Saint-Hilaire.



Geological map of the Poudrette quarry Mont Saint-Hilaire

The unit locally contains inclusions of the Sunrise suite (pyroxene melagabbro and jacupirangite), and Pain de Sucre suite (tabular to granular plagioclase rimmed by alkali feldspar, interstitial nepheline, and mafic clots containing titanaugite, kaersutite, biotite and olivine).

Poikilitic nepheline syenite

A poikilitic texture is locally strikingly developed in small bodies of nepheline syenite. If one mineral is systematically enclosed by another, then the enclosed phase must have been the first to crystallize. In the poikilitic nepheline syenite at Mont Saint-Hilaire (Fig. 5), euhedral crystals of nepheline nucleated and grew freely in the melt (high-nucleation density), and were surrounded by a host crystal of either microcline perthite or annite (low nucleation-density), which are relatively coarse and entrap many nepheline euhedra. In most cases of the poikilitic texture, the enclosed mineral is randomly arranged. In others, the texture becomes truly graphic, *i.e.*, two minerals (nepheline and alkali feldspar) intergrew simultaneously.

There are four medium- to coarse-grained bodies of poikilitic nepheline syenite in the Poudrette quarry, located either between the porphyritic nepheline syenite and country rock or intruding the porphyritic nepheline syenite (Fig. 5). The poikilitic texture is defined by light grey small euhedral chadacrysts (the enclosed mineral) of nepheline (40%), enclosed in large oikocrysts (the enclosing crystal in a poikilitic texture) of K-feldspar (40%) or mafic minerals (most commonly annite, 20%). Oikocrystic aegirine also occurs, but is uncommon. The development of oikocrystic annite and aegirine clearly points to the late stage of crystallization of mafic minerals, *i.e.*, at or near the solidus.

Poudrette dyke (nepheline syenite pegmatite)

What has become informally known as the Poudrette dyke is a prominent cross-cutting body in the southern part of the quarry (Fig. 5). It is pegmatitic in texture, contains euhedral to subhedral nepheline grains (40%) and very coarse K-feldspar (30%), annite (20%), fibrous aegirine (10%), and an accessory primary eudialyte-group mineral. The

annite, mostly observed near the margins of the Poudrette dyke has a bladed morphological development with up to 3 cm long. The bladed habit is an unusual one for a mica. In contrast to poikilitic nepheline syenite, annite seems to have crystallized early with respect to the nepheline and alkali feldspar in the Poudrette dyke.

The presence of an alkali zirconium-bearing silicate rather than zircon indicates that the magma had become highly enriched in Zr, its agpaitic nature having suppressed the formation of zircon (Barth 1962). Where the pegmatite dyke enlarges, miarolitic cavities occur, with well-formed crystals such as analcime growing on the walls of the cavities. Many parts of the pegmatite have become altered to various degrees during a hydrothermal stage, characterized by the presence of a chlorite-group mineral (perhaps chamosite, the Fe-dominant member) after annite, sulfides (pyrite and chalcopyrite) and fluorite.

Sodalite syenite

Sodalite syenite mostly occurs as isolated bodies (xenoliths) in the poikilitic nepheline syenite (Fig. 5). As the magmas of the East Hill suite are believed to have interacted with brines at a relatively shallow depth in the crust (Currie *et al.* 1986), chlorine probably helped to produce the sodalite, and it also may be responsible for the explosive nature of this rock type (Currie *et al.* 1986).

The poikilitic texture is also commonly developed in sodalite syenite. It is defined by light blue to grey small euhedral chadacrysts of sodalite, enclosed in oikocrysts of feldspar.

The origin of the sodalite syenite, magmatic *versus* hydrothermal (metasomatic), remains controversial, and is worthy of a separate investigation. On one hand, the sodalite is homogeneously distributed in the unit, and the boundaries between it and the enclosing poikilitic nepheline syenite, as observed on the walls of the Poudrette quarry, are sharp, which may point to a magmatic origin. The sodalite syenite may represent a late-stage local buildup of highly evolved, chlorine-bearing melt within partly solidified nepheline syenite. In favour of postmagmatic replacement of nepheline syenite, the progressive replacement of nepheline by sodalite (see below, chapter 5) probably leads to

gradational boundaries at depth, with sodalite the encroaching phase. Also, there is a striking textural similarity with the enclosing poikilitic nepheline syenite (Fig. 5). The state of the annite in such sodalite-rich syenite may shed light on its origin.

Hornfels

Hornfels, fine-grained and dark grey, dark green or even pale blue in color, denotes the contact-metamorphosed sedimentary rocks exposed around the intrusion and included in it.

Biotite has not included in the list of minerals found in hornfels at Mont Saint-Hilaire (Horváth and Gault 1990, Horváth and Pfenninger-Horváth 2000), but hornfels inclusions in the nepheline syenite contain biotite (pleochroic from yellow to brown). The other minerals reported are aegirine, albite, allanite, astrophyllite, hematite, muscovite, pyrite, and rutile (Horváth and Gault 1990). This unit is in contact with the Poudrette dyke, and offshoots of syenitic material were injected in the hornfels. Rajasekaran (1967) reported biotite from the southern part of the hornfels collar. However, he reported no information on its composition.

Marble xenoliths

The marble xenoliths, white to pale green in color, stand out against the porphyritic nepheline syenite host (Fig. 5). Some of these xenoliths show dark, distinct metasomatized contact-zones, consisting mostly of anhedral to euhedral crystals of vesuvianite. In some parts, the xenoliths show a pink contact zone containing meionite (calcic scapolite) (pers. commun., A.E. Lalonde, 2003), and fluorite. Also, diopside is of widespread occurrence in these xenoliths. Fibrous pectolite is found in cavities in the marble. Phlogopite, aegirine, eudialyte, muscovite, natrolite, sodalite, siderite, carletonite and pyrite also have been reported (Horváth and Gault, 1990).

Chapter 3

Materials and Methods

Materials

Hand samples for this investigation were collected from various rock units exposed in the Poudrette Quarry at Mont Sainte-Hilaire, Quebec (Fig. 6). On the basis of visual observations and numerous excursions to the quarry, hand samples were carefully chosen to represent the complete range of freshness, from unaltered to hydrothermally modified rocks. Detailed petrographic analysis of the various units was performed with more than 60 hand samples, from which 38 polished thin sections were prepared. Identification of minerals and estimation of their abundances and compositions were obtained from optical microscopy and electron-microprobe analysis (EMPA; Table 1). Samples were chosen for detailed analysis of the alteration of the micas using X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) (Table 1).

Fig. 6. Geological map of the Poudrette quarry, Mont Saint-Hilaire showing sample locations. Those samples chosen for detailed analysis of the micas using EMPA, XRD, and HRTEM are labelled.



Geological map of the Poudrette quarry Mont Saint-Hilaire

TABLE 1. SAMPLES INVESTIGATED, POUDRETTE QUARRY, MONT SAINT-

HILAIRE

UNITS	OM*	EMPA*	XRD*	HRTEM*
Poikilitic nepheline syenite			I	L
AZ-1	•			
AZ-2 (F)	•	•		
AZ-3	•			
MSH-7	•			
MSH-20	•			
MSHA-1 (A)	•	•		
MSHA-3	•			
MSHA-4	•			
MSHA-5	•			
MSHA-6 (A)	•	•		
MSHT-7 (F)			•	•
Poudrette dyke		•	•••••	
STH-1	•			
STH-2	•	•		
STH-3a	•			
STH-3b	•			
STH-3c	•	•		
STH-4a	•			
STH-4b	•			
MSH-1	•			
MSH-2	•			
MSH-3	•			
MSH-4	•			
MSH-5 (B)	•	•		
MSH-6 (B)	•			
MSH-15	•			
MSH-16	•	•		
MSH-17	•			
MSH-21	•			
MSH-23	•			
MSH-A	•			
MSHA-2	•		·····	
MSHT-1 (A)			•	•
MSHT-2 (A)			•	•

MSHT-3 (A)			•	•
MSHT-4 (A)			•	•
Porphyritic nepheline syenite			1	
MSH-11	•			
MSH-13	•			
MSH-19	•	•		
Sodalite syenite		I.,		,
MSH-10	•			
MSH-22	•			
MSH-18 (PAnn)	•	•		
Hornfels		.I		L
MSH-24	•	•		
MSH-26	•			
MSH-27	•			

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* OM, optical microscopy * EMPA, electron-microprobe analysis * XRD, X-ray diffraction
*HRTEM, high-resolution transmission electron microscopy
* F, fresh * A, altered * B, blade *PAnn, poikilitic annite

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Sample preparation for X-ray diffraction and high-resolution transmission electron microscopy

I prepared oriented samples for XRD analysis from 20-30 mg of the <2.0 μ m size fraction of the mica dispersed in ~1.5 mL of deionized H₂O, pipetted onto glass slides and air-dried at room temperature. Then, I solvated these samples with ethylene glycol (EG) in vapour pressure at 60°C for 24 hours and immediately X-rayed. I treated mica flakes with octadecylammonium cations (see below), dispersed in ~1.5 mL of a 1:1 95% ethanol – deionized H₂O solution, pipetted onto glass slides, and allowed to dry at room temperature.

Approximately 100 mg of flakes of mica were hand-picked from selected hand-samples for detailed structural investigation using XRD and HRTEM. Selection criteria were based primarily upon visual observation and results from EMPA. The flakes were lightly ground to a uniform size using an agate mortar and pestle in 95% ethanol. To minimize potential damage to the mica structure, specimens were ground for a maximum of 10 minutes. The resulting mica-ethanol slurry was washed in deionized water and sieved to isolate and concentrate the <2.0 μ m size fraction.

For imaging in HRTEM, I embedded the flakes of mica in thermally curing, lowviscosity aliphatic EPON resin following a procedure modified from Lee *et al.* (1975). Embedding of the samples in EPON is a five-day procedure involving slow infiltration and impregnation with intermediate solutions of EPON resin to ensure maximum infiltration. I placed approximately 10-20 mg of mica in 1.5 mL Eppendorf microtest tubes and dehydrated by adding 1 mL propylene oxide to remove adsorbed water and agitated for two hours using mechanical roller. Care must be taken to dehydrate the samples and to avoid excessive exposure to moisture, as the embedding medium may not polymerize completely. Propylene oxide is also used as an intermediate solvent and enables rapid infiltration of the material by the EPON resin. After high-speed centrifugation (15,000 rpm), the propylene oxide was decanted, and fresh propylene oxide added and agitated overnight. On the second day, after high-speed centrifugation (15,000 rpm), the propylene oxide was decanted, and a 30:70 mixture of EPONpropylene oxide was added to the microtest tubes, and mixed for 24 hours to ensure complete impregnation. On subsequent days, I repeated the above procedure with 50:50 and 70:30 mixtures of EPON-propylene oxide and mixed for 24 hours, respectively. The last infiltration involved 100% EPON. After mixing, the 100% EPON-mica mixture was placed under vacuum to remove air bubbles trapped in the resin, transferred to flat embedding moulds and thermally cured at 65°C for 24 hours. This slow curing allowed the mica flakes to settle and to orient themselves with the {001} parallel to the base of the mould.

I trimmed the cured blocks of resin with a razor blade into the approximate shape of a truncated pyramid with a side length of no more than 0.6 mm. The top face of the truncated pyramid was initially trimmed to a uniform smoothness using a Reichert Ultracut AV ultramicrotome and a glass knife. Ultrathin sections of a thickness of ~70 - 100 nm thick were cut from this face, with the basal plane surface oriented perpendicular to the knife-edge and to the cutting direction, using a Diatome diamond knife. I transferred selected ultrathin-sections to the center of 300-mesh, carbon-coated Cu grids with a formvar support film by carefully touching the grids to the surface of the water on which the sections were floating. I carefully used blotter paper to remove excess water.

Treatment of mica with octadecylammonium cations

For XRD analysis, ~50 mg of mica separates were placed in 1.5 mL Eppendorf micro test tubes and ~1 mL of octadecylammonium cations added. Samples were incubated at 65° C for 24 hours, and repeatedly agitated during this period to resuspend the material, centrifuged at high speed (15,000 rpm); the supernatant liquid was decanted, and the process was repeated. After the second 48-hour incubation, *i.e.*, 5-day exchange period, the samples were twice washed with a 1:1 solution of 95% ethanol – H₂O, and then washed 12 times in 95% ethanol to remove excess alkylammonium salts and alkylamines (Lagaly 1994).

The stoichiometric exchange of interlayer cations in 2:1 layer silicates with n-alkylammonium cations enables the estimation of the density of interlayer cations, layer charge and charge distribution of expandable 2:1 layer silicates, *e.g.*, smectite-group and vermiculite minerals (Lagaly and Weiss 1969, 1970, Lagaly 1981, 1982) and the

expandable component of illite-smectite (Lagaly 1979, Cetin and Huff 1995a; Sears et al. 1998). Treatment with *n*-alkylammonium cations also serves to stabilize the interlayers of expandable 2:1 clay minerals that otherwise collapse under the electron beam in the high vacuum of the transmission electron microscope (TEM). Intercalation of other organic compounds, such as ethylene glycol and glycerol, leads to samples that are not stable in TEM (Ahn and Peacor 1986a, Bell 1986, Vali and Köster 1986). The nalkylammonium cation-exchange reaction and the degree of expansion are functions of alkyl-chain length ($6 \le n_C \le 18$, where n_C is the number of carbon atoms in the alkyl chain with the general formula $Cn_{C}H2n_{C+1}NH^{3+}$) and the density of the interlayer charge. They are also influenced by the temperature of reaction, solution concentration, duration of incubation, chemical pre-treatment, particle size and morphology, properties of the mineral, including the location of layer charge (tetrahedral versus octahedral), and conditions of washing (Lagaly 1981, 1984, Laird et al. 1987, Vali et al. 1991, Sears et al. 1998). Short- and intermediate-chain alkylammonium cations ($6 \le n_C \le 11$) are capable of rapidly intercalating in low- and high-charge 2:1 silicate layers, whereas long-chain alkylammonium cations ($12 \le n_{\rm C} \le 18$) are capable of selectively exchanging interlayer K and other cations, and thus, of expanding the interlayers of higher-charge 2:1 layer silicates such as muscovite, biotite, phlogopite and illite, and the higher-charge component of mixed-layer illite-smectite, which are not expandable with ethylene glycol or glycerol (Weiss 1963, Mackintosh et al. 1971, 1972, Vali et al. 1991, 1992, Sears et al. 1998).

An aqueous solution containing of 0.05 N octadecylammonium cations was prepared by dissolving octadecylamine hydrochloride in deionized water preheated to 65° C. Two procedures for the alkylammonium cation-exchange were used on the mica separates: (i) before XRD analysis following the procedure of Rühlicke and Kohler (1981), and (ii) after embedding in EPON and preparation of ultrathin sections (Vali and Hesse 1990, Sears *et al.* 1998).

For imaging in HRTEM, the copper grids containing the ultrathin sections were transferred to 1.5 mL microtest tubes containing 1.0 mL of the octadecylammonium cation-solution diluted to 50% of the original concentration. The test tubes were placed in an oven at 65° C for 20 minutes and agitated every few minutes to ensure complete
exchange of cations. The grids were washed 14 times with deionized H_2O preheated to $65^{\circ}C$.

