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THE METAMORPHISM OF SULFIDE-BEARING
PELITIC ROCKS FROM SNOW LAKE, MANITOBA

BY

IAN HUTCHEON, B.Sc., M.Sc.

A thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfilment of the requirements
for the degree of Doctor of Philosophy.

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Ottawa, Ontario

April, 1977

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ABSTRACT

Detailed geological mapping (1:8000) has been conducted near the Stall Lake and Anderson Lake mines in the vicinity of Snow Lake, Manitoba. Massive sulfides occur with pelitic rocks enclosed by metavolcanic rocks of the Amisk Group in the Churchill structural province. The metavolcanic rocks range from basaltic to rhyolitic compositions and display no recognizable differentiation trend.

Two periods of deformation can be recognized in micaceous rocks. F_1 folds are isoclinal, trending east-west, and are possibly coaxial with upright, northeast plunging F_2 folds. Lineations are parallel to F_2 fold axes and the underlying Stall and Anderson Lake ore bodies.

The major mineral assemblage in the pelitic rocks associated with the sulfides is:

staurolite-biotite-chlorite-muscovite-quartz-sillimanite-pyrite-pyrrhotite with or without magnetite.

Examination of sulfide-bearing biotite-chlorite-staurolite-muscovite rocks shows that the mole fraction of iron in these minerals decreases with increasing sulfur or oxygen fugacities at constant pressure and temperature.

The thermodynamic properties of (Zn,Fe)S solid solutions were calculated using a Margules solution model fitted to the data of Barton and Toulmin (1966) and used to calculate P-T-X relations for sphalerite-pyrite-pyrrhotite. Compositions of sphalerite from Scott (1976) give metamorphic pressures between 5 and 6 kb, consistent with

5.5 kb estimated by Froese and Gasparri (1975). Temperatures, estimated from the simultaneous solution of the pyrite-pyrrhotite-magnetite buffer and an equilibrium among biotite, muscovite, sillimanite and magnetite, range from 565 to 630.C.

A petrogenetic grid for the system K-Fe-Al-Si-O-H was constructed at 2000 and 5000 bars from the equilibria:

(James, pers. comm.; Richardson, 1968)

(Rutherford, 1970)

(Hsu, 1968; Turnock and Eugster, 1962).

(Wones et al, 1971)

(Chatterjee and Johannes, 1974).

A second grid was constructed using the equilibrium:

(Richardson, 1968)

The model defined by the equilibria above was used with a Temkin solution model and microprobe analyses to confirm previous estimates of metamorphic conditions. The daphnite and biotite-muscovite equilibria are consistent with other estimates, but both staurolite equilibria give temperatures of 700 C, approximately 100 C higher than all other estimates.

The compositions of H-O-S gases were also considered and under 700 C the gas coexisting with pyrrhotite-magnetite or pyrrhotite-pyrite-magnetite can be treated as a binary mixture of H_2 and H_2O . Pyrite-pyrrhotite or pyrite-magnetite coexist with H-O-S gases which contain significant amounts of sulfur species and silicate equilibria can no longer be treated as taking place in a binary H_2 - H_2O gas.

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Appendix I

Mineral Assemblages in Pelitic
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Appendix II

Chemical Analyses of Volcanic
Rocks

Appendix III

Electron Microprobe Analyses of
Minerals from Stall and Anderson
Lake Mines

Abbreviations of Mineral Names

al	almandine
an	annite
at	anthophyllite
bi	biotite
ch	chlorite
cp	chalcopyrite
da	daphnite
ga	gahnite
gr	graphite
gt	garnet
il	ilmenite
kf	potassium feldspar
ky	kyanite
mt	magnetite
mu	muscovite
pc	plagioclase
po	pyrrhotite
py	pyrite
qz	quartz
si	sillimanite
sp	sphalerite
st	staurolite
to	tourmaline

INTRODUCTION

The Snow Lake area in Manitoba (Figure 1-3) offers an excellent opportunity to study the metamorphism of pelitic rocks containing disseminated sulfides and oxides, associated with stratiform massive sulfide deposits. A detailed map (Figure 1-1, in pocket) of the area between the Anderson Lake and Stall Lake mines of the Hudson Bay Mining and Smelting Company, was completed by the author in 1972, while employed by the Geological Survey of Canada, under the supervision of Dr. E. Froese. In the fall of 1973 drill core was collected from both mines.

Froese and Gasparrini (1975) have defined three isograds, based on reactions inferred between the silicate minerals in four metamorphic mineral zones: biotite-chlorite, biotite-chlorite-staurolite, biotite-staurolite-sillimanite and biotite-garnet-sillimanite. The reaction which defines the isograd between the two intermediate metamorphic zones:

chlorite + staurolite + muscovite + quartz

biotite + sillimanite + H₂O (1)

occurs near the Anderson Lake and Stall Lake mines, and is the same reaction described by Guidotti (1974) in pelitic rocks from the Rangely Quadrangle, Maine. Froese and Gasparrini and Guidotti have documented Fe/Mg ratios, in coexisting silicates, which vary with changing metamorphic grade. Guidotti (1974) and Bachinskii (1975) have related increasing modal amounts of sulfides to Mg enrichment of the coexisting silicates.

The objectives of this study are:

- (1) To study the geology of metamorphosed, stratabound massive sulfide deposits and the associated rocks.
- (2) To determine what relationships exist, at constant total pressure and temperature, between the Fe-Mg ratio of coexisting silicates and the vapor composition inferred from the associated opaques.
- (3) To estimate the metamorphic conditions (temperature and total pressure) at the Stall Lake and Anderson Lake mines.
- (4) To construct a model for the metamorphism of pelitic rocks which includes the minerals found at Snow Lake, and apply the model to rocks in the Snow Lake area in Manitoba.
- (5) To quantitatively examine the relationships between silicate compositions and the composition of the H-O-S vapor phase.

Chapter 1 describes the geologic setting of the Snow Lake area, the geology of the detailed map area with reference to the lithologies of the Amisk volcanic and pelitic rocks, and the geology of the Stall Lake and Anderson Lake mines.

Chemical analyses of thirty seven samples of metavolcanic rocks from the Amisk Group are presented in Chapter 2. This information is used to briefly describe the primary environment of deposition of the volcanic rocks, pelitic sedimentary rocks and the associated massive sulfides.

The mineral assemblages in metavolcanic and pelitic rocks at the surface, and pelitic rocks from the mines are detailed in Chapter 3. The Anderson Lake and Stall Lake mines are close to mineral reaction (1) and were metamorphosed at approximately the same temperature and total pressure. The observed variation in $Fe/(Fe+Mg+Zn)$ for biotite, staurolite and chlorite can be related to the coexisting opaque

mineral assemblage, indicating that the compositions of the coexisting silicates are a function of fO_2 and fS_2 . The pressure and temperature of metamorphism and the stabilities of end-member equilibria in the system K-Fe-Al-Si-O-H are required to quantitatively study the relationship between silicate compositions and the composition of the coexisting H-O-S vapor phase.

In Chapter 4 the temperature and total pressure of metamorphism are estimated. The P-T-X phase relations of the assemblage sphalerite-pyrite-pyrrhotite, in the system Fe-Zn-S were calculated using activity coefficients for ZnS and FeS in sphalerite, derived from a two-constant (subregular) Margules solution model, fit to the data of Barton and Toulmin (1966), and thermodynamic data. The composition of sphalerite from the Stall Lake mine provides an estimate of the total metamorphic pressure between 5 and 6 kb. Equilibria among biotite, muscovite, sillimanite, quartz and magnetite, and pyrite, pyrrhotite and magnetite were solved simultaneously for fO_2 and temperature at constant total pressure. A Temkin (1945) ideal solution model was used to estimate the activity of annite in biotite. Because the equilibria intersect at a shallow angle, the uncertainty in the temperature estimate is large. The temperature also changes with the assumed Fe^{3+} content of biotite. For $Fe^{3+}/Fe^{3+}+Fe^{2+} = 0.1$, the estimated temperature is 570 C; if $Fe^{3+}/Fe^{3+}+Fe^{2+} = 0.2$, the estimated temperature is 630 C. These conditions agree well with 5.5 kb and 600 C, estimated for the Stall Lake mine by Froese and Gasparrini (1975) from the pelitic assemblages.

Experiments in the Fe end-member system are often directly compared to pelitic rocks observed in the field. If the equilibria in the system K-Fe-Al-Si-O-H are considered in $H_2 - H_2O$ mixtures, the stable assemblages can be determined from published experimental data.

Because minerals in natural pelitic rocks contain more components than the ideal system, the assemblages are not directly comparable. In Chapter 5 the stable equilibria for the system K-Fe-Al-Si-O-H are determined.

In Chapter 6 the assemblages observed in naturally occurring pelitic rocks from the Stall Lake and Anderson Lake mines are related to the stabilities of end-member equilibria determined in Chapter 5. The activities of ideal end-members dissolved in minerals, are estimated using ideal solution models and mineral analyses, and included in the equilibrium constants of the ideal equilibria. The calculation of $p_{H_2} + p_{H_2O}$ for the assemblages pyrite-pyrrhotite, pyrite-magnetite and pyrrhotite-magnetite indicates that for the estimated metamorphic conditions in the Snow Lake area, $p_{H_2} + p_{H_2O}$ may be substantially less than P_{total} for pyrite-pyrrhotite and pyrite-magnetite bearing rocks. One sample contains a mineral assemblage which implies a number of simultaneous equilibria, and fixes f_{S_2} and f_{O_2} if temperature and total pressure are specified. The H-O-S vapor composition is calculated at each temperature and the equilibria are solved simultaneously for temperature and X_{H_2} at constant total pressure. The value of p_{H_2O} at each temperature is specified by the coexisting buffer assemblage. Another sample coexists with a mineral assemblage that implies some simultaneous silicate-sulfide equilibria. A water conservative equilibrium between biotite-muscovite-sillimanite-quartz-pyrite allows the calculation of f_{O_2} and f_{S_2} if pyrite coexists with pyrrhotite. The activities of end-members in minerals can be estimated from the compositions and the sulfide-silicate equilibrium may be employed to calculate p_{H_2O} in an H-O-S vapor. This value for p_{H_2O} can be solved

for simultaneously with a dehydration equilibrium. The temperatures obtained by these methods are between 570 and 630 C, comparable to the previous estimates.

CHAPTER 1 GEOLOGY OF THE SNOW LAKE AREA

1-1 INTRODUCTION

Snow Lake is located within a 150 km belt of metamorphosed volcanic and sedimentary rocks that trends east-west to Flin Flon, 100 km to the west (Figure 1-3). The belt contains Amisk Group volcanic rocks and sedimentary rocks of the Missi group and is in the Churchill structural province of the Canadian Shield, near the Churchill-Superior boundary. To the south Paleozoic carbonates cover the Precambrian and to the north the belt is bounded by the Kisseynew gneiss complex. The rocks at Snow Lake are considered to be approximately equivalent in age and depositional environment to those at Flin Flon, but they are higher in metamorphic grade (Howkins and Martin, 1970). Stauffer *et al* (1975) conclude from chemical analyses of mafic volcanic rocks, that the Amisk Group, near Flin Flon represents an Aphebian (?) island arc deposit.

The disseminated and massive sulfides in the Anderson Lake and Stall Lake mines (Figure 1-4) are in pelitic host rocks and provide an opportunity to study the metamorphism of silicate-sulfide assemblages. Chemical analyses of the enclosing volcanic rocks indicate that they range in composition from tholeiitic to calc-alkaline rhyolites, andesites and basalts.

