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GEOLOGY OF THE NEW FOX ALTERATION ZONE

Laurie Lake, Manitoba

by

Bruce A. Barham, B.Sc (Hons.)

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

Department of Geology

Carleton University

Ottawa, Ontario

April 6, 1987

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Thesis

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Abstract

In the Laurie Lake-Dunphy Lakes area of the Lynn Lake Greenstone Belt, unusual rocks characterized by coarse-grained garnet, cordierite, orthoamphibole, and in some cases sillimanite and staurolite, occur. At the New Fox Alteration Zone, these rocks represent metasomatized and subsequently metamorphosed equivalents of mostly mafic to intermediate hornblende-bearing volcanic rocks, but are also developed in more felsic hornblende-bearing sedimentary and volcaniclastic rocks. Weakly altered to unaltered host rocks are characterized by calcic minerals including hornblende, epidote, titanite and andesine. The predominant type of altered rocks forms a stratiform layer characterized by calcium-poor mineral assemblages rich in gedrite, garnet and cordierite. Hornblende-bearing rocks are everywhere separated from Ca-poor gedrite-bearing rocks by cummingtonite-andesine rocks intermediate in calcium content. The progressive destruction of primary volcanic structures provides compelling evidence for derivation of the Ca-poor rocks by in situ hydrothermal alteration. Siliceous alteration and Ca-enriched alteration, containing clinopyroxene, are developed at the margins of the main stratiform zone of Ca-depleted rocks.

Mineral analyses from thirteen rocks are presented and it is shown that the distribution equation valid for ideal binary solutions

$$K_D = (x_{Mg}^A / (1 - x_{Mg}^A)) ((1 - x_{Mg}^B) / x_{Mg}^B)$$

where $x_{Mg} = Mg/(Mg+Fe^{+2})$ and A and B are ferromagnesian phases, adequately describes the distribution of Mg and Fe^{+2} . Amongst the five ferromagnesian phases cordierite, biotite, gedrite, cummingtonite and garnet, two naturally occurring four phase assemblages have the following distribution relationships

X_{Mg} :

cordierite^{1.81} biotite^{1.46} gedrite^{3.63} garnet
biotite^{1.18} cummingtonite^{1.38} gedrite^{3.63} garnet

where the numbers refer to the distribution coefficient (K_D).

In hornblende-cummingtonite assemblages, K_D varies with X_{Mg} which decreases with increased Mg tschermakite substitution ($Al^{IV}Al^{VI} = MgSi$) in hornblende. Considering Fe-rich mineral assemblages with garnet, the distribution relationships are:

X_{Mg} :

biotite $\approx$ cummingtonite^{1.16} hornblende^{4.45} garnet

Mineral assemblages in the New Fox Alteration Zone reflect medium grade metamorphism. Deduced conditions correspond to those of the sillimanite-muscovite zone and are consistent with a regional northeast-southwest increase in metamorphic grade. Garnet-biotite and garnet-cordierite exchange thermometry and qualitative estimates of pressure and X_{H_2O} give the following conditions of metamorphism;

$$T \approx 600^\circ C$$

$$P = 4-5 \text{ kb}$$

$$X_{H_2O} \approx 1$$

Suitable quartz-chlorite protoliths for the Fe-rich and Ca-depleted rocks typical of the New Fox Alteration Zone are observed in the geologic record and are being formed presently in active hydrothermal systems. A brief review of current basalt-seawater experiments and observations of active geothermal systems suggests that unmodified seawater would not be capable of producing the required iron-rich chloritic protoliths.

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I would like to express gratitude to Dave Baldwin for suggesting this study and taking a continued interest in it. Jim Chornoby and Rick Sawyer of Sheritt Gordon Mines Limited encouraged the study and allowed access to their accumulated information on the area. Lorne Adamitz provided enthusiastic assistance during the mapping.

My interest in petrology was greatly augmented through working for George Skippen as a teaching assistant. Much of the study is formulated after the work of Ralph Kretz, and his influence was instrumental to the content of the text. The suggestions of Dave Watkinson improved text content, format and flow.

I have benefitted immeasurably from a close working and social relationship with Edgar Froese; for his contribution and guidance throughout this study, I am deeply grateful. Bill Morrison kindly provided the use of his computer during the writing and editing stages. To these, and all the rest of my friends, family and contemporaries, I express thanks for their intangible contribution.

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Chapter 1: Introduction

1-1: Statement of Problem

Coarse-grained rocks of unusual composition, characterized by the presence of garnet, staurolite, cordierite, sillimanite and pale bronze or green amphibole were described from the Dunphy Lakes area of the Lynn Lake Greenstone Belt by Stanton (1949). One occurrence of such rocks is now known as the New Fox Alteration Zone (NFAZ). Stanton's (1949) work was incorporated in a report by Milligan (1960), but the occurrences of these rocks were not shown on the revised maps. Mustard (1974) reported cordierite-anthophyllite rocks from several localities in the Laurie Lake-Dunphy Lakes area, including the Lar Deposit (Elliot, 1984; Elliot and Appleyard, 1985) and attributed them to metamorphism of chlorite-rich zones. Lustig (1979) described metamorphosed alteration zones at the Fox Mine. In the recent mapping of Gilbert et al. (1980), some occurrences of rocks of unusual composition, reported by Stanton (1949), were recognized as altered volcanic rocks. Other occurrences, including rocks of the NFAZ, were merely indicated as porphyroblastic schist and their origin was not discussed. Gale (1983) used the designation New Fox occurrence and commented that the genesis of these porphyroblastic schists had not been determined, although he regarded similar rocks at the Lar deposit as constituting an alteration zone. Stewart and Brewer (1984) briefly described the New Fox occurrence and on an unpublished map, dated December 1984, an alteration zone is shown. The New Fox occurrence was mentioned by Gunter and Yamada (1985) and dealt with briefly by Barham (1986) and by Barham and Froese (1986).

An understanding of the alteration zone requires the documentation of alteration types and their relation to unaltered rocks. In a metamorphic terrane, the phase relations and conditions of metamorphism must

be established. During the summer of 1985, the New Fox Alteration Zone was mapped and emphasis on transitions between altered and unaltered rocks established the field relations of alteration types. Standard petrographic documentation of representative rocks was undertaken to study mineral compatibilities in altered and unaltered rocks. The composition of minerals from various assemblages was obtained by electron-microprobe analysis enabling a discussion of phase relations at imposed metamorphic conditions. The origin of the unusual rocks of the New Fox Alteration Zone is considered in light of these results.

1-2: Regional Setting

The Lynn Lake Greenstone Belt (LLGB) of Archean age (Clark, 1980; Baldwin et al., 1985) lies within the southern Churchill Province of Manitoba. The belt is a domain of metamorphosed volcanic, sedimentary and plutonic rocks bounded by the Kisseynew Sedimentary Gneiss Belt to the south and the Southern Indian Gneiss Belt to the north. Figure 1 presents the regional geology of the westernmost LLGB in the Laurie Lake-Dunphy Lakes area. The New Fox Alteration Zone occurs in a unit of sedimentary and volcanic rocks on the northern margin of the belt.

Reconnaissance mapping in the Lynn Lake area led to the recognition of an older pre-Sickle Group of volcanic rocks unconformably overlain by the Sickle Series of quartzofeldspathic sediments (Norman, 1934; Henderson et al., 1936; Downie, 1936). In a detailed study, Bateman (1942, 1945) used the term Wasekwan Series for pre-Sickle rocks in the vicinity of McVeigh Lake and recognized post-Wasekwan intrusive rocks, possibly of pre-Sickle age. Allan (1946) extended the term Wasekwan to include pre-Sickle rocks near the town of Lynn Lake. Stanton (1949) and Milligan (1952) suggested that the pre-Sickle rocks of the Laurie Lake-Dunphy Lakes area are continuous with the Wasekwan of Lynn Lake. Campbell (1969) revised the names to Wasekwan and Sickle Groups.

(facing page 3)

Figure 1: General geology of the Laurie Lake-Dunphy Lakes region. Symbols are on high grade side of metamorphic zone boundaries. (after Gilbert et al., 1980; modified after Jackson and Gordon, 1986; inset simplified after Syme, 1985).

The early geological work in the region, as well as the results of an extensive mapping program by the Manitoba Mines Branch, were summarized by Milligan (1960). More recent revisions and additions, based on a four-year mapping program by the Manitoba Mineral Resources Division, were presented by Zwanzig (1976) and Gilbert *et al.* (1980). Syme (1985) detailed the petrochemistry of the LLGB and emphasized similarities with Cenozoic island arc environments.

In most areas, the Sickle Group separates Wasekwan volcanic and sedimentary rocks from the Kiseynew Gneiss Belt, but in the Laurie Lake area (Fig. 1), the Wasekwan Group may be traced southwestwards into the Kiseynew terrane (Zwanzig, 1976). The transition is accompanied by changes in structural style, lithology and an increase in metamorphic grade from northeast to southwest (Zwanzig *et al.*, 1980; Gilbert *et al.*, 1980; Jackson and Gordon, 1986). High grade correlatives of Wasekwan Group rocks in the southern part of Figure 1, are known as the Burntwood River Metamorphic Suite. Table 1 gives an interpretation of the tectonic evolution of the Lynn Lake region taken from Gilbert *et al.* (1980).

In the Lynn Lake region, deformation and plutonism occurred during (D1) and after (D2) deposition of Wasekwan Group rocks. Sickle Group sediments were unconformably deposited on deformed Wasekwan Group rocks. A later deformation (D3), affecting rocks of both groups at the margins of the greenstone belt, produced recumbent folds in Sickle Group sediments. D3 structures were folded by north- and east-trending folds into domal complexes (D4, Table 1, Fig. 1). Folding was accompanied by regional foliation development and metamorphism (Gilbert *et al.*, 1980).

In the Laurie Lake region the early deformations are not readily discernible and northeast trending D4 structures and attendant medium to high grade metamorphic assemblages dominate the rocks (Gilbert *et al.*, 1980; Jackson and Gordon, 1985; Table 1). D4 folds (D2 of north margin

Table 1: Tectonic Evolution of the Lynn Lake region***	
Lynn Lake Greenstone Belt	Kissaynew Sedimentary Gneiss Belt (north margin)
faulting, northerly, northwest	
D5 continued development of foliation, cataclasis (northeasterly); open cross folding	folding, faulting (northeasterly) D3
pegmatite intrusion	
felsic - intrusion ** 1765 ± 100 Ma	
metamorphism locally retrograde	
D4 shearing, faulting (east & northeasterly) formation of basins & domes (north & east) trending → development of foliation, regional metamorphism	D2
mafic to felsic intrusion	
D3 thrusting at margins of belt e.g. Tod Lake	recumbent folding e.g. Laurie Lake D1
diorite intrusion	
sedimentation	
Sickle Group (Shallow water, terrestrial)	Sickle Metamorphic Suite
D2 uplift, erosion, faulting, tilting Pre - Sickle Intrusion * 1876 ± 6 Ma	
D1 folding, faulting (east-northeasterly)	Burntwood River Metamorphic Suite
Wasekwan Group mafic to felsic intrusion mafic to felsic volcanism * 1910 ± 15 Ma felsic volcanism, sedimentation mafic volcanism	deep water sedimentation
*** - after Gilbert et al. (1980)	
** - Rb-Sr whole rock age, Clark (1980)	
* - U-Pb zircon age, Baldwin et al. (1985)	

of Kisseynew terrane, Table.1) postdate regional foliation development and thus deform secondary foliations and pre- to syn-tectonometamorphic pegmatites (Jackson and Gordon, 1985). Lineations are coaxial with minor D₃ folds and are interpreted as synchronous with foliation folding. Linear fabric not coaxial with D₄ folds is interpreted as refolding of earlier large scale folds (Thomas, 1980).

The metamorphic gradient of the LLGB was approximately deduced by Gilbert et al. (1980) and Zwanzig et al. (1980). Metamorphic grade increases from upper greenschist or lower amphibolite facies near Lynn Lake to upper amphibolite facies in the Laurie Lake area. In the Laurie Lake-Dunphy Lakes area, Zwanzig et al. (1980) marked the first appearance of sillimanite in greywacke (Fig. 1). Most of the Laurie Lake-Dunphy Lakes area lies within the sillimanite zone (Fig. 1) but coarse-grained, euhedral andalusite occurs in biotite schist from Dunphy Lakes. Fifty kilometres east of the Fox Mine (Fig. 1), in the alteration zone of the Nicoba deposit, kyanite is stable with andalusite (Barham, 1985). Between these areas, andalusite-bearing assemblages are common (Gilbert et al., 1980) and the possibility of a kyanite-andalusite-sillimanite transition in the LLGB exists.

Milligan (1952) and Zwanzig et al. (1980) mapped a large fault (Tod Lake Fault) which extends from Dunphy Lakes to south of South Bay of Laurie Lake (Fig. 1). Jackson and Gordon (1986) mapped an isograd in Sickle Group sediments tentatively based on the reaction

The isograd has a dextral offset of 3.5 km along this fault.

Reaction (1) marks the boundary between medium and high grade metamorphism (Winkler, 1979) in the Laurie Lake-Dunphy Lakes area. In mafic rocks, epidote is stable to the low temperature part of high grade metamorphism (Jackson and Gordon, 1985). Upgrade from reaction isograd

(1), rocks become progressively more migmatitic with increases in the variety and amount of leucosome present, in the grain size of mesosomes, and in the increasingly aluminous nature of the melanosomes (Jackson and Gordon, 1985, 1986). Southwest of the line marking the approximate limit of extensive anatexis (Fig. 1), leucosome in greywacke-gneiss forms about 40% of the rock by volume (Gilbert et al., 1980).

Jackson and Gordon (1986) established that metamorphic pressures and temperatures increased from about 4.5 kb and 650°C near the NFAZ on the Laurie River, to about 5.5 kb and 750°C near the southern end of South Bay, consistent with a regional northeast-southwest increase in metamorphic grade.

Chapter 2: Geology of the New Fox Alteration Zone

2-1: Introduction

The New Fox Alteration Zone (NFAZ) outcrops within a south-facing, steeply north-dipping sequence of hornblende-bearing volcanic and sedimentary rocks of the Wasekwan Group (Fig. 2, in pocket). Facing direction is indicated by graded bedding in sediment gravity flows and by volcanic pillow morphology. Intrusive rocks north of the field area are interpreted by Gilbert *et al.* (1980) to be post-Sickle in age (Fig. 1). At the NFAZ, crosscutting intrusive rocks are interpreted to have a similar age but a pre-Sickle age cannot be ruled out.

Interpretation of structural elements suggests at least two deformations, one preceding (D4) and one postdating (D5) peak metamorphic temperatures. A prominent east-west foliation deforms Wasekwan Group rocks and crosscutting intrusive rocks. This foliation is folded by observed minor northeast plunging folds. In Table 1, this foliation is shown as corresponding to D4 of the LLGB which correlates with D2 of the north margin of the Kisseynew Sedimentary Gneiss Belt. Evidence for an earlier deformation is inconclusive. Thus in the vicinity of the New Fox Alteration Zone, post-Sickle intrusion was followed by D4 foliation development and folding. However, D4 folding appears to have outlasted D4 foliation development. Structural elements closely correspond to those described by Jackson and Gordon (1985, 1986) for the Laurie Lake area.

2-2: Structure

D4 foliation is subparallel to lithologic contacts and dips steeply. Observed minor folds deform D4 foliation and are closed to isoclinal, north-east trending and steeply plunging (Plate 1A). Lineations (mineral, clast elongation) are coaxial with minor folds. Figure 3A,B

Figure 3: Equal area plots of structural elements. A: poles to 130 foliations, B: Linear elements, C: Evidence for a late deformation.

shows equal area plots of all lineations (fold axis, mineral and clast elongation) and poles to foliations. The lineations define a pole to the girdle of poles to foliations suggesting that development of the lineations was synchronous with folding of foliations.

One minor isoclinal fold in the south-central part of the map area plunges southwest. Gilbert et al. (1980) describe an early deformation (D1) which produced isoclinal folds in Wasekwan Group rocks; this fold may represent a D1 fold reoriented during D4.

Peak metamorphic temperatures were achieved following D4 folding. Minerals in rocks with strong foliation are recrystallized. Hornblende and cummingtonite-rich rocks are typically nematoblastic. Orthoamphibole is nematoblastic in rocks with cummingtonite and garnet. In rocks with cordierite, orthoamphibole generally occurs as coarse, radiating bundles without apparent foliation, although some strongly foliated and lineated cordierite-orthoamphibole rocks do occur.