X-ray diffraction and high-resolution transmission electron microscopy analysis

X-ray powder diffraction and high-resolution transmission electron microscopy were performed on <2.0 μ m size fraction of mica either solvated with or without ethylene glycol, or exchanged with n-alkylammonium-ion solution.

X-ray diffraction analysis was performed on a Rigaku D/Max 2400 automated diffractometer equipped with a graphite diffracted-beam monochromator (CuK α radiation) using the following analytical conditions; operating voltage of 40 kV, beam current of 160 mA, step-size of 0.01° 2 θ , counting time of 1 second per step, 0.15 mm receiving slit, and a scanning range of 2 to 40° 2 θ . The minerals present were identified by comparing the patterns obtained to reference patterns of randomly mounted specimens contained in the Joint Committee on Powder Diffraction Standards (JCPDS). The raw XRD files (MDI format) were processed with JADE+ (Materials Data, Inc, Livermore, CA) and exported as Hewlett-Packard Graphics Language (HPGL file), which may result in slight distortion of the XRD scan when imported into CorelDRAWTM (version 10). Analysis was performed on the original raw files.

All ultramicrotomed samples were imaged in bright-field illumination at high resolution with a JEOL JEM-2011 TEM equipped with FasTEMTM at an accelerating voltage of 200 kV with an objective aperture of 50 μ m. The phase contrast of one-dimensional lattice-fringe images of 2:1 layer silicates with focus conditions approximating Scherzer defocus depends on the structure and thickness of the specimen and instrumental conditions. Magnification ranged between 400,000 and 800,000X. Images were acquired with a Gatan DualView 300W 1.3k × 1k CCD camera. The digital images were archived in the digital micrograph format and exported as TIF files to retain the high-resolution format of the original images. Although only a few digital images are presented, results are based on hundreds of images taken, and represent some commonly observed features.

As with the XRD scans, the digital images were processed using CorelDrawTM (version 10) to improve contrast and brightness, and imported into Microsoft Word XP.

Electron-microprobe analysis

For electron-microprobe analysis, samples (Table 1) were selected from poikilitic nepheline syenite, Poudrette dyke, porphyritic nepheline syenite, sodalite syenite, and hornfels. The samples were selected on the basis of two main criteria: freshness, and morphology of annite. Owing to advanced alteration in some samples, friable specimens needed to be impregnated with low-viscosity Epoxy resin before cutting. Cutting was done with a diamond saw. The specimens then trimmed to the size required for polished thin sections, from a parallel-sided slice (typically a few mm thick). Carbon coating was applied to prevent charging. The spots to be analyzed were selected on the basis of color of annite, keeping in mind signs of bleaching at the margin of the annite where a fluid phase can circulate.

The mica in nine samples was analyzed using a JEOL-8900L electron microprobe in wavelength dispersion mode, at an accelerating voltage of 15 kV, a beam current of 8 nA, and a beam diameter of 5 μ m. The mineral standards used were orthoclase (K, Al), albite (Na), diopside (Si, Mg, Ca), hematite (Fe), spessartine (Mn), rutile (Ti), fluorite (F), vanadinite (Cl), zircon (Zr), barite (S), and apatite (P). The line (order) used in each case was Ka (1). The accessory minerals were identified by energy-dispersion spectrometry (EDS).

Chapter 4

Literature review

General formula, site allocation and crystal chemistry of biotite

Biotite is now used as a series name (Rieder *et al.* 1998) to describe a solid solution among four end-members: annite and phlogopite (Fe-Mg AlSi₃ micas) and siderophyllite and eastonite (Fe-Mg-Al Al₂Si₂ micas) (Fig. 7). These end-members define a quadrilateral, bound by two independent substitutional vectors: Mg-Fe exchange and (Mg,Fe) Si = ^{VI}Al ^{IV}Al exchange (Tschermak substitution). In Figure 7, the quadrilateral is shaded. The fields of tetra-ferriphlogopite and tetra-ferri-annite also are shown. According to IMA rules of nomenclature, only the two end-members are given a name in a continuous binary solid-solution series, and the compositional range of the species is taken to apply from that of the end-member to 50 mol.% of the series; this is generally known as the "50% rule". For this reason, the fields of tetra-ferriphlogopite and tetraferri-annite are shown to terminate at 0.5 *apfu* Al.

Additional compositional variability of biotite is made possible by substitution at four distinct structural sites: tetrahedral, octahedral, interlayer and hydroxyl sites. The multiplicity of sites leads to a wide range of compositional variability of natural igneous biotite as a function of melt composition, temperature, pressure, fugacity of oxygen in the melt, and fugacity of H₂O, fluorine, and chlorine in the volatile phase.



Fig. 7. The biotite quadrilateral (shaded) and its relationship to the fields of tetraferriphlogopite and tetra-ferri-annite. The occupants of the tetrahedral sites are enclosed in square brackets.

The composition of biotite, therefore, can be very useful to evaluate these factors through the assessment of crystal-melt or crystal-fluid equilibria.

As summarized by Rieder *et al.* (1998), the unit structure of a mica consists of one sheet of octahedra (*Os*) sandwiched between two opposing sheets of tetrahedra (*Ts*), which form adjacent layers separated by interlayer cations (*I*). This produces the sequence I - Ts- Os - Ts - I - Ts - Os - Ts... The simplified formula can be written as:

*I M*₂₋₃
$$\Box$$
 ₁₋₀ *T*₄ O₁₀ *A*₂

where *T* (tetrahedrally coordinated cations) = Si, Al, Fe³⁺, B, Be *M* (octahedrally coordinated cations) = Fe²⁺, Fe³⁺, Mg, Mn²⁺, Mn³⁺, Al, Li, Zn, Ti, Cr, V, \Box (vacancy) *A* = OH, F, Cl, O, S *I* = K, Na, Rb, Cs, NH₄, Ba, Ca, \Box

The most commonly occurring elements in the formula unit above are set in bold face. The order of their presentation reflects the relative importance of the elements at each site at Mont Saint-Hilaire. The number of formula units (Z) in a unit cell is 2 in a 1M structure. Trioctahedral micas have three octahedrally coordinated cations in a formula unit, whereas dioctahedral micas have only two of their three octahedral sites occupied. Most samples of mica of course do not contain exactly 3.0 or 2.0 octahedral cations per formula unit. A trioctahedral mica like annite or phlogopite can show restricted solid-solution toward dioctahedral end-members, the extent of the departure from the ideal value being a function of temperature (Monier and Robert 1986).

In biotite, Si and Al occupy the four tetrahedral sites in a formula unit; the ionic radius of Al^{3+} in tetrahedral coordination is larger than that of Si⁴⁺ (0.39 *versus* 0.26 Å). The substitution of Al^{3+} for Si⁴⁺ in the tetrahedral site thus can be expected to increase sheet thickness and lateral dimensions. Ferric iron also can be accepted in the tetrahedral site. The incorporation of ^{IV}Fe³⁺ is especially important in an environment where there is insufficient Al and Si, for example in the Alto Paranaíba igneous province, southeastern Brazil, the magnesium-rich biotite contains a very high proportion of ^{IV}Fe³⁺, up to 0.92

apfu (Brigatti *et al.* 2001), *i.e.*, it is tetra-ferriphlogopite (Fig. 7). At Mont Saint-Hilaire, such low-Al, high-Fe or high-Mg mica can be expected in the marble xenoliths only, but none was found in this investigation.

Manganese can substitute for Fe^{2+} in the octahedral site. The proportion of Mn reflects the extent of fractionation of the magma. The relatively large ionic radius of ^{VI}Mn²⁺, 0.84 Å, causes it to systematically partition in favour of the residual melt. In the Klokken syenite, in Greenland, for example, the amount of Mn in biotite increases from ~0.01 *apfu* in gabbros to ~0.05-0.06 *apfu* in laminated syenites (Parsons *et al.* 1991). In comparison with the other occupants of the octahedral position mentioned so far, ^{VI}Li (0.74 Å) is less plentiful in the magma. The ratio Li/Mg progressively increases in mica (Tischendorf *et al.* 1999), such that Li micas can be expected at Mont Saint-Hilaire at the late stages of crystallization. Li-bearing micas, currently being investigated at Mont Saint-Hilaire by A.E. Lalonde (pers. commun., 2002) were not included in this study.

Titanium also is incorporated in the octahedral sites of the biotite, where it replaces Mg or Fe²⁺ preferentially at the *M1* site (Brigatti *et al.* 1991). The distortion of the *M1* site increases as the amount of Ti increases. For samples with more than 0.5 *apfu* Mg in octahedral sites, the refined occupancies of the *M1* sites show that the amount of Ti⁴⁺ is balanced by octahedral vacancies. The *M2* sites remain like those in Mg end-members because of preferential ordering of Mg. As a result, the thickness of the sheet of octahedra in Ti, Mg-rich biotite is smaller than that in Fe-rich biotite (Brigatti *et al.* 1991). In another study on biotite, Dymek (1983) found that in pelitic to mafic metamorphic rocks from Greenland, incorporation of Ti and, to a lesser extent, Al, at octahedral sites involves vacancy formation. It is evident that Ti content in biotite co-existing with an iron-titanium oxide phase is sensitive to oxygen fugacity (Patiño Douce 1993). This dependence makes it possible to estimate reliable values of oxygen fugacity from biotite-oxide assemblages, which are widespread in metamorphic and plutonic igneous rocks. The breakdown reaction of annite to K-feldspar + magnetite + ilmenite + H₂O is also capable of serving as a sensitive H₂O barometer.

The relative importance of volatile species (H₂O, F and Cl) is expressed by the extent of corresponding substitution at the hydroxyl site. Fe^{2+} -F avoidance has been noted in biotite for some time (Ramberg 1952, Ekström 1972, Rosenberg and Foit 1977).

Ramberg (1952) explained it by stronger bonding between Mg and F than between Fe and F, owing to the smaller size of the Mg^{2+} , and documented this behaviour by the exothermic model reaction:

$Mg(OH)_2 + FeF_2 = MgF_2 + Fe(OH)_2$

Rosenberg and Foit (1977) explained this model of Fe^{2+} -F avoidance by invoking crystalfield theory. The crystal-field splitting parameters of FeO and Fe(H₂O)²⁺ indicate similar stabilization energies for Fe^{2+} versus O²⁻, (OH)⁻ and H₂O, and convey equal favorability for Fe²⁺ linkage to these anions. On the other hand, crystal-field stabilization energy of Fe-F is smaller, which promotes relative instability of Fe-F bonds (Rosenberg and Foit 1977). In synthetic materials, Munoz and Ludington (1974) found annite to be less effective in accommodating fluorine from a coexisting fluid phase than phlogopite, in accordance with observations in natural assemblages of the highest degree of fluorine enrichment in magnesian, rather than ferroan biotite (Rosenberg and Foit 1977). Those authors documented in a experimental study that in most syenites and syenodiorites, F/(F + OH) in biotite thus decreases with increasing Fe, from 1.5% F in phlogopite to <0.1% F in annite.

In spite of the predicted preference of OH for Fe-dominant trioctahedral micas, Shen *et al.* (2000) have established the existence of fluorannite, of end-member composition $KFe^{2+}_{3}AlSi_{3}O_{10}F_{2}$, in the Huangshan granite, People's Republic of China, accompanied by quartz, hafnian zircon, columbite-tantalite, fluorite and magnetite. They found the *1M* polytype (Shen *et al.* 2000). In this case, the F-Fe avoidance has apparently not been effective at all, possibly owing to disequilibrium (*i.e.*, rapid growth) of the mica in that pluton.

In a F-bearing synthetic system, the degree of $OH \rightarrow F$ substitution in trioctahedral ferrous micas has been also investigated by Boukili *et al.* (2001). The compositions investigated correspond to annite and ferroan eastonite. They documented that $OH \rightarrow F$ substitution induces local adjustments in cation occupancies and, as a result, a dimensional adaptation of the sheets of tetrahedra, which in turn controls the fluorine solubility in the micas they studied. Their results also show that Fe^{3+}/Fe_{total} in F-bearing micas is not only controlled

by $f(O_2)$, but also by structural constraints. The fluorine content of biotite has to be taken into account to estimate oxygen fugacities prevailing in the rocks, in their opinion.

Local structure also is important in controlling anion occupancy in micas. For example, the degree of incorporation of Cl in OH-dominant biotite depends on the symmetry of the ring of six tetrahedra. The closer the symmetry of the ring is to the ideal hexagonal symmetry, the greater the extent of Cl replacing OH. Therefore, the incorporation of Cl in annite, in which the symmetry of the ring is close to the ideal hexagonal symmetry (Munoz 1984), is expected to be more extensive than in phlogopite.

In biotite, the amount of K ranges from 7 to 9 wt.% K₂O, and commonly attains the maximum value of 1.0 *apfu*. Na is relatively low (~1% Na₂O), and generally about 0.1 *apfu* (Speer 1984). A remarkable example of "ferriphlogopite" (2.457 *apfu* Mg) was discovered in melilite-bearing eruptive rocks from Cupaello, Italy; it has an excess of silica (Si > 3 *apfu*) and alkalis [(Na + K) > 1 *apfu*)]. It is the first known example of a layer silicate with octahedrally coordinated sodium (Hazen *et al.* 1981), the presence of which was proved with an analysis of the structure. No evidence of a mica with [(Na + K) > 1 *apfu*)] was found at Mont Saint-Hilaire.

Iron-rich biotite in nepheline syenite and in nepheline syenite pegmatite shows virtually no Ca in the interlayer site (Kunitz 1924, Deer 1937). The maximum reported occupancy $(0.13 \ apfu)$ is from quartz latite (Larsen *et al.* 1937). In an agpaitic system such as the East Hill suite at Mont Saint-Hilaire, the amount of Ca in mica is expected to be very low, and presumably controlled by the relative lack of Ca and the high proportion of K and Na in the melt. The same can be said of barium, as there is evidence of removal of Ba via the phlogopite-kinoshitalite solid-solution series in more mafic units of the complex (see below).

Biotite encountered in gabbro from the Brome complex

In a study of biotite in the alkali gabbro members of the Brome complex (intrusive center #9 in Fig. 2), Henderson and Foland (1996) found that on the basis of the average result of 56 electron-microprobe analyses, the "biotite" is in fact a phlogopite-kinoshitalite solid-solution, which varies in Fe/(Fe + Mg) from 0.16 to 0.47 and 1.48 to 1.80 *apfu* total Al). This biotite is thus uncommonly depleted in K (0.54 to 0.13 *apfu*) and Si (2.54 to 1.97 *apfu*), and enriched in Ba (0.26 to 0.85 *apfu*) and Ti (0.32 to 0.87 *apfu*). They also characterized the biotite by means of element-specific and X-ray absorption spectroscopic techniques to provide information on the coordination states of Fe and Ti. Ferric iron makes up a maximum of 10% of the total Fe. Henderson and Foland (1996) considered this biotite to have formed at a late stage of crystallization of the gabbro. Crystallization proceeded under slightly oxidizing conditions, but this does not imply high $f(H_2O)$ in their opinion, as indicated by the relatively low content of OH and high "oxy-biotite" component in the Brome biotite. They also documented a low proportion of F (0.07 *apfu*) and Cl (0.005 *apfu*) in the biotite of the gabbro.