1-2 PREVIOUS WORK

J. B. Tyrell first entered the area around Snow Lake, traversing along the Grass River in 1896. Bruce (1916) and Alcock (1917) did reconnaissance mapping from Reed Lake to Wekusko Lake, 5 km southeast of Snow Lake. Alcock (1917, 1920)

Figure 1-3 The map of Manitoba, showing the location of Snow Lake in the Churchill Structural province.

Figure 1-4 Geological map of the Snow Lake area, after Froese and Noore (1972).

first reported the kyanite-bearing rocks near Anderson Lake. Harrison (1949) reported on the geology of the gold and massive sulfide deposits in the area. Russell (1957) did a structural study of the area between Anderson Lake and Osborne Lake. Bailes (1971) has compiled the geology of the Flin Flon-Snow Lake-Sherridon area. Moore and Froese (1972) and Moore and Froese (1972b) remapped the area from Chisel Lake to Osborne Lake and described the tectonic and metamorphic environment of the rocks around Snow Lake. Froese and Gasparrini (1975) describe the mineral zones and metamorphic isograds in the pelitic rocks. Sangster (1972) obtained radiometric age dates of lead minerals from ores of the Hanson Lake-Flin Flon-Snow Lake belt and Bell et al (1975) obtained Rb-Sr whole rock radiometric age dates from the volcanic rocks at Snow Lake. Both studies indicate the rocks are Archean in age. Bristol (1974) and Scott (1976) have done sphalerite geobarometry on the Stall Lake deposit.

Coats et al (1970) described the structure of Amisk rocks and associated massive sulfides in the Stall Lake mine of Stall Lake Mines Ltd., southeast of the Hudson Bay Mining and Smelting Company's Stall Lake deposit. Martin (1966) did a structural study of the Chisel Lake orebody. Howkins and Martin (1970) have compared the geology of the Snow Lake ore deposits to the geology of the Flin Flon deposits.

1-3 LOGISTICS

The area from Anderson Lake to the east of Stall Lake and north to Snow Creek (Figure 1-1, in pocket) was mapped at an

approximate scale of 1:8000. Mapping was done on foot and access was provided by gravel roads and railway and power lines. Air photographs, enlarged to 1" = 667' (approximately 1:8000) were used for geographic control. Peter Goetz provided able assistance in the field.

In the fall of 1973 Hudson Bay Mining and Smelting provided access to diamond drill core and plans from both the Anderson Lake and Stall Lake mines. The petrography of these rocks has been studied in detail.

1-4 GEOLOGIC SETTING OF THE SNOW LAKE AREA

Stratigraphic Setting

Table 1-1 shows the stratigraphy of the Snow Lake area. The stratified rocks around Snow Lake can be divided into the Amisk metavolcanic and Missi metasedimentary groups. There is no direct correlation with the Amisk and Missi type sections near Flin Flon, but the rocks are similar in lithologic and stratigraphic relationships. Massive sulfide deposits near Snow Lake are associated with felsic pyroclastic and pelitic rocks of the Amisk.

North of Squall and Herblet Lakes (Figure 1-4) are quartz monzonite gneiss domes overlain by metamorphosed pillow basalts, tuffs, agglomerates and fragmental andesites of the Amisk Group. "Quartz eye Granites" described by Harrison (1949) are metamorphosed felsic fragmental volcanic rocks and subvolcanic intrusions with quartz phenocrysts. The Missi psammites are described by Moore and Froese (1972) as fine grained quartzo-feldspathic rocks, containing minor amounts of pelitic rock. They overlie the Amisk

Table 1-1 Stratigraphy of the Snow Lake Area
(After Froese and Moore, 1972)

Intrusive Rocks		Large gabbroic to quartz monzonitic intrusions, smaller mafic intrusions, and sills in the Amisk and Missi Groups.
Missi Group		Psammite Pelite Psammite and pelite
Amisk Group		"Quartz eye" granitic rocks Pelites Undifferentiated extrusions Felsic pyroclastic rocks Mafic pyroclastic rocks Mafic flow rocks Quartz monzonite gneiss domes into Amisk volcanic rocks
	1510 my	
	1720 my	
	1750 1720 1690 my	

with gentle unconformity and transgress northeast onto the quartz monzonite gneiss domes. Cross-bedding is common and foreset beds indicate a source to the north. Metamorphosed dioritic and gabbroic intrusions occur in the Amisk and Missi groups.

Moore and Froese (1972) and Stauffer and Mukherjee (1971) suggest an Aphebian age for the Flin Flon-Snow Lake belt. Stauffer and Mukherjee report an age of 1775 ± 89 my., appropriate to the Hudsonian orogeny. Sangster (1972) reports model lead radiometric ages from 1780 to 1900 ± 44 my. for sulfide ores from the belt, further indicating an Aphebian age for the sulfides and enclosing rocks. Bell *et al* (1975) obtain an age between 1690 and 1750 my. for whole-rock Rb-Sr isochrons from the Snow Lake volcanic rocks.

Structural Geology

Moore and Froese (1972) describe three deformation events. F_1 , subparallel to compositional layering, forms the prominent planar fabric in the Amisk rocks. They describe two F_1 anticlines, the Nor-Acme anticline north of Snow Lake and a proposed F_1 anticline between Anderson and Stall Lakes. F_2 folds produce the dominant northeast structural grain and are well documented in the Missi rocks south of the study area. Mineral lineations, L_1 , are subparallel to the northeast plunging F_2 fold axes and the cigar-shaped orebodies at Stall and Anderson Lakes. Moore and Froese (1972) suggest F_1 and F_2 are coaxial or L_1 lineations are rotated parallel to F_2 fold axes. Moore and Froese ascribe open folds and warps associated with the formation of the gneiss domes to F_3 .

Metamorphism

The most comprehensive account of the metamorphism at Snow Lake is given by Froese and Gasparrini (1975). They have defined three isograds in pelitic rocks, related to reactions inferred between the silicate minerals in four metamorphic zones. The chlorite-biotite and chlorite-biotite-garnet zones are indistinguishable and are replaced by biotite-chlorite-staurolite according to reaction (1).

With increasing metamorphic grade chlorite and staurolite react according to reaction (2).

and the assemblage biotite-staurolite-sillimanite is stable. Froese and Gasparrini (1975) state that this reaction is close to the kyanite-sillimanite transition and show the corresponding biotite-sillimanite isograd in the vicinity of the Anderson Lake and Stall Lake mines. Further increase in metamorphic grade makes staurolite unstable according to reaction (3).

and the biotite-sillimanite-staurolite zone is replaced by the biotite-sillimanite-garnet zone.

Froese and Gasparrini estimate the metamorphic conditions in the Snow Lake area as 600 C and 5.5 kb from the intersection of reaction (2) and the kyanite-sillimanite transition. Bristol

(1974) and Scott (1976) report 5 and 7 kb. respectively from the sphalerite geobarometer. Thompson (1976) predicts the temperature 630 C at 5 kb for reaction (2).

1-5 GEOLOGY OF THE STUDY AREA

Local Stratigraphy

Top determinations in pillow basalts and mafic tuff face north and are restricted to the southern half of the area. The proposed stratigraphy for the study area is reported in Table 1-2. The massive sulfides are associated with pelitic rocks enclosed by felsic pyroclastic rocks containing quartz phenocrysts. Pillow lavas 500 m thick overlie the felsic rocks and give way to nondescript mafic flows and mafic agglomerates to the east and mafic agglomerates to the west. The agglomerates contain graded-bedded mafic tuff layers up to 10 m thick. A 300 to 400 m thick sequence of interbedded felsic and intermediate tuffs and agglomerates, with and without quartz phenocrysts lies on top of the mafic rocks and pinches to 20 m on the western map boundary. Mafic agglomerates, which thicken very rapidly to the west to 1000 m at the western boundary of the study area, overlie the felsic and intermediate rocks. To the east, the mafic agglomerates are intercalated with mafic tuffs, felsic volcanics and nondescript mafic rocks, probably flows and subvolcanic intrusions. To the north, along Snow Creek, the volcanics are overlain by pelitic schists.

The massive sulfide orebodies at Anderson and Stall Lakes are associated with the lowermost pelite. Figures 1-5, 6, 7 and 8 are plans of two levels from the Anderson Lake and Stall Lake mines.

Table 1-2 Stratigraphy of the Study Area

Rock Unit	MAP NUMBER	DESCRIPTION
Pelitic Schist	1a	Porphyroblastic garnet-biotite-staurolite schist.
Mafic Volcanic Rocks	3c	Flows and subvolcanic intrusions into underlying tuffs, felsic rocks and mafic agglomerates.
Mafic Agglomerate	3b	Thickens rapidly to the west. Fragments up to 3 cm. Some interbedded mafic tuffs, tops to the north.
Felsic and Intermediate Tuffs and Agglomerates	2b,2a	Fragments up to 25 cm and some poorly developed compositional layering. Some outcrops contain quartz phenocrysts.
Mafic Agglomerate	3b	Along strike from pillow lavas.
Mafic Pillow Lavas	3a	Well developed pillows, up to 70 cm, elongate down plunge to northeast. Tops to north.

Table 1-2 (cont.)

Felsic and Intermediate Pyroclastic Rocks	2a,2b	Dominantly agglomerates, fragments up to 1 m. Some F ₁ folds in outcrop. In- terbedded with pelites.
Pelitic Schists	1a,1b	Staurolite-biotite schists (1) and kyanite-chlorite schists (1) exposed at sur- face. This unit encloses the massive sulfide depo- sits.

STALL LAKE MINE

E MINE 1500 FOOT LEVEL

- Massive and Disseminated Sulfides
- Kyanite - Mg chlorite Schist
- Staurolite - Chlorite - Biotite Schist
- Garnet - Hornblende Gneiss and Amp

+ 5600 N

+

4800 E

+

0 FEET 200
0 METERS 50

5200 E

+

2d

- Massive and Disseminated Sulfides
- Kyanite - Mg chlorite Schist
- Staurolite - Chlorite - Biotite Schist
- Garnet - Hornblende Gneiss and Amphibolite

+

5200E

+

Figure 1-5

- Massive and Diss
- Kyanite Mg c
- Staurolite Ch
- Garnet Hornbl

0 FEET 200
0 METERS 50

- ▲ Massive and Disseminated Sulfides
- ▮ Kyanite Mg chlorite Schist
- ▮ Staurolite Chlorite Biotite Schist
- ▮ Garnet Hornblende Gneiss and Amphibolite

2d

4800 L
+ 6200 N

STALL LAKE MINE

2550 FOOT L.

2550 FOOT LEVEL

Figure 1-6

ANDERSON LAKE MINE
1600 FOOT LEVEL

Figure 1-7

2650 F

LAKE MINE . 2650' FOOT LEVEL

Figure 1-8

showing the approximate distribution of rock types in both mines. Only minor amounts of volcanic rocks occur with the pelitic rocks and massive sulfides, indicating the orebodies formed during a period of quiescence in the volcanic activity.

Pelitic Schists (Units 1a and 1b Figure 1-1)

Two compositionally distinct pelitic schists can be mapped in the study area. A magnesian pelitic schist containing kyanite and chlorite outcrops on the north shore of Anderson Lake. A more iron-rich staurolite schist outcrops near Anderson Lake and along Snow Creek. Both rock types are found in the Anderson Lake and Stall Lake mines.