A later deformation (D5) is evident in some outcrops where a penetrative foliation cuts earlier formed (D4) foliation. A parallel, shallow, northeast plunging orthoamphibole lineation accompanies D5 foliation in some rocks of appropriate composition. In Figure 3C, two observations of D4 foliation transected by D5 penetrative foliation are plotted. Several measurements of an intersection lineation measured in the plane of D4 foliation are plotted in Figure 3C and presumably formed during D5. Gilbert et al. (1980) report a weak hornblende foliation which truncates earlier foliation parallel to stratification.

In the central area, lithologic units define a north-plunging, open synclinal structure probably related to NE cross folding during D5 (Fig. 2, Table I). Discontinuities of lithologic contacts across topographic depressions suggest dextral faulting. Stanton (1949) also showed a fault with apparent dextral offset in the western topographic depres-

sion. In outcrops nearby, late to post-metamorphic shear zones crosscut earlier foliation (Fig. 3B, Plate 1B). The shear zones have the same recrystallized mineral assemblage as the host rock. The postulated faults, shear zones and rarely observed D5 foliation are approximately parallel and considered to be synchronous. Structural elements in metasomatized rocks reflect the same tectonometamorphic history as revealed in host rocks.

2-3: Lithology

The NFAZ is developed in interlayered volcanic and sedimentary rocks of the Wasekwan Group in a border zone adjacent to a large intrusion of post-Sickle granodiorite. Stanton (1949) mapped the area in this vicinity as 'hybrid rocks' to draw attention to the disruption of Wasekwan Group rocks by later intrusions. On the basis of field relations, it can be shown that rocks of unusual composition are metasomatically derived from volcanic or sedimentary rocks. Some rocks have enhanced concentrations of quartz and others are enriched in calcic minerals. Comparison of weakly altered to unaltered rocks with strongly altered rocks shows Ca-depletion to be the dominant alteration. The present composition of Ca-depleted rocks requires chloritic protoliths and postulated metamorphism of a chloritic alteration zone is consistent with field relations. The central part of the thesis area is least disturbed by the late intrusions and the lithologic units shown in Figure 2 form a local stratigraphic succession.

Unit 1 consists of well-layered to massive hornblende-plagioclase-biotite psammite. These rocks are best exposed in the eastern outcrop area of Fig. 2, and similar rocks occur in the northernmost part of the central area. The contact with unit 2 is not exposed but there is an abrupt change to rock types of unit 2.

Mafic to intermediate volcanic flows and subordinate volcanoclastic

rocks of unit 2 overlie unit 1. Massive quartz-plagioclase-hornblende-amphibolite is the dominant rock type in unaltered outcrops, but discontinuous outcrops of pillowed volcanic rock occur throughout this unit. Pillows are particularly well preserved south of the lake in the central outcrop area and suggest south-facing tops. There it is possible to distinguish an upper flow of concentrically zoned, amygdaloidal pillowed rock from a lower flow consisting of tightly packed, homogeneous pillows (Plate 1C, 1D). Intercalated with the massive and pillowed flow rock is subordinate layered amphibolite. In several places, a monolithic mafic volcanic psephite (fragment size > sand) is observed near the contact with unit 3 (Fig. 2).

Unit 3 includes sedimentary and volcanoclastic rocks of variable composition. Principal lithologic types are layered quartz-hornblende-plagioclase psammite, heterolithic psammite and matrix-supported heterolithic psephite. The heterolithic rocks contain quartzofeldspathic sedimentary and felsic volcanic clasts and may include mafic volcanic clasts in a quartzofeldspathic matrix. Individual beds may display normal grading with parallel laminated bed tops (Plate 1E) giving south-facing stratigraphic tops. Monolithic felsic volcanic psephite occurs in the eastern outcrop area and has been assigned to this unit. Layered mafic to intermediate hornblende-plagioclase psammite also occurs.

Unit 4 consists of layered and massive, rusty-weathering plagioclase-biotite-hornblende psammite which commonly contains concentric hornblende-plagioclase lenses (Plate 1F). The contact with unit 3 is gradational over a narrow stratigraphic thickness with interbedding of thin rusty-weathering and buff-grey weathering beds. Finely disseminated hematite imparts the rusty colour to these rocks. Unit 4 is truncated at its top by post-Sickle intrusions.

2-4: Intrusive Rocks

Irregular bodies of intrusive rock ranging in composition from diorite to granite (field names) cut all supracrustal rock. These intrusive rocks are probably related to the large body of post-Sickle granodiorite immediately north of the map area (Fig. 1). Near the contacts with Wasekwan Group rocks, a heterolithic intrusion breccia is commonly formed (unit 5c, Fig. 2). D₄ foliation is continuous through post-Sickle intrusions and included xenoliths (Plate 1G). Tonalite dykes, some strongly deformed, are common within supracrustal rocks (Plate 1H). Crosscutting relationships of tonalite dykes support two ages of intrusion.

2-5: Alteration

Three principal alteration types are recognized at the NFAZ. Ca-depleted rocks are preferentially developed in a stratiform layer in mafic to intermediate volcanic rocks of unit 2 but also occur above and below this unit in sedimentary and volcanoclastic rocks. Patches of weakly altered to unaltered hornblende-bearing rocks are common within Ca-depleted rocks and the proportion of Ca-depleted rocks increases towards the top of unit 2 (Fig. 2). Ca-rich alteration and siliceous alteration is irregularly developed at the margins of the main zone of Ca-depleted rocks.

Mafic volcanic rocks commonly display epidotized patches, particularly in pillow cores. This alteration is of regional extent in rocks of the Wasekwan Group (Syme, 1985) and, at the NFAZ, appears to be earlier than locally observed siliceous alteration and Ca-Na depletion. Calcium-enriched alteration is also observed as rare, irregular hornblende-epidote-clinopyroxene veins in hornblende-amphibolites. Similar alteration is more extensively exposed in the alteration zone of the Lar deposit (Fig. 1, Elliot and Appleyard 1985). The epidotized patches and

Plate 1: Host rocks of the New Fox Alteration Zone

Plate 1A: Minor fold in Wasekwan Group rocks.

Plate 1B: Late- to post-metamorphic shear zone in cordierite-gedrite rock. The mineral assemblage in the portion of the rock with reduced grain size is also cordierite-gedrite.

Plate 1C: Concentrically zoned, amygdaloidal, pillowed, hornblende-amphibolite. Stratigraphic tops indicated towards top of photograph (unit 2).

Plate 1D: Hornblende-amphibolite characterized by small, massive pillows (compare with 1C above). Note the cummingtonite-plagioclase rich interpillow areas (unit 2)

Plate 1E: Sediment gravity flow displaying fining upward grading of dark amphibolite clasts and laminated bed top. Stratigraphic tops indicated towards left edge of photograph (unit 3).

Plate 1F: Calcic hornblende-plagioclase lenses in Unit 4.

Plate 1G: Post-Sickle tonalite intrusion breccia with heterolithic clasts of Wasekwan Group rocks. Note D4 foliation is continuous through the rock (unit 5c).

Plate 1H: Boudined tonalite dyke in coarse-grained, layered, cordierite-garnet-gedrite rock.

11/11/77

A

B

C

D

E

F

G

H

calcic veins are not exposed in the same areas and any relation between them is unclear.

Some poorly exposed quartz-rich rocks are present along a part of the contact of units 2 and 3 (Fig. 2). Patches of layered and fragmental rocks composed of medium-grained granoblastic quartz-plagioclase, commonly with magnetite, occur within biotite-hornblende-quartz-plagioclase psammite and psephite. Zones of Ca-depleted rocks, described below, are present within the siliceous rocks. Some layered very quartz-rich rocks may be related to chemical sedimentation, but field relations are inconclusive.

In mafic volcanic rocks, patches of magnetite-garnet-plagioclase-quartz and magnetite-plagioclase-quartz rock are present (Plate 2A). Some outcrops of quartz-rich rocks display epidote clots and ghost structures suggestive of replacement of pillowed volcanic rock (Plate 2B). Early deformed quartz-veins may be related to siliceous alteration (Plate 2C). Cumingtonite-quartz-plagioclase rocks are common and may be transitional between siliceous alteration and Ca-depleted rocks.

Gilbert *et al.* (1980) reported chert occupying interpillow voids in basalts from the Cockeram Lake - Fraser Lake area of the Lynn Lake Greenstone Belt. Interpillow areas at the NFAZ are commonly occupied by medium-grained granoblastic quartz-plagioclase rock with or without cumingtonite, hornblende and magnetite. These compositions are probably related to selective in situ alteration of an interpillow rock such as hyaloclastite, rather than chert precipitation.

The dominant alteration at the NFAZ is marked by progressive depletion in calcium and sodium. The first manifestation is the appearance of cumingtonite, commonly as patches with diffuse contacts (Plate 2A) or in pillow cores and margins (Plates 2D). Such alteration has also been reported from the Laurie Lake region (Jackson and Gordon, 1985) but

not associated with the more advanced stages of alteration.

More intensely altered rocks are composed predominantly of quartz-cummingtonite-plagioclase with patchy gedrite, garnet and magnetite. Primary structures, other than quartz-amygdales, are generally obliterated. However, in one outcrop, a one metre wide massive gedrite-garnet zone transgresses deformed pillow volcanic rock characterized by the assemblage plagioclase-cummingtonite-hornblende (Plate 2E). Pillows marginal to the massive zone are enriched in cummingtonite and the interpillow regions are more strongly altered to garnet-gedrite (Plate 2F). Primary structures are obliterated in the massive zone.

Intense alteration allows the appearance of large areas of quartz-garnet-gedrite rock, some of which is very garnet-rich (Plate 3A). The transition from hornblende to gedrite-bearing rocks, where abrupt, is represented by a narrow cummingtonite-rich boundary (Plate 3B).

The most intense calcium-sodium depletion results in the appearance of cordierite-garnet-gedrite rocks characterized by porphyroblasts of garnet, radiating gedrite and aggregates of cordierite (Plates 3C). These rocks are very heterogeneous displaying extreme local variation in bulk $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio, as indicated by alternating garnet-rich and cordierite-rich layers and patches (Plate 3D, 3E). Compositional layers alternate at decimetre to outcrop scale, but relatively large areas of garnet-rich and cordierite-rich (Plate 3F) rocks also occur.

Retrograde chlorite is common in the most intensely altered rocks and plagioclase is generally absent. Biotite is a common additional mineral in altered rocks and is usually evenly distributed, but also occurs in biotite-rich lenses. Tourmaline, pyrrhotite, chalcopyrite and pyrite are present in trace amounts in some outcrops of altered rock. Magnetite is common in all rock types and in some altered rocks occurs as large euhedral crystals (up to 1 cm).

(facing page 19)

Plate 2: Characteristics of altered rocks-A

PLATE 2A: PATCHES OF MAGNETITE-GARNET-PLAGIOCLASE-QUARTZ (A) IN MAFIC VOLCANIC ROCK WITH REMNANT PILLOWS. IN LIGHTER-COLOURED PORTIONS OF THE ROCK (B) CONTAINING CUNNINGTONITE, PILLOWS ARE OBSCURED.

PLATE 2B: PLAGIOCLASE-QUARTZ ROCK WITH EPIDOTE PATCH (EP). OVAL RIDGE AROUND EPIDOTE PATCH MAY REPRESENT REPLACED PILLOW MARGIN (SEE PLATE 2D).

PLATE 2C: INTENSE PYRAMITIC FOLDING OF QUARTZ-PLAGIOCLASE DYKES IN HORNBLende-PLAGIOCLASE AMPHIBOLITE. THESE DYKES MAY BE RELATED TO EARLY SILICIOUS ALTERATION.

PLATE 2D: MAFIC VOLCANIC ROCK WITH QUARTZ-PLAGIOCLASE FILLED INTERPILLOW AREAS AND CUNNINGTONITE-RICH PILLOW MARGINS (GREY). DARK AREAS ARE HORNBLende-BEARING. SOME PILLOWS HAVE EPIDOTE CONES (EP).

PLATE 2E: DEFORMED CUNNINGTONITE-PLAGIOCLASE-HORNBLende PILLOWED VOLCANIC ROCK.

PLATE 2F: STRONGLY ALTERED ROCK WITH QUARTZ-PLAGIOCLASE-CUNNINGTONITE REMNANT PILLOWS. LENSES OF COARSER GARNET-GRANITE PROBABLY OCCUPY INTERPILLOW SPACES.

(facing page 21)

Plate 3: Characteristics of altered rocks-B

PLATE 3A: VERY GARNET-RICH GARNET-GEODITE ROCK.

PLATE 3B: CUMINGTONITE-RICH ROCK (GREY) SEPARATING CORDIERITE-GARNET-GEODITE ROCK FROM UNALTERED PLAGIOCLASE-HORNBLende AMPHIBOLITE (DARK).

PLATE 3C: CORDIERITE-GARNET-GEODITE ROCK.

PLATE 3D: COMPOSITIONALLY LAYERED CORDIERITE-GARNET-GEODITE ROCK.

PLATE 3E: COMPOSITIONALLY LAYERED CORDIERITE-GARNET-GEODITE ROCK.

PLATE 3F: CORDIERITE-GEODITE ROCK.

Weakly altered to unaltered rocks at the NFAZ are composed primarily of minerals rich in Ca. Strongly altered rocks commonly do not contain calcium-bearing minerals. The gradual obliteration of primary volcanic structures suggests in situ alteration of predominantly mafic to intermediate volcanic precursors, although sedimentary and felsic volcanic rocks have also been altered. Small scale structures in volcanic rocks confirm the influence of primary porosity, such as interpillow voids. Siliceous rocks are concentrated near the top of the volcanic rocks and near the base of heterolithologic unit 3 and some of these siliceous rocks may be chemical sediments. Gedrite-cummingtonite-garnet rocks are present in these siliceous rocks and in some places appear to cut them. In the pillowed unit, quartz-rich patches may crosscut cummingtonite-rich alteration (Plate 2A). Some observations suggest that siliceous alteration postdates early epidote alteration (Plate 2B).

At the NFAZ, altered rocks have undergone the same structural and metamorphic history as their host rocks suggesting that the alteration predates regional tectonometamorphism. The alteration zone likely resulted from in situ hydrothermal alteration related to subseafloor hydrothermal convection.

2-6: Compatible Mineral Assemblages

Minerals which commonly occur in contact and without obvious textural signs of incompatibility, such as reaction rims, are taken to be in textural equilibrium. Staurolite occurs as armoured relics in cordierite and chlorite occurs in patches and replaces earlier formed minerals; these textures are taken to indicate that these minerals are not part of the stable mineral assemblage. In some rocks, hornblende and gedrite occur in close proximity, but are never observed in contact; at the imposed conditions of metamorphism, these minerals are taken to be incompatible.

Table 2 gives a list of minerals observed at the NFAZ as well as a tabulation of mineral and end member component abbreviations used in the text (Kretz, 1983). In Table 3, a list of compatible mineral assemblages is presented. ACF diagrams for Fe-rich, intermediate and Mg-rich bulk compositions, provide an approximate relationship between mineral assemblage, bulk composition and Ca-depletion (Fig. 4ABC). FeO and MgO behave as separate components and grouping them leads to crossing tie lines (Fig. 4).

Unaltered mafic volcanic rocks are composed primarily of Pl-Hbl (Plate 4A) but commonly contain some epidote. Irregular calcic veinlets in amphibolites, probably related to hydrothermal alteration, contain the assemblage Cpx-Ep-Hbl (Fig. 4). Magnetite is common in hornblende-bearing rocks, in many instances displaying quartzofeldspathic haloes (Plate 4B) which suggests oxidation of Fe silicates. A representative reaction can be balanced in terms of end members:

In some rocks, biotite and epidote are also present as reactants in reaction (2).