The compositions of coexisting olivine, clinopyroxene, amphibole, ilmenite and magnetite all show only limited variation in Mg and Fe compared to the biotite. The abnormally low An contents of plagioclase (83/59) of the alkali gabbro, compared with the degree of evolution shown by contemporaneous mafic phases (olivine and augite), could perhaps be related to the relatively low activity of H₂O, in the opinion of the authors. This, in turn, would lead to displacement of the plagioclase solidus toward more sodic compositions. Therefore, it is possible that the Brome Ba-Ti-rich biotite formed at relatively high temperature and elevated $f(O_2)$, and low total pressure, low $f(H_2O)$, and perhaps relatively high $f(CO_2)$ (Henderson and Foland 1996).

Biotite encountered in gabbro from the Mont Saint-Hilaire complex

In an investigation of the petrogenesis of the gabbros from the Sunrise suite at Mont Saint-Hilaire, Greenwood and Edgar (1984) reported information on biotite from two units. Phlogopite in kaersutite-biotite gabbro varies in Fe/(Fe + Mg) from 0.19 to 0.21,

and in total Al, from 1.19 to 1.23 *apfu*. The phlogopite varies significantly in Ti (0.35 to 0.40 *apfu*). It developed as an overgrowth on opaque minerals. The phlogopite from leucogabbro varies in Fe/(Fe + Mg) from 0.17 to 0.26, and shows a larger variation in Ti content, from 0.20 to 0.47 *apfu*.

Biotite encountered in nepheline syenite from the Mont Saint-Hilaire complex

In a survey of mineral treasures from Mont Saint-Hilaire, Mandarino and Anderson (1989) recognized six species of mica in rocks of the East Hill suite. Annite is the dominant mica encountered. What they called biotite occurs mostly in pegmatite and in cavities in the marble, and muscovite- $2M_1$ also is found in cavities, in the igneous breccia and hornfels. They also reported the existence of fluorine-dominant phlogopite in marble xenoliths (a new mineral species?), and two lithium-bearing micas, polylithionite KLi₂AlSi₄O₁₀(F,OH)₂, in cavities in pegmatites and marble xenoliths, and tainiolite-1M, KLiMg₂Si₄O₁₀F₂, in cavities near a contact with breccia xenoliths.

They reported compositions for two annite specimens from nepheline syenite pegmatite dyke (Ann-4 and Ann-5: Table 2). These specimens differ significantly in their content of F (0.42, 2.20 wt.%). Note also that they indicated an opinion ^{IV}Fe³⁺ to be absent, but vacancies in the *T* site are not generally considered possible. Thus Mandarino and Anderson should have proposed a full *T* site, which implies that some of the Fe²⁺ reported should be converted to Fe³⁺ to fill the *T* site.

Lalonde *et al.* (1996) also documented the occurrence of Fe-dominant trioctahedral micas in the East Hill suite, as exposed in the Poudette quarry. They used electron-microprobe analyses, Mössbauer spectroscopy, X-ray diffraction, and optical measurement to characterize their samples. They found micas ranging in Fe/(Fe + Mg) from nearly pure end-member annite to phlogopite (0.98 to 0.29). Their study was based on eight analyzed specimens (Table 3): 1) Phlogopite is found as an accessory mineral in a marble xenolith. 2) Four samples are labelled biotite, but here renamed (in parentheses, on the basis of IMA nomenclature) according to the chemical data they provided. Biotite-a (phlogopite) occurs in a xenolith of foliated gabbro found in nepheline syenite.

Sample	Ann-4	Ann-5
Si apfu Al ΣT	2.80 1.14 0.06 4.00	2.97 0.94 0.09 4.00
$ \begin{array}{l} \text{Ti} \\ \text{Fe}^{2+} \\ \text{Mn}^{2+} \\ \text{Mg} \\ \sum M \end{array} $	0.10 2.62 0.20 0.09 3.01	$\begin{array}{c} 0.15 \\ 1.61 \\ 0.14 \\ 1.00 \\ 2.90 \end{array}$
Ca Na K Σ I	0.00 0.04 0.92 0.96	0.00 0.03 0.91 0.94
$ \begin{array}{c} \text{OH} \\ \text{F} \\ \text{Cl} \\ \boldsymbol{\Sigma} \\ \boldsymbol{A} \end{array} $	1.87 0.11 0.00 1.98	1.44 0.55 0.00 1.99
Fe/(Fe + Mg) (Na + K)/Al	0.96 0.84	0.62 1.00

TABLE 2. CHEMICAL ANALYTICAL DATA FOR ANNITEFROM THE POUDRETTE QUARRY*

* Data of Mandarino and Anderson (1989). The compositions are reported in terms of atoms per formula unit (apfu), calculated on the basis of 11 atoms of oxygen. The symbols T, M, I and A are used here as defined in the IMA report of the Mica Subcommittee (Rieder *et al.* 1998).

Sample IMA	Phl	Bt-a	Bt-b	Bt-c	Bt-d	Ann-x	Ann	Sdp
nomenclature	Phl	Phl	Ann	Ann	Ann	Ann	Ann	Sdp
Si <i>apfu</i>	3.10	2.70	2.97	3.03	2.93	2.79	2.82	2.50
Al	0.90	1.23	0.90	0.85	0.84	1.08	0.97	1.43
Fe^{3+}	0.00	0.06	0.12	0.10	0.22	0.12	0.19	0.07
ΣT	4.00	3.99	3.99	3.98	3.99	3.99	3.98	4.00
Al Ti Fe ³⁺ Fe ²⁺ Mn ²⁺ Mg ΣM	$\begin{array}{c} 0.03 \\ 0.00 \\ 0.00 \\ 0.84 \\ 0.02 \\ 2.04 \\ 2.93 \end{array}$	$\begin{array}{c} 0.00\\ 0.41\\ 0.00\\ 1.02\\ 0.01\\ 1.35\\ 2.79\end{array}$	$\begin{array}{c} 0.04 \\ 0.15 \\ 0.07 \\ 1.40 \\ 0.14 \\ 1.01 \\ 2.81 \end{array}$	$\begin{array}{c} 0.00\\ 0.14\\ 0.09\\ 1.42\\ 0.11\\ 1.00\\ 2.76\end{array}$	$\begin{array}{c} 0.03 \\ 0.06 \\ 0.12 \\ 1.75 \\ 0.37 \\ 0.57 \\ 2.90 \end{array}$	$\begin{array}{c} 0.00\\ 0.09\\ 0.12\\ 1.84\\ 0.13\\ 0.07\\ 2.25 \end{array}$	$\begin{array}{c} 0.00\\ 0.07\\ 0.28\\ 2.24\\ 0.17\\ 0.07\\ 2.83 \end{array}$	0.65 0.01 0.09 1.94 0.11 0.05 2.85
Ca Na K Σ I	0.00 0.02 0.92 0.94	$\begin{array}{c} 0.00 \\ 0.06 \\ 0.86 \\ 0.92 \end{array}$	0.00 0.03 0.91 0.94	0.00 0.03 0.94 0.97	0.00 0.03 0.84 0.87	0.00 0.06 0.82 0.88	0.00 0.07 0.93 1.00	$0.00 \\ 0.04 \\ 0.90 \\ 0.94$
$ \begin{array}{c} \text{OH} \\ \text{F} \\ \text{Cl} \\ \boldsymbol{\Sigma} \boldsymbol{A} \end{array} $	1.21	1.80	1.44	1.46	1.63	1.87	1.84	1.87
	0.77	0.11	0.55	0.50	0.36	0.11	0.14	0.10
	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.02
	1.98	1.91	1.99	1.99	1.99	1.98	1.98	1.99
Fe/(Fe + Mg)	0.29	0.44	0.61	0.61	0.78	0.96	0.97	0.97
(Na + K)/Al	1.01	0.74	1.00	1.14	1.00	0.81	1.03	0.45

TABLE 3. CHEMICAL ANALYTICAL DATA FOR EIGHT SAMPLES OF DARK MICA FROM THE POUDRETTE QUARRY *

* Data of Lalonde *et al.* (1996). The compositions are reported in terms of atoms per formula unit (*apfu*), calculated on the basis of 11 atoms of oxygen. The symbols T, M, I and A are used here as defined in the IMA report of the Mica Subcommittee (Rieder *et al.* 1998). Ann: annite, Phl: phlogopite, Sdp: siderophyllite.

Biotite-b (annite), biotite-c (annite), and biotite-d (annite) are from a granular micaceous rock, composed of 75% euhedral to subhedral pseudohexagonal crystals of mica. This rock is found as a mafic segregation in nepheline syenite.

According to the authors, this material most likely resulted from the crystallization of a H_2O -rich mafic residual melt within pockets in the nepheline syenite. Biotite-d (annite) is found in a micaceous granular rock (also a xenolith) associated with K-feldspar and albite in a "remobilized syenite dyke". 3) Annite and annite-x (ferrian annite) are found, respectively, in nepheline syenite and in a nepheline syenite dyke. 4) Siderophyllite occurs in a late dyke of what they called "albitite".

They discovered, by Mössbauer spectroscopy, that a relatively high proportion of ^{IV}Fe³⁺ is a feature of the annite at Mont Saint-Hilaire. The proportion of ^{IV}Fe³⁺ to Fe_{total} varies from 0.03 in siderophyllite to 0.05 in annite-x (ferrian annite). Lalonde *et al.* (1996) explained the high content of ^{IV}Fe³⁺ in annite by the deficiency of Si and Al to fill tetrahedral sites during primary crystallization in this peralkaline system. Moreover, they documented a bimodal proportion of total Al contents (roughly 1.0 *apfu* in annite and 2.1 *apfu* in siderophyllite based on 11 oxygen atoms). In most of their specimens, total Al is less than 1 *apfu* (ideally it should be 1.0 *apfu*). This is in part because ^{IV}Al³⁺ contents are relatively low, but also because all samples have practically no ^{VI}Al³⁺, 0 to 0.08 *apfu*. The micas of the East Hill suite thus are relatively poor in Al (Lalonde *et al.* 1996), and are in some cases themselves peralkaline (Table 3).

In their data set, manganese shows a general increase from 0.03 *apfu* in phlogopite, and peaks at 0.75 *apfu* in annite from the nepheline syenite. From there onward in terms of Fe/(Fe + Mg), Mn drops back to 0.26 *apfu* in ferrian annite and 0.35 *apfu* in annite specimens, which suggests late depletion of Mn in the most evolved magmas, probably brought about by the crystallization of Mn-rich phases such as sérandite and rhodochrosite (Lalonde *et al.* 1996). The same late depletion has been encountered at Klokken, in Greenland (previous section). Titanium contents show the reverse trend to Mn in that it generally decreases in concentration from the biotite of the gabbro (0.82 *apfu*) to that of the syenites and albitite (0.03 *apfu*) (Lalonde *et al.* 1996).

Lalonde *et al.* (1996) found two morphological developments of annite in the nepheline syenite. Their ferrian annite occurs as unusual bladed crystals up to 4 cm long in a

nepheline syenite dyke (presumably what is now known informally as the "Poudrette dyke") composed of microcline, nepheline, aegirine and an accessory eudialyte-group mineral. They attributed the bladed habit of the crystals to the preferential development of $\{010\}$, but did not explain the habit. On the other hand, normal annite (*i.e.*, less ^{IV}Fe³⁺) occurs in massive nepheline syenite as black euhedral (hexagonal) to subhedral crystals that can attain 6 cm across and 2 cm in thickness. They did not discuss the poikilitic variety of annite in their work.

They concluded that the great variety of mica composition encountered in the Poudrette quarry at Mont Saint-Hilaire reflects the highly heterogeneous conditions that prevailed during magmatic and postmagmatic stages of crystallization in this sector of the intrusive body.

Chapter 5

Petrography, and chemical composition of annite at Mont Saint-Hilaire

In this chapter, I present a petrographic description of the samples of the important units exposed in the Poudrette quarry, with a focus on the morphology of the annite crystals (Table 1). I will show photos of representative specimens of each major unit, along with related photomicrographs of thin sections, and present the results of electron-microprobe analyses of the annite. The compositional data will be plotted in the biotite quadrilateral. In all, 44 samples were examined (Table 1).

Poikilitic nepheline syenite

Fresh poikilitic nepheline syenite

From the point of view of the morphology of annite, the unit identified in chapter 2 as poikilitic nepheline syenite is prominent in the quarry. Thus it has been a focus of my investigation, and is described first. In sample AZ-2, which is representative, the poikilitic texture is defined by small (2 mm) euhedral chadacrysts (included phase) of nepheline (20%), enclosed either in oikocrysts of off-white tabular lustrous perthitic

microcline (35%) or in oikocrysts of annite, up to 5 cm across (Fig. 8). Small blocky white crystals of perthitic microcline with a duller luster are randomly distributed in the rock. The perthitic intergrowths of film-like albite are not clearly distinguished from the microcline host.

The photomicrograph AZ-2 (Fig. 9) shows a close-up of the poikilitic texture with annite as the host mineral surrounding euhedral, grey crystals of nepheline, one more or less perpendicular to its c axis and the other parallel to its c axis. The light grey nepheline seems homogeneous in plane light. It also contains scattered micro-inclusions of unzoned acicular aegirine (circled in Fig. 9). These inclusions are fine grained, and have a common orientation in the nepheline.

A network of subparallel cracks, combined with some irregular cross-cutting cracks, characterizes the crystals of nepheline. Along most cracks, there is an incipient alteration to an isotropic material, tentatively identified as sodalite, which also is irregularly distributed as patches surrounding the micro-inclusions of aegirine.

The oikocrystic annite in AZ-2 (Fig. 8) is black and lustrous, and a minor constituent (<10% by volume) of the coarse-grained light grey nepheline syenite. In addition to its involvement in the poikilitic texture, a small proportion of the annite also appears in scattered isolated grains (Fig. 8).

The annite contains two domains, dark brown and reddish brown (Fig. 9). The reddish brown area seems primary, more homogeneous in color and covers most of the area (60%) in the grains, averaged over the entire thin section. The dark brown area (40%) defines more irregular patches elongate along the cleavage planes. The interface between the domains is gradational. The interface between annite and nepheline is generally straight.

The composition of the annite is reported in the two domains, reddish brown (AZ2 -3, 4) and dark brown (AZ2-1, 2). Table 4 shows the average composition of ten points within each domain. The electron beam was focused on areas away from grains of included phases, for example ilmenite and magnetite.

The composition of the annite in the two domains emphasizes how subtle are variations between reddish brown and dark brown annite. The proportion of Al (1.07 to 1.01 *apfu*, atoms per formula unit), Ti (0.11 to 0.05 *apfu*), Mg (0.06 to 0.03 *apfu*) decreases from the

reddish brown to the dark brown domains, but the two domains are identical in Mg and Al if standard deviations (σ) for these constituents are kept in mind. The depletion in Ti in the dark brown domains may in fact be significant. Ferric iron was assigned to the tetrahedral site to fill the *T* site to 4.00 *apfu*. As information on Fe²⁺/ Fe³⁺ is not available, an estimate of gains or losses of Fe content is not possible. The mica is very close to the annite end-member, and the proportions of F and Cl are very low. Magnetite and ilmenite (identified by energy-dispersion spectra, EDS) precipitated as minute particles within the cleavage of the dark brown annite, presumably in response to an influx of fluid, which induced oxidation.

Fig. 8. Fresh poikilitic nepheline syenite AZ-2.

Fig. 9. Photomicrograph of poikilitic nepheline syenite AZ-2. Areas 1, 2, 3, and 4 mark the locus of the spot analyses.