The kyanite-chlorite schist (1a) is very coarse grained with kyanite porphyroblasts up to 10 cm in a matrix of quartz and very pale green chlorite, with minor amounts of biotite. This unit is usually in contact with the massive sulfides in both mines, particularly the Anderson Lake mine. The dumps at both mines display a varied mineralogy with cordierite, gahnite, anthophyllite, gypsum, anhydrite, calcite, garnet and staurolite bearing rocks described by Sabina (1971). One large sample, collected by the author from the Stall Lake dump, contains garnet, staurolite, chlorite, biotite, anthophyllite, cordierite, gahnite, pyrrhotite, pyrite and chalcopyrite. The exact location of the sample is unknown. Examination of precisely located drill core samples from underground at both mines using a petrographic microscope, X-ray diffraction and the electron microprobe failed to locate any cordierite bearing samples. Rocks with anthophyllite or gahnite are not common.

The staurolite schist (1b) is the most abundant pelitic rock underground in both mines and in surface exposures. In addition to staurolite these rocks contain biotite, chlorite, garnet and rarely muscovite or aluminosilicate (sillimanite or kyanite). A hercynite-gahnite spinel solid solution was observed in two polished thin sections from the Stall Lake mine.

Felsic and Intermediate Volcanic Rocks (Units 2a, 2b)

These rocks are poorly layered tuffs or agglomerates with felsic fragments up to 70 cm in a slightly more mafic matrix. Lichen obscures clean weathered surfaces making identification of primary features difficult.

Minor amounts of mica (biotite and muscovite) define the F_1 and F_2 foliations observed in the study area. Quartz phenocrysts up to 1 cm in diameter are polygonized with sutured grain boundaries in thin section. These rocks have 60-65 percent quartz, 20 percent untwinned plagioclase altered to sericite and epidote, and minor amounts of biotite, hornblende, potassium feldspar, muscovite, garnet, opaques and retrograde chlorite and calcite. This unit contains a progressively greater amount of hornblende to the east.

Mafic Pillow Lavas (Unit 3a)

The pillowed unit is a maximum of 400 m thick and pinches out to the east and west. Pillows seen on weathered outcrops have a maximum diameter of 1 m and are elongate parallel to the northeast plunging mineral lineations and the elongation of the stratigraphic

ically underlying Stall Lake ore zones.

In thin section, pillow rims are more mafic, containing more hornblende than the cores or interstices. The rims may also contain 1 to 2 mm pink euhedral garnets. The approximate modal composition is, blue-green hornblende 50 to 60 percent, untwinned plagioclase 30 percent with minor amounts of quartz, garnet, biotite, apatite, opaques and retrograde chlorite and calcite.

Mafic Agglomerate (Unit 3b)

The mafic agglomerate has a dark, fine grained matrix and may contain up to 70 percent fragments from 1 to 10 cm. The fragments include fine grained mafic types and mafic porphyritic rock with relict plagioclase phenocrysts up to 5 mm. The relict plagioclase phenocrysts are useful in identifying poorly exposed outcrops of the mafic agglomerate.

Fragments are usually slightly elongate parallel to F_1 , and near the Anderson Lake mine there are folded fragments with axial planes parallel to F_1 .

Thin section examination shows the mafic agglomerates have 35 to 45 percent euhedral, blue-green hornblende. Relict plagioclase phenocrysts are about 5 mm and strongly sericitized with albite twins. The mafic agglomerates also contain minor amounts of garnet, quartz, epidote, biotite, opaques and chlorite.

Mafic Tuff (Unit 4)

Mafic tuff layers, up to 10 m thick, outcrop in the mafic agglomerates. The tuffs have alternating mafic and slightly more felsic layers from 0.5 to 3 cm thick. Primary soft sediment

deformation features, cross bedding and graded bedding in the tuffs provide reliable "top" criteria.

In thin section, the mafic tuffs contain hornblende-rich layers alternating with layers containing a higher proportion of quartz and feldspar. The hornblende is blue-green and euhedral. Twinned plagioclase grains and minor quantities of biotite, quartz and opaques are also observed.

Massive Mafic Volcanics (Unit 3c)

The massive mafic rocks exhibit no primary structures or textures except possible relict plagioclase phenocrysts. They do have some intrusive cross-cutting contacts with the mafic agglomerate.

In thin section, euhedral relict plagioclase phenocrysts have well-developed albite twins, partially obliterated by recrystallization. In some grains twin individuals form separate grains with recrystallized, sutured grain boundaries. Blue-green hornblende is approximately equal in modal percent to plagioclase, forming from 40 to 50 percent of the rock. There are minor quantities of cummingtonite intergrown with hornblende.

Hornblendite (Unit 5)

An intrusive sill of hornblendite, up to 40 m thick, cuts felsic agglomerates near the main Snow Lake road. Clusters up to 2 cm of euhedral blue-green hornblende, suggestive of glomeroporphyritic texture, with minor inclusions of cummingtonite, form 80 percent of the rock. The matrix of polygonized quartz and

plagioclase contains approximately 10 percent equant euhedra of colorless epidote and trace amounts of red-brown biotite.

Textures

Figure 1-9 shows textures typical of rocks from the Snow Lake area. H 56, a porphyritic quartz agglomerate, has elongate, recrystallized quartz phenocrysts parallel to the biotite foliation. Garnet forms skeletal porphyroblasts up to 3 mm. Quartz and potassium feldspar form the matrix.

H 115, in Figure 1-9, is a sketch from a thin section of a pillow rim in a pillowed basalt. Garnet forms euhedral 5 mm porphyroblasts in a matrix of euhedral 3 mm long hornblende prisms. Plagioclase and quartz form a matrix with triple junction grain boundaries. Minor amounts of chlorite and opaques are present.

S263-75 and S267-55 are pelitic rocks from the Stall Lake mine, but the textures observed are similar to textures observed in surface samples. In 263-75 sillimanite forms as fibrous mats, bordering euhedral biotite. Staurolite forms poikiloblastic porphyroblasts up to 2 cm. Chlorite and muscovite are well crystallized grains, approximately 2 mm in length, parallel to the foliation. The matrix is generally a mosaic of quartz grains with minor plagioclase.

S267-55 is a staurolite-chlorite-biotite schist with garnet relicts. The garnet in samples with the above assemblage is mantled by quartz and plagioclase and is rarely found in contact with any other iron-magnesium silicates. These garnets are

1mm

1mm

1mm

S263-75
(S7)

1mm

S267-5
(S8)

Figure 1-9 Sketches of textures in metamorphic rocks from the Snow Lake area.

interpreted as relicts from lower metamorphic grade.

The mineral assemblages of rocks from outcrop and the mines are presented in Appendix 1. Figure 1-2 is a location map with sample numbers for surface samples. Underground samples can be located on Figures 1-5, 6, 7 and 8. The sample numbers give the sample location. The letter "A" indicates the sample is from the Anderson Lake mine, "S" indicates a sample from the Stall Lake mine. The first number after the letter is the number of the drill hole as recorded on Figures 1-5 to 1-8, the second number is the footage along the drill hole. For example, A172-55 indicates a sample from diamond drill hole 172 in the Anderson Lake mine, 55 feet from the collar of the hole. The letters "TH" after the first letter refer to a short "test hole".

Structural Geology of the Study Area

Only F_1 , F_2 and L_1 can be observed in the study area. F_1 folds can be identified only on a hand specimen or outcrop scale. The F_1 foliation is subparallel to compositional layering. The anticlinal F_1 isocline, proposed by Moore and Froese (1972) between Anderson and Stall Lakes could not be substantiated by detailed mapping. The evidence against the structure is as follows:

- (1) All top determinations in tuffs and pillow lavas, although restricted to the southern part of the area, face north.
- (2) The pelites between Anderson and Stall Lakes contain sulfides and both Mg-rich (kyanite-chlorite) and Fe-rich (staurolite-biotite) compositions are present. The northern band

Figure 1-10 (a) Poles to F_1 foliations. (b) Poles to compositional layering. (c) Poles to F_2 foliations. (d) L_1 lineations.

of pelite is not associated with known sulfide mineralization and only Fe-rich pelitic rocks outcrop.

(3) The southern pelites are enclosed by felsic pyroclastic rocks while the northern pelites are most closely associated with mafic flows and pyroclastics.

(4) There is no apparent symmetry in the rock types, aside from the pelites. Pillow lavas, for example, can only be identified in the southern part of the area.

Rapid lateral changes in rock units are commonly associated with volcanic rocks, therefore symmetry of outcrop distribution cannot be used to refute the proposed isocline, but all the evidence considered together does not support the proposed F_1 isocline of Moore and Froese (1972). Poles to F_1 foliations in the study area are shown in Figure 1-10a and poles to compositional layering are shown in Figure 1-10b.

F_2 causes open folding of F_1 in the study area, with F_2 axial planar cleavage, observed in micaceous rocks, nearly perpendicular to F_1 . Figure 1-10c shows poles to F_2 foliations and Figure 1-10d shows the plunge of mineral lineations (L_1) in the study area.

CHAPTER 2 CHEMICAL PETROLOGY OF AMISK VOLCANIC ROCKS

2-1 INTRODUCTION

The chemistry of Amisk volcanic rocks near Flin Flon has been studied by Froese (1969) and Stauffer et al (1975). Froese describes the Amisk as Archean volcanics derived from geosynclinal magmatism. Stauffer et al took 20 analyses from Froese and 40 new analyses of Amisk rocks; removed CO_2 , H_2O , S, CuO and ZnO ; made an arbitrary correction for iron sulfides and recalculated the analyses to 100 percent. Using the "igneous spectrum" diagram of Hughes (1972), modified to include Cenozoic island arc tholeiites, they eliminated all but six analyses of mafic rocks on the basis of post-depositional alteration. Based on the tholeiitic composition of these six analyses and the presence of pillow lavas, waterlain tuffs and turbidites, Stauffer et al conclude that the Amisk Group, near Flin Flon has a tholeiitic island arc affinity. Previously no chemical data has been available for Amisk volcanic rocks at Snow Lake.

2-2 METAVOLCANICS FROM THE AMISK GROUP, SNOW LAKE

Thirty-seven samples of Amisk volcanics, including all mappable rock types and covering the area mapped by the writer were analyzed by the Geological Survey of Canada using X-ray fluorescence and rapid chemical analysis techniques. The samples chosen for analysis were fresh and unsheared, weathered surfaces were trimmed before analysis. The analyses reported in Appendix 2 were classified using a computer program based on the classification of Irvine and Baragar (1971). Table 2-1 shows the field name and the

name assigned by chemical classification.

Field names for the metavolcanic rocks correspond well with names based on chemical data. Felsic agglomerates, with and without quartz phenocrysts, range from dacite to andesite, according to the chemical classification. These rocks have been subjected to upper amphibolite facies metamorphism, which probably masks post-depositional alteration. However the rocks have very little CO_2 or H_2O and may not have been significantly altered. Stauffer *et al* (1975) concluded that altered metavolcanic rocks near Flin Flon are depleted in SiO_2 , CaO , MgO , Na_2O and K_2O compared to their unaltered counterparts. The samples from Snow Lake did not appear altered in hand specimen or thin section, but some felsic rocks may have been silicified. Sample H-182, an agglomerate with quartz phenocrysts, contains 80.9 weight percent SiO_2 and approximately 75 volume percent quartz, indicating it is silicified.