Calcium leaching of Fe-rich and intermediate compositions (Fig. 4A,B) leads to compositions in which Grt-Cum-Hbl and Hbl-Cum are stable. Qtz-Cum-Pl assemblages are common in slightly more altered rocks. Some Qtz-Cum-Pl rocks contain trace amounts of hornblende as pleochroic patches in larger cummingtonite grains (Plate 4C). Figure 4A,B illustrates the nature of a continuous reaction which may govern the stability of hornblende in rocks of this composition. The most aluminous hornblende is from assemblages with cummingtonite, plagioclase and garnet and increasing temperature or dehydration will cause the hornblende composition to retreat to lower Al content, producing more plagioclase

Table 2: Mineral Abbreviations

almandine	Alm	ilmenite	Ilm
*aluminosilicate	Als	K feldspar	Kfs
andalusite	And	Kyanite	Ky
annite	Ann	magnetite	Mag
anorthite	An	moscovite	Ms
anthophyllite	Ath	orthoamphibole	Oam
apatite	Ap	phlogopite	Phl
biotite	Bt	plagioclase	Pl
*carbonate	Cb	pyrope	Prp
chalcopyrite	Ccp	pyrite	Py
chlorite	Chl	pyrrhotite	Po
clinopyroxene	Cpx	quartz	Qtz
cordierite	Lrd	rutile	Rt
cummingtonite	Cum	sillimanite	Sil
epidote	Ep	spessartine	Sps
garnet	Grt	staurolite	St
gedrite	Ged	tourmaline	Tur
grossularite	Grs	titanite	Ttn
hematite	Hem	hervycite	Hc
hornblende	Hbl	zircon	Zrn

In text, mineral abbreviations are capitalized, and components in solution have lower case abbreviations (after Kretz (1983), except *)

	Lpx	EP	Hbl	Cum	Grt	Lnd	Qtz	Pl	St	Chl	Ap	Ms	Kfs	Ch	Tr	Mon	Mag	Ilm	Hem	Py	Ccp	Po	Ht
NFF-27							17	25	55														
NFF-33	10	30	50																				
NFF-36		10	15				10	15	47							3							
NFF-21		3	10					50	35		2					tr							
NFF-20		1	30				2	15	50														
NFF-9			35				10		54														
NFF-35			54				tr	4	40														
NFF-5			45				tr	5	49														
NFF-16			7				20	30	40							1							
NFF-10A			50					28	18							2							
NFF-13			30				25	6	50														
NFF-12			3				1	1	24														
NFF-12			55	20			4	15	45														
NFF-31			30	4				30	40														
NFF-19A			tr	25				25	7	35													
NFF-10			10	5			25	30	30														
NFF-1			tr	25			5	7	12														
NFF-8			5	70																			
NFF-2				38			5	15	35							12							
NFF-7				10			5	10	74							1							
NFF-19B			8	30				12	36														
NFFM-1			5	35				8	95														
NFF-14			15	20			2	40	22														
NFF-6			30	4			1	23	40														
NFF-30			2	30	5		tr	21	40														
NFFM-4			25	25	10			17	20														
NFF-28			15	15	5		2	15	35														
NFF-26					10	15	1	27	20														
NFF-17					2	10	30	27	30														
NFFM-3					5	5	5	10	5														
NFFM-6					10	5	7	10	65														
NFF-16					8	40	20	22	5														
NFFM-4					40	25	15	16															
NFFM-1A					25	40	20	6															
NFF-32					35		30	15	20														
NFF-32A					30		24	12	32														
NFF-14A					25		40	10	20														

Table 3: Observed Mineral Assemblages (visual estimates of modal proportion) where only covered thin sections are available

Analyses of silicate minerals appear in the Appendices. ▲ - retrograde mineral 0 - exsolution lamellae in Ilmenite
 Hbl not seen in contact with Grt ② - armoured relic, St in Grt, Py in Mag + Fe hydroxide(?) + exsolution lamellae in Magnetite

(facing page 27)

Figure 4: ACF diagrams for the amphibolite facies (A = Al_2O_3 , C = CaO, F = FeO + MgO). A: Fe-rich bulk compositions, B: intermediate bulk compositions, C: Mg-rich bulk compositions.

and cummingtonite (Robinson *et al.*, 1982). The reaction may be represented as

Cummingtonite contains virtually no Al and this reaction transfers Al from octahedral coordination in hornblende to tetrahedral coordination in plagioclase. Decompression should also favour the reactants of reaction (3) (Robinson *et al.*, 1982).

Further Ca leaching allows the formation of gedrite, commonly coexisting with cummingtonite and garnet (Plate 4D, Fig. 4B). In more magnesian rocks, garnet is absent (Fig. 4C). Figure 4C is drawn to allow coexistence of Hbl-Pl with low-Al orthoamphibole in low-Al magnesian rocks; however the appropriate bulk compositions are not present at the NFAZ.

Intense leaching of Ca gives mineral assemblages commonly devoid of plagioclase. In intermediate bulk compositions, Crd-Grt-Ged is stable (Plate 4E, Fig. 4B). Some rocks with this mineral assemblage contain grains of staurolite armoured by cordierite (Plate 4F). Intensely altered, very magnesian rocks contain the assemblage Crd-Ged (Plate 4G, Fig. 4C).

Most mineral assemblages at the NFAZ are adequately accounted for by progressive leaching of Ca from predominantly mafic volcanic rocks of intermediate bulk Fe/(Fe+Mg) ratio. Very magnesian Crd-Ged rocks and ferruginous Ged-Grt rocks probably require Mg and Fe enrichment, respectively.

Magnetite and ilmenite are present as subhedral to euhedral grains in virtually all rocks sampled at the NFAZ. They commonly occur together in oxide patches (Plate 4H) and also as separate matrix grains. Pyrite occurs frequently, usually with some chalcopyrite and always

armoured by magnetite and/or a convoluted mass of fine-grained, optically indiscernible material (Fe hydroxides?). Pyrrhotite was identified in three samples in apparent textural equilibrium with silicate minerals. Chalcopyrite also occurs in trace amounts as inclusions in garnet, gedrite and magnetite, as well as forming rare matrix grains.

A variety of exsolution textures were recognized in opaque grains. Hematite lamellae are common in ilmenite grains and also occur in magnetite (Plate 4H). Rare ilmenite and herynite exsolution lamellae are recognized along crystallographic planes in magnetite.

Plate 4: Textural features of New Fox Alteration Zone
Rocks in thin section

Plate 4A: Quartz-hornblende-plagioclase rock.

Plate 4B: Magnetite-quartz-hornblende-plagioclase rock with plagioclase-rich haloes around magnetite.

Plate 4C: Quartz-cummingtonite-plagioclase rock. Dark patches in centres of larger cummingtonite grains are hornblende.

Plate 4D: Quartz-garnet-gedrite-cummingtonite-plagioclase rock.

Plate 4E: Quartz-cordierite-garnet-gedrite rock.

Plate 4F: Remnant staurolite in cordierite in a quartz-cordierite-biotite-gedrite-garnet rock.

Plate 4G: Foliated quartz-gedrite-cordierite rock. Note oriented magnetite and ilmenite inclusion trails.

Plate 4H: Ilmenite-magnetite oxide patch. Crystallographically controlled exsolution lamellae in magnetite are hematite.

Scale for Plate 4A to Plate 4G:

0 1
mm

Scale for, Plate 4H:

0 0.5
mm

Chapter 3: Metamorphic Mineralogy

3-1: Introduction

In this chapter, the mineral analyses from 13 rocks are presented to examine the variation in composition of silicate phases. Graphical techniques are employed to demonstrate a close approach to thermodynamic equilibrium among phases which occur frequently in contact and without obvious textural indications of incompatibility. Electron microprobe analyses were performed by M. Bonardi of the Geological Survey of Canada. Appendix A contains electron microprobe data for minerals from 10 rocks and a discussion of the operating conditions and accuracy of the results. Some titrimetric determinations of FeO in hornblende were performed at the University of Ottawa under the direction of John Loop and are combined with electron microprobe results in Appendix B. The precision of the results is treated in the appendices after a method discussed by Kretz (1985).

3-2: Treatment of Analyses

Electron microprobe analyses of complex Fe-Mg silicates are commonly reported on the basis of assuming all iron to be ferrous. Some minerals in question here are conveniently and justifiably treated in this fashion, but in the case of hornblende, and to a lesser extent, biotite and aluminous orthoamphibole, ferric iron is commonly a significant component (Hawthorne, 1981, 1983; Essene, 1982).

Mineral separates of hornblende from three simple hornblende-plagioclase amphibolites were chosen for titrimetric determination of ferrous iron by the method described in Appendix B. Ferric iron was determined by difference from total iron as obtained by electron microprobe analysis. An average $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio for the three wet determinations of 0.44 was applied to most other hornblende specimens. However, in

comparing garnet-present and garnet-absent assemblages, the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio of hornblende is significantly lower if coexisting with garnet (Graham and Powell, 1984). Jen and Kretz (1980) report Fe_2O_3 determinations in hornblendes from five Hbl-Grt pairs from the Adirondack region. Their average $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio of 0.24 was applied to hornblende from samples NFF-1 and NFF-10.

For aluminous orthoamphibole and biotite, all Fe is treated as FeO and the limitations of this assumption are discussed in the text. All analyses were recalculated on the basis of appropriate numbers of oxygen (Deer et al., 1966).

3-3: Classification of Mineral Species

3-3a: Amphiboles

Individual point analyses of some orthorhombic amphiboles show considerable variation in major element composition. Total Fe is nearly constant but Na and Al vary inversely with Si and Mg. Microscopically, orthoamphiboles are uniformly pleochroic and display no textures suggestive of two coexisting species (Spear, 1980). Optically indiscernible exsolution lamellae may be present. Robinson et al. (1982) presented detailed analyses of zoned grains showing this chemical variation and considered it to represent retrogression of high Na-Al gedrite to lower Na-Al compositions.

Figure 5 was constructed by averaging high-Al and low-Al point analyses of inhomogeneous grains and plotting tetrahedral Al versus $\text{Fe}/(\text{Fe}+\text{Mg})$. The low-Al averages consistently plot within the high-Al part of the anthophyllite field and the high-Al averages fall in the gedrite field. This inhomogeneity probably resulted from intersection of the crest of the orthoamphibole solvus, and exsolution of submicroscopic anthophyllite lamellae during cooling of the rocks.

Other orthoamphibole analyses of similar $\text{Fe}/(\text{Fe} + \text{Mg})$ show little

Figure 5: Compositional inhomogeneity of orthoamphiboles.

variation in Si, Al, Mg and Na, and plot as gedrites in Figure 5. The most magnesian orthoamphibole plots narrowly within the gedrite field, consistent with less edenite ($\text{NaAl}^{\text{IV}} = \square \text{Si}$) and Mg tschermakite ($\text{Al}^{\text{VI}}\text{Al}^{\text{IV}} = \text{MgSi}$) exchange with decreasing $\text{Fe}/(\text{Fe}+\text{Mg})$ (Spear, 1980).

At peak metamorphic conditions, presently inhomogeneous orthoamphiboles are considered to have been homogeneous hypersolvus gedrites. As such, an attempt should be made to integrate the low-Al and high-Al points because the peak metamorphic composition should be inbetween them. However, the low-Al points are present only in some grains suggesting that exsolution lamellae, if present, are probably so fine that they are usually not resolved by the electron probe. The high-Al points are considered to reflect peak metamorphic compositions and low Na-Al point analyses were rejected in considering phase relations. Averages of these low-Al points appear with the appropriate high-Al average in Appendix A.

Spear (1980) estimates the crest of the orthoamphibole solvus to be at $600 \pm 25^\circ\text{C}$ and $\text{Fe}/(\text{Fe}+\text{Mg})$ of 0.40. If the interpretation of inhomogeneity is correct, analyses of gedrite grains suggest a quench temperature of higher than 600°C . This is further on shown to be consistent with phase relations and temperatures from exchange thermometry.

Analyses of amphiboles are plotted on the classification diagrams of Leake (1978) in Figure 6. Orthoamphibole analyses (High-Al averages) fall within the aluminous gedrite field. Calcic amphiboles, for which there are wet chemical determinations of Fe^{+2} , are found to be high Na, Al^{+3} , and Fe^{+3} edenite and magnesian hastingtonite varieties but are referred to hereafter by the field name hornblende. Iron in Fe-Mg-Mn monoclinic amphibole can be accurately treated as all ferrous (Hawthorne, 1981, 1983) and analyses of these minerals give intermediate $\text{Fe}/(\text{Fe}+\text{Mg})$ ratios.

Calcic Amphiboles: $(Na+K) \geq 0.5, Ti < 0.50, Fe^{+3} \leq Al^{IV}$

Figure 6: Amphibole classification diagrams (Leake, 1978).

3-3b: Garnets

Analyzed garnets are predominantly almandine (alm_{69-77}) with moderate amounts of grossularite (grs_{3-9}) and spessartine (sps_{1-6}) components. Compositional zoning in two garnets is shown in Figure 7 (analyses in Appendix A). Rim compositions are depleted in pyrope and $\text{Fe}/(\text{Fe}+\text{Mg})$ increases at the margins of the grains. Jackson and Gordon (1986) report spessartine-rich and pyrope-depleted rims from Laurie River southwest of the NFAZ (Fig. 1). Spessartine component gives a flat profile in garnets from the NFAZ. In view of the tendency for $\text{Mg}/(\text{Mg}+\text{Fe})$ to increase with metamorphic grade (Thompson, 1976; Essene, 1982; Tracy, 1982), Mg-depleted garnet rims will be considered retrograde adjustment for the purposes of applying an exchange geothermometer.

3-3c: Sheet Silicates

Biotite compositions are plotted in the biotite quadrilateral in Figure 8A and define a trend to more aluminous compositions with increasing $\text{Fe}/(\text{Fe}+\text{Mg})$. A biotite inclusion in garnet from a biotite free Grt-Crd-Ged rock is considerably more iron-rich than biotite that coexists with Grt-Crd-Ged in other rocks. Retrograde chlorite compositions fall within the magnesian ripidolite field (Fig. 8B). A chlorite inclusion from the same garnet, is the most iron-rich chlorite found and is more iron-rich and aluminous than matrix retrograde chlorite. The chlorite and biotite inclusions may represent phases shielded from complete reaction.

3-3d: Other minerals

Plagioclase composition varies within narrow limits from An_{38} to An_{45} and is not related to mineral assemblage or bulk composition. Cordierite and included staurolite show little variation in composition. A titanite analysis from sample NFF-5, is listed in Appendix B. Opaque grains were identified in polished section using reflected light micro-

Figure 7: Compositional profiles through garnet

Figure 8: Classification of sheet silicates. A: Biotite quadrilateral, B: Chlorite classification.

scopy and are listed with the total mineral assemblage in Table 3.

3-4: Evaluation of $\text{Fe}^{+2}:\text{Mg}$ exchange equilibrium

3-4a: Introduction

Ferromagnesian minerals are predominant constituents of New Fox rocks and, at the imposed conditions of metamorphism, the relative distribution of ferrous iron and magnesium between coexisting minerals will be governed by solid-solid exchange reactions. As an example, consider the commonly observed mineral pair cummingtonite-gedrite, for which the following equilibrium may be written;

or on the basis of one atom of Fe and Mg per formula unit;

At given P and T, reaction equilibrium is given by

$$\bar{G}_{\text{Fe-Cum}} + \bar{G}_{\text{Mg-Ged}} = \bar{G}_{\text{Mg-Cum}} + \bar{G}_{\text{Fe-Ged}}$$

where $\bar{G}$ is the partial molar Gibbs free energy, or chemical potential.

Also;

$$\Delta G^0 = -RT \ln K - \int_{P=1}^P \Delta V dP$$

where K is the equilibrium constant in terms of activities, ΔG^0 is the standard Gibbs free energy of reaction and ΔV is the volume change of reaction. The standard state is the pure substance at 1 bar and the temperature of interest. The unit activity state is the pure substance at specified P and T. A common approximation is that the volume term is independent of pressure and temperature over a limited range (Skippen, 1975; Froese, 1976), and the relation reduces to

$$\Delta G^0 = -RT \ln K - \Delta V(P-1)$$

For equilibrium (5)

$$K = (a_{\text{Mg-Cum}}^{\text{Cum}}) (a_{\text{Fe-Ged}}^{\text{Ged}}) / (a_{\text{Fe-Cum}}^{\text{Cum}}) (a_{\text{Mg-Ged}}^{\text{Ged}})$$

where a is the activity.