Sample	AZ-2-1 Reddis	AZ-2-2 sh brown	AZ-2-3 Dark	AZ-2-4 brown
SiO ₂ wt %	35 09(15)	35 14(26)	35 44(22)	35 34(18)
TiO ₂	1.77(7)	1.81(8)	1.01(25)	0.87(3)
Al	11.34(43)	10.75(78)	10.37(24)	10.22(9)
FeO	36.91(24)	36.73(80)	37.69(77)	38.22(52)
MnO	1.93(20)	2.83(60)	2.59(46)	2.71(41)
MgO	0.53(3)	0.52(6)	0.33(22)	0.25(16)
CaO	0.06(3)	0.04(3)	0.06(3)	0.07(3)
Na ₂ O	0.34(6)	0.29(6)	0.27(4)	0.32(4)
K ₂ Ó	8.36(18)	8.64(2́4)	8.32(41)	8.22(35)
H ₂ O	3.51	3.52	3.52	3.53`´
F	0.23(9)	0.21(8)	0.14(8)	0.10(6)
Cl	0.02(1)	0.02(1)	0.01(1)	0.02(1)
O=F, Cl	0.10	0.09	0.06	0.05
Total	100.00	100.41	99.70	99.82
Si <i>apfu</i>	2.90	2.91	2.97	2.97
Al	1.10	1.05	1.02	1.01
$\underline{F}e^{3+}$	0.00	0.04	0.01	0.02
ΣT	4.00	4.00	4.00	4.00
Ti	0.11	0.11	0.06	0.05
Fe ²⁺	2.55	2.50	2.63	2.66
Mn^{2+}	0.13	0.19	0.18	0.19
Mg	0.06	0.06	0.04	0.03
ΣM	2.85	2.86	2.91	2.93
Ca	0.00	0.00	0.00	0.00
Na	0.05	0.04	0.04	0.05
K -	0.88	0.91	0.89	0.88
ΣI	0.93	0.95	0.93	0.93
ОН	1.93	1.93	1.95	1.96
F	0.06	0.05	0.03	0.02
CI	0.00	0.00	0.00	0.00
	1.99	1.98	1.98	1.98
Fe/(Fe + Mg)	0.97	0.97	0.98	0.98
(Na + K)/Al	0.84	0.90	0.91	0.92

TABLE 4. CHEMICAL ANALYTICAL DATA FOR ANNITE IN
FRESH POIKILITIC NEPHELINE SYENITE

The structural formula is calculated on the basis of 11 atoms of oxygen. Particles of opaque minerals are avoided in the choice of spots for analyses. The average composition of ten points is shown within each domain. The amount of H_2O is calculated by stoichiometry. Total Fe expressed as FeO. Fe³⁺ assigned to *T* site to achieve full occupancy. One standard deviation is shown in parentheses, and pertains to the last digits quoted.

Two crystals of aegirine are present in the section (Fig. 9). One shows hourglass zoning, with a dark green center, and light green and yellowish green sectors. The other one, in the top left corner, also is zoned, but its orientation is not appropriate to show sector zoning. Both are intergrown with annite, and the interface between them is highly irregular. Piilonen *et al.* (1998) found zonation to be a common characteristic of the sodic pyroxene in syenitic rocks exposed in the Poudrette quarry, and documented a range of composition from aegirine-augite to end-member aegirine. However, they found the zoning to be concentric rather than of sector type, with a core enriched in Ca + Zr, and a rim enriched in Na + Ti. Their observations pertain to sodic pyroxene in dyke rocks, however, not in the poikilitic-textured unit.

Interpretations

The euhedral crystals of nepheline indicate unimpeded growth in the magma at an early stage of crystallization. Nepheline thus was the liquidus phase in this unit. After the formation of nepheline, large laths of K-feldspar, inferred to have been sanidine (prior to exsolution and Al-Si ordering) and domains of annite engulfed the nepheline crystals, to form the strikingly poikilitic texture. The relative sequence of crystallization of annite, which occurs in subordinate amount, and sanidine cannot be determined, as the two "hosts" of the poikilitic texture are largely present in separate domains. Nevertheless, they clearly are later than nepheline.

The intergrowth of annite and aegirine indicates that aegirine crystallized synchronously with annite from the melt that had become relatively enriched in Fe after extraction of nepheline. Sector zoning in aegirine is a sign of rapid growth (Larsen 1981), consistent with the epizonal character of the pluton.

Early subsolidus changes have affected the nepheline, the sanidine and the annite. The cracks in nepheline offered an avenue of introduction for a fluid phase. The localized development of sodalite implies the fluid phase was Cl-bearing. Possibly another sign of nepheline-fluid interaction is the development of the scattered inclusions of unzoned acicular aegirine with a common orientation prior to its localized conversion to sodalite.

The inclusions may be related to early expulsion of Fe^{3+} expected in the structure of nepheline, as a result of ordering reactions.

This rock, characterized by the absence of albite except as a component of perthite, is an example of a hypersolvus nepheline syenite. At the conditions of crystallization, a gap in temperature separated the solidus and the solvus.

The sanidine crystals are inferred to have begun exsolving sodic feldspar at a temperature of 570°C (Parsons and Brown 1984). The phase diagram shows that after exsolution, the K-rich phase is expected to have inverted to microcline at roughly 450°C.

Altered poikilitic nepheline syenite

Rock MSHA-6 in Figure 10 is an example of the same rock subjected to more obvious hydrothermal alteration. It is medium to coarse grained, and resembles AZ-2, except for a greater contrast in color between alkali feldspar and "nepheline". Annite keeps its black color, but is not as lustrous as in AZ-2. The nepheline crystals retain their shape, but have become bluish grey (Fig. 10) in hand specimen.

The photomicrograph MSHA-6 (Fig. 11) shows euhedral crystals of what used to be "nepheline", enclosed by poikilitic annite and associated aegirine.

In the plane-polarized light (PPL), the euhedral crystals of "nepheline" contain irregular cream-color bulbous domains, which seem to grow inward from the periphery. The mineral seems to be natrolite; the properties are: colorless in PPL, acicular on c, and grey in hand specimen (Phillips and Griffen 1981, p. 376), moderate relief (Nesse 1991, p. 291). The interface between these two domains, natrolite and nepheline, is scalloped in shape. The core area contains irregularly shaped residues of cracked nepheline. Also a mass of acicular crystals with a spherulitic texture can be observed.

The perthitic texture is coarser in this rock than in AZ-2, and contains vein and patch perthite, usually associated with areas of natrolite.

The annite contains three domains, reddish brown, dark brown, and yellowish brown. The reddish brown domain has become less voluminous than in the precursor rock, and takes on the appearance of scattered islands. The dark brown area maintains its homogeneous

Fig. 10. Altered poikilitic nepheline syenite MSHA-6.

Fig. 11. Photomicrograph of altered poikilitic nepheline syenite MSHA-6. Areas 1 and 2 mark the locus of the spot analyses.





color along the cleavage planes, and resembles that in the fresher material (AZ2-3, 4). The yellowish brown domains, heterogeneous, have become dominant, at the expense of the darker precursor, on the basis of observations over the entire thin section.

In this rock, I determined the composition of annite in two domains, dark brown (MSHA6-1) and yellowish brown (MSHA6-2). Table 5 shows the average composition of six points within each domain. Ferric iron was assigned to the tetrahedral site to fill the T site to 4.00 *apfu*.

Note that in the yellowish brown domains, the annite has apparently lost about 15% of its potassium. However, consideration of the large spread of values for K, as well as for Fe and Si, suggests that the yellowish brown domains likely consist of an interlayering of annite and chamosite. The annite component of the mixture, to judge from the composition of the dark brown domains (Table 5), is very close to the annite end-member.

Sample	MSHA-6-1 Dark brown	MSHA-6-2 Yellowish brown
SiO ₂ wt.%	34.35(19)	33.50(1.73)
TiO ₂	1.31(11)	1.38(9)
$Al_2\tilde{O}_3$	11.15(6)	11.46(43)
FeO	37.37(30)	38.13(1.44)
MnO	1.75(23)	1.96(28)
MgO	0.26(7)	0.59(43)
CaO	0.00(1)	0.07(10)
Na ₂ O	0.47(4)	0.43(6)
K ₂ Õ	9.06(5)	7.72(2.19)
H ₂ O	3.51	3.50
\mathbf{F}^{-}	0.09(6)	0.05(2)
Cl	0.02(1)	0.02(1)
O=F, Cl	0.04	0.03
Total	99.30	98.78
Si apfu	2.90	2.84
Al	1.10	1.14
$\underline{F}e^{3+}$	0.00	0.02
ΣT	4.00	4.00
Ti	0.08	0.08
Fe ²⁺	2.63	2.68
Mn^{2+}	0.12	0.14
Mg	0.03	0.07
ΣM	2.86	2.99
Ca	0.00	0.00
Na	0.07	0.07
K	0.97	0.83
ΣI	1.04	0.90
ОН	1.97	1.98
F	0.02	0.01
Cl	0.00	0.00
ΣA	1.99	1.99
Fe/(Fe + Mg)	0.98	0.97
(Na + K)/Al	0.93	0.78

TABLE 5. CHEMICAL ANALYTICAL DATA FOR ANNITE IN ALTERED POIKILITIC NEPHELINE SYENITE

The structural formula is calculated on the basis of 11 atoms of oxygen. Particles of opaque minerals are avoided in the choice of spots for analyses. The average composition of six points is shown within each domain. The amount of H_2O is calculated by stoichiometry. Total Fe expressed as FeO. Fe³⁺ assigned to *T* site to achieve full occupancy. One standard deviation is shown in parentheses, and pertains to the last digits quoted. Fe³⁺ assigned to *T* site to achieve full occupancy.

Irregular arrays of 125-150 μ m across of micro-inclusions of magnetite and ilmenite line the cleavage in the dark brown domains, as documented by EMPA, and decorate the sheet structure of the annite. In contrast, the margins of annite and nepheline are not rimmed by iron oxides.

As in sample AZ-2, the pale green crystal of aegirine continues the rim around the nepheline where annite is absent. It also shows an intergrowth with poikilitic annite. Zoning is not as prominent as in AZ-2.

Interpretations

The crystal of nepheline was first partially replaced by natrolite, a zeolite-group mineral, presumably along cracks. This replacement may well proceed according to the idealized reaction (Delvigne 1998, p. 102):

$$2$$
NaAlSiO₄ + SiO₂ + 2 H₂O = Na₂Al₂Si₃O₁₀ $.2$ H₂O

Natrolite is commonly a pseudomorph after nepheline (Delvigne 1998, p. 102). The cracks noted in the previous specimen help the fluid phase to have easy access to the nepheline.

Annite shows signs of oxidation, namely the appearance of magnetite (dominant oxide phase) with ilmenite (identified by EDS analyses). The annite resembles Ann-x (bladed annite) and Ann (euhedral annite) found by Lalonde *et al.* (1996) in a late syenite dyke in the Poudrette quarry. In specimen MSHA-6, the oikocrystic annite in the yellowish brown domain shows the same composition as Ann-x in Lalonde *et al.* (1996) in terms of major elements; however, MSHA-6 contains slightly more Al (1.14 *apfu*), less F (0.01 *apfu*), and more OH (1.98 *apfu*) than specimen Ann-x in Lalonde *et al.* (1996) [Al (1.08 *apfu*), F (0.11 *apfu*), and OH (1.87 *apfu*)]. Also Lalonde *et al.* (1996) found more Fe³⁺ in the *T* site in sample Ann (0.12 *apfu*) on the basis of Mössbauer spectroscopy.

More advanced alteration in poikilitic nepheline syenite

Figure 12 shows a more altered sample of poikilitic nepheline synite in which more nepheline seems to have been preserved than in MSHA-6.

The photomicrographs MSHA-1 (Fig. 13) illustrate a highly altered poikilitic rock. The precursor micaceous material seems to have completely been replaced by highly heterogeneous domains. The subhedral crystals of what used to be "nepheline" are partially replaced by volumes of secondary natrolite, concentrated in its central parts rather than at its periphery. The interface between these two domains, natrolite and nepheline, is an irregular boundary (Fig. 13).

The perthitic texture has become coarser in this rock compared to AZ-2, and contains blocks of perthite domains, usually turbid, in areas affected by alteration.

The crystals of "nepheline" are enclosed by the breakdown products of annite in numerous irregular embayments (more clearly visible under crossed polars). Chlorite (recognized through optical microscopy) is dominant, but magnetite and ilmenite also are present, recognized on the basis of EDS spectra. This material also contains siderite and muscovite (reported by EDS spectra). Owing to its high iron content, chlorite is dark olive green (Nesse 1991, p. 257), and presumably is chamosite.

Fig. 12. Sample MSHA-1, showing advanced alteration in poikilitic nepheline syenite. The marked area has a poikilitic texture.

Fig. 13. Photomicrograph of MSHA-1, showing evidence of hydrothermal alteration affecting the primary minerals.



Mag

Chl

2 mm

Sodalite syenite

The unit identified in chapter 2 as sodalite syenite consists of four isolated bodies enclosed (or partially enclosed) in poikilitic nepheline syenite (Fig. 5). Sample MSH-18 is a typical example of poikilitic sodalite syenite; the poikilitic texture is not present everywhere in this unit, however. Sample MSH-18 is texturally very similar to AZ-2, sodalite-free poikilitic nepheline syenite.

The rock is coarse-grained and mostly composed of blue to grey crystals of sodalite (40%), nepheline (20%), buff-colored perthitic microcline (30%), and mafic minerals (10%), mostly aegirine with subordinate annite. Some samples are devoid of annite (MSH-10, MSH-22). The poikilitic texture is defined by light blue to grey, small (2 mm) "euhedral" chadacrysts of sodalite, enclosed either in oikocrysts of tabular, lustrous perthitic microcline or in oikocrysts of annite, up to 2 cm across (Fig. 14). Small blocky white crystals of perthitic microcline with a duller luster are randomly distributed in the rock. The perthitic intergrowths of film-like albite are not clearly distinguished from the microcline host. There is no evidence of magmatic albite. The rock thus has a hypersolvus texture.

Thin section MSH-10 offers another example of poikilitic sodalite syenite. The poikilitic texture is defined by perthitic microcline and, in subordinate amount, dark green, zoned crystals of aegirine as the host minerals surrounding markedly euhedral (hexagonal), colorless crystals of sodalite. The euhedral crystals of sodalite contain irregular mm-size of light-grey remnant islands of "nepheline". Sodalite seems to grow inward from the periphery of what were grains of nepheline. The crystals of sodalite seem homogeneous in plane light. Thus the sodalite seems entirely of replacement origin in this sample.

All efforts failed to make a proper polished thin section of MSH-18. The annite would simply get plucked out of the matrix during cutting. Therefore, a piece of refractory brick was used to orient isolated flakes of annite perpendicular to the base of a mould. The annite was thus mounted in epoxy. A polished block of MSH-18 was used for analytical work.

In this rock, I determined the composition of two crystals of annite from MSH-18. Table 6 shows the average composition measured at twenty points.

Fig. 14. Poikilitic sodalite syenite MSH-18.