2-3 CHEMICAL CLASSIFICATION OF VOLCANIC ROCKS

Non-fragmental mafic rocks, including all pillowed rocks, can be chemically classed as tholeiitic basalts. Mafic tuffs, agglomerates and intrusive rocks are either tholeiitic or calc-alkaline, high alumina basalts by the method of Irvine and Baragar (1971).

For the purpose of chemical classification Chayes (1975) rejects the use of analyses of andesites and basalts with greater than two weight percent H_2O , or a molar ratio of $2\text{Fe}_2\text{O}_3/\text{FeO}$ greater than unity. The intrusive hornblendite (H 91A) has too

Figure 2-1 Volcanic AFM diagram ($A = Na_2O + K_2O$; $F = FeO + 0.8998 Fe_2O_3$; $M = MgO$; all in weight percent oxide) indicates that the Snow Lake metavolcanic rocks are dominantly tholeiitic.

Figure 2-2 $Ne'Q'O1'$ cation norm diagram ($Ne' = Ne + 3/5Ab$; $Q' = Qz + 2/5Ab + 1/40px$; $O1' = O1 + 3/40px$) indicates that the Snow Lake metavolcanics are subalkaline.

high a ferric:ferrous ratio and H 50, a mafic agglomerate contains too much H_2O . Chayes also rejects andesites with normative $(An \times 100)/(An + Ab)$ (ie. "An content") for plagioclase greater than 58.5 (the average for Cenozoic basalts) and basalts containing plagioclase with An content less than 48 (the average for andesites). Analyses which do not meet Chayes criteria are indicated in Figures 2-1, 2 and 3 by a dot to the right of the symbol. Exclusion of these analyses does not affect the classification of the Amisk metavolcanic rocks from the study area.

Irvine and Baragar (1971) state that more than one type of graphical presentation of chemical data is necessary to classify volcanic rocks. Because the analyses have been classified using the Irvine-Baragar computer program only three graphical representation have been used to demonstrate the generally sub-alkaline, tholeiitic nature of the Snow Lake volcanics. Figure 2-1 shows the mafic rocks are tholeiitic and the felsic rocks are tholeiitic or calc-alkaline. Nearly all analyses fall within the sub-alkaline field of $Ne'-O1'-Q'$ plot (Figure 2-2) and the sub-alkaline field of an alkalis ($Na_2O + K_2O$) versus silica variation diagram (Figure 2-3). Abbreviations of names obtained from chemical classification are indicated beside the sample number in Figure 1-2 for analysed rocks. If the rocks at Snow Lake represent a monoclinal sequence the analyses of the volcanic rocks do not display any differentiation trend. Felsic rocks occur in many parts of the section and are interlayered with mafic rocks on a scale of 10 m, indicating that rocks of very different compositions were deposited over a short time span; probably from more than one

Figure 2-3 The variation of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ with silica (SiO_2) indicates that the Snow Lake metavolcanic rocks are subalkaline.

volcanic center.

2-4 ENVIRONMENT OF DEPOSITION OF VOLCANIC ROCKS AND ASSOCIATED PELITES AND SULFIDES

Bell et al (1975) give similar Proterozoic Rb-Sr whole rock ages for felsic and mafic Amisk Group rocks near the study area, and the granitoid gneiss domes north of the study area. The ages range from 1510 my for a quartz porphyry dacite, south of Anderson Lake, to 1750 my for the gneiss dome north of Herblet Lake. The similarity in ages suggests the gneisses could be remnant magma chambers, coeval with the extrusion of the Amisk volcanic rocks. Moore and Froese correlate the general east-west trend of the Flin Flon-Snow Lake belt with the formation of an Aphebian volcanic arc on the margin of an Archean continent. The lack of an apparent differentiation trend in the Amisk Group near Snow Lake is consistent with volcanism taking place at a continental margin.

The sulfides at Snow Lake are associated with approximately 500 m of pelitic rocks, enclosed by felsic pyroclastic rocks. The deposition of the sulfides, possibly by fumarole activity, took place during a long period of little or no extrusive volcanic activity.

Table 2-1 Volcanic Rock Names

Sample Number	Field name	Name from Chemical Analysis
H9	Quartz porphyry agglomerate	Tholeiitic dacite
H16	Mafic tuff	Calc-alkalai basalt
H18	Mafic agglomerate	Alkalai basalt
H36	Felsic agglomerate	Tholeiitic andesite
H49	Mafic tuff	Calc-alkalai basalt
H50	Mafic agglomerate	Tholeiitic basalt
H53	Mafic intrusive	Calc-alkalai basalt
H56	Quartz porphyry agglomerate	Tholeiitic dacite
H58	Quartz porphyry agglomerate	Tholeiitic dacite
H75	Mafic agglomerate	Calc-alkalai basalt
H76	Quartz porphyry agglomerate	Tholeiitic andesite
H81	Quartz porphyry agglomerate	Tholeiitic andesite
H91	Felsic agglomerate	Calc-alkalai dacite
H91A	Hornblendite	Calc-alkalai basalt
H97	Quartz porphyry agglomerate	Tholeiitic andesite
H102	Pillow basalt	Tholeiitic basalt
H115	Pillow basalt	Tholeiitic basalt
H119	Pillow basalt	Tholeiitic basalt
H120	Quartz porphyry agglomerate	Tholeiitic andesite
H122	Quartz porphyry agglomerate	Tholeiitic endesite
H123	Pillow basalt	Tholeiitic basalt
H129	Pillow basalt	Tholeiitic basalt
H132	Felsic agglomerate	Tholeiitic andesite

Table 2-1 (cont.)

Sample Number	Field Name	Name from Chemical Analysis
H135	Mafic agglomerate	Calc-alkalai basalt
H141A	Mafic agglomerate	Calc-alkalai basalt
H150	Mafic agglomerate	Tholeiitic basalt
H155	Mafic intrusive	Calc-alkalai basalt
H156	Mafic intrusive	Hawaiiite
H158	Mafic intrusive	Calc-alkalai basalt
H166	Mafic agglomerate	Tholeiitic basalt
H171	Pillow basalt	Tholeiitic basalt
H182	Quartz porphyry agglomerate	Calc-alkalai dacite
H186	Mafic intrusive	Tholeiitic basalt
H188	Felsic agglomerate	Tholeiitic andesite
H189	Quartz porphyry agglomerate	Tholeiitic andesite
H196	Mafic agglomerate	Calc-alkalai basalt
H198	Quartz porphyry agglomerate	Tholeiitic andesite

CHAPTER 3 METAMORPHIC PETROLOGY OF PELITIC ROCKS

3-1 INTRODUCTION

The changes in mineral zones, in the Snow Lake area, not associated with changes in bulk composition, have been related to isograds based on the reactions between the coexisting minerals in each zone by Froese and Gasparrini (1975). They define the following reactions between the minerals in each zone, corresponding to the mapped isograds:

Moore and Froese (1972) and Froese and Gasparrini (1975) indicate that metamorphic recrystallization was contemporaneous with the last major structural event. Neither report retrograde textures in the pelitic rocks, implying that the rocks contain the assemblage stable at the last recognizable peak of metamorphic conditions.

Hounsflow and Moore (1967) related high oxygen fugacities to higher Mg contents in coexisting biotite and staurolite. Banno and Kanehira (1961), Froese (1971) and Bachinski (1975) suggest that sulfur is involved in reactions between sulfides and silicates; which cause the silicates to be depleted in Fe, with increasing sulfur fugacity. Guidotti (1974) and Hounsflow and

Figure 3-1 Metamorphic mineral assemblages observed in pelitic rocks from the Snow Lake area. (a) Assemblages in the Stall and Anderson mines. (b) Assemblage in pelites north of isograd defined by reaction (2). (c) Assemblage south of isograd defined by reaction (2).

Moore have dealt with rocks in areas with obvious variations in intensive parameters, indicated by the distribution of mineral assemblages. The compositional relationships these authors describe may be obscured by sample to sample variation of intensive parameters. The samples to be discussed here are from two mines, close to mineral reaction (2) and should represent approximately the same P,T conditions.

3-2 MINERAL ASSEMBLAGES

Polished thin sections of rocks from both mines were examined in transmitted and reflected light. Samples collected from surface outcrops of volcanic and pelitic rocks were examined in transmitted light only. Phases present were considered to be in textural equilibrium if they had grain boundary contacts with one another. Assemblages observed for all rocks are reported in Appendix 1 and Figure 3-1.

No attempt was made to study the metamorphism of the volcanic rocks, but the mineral assemblages for the volcanic rocks are listed in Appendix 1. Garnet-biotite-chlorite $\pm$ staurolite (Figure 3-1c) is observed in thin sections from outcrops of the pelites between Anderson and Stall Lakes. The assemblage kyanite-chlorite-biotite (Figure 3-1a) is observed in the magnesian pelite schist near the northern shore of Anderson Lake. Both assemblages occur south of the isograd correlated with reaction (2) by Froese and Gasparri (1975). The assemblage garnet-staurolite-biotite is observed at the outlet of Snow Creek on the southeast shore of Snow Lake, north of the isograd represented by reaction (2).

Mineral Assemblages in Drill Core Samples

Most rocks from the Anderson Lake and Stall Lake mines contain staurolite-chlorite-biotite (Figure 3-1a) with muscovite, if the rocks are sufficiently aluminous. Some rocks also contain sillimanite and/or kyanite, but there is no textural relationship to indicate which Al_2SiO_5 polymorph is stable. Nearly all combinations of staurolite, biotite, chlorite, sillimanite (kyanite), muscovite, garnet, pyrite, pyrrhotite and magnetite are present with quartz, plagioclase, ilmenite, chalcopyrite and rarely sphalerite, but garnet and chlorite are never in contact. Except in garnet-staurolite-biotite assemblages, garnet grains are mantled by quartz and feldspar (Figure 1-9d). Other authors do not report retrograde metamorphic effects in the Snow Lake area and no retrograde textures were observed, except possible retrograde chlorite in the volcanic rocks. Microprobe analyses indicate homogeneous compositions among grains within a thin section and mineral zoning is absent, except in garnet relicts, verifying the absence of retrograde metamorphic effects and confirming that staurolite-biotite-chlorite is a prograde assemblage, representative of the peak of metamorphic conditions.

All the phases in reaction (2) are present in rocks from both the Anderson Lake and Stall Lake mines. The same assemblage is reported by Guidotti (1974) as marking the transition from the lower to the upper staurolite zone in the Rangely Quadrangle, Maine. Thompson (1976) predicts a metamorphic temperature of 630 C at 5 kb for reaction (2).

3-3 ELECTRON MICROPROBE ANALYSES

Analyses were performed by the author on carbon coated polished thin sections using the Cambridge Instruments Microscan 5 at Carleton University. An accelerating potential of 15 kv and a specimen current of approximately 5×10^{-6} amps were employed. In addition to the gahnite bearing samples, P. R. Mainwaring analyzed some samples previously analyzed by the author. The results indicate good reproducibility. Four or five grains of each mineral in each sample were analyzed at the core, and rim. Except for garnet, no zoning greater than 0.5 oxide weight percent was observed.

Difficulty was encountered in obtaining consistent staurolite analyses, with reasonable totals and appropriate amounts of aluminum and silicon. Using various combinations of standards, analyses were performed on a staurolite analyzed wet chemically by A. W. Hounslow, until a suitable procedure was found. Two analyzed biotites, Evans 1 and Evans 3 were obtained from B. W. Evans, and Evans 3 was used as a standard for K, Na, Fe, Mg, Si and Al in staurolite, biotite and chlorite analyses. An analyzed kaersutite was used for Ti, and various other analyzed silicates were used for Ca and Mn. For staurolite a jadeitic pyroxene was also employed as an Si and Al standard, and an analyzed Fe-Zn sphalerite was used for Zn.