Activity is equal to mole fraction (X) times an activity coefficient (γ) and

$$K = ((X_{\text{Mg-Cum}}^{\text{Cum}}) (X_{\text{Fe-Ged}}^{\text{Ged}}) / (X_{\text{Fe-Cum}}^{\text{Cum}}) (X_{\text{Mg-Ged}}^{\text{Ged}})) \\ ((\gamma_{\text{Mg-Cum}}^{\text{Cum}}) (\gamma_{\text{Fe-Ged}}^{\text{Ged}}) / (\gamma_{\text{Fe-Cum}}^{\text{Cum}}) (\gamma_{\text{Mg-Ged}}^{\text{Ged}}))$$

Assuming ideal ionic solution, activity coefficients are unity and activity is equal to mole fraction. Further assuming the limiting case of a binary solution of Fe^{+2} and Mg (constant Al), the activities may be written as;

$$a_{\text{Mg-Ged}}^{\text{Ged}} = (X_{\text{Mg-Ged}}^{\text{Ged}}) = (\text{Mg}/(\text{Fe}+\text{Mg})) \\ a_{\text{Mg-Cum}}^{\text{Cum}} = (X_{\text{Mg-Cum}}^{\text{Cum}}) = (\text{Mg}/(\text{Fe}+\text{Mg}))$$

and similar relations hold for the Fe end members. The equilibrium constant can now be expressed in the form of atomic fractions

$$K = (\text{Mg}/(\text{Fe}+\text{Mg}))_{\text{Cum}} (\text{Fe}/(\text{Fe}+\text{Mg}))_{\text{Ged}} / (\text{Fe}/(\text{Fe}+\text{Mg}))_{\text{Cum}} (\text{Mg}/(\text{Fe}+\text{Mg}))_{\text{Ged}}$$

The quotient on the right side of the equation is known as the distribution coefficient (K_D); it is equal to the equilibrium constant for ideal solutions. Following the convention of Kretz (1978), and defining X_{Mg} as $\text{Mg}/(\text{Fe}+\text{Mg})$, the quotient may be rewritten;

$$K_D = (X_{\text{Mg}}^{\text{Cum}} / (1-X_{\text{Mg}}^{\text{Cum}})) ((1-X_{\text{Mg}}^{\text{Ged}}) / X_{\text{Mg}}^{\text{Ged}})$$

K_D is a function of T and P and for an assumption of approximately ideal ionic solution, K_D will remain nearly constant at given P and T over all X_{Mg} , as has been shown by Kretz (1978) for some rocks metamorphosed to amphibolite grade. However, many ferromagnesian minerals are not ideal solutions. Amphiboles, for instance, have 4 non-equal octahedral sites which Fe^{+2} and Mg can occupy ($M1, M2, M3, M4$). Still a mineral can display nearly ideal behaviour even if X_{Mg} is not the same on different sites, as Jen and Kretz (1981) demonstrated for orthopyroxene. With non-ideal mixing, K_D may vary with X_{Mg} (Kretz, 1961, 1963) or if the solution is

not binary, with concentration of elements which do not participate in the exchange reaction, such as Al and Fe^{+3} in hornblende (Ramberg, 1952).

K_D is commonly represented by plotting X_{Mg} of coexisting minerals (Kretz, 1961). Figure 9A shows X_{Mg} of cummingtonite versus X_{Mg} of gedrite and demonstrates that $K_D = \text{constant}$ provides a satisfactory description of the relation between X_{Mg} of the two minerals. These data may be plotted as tie lines on a conventional phase diagram, shown in Fig. 9B, as discussed by Froese (1976).

An evaluation of $\text{Fe}^{+2}:\text{Mg}$ exchange equilibrium for New Fox rocks includes the ferromagnesian phases hornblende, cummingtonite, gedrite, garnet, cordierite and biotite. Exchange reactions similar to the example involving cummingtonite and gedrite may be written for any two coexisting minerals. But hornblende does not coexist with cordierite or gedrite, and cummingtonite does not coexist with cordierite. This leaves three commonly observed assemblages of four ferromagnesian phases:

~~Cordierite-Biotite-Gedrite-Garnet~~

~~Biotite-Cummingtonite-Gedrite-Garnet~~

~~Biotite-Cummingtonite-Hornblende-Garnet~~

Several two- and three-phase assemblages are common to more than one four-phase assemblage. Distribution diagrams are constructed for two minerals from any mineral assemblage and K_D is not significantly affected by the other minerals present.

~~3-4b: Cordierite-Biotite-Gedrite-Garnet~~

In any rock with four coexisting ferromagnesian phases there are six two phase combinations (Fig. 10) but K_D will be independent in only three of these combinations. In rocks containing all four phases, X_{Mg} increases in the order;

Figure 9: Graphic expression of $\text{Fe}^{+2}:\text{Mg}$ distribution between cummingtonite and gedrite. A: K_D diagram, B: AFM diagram.

Figure 10: K_D data for cordierite-biotite-gedrite-garnet.

$$x_{Mg}^{Crd} > x_{Mg}^{Bt} > x_{Mg}^{Ged} > x_{Mg}^{Grt}$$

After the convention of Kretz (1978), the symbol $>$ will refer to x_{Mg} and the distribution coefficient for minerals on either side, can be written above this symbol

$$Crd \overset{1.81}{>} Bt \overset{1.46}{>} Ged \overset{3.63}{>} Grt$$

Taking these three K_D as independent, the remaining K_D may be obtained by calculation as follows;

$$Crd \quad 1.81 \times 1.46 = 2.64 (2.61) \quad Ged$$

$$Bt \quad 1.46 \times 3.62 = 5.30 (5.21) \quad Grt$$

$$Crd \quad 1.81 \times 1.46 \times 3.62 = 9.59 (9.41) \quad Grt$$

where the numbers in brackets refer to K_D as determined by considering all two phase assemblages as shown in Figure 10. The data are mutually consistent and provide evidence for a close approach to exchange equilibrium with respect to Fe^{+2} and Mg for these phases.

3-4c: ~~Biotite-Cummingtonite-Gedrite-Garnet~~

Because distribution diagrams for Bt-Ged, Bt-Grt and Ged-Grt have already been presented, only those involving Cum are new to the discussion (Fig. 11). Following established procedure, the three independent K_D are chosen as

$$Bt \overset{1.18}{>} Cum \overset{1.38}{>} Ged \overset{3.63}{>} Grt$$

and calculation gives;

$$Bt \quad 1.63 \overset{(1.46)}{>} Ged$$

$$Cum \quad 5.01 \overset{(5.07)}{>} Grt$$

$$Bt \quad 5.91 \overset{(5.21)}{>} Grt$$

Results provide evidence for establishment of Fe^{+2} :Mg exchange equilibrium.

3-4d: ~~Biotite-Cummingtonite-Hornblende-Garnet~~

Before considering Fe^{+2} :Mg exchange amongst all four phases, the distribution between Hbl and Cum will be discussed in detail and this

Figure 11: K_D data for biotite-cummingtonite-gedrite-garnet.

requires some review of amphibole mineral chemistry.

Hawthorne (1981) gives a standard amphibole formula as

which translated into site terminology gives

Robinson et al. (1982) suggested a reasonable list of crystal chemical limits might be;

K - A-site only	Mg - M1, M2, M3, or M4 site
Na - A-site and M4 site only	Fe ⁺³ - M2, M1 or M3 site
Ca - M4 site only	Ti - M2 site
Mn - M1, M2, M3 or M4 site	Al - M2 or T sites
Fe ⁺² - M1, M2, M3 or M4 site	Si - T sites only

Hawthorne (1981) further stated that octahedral Al and Fe⁺³ are strongly ordered into M2.

Cum contains more Fe and Mg cations per formula unit than coexisting calcic amphibole. However, it is commonly observed that in Mg-rich pairs, $X_{Mg}^{Cum} < X_{Mg}^{Hbl}$, while in Fe-rich pairs, $X_{Mg}^{Cum} \geq X_{Mg}^{Hbl}$ (Robinson et al., 1982). Plots of (Al^{VI} + Ti + Fe³⁺) cations versus Fe/(Fe+Mg) and Fe atoms per formula unit illustrate these observations (Fig. 12A,B). A simple binary exchange reaction does not adequately describe the Fe⁺²:Mg distribution in Hbl-Cum pairs.

Bancroft et al. (1967) and Ghose (1961, 1982) demonstrated that Fe⁺² is strongly ordered into the M4 site of Cum. But in Hbl, M4 is largely filled with Ca and Na, and Fe⁺² and Mg are effectively excluded.

The M2 site of Cum shows a strong preference for Mg (Bancroft et al., 1967). In hornblende of common composition, the highly charged cations Al^{VI}, Fe⁺³, and Ti⁺⁴ are almost exclusively ordered into M2 (Hawthorne, 1983); but Bancroft and Brown (1975) and Kretz (1978) have shown that in the part of the M2 site available for Mg and Fe⁺² occupan-

Figure 12: The variation of $Fe/(Fe+Mg)$ of coexisting hornblende-cummingtonite. $(Al^{VI} + Fe^{+3} + Ti^{+4})^{VI} + (Fe^{+2})^{VI}$ cations versus A: Fe^{+2} per formula unit, B: $Fe/(Fe+Mg)$, C: $Fe/(Fe+Mg)$ of the M1 and M3 sites of amphibole.

cy in hornblende, Mg is favoured over Fe. Thus x_{Mg}^{Hbl} tends to decrease with an increase of octahedral Al. x_{Mg}^{Hbl} exceeds x_{Mg}^{Cum} in the magnesian pair principally because of the lower Al^{+3} , Fe^{+3} , and Ti^{+4} content of magnesian Hbl, allowing more Mg to reside in the M2 site (Fig. 12B).

The M1 and M3 sites of cummingtonite and hornblende show little or no apparent cation ordering with respect to Fe^{+2} and Mg and are virtually entirely filled by these cations in species of common composition (Bancroft *et al.* 1967; Bancroft and Brown, 1975; Kretz, 1978). Robinson *et al.* (1982) suggested a method of testing the Fe^{+2} :Mg distribution between Hbl and Cum by ignoring Fe^{+2} and Mg in M2 and M4 and dealing exclusively with Fe^{+2} and Mg in the M1 and M3 sites. This is accomplished by assuming that Fe^{+2} is perfectly ordered into M4, after assigning Ca to this site (2 cations), and Mg is perfectly ordered into M2, after assigning Al^{VI} , Fe^{+3} and Ti^{+4} to this site (2 cations). The remaining Fe^{+2} and Mg is used to calculate x_{Mg} in M1 and M3 (3 cations). Results of the calculation are shown in Figure 12C. The tie line slopes for Fe-rich pairs, shown in Figure 12B, are reproduced in Figure 12C and the tie line for the Mg-rich pair now has a similar slope. Despite the fact that the assumptions overestimate ordering patterns (Hawthorne, 1983; Kretz, 1978), results suggest the variation of K_D with x_{Mg} exhibited by Hbl-Cum pairs may be partially accounted for by considering the effect the Mg tschermakite substitution mechanism ($Al^{IV}Al^{VI} = MgSi$).

Distribution diagrams involving hornblende are shown in Figure 13. The diagram for Hbl-Cum shows the non-ideal mixing effect discussed previously. K_D is also plotted on the basis of x_{Mg} values determined for the M1 and M3 sites. This distribution curve shows Mg to be favoured by Cum over all x_{Mg} .

In Fe-rich rocks, all four phases coexist and

$$x_{Mg}^{Bt} \approx x_{Mg}^{Cum} > x_{Mg}^{Hbl} > x_{Mg}^{Grt}$$

Figure 13: K_D data for biotite-cummingtonite-hornblende-garnet.

Considering data only from samples NFF-10 and NFF-1, with garnet;

$$\text{Bt} \approx \text{Cum}^{1.16}_{>} \text{Hbl}^{4.45}_{>} \text{Grt}$$

and calculation gives

$$\text{Bt } 1.16_{\approx} (1.0) \text{ Hbl}$$

$$\text{Cum } 5.15_{>} (5.07) \text{ Grt}$$

$$\text{Bt } 5.15_{>} (5.21) \text{ Grt}$$

which is consistent with data presented previously.

K_D data from 3 independent combinations of 4 ferromagnesian phase assemblages are mutually consistent with a close approach to the establishment of exchange equilibrium with respect to Fe^{+2} and Mg. It is reasonable to infer that rocks of the NFAZ equilibrated and quenched under nearly constant conditions of P and T. These physical conditions are discussed in chapter 4.

3-5: Chemography of observed mineral assemblages

Having demonstrated a close approach to exchange equilibrium, it would be convenient to find an applicable graphical representation that embodies the range of mineral assemblages and bulk compositions observed at the NFAZ. Phase relations in these rocks involve at least nine components: SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MgO , CaO , Na_2O and H_2O . Manganese is present in small concentrations in some phases, but to a first approximation can be neglected. The addition of K_2O gives rise to one additional phase (Albee, 1965), in this case Bt, and will be considered later.

Several projections accommodating the components of interest have been employed in the graphical analysis of low variance K-poor pelitic rocks (Robinson et al., 1982). Most of these are derived from the tetrahedron, $\text{CaO-Al}_2\text{O}_3\text{-FeO-MgO}$, by projection from plagioclase onto the AFM face. A diagram of this kind, introduced by Froese (1969), has been successfully employed in a number of studies and is used to portray

phase relations in New Fox rocks.

If the chemical potential, or partial molar Gibbs free energy (G) of a component is kept constant, it is not represented in the phase diagram and may be regarded geometrically as a projection point. At constant P and T , the partial molar Gibbs free energy of a gas species in an ideal gaseous solution is determined by specifying its partial pressure. For a solid constituent, the molar free energy is determined by its presence as a pure phase or as a component in a phase of fixed composition.

In rocks containing quartz, magnetite and ilmenite, G of SiO_2 , $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ and $\text{FeO} \cdot \text{TiO}_2$ are determined, assuming pure phases. The presence of plagioclase of fixed composition together with quartz fixes G of $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (Froese, 1978). Thus in rocks containing quartz, magnetite, ilmenite and plagioclase of constant composition, phase relations may be projected onto the AFM face of the ACFM tetrahedron with AFM defined by Froese (1969) as

$$A = \text{Al}_2\text{O}_3 - (\text{Na}_2\text{O} + \text{CaO})$$

$$F = \text{FeO} - (\text{Fe}_2\text{O}_3 + \text{TiO}_2)$$

$$M = \text{MgO}$$

The variance of specific assemblages in this space follows from the phase rule. Table 3 in Chapter 2 shows that most rocks sampled at the NFAZ contain magnetite and ilmenite. However, some of the hornblende-bearing rocks presented in the following diagrams do not contain oxide minerals. As well, magnetite is observed to host herynite exsolution lamellae in some rocks and plagioclase is absent in cordierite-bearing rocks. Thus the constraints of the projection are not fully met for all assemblages, but their exclusion does not alter phase relations. The effect of mixing herynite and hematite components in magnetite and ilmenite is not considered here, but is addressed qualitatively in

Chapter 4.

Phase relations in Crd-bearing rocks are shown in Figure 14A. In aluminous rocks of intermediate Fe/(Fe + Mg) ratio, Crd coexists with Grt and Ged. Dashed tie lines are shown to staurolite which occurs as armoured relics in Crd in several samples with this mineral assemblage. This association suggests the incompatibility of St and Ged and indicates that the metamorphic temperature exceeded that of the reaction;

This reaction may be balanced utilizing the mineral analyses given for samples NFFM4A and NF3-16 (Appendix A). Because Ged contains some Na, and Grt contains some Ca, small amounts of albite (Ab) and anorthite (An) components are required to balance the reaction. Assuming anhydrous cordierite, stoichiometric ilmenite, and ignoring Mn, the stoichiometric coefficients are

Ged	St	Qtz	An		Grt	Crd	Ilm	Ab	H ₂ O
1	0.4	3.8	0.1	NFFM4A	0.8	1.6	0.01	0.5	1
1	0.4	4.0	0.2	NF3-16	0.7	1.7	0.01	0.4	1

In the most magnesian aluminous compositions observed, Crd - Ged is the stable assemblage. Like Hbl, Bt, and Chl, Ged tends to be less aluminous with increasing X_{Mg} .

Figure 14B depicts phase relations involving Cum and Ged. Grt is present only in Fe-rich compositions. Aluminous minerals, Grt and Ged vary significantly only in A-value. Grt from NFF-28 (lower point) contains more Ca and Mn than Grt from NFFMA (Appendix A).

Mineral analyses from Hbl-bearing assemblages are plotted in Figure 14C. In iron-rich and aluminous compositions, Hbl coexists with Grt and Cum. Grt is not present in more magnesian rocks. Hbl is more aluminous with decreasing X_{Mg} as has been previously discussed. The least aluminous Hbl is from a hornblende-plagioclase amphibolite. This rock

Figure 14: Mineral assemblages plotted on an AFM diagram. A: Cordierite-bearing assemblages, B: Cumingtonite-gedrite assemblages, C: Hornblende-bearing assemblages.

- Staurolite
- Cordierite
- Garnet
- Gedrite
- Cummingtonite
- Hornblende (corrected for Fe_2O_3)
- ▲ Hornblende (titrimetric FeO)

$A = \text{Al}_2\text{O}_3 - (\text{CaO} + \text{Na}_2\text{O})$

$F = \text{FeO} - (\text{Fe}_2\text{O}_3 + \text{TiO}_2)$

$M = \text{MgO}$

+ Quartz

+ Plagioclase of constant composition (An_{40})

+ Magnetite

+ Ilmenite

contains trace amounts of magnetite and ilmenite and also some titanite, however, a tie line to titanite has not been shown.

Hbl and Grt from the three phase Hbl-Grt-Cum assemblages show considerable variation in A-value. Grt from NFF-1 (lower point) contains more Ca and Mn and less Al than Grt from NFF-10. The X_{Mg} ratios of these Grt also varies significantly and may reflect different quench temperatures. Hbl and Cum from these rocks have nearly identical X_{Mg} values.