There is no difference in the composition of the annite in terms of Cl between this unit and the other units exposed in the quarry. It is as close to the annite end-member as the mica in the sodalite-free poikilitic unit, but Al seems to be slightly deficient, and the inferred amount of ^{IV}Fe³⁺, necessary to achieve an occupancy of 4.00 *apfu*, considerably greater. Interestingly, the inferred level of Fe³⁺ matches some measured values of Fe³⁺ in the dataset of Lalonde *et al.* (1996), as shown in Table 3.

Sample	MSH-18
SiO ₂ wt.%	34.77(32)
TiO ₂	1.00(8)
Al_2O_3	9.96(14)
FeO	40.22(28)
MnO	2.10(6)
MgO	0.30(1)
CaO	0.05(3)
Na ₂ O	0.40(12)
K ₂ O	8.68(37)
H ₂ O	3.37
F	0.42(7)
	0.03(3)
O=F, CI	0.18
Total	101.12
Si apfu	2.90
Al	0.97
Fe ³⁺	0.13
ΣT	4.00
Ti	0.06
Fe^{2+}	2.67
Mn^{2+}	0.15
Mg	0.03
ΣM	2.91
Ca	0.00
Na	0.06
K	0.92
ΣI	0.98
OH	1.89
F	0.11
Cl	0.00
ΣA	2.00
Fe/(Fe + Mg)	0.98
(Na + K)/AI	1.01

TABLE 6. CHEMICAL ANALYTICAL DATA FOR ANNITE IN
SODALITE SYENITE

The structural formula is calculated on the basis of 11 atoms of oxygen. Particles of opaque minerals are avoided in the choice of spots for analyses. The average composition of twenty points is shown. The amount of H_2O is calculated by stoichiometry. Total Fe expressed as FeO. Fe³⁺ assigned to *T* site to achieve full occupancy. One standard deviation is shown in parentheses, and pertains to the last digits quoted.

Poudrette dyke (nepheline syenite pegmatite)

This map unit represents the last stage of intrusion of the nepheline-bearing syenitic magma. In this section, I present descriptions of three samples, MSH-5, STH-2, and STH-3c. Sample MSH-5 is the representative of the margin of the dyke, whereas the other two were taken near the center of the dyke.

MSH-5 (bladed habit)

Rock MSH-5 in Figure 15 is a typical example of the coarse-grained and hololeucocratic nepheline syenite exposed in the Poudrette dyke. Large crystals up to 3 cm in length of white-grey nepheline (50%), cm-sized domains of white lustrous perthitic K-feldspar (30%) with a plumose texture (curved bladed crystals), and randomly oriented blades of fresh black annite (20%) up to 2 cm long are the dominant minerals. Lustrous reddish brown crystals of a eudialyte-group mineral can locally be observed in MSH-5. This mineral is anhedral in grains ranging from mm size up to 4 cm.

The unusual bladed morphological development of the annite is characterized by marked elongation in one direction, {010}. In addition to the prominent bladed habit, some annite "crystals" consists of two blades growing parallel to each other (likely joined in the third dimension), with interstitial nepheline and K-feldspar grains between them (Fig. 15). These blades or composite blades are randomly oriented with respect to the outer contact of the dyke. In some cases, the growth of the two parallel blades is accompanied by another blade, which results in an unusual U-shape of the cluster.

The photomicrograph MSH-5 (Fig. 16) shows one grain of the bladed annite accompanied by nepheline, K-feldspar, albite, and iron oxide (likely magnetite) under microscope. The section is perpendicular to blade elongation (Fig. 17).

The annite contains three domains, reddish brown (MSH-5-1, 2), dark brown (MSH-5-3, 4), and yellowish brown (MSH-5-5, 6). The reddish brown domains seem primary, homogeneous, and residual, whereas these and the dark brown domains resemble scattered islands.

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Fig. 15. Nepheline syenite pegmatite MSH-5. Poudrette dyke. Examples of bladed annite are encircled.

Fig. 16. Photomicrograph of MSH-5. Areas 1, 2, 3, 4, 5, and 6 were chemically analyzed.





Fig. 17. A blade of annite in which the section is cut perpendicular to blade elongation, as in Figure 16.

The youngest generation of the annite, the yellowish brown domains (Fig. 16), encroaches upon the previous two to become dominant. The boundary between the domains is gradational. Cleavage planes are clearly visible, continuous across domains, and perpendicular to the elongation of the crystal (Fig. 17). Magnetite (dark grey) is especially encountered at the margin of the grain. Where coarse-grained, it is likely primary. Contrary to what one might conclude from the hand specimen, the annite does not seem fresh, but has clearly been affected by the fluid phase.

In this rock, I determined the composition of annite in three domains, reddish brown (MSH-5-1, 2), dark brown (MSH-5-3, 4), and yellowish brown (MSH-5-5, 6). Table 7 shows the average composition of ten points within each domain.

There is not much difference in composition among domains, which differ so strikingly in color. In detail, however, all the Mg has gone in the latest annite. The Al content in yellowish domains seems to have increased by 10% of the original amount. The proportion of F and Cl is negligible; however, Cl seems to have been added to the mica's structure. Ferric iron was assigned to the tetrahedral site to fill the *T* site to 4.00 *apfu*. No statement is possible about Fe²⁺: Fe³⁺ ratio. However, in view of the findings of Lalonde *et al.* (1996), and the coexistence of the annite with primary magnetite (Fig. 16), it is legitimate to propose the presence of small amounts of Fe^{3+} in the annite's structure. The inferred amounts of ^{IV}Fe³⁺ (Table 7) are in the same range as the measured amounts reported by Lalonde *et al.* (1996).

Sample	MSH-5-1 Reddis	MSH-5-2 h brown	MSH-5-3 Dark	MSH-5-4 brown	MSH-5-5 Yellowi	MSH-5-6 sh brown
SiO ₂ wt.%	34.25(23)	34.29(15)	34.11(28)	34.48(36)	33.91(33)	33.90(30)
TiO ₂	1.08(13)	$1.02(3)^{2}$	0.99(17)	1.01(2)	1.59(30)	1.57(35)
$Al_2 \tilde{O}_3$	10.92(43)	10.07(27)	9.82(105) 9.77(74)	11.73(16)	11.84(39)
FeO	38.86(62)	39.85(19)	40.58(78)	40.48(91)	39.22(33)	38.88(23)
MnO	1.46(34)	2.63(29)	2.14(57)	1.84(12)	1.36(7)	1.57(13)
MgO	0.45(6)	0.37(6)	0.38(10)	0.61(7)	0.05(2)	0.06(3)
CaO	0.02(2)	0.01(2)	0.02(2)	0.01(1)	0.00(1)	0.00(1)
Na ₂ O	0.26(7)	0.34(3)	0.27(5)	0.25(2)	0.26(3)	0.24(3)
K_2O	9.11(35)	8.81(17)	9.05(25)	9.12(15)	9.34(14)	9.35(5)
$H_2^{-}O$	3.42	3.41	3.38	3.39	3.37	3.36
F	0.26(10)	0.30(8)	0.29(12)	0.37(7)	0.19(7)	0.21(9)
Cl	0.05(2)	0.02(4)	0.11(19)	0.01(1)	0.50(5)	0.48(2)
O=F, Cl	0.12	0.13	0.15	0.16	0.19	0.2
Total	100.02	100.99	100.99	101.18	101.33	101.27
Si <i>apfu</i>	2.87	2.87	2.87	2.88	2.81	2.80
Al	1.08	0.99	0.97	0.96	1.14	1.15
$\underline{F}e^{3+}$	0.05	0.14	0.16	0.16	0.05	0.05
ΣT	4.00	4.00	4.00	4.00	4.00	4.00
Ti	0.06	0.06	0.06	0.06	0.10	0.09
Fe ²⁺	2.67	2.66	2.69	2.67	2.66	2.65
Mn^{2+}	0.10	0.18	0.15	0.13	0.09	0.11
Mg	0.05	0.04	0.04	0.07	0.00	0.00
ΣM	2.88	2.94	2.94	2.93	2.85	2.85
Ca	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.04	0.05	0.04	0.04	0.04	0.04
K	0.97	0.94	0.97	0.97	0.98	0.98
ΣI	1.01	0.99	1.01	1.01	1.02	1.02
OH	1.92	1.91	1.90	1.90	1.87	1.87
F	0.07	0.08	0.07	0.10	0.05	0.05
Cl	0.00	0.00	0.01	0.00	0.07	0.06
ΣA	1.99	1.99	1.98	2.00	1.99	1.98
Fe/(Fe + Mg	g) 0.94	0.92	0.93	0.93	0.96	0.95
(Na + K)/Al	0.93	1.00	1.04	1.05	0.90	0.89

TABLE 7. CHEMICAL ANALYTICAL DATA FOR BLADED ANNITE IN THE POUDRETTE DYKE

The structural formula is calculated on the basis of 11 atoms of oxygen. Particles of opaque minerals are avoided in the choice of spots for analyses. The average composition of ten points is shown within each domain. The amount of H_2O is calculated by stoichiometry. Total Fe expressed as FeO. Fe³⁺ assigned to *T* site to achieve full occupancy. One standard deviation is shown in parentheses, and pertains to the last digits quoted.

STH-2

Sample STH-2 in Figure 18, taken near the core of the dyke, is coarser than MSH-5, and it contains large grey crystals of nepheline (40%) up to 3 cm in length, blocky crystals of white perthitic microcline (30%), and localized blue crystals of sodalite. In this rock, the annite (20%) is not bladed but shows re-entrant features (white arrow in Fig. 18). The re-entrant area is filled with either nepheline or microcline perthite. Crystals of aegirine, not clearly visible, are intergrown with annite.

The photomicrograph STH-2 (Fig. 19) shows one grain of annite locally intergrown with aegirine. As in sample MSH-5, the annite does not seem completely fresh, and it has been affected by a fluid phase. There are minor signs of bleaching at the margin of annite next to albite reported by EDS spectra in EMPA.

In this rock, I determined the composition of the annite in one area covering two zones, bleached and brown. I set up the points along a traverse for analysis from the bleached area toward the orange-brown area (black arrow in Fig. 19). Table 8 shows the average composition of three points within the bleached area and seven points within the brown area. No effort was made to evaluate the composition of the irregular darker brown internal domains.

In the bleached rim, Al seems to have increased slightly (~25%), as in sample MSH-5, whereas the Fe and Mg may have been leached slightly. The drop in (Na + K) / Al is due to addition of Al (^{IV}Al and ^{VI}Al) rather than removal of alkalies. Consideration of the standard deviations associated with Si, Al and Fe suggests that the bleached zone contains interlayers of other species, like chamosite and a dioctahedral mica.

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Fig. 18. Sample STH-2 pegmatitic nepheline syenite, Poudrette dyke. Re-entrants of annite (white arrow) show that the feldspar and nepheline crystallized after the annite.

Fig. 19. Photomicrograph of STH-2. Black arrow shows the points along a traverse for analysis from the bleached rim toward the orange-brown area.



Sample	STH-2		
I	Brown	Bleached	
SiO ₂ wt.%	34.64(16)	33.80(1.53)	
TiO ₂	1.30(16)	0.80(6)	
Al_2O_3	10.22(18)	15.15(3.52)	
FeO	39.47(38)	36.34(1.79)	
MnO	2.05(19)	1.50(34)	
MgO	0.56(5)	0.40(13)	
CaO	0.00(1)	0.00(1)	
Na ₂ O	0.36(5)	0.19(6)	
K ₂ Õ	8.96(13)	9.38(11)	
H ₂ O	3.53	3.63	
F	0.11(7)	0.02(3)	
Cl	0.01(1)	0.09(1)	
O=F, Cl	0.05	0.03	
Total	101.56	101.42	
Si <i>apfu</i>	2.90	2.76	
Al	1.00	1.24	
Fe ³⁺	0.10	0.00	
ΣT	4.00	4.00	
Al	0.00	0.22	
Ti	0.08	0.05	
Fe ²⁺	2.65	2.48	
Mn^{2+}	0.14	0.10	
Mg	0.07	0.04	
ΣM	2,94	2.89	
Ca	0.00	0.00	
Na	0.05	0.03	
Κ	0.95	0.97	
ΣI	1.00	1.00	
OH	1.97	1.98	
F	0.03	0.00	
Cl	0.00	0.01	
ΣA	2.00	1.99	
Fe/(Fe + Mg)	0.97	0.98	
(Na + K)/AI	1.00	0.68	

TABLE 8. CHEMICAL ANALYTICAL DATA ON ANNITEWITH RE-ENTRANT FEATURES INTHE CORE ZONE OF THE POUDRETTE DYKE (STH-2)

The structural formula is calculated on the basis of 11 atoms of oxygen. Particles of opaque minerals are avoided in the choice of spots for analyses. The average composition of ten points is shown within each domain. The amount of H_2O is calculated by stoichiometry. Total Fe expressed as FeO. Fe³⁺ assigned to *T* site to achieve full occupancy. One standard deviation is shown in parentheses, and pertains to the last digits.

STH-3c

Rock STH-3c (Fig. 20) contains mostly, large blocky crystals of white perthitic microcline (60%) and subordinate amounts of light grey of nepheline (30%). In the photograph, two blades of annite (10%) define an unusual "boxed-shaped" array, with enclosed nepheline and microcline perthite. In this "boxed-shaped" array, walls are made of two separate bladed crystals, with segments oriented at 90° to each other and with elongation in one direction {010}, grown separately from the melt.

The photomicrograph STH-3c (Fig. 21) shows a close-up of the bladed annite as the host mineral surrounding a crystal of nepheline. In plane-polarized light (PPL), the euhedral crystal of "nepheline" contains irregular cream-color domains. The secondary mineral seems to be natrolite (with the same properties explained as in MSHA-6). The interface between these two domains, natrolite and nepheline, is gradational. The core area contains irregularly shaped residues of cracked nepheline.

In this rock, I determined the composition of annite in two domains, light brown (STH-3c-1) judged to be primary, and dark brown (STH-3c-2). Table 9 shows the average composition of ten points within each domain.

As in other samples, there is really not much difference in composition between the two domains. They overlap completely at the 1σ level (Table 9). The proportion of Cl is negligible. The fluorine content is a bit higher than that of the other samples, 10-15% of the fluorannite component. The reason may well be explained by the location of the sample, as it has been picked up from the center of the dyke, where the orthomagmatic fluid phase has a larger residence-time and has become fluorine-rich. Both samples are close to end-member annite.

A few interpretations can be made at this point. The crystal of nepheline enclosed in annite indicates restricted growth in the magma at a late stage of crystallization. The intergrowth of annite and aegirine indicates that aegirine crystallized synchronously with annite from the evolved melt. The cracks noted help the fluid phase to have easy access to the interior of the nepheline grains.

Nepheline was first partially replaced by natrolite, presumably along cracks. There is also an incipient alteration to an isotropic material, tentatively identified as sodalite, which

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also is irregularly distributed along most cracks. The localized presence of sodalite implies that the fluid phase introduced Cl, yet the annite contains none. It seems at the low temperature of sodalite formation, there was no possibility of reducing anion exchange of Cl for OH in the annite.

Fig. 20. Box-like array of annite crystals in nepheline syenite STH-3c. Poudrette dyke. This array is possibly a variant of the bladed habit seen closer the outer contact of the dyke.

Fig. 21. Photomicrograph of STH-3c; 1 and 2 are the areas where spot analyses were made.