Data were reduced using EMPADR VII (Rucklidge and Gasparri, 1969) modified by D. H. Watkinson and W. Yzerdraat for use on the XEROX computer at Carleton University. SUPERRECAL (Rucklidge, 1971) was used to calculate structural formulae for biotite and

chlorite analyses and stoichiometric water contents for biotite analyses. Mineral analyses and structural formulae are reported in Appendix 3.

3-4 ELEMENT PARTITIONING

Many authors have observed that Mg/Fe ratios in coexisting silicate minerals may be related to temperature, pressure and the fugacities of oxygen and sulfur. Hounslow and Moore (1967) have related increasing f_{O_2} to decreasing Fe-content of coexisting staurolite and biotite. Guidotti (1974) and Froese and Gasparrini (1975) describe coexisting minerals with Mg/Fe ratios which appear to be related to increasing metamorphic grade. The distribution of Fe and Mg between garnet and cordierite has been calibrated as a method for estimating temperature and pressure by Hensen (1971), Currie (1971) and Hutcheon et al (1974). Bachinski (1975) and Guidotti (1974) have found that higher modal amounts of sulfides can be correlated with increasing Mg/Fe ratios in coexisting silicates.

Figure 3-2 shows the compositions of staurolite, biotite and chlorite, coexisting with muscovite and quartz in rocks from the Anderson Lake (prefixed by "A") and Stall Lake (prefixed by "S") mines. Temperature and total pressure are assumed to be the same for all rocks. There is a significant, systematic variation of X_{Fe} for the minerals in each rock; and this variation can be correlated with the coexisting opaque assemblage. Samples A3, A8 and S6 contain pyrite, sample S7 contains pyrite, pyrrhotite and magnetite and A2, A4 and A7 contain pyrite and pyrrhotite.

Figure 3-2 The compositions of coexisting staurolite-biotite-chlorite in quartz-muscovite bearing rocks. Samples S6, A8 and A3 contain pyrite. S7 contains pyrite-pyrrhotite-magnetite and the remainder contain pyrite-pyrrhotite.

All mineral analyses are reported in Appendix 3.

Figure 3-3 has been constructed for the approximate metamorphic conditions; $P = 5 \text{ kb}$, $T = 600 \text{ C}$, as suggested for the Stall Lake mine in the Snow Lake area, by Froese and Gasparrini (1975). The data for the equilibria between iron sulfides and iron oxides were taken from Froese (1976). Accepting the above data it can be shown qualitatively that changing X_{Fe} in the silicates can be correlated with changes in $f\text{O}_2$ or $f\text{S}_2$ implied by the coexisting opaque assemblage. Sample S7, with pyrite-pyrrhotite-magnetite, has fixed $\log f\text{O}_2 = -16.45$ and $\log f\text{S}_2 = -1.77$ at the assumed metamorphic conditions. A2, A4 and A7 have $\log f\text{S}_2 = -1.77$ fixed by the coexistence of pyrite and pyrrhotite, but $\log f\text{O}_2$ is only restricted to values below the stability of magnetite. S7, which must have a higher value of $f\text{O}_2$ than A2, A4 and A7 has a lower X_{Fe} for all minerals, indicating the concentration of Fe in chlorite, biotite and staurolite is a function of $f\text{O}_2$. A8 and S6 contain pyrite and $f\text{O}_2$ is restricted to values below the stability of magnetite; $f\text{S}_2$ is restricted to values higher than the stability of pyrrhotite. For these two samples, $f\text{S}_2$ must be higher than for the other samples and they have the lowest X_{Fe} values for coexisting chlorite-biotite-staurolite.

The microprobe analyses in Appendix 3 show that Mg increases significantly in chlorites and biotites with low values of X_{Fe} . In staurolite, Zn increases, implying that Zn, rather than Mg, which remains relatively constant, substitutes for Fe. Griffen and Ribbe (1973) report that Zn substitutes in the Fe^{IV} and Al^{VI} sites in staurolite. Staurolite analyses, in Appendix 3, with

Figure 3-3 The stability of iron sulfides and oxides at 5000 bars and 600 C as a function of $\log f_{O_2}$ and $\log f_{S_2}$ from the data of Froese (1975). Only sample S7 has f_{O_2} and f_{S_2} specified. A3, 8 and S6 have f_{S_2} specified.

high Zn values, are slightly lower in Al and markedly lower in Fe than staurolites with low Zn contents. Figure 3-4 shows X_{Mg} in biotite and chlorite plotted against X_{Zn} in staurolite. Because the octahedral Al content of chlorite and biotite may be a function of bulk composition (Guidotti *et al.*, 1975), the points have been separated into muscovite and non-muscovite bearing rocks. It is clear that, for muscovite bearing rocks, X_{Mg} in chlorite or biotite bears a direct relationship to the amount of Zn in staurolite, in contrast with the results of Guidotti (1974) who reports that Zn in staurolite has no effect on Mg/Fe ratios in coexisting biotite and staurolite. Figures 3-5 and 3-6 show K_D for various analyzed mineral pairs.

The variation in the composition of iron-magnesium silicates with changes in fO_2 and fS_2 implied by the opaque assemblages supports Thompson's (1972) contention that fO_2 and fS_2 are locally buffered by equilibria taking place in the rock during metamorphism, rather than being externally controlled and subject to gradients over large areas. Greenwood (1975) has verified Thompson's suggestions for CO_2 - H_2O in carbonate rocks and H_2 - H_2O in pelitic rocks. The observed variations in mineral compositions at fixed pressure and temperature are related to the composition of the H-O-S vapor phase. To undertake a quantitative study of this problem, certain information is required. Some estimate must be made of the temperature and total pressure at the peak of metamorphism. In the next chapter the thermodynamic properties of (Zn, Fe)S solid solutions will be used to calculate P-T-X relations for the assemblage pyrite-pyrrhotite-sphalerite and

Figure 3-4 X_{Mg} in chlorite and biotite vs X_{Zn} in staurolite. The mole fraction of Mg in biotite and chlorite is related to the mole fraction of Zn in staurolite. Squares indicate biotite, triangles are chlorite. The open symbol indicates muscovite bearing rocks.

Figure 3-5 (a)

Figure 3-5 (b) Captions on next page.

Figure 3-6

Figure Captions for Figures 3-5, and 3-6

Figure 3-5 (a) Distribution of Fe between staurolite and biotite in samples from Stall and Anderson mines. (b) Distribution of Fe between staurolite and chlorite.

Figure 3-6 Distribution of Fe between chlorite and biotite.

Mole fractions are calculated as follows:

staurolite $(\text{Fe}/\text{Fe}+\text{Mg}+\text{Zn}+\text{Ti}+\text{Mn})$

chlorite $(\text{Fe}/\text{Fe}+\text{Mg}+\text{Mn}+\text{Ti}+\text{Al}^{\text{VI}})$

biotite $(\text{Fe}/\text{Fe}+\text{Mg}+\text{Mn}+\text{Ti}+\text{Al}^{\text{VI}})$

The closed circles represent rocks with no muscovite or sillimanite, the closed triangles represent sillimanite bearing rocks, the closed squares are rocks with muscovite and the open squares indicate muscovite-sillimanite bearing rocks.

thereby obtain an estimate of total pressure. The coexistence of biotite-muscovite-sillimanite-quartz-magnetite-pyrite-pyrrhotite in certain samples will be used to estimate the metamorphic temperature.

In the past, researchers have applied experimental work on iron end-member silicates, experiments with silicates of arbitrary iron-magnesium ratios, or experiments in which the composition of the phases is arbitrary, directly to pelitic assemblages observed in the field, with the common assumption that $P_{H_2O} = P_{total}$. The direct application of experiments of this type to naturally occurring assemblages in pelitic rocks is not valid because:

(1) Minerals in pelitic rocks rarely have ideal end-member compositions, or the compositions arbitrarily chosen in an experiment and; minerals in pelitic rocks may have substantial amounts of Ca, Mn, Ti, Na and Zn, in addition to the K, Fe, Si, Al, Mg, O and H present in most experimentally studied systems.

(2) The presence of sulfides, oxides and graphite in many pelitic rocks indicates that equilibrium takes place in a C-O-H-S vapor, whereas most experiments are conducted in O-H mixtures.

A summary of a thermodynamically valid approach to the problem of relating experimental data to naturally occurring sulfide bearing pelitic rocks from the Snow Lake area is given below. For the minerals biotite, chlorite, staurolite, garnet, sillimanite, magnetite and quartz; the stabilities of end-member equilibria in the system K-Fe-Al-Si-O-H can be determined from published experimental data. Using ideal solution models, and

the compositions of minerals obtained from microprobe analyses, the end-member equilibria can be adjusted for the change in activity of components which are present dissolved in minerals. Using thermodynamic data, magnetite in a relevant equilibrium can be replaced by pyrite. The resulting sulfide-silicate equilibrium can be solved simultaneously with a dehydration equilibrium to give estimates of temperature and the composition of the vapor phase, if total pressure can be specified. In Chapter 5 the stabilities of the necessary end-member equilibria are determined and in Chapter 6 these equilibria are applied to rocks from the Snow Lake area.

CHAPTER 4 ESTIMATES OF METAMORPHIC PRESSURE AND TEMPERATURE IN THE SNOW LAKE AREA

4-1 INTRODUCTION

In this chapter the temperature and total pressure of metamorphism at the Stall Lake and Anderson Lake mines are estimated. The composition of (Zn, Fe)S solid solutions, coexisting with pyrite-pyrrhotite has been experimentally calibrated by Scott (1973). Based on sphalerite compositions from the Stall Lake mine, Scott (1976) estimates 7 kb total pressure, significantly higher than 5.5 kb estimated by Froese and Gasparri (1975) from the intersection of reaction (2) (Chapter 3) and the kyanite-sillimanite transition. To resolve this discrepancy an independent study of the P-T-X relationships of sphalerite-pyrite-pyrrhotite was conducted. A two-constant Margules solution model was applied to the one atmosphere experimental data of Barton and Toulmin (1966) to extract activity coefficients for FeS and ZnS in sphalerite. Using the molar volumes of pyrrhotite and sphalerite and the compressibilities and thermal expansions estimated by Scott (1973), the phase relations of sphalerite solid solutions can be calculated. Compositions of sphalerite from the Stall Lake mine, reported in Scott (1976), provide estimates of the total pressure between 5 and 6 kb, using the calculated P-T-X relationships in this study.

If temperature and total pressure are fixed, the assemblages biotite-sillimanite-muscovite-magnetite-quartz and pyrite-pyrrhotite-magnetite allow the calculation of fO_2 if the activity of annite in

biotite (a_{an}^{bi}) is calculated from microprobe analyses using an ideal solution model. At the pressure specified by the sphalerite geobarometer, fO_2 is a function of temperature and the assemblages listed above can be solved simultaneously to give fO_2 and temperature. The temperature estimate for one sample from the Stall Lake mine, which contains both assemblages, is between 570 and 630 C, depending on the amount of Fe^{3+} assumed to be present in biotite. The fO_2 -temperature curves for both assemblages have similar slopes, making their intersection very sensitive to a_{an}^{bi} .