An interpretation of phase relations is presented in Figure 15. The diagram is based on seventeen mineral analyses chosen to reflect the range of mineral compositions presented previously. Tie lines are drawn for commonly observed trivariant (if $a_{H_2O}=f(P,T)$ or $=1$) assemblages and are based on K_D as obtained from the distribution diagrams, except in the case of Hbl-Cum, where tie lines are schematic but constrained by reported analyses. The requirements of the diagram are violated in that oxide minerals are absent in sample NFF-12 (magnesian Hbl-Cum pair) and plagioclase was not observed in Crd-bearing rocks. The addition of plagioclase should not affect X_{Mg} ratios (Robinson et al., 1982) in minerals of low content of CaO and Na₂O. Deduced metamorphic conditions shown on Figure 15 are discussed in Chapter 4.

The aluminous compositions necessary to test the stability of staurolite do not occur at the NFAZ. In some rocks, small amounts of quartz are present with St as inclusions in Crd. Presumably, if the temperature exceeded that of the terminal reaction for staurolite

small amounts of sillimanite would be present in these rocks. Consequently, St is shown to be stable in Figure 15. Tie lines for St-Crd are based on $K_D = 7.64$ taken from this study. Grt-St tie lines are based on $K_D = 1.54$, taken from four low MnO and CaO Grt coexisting with

Figure 15: Interpretation of phase relations: An AFM diagram for the New Fox Alteration Zone.

St from Hounslow and Moore (1967).

Phase relations in very magnesian rocks are not shown in Figure 15. The assemblage Cum-Oam-Crd has been reported from altered rocks near Snake Lake (S.L. Jackson, pers. comm., 1987, Fig. 1). This assemblage has been reported previously by Tella and Eade (1978). In very magnesian rocks at similar grade, Robinson and Jaffe (1969) report the assemblage Crd-Oam-Hbl.

Biotite is stable in all assemblages depicted in Figure 15. Figure 16A is an AKF diagram and shows that the biotite composition surface and tie lines from aluminous silicates to Bt shield orthoamphibole-bearing compositions from muscovite or K feldspar. This shield appears to be present throughout a large P-T range and explains why Ms (or Kfs) - orthoamphibole assemblages have not been reported (Robinson *et al.*, 1982). Consequently, it has proved advantageous to use two separate projections to portray mineral compatibilities in potassic (Ms and/or Kfs present) and K-poor (Bt only K-bearing phase) aluminous rocks (Froese, 1978, Bailes and McRitchie, 1978).

Froese (1969, 1972, 1978) suggested a method which allows the display of mineral compatibilities in both K-rich and K-poor aluminous rocks on a single diagram. This is accomplished through a subdivision of the biotite composition surface as seen from the AFM face of the AKFM tetrahedron.

To treat phase relations in this space, a component is introduced;

$$K = K_2O \cdot Al_2O_3$$

and A is redefined;

$$A = Al_2O_3 - (Na_2O + CaO + K_2O)$$

Thus the introduction of component $K_2O \cdot Al_2O_3$ gives rise to one additional phase, Bt, and the variance of specific assemblages remains the same.

Figure 16: Chemography of biotite-bearing rocks. A: AKF diagram, B: Biotite compositions in AFM space, C: An interpretation of the biotite composition surface.

In Figure 16C a biotite composition surface has been constructed from four preferred biotite analyses (Fig. 16B) and completed schematically after the treatment of Froese (1978, 1980) and Froese and Moore (1980). Four-phase assemblages in the AKFM tetrahedron are represented by subtetrahedra having one apex on the biotite composition surface. Similarly, three-phase assemblages subtend a line and two-phase assemblages an area.

The Bt composition surface is truncated along bevelled edges from which tie lines extend towards the $K_2O - Al_2O_3$ join, to Ms in aluminous compositions and Kfs in more mafic compositions. Because of the small variation in component A, co-ordinates are chosen as $M/(F+M)$ and $A/(F+M)$ which allows an exaggeration of the $A/(F+M)$ axis (Froese, 1978).

A small staurolite field is shown on the Bt composition surface. This topology is valid if metamorphic temperatures did not exceed that of reaction (7). The topology of the appropriate Thompson (1957) projection may be worked out from consideration of minerals stable with Ms along the top edge of the Bt-composition surface and is consistent with the regional work of Jackson and Gordon (1985,1986) and Gilbert *et al.* (1980).

Mineral compatibilities in AFM compositional space are constant. The distribution of ferrous iron and magnesium between coexisting ferromagnesian minerals is consistent with metamorphism at constant P and T. Limited variation in composition amongst minerals plotting as three phase assemblages on the face of the AFM projection (Figs. 14,15) at fixed P and T suggests nearly constant a_{H_2O} .

Chapter 4: Physical Conditions of Metamorphism

The data presented in chapter 3 provide compelling evidence for a close approach to thermodynamic equilibrium at near constant conditions of P, T, and $^a\text{H}_2\text{O}$. In this chapter, an attempt is made to elucidate these conditions.

4-1: Exchange Thermometry

As has been discussed previously, X_{Mg} of coexisting Bt and Grt are governed by the exchange reaction

Recalling the general statement of equilibrium

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K - \Delta V (P-1)$$

and assuming ideal mixing over octahedral sites, activities are equal to mole fraction, and for the reaction as written $K = K_D$, giving upon rearrangement

$$\ln K_D = -\Delta H^0 / RT + \Delta S^0 / R - \Delta V (P-1) / RT$$

This formula shows that K_D will vary with T and P. Because ΔH^0 and ΔS^0 vary little with T, plotting $\ln K + \Delta V(P-1)/RT$ vs. $1/T$ yields a straight line with slope $-\Delta H^0/R$.

This relation has been determined by various methods, but for medium and high grade rocks, the experimental calibration of Perchuk and Lavrent'eva (1983) yields favourable results (Perkins and Chipera, 1985). The experimental calibration of Ferry and Spear (1978), calibrated for the pure Mg-Fe system (equilibrium 8), is also applied. Perchuk and Lavrent'eva's (1983) calibration accounts for Mn dilution and thus X_{Mg} for their thermometers is defined as $\text{Mg}/(\text{Mg}+\text{Fe}+\text{Mn})$, and reaction (8) will involve Mn. Perchuk and Lavrent'eva (1983) also

calibrated a Crd-Grt thermometer which is applied in this study.

Results for $P=4.5$ Kb for five Grt-Bt pairs and three Crd-Grt pairs are presented in Table 4. The selection of a pressure is discussed in the following section. Zoned garnets (Fig. 7) give higher core temperatures for all calibrations. All other samples show less than 1 wt. % internal variation in CaO, MnO, FeO, MgO and TiO_2 and average analyses were used.

The rim temperatures from sample NFFMA and NFFM4A are a result of pyrope-poor rim compositions. It is well established that K_D for Grt-Bt pairs decreases with increasing metamorphic temperature (Parchuk and Lavrent'eva, 1983; Essene 1982) and Mg-poor Grt rims probably represent a retrograde adjustment (Tracy, 1982). These temperatures were rejected before an average was calculated. The Crd-Grt temperature for sample NF3-16 is not consistent with other results and is rejected. Recognition of significant quantities of Fe^{+3} in biotite would raise calculated temperatures by reducing Fe^{+2} and increasing x_{Mg}^{Bt} .

The remaining results give average temperatures ($^{\circ}C$) of;

Garnet-Biotite: 622 ± 112 (2 std. dev.) Ferry and Spear (1978)

612 ± 60 (2 std. dev.) Parchuk and Lavrent'eva (1983)

Garnet-Cordierite: 591

Parchuk and Lavrent'eva (1983)

The Grt-Bt temperatures of Ferry and Spear (1978) and Parchuk and Lavrent'eva (1983) are in agreement, however, the latter are preferred because of the relatively low standard deviation. Grt-Crd temperatures are in reasonable agreement with Grt-Bt temperatures.

Temperatures around $600^{\circ}C$ agree with phase relations and upper sillimanite-muscovite zone metamorphism as suggested by the regional gradient (Fig. 1). Jackson and Gordon (1986) obtained minimum Grt-Bt temperatures of $650^{\circ}C$ using Ferry and Spears' (1978) calibration about 3 km south-west of the NFAZ on the Laurie River (Fig. 1). Thus results

are broadly consistent with a regional NE-SW increase in metamorphic temperatures (Jackson and Gordon 1986; Zwanzig, 1976).

4-2: Metamorphic Pressures from the Petrogenetic Grid

Some mineral assemblages stable at the NFAZ suggest moderate temperatures at peak metamorphism. In combination with the unpublished petrogenetic grids of D.M. Carmichael (1978, 1984) and the work of Froese and Hall (1983) a reasonable estimation of ambient pressures at peak metamorphic temperatures is achieved.

In mafic rocks, the assemblage Grt-Cum-Hbl may be typical of intermediate pressures during medium grade metamorphism (Froese, 1980) as suggested by work in the Snow Lake, Manitoba area (Bailes and McRitchie, 1978). Robinson *et al.* (1982) review published petrogenetic grids relevant to orthoamphibole bearing rocks and find that all grids place Grt-Crd-Oam assemblages at lower pressures. In equivalent higher pressure assemblages, Oam-aluminosilicate is stable.

In Figure 17 an attempt has been made to construct a composite petrogenetic grid which accounts for common medium grade mineral assemblages in mafic, K-poor pelitic and pelitic rocks. Invariant points 2-4 are familiar from the work of Korikovsky (1970) and invariant points 12-16 from Hess (1969). An unpublished grid of D. M. Carmichael (see Bailes and McRitchie, 1978) linked invariant points in K-poor rocks (2-4) to invariant points in pelitic rocks (12-13) via Ms-absent reactions. The framework of Figure 17 is taken from an updated and calibrated version of this grid constructed by D.M. Carmichael in 1984.

Froese and Hall (1983) derived a grid for K-poor pelitic and mafic rocks which includes invariant points 2-11. They give a detailed account of assemblages justifying the stability of previously published and new invariant points. Froese and Hall (1983) introduced invariant points 6-11 which provide the link between reactions in K-poor and mafic

rocks. Invariant points 5-11 are placed schematically in the framework of invariant points 1-4 and 12-16 guided only by Schreinemaker's rules (Zen, 1966).

Reactions involving anthophyllite have been ignored and invariant point 6 is metastable with respect to anthophyllite. Spear (1977), Percival et al. (1982) and Spear and Rumble (1986) derived grids which accomodate reactions involving Ged and Ath. Inherent limitations of Fig. 17 are the assumptions of constant mineral composition, the plagioclase projection, that a_{H_2O} is a smoothly varying function of P and T and neglecting details of the orthoamphibole solvus.

The reaction

suggested by textures in samples NFFM4A and NF3-16 links invariant points 2 and 4. Invariant point 2 is placed near the And field to accomodate mineral assemblages observed at the Coronation Mine near Flin Flon, Manitoba (Froese, 1969) and from the Buchan Dalradian area (Hudson and Harte, 1985) where And is the stable aluminosilicate. Other studies have suggested that this invariant point is in the Sil field (eg. File Lake area, Bailes and McRitchie, 1978). Carmichael (pers. comm., 1984) would place invariant point 2 high in the Sil field near the Ky-Sil transition.

If the coordinates of invariant point 1 are accepted as those determined by Holdaway (1971) (501°C, 3.8 kb), metamorphic pressures at the NFAZ, in light of reaction (6) are greater than 3.5 kb and less than 5 kb. Jackson and Gordon (1986) obtained lower pressure estimates of 4.5 kb 3 km south-west of the NFAZ on the Laurie River (Fig. 1) using the Pl-Grt-Al₂SiO₅-Qtz geobarometer of Ghent et al. (1979). An estimate of 4.5 kb is consistent with phase relations at peak metamorphism and temperatures around 600°C.

3-3: The fluid phase

A common assumption amongst petrologists studying rocks dominated by dehydration reactions during prograde metamorphism is $P_{fl} = P_{tot}$ and $X_{H_2O} = 1$. Phase relations at the NFAZ are consistent with uniform fugacities of H_2O and the agreement between temperatures based on exchange reactions and conditions deduced from the reaction grid suggest that fluid composition did not deviate markedly from pure H_2O . Phases present in minor amounts, however, indicate the presence of species other than H_2O and limited variation in oxygen and sulphur fugacities.

Textural criteria and the consistency of opaque mineral assemblages suggest equilibrium amongst oxide and silicate phases. The stabilities of oxide and sulphide phases may be represented on a $\log fO_2 - \log fS_2$ diagram (Holland, 1959). Construction of such diagrams has been covered at length elsewhere (Korzhinskii, 1959; Froese, 1976, 1977, 1981; Ferry and Burt, 1982; Nesbitt, 1986a, 1986b).

In Figure 18, the stabilities of the Fe oxides and sulphides are plotted on a $\log fO_2 - \log fS_2$ diagram for $P = 4.5$ kb and $T = 600^\circ C$ after a method suggested by Froese (1981) and using the thermochemical data presented for reactions (9-16) in Table 5. The calculated diagram is based on the experimental study of pyrrhotite-pyrite phase relations of Toulmin and Barton (1964). They provide empirical equations relating fS_2 and a_{FeS} to mole fraction and T at one atmosphere. After Froese and Gunter (1976, 1978), the pyrrhotite composition is expressed in the system $FeS-\square S$, where $\square$ stands for vacancy. In calculating the positions of reaction curves, repeated use is made of the relation

$$\Delta G^\circ = -RT \ln K - \Delta V_g(P-1)$$

For reactions (1) and (3), ΔG° is calculated from known values of fS_2 and a_{FeS} at one atmosphere (Toulmin and Barton, 1964). ΔG° of other reactions in Table 5 are taken from the tabulated thermochemical data of

Robie et al. (1978). ΔV_g for reactions (9) and (11-19) were obtained from Robie et al. (1978), and reaction (10) from Froese (1976). Stoichiometric magnetite has been assumed.

The stabilities of the Fe-Ti oxides, based on reactions (17-19) (Table 5), have also been plotted in Figure 18. Assuming pure phases, the slopes of the reactions in $\log fO_2$ - $\log fS_2$ space follows from the reaction equation. For reaction (17), ΔG° is calculated using thermochemical data for troilite (Robie et al., 1978), and the effect of the changing activity of FeS has not been accounted for. The trace of this reaction will be curved with slope < 1 (Froese, 1977). The position of reaction (19) as shown in the magnetite field of Figure 18 is metastable (E. Froese, pers. comm.). With dissolved hematite in ilmenite and magnetite, as is the case at the NFAZ, the actual position of the reaction may lie in the hematite stability field (Rumble, 1976; Froese, 1977).

Ilmenite, usually with some hematite exsolution lamellae, and magnetite characterize the opaque mineral assemblages of most NFAZ rocks (Table 3). Pyrrhotite is present in some samples in apparent textural equilibrium with silicate minerals. This restricts metamorphic conditions to relatively low oxygen and sulphur fugacities (Fig. 18). Pyrite-chalcopyrite aggregates with magnetite and Fe-Hydroxide(?) reaction rims could reflect decreasing fS_2 conditions and the oxidation of pyrite according to reaction (14). However, the reactions have not proceeded to completion and the poorly crystallized nature of the reaction rims are more readily reconciled with retrogressive conditions. The aggregates are not in textural equilibrium with the silicate mineral assemblage and pyrite is not expected to coexist with the relatively Fe-rich silicates present in most mineral assemblages (Froese, 1971; Nesbitt, 1986a, 1986b).

Apatite is common in all rock types at the NFAZ and tourmaline was encountered in many altered rocks in outcrop. Graphite and carbonate are present in trace amounts in some hornblende-bearing rocks. These observations confirm dilution of the fluid phase by P and CO_2 in relatively unaltered rocks and P and B in altered rocks. Cl^- and F could be present in the hydroxyl site of amphibole and would have some concentration in the metamorphic fluid.

The zonation of $f\text{O}_2$ - $f\text{S}_2$ sensitive minerals observed in many alteration zones of metamorphosed sulphide deposits (Nesbitt, 1986a, 1986b) is not evident at the NFAZ. Consistent magnetite-ilmenite oxide mineral assemblages suggest that ambient $f\text{O}_2$ - $f\text{S}_2$ conditions were restricted to the magnetite-ilmenite stability field of Figure 18. However, the stability fields of these oxides are larger than that depicted due to dissolved hematite in ilmenite and hematite and hercynite in magnetite. Late hematite rims on Fe-oxides and disequilibrium sulphide textures presumably represent retrogressive adjustment.

In the Laurie Lake area, Jackson and Gordon (1986) suggest that $X_{\text{H}_2\text{O}}$ may have been less than 0.8 to reconcile exchange P-T estimates with reaction isograd (1) in Figure 1, which extends below the intersection of the Ms-out reaction and the granite minimum (invariant point 16, Fig. 17). At the NFAZ, mineral compositions, assemblages and P-T estimates are consistent with a metamorphic fluid phase dominated by water with small concentrations of CO_2 , B and P. Sulphur fugacities along the pyrrhotite-magnetite boundary of Figure 18 are so low that only a little H_2S and SO_2 should be present (Eugster and Skippen, 1967; Froese, 1977). Most rocks were metamorphosed with ambient $f\text{O}_2$ conditions within the magnetite stability field.