Sample	STH-3c-1 Light brown	STH-3c-2 Dark brown
SiO ₂ wt.%	34.98(24)	35.17(36)
TiO ₂	1.77(13)	1.48(29)
$Al_2\tilde{O}_3$	11.23(57)	10.66(1.30)
FeO	37.87(35)	38.22(41)
MnO	2.02(14)	2.36(78)
MgO	0.81(6)	0.60(22)
CaO	0.00(1)	0.00(1)
Na ₂ O	0.40(9)	0.20(9)
K ₂ Õ	9.11(18)	9.38(22)
H ₂ O	3.38	3.44
F	0.58(8)	0.42(20)
Cl	0.02(1)	0.01(1)
O=F, Cl	0.25	0.18
Total	102.41	102.30
Si apfu	2.84	2.9
Al	1.07	1.03
Fe ³⁺	0.09	0.07
ΣT	4.00	4.00
Ti	0.10	0.09
Fe ²⁺	2.48	2.55
Mn^{2+}	0.14	0.16
Mg	0.09	0.07
ΣM	2.81	2.87
Ca	0.00	0.00
Na	0.06	0.03
Κ	0.94	0.98
ΣI	1.00	1.01
OH	1.84	1.90
F	0.15	0.10
Cl	0.00	0.00
ΣA	1.99	2.00
Fe/(Fe + Mg)	0.91	0.97
(Na + K)/AI	0.93	0.98

TABLE 9. CHEMICAL ANALYTICAL DATA FOR ANNITE WITH BOX-LIKE ARRAY IN THE CORE OF THE POUDRETTE DYKE (STH-3c)

The structural formula is calculated on the basis of 11 atoms of oxygen. Particles of opaque minerals are avoided in the choice of spots for analyses. The average composition of ten points is shown within each domain. The amount of H_2O is calculated by stoichiometry. Total Fe expressed as FeO. Fe³⁺ assigned to *T* site to achieve full occupancy. One standard deviation is shown in parentheses, and pertains to the last digits quoted.

Interpretations

In the Poudrette dyke, the light-colored minerals, nepheline and K-rich feldspar, occupy the interstitial space between earlier grains of annite, and thus belong to a later period of crystallization than the annite. In the other words, K-feldspar and nepheline crystallized last from the melt, at a stage when almost all the annite (and aegirine) had already formed. This rock is assumed to be hypersolvus nepheline syenite.

In MSH-5, the reddish brown domains, lined up along the cleavage, show that there was easy access to the interior of grains by the fluid phase in circulation below the solidus. The dark brown domains with the inclusions of magnetite can be considered as superimposed on the reddish brown ones, sharing almost the same composition. The granules of magnetite originated by localized dissolution and oxidation of the annite.

The yellowish brown domains in the annite indicate an even later process of alteration, which led to bleaching. The bleached annite has become slightly more aluminous than the precursor. The replacement usually occurs along the periphery of the flakes close to albite grains, and extends irregularly toward the center of the blade along the cleavage, which controlled access of the fluid phase. The yellowish brown or bleached annite progressively isolates the darker domains. Peripherial granules of magnetite and ilmenite express the portion of the original iron content of the annite crystal that is missing in the structure of the bleached hydrothermally equilibrated annite.

Hibbard (1995) proposed that bladed annite is likely to form by rapid growth in an undercooled environment, commonly in situations of magma-mixing and hybridization. In other environments, unusual elongations have been documented for magnetite and halite crystals in the rapid crystallization environment at fumaroles in Merapi Volcano, Indonesia (Symonds *et al.*, 1987). In another study, Nilgun *et al.* (1996) noted the appearance of blade-shaped mafic minerals toward the margin of a gabbro body in central Turkey. unusual elongations also has been reported by Henriquez and Martin (1978) in crystal-growth textures in magnetite flows and feeder dykes, El Laco, Chile.

Thus in the dyke, the occurrence of bladed morphology of the annite and the plumose K-feldspar near the contact is an expected manifestation of rapid loss of heat from the

magma to a cooler enclosing country-rock. Therefore, these blades seem to be a rapidgrowth feature.

In STH-3c, and STH-2 taken close to the center of the dyke, the grain size of these dominant minerals is greater than in MSH-5. The perthite is blocky and rather than plumose or branching, and the nepheline is coarser. The annite is less strongly skeletal, presumably because of slower growth.

In contrast with poikilitic nepheline syenite, in which annite crystallized last, the bladed morphology of annite indicates that the melt crystallized annite as a liquidus phase. Therefore, the rock is hypersolvus nepheline syenite in which order of crystallization was "normal". The slower cooling in the core zone is reflected also in more through recrystallization of the annite.

In MSH-5, from the contact zone, the color is not as homogeneous as the STH-2 and STH-3c from the center of the dyke. The reason may well be that in the samples from the center of the dyke, the fluid had more time to remain in contact with the annite and to affect the entire grain.

Porphyritic nepheline syenite

This map unit represents the dominant unit exposed in the Poudrette quarry. Rock MSH-19 in Figure 22 is a typical example of porphyritic nepheline syenite. The rock is dark grey, petrographically homogeneous, and contains blocky phenocrysts of whitish to greenish perthitic microcline (40%) with film-like albite, dark green aegirine enclosed in a medium- to fine-grained matrix of feldspar, nepheline and mafic minerals, mostly aegirine and subordinate amount of annite, and white localized crystals of analcime, which grows in cavities.

The photomicrograph MSH-19 (Fig. 23) shows a close-up of a light brown phenocryst or xenocryst of aegirine-augite. It shows hourglass zoning, with a dark brown center, and light brown sectors (not visible in the photomicrograph). Its orientation in Figure 23 is not appropriate to show sector zoning. The aegirine-augite encloses prisms of an apatite-group mineral (Fig. 23). In the matrix, aegirine predominates over annite; it forms small isolated prisms and anhedral grains, and an overgrowth on the small aegirine-augite -phenocrysts in the groundmass, and on the coarser phenocrysts of aegirine-augite.

The annite is reddish brown, amounts to $\sim 5\%$ randomly oriented among the crystals of aegirine. The annite crystals (~ 0.6 mm) seem homogeneous at high power. Locally, annite and aegirine are intergrown, and the interface between them is highly irregular.

Microcline perthite is the dominant mineral in the matrix. The perthitic intergrowths of film-like albite are not clearly distinguished from the microcline host. White, scattered, anhedral crystals of nepheline, with some irregular cross-cutting cracks, seem homogeneous and fresh in plane light.

I determined the composition of the annite in this rock. Table 10 shows the average composition of twelve points. Compositionally, in all respects except its Mg and Fe contents, the annite resembles other compositions reported earlier. The annite has a Fe/(Fe + Mg) of 0.74 without evidence of zonation, and thus is considerably removed from the annite end-member. Strictly on the basis of Fe/(Fe + Mg) of the biotite, therefore, the unit is considerably less evolved than those discussed earlier. The porphyritic nepheline syenite is probably the oldest and most primitive syenitic unit exposed in the quarry.

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Fig. 22. Porphyritic nepheline syenite MSH-19.

Fig. 23. Photomicrograph of MSH-19. Areas of Ann were chemically analyzed.



2 mm

Sample	MSH-19
SiO ₂ wt.%	35.09(30)
TiO ₂	3.01(13)
$Al_2 \dot{O}_3$	11.63(24)
FeO	29.33(31)
MnO	1.32(2)
MgO	5.74(17)
CaO	0.08(8)
Na ₂ O	0.38(7)
K ₂ Õ	9.14(39)
H ₂ O	3.7
F	0.04(4)
Cl	0.02(1)
O=F, Cl	0.02
Total	99.98
Si apfu	2.83
Al	1.10
Fe ³⁺	0.07
ΣT	4.00
Ti	0.18
Fe^{2+}	1.91
Mn^{2+}	0.09
Mg	0.69
ΣM	2.87
Ca	0.00
Na	0.06
K	0.94
ΣI	1.00
OH	1.98
F	0.01
Cl	0.00
ΣA	1.99
Fe/(Fe + Mg)	0.74
(Na + K)/Al	0.90

TABLE 10. CHEMICAL ANALYTICAL DATA FOR ANNITE IN PORPHYRITIC NEPHELINE SYENITE

The structural formula is calculated on the basis of 11 atoms of oxygen. Particles of opaque minerals are avoided in the choice of spots for analyses. The average composition of twelve points is shown. The amount of H_2O is calculated by stoichiometry. Total Fe expressed as FeO. Fe³⁺ assigned to *T* site to achieve full occupancy. One standard deviation is shown in parentheses, and pertains to the last digits quoted.

Hornfels

This sample was taken close to the contact with the Poudrette dyke (shown in Fig. 6). Rock MSH-24 in Figure 24 is a typical example of a large block of fine-grained hornfels. It is banded with bluish, light grey, and dark grey bands. In addition, veins of injected syenitic material, locally cross-cutting (pale grey to white), are conformable to the contact between the bands. Each injected vein is separated from the adjacent hornfelsic rock by a dark margin. This hornfels is locally alkali-metasomatized, and in some parts, it contains bluish or greenish veinlets, presumably colored by arfvedsonite or aegirine.

The photomicrograph shows two parts. The hornfels, the fine-grained upper part of Figure 25, shows small platy crystals of randomly oriented annite. The lower part shows fine-grained syenitic material, which comprises clusters of green aegirine along with light to dark brown crystals of annite. Table 11 shows the average composition of annite from hornfels (n = 12). The mica in the syenite was not analyzed.

Compositionally, in all respects except its Mg and Fe contents, the annite in hornfels resembles other compositions reported earlier. It has a Fe/(Fe + Mg) of 0.54, and thus is considerably removed from the annite end-member, and close to the limiting value between the fields of annite and phlogopite. Also, in comparison with the other units, the proportion of F is markedly higher in this more magnesian annite. The source of fluorine is presumably due to proximity to a syenite vein, but incorporation of more F in the mica reflects its more magnesian composition.

Fig. 24. Hornfels sample MSH-24. The black oval identifies the area in which annite grains were analyzed.

Fig. 25. Photomicrograph of sample MSH-24. The circle identifies the area in which the spot analyses were made.



Sample	MSH-24
SiO ₂ wt.%	37.05(69)
TiO ₂	2.37(15)
Al_2O_3	11.91(55)
FeO	22.99(68)
MnO	1.31(3)
MgO	10.81(61)
CaO	0.01(2)
Na ₂ O	0.36(8)
K ₂ O	9.70(10)
H ₂ O	3.43
F Cl	1.02(21)
	0.02(2)
0≡F, Cl	0.43
Total	100.55
Si apfu	2.80
Al	1.06
Fe ³⁺	0.14
ΣT	4.00
Ti	0.13
Fe ²⁺	1.31
Mn^{2+}	0.08
Mg	1.22
ΣM	2.74
Ca	0.00
Na	0.05
K	0.93
	0.98
OH	1.75
F	0.24
	0.00
	1.99
Fe/(Fe + Mg)	0.54
(Na + K)/AI	0.92

TABLE 11. CHEMICAL ANALYTICAL DATA FOR ANNITE IN A BANDED HORNFELS WITH INJECTED SYENITIC MATERIAL

The structural formula is calculated on the basis of 11 atoms of oxygen. Particles of opaque minerals are avoided in the choice of spots for analyses. The average composition of twelve points is shown. The amount of H_2O is calculated by stoichiometry. Total Fe expressed as FeO. Fe³⁺ assigned to *T* site to achieve full occupancy. One standard deviation is shown in parentheses, and pertains to the last digits quoted.

Chapter 6

Degradation of mica: evidence from X-ray diffraction and highresolution transmission electron microscopy

Mica separated from selected rock samples collected from the Poudrette Quarry at Mont Saint-Hilaire was investigated by X-ray powder diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) to document the extent of mineral alteration by hydrothermal fluids associated with magmatic intrusions. The mica was separated from rock samples that have been classified as poikilitic nepheline syenite (MSHT-7), syenitic pegmatite (MSHT-1, MSHT-3, MSHT-4), and sodalite syenite (MSHT-2). The mica that was separated from these rocks was judged to be annite from the macroscopic observation of hand specimens, and optical microscopy (OM) and electron microprobe analysis (EMPA) of thin sections from similar rocks and represent the various stages of hydrothermal alteration, *i.e.*, non-altered material, moderately altered material, and highly altered material. Comparison of samples analyzed by XRD and HRTEM was accomplished by treating the <2.0 μ m size fractions of the lightly ground annite with octadecylammonium cations ($n_{\rm C} = 18$), *i.e.*, long-chain alkylammonium cations. While not a widely employed or routine treatment to characterize high-charge 2:1 layer silicates, the application of *n*-alkylammonium cations of various chain-lengths ($6 \le n_C \le 18$) has been used in XRD and TEM investigations to identify and distinguish among a variety of expandable and non-expandable 2:1 clay minerals, particularly smectite-group phases,

vermiculite, illite and mixed-layer illite-smectite (I-S) (*e.g.*, Vali *et al.*, 1994; Sears *et al.*, 1998).

The treatment of 2:1 layer silicates with *n*-alkylammonium cations stabilizes the interlayers of expandable 2:1 layer silicates and amplifies the compositional differences of interlayers having different densities of charge. Treatment of expandable 2:1 layer silicates with other organic molecules such as ethylene glycol and glycerol, an approach typically used in the XRD analysis of clay minerals, does not yield stable lattice spacings under the operating conditions of the TEM, nor do they enable of expansion of interlayers of highly charged 2:1 layer silicates. The *n*-alkylammonium cation-exchange reaction and degree of expansion of interlayers of 2:1 layers are largely functions of alkyl-chain length and the density of interlayer charge (see Sears et al., 1998). Short- and intermediatechain alkylammonium cations ($6 \le n_C \le 11$) are capable of rapidly intercalating in lowand high-charge 2:1 layer silicates, e.g., smectite-group phases and vermiculite. Longchain alkylammonium cations ($12 \le n_{\rm C} \le 18$) are capable of selectively exchanging interlayer K and low-hydration cations, and thus of expanding the interlayers of highercharge 2:1 layer silicates such as mica (e.g., biotite, phlogopite) and other weathered, degraded, altered or poorly crystalline phyllosilicates, illite, glauconite and the highercharge components of I-S that are not expandable with ethylene glycol or glycerol (e.g., Mackintosh et al., 1971, 1972; Vali et al., 1991, 1992; Sears et al., 1998, 1998b).

Non-altered material

Sample MSHT-7 is typical of annite obtained from rock samples that were classified as poikilitic nepheline syenites. The XRD pattern of the <2.0 μ m size fraction of MSHT-7 after air-drying and solvation with ethylene glycol shows an integral series of sharp reflection of ~0.99 (001), 0.50 (002), and 0.334 (003) nm. These reflections are typical of unaltered annite (Fig. 26).

Lattice-fringe images of the <2.0 μ m size fraction of MSHT-7 upon treatment with n_c = 18 show apparently coherent stacks of mica layers that contain 5 to 22 non-expanded interlayers (Fig. 27). Owing to the limited amount of annite that was available from this sample, no XRD pattern was obtained of the sample after exchange with n_c = 18. The apparently coherent stacks of 2:1 layers observed in the lattice-fringe images are

terminated by stacking faults or defects in the mica structure. No expanded interfaces or coherent sequences of 2:1 layers with expanded interlayers, as are commonly encountered in biotite and other altered phyllosilicates upon treatment with $n_C = 18$, were observed (Vali *et al.* 1992). The arrangement of sequences of 2:1 silicate layers observed in the lattice-fringe images explain in the sharp ~1.0 nm basal reflection observed in the XRD pattern (Fig. 26).