4-2 INTRODUCTION TO SPHALERITE GEOBAROMETRY

Kullerud (1953) recognized the potential usefulness of the FeS content of sphalerite as an indicator of the conditions of sulfide deposition. Barton and Toulmin (1966), Scott and Barnes (1971) and Scott (1973) have investigated the equilibrium between pyrite, hexagonal pyrrhotite and sphalerite at various temperatures and pressures. Scott (1973) has proposed from experimental work, that in the range from 300 to 600 C and pressures up to 5 kb, the mole fraction of FeS in sphalerite is independent of temperature. Scott's geobarometer has seen widespread use as an indicator of the total pressure of metamorphism of sulfide orebodies (Bristol, 1974; Lusk, Campbell and Krouse, 1975; Scott, 1976).

From mineral zones in pelitic rocks, Froese and Gasparrini (1975) estimate pressures near Stall Lake, Manitoba (Figure 4-10) at approximately 5.5 kb. Using the sphalerite geobarometer Scott (1976) obtains 7 kb.

In this study the data of Barton and Toulmin (1966, Table 3)

have been used to calculate temperature dependent activity coefficients for FeS and ZnS in sphalerite by applying a two-constant Margules (sub-regular) solution model. The activity coefficients have been combined with molar volume data and data for the pyrite-pyrrhotite equilibrium (Toulmin and Barton, 1964; Froese and Gunter, 1976) to calculate phase relations for pyrite, pyrrhotite and sphalerite.

4-3 DETERMINATION OF TEMPERATURE DEPENDENT ACTIVITY COEFFICIENTS FOR FeS AND ZnS IN SPHALERITE

Standard State

In this paper the standard state of FeS sphalerite and stoichiometric FeS pyrrhotite (troilite) is defined as the pure component at one atmosphere. The chemical potential of FeS sphalerite ($\mu_{\text{FeS}}^{\text{sp}}$) is defined by:

$$\mu_{\text{FeS}}^{\text{sp}} = \mu_{\text{FeS}}^{\text{sp}*} + RT \ln x_{\text{FeS}}^{\text{sp}}$$

and similarly for pyrrhotite:

$$\mu_{\text{FeS}}^{\text{po}} = \mu_{\text{FeS}}^{\text{po}*} + RT \ln x_{\text{FeS}}^{\text{po}}$$

for an ideal solution, where $\mu_{\text{FeS}}^{\text{sp}*}$ is the chemical potential of FeS with the sphalerite structure and $\mu_{\text{FeS}}^{\text{po}*}$ is the chemical potential of FeS with the pyrrhotite structure. For non-ideal solutions:

$$\mu_{\text{FeS}}^{\text{sp}} = \mu_{\text{FeS}}^{\text{sp}*} + RT \ln \gamma_{\text{FeS}}^{\text{sp}} x_{\text{FeS}}^{\text{sp}}$$

$$\mu_{\text{FeS}}^{\text{po}} = \mu_{\text{FeS}}^{\text{po}*} + RT \ln \gamma_{\text{FeS}}^{\text{po}} x_{\text{FeS}}^{\text{po}}$$

where γ is defined as the activity coefficient, consistent with Denbigh (1971, p. 270) and $\gamma.X$ = activity. The unit activity state is defined for pyrrhotite and sphalerite so that at unit concentration the activity is equal to one at any pressure and temperature of interest.

For the equilibrium:

$$K_{(4)} = \frac{a_{\text{FeS}}^{\text{sp}}}{a_{\text{FeS}}^{\text{po}}}, \text{ and:}$$

$$\begin{aligned} \Delta G_{(4)}^0 &= -RT \ln K_{(4)} - \Delta V_s (P-1) \\ &= -RT (\ln a_{\text{FeS}}^{\text{sp}} - \ln a_{\text{FeS}}^{\text{po}}) - \Delta V_s (P-1) \end{aligned}$$

For equilibrium (1) $a_{\text{FeS}}^{\text{po}}$ can be calculated at different pressures and temperatures using the solution model of Froese and Gunter (1976) based on the data of Toulmin and Barton (1964). The values of $a_{\text{FeS}}^{\text{po}}$ given by Barton and Toulmin (1966) were used to determine the constants for the Margules solution model, but for ease of application Froese and Gunter's solution model was used in subsequent calculations. A recent study by Rau (1976) is within 0.3 log $a_{\text{FeS}}^{\text{po}}$ of Toulmin and Barton for a specified fs_2 and temperature.

To obtain $\Delta G_{(4)}^0$ it is necessary to find values for $a_{\text{FeS}}^{\text{sp}}$. This may be done by expressing the variation of $\ln \gamma_{\text{FeS}}^{\text{sp}}$ and

$\ln \gamma_{\text{ZnS}}^{\text{sp}}$ with composition in terms of a power series, as suggested by Carlson and Colburn (1942). By this method:

$$RT \ln \gamma_{\text{FeS}}^{\text{sp}} = (2\bar{G}_{\text{ZnS}}^{\text{ex}} - \bar{G}_{\text{FeS}}^{\text{ex}}) x_{\text{ZnS}}^{\text{sp}2} + 2(\bar{G}_{\text{FeS}}^{\text{ex}} - \bar{G}_{\text{ZnS}}^{\text{ex}}) x_{\text{ZnS}}^{\text{sp}3} \quad (5)$$

$$RT \ln \gamma_{\text{ZnS}}^{\text{sp}} = (2\bar{G}_{\text{FeS}}^{\text{ex}} - \bar{G}_{\text{ZnS}}^{\text{ex}}) x_{\text{FeS}}^{\text{sp}2} + 2(\bar{G}_{\text{ZnS}}^{\text{ex}} - \bar{G}_{\text{FeS}}^{\text{ex}}) x_{\text{FeS}}^{\text{sp}3} \quad (6)$$

where $\bar{G}_{\text{FeS}}^{\text{ex}}$ is the excess free energy of FeS at infinite dilution.

If: $\bar{G}_{\infty}^{\text{ex}} = \bar{H}_{\infty}^{\text{ex}} - \bar{S}_{\infty}^{\text{ex}} T$

the expressions for $RT \ln \gamma$ can be substituted into equilibrium (4) and an equation in three unknowns, $\Delta G_{(4)}^0$, $\bar{G}_{\text{FeS}}^{\text{ex}}$, and $\bar{G}_{\text{ZnS}}^{\text{ex}}$ is obtained. Assuming a linear temperature dependence of these unknowns:

$$\Delta G_{(1)}^0 = \Delta H^0 - T \Delta S^0$$

$$\bar{G}_{\text{FeS}}^{\text{ex}} = \bar{H}_{\text{FeS}}^{\text{ex}} - T \bar{S}_{\text{FeS}}^{\text{ex}}$$

$$\bar{G}_{\text{ZnS}}^{\text{ex}} = \bar{H}_{\text{ZnS}}^{\text{ex}} - T \bar{S}_{\text{ZnS}}^{\text{ex}}$$

Data at 1104, 1001, 1000 and 925 C in Table 3 of Barton and Toulmin (1966) have been excluded because of the presence of wurtzite in the experimental runs. Data at 555 C were excluded because Barton and Toulmin report difficulty in obtaining equilibrium. For each of the remaining 114 experimental determinations there exists an equation in six unknowns. The 114 equations

Figure 4-1 Chemical potential vs $\ln X_{\text{FeS}}^{\text{sp}}$. The standard state and the unit activity state are chosen so that the value of $a_{\text{FeS}}^{\text{sp}}$ is unity for pure FeS with the structure of sphalerite. The standard state of FeS in sphalerite chosen as FeS with the structure of pyrrhotite (Barton and Toulmin, 1966) means that the activity of FeS in sphalerite ($a_{\text{FeS}}^{\text{sp}}$) is not equal to one for pure FeS sphalerite.

Figure 4-1a The data of Barton and Toulmin (1966) at 850 and 700 C

have been solved by least squares to obtain:

$$\Delta G_{(4)}^0 = 1166. - .125 T$$

$$\frac{\bar{G}_{\infty}^{\text{ex}}}{\text{ZnS}} = -3235. + 4.006 T$$

$$\frac{\bar{G}_{\infty}^{\text{ex}}}{\text{FeS}} = -212. + 1.377 T$$

4-4 MIXING PROPERTIES OF SPHALERITE SOLID SOLUTIONS

Barton and Toulmin equate $a_{\text{FeS}}^{\text{po}}$ with $a_{\text{FeS}}^{\text{sp}}$, thereby assuming that troilite is the standard state for FeS in sphalerite.

Figure 4-1 shows $RT \ln a_{\text{FeS}}^{\text{sp}}$ from this study plotted against $x_{\text{FeS}}^{\text{sp}}$. The unit activity state of FeS sphalerite is equal to:

$$\mu_{\text{FeS}}^{\text{sp}*} = -RT \ln a_{\text{FeS}}^{\text{sp}} + \mu_{\text{FeS}}^{\text{sp}}$$

where the activity is defined as one for a mole fraction of unity. On Figure 4-1, $\mu_{\text{FeS}}^{\text{po}*}$ is also plotted, clearly $x_{\text{FeS}}^{\text{sp}}$ is not unity when $a_{\text{FeS}}^{\text{sp}}$ equals one for the standard state of FeS in sphalerite chosen as pyrrhotite. The difference

$$\mu_{\text{FeS}}^{\text{sp}*} - \mu_{\text{FeS}}^{\text{po}*} \text{ is equal to } \Delta G_{(4)}^0$$

since $\mu^* = \mu^0$ at one atmosphere.

Fleet (1975) has chosen a standard state the same as the one chosen in this study and graphically integrated the Gibbs-Duhem equation at 850 C using the data of Barton and Toulmin. Fleet accepts Barton and Toulmin's assumption of non-temperature dependence of $a_{\text{FeS}}^{\text{sp}}$. Figure 4-2 shows the activities determined

Figure 4-2 Activity vs x_{ZnS}^{sp} at 850 C and 1 atm. compared to Fleet (1975). Broken lines indicate metastable compositions.

Figure 4-3 Free Energy vs x_{ZnS}^{sp} at 850 C and 1 atm, compared to Fleet (1975). G^{ex} is the excess free energy of mixing. G^{mx} is the free energy of mixing.

by Fleet compared to those in this study. There are minor differences in the ZnS rich area, especially for $a_{\text{ZnS}}^{\text{sp}}$, but the activities are comparable.

The free energy of mixing:

$$\Delta G^{\text{mx}} = X_{\text{FeS}}^{\text{sp}} RT \ln \gamma_{\text{FeS}}^{\text{sp}} X_{\text{FeS}}^{\text{sp}} + X_{\text{ZnS}}^{\text{sp}} RT \ln \gamma_{\text{ZnS}}^{\text{sp}} X_{\text{ZnS}}^{\text{sp}}$$

and the excess free energy of mixing:

$$\Delta G^{\text{ex}} = X_{\text{FeS}}^{\text{sp}} RT \ln \gamma_{\text{FeS}}^{\text{sp}} + X_{\text{ZnS}}^{\text{sp}} RT \ln \gamma_{\text{ZnS}}^{\text{sp}}$$

are compared at 850 C, 1 atm to those determined by Fleet in Figure 4-3. The difference between Fleet's values and those in this study is always less than 50 calories for a given sphalerite composition. Figure 4-4 shows that $RT \ln \gamma$ versus composition is comparable to Fleet, except in the region of infinite dilution. As Fleet shows (Fe, Zn)S solutions are nearly symmetric at 850 C, but Figure 4-5 shows the solution is asymmetric with $\ln \gamma_{\text{ZnS}}^{\text{sp}}$ greater than $\ln \gamma_{\text{FeS}}^{\text{sp}}$ at some temperature between 850 and 950 C and progressively greater at higher temperatures. At 850 C, and lower temperatures, $\ln \gamma_{\text{ZnS}}^{\text{sp}}$ is less than $\ln \gamma_{\text{FeS}}^{\text{sp}}$, the difference increasing with decreasing temperatures. The temperature dependence of activity is demonstrated in Figure 4-6, which shows the activities of FeS and ZnS in sphalerite at 750, 850 and 950 C and 1 atm.