Chapter 5: Discussion

The unusual composition of Crd-Oam rocks led Seki (1957) to comment that "chemically similar rocks are unknown amongst igneous, sedimentary or metamorphic types". This has led to a plethora of proposed exotic origins for these rocks. The present discussion considers only aspects relevant to the NFAZ. A historical perspective of proposed origins is presented by Robinson et al. (1982) and by Froese (1985). In most cases, field evidence suggests that Crd-Oam rocks attained their bulk compositions prior to metamorphism (Robinson et al., 1982). Crd-Ged rocks and related compositional variants at the NFAZ have undergone the same structural-metamorphic history as their host rocks and there is little doubt that their present composition is inherited from a premetamorphic protolith. The systematic changes in mineral assemblages and gradual obliteration of primary features provide compelling evidence for progressive in situ hydrothermal alteration. It remains to find suitable protoliths and speculate on their origin.

The spatial relation of Crd-Oam rocks to massive sulphide orebodies led some workers to suggest that these rocks could represent metamorphosed chloritic alteration zones (Froese, 1969, Whitmore, 1969, de Rosen-Spence, 1969). In fact, this is now widely accepted (Franklin et al., 1981) and practically applied in exploration. Quartz - Mg chlorite assemblages are the principal constituents of many low-grade alteration zones and provide suitable protoliths for Crd-Ged rocks such as are present at the NFAZ. However many of the rocks under consideration are Grt-rich and require other protoliths. Furthermore Grt and Crd-rich Ged-bearing rocks are often intimately interlayered requiring drastic local variation in bulk $Fe/(Fe+Mg)$ ratios.

Bachinski (1976, 1977) provided data on Fe-rich chlorite alteration

zones from cupriferous iron sulphide deposits hosted by ophiolitic rocks in Newfoundland. He reported variation in chlorite composition within single deposits which span nearly the entire range of compositions shown on the AFM diagram for NFAZ rocks in Figure 19A. At the lower greenschist grades of metamorphism, represented by the Newfoundland occurrences, the chlorites of the weakly altered to unaltered basaltic host rocks are always more magnesian than those of the altered quartz-chlorite rocks. An average analysis of these quartz-chlorite rocks (Bachinski, 1977) is plotted in Figure 19B.

Bernard et al. (1982) presented data on 'chloritites'(sic) from a variety of European massive sulphide deposits developed in variable lithologies. These are rocks composed primarily of quartz-chlorite and many are interpreted as sedimented altered material. Chlorite compositions from several deposits in the Huelva Province in Spain and the Pierrefitte - Nestalas district of the High Pyrenees in France are sufficiently Fe-rich to correspond in composition to Grt-rich rocks at the NFAZ (Fig. 19A). Cumingtonite- or grunerite-magnetite-quartz rock, interpreted to be of exhalative origin, was reported from greenschist grade deposits in the Pierrfitte-Nestalas district as lenses associated with Fe-rich 'chloritites' and biotite-rich alteration.

Mottl (1983) summarized work on altered basalts dredged from the seafloor. Some intensely altered quartz-chlorite rocks, apparently altered in an area of upwelling hydrothermal fluids, have very iron-rich bulk compositions (Fig. 19B) and contain very Fe-rich chlorites (Fig. 19A). For comparison, the composition of a quartz-chlorite rock, presumably altered through interaction with downward migrating, relatively unmodified seawater is also plotted in Figure 19B; it is much more magnesian than the "upflow zone" quartz-chlorite rocks.

Figure 19A,B illustrates that suitable protoliths for Ca-poor NFAZ

Figure 19: Chlorite compositions and bulk compositions of some iron-rich quartz-chlorite rocks plotted on an AFM diagram for the New Fox Alteration Zone. A: Chlorite compositions, B: Bulk compositions, (inset: phase relations in Ca-poor altered rocks).

A. CHLORITE COMPOSITIONS FROM SOME Qtz-CHLORITE ROCKS ASSOCIATED WITH HYDROTHERMAL ACTIVITY

$A = Al_2O_3$

$F = FeO$

$M = MgO$

B. BULK ROCK COMPOSITIONS OF SOME Qtz-CHLORITE ROCKS ASSOCIATED WITH HYDROTHERMAL ACTIVITY

rocks, characterized by Fe-rich chlorite, occur associated with near seafloor hydrothermal processes. Vallance (1967) described the transformation of quartz-chlorite alteration in basaltic rock to cordierite-orthoamphibole rock in the contact aureole of a granite at Yalwal, New South Wales, Australia. Three analyses of cordierite-orthoamphibole rock from this study are plotted in Figure 19B. The rocks are very iron-rich and do not contain garnet, although almandine occurs in some other Crd-Oam rocks (Vallance, 1967). In addition, cummingtonite is developed in some rocks. These data indicate that Crd-Oam assemblages at relatively low P and T are stable in rocks of high $\text{Fe}/(\text{Fe}+\text{Mg})$, and suggest that garnet could be expected at higher metamorphic grade. Williams (1983) remarked on the significance of garnet-rich gedrite rocks in a description of the Anintei-ro-Bama Cu deposits of northwestern Spain. Garnet-rich Grt-Ged rocks and cummingtonite-rich rocks are interpreted as metamorphosed equivalents of chlorite-rich rocks.

Ragnarsdóttir et al. (1984) provided an excellent description of an active geothermal system at Svartsengi, Iceland, and reviewed work on geothermal systems on the Reykjanes Peninsula. Alteration in these systems involves several steps. At low temperatures, magnesium-rich smectites are formed. At deeper levels and higher temperatures, Fe-rich smectite forms, and at 230°C , Fe-rich smectite is transformed to Fe-rich chlorite. Mass transfer calculations indicate that alteration of augite-Ca plagioclase-phyric tholeiite to an oxide-calcite-quartz-epidote-albite-ripidolite rock involves the transfer of large amounts of Fe and Si to the fluid. Constant pressure and temperature activity-activity diagrams were used to demonstrate that alteration phases maintain a state close to equilibrium with the evolving geothermal fluid.

Thus, alteration zones characterized by Fe-rich alteration products are observed in diverse geologic settings and in many cases associated

with base-metal mineralization. Ragnarsdóttir et al. (1984) and Mottl (1983) demonstrated that processes responsible for iron-rich alteration products are operating in active geothermal areas. The classic work of Vallance (1967) provides a direct link between Fe-rich chloritic alteration and all the principal minerals observed at the NFAZ in Ca-poor altered rocks.

Bachinski (1976) and Bernard et al. (1982) showed that the Fe/(Fe+Mg) ratio of chlorite can vary radically within individual alteration zones; however, the distribution of Fe and Mg-rich chlorites is not detailed. At higher grades of metamorphism, assemblages would reflect the nature of the distribution. Relatively large areas of Mg- and Fe-rich rocks occur at the NFAZ but the prevailing relationship is intimate intermingling of Grt- and Crd-rich Ged rocks at the decimetre to outcrop scale. Presumably an intensive study of chlorite compositions from an appropriate alteration zone would reveal a lower grade analogue of this bulk Fe/(Fe+Mg) distribution. Commonly, a more uniform transition from marginal Fe-rich chlorites, to Mg-rich chlorites near the site of discharge is reported (Franklin, 1986; Ragnarsdóttir et al., 1984).

Having established that suitable Fe-rich chloritic protoliths are not uncommon, some insight into the nature of the agent of metasomatism might be gained through a brief review of pertinent fluid-rock experimental work. Mottl (1983) summarized experimental work on basalt-seawater interaction. Despite the fact that the experiments were run as closed systems, and the concept of water/rock ratio cannot be applied to natural systems with any rigour (Ragnarsdóttir et al., 1984), the results succeeded in reproducing many common alteration assemblages. At high water/rock mass ratios (>50), and 300°C, only quartz and chlorite form as reaction products. Calcium and sodium are strongly leached from

the rocks and Mg is stripped from seawater by reactions generating abundant H^+ . The resultant low pH would ensure the stability of metal-chloride complexes in the environment of alteration. Thus seawater-basalt interaction at high temperatures and high water/rock ratios may be capable of producing the Mg chlorite-quartz precursors of Crd-Oam rocks in an environment conducive to base metal transport. Mottl (1983) also remarked that the Mg content of chlorite increased at high water/rocks ratios.

Schulien (1980) calibrated an exchange reaction between biotite and chloride fluids and showed that at 500-700°C, Fe^{+2} is strongly fractionated into the fluid resulting in a Mg-enriched biotite. The effect is enhanced by increasing temperature. Eugster (1985) discussed the same trends in carbonates, but at around 350°C, fractionation trends are reversed with Mg enriched over Fe in the chloride fluids. Eugster (1985) suggested that similar behaviour might be expected for other silicates and cited the observation of Fe-rich silicates growing in diagenetic seawater-dominated Mg-rich fluids as an indication of this general fractionation reversal. The exchange reaction for chlorite

might proceed to the right at temperatures $> 500^\circ C$ and to the left at much lower temperature. At temperatures ranging as low as $70^\circ C$, almost complete removal of Mg from seawater is observed in experiments with basalt (Mottl, 1983). In any case, a reversal in fractionation trends is not evident in the temperature range of seawater-basalt experiments (approx. $70-400^\circ C$). If significant chloride concentration and moderate to high temperatures are assumed, fluids responsible for the production of large amounts of Fe-rich chlorite must be very Fe-rich.

Experimental work demonstrated that Mg-rich seawater undergoes irreversible cation exchange with basalt at elevated temperatures resul-

ting in an evolved fluid of higher Fe/(Fe+Mg) ratio. In fact, the ability of basalt to fix Mg from seawater at elevated temperatures is so dramatic that Mg is virtually undetectable in exhalations from hydrothermal vents on the seafloor (Franklin, 1986). This Franklin (1986) regarded as evidence for the formation of typical massive sulphide deposits and attendant Mg-enriched crosscutting alteration pipes according to the two-fluid model of Roberts and Reardon (1978), wherein a high-T, upwelling metal-bearing fluid depleted in Mg interacts at shallow levels with cold, Mg-rich relatively unmodified seawater. Even in the absence of readily exchanged cations such as calcium (Mottl, 1983), chloride fluids such as seawater should preferentially extract Fe from the rocks at high temperatures (Schulien, 1980; Eugster, 1985). Rocks from quartz-chlorite "upflow zone breccias" with Fe-rich chlorites (Fig. 19A,B) are interpreted to have resulted from direct interaction with an evolved, Mg-depleted, Fe-Mn-H₂S-Cu-Zn rich chloride solution in an upwelling zone of hydrothermal fluids (Mottl, 1983). If metamorphism of the precursors of the iron-rich rocks at the NFAZ has been isochemical, the agent of metasomatism was an evolved Fe-rich fluid, possibly derived from seawater. The work of Ragnarsdóttir et al. (1984) demonstrated such possibility.

Unusually quartz- and plagioclase-rich rocks at the NFAZ probably have a greater distribution than that shown in Fig. 2 because they are not readily recognized in metamorphosed felsic rocks. They are concentrated stratigraphically above the Ca-Na- depleted rocks and in some places appear to be cut by later gedrite- and cummingtonite-bearing rocks. Replacement textures in pillowed rocks demonstrate that at least some siliceous rocks reflect the addition of Si to the rock. However, any temporal or genetic relationship between siliceous rocks and the Fe- and Mg-rich rocks is unclear. Many intensely altered Ca-depleted rocks

are quartz-poor. In the following discussion, some occurrences of altered rocks suggesting the parallel development of siliceous and chloritic alteration are compared to the NFAZ.

The geologic setting and alteration assemblages of some Cu-Zn deposits in the Trondheim district in Norway bear resemblance to the NFAZ. There massive sulphide ore occurs associated with amphibolites and in contact with Hbl-Cum-Grt rocks in the stratigraphic footwall. Locally these rocks are anthophyllite-bearing. Overlying the deposits, a 'hydrothermal quartzite' is commonly developed (Nilson and Mukherjee, 1972; Franklin et al., 1981). Williams et al. (1985) and Williams (1986) described siliceous Grt-Cum rocks, presumably the result of metamorphism of siliceous silicate-facies iron formation. Significantly, many of the examples of metamorphosed Fe-rich altered rocks and metamorphosed Fe-rich sediments are related to stratiform base metal mineralization (Williams, 1986). The stratiform zone of patchy Mag-Pl-Qtz rocks at the NFAZ may represent an exhalative layer. However, a replacement origin, such as can be documented for some siliceous zones in pillowed mafic rocks, cannot be ruled out.

Fe-rich alteration occurs in the Snow Lake area in relatively large areas of alteration termed lower semi-conformable alteration zones (LSZ) which underlie massive sulphide deposits with more familiar crosscutting alteration pipes (Walford and Franklin, 1982). Stratigraphically below the Chisel Lake deposit, garnet-chlorite rocks are spatially associated with extensive zones of silicified rocks developed in a mafic volcanic and volcanoclastic sequence (R. Skirrow, pers. comm., 1987). Skirrow considers a Mg-depleted and Si-enriched modified seawater fluid, which could result from basalt-seawater interactions at high temperatures (Mottl, 1983), as a potential source of alteration components.

Silicification appears to be a significant component of many LSZ

(Gibson et al., 1983; MacGeehan and MacLean, 1980; Leshar et al., 1986) and it has been suggested that these zones represent reservoir rocks from which leached metals entered the ore-forming fluid (Spooner, 1977; MacGeehan and MacLean, 1980). Gibson et al. (1983) suggested that silicified rocks formed a relatively impermeable cap to buoyant hydrothermal fluids. Synvolcanic faulting breached the zone of alteration allowing pressurized fluids to rise, producing silicified breccias. Rocks very near the synvolcanic faults were chloritized. Albite-rich and epidote-rich alterations, characteristic of low water-rock ratios (Mottl, 1983), are also common in these zones.

In summary, the overall character of alteration at the NFAZ suggests interaction of primary rocks with a Mg-depleted and Fe-enriched fluid possibly derived from seawater. Local redistribution of Fe components of the unaltered rocks might account for some of the local variation in bulk $\text{Fe}/(\text{Fe} + \text{Mg})$ ratio of alteration products (Mottl, 1983). Interaction with a second relatively unmodified Mg-rich fluid, controlled by permeability, could produce highly variable chlorite compositions such as Bachinski (1976) has documented. Extreme bulk compositions represented by Grt-Ged and Crd-Ged rocks are volumetrically far more abundant than intermediate Grt-Crd-Ged rocks. This observation is compatible with a two fluid model which implies relative proximity to the seafloor.

Siliceous alteration is developed at the margins of the main alteration zone and mostly overlies Ca-Na depleted rocks. These rocks may have locally formed a relatively impervious cap to hydrothermal fluids (Gibson et al., 1983). Thus, the NFAZ contains many of the principal components and geologic relationships identified in lower semi-conformable alteration zones (Franklin, 1986) and could represent a highly metamorphosed analogue of alteration zones such as are developed below

base-metal deposits in the Snow Lake area.

The local stratigraphy of the Lar deposit (Elliot, 1984) is similar to that at the NFAZ, and a favourable stratigraphic horizon may connect these occurrences of altered rocks. Orthoamphibole-bearing rocks occur in rocks between the Lar deposit and the NFAZ (Mustard, 1974, Stewart and Brewer, 1985). The alteration assemblages associated with some exhalative deposits of Cu and Zn demonstrate that the conditions responsible for at least the spatially related development of siliceous and Fe-rich alteration are often met in near seafloor processes. Alternatively, the possibility should be investigated that alteration represents a lower-semiconformable zone and a favourable horizon might exist at some stratigraphically higher level.

Chapter 6: Conclusions

1) Coarse grained gedrite, garnet, cummingtonite and cordierite-bearing rocks have undergone the same structural-metamorphic history as their host rocks. The progressive destruction of primary volcanic structures, such as pillows, indicates that the rocks were metasomatically derived from predominantly mafic to intermediate volcanic rocks. Their present composition requires chloritic precursors if metamorphism has been isochemical. A model of metamorphism of a chloritic alteration zone related to sub-seafloor hydrothermal convection is consistent with field relations.