Fig. 26. X-ray patterns of the MSHT-7 <2.0 μ m fraction; a) air-dried, b) solvated with ethylene glycol. See text for further explanation.



Fig. 27. Lattice-fringe image of the <2.0 μ m size fraction of sample MSHT-7 after treatment with $n_{\rm C}$ = 18 cations shows apparently coherent stacks of 2:1 layers that contain 5 to 22 non-expanded interlayers (black arrows). The stacks of 2:1 layers are terminated by stacking faults or defects in the mica structure (white arrows).

Moderately altered material

Samples MSHT-1 and MSHT-3 are typical of annite obtained from rock samples classified as altered syenitic pegmatite in the core zone of the Poudrette dyke. The XRD patterns of both these samples after air-drying show an integral series of sharp reflections of ~0.997 (001), 0.50 (002) and 0.335 (003) nm (Figs. 28, 29), as in MSHT-7. These reflections are typical of annite, as indicated by comparison with diffraction patterns of reference and standard phyllosilicates contained in the mineral Powder Diffraction Files (PDF) database. After solvation with ethylene glycol, the d(001) reflection shifted to the slightly higher 2 θ value, 1.006 nm, which suggests the presence of a minor component of an expandable 2:1 layer silicate (<5%). Also observed in the XRD pattern of MSHT-1 are a nearly integral series of reflections of ~1.43 (001), 0.723 (002) and 0.360 (003) nm. Comparison of the experimental diffraction patterns with reference and standard diffraction files in the PDF database suggests these reflections are characteristic of a chlorite-group phase. Also, optical microscopy of thin sections from related samples indicates the presence of a chlorite-group phase after annite (Fig. 11), likely chamosite, the Fe-dominant member of the chlorite group.

Unfortunately, owing to the limited amounts of annite available from these samples, no XRD patterns were prepared of the sample after exchange with $n_{\rm C} = 18$. Lattice-fringe images of MSHT-1 and MSHT-3 after treatment with $n_{\rm C} = 18$, however, both show thick stacks of apparently coherent sequences of 2:1 layers with interfaces expanded with $n_{\rm C} = 18$ that are typical of altered mica, and smaller stacks of apparently coherent sequences of 2:1 layers that contain four to five non-expanded interlayers (Figs. 30, 31). The interfaces between adjacent packets of 2:1 layers have intercalated $n_{\rm C} = 18$ and show a layer thickness of ~2.1 - 2.2 nm, suggesting a high-charge expandable 2:1 layer silicate (*e.g.*, vermiculite-like) density of interlayer charge. This arrangement of sequences of 2:1 silicate layers would explain the sharp ~1.0 nm reflection observed in the XRD pattern, and may help to explain the small amount of expandable 2:1 layers observed in the XRD patterns after solvation with ethylene glycol, *i.e.*, shift of d(001) from 0.997 to 1.006 nm (Fig. 29).



Fig. 28. X-ray patterns of the <2.0 μ m fraction from sample MSHT-1; a) airdried, b) solvated with ethylene glycol. See text for further explanation.



Fig. 29. X-ray patterns of the <2.0 μ m fraction from sample MSHT-3; a) airdried, b) solvated with ethylene glycol. See text for further explanation.



Fig. 30. Lattice-fringe image of the <2.0 μ m size fraction from sample MSHT-1 after treatment with $n_{\rm C} = 18$ cations shows stacks of apparently coherent sequences of 2:1 layers with three to five non-expanded interlayers and interfaces expanded with $n_{\rm C} = 18$ (black arrows). The interfaces intercalated with $n_{\rm C} = 18$ have a thickness of approximately 2.1 – 2.2 nm (white arrows).



Fig. 31. Lattice-fringe image of the <2.0 μ m size fraction of sample MSHT-3 after treatment with $n_{\rm C}$ = 18 cations shows small stacks of apparently coherent sequences of 2:1 layers consisting of two to five non-expanded interlayers (black arrows). No coherent sequences of 2:1 layers with interlayers intercalated with $n_{\rm C} = 18$, as are commonly observed in mica and other altered phyllosilicates upon treatment with $n_{\rm C} = 18$ (Vali *et al.* 1992; Sears et al. 1998).

Highly altered material

Samples MSHT-2 and MSHT-4 are typical of the annite obtained from rock samples classified as either altered sodalite syenite or nepheline syenite pegmatite (Poudrette dyke), respectively. The XRD patterns of the <2.0 μ m size fraction of MSHT-2 and MSHT-4 after air-drying and solvation with ethylene glycol show nearly identical sets of integral sharp reflections of ~1.014 (001), 0.505 (002), and 0.337 (003) nm, and ~1.009 (001), 0.502 (002), and 0.336 (003) nm, respectively (Figs. 32, 33). These reflections are typical of annite. Also observed in MSHT-2 is a nearly integral series of reflections of 1.457 (001), 0.634 (002), 0.485 (003), 0.362 (004), and 0.293 (005) nm. Comparison of these reflections with reference and standard chlorite-group diffraction files in the PDF database suggests a Fe-rich chlorite-group phase, presumably chamosite.

The XRD patterns of samples MSHT-2 and MSHT-4 upon exchange with $n_{\rm C}$ = 18 cations are of poor quality, owing to the difficulty in obtaining nearly perfectly oriented mounts from coarse-grained *n*-alkylammonium mica dispersed in 95% ethyl alcohol and allowed to dry at room temperature. The diffraction pattern for MSHT-2, however, clearly shows two sets of nearly integral, broad reflections (Fig. 32). The first set is ~3.37 (001), 1.72 (002), 1.14 (003), 0.87 (004), and 0.56 (006) nm, and suggests the intercalation of $n_{\rm C}$ = 18 cations with a paraffin-type arrangement of alkyl chains in the interlayers, *i.e.*, a discrete, highly charged 2:1 layer of an "octadecylammonium annite" (Sears *et al.*, 1998). The second set of nearly integral reflections of ~1.006 (001), 0.50 (002), 0.336 (003), and 0.251 (004) nm represents the component of annite that has not intercalated $n_{\rm C}$ =18 in the interlayers. The slight shifts in the integrality of higher-order peaks suggest that they are the sum contributions of the reflections from both "octadecylammonium annite" and annite.

Fig. 32. X-ray patterns of the <2.0 μ m fraction from sample MSHT-2; a) air-dried, b) solvated with ethylene glycol, and c) exchanged with $n_{\rm C}$ = 18 cations. See text for further explanation.


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Fig. 33. X-ray patterns of the <2.0 μ m fraction from sample MSHT-4; a) air-dried, b) solvated with ethylene glycol, and c) exchanged with $n_{\rm C} = 18$ cations. See text for further explanation.



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The XRD pattern of sample MSHT-4 upon exchange with $n_{\rm C} = 18$ is similar to MSHT-2 in showing two sets of nearly integral, broad reflections (Fig. 33). The first set is ~3.42 (001), 1.72 (002), 1.13 (003), and 0.911 (004) nm, and like MSHT-2, indicates the intercalation of $n_{\rm C} = 18$ with a paraffin-type arrangement of alkyl chains in the interlayers. This suggests a discrete, highly charged 2:1 layer mineral of an "octadecylammonium mica" (Sears *et al.*, 1998). The second set of nearly integral reflections of ~1.001 (001), 0.50 (002), 0.337 (003), and 0.251 (004) nm represents the component of annite that has not intercalated $n_{\rm C} = 18$ in the interlayers. Also observed in MSHT-2 upon treatment with $n_{\rm C} = 18$ cations is a series of integral reflections of ~1.50 (001), 0.719 (002), and 0.360 (003) nm that is characteristic of a chlorite-group phase, presumably chamosite, as evident in the diffraction pattern of the untreated sample after air-drying. The chlorite thus does not react with treatment with $n_c = 18$ cations. The other reflections in the XRD patterns of both MSHT-2 and MSHT-4 at higher 20 are likely reflections from the non-00*l* faces of mica, *i.e.*, hk0 or hkl.

Lattice-fringe images of MSHT-2 and MSHT-4 upon treatment with $n_{\rm C} = 18$ show large particles consisting of thick mixed-layer sequences of parallel 2:1 layers that contain (i) 2:1 layers with non-expanded interlayers of ~1.0 nm that are characteristic of nonexpanded annite, (ii) 2:1 layers with interlayers intercalated with $n_{\rm C} = 18$ that have a paraffin-type arrangement of alkyl chains and having a d (001) = ~3.4 nm (*i.e.*, "octadecylammonium mica"), and (iii) double layers (*i.e.*, two 2:1 layers) alternating non-expanded and $n_{\rm C} = 18$ -expanded interlayers with the alkyl chains in a pseudotrimolecular arrangement and having a d (001) = ~3.2-3.3 nm (Fig. 34). Also present are thinner packets of 2:1 layers consisting of three to ten non-expanded interlayers characteristics of annite [*i.e.*, d (001) = ~1.0 nm]. It is readily apparent in the lattice-fringe images of the annite from the highly altered specimens that the amount of the $n_{\rm C} = 18$ intercalated 2:1 layers has significantly increased in comparison to the nonaltered and moderately altered samples.

The nearly integral series of reflections based on d(001) = -3.4 nm in the XRD patterns in both samples MSHT-2 and MSHT-4 upon treatment with $n_c = 18$ cations is observed only in altered mica (*i.e.*, biotite, phlogopite, muscovite), vermiculite, rectorite-like R1ordered phase, and in illite with less than 10% expandable layers after treatment with long-chain alkylammonium cations ($n_c \ge 12$) (Vali *et al.*, 1991, 1992; Cetin and Huff 1995a; Sears *et al.*, 1997,1998).



Fig. 34. Lattice-fringe image of <2.0 μ m size fraction from sample MSHT-2 after treatment with $n_{\rm C}$ = 18 cations shows apparently coherent sequence of 2:1 layers with non-expanded interlayers (black arrows), 2:1 layers with interlayers intercalated with $n_{\rm C}$ = 18 cations (white arrows), and double layers (white diamonds).



Fig. 35. Lattice-fringe image of the <2.0 μ m size fraction from sample MSHT-4 upon treatment with $n_{\rm C} = 18$ cations shows thin stacks of 2:1 layers with three to six non-expanded interlayers (black arrows).

It is apparent, however, that the *d* values measured in the lattice-fringe images of samples MSHT-2 and MSHT-4 correlate with those measured in the XRD patterns and suggest that the broad reflections of d(001) = -3.4 nm are the result of the combination of both the "octadecylammonium mica" and the R1 ordered structure (Vali *et al.* 1994; Sears *et al.* 1998).

Chapter 7

Discussion

In Poudrette quarry at Mont Saint-Hilaire, the trioctahedral mica present provides a sensitive monitor of magmatic to subsolidus stages of evolution in this highly differentiated system. Whereas phlogopite crystallized in gabbroic rocks earlier in the evolution of the igneous complex, as well as in marble xenoliths, annite is the main control of Fe/(Fe + Mg) in many igneous rocks exposed in the quarry, and thus is a valid indicator of geochemical evolution of the residual magma.

Here, I discuss the implication of my findings concerning the composition of mica as well as its habit with respect to conditions at the late magmatic stage. I also discuss compositional changes due to post-magmatic degradation, pseudomorphism of the mica in contact with the hydrothermal fluid as the pluton cooled, and compositional features of the annite in the hornfels.

Late magmatic stage

Compositional features

In the single sample of porphyritic nepheline syenite examined, the annite shows no evidence of zonation, and has a Fe/(Fe + Mg) value of 0.74 (MSH-19 in Fig. 36). It thus



Fig. 36. Plot of part of the biotite quadrilateral, expanded to cover Al-free compositions, showing the compositions of annite known from the literature and determined in this investigation.

is considerably removed from the annite end-member. On the basis of Fe/(Fe + Mg) of the annite, therefore, the unit is considerably less evolved than the other igneous units exposed in the quarry, in which this value approaches 1. The porphyritic nepheline syenite [foyaite in Rajasekaran's (1967) system of nomenclature] thus is the most primitive syenitic unit exposed in the quarry. Rajasekaran (1967) reported a whole-rock Fe/(Fe + Mg) value of 0.86 for a representative sample.

In the annite samples from the Poudrette dyke, the fresh parts (reddish brown and brown domains) seem primary, homogeneous, and residual. Fe/(Fe + Mg) increases slightly from the outer contact (0.94) to the core zone (coarser, 0.97) (MSH-5, and STH-3c, STH-2; respectively, in Fig. 36). Therefore, the samples from the core zone are closer to the annite end-member than in the rim zone, and presumably reflect the importance of *in situ* fractional crystallization.

The most evolved unit sampled in this study is the hypersolvus poikilitic nepheline syenite (AZ-2, MSHA-6 in Fig. 36). In this unit, most compositions of annite cluster even closer to the end-member: $Fe/(Fe + Mg) \approx 0.98$ (Fig. 36). Such batches of syenitic melt were more strongly agpaitic (agpaitic index 1.2 or more: Rajasekaran 1967), and the two mafic minerals, annite and aegirine, appeared generally close to the solidus, thus explaining the oikocrystic nature of the annite (with aegirine).

On the basis of field relationships, the Poudrette dyke seems the latest to be emplaced, and thus could be expected to contain the most evolved magma in the system. However, with respect to annite composition, the poikilitic nepheline syenite is more evolved than the Poudrette dyke. Clearly, therefore, the batch of magma that congealed as the Poudrette dyke intruded the evolved roof-zone rocks of the Mont Saint-Hilaire complex, and was presumably derived from deeper in the laccolithic body.

The presence of Ti silicate minerals in the Poudrette dyke, such as minerals of the astrophyllite group and mangan-neptunite, indicates an increase of Ti in the agpaitic magma. However, Figure 37 shows that the amount of Ti in annite decreases with increasing Fe/(Fe + Mg). This deplition must then reflect a crystal-chemical reason, not a geochemical one; Mg-rich micas are known to better accommodate Ti (Lalonde *et al.* 1996, Brigatti *et al.* 2001).



Fe/(Fe+Mg)

Fig. 37. Geochemical data on annite taken from the literature and determined in this investigation. a) Ti in *apfu* (atoms per formula unit) *versus* Fe/(Fe + Mg), and b) Mn in *apfu versus* Fe/(Fe + Mg). The arrows represent the general trend only and are not calculated.

The Ti contents are known to be much higher in the phlogopite of the mafic rocks than in the annite of the syenites, as reviewed in Chapter 4 and shown in Figure 37a.

Manganese in annite at Mont Saint-Hilaire also is an excellent indicator of the degree of fractionation of the melts. The Mn content of annite shows the reverse trend (with reference to Ti) and generally increases from the porphyritic nepheline syenite toward the most evolved units.

The most Mn in annite recorded in this investigation is 0.2 *apfu*. The data point at 0.37 *apfu* in the data set of Lalonde *et al.* (1996) (Fig. 37b) is anomalous in this respect. The rock hosting such mica is described as a dark micaceous granular material containing more than 75% mica (A.E. Lalonde, personal communication, 2001). Perhaps the reason for the anomalous buildup in Mn and depletion of Ti in their sample (Fig. 37a) is to be sought in its complex history, involving remobilization (partial melting?) of syenitic material, their sample (biotite-d) representing the residue.