4-5 DETERMINATION OF PRESSURE DEPENDENT ACTIVITY COEFFICIENTS AND THE EFFECT OF PRESSURE ON THE SPHALERITE-PYRITE- PYRRHOTITE EQUILIBRIUM

To calculate the molar volume of FeS and the partial molar

Figure 4-4: $RT \ln \gamma$ vs $x_{\text{ZnS}}^{\text{sp}}$ at 850 C and 1 atm. compared to Fleet (1975). Note that Fleet does not obtain γ at infinite dilution.

Figure 4-5 $RT \ln \gamma$ vs x_{ZnS}^{sp} at 750, 850 and 950 C and 1 atm. The solution is nearly symmetric at 850 C, but is asymmetric in opposite senses for 750 and 950 C.

Figure 4-6 The activity of FeS and ZnS at 750, 850 and 950 C and 1 atm. The activities of FeS and ZnS in sphalerite are temperature dependent.

volumes of FeS and ZnS in sphalerite, volumes were calculated in 5 mole percent intervals from 0 to 55 mole percent FeS, from the expression in Barton and Toulmin (1966):

$$a_0 = 5.4093 + .0005637 (\% \text{FeS}) - .000004107 (\% \text{FeS})^2.$$

A polynomial was fitted to the volumes obtained at the twelve points to give:

$$\begin{aligned} \text{Volume (cm}^3\text{)} = & 23.831 + 0.7452 x_{\text{FeS}}^{\text{sp}} - 0.5366 x_{\text{FeS}}^{\text{sp}^2} \\ & - 0.006835 x_{\text{FeS}}^{\text{sp}^3} \end{aligned}$$

The volume equation was differentiated to obtain:

$$\frac{dv}{dx}_{\text{FeS}}^{\text{sp}} = 0.7452 - 1.0731 x_{\text{FeS}}^{\text{sp}} - 0.02051 x_{\text{FeS}}^{\text{sp}^2}$$

This differential was evaluated at $x_{\text{FeS}}^{\text{sp}} = 0$ and $x_{\text{FeS}}^{\text{sp}} = 1$ to obtain the partial molar and excess partial molar volumes in Table 4-1. The polynomial for the volume was evaluated at $x_{\text{FeS}}^{\text{sp}} = 1$, to obtain the molar volume of FeS sphalerite. The relationship between molar volume, partial molar volume, excess partial molar volume and composition is shown in Figure 4-7.

The excess partial molar volume at infinite dilution may be included in the $\bar{G}_{\infty}^{\text{ex}}$ term to allow calculation of activity coefficients at any pressure and temperature, since:

$$\bar{G}_{\infty}^{\text{ex}} = \bar{U}_{\infty}^{\text{ex}} + P\bar{V}_{\infty}^{\text{ex}} - T\bar{S}_{\infty}^{\text{ex}}$$

and:

$$\bar{G}_{\infty}^{\text{ex}}_{\text{ZnS}} = - 3235. + 4.006 T + 0.0131 P \quad (7)$$

$$\bar{G}_{\infty}^{\text{ex}}_{\text{FeS}} = - 212. + 1.377 T + 0.0130 P \quad (8)$$

TABLE 4-1 Molar Volumes, Partial Molar Volumes and Excess Partial Molar Volumes for ZnS and FeS at Infinite Dilution.

	$V_{\text{FeS}}^{\text{sp}}$	$V_{\text{ZnS}}^{\text{sp}}$	$\bar{V}_{\infty}^{\text{sp}}_{\text{FeS}}$	$\bar{V}_{\infty}^{\text{sp}}_{\text{ZnS}}$	$\bar{V}_{\infty}^{\text{sp}^{\text{ex}}}_{\text{FeS}}$	$\bar{V}_{\infty}^{\text{sp}^{\text{ex}}}_{\text{ZnS}}$
cm ³	24.033	23.831	24.576	24.381	0.544	0.550
cal/bar ^a	0.5741	0.5693	0.5871	0.5824	0.0130	0.0131

Figure 4-7 Volume vs sphalerite composition showing the relationship of molar volume, partial molar volume and excess partial molar volume. The broken part of the curve indicates metastable compositions. Tangents to the molar volume curve at $X_{\text{FeS}}^{\text{sp}} = 0$ and $X_{\text{FeS}}^{\text{sp}} = 1$ define the partial molar volumes at infinite dilution. The excess partial molar volume is the difference between the molar volume and the molar volume at infinite dilution.

Using the molar volume of FeS pyrrhotite and FeS sphalerite at 25 C, ΔV solids for equilibrium (4) is:

$$V_{\text{FeS}}^{\text{sp}} - V_{\text{FeS}}^{\text{po}} = 24.033 \text{ cm}^3 - 18.198 \text{ cm}^3 = 5.835 \text{ cm}^3$$

$$(0.1394 \text{ cal/bar})$$

and $\Delta G_{(4)}^0$ at any temperature and pressure is:

$$\Delta G_{(4)}^0 = 1166. - 0.1248 T + 0.1394 (P - 1) \quad (9)$$

Equations (7), (8) and (9) may be used to calculate the sphalerite-pyrite-pyrrhotite equilibrium as follows.

Using the data of Froese and Gunter (1976) $a_{\text{FeS}}^{\text{po}}$ is calculated for the desired temperature and pressure. The equilibrium constant for (4) is calculated at P and T from equation (9). Knowing $K_{(4)}$ and $a_{\text{FeS}}^{\text{po}}$; $a_{\text{FeS}}^{\text{sp}}$ may then be calculated:

$$a_{\text{FeS}}^{\text{sp}} = \frac{K_{(4)}}{a_{\text{FeS}}^{\text{po}}}$$

From (7) and (8) the values of $\bar{G}_{\text{FeS}}^{\text{ex}}$ and $\bar{G}_{\text{ZnS}}^{\text{ex}}$ may be calculated and substituted into equation (2) to obtain $\gamma_{\text{FeS}}^{\text{sp}}$. Assuming values for $x_{\text{FeS}}^{\text{sp}}$, where $x_{\text{ZnS}}^{\text{sp}} = 1 - x_{\text{FeS}}^{\text{sp}}$, a second value for $a_{\text{FeS}}^{\text{sp}}$ may be obtained. The values of $x_{\text{FeS}}^{\text{sp}}$ (and therefore $x_{\text{ZnS}}^{\text{sp}}$) may then be iterated until the two values of $a_{\text{FeS}}^{\text{sp}}$ are equal.

This provides the temperature, pressure and composition of sphalerite in equilibrium with pyrite and pyrrhotite. A FORTRAN IV program was written to perform the iterations required and is listed in Appendix 4.

The data obtained have been used to produce the P-T-X relations in Figure 4-8. Scott's 1 bar and 5 kb experimentally

Figure 4-8 T-X projection of isobars for the sphalerite-pyrite-pyrrhotite equilibrium. The molar volumes are not corrected for isothermal compressibility and thermal expansion. The broken part of the isobars indicates the temperature range over which the isobars are extrapolations of the solution model. Solid curves are from Scott (1973).

determined isobars are shown for comparison.

Thermal Expansion and Compressibility

Scott (1973) demonstrated that thermal expansion and isothermal compressibility have an appreciable effect on the calculated P-T-X relations between pyrite, pyrrhotite and sphalerite. Using data given in Scott (1973, Tables 3 and 4) the molar volumes of sphalerite and pyrrhotite may be corrected for thermal expansion and compressibility. The data were also applied to the excess partial molar volumes in the calculations of activity coefficients, but they have a negligible effect.

Because the expansion and compressibility data for sphalerite are for ZnS, not FeS the calculations were done twice. The first set of calculations assumed that the volume change was proportional to the respective volumes of the end-members. The second set of calculations assumed that the volume of ZnS and FeS sphalerite change by the same absolute value. The two assumptions have a negligible effect on the P-T-X relations.

Examination of Figure 4-9 shows that for $x_{\text{FeS}}^{\text{sp}}$ approximately 0.13 and in the temperature range 575-700 C (within the experimental temperature range of Barton and Toulmin) the calculated 5 kb isobar is approximately $0.012 x_{\text{FeS}}^{\text{sp}}$ (1.2%) lower than the experimentally calibrated 5 kb isobar of Scott (1973). The extrapolation of the 1 atm isobar below the temperature range of Barton and Toulmin's data does not bend to the vertical as does Scott's 1 atm isobar. This is an artifact of the extrapolation of the solution model data. The 5 kb isobar is nearly vertical

Figure 4-9 T-X projection of isobars for the sphalerite-pyrrhotite-pyrite equilibrium. Molar volumes are corrected for thermal expansion and isothermal compressibility. The broken lines on each isobar indicates the temperature over which the isobars are extrapolations of the solution model. Short dashed lines are isobars from Scott (1973).

- Point 1: composition of sphalerite from Chisel Lake mine.
- Point 2: composition of sphalerite from Stall Lake mine.
- Point 3: composition of sphalerite from Osborne Lake mine.

Sphalerite compositions are reported in Scott (1976), temperature estimates at each mine are from Froese and Gasparrini (1975).

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Figure 4-10 Metamorphic isograds at Snow Lake, Manitoba, after Froese and Gasparinni (1975).

and in reasonable agreement with Scott (1973). It should be stressed that the calculated isobars are extrapolations based on estimated thermodynamic properties and properties of the (Zn, Fe)S solid solution retrieved from higher temperatures.

4-6 METAMORPHIC CONDITIONS AT SNOW LAKE, MANITOBA

Based on the intersection of the kyanite-sillimanite transition and estimated P, T conditions for the mineral reaction:

$$\text{staurolite} + \text{chlorite} + \text{muscovite} = \text{biotite} + \text{sillimanite} + \text{H}_2\text{O}$$

Froese and Gasparrini (1975) estimate the total pressure at the Anderson Lake and Stall Lake mines near Snow Lake, Manitoba to be approximately 5.5 kb. Scott (1976) estimates the pressure to be 7 kb from the experimental calibration of the sphalerite geobarometer. In Figure 4-9 the point indicated by the number "2" corresponds to the composition of sphalerite from the Stall Lake mine as reported by Scott (1976). The point numbered "1" is the composition of sphalerite from the Chisel Lake mine in the chlorite-staurolite-biotite zone and point "3" is the composition of sphalerite from the Osborne Lake mine in the biotite-sillimanite-almandine zone. The total pressure at the peak of metamorphism in the area of Stall Lake mine estimated from the solution model data is approximately 5 to 6 kb in agreement with the pressure estimated from the pelitic rocks by Froese and Gasparrini (1975). The temperatures at which the sphalerite composition from each locality is plotted are those estimated by Froese and Gasparrini.

4-7 TEMPERATURE OF METAMORPHISM

Standard State

To obtain a temperature estimate for the Stall Lake and Anderson Lake mines, the equilibrium constant, K (as defined in Chapter 5) for equilibrium (6) in Table 5-6 is required. To facilitate the manipulation of data by XCDFOR, a FORTRAN IV program to calculate isobaric T-X (vapor composition) diagrams (Skippen and Yzerdraat, 1973), a standard state pressure for the solids of 2000 bars must be adopted. For the remainder of this Chapter and in Chapters 5 and 6, the standard states for the chemical potential are defined as follows:

SOLIDS: the free energy of the pure phase with the composition of the component at 2000 bars and the temperature of interest.