2) Several alteration types are recognized at the NFAZ. The present mineral assemblages of these metasomatized rocks indicate the principal chemical fluxes operating during alteration:

a) ~~Ca-enrichment~~: epidote-rich and clinopyroxene-bearing alterations

b) Siliceous alteration: Si was demonstrably added to some rocks. Siliceous rocks in the stratiform layer overlying the mafic volcanic rocks may have formed from exhalative hydrothermal activity.

c) Ca(Na)-depletion: depletion of Ca in mafic to intermediate volcanic rocks accounts for most of the observed cummingtonite- and gedrite-rich rocks at the NFAZ. Extreme gedrite-rich variants, accompanied by high modal amounts of either Grt or Crd, represent zones of Fe and Mg enrichment, respectively. Ca-bearing minerals are rare in intensely altered rocks and were not observed with cordierite.

3) K_D data from three combinations of four ferromagnesian phase assemblages are mutually consistent with a close approach to exchange equilibrium with respect to Fe^{+2} and Mg. In cordierite-bearing rocks, X_{Mg} increases in the order

Crd $\overset{1.81}{>}$ Bt $\overset{1.46}{>}$ Ged $\overset{3.63}{>}$ Grt

where the numbers refer to the distribution coefficient. In cummingtonite-gedrite rocks, the following distribution relationships are observed;

$$\text{Bt } 1.18 \text{ Cum } 1.38 \text{ Ged } 3.63 \text{ Grt}$$

For hornblende-cummingtonite assemblages, a binary ideal solution model does not adequately describe the $\text{Fe}^{+2}:\text{Mg}$ distribution. In the most iron-rich pair Cum 1.17 Hbl and in a magnesian pair Cum 0.66 Hbl. $K_D = \text{constant}$ provides a satisfactory description of the distribution between the M1 and M3 sites of Hbl-Cum pairs and the deviation from ideality over all sites can be partially understood by taking the effects of the Mg tschermakite ($\text{Al}^{\text{VI}}\text{Al}^{\text{IV}}=\text{MgSi}$) substitution mechanism into account. For iron-rich Hbl-Cum-Grt rocks

$$\text{Bt} \approx \text{Cum } 1.16 \text{ Hbl } 4.45 \text{ Grt}$$

Phase relations of ferromagnesian minerals are consistent with nearly constant conditions of P, T, and $a_{\text{H}_2\text{O}}$.

4) Garnet-Biotite and Garnet-Cordierite thermometry and qualitative estimates of P and $X_{\text{H}_2\text{O}}$ suggest the following conditions at peak metamorphism;

$$T = 550 - 670^\circ\text{C}$$

(2 std. dev., calibration-Perchuk and Lavrent'eva, 1983)

$$P = 4-5 \text{ Kb}$$

$$X_{\text{H}_2\text{O}} \approx 1$$

Low oxygen and sulphur fugacities corresponding to the field of magnetite-ilmenite stability prevailed during the peak of metamorphism. Deduced conditions are consistent with a regional metamorphic gradient increasing towards the southwest.

5) Suitable protoliths for Crd-Ged rocks such as occur at the NFAZ are provided by quartz-Mg chlorite assemblages that are familiar from low-grade hydrothermal alteration zones of diverse geologic settings and

are commonly associated with base-metal mineralization. Very garnet-rich gedrite rocks have formed by metamorphism of Fe-rich silicate protoliths. Low grade Fe-rich chloritic alteration occurs in diverse geologic settings and could provide suitable protoliths for rocks at the NFAZ. Recent investigations into low grade Fe-rich alteration zones and active geothermal systems suggest that an evolved, Mg-depleted, Fe-enriched fluid interacted with unaltered rocks. The origin of extreme variation in bulk $\text{Fe}/(\text{Fe}+\text{Mg})$ ratio of intensely altered NFAZ rocks remains problematic; possibly a Mg-rich fluid also interacted with the rocks.

6) Cummingtonite-rich alteration, some accompanied by Fe-rich chlorite alteration and at higher grades, garnet- and orthoamphibole-rich variants and associated siliceous rocks, is the typical alteration of base-metal deposits in many areas. Occurrences of cummingtonite-rich rocks should be considered in mining exploration. Similarly, garnet-rich rocks associated with cummingtonite or orthoamphibole in many cases provide an indication of fossil hydrothermal activity.

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Appendix A: The composition of minerals from 10 rocks

On the following pages, compositional data for minerals from 10 samples (NFFM-3, NF3-16, NFFM4A, NFF-32A, NFF-28, NFFMA, NFF-12, NFFM-1, NFF-1, NFF-10) are presented. In addition a table is presented which gives the compositions of averaged high-Al and low-Al point analyses of inhomogeneous orthoamphibole analyses. The last table gives the compositions of garnets which are zoned.

The analyses were obtained using a Material Analysis Company electron microprobe equipped with a Kevex dispersive spectrometer and automated to produce simultaneous multielement analysis and data reduction (Plant and Lachance, 1973). Operating conditions were as follows: 20 kV accelerating voltage, specimen current of 10 nanoamperes measured on a standard kaersutite and a counting time of 100 seconds. The feldspars were analyzed for Na, Al, Si, K, Ca and Fe. All other minerals were analysed for Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Na and K. Under the above conditions of analysis, the determinations have a relative accuracy of ± 1 to ± 2 % for the major elements and up to ± 10 % for elements of low concentration (<5 wt. %). Analyses were taken at the centre and the edge of each mineral grain to check for possible zoning.

The precision of the technique operating under the above conditions is very good. Much of this thesis is concerned with the distribution of Fe^{+2} and Mg, and the precision of the results for these two elements will be examined after the treatment of Kretz (1985).

Under good operating conditions, repeat analyses for any element will show a total range of 4 counts per second (c.p.s.) (G. Pringle, Geological Survey of Canada, pers. comm.). Standards of known concentration are periodically calibrated to a count rate. The analytical setup during analyses of some of the minerals presented in the following

tables, and in Appendix B, for the kaersutite standard was:

147 c.p.s. on 12.96 wt. % MgO

121 c.p.s. on 11.20 wt. % FeO

Accepting ± 2 c.p.s. as an estimate of 2 standard deviations (2s) gives the following deviation, valid between concentrations of 5 and 35 wt. %;

$$\text{MgO} \pm 0.20 \text{ wt. \%} = 2s$$

$$\text{FeO} \pm 0.30 \text{ wt. \%} = 2s$$

These can be converted to an estimate of s on proportional amounts of atoms of Fe and Mg utilizing the propagation of error equation;

$$s_x = ks_x$$

where x is the wt. % of the oxide and k is a constant, in this case the molecular weight of the oxide;

$$s_{\text{Mg}} = 0.003$$

$$s_{\text{Fe}} = 0.002$$

The uncertainties can be propagated through a ratio such as $x/(x+y)$ using the equation;

$$s_{x/(x+y)} = \sqrt{(y^2 s_x^2 + x^2 s_y^2)} / (x + y)^2$$

In this case the relation is $\text{Mg}/(\text{Mg} + \text{Fe})$ and x and y are Mg and Fe respectively. The solution to this equation will vary with X_{Mg} , however X_{Mg} of most of the minerals shows limited variation and $s = \text{constant}$ is applicable. Given the assumption of ± 2 c.p.s. as an estimate of 2s, propagation of error equations (Kretz, 1985) for minerals presented in distribution diagrams give the following uncertainty in X_{Mg} :

Mineral	2s
Cordierite	0.010
Gedrite	0.004
Biotite	0.004
Garnet	0.006
Cummingtonite	0.006

These results represent a confidence limit of 0.95, which is considered liberal because averaging 4-10 point analyses of homogeneous grains would probably allow for a confidence limit of 0.95 to approach 1s (Kretz, 1985). The precision of X_{Mg} of hornblende is considered in Appendix B.

	N F F M - 3					N F 3 - 1 6					**St	*Chl
	Ged	Grt	Crđ	Bt	*Chl	Ged	Grt	Crđ	Bt			
SiO2	45.39	36.96	49.09	38.29	25.01	43.45	35.94	49.07	37.46	26.92	25.59	
TiO2	0.29	0.03	0.03	1.84	0.12	0.16	0.05	0.07	1.50	0.54	0.12	
Al2O3	11.94	20.07	32.05	16.88	21.97	13.22	19.81	32.34	17.15	52.51	22.20	
Cr2O3	0.07	0.04	0.05	0.00	0.06	0.07	0.06	0.06	0.02	---	0.04	
FeO	23.90	32.99	6.63	16.20	21.76	25.42	36.09	7.01	17.76	15.58	21.27	
MnO	0.32	0.88	0.07	0.02	0.13	0.09	0.51	0.09	0.02	0.06	0.03	
MgO	14.32	6.37	10.06	13.89	18.60	12.92	4.57	10.01	13.00	2.75	19.27	
CaO	0.57	2.14	0.04	0.13	0.07	0.48	1.79	0.05	0.13	---	0.04	
Na2O	1.32	0.15	0.14	0.32	0.19	1.70	0.20	0.12	0.66	---	0.00	
K2O	0.05	0.01	0.02	8.76	0.02	0.02	0.04	0.06	8.45	---	0.02	
oxygen	98.50	99.64	98.18	96.33	87.93	97.53	99.06	98.88	96.15	98.23	88.58	
Si	6.695	5.923	5.028	5.634	5.170	6.511	5.884	5.003	5.571	7.546	5.220	
Al	2.076	3.790	3.869	2.928	5.355	2.335	3.822	3.886	3.006	17.243	5.338	
Ti	0.033	0.004	0.002	0.204	0.019	0.018	0.006	0.005	0.169	0.115	0.019	
Mg	3.149	1.522	1.535	3.047	5.733	2.887	1.115	1.522	2.883	1.148	5.861	
Mn	0.040	0.119	0.006	0.003	0.024	0.011	0.071	0.008	0.003	0.013	0.005	
Cr+2	0.008	0.005	0.004	0.000	0.009	0.008	0.008	0.005	0.002	---	0.006	
Fe	2.948	4.421	0.568	1.994	3.762	3.185	4.940	0.598	2.209	3.651	3.629	
Ca	0.090	0.367	0.004	0.020	0.016	0.077	0.314	0.005	0.020	---	0.009	
Na	0.377	0.047	0.028	0.092	0.077	0.494	0.064	0.024	0.189	---	0.000	
K	0.009	0.002	0.002	1.644	0.006	0.038	0.008	0.008	1.604	---	0.006	
Fe/(Fe+Mg)	0.484	0.744	0.270	0.395	0.396	0.525	0.816	0.282	0.434	0.761	0.382	
Fe/(Fe+Mg)	15.425	16.200	11.046	15.566	20.171	15.564	16.232	11.064	15.654	29.716	20.093	

* - retrograde mineral

** - armoured relic in cordierite

--- - not determined

	N F F M 4 A							N F F - 3 2 A			
	Ged	Grt	Crd	**St	*Chl	OChl	O Bt	Ged	Crd	Bt	
SiO2	44.24	37.67	47.44	27.35	25.20	23.95	36.19	48.32	47.47	37.85	
TiO2	0.19	0.00	0.06	0.71	0.18	0.17	1.90	0.21	0.08	1.68	
Al2O3	15.16	21.47	34.14	53.37	23.02	23.45	17.94	9.20	34.24	16.45	
Cr2O3	0.07	0.08	0.02	0.01	0.11	0.08	0.05	0.07	0.06	0.07	
FeOt	24.30	33.52	6.66	14.14	20.41	22.89	19.53	20.53	5.25	13.47	
MnO	0.06	0.39	0.05	0.05	0.03	0.08	0.00	0.19	0.09	0.01	
MgO	13.05	5.40	9.76	2.74	19.22	17.01	10.91	18.18	10.99	16.59	
CaO	0.33	1.07	0.00	0.00	0.03	0.00	0.00	0.27	0.00	0.00	
Na2O	1.85	0.00	0.52	0.53	0.00	0.00	0.21	1.06	0.87	0.51	
K2O	0.00	0.00	0.02	0.00	0.02	0.02	8.80	0.03	0.04	8.12	
oxygen	99.27	99.59	98.67	98.89	88.21	87.65	95.52	98.06	98.06	98.74	
Si	6.455	5.989	4.851	7.552	5.140	4.993	5.475	6.987	4.817	5.586	
Al	2.206	4.024	4.115	17.370	5.534	5.763	3.199	1.568	4.095	2.862	
Ti	0.021	0.000	0.005	0.047	0.028	0.027	0.216	0.022	0.006	0.186	
Mg	2.839	1.279	1.487	1.126	5.842	5.289	2.460	3.919	1.662	3.649	
Mn	0.008	0.053	0.004	0.011	0.005	0.014	0.000	0.023	0.008	0.001	
Cr	0.008	0.010	0.002	0.001	0.018	0.013	0.005	0.008	0.005	0.008	
Fe+2	2.965	4.457	0.570	3.266	3.481	3.992	2.472	2.483	0.445	1.662	
Ca	0.052	0.182	0.000	0.000	0.007	0.000	0.000	0.042	0.000	0.000	
Na	0.524	0.000	0.104	0.284	0.000	0.000	0.062	0.297	0.170	0.146	
K	0.000	0.000	0.002	0.000	0.005	0.004	1.699	0.006	0.006	1.529	
	15.479	15.990	11.139	29.757	20.059	20.094	15.587	15.354	11.215	15.630	

Fe/(Fe+Mg) 0.511 0.777 0.277 0.744 0.373 0.430 0.501 0.388 0.211 0.313

*- retrograde mineral **- armoured relic in cordierite o - inclusion in garnet

	N F F - 2 8				* Chl				N F F M A			
	Cum	Ged	Grt	Bt				Pl	Cum	Ged	Grt	Bt
SiO ₂	53.08	45.21	36.49	37.64	25.91	56.53			52.60	43.88	38.08	37.29
TiO ₂	0.06	0.18	0.05	2.03	0.08	--			0.09	0.34	0.00	1.61
Al ₂ O ₃	2.25	10.93	20.08	17.23	22.13	27.89			2.49	12.67	21.66	17.51
Cr ₂ O ₃	0.05	0.05	0.02	0.02	0.00	--			0.05	0.13	0.05	0.04
FeO	24.95	25.62	33.51	16.82	20.22	0.17			25.19	25.08	31.97	16.70
MnO	0.39	0.56	2.84	0.03	0.04	--			0.34	0.40	1.78	0.01
MgO	16.89	13.21	4.42	13.54	20.50	--			17.30	13.55	4.60	13.29
CaO	0.59	0.66	2.49	0.11	0.02	9.32			0.34	0.40	2.09	0.00
Na ₂ O	0.35	1.41	0.00	0.57	0.08	6.11			0.05	1.75	0.00	0.19
K ₂ O	0.01	0.03	0.08	8.29	0.05	0.20			0.00	0.04	0.00	8.83
	98.62	98.84	99.98	96.28	89.03	100.22			98.46	98.27	100.24	95.47

	oxygen											
	23	23	24	22	28	32	23	23	24	24	22	22
Si	7.745	6.765	5.905	5.555	5.231	10.131	7.688	6.532	6.019	5.557		
Al	0.386	1.927	3.829	2.998	5.266	5.893	0.429	2.223	4.035	3.076		
Ti	0.007	0.020	0.006	0.226	0.012	--	0.010	0.038	0.000	0.180		
Mg	3.675	2.946	1.066	2.979	6.169	--	3.769	3.007	1.082	2.953		
Mn	0.048	0.071	0.389	0.004	0.006	--	0.043	0.050	0.238	0.001		
Cr	0.006	0.006	0.003	0.003	0.000	--	0.006	0.015	0.007	0.005		
Fe ⁺²	3.045	3.205	4.534	2.076	3.414	--	3.079	3.122	4.223	2.082		
Ca	0.092	0.106	0.432	0.018	0.004	1.789	0.054	0.069	0.355	0.000		
Na	0.099	0.409	0.000	0.163	0.033	2.123	0.016	0.505	0.000	0.056		
K	0.002	0.006	0.017	1.561	0.012	0.046	0.000	0.008	0.000	1.678		
	15.105	15.461	16.181	15.583	20.147	19.982	15.093	15.569	15.961	15.589		

Fe/(Fe+Mg) 0.453 0.521 0.810 0.411 0.356 An₄₅ 0.450 0.509 0.789 0.413

* - retrograde mineral

--- not determined

	N F F - 1 2				N F F M - 1				
	Hbl	Cum	Bt	P1	Hbl	*Cum	**Cum	Ged	P1
SiO2	47.02	54.78	39.13	57.82	42.33	53.21	53.43	46.29	56.85
TiO2	0.33	0.05	1.36	0.00	0.44	0.09	0.11	0.24	-
Al2O3	10.46	1.16	16.74	26.47	14.23	2.26	2.59	13.53	26.84
Cr2O3	0.18	0.07	0.20	0.00	0.24	0.08	0.07	0.00	-
FeOt	12.77	20.09	13.17	0.24	19.28	23.73	22.66	24.79	0.32
FeO	9.12				13.78				
Fe2O3	4.06				6.12				
MnO	0.18	0.40	0.00	0.00	0.32	0.52	0.46	0.71	-
MgO	14.40	20.80	18.83	0.00	9.01	17.78	18.63	12.99	-
CaO	11.44	1.18	0.34	8.01	10.74	0.91	0.62	0.64	8.41
Na2O	1.33	0.33	0.31	7.16	1.57	0.00	0.01	1.74	6.93
K2O	0.18	0.03	5.88	0.06	0.21	0.02	0.03	0.05	0.06
	98.29	98.89	95.96	99.76	98.37	98.62	98.61	98.77	99.39

	23	23	22	32	23	23	23	23	32
Si	6.728	7.801	5.603	10.900	6.232	7.724	7.705	6.518	10.268
Al	1.764	0.195	2.825	5.902	2.475	0.387	0.440	2.358	5.711
Ti	0.036	0.005	0.147	---	0.049	0.010	0.012	0.027	---
Mg	3.072	4.416	4.019	---	1.982	3.848	4.005	2.864	---
Mn	0.022	0.048	0.000	---	0.040	0.063	0.056	0.089	---
Cr ⁺²	0.020	0.008	0.022	---	0.028	0.009	0.008	0.000	---
Fe ⁺³	1.091	2.392	1.577	---	1.700	2.881	2.733	3.065	---
Fe	0.437				0.680				
Ca	1.754	0.180	0.053	1.620	1.698	0.142	0.095	0.101	1.629
Na	0.369	0.091	0.086	2.620	0.449	0.000	0.004	0.499	2.425
K	0.033	0.005	1.074	0.015	0.040	0.004	0.005	0.009	0.015
Fe/(Fe+Mg)	0.262	0.351	0.282	An ₃₈	0.462	0.428	0.406	0.517	An ₄₀

--- - not determined * - proximal to Hbl ** - proximal to Ged

Hornblende corrected for Fe₂O₃ assuming Fe₂O₃/FeO of 0.44 taken from analyses with titrimetric FeO (see Appendix B).