Lalonde *et al.* (1996) documented three compositions of annite (biotite-b, biotite-c, and biotite-d) that contain less than 1 *apfu* Σ Al (Fig. 36). No such points were encountered in this investigation. Biotite-b and biotite-c, like biotite-d, come from granular micaceous rocks associated with nepheline syenite. Such rocks are not standard igneous rocks. As mentioned above, they may represent residues after partial melting of "standard igneous rocks" or products of their metasomatic modification (glimmerite?) in contact with a peralkaline fluid phase.

In this discussion of the composition of evolved magmas, the sodalite-dominant variant of the poikilitic feldspathoidal syenite has not been mentioned because the sodalite is attributed a post-magmatic origin. Rajasekaran (1967) called such material "aegirine ditroite" (see also Sørensen 1974, p. 563).

Textural features

In contrast with poikilitic nepheline syenite, the annite from the Poudrette dyke shows the bladed {010} morphology, which indicates that annite was a liquidus phase in this slightly less evolved melt. The light-colored minerals, nepheline and perthitic K-feldspar (originally sanidine), occupy the interstitial space between earlier grains of annite, and thus belong to a later period of crystallization than the annite. The rock is a hypersolvus nepheline syenite in which the order of crystallization was "normal".

The appearance of blade-shaped annite in the Poudrette dyke (MSH-5), near its outer contact, is an expected manifestation of the rapid loss of heat to a cooler country-rock. Therefore, these blades seem to be a feature of rapid growth, as discussed in Chapter 5, along with the plumose habit of the K-feldspar. Also in STH-3c and STH-2, taken close to the center of the dyke, the grain size of these dominant minerals is greater than near the contact. Furthermore, the crystals of K-feldspar are blocky rather than plumose or branching. The annite is less strongly skeletal and more aquant on the whole, presumably because of a slower rate of growth. The bladed habit of annite can thus be expected in rapidly cooled batches of magma following the "normal" sequence of crystallization (*i.e.*, mafic mineral first).

As is common in some highly evolved agpaitic systems, the iron-enriched mafic mineral is not invariably the liquidus phase. For example, in the poikilitic nepheline syenite, nepheline was the liquidus phase, which explains its unimpeded growth as euhedral crystals in the magma at an early stage of crystallization. After extraction of nepheline, the melt thus became relatively enriched in Fe, and from it, annite crystallized along with aegirine and K-feldspar. The poikilitic texture shows that annite is in fact a near-solidus phase. Implicit in this reconstruction is the idea that in such evolved agpaitic systems, the magmas become more and more enriched in iron, not more and more depleted in it. In other words, after a long interval of fractional crystallization where the magma became progressively more Mg- and Fe-depleted, the final stages of evolution involve agpaitic melts in which Fe starts increasing because of fractionation of the felsic minerals as near-liquidus phases. Ultimately, this trend reflects the decreasing upper stability of annite as its Fe/(Fe + Mg) increases and as the system becomes more oxygenated. Wones and

Eugster (1965) showed that the upper stability of end-member annite at the magnetite-hematite buffer may be as low as 420°C (600°C at the Ni–NiO buffer). An obvious question concerns the correlation between the habit of annite and melt composition. I can conclude that it is the melt composition that controls the order of crystallization, which then in turn controls the habit of the annite.

Post-magmatic modifications

The evolved magma crystallized nepheline, sanidine, annite and aegirine. Of these, three minerals are anhydrous, and one contains a small amount of hydroxyl. Thus, one predicts that an aqueous fluid will appear at the solidus, and most probably earlier. Such a fluid phase will tend to escape easily, and could well bring with it Na, F, and Cl. Hydrogen also is expected to leave preferentially during degassing, as has been implied for the Brome complex by Henderson and Foland (1996). At the subsolidus stage, the hot rocks thus can be expected to interact with a hot aqueous and oxygenated fluid released from subjacent batches of magma.

In a closed system, oxygen fugacity is predicted to decrease with a drop in temperature (path II of Wones and Eugster 1965, Fig. 13), such as at the Klokken complex, Greenland (Parsons 1981), presumably owing to the drier state of the magma. However, the Mont Saint-Hilaire epizonal laccolith clearly was not a closed system, but rather one open to the atmosphere and to the enclosing rocks. It cooled along a path marked by increasing $f(O_2)$, *i.e.*, closer to path I of Wones and Eugster (1965).

In fresh *poikilitic nepheline syenite* (AZ-2), early subsolidus changes have affected the annite, which shows a slight decrease in K content (0.89 *apfu*). In more advanced alteration in poikilitic nepheline syenite (MSHA-6), the annite shows signs of oxidation, namely the appearance of magnetite (dominant oxide phase) with ilmenite. The annite presumably also becomes oxidized, in this environment. In advanced alteration in poikilitic nepheline syenite (MSHA-1), the precursor micaceous material seems to have completely been replaced by highly heterogeneous domains of chlorite (dominant), magnetite, and ilmenite. As the mica is close to end-member annite, it likely altered to chamosite, the Fe-dominant member of the chlorite group.

In the sample of sodalite syenite, the progressive replacement of nepheline by sodalite led to gradational boundaries, with sodalite the encroaching phase. As has already mentioned (Chapter 2), there is also a strong textural similarity between sodalite syenite and the enclosing poikilitic nepheline syenite in the southeastern part of the quarry, which is explained by the hydrothermal origin of this unit. The texture is igneous, but the minerals present are judged to have been readjusted or transformed at a subsolidus stage.

In the samples from the *Poudrette dyke*, there is not much difference in annite composition among the various domains, which differ so strikingly in color (Fig. 16). In MSH-5, the color is not as homogeneous as in STH-2 and STH-3c (core-zone samples). The reason may well be that near the core zone, the fluid phase has had more time to interact with the annite and to have a relatively equalizing effect on it, which also explains the predominance of the bleached domains in annite near the core zone of the pegmatite.

Bleached zones formed by pseudomorphic replacement of the darker brown annite. In MSH-5, peripheral granules of magnetite and ilmenite express the portion of the original iron content of the annite crystal that was rejected from the structure of the bleached, hydrothermally equilibrated annite. In detail, the Al content in the bleached domains seems to have increased (relatively) by 10 and 25% of the original amount, in MSH-5 and STH-2, respectively (points shifted to 1.2 *apfu* and 1.5 *apfu* in Fig. 36), whereas the Fe and Mg may have been leached slightly. Also owing to the relative increase in Σ Al, the agpaitic index of the mica is markedly lower in the bleached domains. The proportion of F and Cl remains negligible; however, the F content is a bit higher in core annite STH-3c, by 10-15%, perhaps a result of its slightly greater Mg content (less Fe²⁺-F avoidance). On the other hand, in STH-3c, the localized presence of sodalite implies the presence of Cl (a large anion) in the fluid phase, whereas the annite contains none. This finding has a crystal-chemical reason: there was no possibility of anion exchange of Cl for OH in the annite at the low temperature of sodalite formation.

Lalonde *et al.* (1996) reported that annite from dyke rocks of the Poudrette quarry contains 10-19% of the iron as ^{IV}Fe³⁺. They attributed this enrichment in ^{IV}Fe³⁺ to a relative deficiency of ^{IV}Al in the system. An alternative hypothesis may be that the oxidation (*i.e.*, loss of hydrogen) had already started to cause Fe²⁺ to convert to Fe³⁺ in

the magma, so that the annite had to accept Fe^{3+} , as the magma by then contained such tetrahedrally coordinated units. During degassing, an H₂O-rich fluid phase separates from the felsic magma (Taylor *et al.* 1983), which in turn results in oxidation due to relative loss of hydrogen (*i.e.*, dehydrogenation of the melt phase: Henderson and Foland 1996, and Czamanske and Wones 1973). Note that the annite (Fig. 36) has shifted into two different directions: in the Poudrette dyke, it gained Al, and in the poikilitic nepheline syenite, it lost Al somewhat. The latter shift is attributed to the stronger peralkalinity of the fluid phase in the most evolved unit. Such a fluid can mobilize (dissolve) Al.

Feeley and Sharp (1996) have provided clear evidence for dehydrogenation of biotite phenocrysts in dacitic igneous rocks. In particular, they found unusually low OH contents and high Fe^{3+}/Fe^{2+} values in their biotite. It seems clear that the annite at Mont Saint-Hilaire can be expected also to have lost hydrogen. In general, under oxidizing conditions, annite decomposes to K-feldspar (sanidine), magnetite (or hematite) and hydrogen gas *via* a metastable phase rich in ferric iron and poor in hydrogen, namely "oxyannite" (Wones and Eugster, 1965). This "oxyannite" can be obtained through one of two mechanisms, i) loss of H₂ by replacement of OH-^{VI}Fe²⁺ by O-^{VI}Fe³⁺ (Eugster and Wones, 1962), which results in the hypothetical end-member KFe²⁺Fe³⁺₂AlSi₃O₁₂, and ii) loss of H₂ by conversion of all the Fe²⁺ to Fe³⁺, with loss of K, which results in the hypothetical end-member KFe¹⁺Fe³⁺₂AlSi₃O₁₂, and ii) loss of H₂ by conversion of all the Fe²⁺ to Fe³⁺, with loss of K, which results in the hypothetical end-member KFe¹⁺Fe³⁺₂AlSi₃O₁₂, and ii) loss of H₂ by conversion of all the Fe²⁺ to Fe³⁺, with loss of K, which results in the hypothetical end-member KFe¹⁺Fe³⁺₂AlSi₃O₁₂, and ii) loss of H₂ by conversion of all the Fe²⁺ to Fe³⁺, with loss of K, which results in the hypothetical end-member \Box Fe³⁺₃AlSi₃O₁₂. It is possible that an intermediate phase between i and ii has formed during hydrothermal alteration at Mont Saint-Hilaire, to explain the incipient loss of K in the interlayer.

On the basis of XRD and HRTEM study of altered annite (MSHT-2) it is likely that once structural defects in annite had increased to a certain level during the oxidation process, especially at more advanced stages of alteration, the 2:1 layered annite partly decomposed and re-assembled to form vermiculite-like layers, as is evident from XRD and HRTEM results (Chapter 6, Fig. 30). The formation of magnetite or ilmenite is a clear indication of oxidation in this complex (Chapter 5, *e.g.* samples MSHA-6 and MSHA-1). If this hypothesis is correct, most of the previous experimental studies of the mechanisms of biotite oxidation applying Mössbauer spectroscopy and X-ray diffraction should be reconsidered, because these methods cannot detect the presence of the type of defect reported in the present study.

Such decomposition of biotite by dehydrogenation is initiated with the formation of the planar defects conformable with the cleavage of the host annite. These defects may well be considered as symptoms of initial stages of the transformation of the mica to other minerals, *e.g.* mica to chlorite and vermiculite. Kogure and Nespolo (2000) reported two kinds of planar defects, one characterized by the excess of Fe and Mg and the other due to the deficiency of these elements, owing to the oxidation of biotite in the specimen of an "oxybiotite" (dehydrogenated biotite with ferric iron) from the Ruiz Peak rhyodacite, New Mexico.

Compositional features of the annite in the hornfels

In hornfels, in comparison with the other units, the annite is markedly more magnesian, and it is much richer in F. This finding can be explained by appealing to a lack of repulsion between Fe^{2+} and F in the octahedral positions. The local addition of the fluorine may well be due to the injection of synchritic magma in the hornfels (Fig. 24).

Chapter 8

Conclusions and suggestions for future work

Ten main conclusions emerge from this work:

- The annite present in the intrusive units exposed in the Poudrette quarry ranges in Fe/(Fe + Mg) from 0.74 to 0.98.
- 2) The F and Cl contents encountered are negligible in annite, although these constituents were present in the environment of growth.
- 3) The amount of Ti increases, and the amount of Mn decreases, with increasing Fe/(Fe + Mg) of the annite. The reason is crystal-chemical in the case of Ti, but geochemical in the case of Mn.
- 4) The arrangement of intrusive bodies (Fig. 6) and petrographic homogeneity of porphyritic and poikilitic nepheline syenites do not support derivation of individual units by crystal fractionation *in situ*. They were probably formed in different parts of the magma chamber, were subsequently but separately injected into their present position, and did not experience any significant interaction.
- 5) The porphyritic nepheline syenite [foyaite in Rajasekaran's (1967) system of nomenclature] is the most primitive syenitic unit exposed in the quarry.
- 6) With respect to annite composition, the poikilitic nepheline syenite is more evolved than the nepheline syenite in the Poudrette dyke. Therefore, the batch of magma that congealed as the Poudrette dyke intruded the evolved roof-zone rocks

of the Mont Saint-Hilaire complex, and was presumably derived from deeper in the laccolithic body.

- 7) It is the melt's composition that controls the order of crystallization, which then in turn controls the habit of the annite. The rock from the Poudrette dyke is a hypersolvus nepheline syenite in which the bladed annite was a liquidus phase; therefore the order of crystallization was "normal".
- 8) A "reverse" trend of crystallization (*i.e.*, mafic minerals last) characterizes the poikilitic nepheline syenite, a more strongly agaitic unit.
- 9) In the sodalite syenite, the progressive replacement of nepheline by sodalite led to gradational boundaries, with sodalite the encroaching phase. There is a strong textural similarity between sodalite syenite and the enclosing poikilitic nepheline syenite in the southeastern part of the quarry, which is explained by the hydrothermal origin of this unit. The texture is igneous, but the minerals present are judged to have been re-adjusted or transformed at a subsolidus stage. Note that this conclusion needs to be tested with more specimens of sodalite-bearing syenite exposed in the quarry.
- 10) Preliminary HRTEM investigations reveal the development of subtle oxidationinduced changes in the annite, leading to modification of bonding in the interlayer site, and giving rise to "vermiculite"-like sequences.

As for the future, the mica in the marble xenoliths and in partially melted hornfels would be appropriate subjects for further study. These units are likely to be the source of Mgrich, and in the case of the hornfels, more Al-rich biotite, tending toward the siderophyllite-eastonite join. In such micas, Fe^{2+} - F avoidance should be relaxed, and I would expect much higher F contents. Interestingly, Mandarino and Anderson (1989, Table E33) reported a mica with 5.38% with F by weight (electron-microprobe data). This mica has the composition of:

$$(K_{0.86}Na_{0.02}) (Mg_{2.30}Fe^{2+}_{0.13}Ti_{0.01}) (Si_{3.31}Al_{0.56}) O_{10} (F_{1.16}OH_{0.83})$$

This is in fact not phlogopite, as the authors claimed. Rather the mica has as its endmember the fluorine-dominant analogue of phlogopite, *i.e.*, the Mg-dominant analogue of fluorannite, but it is strongly subaluminous. This material will constitute a new species once it is well characterized.

It seems clear that HRTEM studies can reveal various new structures in oxidized derivatives of mica that could not be documented using other techniques. Although their volume ratio in the specimen in many cases is small, these structures can provide new insight about fields of stability and mechanisms of transformation.

The specimens described in this thesis focused on a specific mica, annite. Not only is annite one of the most important rock-forming minerals, but also it is stable when bombarded with electrons during HRTEM studies. The investigation should be expanded to other micas known to occur in the quarry, although radiation-damage problems may well be encountered, especially in Li-bearing micas. In particular, more work needs to be done on the nature of the "vermiculite"-like product; in the strict sense, vermiculite is a K-free, Mg-dominant derivative of phlogopite. What is the nature of its Fe-dominant equivalent?

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