	N F F - 1				N F F - 1 0				
	Hbl	Cum	Grt	Pl	Hbl	Cum	Grt	Bt	Pl
SiO ₂	41.87	51.92	36.25	58.43	41.88	52.42	37.87	36.07	57.29
TiO ₂	0.40	0.11	0.08	---	0.50	0.14	0.00	1.82	---
Al ₂ O ₃	14.04	2.28	19.68	26.21	15.16	1.72	21.66	16.66	27.19
Cr ₂ O ₃	0.09	0.07	0.02	---	0.05	0.04	0.13	0.03	---
FeO _T	20.97	27.99	35.42	0.21	20.62	28.53	32.57	21.67	0.11
FeO	17.25				16.96				
Fe ₂ O ₃	4.14				4.07				
MnO	0.09	0.31	1.91	---	0.13	0.29	1.36	0.01	---
MgO	7.85	14.92	3.07	---	7.77	15.18	4.10	11.25	---
CaO	10.55	0.96	3.33	7.87	10.39	0.50	2.59	0.00	8.83
Na ₂ O	2.13	0.02	0.24	7.15	1.61	0.00	0.00	0.40	6.63
K ₂ O	0.34	0.04	0.01	0.13	0.37	0.00	0.00	8.83	0.10
	98.32	98.62	100.01	99.99	98.47	98.82	100.23	96.72	100.14

oxygen	23	23	24	32	23	23	24	22	32
Si	6.265	7.699	5.916	10.467	6.220	7.758	5.996	5.463	10.265
Al	2.476	0.399	3.785	5.533	2.653	0.300	4.047	2.974	5.742
Ti	0.045	0.012	0.010	---	0.056	0.015	0.000	0.207	---
Mg	1.749	3.298	0.747	---	1.720	3.348	0.969	2.539	---
Mn	0.011	0.039	0.264	---	0.016	0.036	0.183	0.001	---
Cr ⁺²	0.011	0.009	0.003	---	0.015	0.005	0.017	0.004	---
Fe ⁺³	2.158	3.472	4.834	---	2.106	3.532	4.319	2.745	---
Fe	0.466				0.455				
Ca	1.691	0.152	0.582	1.510	1.653	0.080	0.440	0.000	1.694
Na	0.618	0.006	0.076	2.485	0.464	0.000	0.000	0.116	2.302
K	0.065	0.007	0.002	0.029	0.070	0.000	0.000	1.705	0.023
	15.555	15.092	16.220	20.024	15.423	15.074	15.972	15.752	20.036

Fe/(Fe+Mg) 0.552 0.513 0.866 An₃₈ 0.550 0.513 0.817 0.519 An₄₂

----- not determined

Hornblende corrected for Fe₂O₃ assuming Fe₂O₃/FeO of 0.24 averaged from Hbl coexisting with Grt in Jen and Kretz (1981).

Averaged high Na-Al (Ged) and low Na-Al (Ath(?)) point analyses of inhomogeneous orthoamphibole analyses.

	N F F M - 1		N F F - 2 8		N F F M A		N F F M - 3	
	Ged	Ath(?)	Ged	Ath(?)	Ged	Ath(?)	Ged	Ath(?)
SiO ₂	46.29	47.40	45.21	48.03	43.88	48.79	45.39	48.42
TiO ₂	0.24	0.20	0.18	0.20	0.34	0.13	0.29	0.16
Al ₂ O ₃	13.53	8.97	10.93	8.09	12.67	7.98	11.94	7.92
Cr ₂ O ₃	0.00	0.00	0.05	0.05	0.13	0.02	0.07	0.05
FeO	24.79	24.13	25.62	25.52	25.08	24.97	23.90	23.96
MnO	0.71	0.65	0.56	0.41	0.40	0.29	0.32	0.30
MgO	12.99	14.98	13.21	14.39	13.55	15.66	14.32	15.84
CaO	0.64	0.47	0.66	0.44	0.43	0.24	0.57	0.44
Na ₂ O	1.74	1.39	1.41	0.88	1.75	0.85	1.32	0.85
K ₂ O	0.05	0.02	0.03	0.05	0.04	0.04	0.05	0.05
	98.77	98.21	98.84	98.05	98.27	98.95	98.50	98.49

number of ions on the basis of 23 oxygen

Si	6.518	6.994	6.765	7.117	6.532	7.136	6.695	7.122
Al	2.358	1.560	1.926	1.413	2.223	1.370	2.076	1.373
Ti	0.027	0.022	0.020	0.023	0.038	0.014	0.033	0.018
Mg	2.864	3.295	2.946	3.179	3.007	3.402	3.149	3.473
Mn	0.089	0.081	0.071	0.051	0.050	0.035	0.040	0.037
Cr	0.000	0.000	0.006	0.010	0.015	0.002	0.008	0.006
Fe ⁺²	3.065	2.997	3.205	3.162	3.122	3.042	2.948	2.947
Ca	0.101	0.074	0.106	0.070	0.069	0.038	0.090	0.069
Na	0.499	0.398	0.409	0.253	0.505	0.240	0.377	0.242
K	0.009	0.004	0.006	0.001	0.008	0.007	0.009	0.009
	15.450	15.425	15.461	15.280	15.569	15.286	15.425	15.296
Fe/(Fe+Mg)	0.517	0.475	0.521	0.499	0.509	0.472	0.484	0.459

Compositional zoning in garnet.

	N F F M - 4 A						N F F M A			
	RIM	C	O	R	E	RIM	AVG.	CORE	RIM	AVG.
SiO ₂	37.24	38.29	37.29	37.59	37.62	37.96	37.67	38.15	38.02	38.08
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	21.18	21.73	21.37	21.65	21.11	21.78	21.47	21.75	21.57	21.66
Cr ₂ O ₃	0.10	0.13	0.11	0.16	0.00	0.00	0.08	0.00	0.11	0.05
FeO	34.04	34.06	32.84	33.85	33.08	33.23	33.52	31.76	32.18	31.97
MnO	0.38	0.37	0.50	0.36	0.34	0.39	0.39	1.76	1.80	1.78
MgO	4.88	5.78	5.34	5.73	5.64	5.07	5.40	5.16	4.03	4.60
CaO	1.34	0.64	0.95	0.98	0.84	1.66	1.07	1.86	2.33	2.09
Na ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	99.10	101.00	98.40	100.32	98.63	100.09	99.59	100.44	100.04	100.24

number of ions on the basis of 24 oxygen

Si	5.980	5.996	5.992	5.941	6.026	5.998	5.989	6.004	6.034	6.019
Al	4.008	4.012	4.047	4.033	3.986	4.056	4.024	4.036	4.034	4.035
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mg	1.155	1.349	1.279	1.350	1.347	1.194	1.279	1.210	0.953	1.082
Mn	0.051	0.049	0.068	0.048	0.046	0.052	0.053	0.234	0.242	0.238
Cr	0.013	0.016	0.014	0.020	0.000	0.000	0.010	0.000	0.014	0.007
Fe	4.571	4.461	4.413	4.474	4.431	4.391	4.457	4.181	4.270	4.225
Ca	0.231	0.107	0.164	0.166	0.145	0.281	0.182	0.313	0.396	0.355
Na	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	16.009	15.990	15.997	16.032	15.981	15.972	15.994	15.978	15.943	15.961
Fe/(Fe+Mg)	0.798	0.768	0.775	0.767	0.767	0.786	0.777	0.776	0.818	0.796

Appendix B: A titrimetric determination of ferrous iron for Hornblende from three rocks

Fragments of rock from three hornblende-plagioclase amphibolites (NFF-9, NFF-5, NFF-35) were chosen for study. The samples were crushed and a 99% purity of separation was achieved by use of a Frantz magnetic separator. For sample NFF-9, hand picking of biotite impurity was required. The determination of ferrous iron for hornblende separates followed the modified Wilson cold acid decomposition method (Wilson, 1960). The sample was weighed in nalgene containers and 5 ml of ammonium metavanadate (NH_4VO_3) was added. A further 10 ml of hydrofluoric acid was added and the sample was allowed to digest overnight. The next day, 10 ml of sulphuric-phosphoric acid solution was added to each sample. The contents were then transferred into a boric acid solution to which a further 10 ml of ferrous ammonium sulphate solution was added. After addition of 2 ml of barium diphenylamine sulphonate indicator, titration with standard potassium dichromate solution was performed until a grey end point was observed. The results of the study for the three hornblende samples and a reference standard (SY-3) appear in the table following this text. On the following page, the results are applied to electron microprobe analyses which gives total iron, and thus ferric iron may be determined by difference.

An estimate (s) of the population standard deviation can be obtained from duplicate determinations (x_1 and x_2) of similar samples (N) (Kretz, 1985);

$$s^2 = [\sum (x_1 - x_2)^2] / 2N$$

For the three duplicate determinations of ferrous iron from similar hornblende samples presented in the following table;

$$s_{\text{FeO}}^2 = 0.0362 : s_{\text{FeO}} = 0.20$$

The average concentration for the standard (SY-3; 3.59 wt. % FeO) is

indistinguishable from the accepted concentration (SY-3 = 3.58 wt. % FeO) (Govindaraju, 1984), and thus results are considered to be good. Additional error arises from small amounts of contaminating minerals in the separations, and from sample preparation and digestion (Kretz, 1985).

Propagating the error in FeO, determined here, and MgO (Appendix A) through the equation which estimates s for the ratio $Mg/(Mg+Fe)$ (Appendix A) gives;

$$s_{Mg}^{Hbl} / (Mg+Fe) = 0.005$$

Because the analyses are duplicate, a 95 % confidence limit is about 1.4s ($0.005(1.4) = 0.007$) (Kretz, 1985). This uncertainty is essentially constant over the concentration range of interest. Considerably more uncertainty arises from the application of these results to hornblende analyses for which only FeO_t is known (Appendix A).

Titrimetric determination of ferrous iron for three hornblendes

Sample	wt. sample	end (ml)	start (ml)	difference, minus	6.92	wt. % FeO
NPF-5	0.1181 gm	38.20	13.06	25.14	18.22	14.22
NPF-5	0.1103	32.21	8.00	24.31	17.39	14.53
NPF-9	0.1070	35.72	15.32	20.40	13.48	11.61
NPF-9	0.1020	33.30	13.50	19.80	12.88	11.64
NPF-35	0.1089	37.70	16.39	21.31	14.39	12.18
NPF-35	0.1075	38.28	17.50	20.78	13.86	11.88
SY-3	0.2031	29.50	14.90	14.60	7.68	3.49*
SY-3	0.2103	30.84	15.50	15.34	8.42	3.69*
Blank		16.72	9.78	6.94		
Blank		24.40	17.49	6.91 (avg. blank = 6.92)		

* - accepted value = 3.58 wt. % FeO (Govindaraju, 1984)

$$\text{wt. \% FeO} = ((V_s - V_b) / (1000 \times W_s)) \times N \times 71.846 \times 100$$

where: V_s = ml for sample; V_b = ml for blank

W_s = weight of sample; mol. wt. FeO = 71.846

N = normality of $K_2Cr_2O_7$

$$= (\text{wt. of } K_2Cr_2O_7 / (294.22/6)) \times (\text{volume (litres)})^{-1}$$

$$= (0.6290 / 49.037) \times 1 = 0.0128$$

	N F F - 3 5		N F F - 5		N F F - 9			
	Hbl	Pl	Hbl	Pl	Ttn	Hbl	Bt	Pl
SiO2	45.99	58.42	43.67	57.36	30.13	44.43	36.57	57.87
TiO2	0.34	---	0.70	---	38.42	0.59	2.18	---
Al2O3	10.48	25.99	10.69	27.15	1.75	10.42	15.42	26.80
Cr2O3	0.16	---	0.21	---	0.03	0.11	0.16	---
FeO _T	16.26	0.09	19.67	0.17	0.36	16.98	18.54	0.16
FeO	12.03	---	14.38	---	---	11.63	---	---
Fe2O3	4.73	---	5.93	---	---	5.99	---	---
MnO	0.22	---	0.31	---	0.00	0.24	0.29	---
MgO	13.23	---	9.83	---	0.39	11.65	13.21	---
CaO	9.88	7.88	11.64	8.92	28.05	11.83	0.00	8.57
Na2O	1.99	7.16	1.58	6.20	0.05	1.20	0.02	6.23
K2O	0.22	0.10	0.89	0.20	0.09	1.07	9.36	0.18
	98.25	99.64	99.17	99.99	99.27	98.51	95.74	99.81

----- not determined

Fe₂O₃ = FeO_{total} (electron microprobe) - FeO (titrimetric)

to Laurie Lake

Post-Sickle intrusive rocks

- 5) a) diorite b) tonalite c) tonalite intrusion breccia with abundant xenoliths of Wasekwan Group rocks d) granodiorite-granite e) quartz and feldspar porphyritic intrusion

Wasekwan Group rocks

- 1) hornblende-bearing psammite with calcareous lenses

- 5) a) diorite b) tonalite c) tonalite intrusion breccia with abundant

Wasekwan Group rocks

3) hornblende-bearing psammite with calcareous lenses

- 5) a) diorite b) tonalite c) tonalite intrusion breccia with abundant xenoliths of Wasekwan Group rocks d) granodiorite-granite
e) quartz and feldspar porphyritic intrusion

Wasekwan Group rocks

4) hornblende-bearing psammite with calcareous lenses

- a) layered psammite b) massive psammite

3) felsic to mafic metasedimentary and metavolcaniclastic rock

- a) layered psammite b) heterolithic psammite and psephite
c) felsic volcanic psephite d) layered amphibolite

2) mafic to intermediate metavolcanic flows and metavolcaniclastic rocks

- a) pillowed volcanic rocks b) volcanic psephite
c) layered amphibolite d) massive amphibolite

1) layered and massive biotite-quartz-hornblende-plagioclase psammite

Alteration

- approximate distribution of cordierite-garnet-gedrite and plagioclase-cummingtonite alteration
- zones of weakly altered to unaltered hornblende-bearing rocks are equally abundant within the patterned area

- approximate distribution of siliceous alteration
- includes patches of gedrite- and cummingtonite-bearing alteration

- outcrop area (f.h.-frost heave)
- geologic contact (approximate, gradational, unconformable)
- inferred fault
- minor fold e.g. minor S-fold with axis plunging 60 degrees and axial plane dipping 85 degrees
- overturned bedding, tops in direction of arrow
- bedding (inclined, vertical)
- overturned pillows, tops known
- foliation (inclined, vertical)
- plunge of mineral lineation within plane of foliation
- plunge of deformed clast
- compositional layering (inclined, vertical)
- lake or pond
- swamp
- drill road

il, unce
additional, uncertain)

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axis plunging
g 85 degrees
on of arrow

foliat
plane of foliation

vertical)

FIGURE 2: GEOLOGY OF THE NEW FOX ALTERATION ZONE

END

30-06-88

FIN