GASES: the free energy of the ideal gas with the composition of the component at unit fugacity and the temperature of interest.

The symbol ΔG° will be used to refer to the free energy change of an equilibrium for the standard pressure of 2000 bars on the solid phases and unit fugacity for volatile phases.

The coexistence of biotite-muscovite-sillimanite-magnetite-quartz implies the equilibrium:

which can be obtained from equilibrium (6) in Table 5-6 by adding the K for the dissociation of water from Zen (1973):

$$\log K = 12447.90889 T^{-1} - 1.51609 \log T + 0.00016 T + 2.00131$$

where T is in Kelvin and log is the base 10 logarithm.

The equilibrium constant for (10) is:

$$K_7 = \frac{1}{a_{an}^{bi} \cdot fO_2^{1/2}}$$

which can be calculated at 2000 bars and adjusted to 5000 bars using the "C" term from the data in Table 5-6. The activity of annite in biotite (a_{an}^{bi}) can be calculated from a mineral analysis using the Temkin ideal ionic solution model in Chapter 5, allowing fO_2 to be calculated at any specified P and T.

The coexistence of pyrite and magnetite implies the equilibrium:

The free energy of formation of pyrite at one atm is given by Barton and Toulmin (1964) as:

Since $\Delta G^0 = -RT \ln K$ at equilibrium, $\log K_9$ can be calculated at one atm and any temperature and adjusted to 5000 bars using the change in molar volume of solids ($\Delta V_s = 0.6521$) from Robie and Waldbaum (1968).

Haas and Robie (1973) give new data for the free energy of

formation of magnetite at one atmosphere. A straight line, fitted to six data points between 298.15 and 1500 K, gives the following equation for equilibrium (13):

$$\Delta G_f^0 = -263399. + 73.850 T$$

and $\log K_{10}$ can be calculated at 1 atm and adjusted to 5000 bars using $\Delta V_s = 0.2792$ (Robie and Waldbaum, 1968). Subtracting (13) from three times (12) will give (11). If fS_2 can be obtained, fO_2 can be calculated at any temperature and 5000 bars since:

$$K_{11} = \frac{fO_2^2}{fS_2^3}$$

Sample S7 (Appendix 1), from the Stall Lake mine, contains all the minerals in equilibria (10) and (11), in addition to pyrrhotite; which fixes the value of fS_2 at any temperature and total pressure, allowing the calculation of fO_2 . Curves of fO_2 vs. T for equilibria (10) and (11) may be plotted at the estimated 5 kb pressure from the sphalerite geobarometer; and these curves have an intersection which represents the simultaneous solution of the two equilibria. Figure 4-11 shows the two curves, which intersect at a shallow angle. In Chapter 5, the amount of ferric iron (Fe^{3+}) in biotite is selected as 10% of the total iron ($\text{Fe}^{2+} + \text{Fe}^{3+}$) on the basis of published biotite analyses. The amount of ferric iron assumed in biotite changes the activity of annite in biotite as described in Chapter 5. In Figure 4-11, the

Figure 4-11 Intersection of f_{O_2} -T for equilibrium (11), Chapter 4 and the pyrite-pyrrhotite-magnetite assemblage (dashed lines). The numbers on the silicate equilibrium curves correspond to $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios.

fO_2 - T curves for equilibrium (10) are plotted at $(Fe^{3+}/Fe^{3+} + Fe^{2+}) = 0.1, 0.2$ and 0.3 intervals. The simultaneous solutions of equilibria (10) and (11) at 5 kb are 580 C for $(Fe^{3+}/Fe^{3+} + Fe^{2+}) = 0.1$ and 630 C for $(Fe^{3+}/Fe^{3+} + Fe^{2+}) = 0.2$. The curve for $(Fe^{3+}/Fe^{2+} + Fe^{3+}) = 0.3$ does not intersect the fO_2 - T curve for the pyrite-pyrrhotite-magnetite assemblage between 500 and 700 C, but this is probably an excessive estimate of Fe^{3+} in biotites from the Stall Lake mine.

4-8 PHASE DIAGRAM FOR ALUMINOUS BIOTITE

Introduction

The data used to calculate the equilibrium conditions for (10) can be used to calculate the variation in composition of Fe-Mg-Al biotites. Foster (1960) suggested a relationship between the Fe-Mg ratio of biotite and its octahedral Al (Al^{VI}) content. Guidotti et al. (1975) have demonstrated that the Al content of biotite, coexisting with muscovite, is not related to the Fe-Mg ratio; and that Foster's proposed correlation resulted from Mg-rich biotites (phlogopites) obtained from Al-poor bulk compositions. Hazen and Wones (1972) suggest that for nearly pure Fe annite-siderophyllite biotites there may be a relationship between Fe content and Al^{VI} content. Annite ($KFe_3AlSi_3O_{10}(OH)_2$) and phlogopite ($KMg_3AlSi_3O_{10}(OH)_2$) are commonly used as end-members to describe Fe-Mg solid solution in the biotite series. Rutherford (1973) chose the hypothetical end-member Aluminum biotite $KAl_3Al_4O_{10}(OH)_2$ to describe tetrahedral and octahedral Al substitution in biotite. Using the annite breakdown (Wones et al., 1971),

the muscovite breakdown (Chatterjee and Johannes, 1974) and a Temkin ideal solution model, a ternary phase diagram for Fe-Mg-Al biotites can be constructed for the metamorphic conditions 600 C and 5 kb; as estimated for the Stall Lake mine.

The aluminum content of biotite should be different for the assemblages:

quartz-magnetite-K feldspar-biotite

quartz-magnetite-K feldspar-muscovite-biotite

quartz-magnetite-muscovite-biotite

quartz-magnetite-muscovite-sillimanite-biotite

which correspond to increasingly aluminous bulk compositions.

Contours of $\log fO_2$ on the annite-phlogopite join were calculated from the data of Wones et al (1971) using the $\log K$ for equilibrium (6), in Table 5-6, and the equilibrium constant for the dissociation of water. The activity of annite was calculated for integer values of $\log fO_2$, for equilibrium (10) and converted to x_{an}^{bi} (the mole fraction of annite in biotite) using a Temkin solution model.

The area of the phase diagram (Figure 4-12) where K feldspar-quartz-magnetite-Fe Mg Al biotite and vapor coexist was contoured by including x_{Al}^{bi} (the mole fraction of aluminum biotite) in 0.05 increments. Assuming the variation in fH_2O with changing fO_2 is negligible; using $\log K$ for equilibrium (7) in Table 5-6 and the new a_{an}^{bi} , calculated from the Temkin model for varying x_{Fe} in biotite; a new value of $\log fO_2$ can be calculated. If $Fe/Fe + Mg$ is plotted against $\log fO_2$, the value of $Fe/Fe + Mg$ can be read off at even values of $\log fO_2$ for each increment of Al-biotite.

$T = 600\text{ }^{\circ}\text{C}$

$P_{\text{H}_2\text{O}} + P_{\text{H}_2} = 5\text{ kb.}$

biotite coexists with
quartz and magnetite

Figure 4-12 Phase diagram for aluminous Fe-Mg biotite at 600 °C and 5 kb. The contours are values of $\log f\text{O}_2$ and indicate that biotites become depleted in Fe as $f\text{O}_2$ increases.

The Fe/Fe + Mg ratio can be converted to Fe/Fe + Mg + Al, and for integer values of log fO_2 , the composition of the coexisting Fe-Mg-Al biotite may be plotted on the ternary phase diagram (Figure 4-12).

Sillimanite-Biotite-Muscovite Boundary

For the assemblage biotite-sillimanite-muscovite-magnetite-quartz it can be assumed (Guidotti *et al.*, 1975) that the Al^{VI} content of biotite is specified for a given pressure and temperature. The above assemblage implies the equilibrium:

and $K_{14} = a_{Al-bi}^{bi}$. One sample, S7, from the Stall Lake mine contains the assemblage listed above, and a_{Al-bi}^{bi} can be calculated from the biotite analysis in Appendix 3; and x_{Al-bi}^{bi} can be calculated since:

$$a_{Al-bi}^{bi} = \left(\frac{Al}{Al + Fe + Mg} \right)^3 \cdot \left(\frac{Al}{Si + Al} \right)^4$$

A plot of a_{Al-bi}^{bi} vs octahedral Al in biotite can be prepared for coupled Fe-Al for Al-Si substitutions in the ideal end-members annite and Al biotite. The activity of Al biotite is then calculated from the formula given above for the biotites in sample S7 and the appropriate mole fraction of Al biotite is taken from the activity-mole fraction plot. The boundary where sillimanite-muscovite-biotite-magnetite coexist is plotted in Figure 4-12.

Contours of $\log fO_2$ in the Muscovite Field

For the muscovite breakdown reaction, $\log K$ is given for the data of Chatterjee and Johannes (1974) for equilibrium (5) in Table 5-6. This equilibrium may be subtracted from the biotite reaction to give equilibrium (10), as was done in the previous section, and (10) may be combined with (14) to give:

and

$$K_{15} = \frac{1}{a_{\text{an}}^2 \cdot a_{\text{Al-bi}}^{\text{bi}} \cdot fO_2}$$

Since K_{15} is known, and $a_{\text{an}}^{\text{bi}}$ and $a_{\text{Al-bi}}^{\text{bi}}$ can be calculated from a mineral analysis using a Temkin solution model, fO_2 can be calculated and the muscovite-biotite-magnetite field of Figure 4-12 can be contoured by the same procedure used to contour the K feldspar field. Where equal contours of $\log fO_2$ intersect marks the line where muscovite-K feldspar-biotite-magnetite-quartz and vapor coexist. It is apparent from Figure 4-12 that increasing fO_2 at fixed pressure and temperature requires the biotite become more Fe-poor to maintain equilibrium.

CHAPTER 5 CALCULATED EQUILIBRIA FOR Fe END-MEMBER ALUMINOUS SILICATES

5-1 THEORY

Five algebraically independent equilibria can be used to evaluate equilibrium relationships among biotite, chlorite, staurolite, garnet, sillimanite, muscovite, quartz and magnetite in the system, K-Fe-Al-Si-O-H. Any suitable reaction, for which data are available, may be used. In this study independent equilibria have been recalculated to a breakdown of Fe-alumino-silicate to magnetite, sillimanite and quartz. The following assumptions have been made:

- (1) Quartz is present in excess; therefore no quartz absent equilibria are considered.
- (2) $p_{H_2} + p_{H_2O} = P$ total (for the construction of T-X diagrams).
- (3) Because potassium feldspar has not been observed as a stable, prograde metamorphic mineral in the pelitic rocks studied, equilibria (4) and (5) in Table 5-6 are used to introduce biotite and muscovite and eliminate potassium feldspar. Any equilibrium with biotite necessarily includes muscovite to accommodate potassium in the mass balance.

If P total is specified and temperature and X_{H_2} are allowed to vary independently, an isobaric invariant assemblage contains a maximum of 5 phases, plus quartz and fluid. Degenerate invariant points may contain fewer phases (Zen, 1966). Univariant assemblages contain 4 phases plus quartz and fluid. If biotite and muscovite coexist and quartz is present in excess, there are 15 isobaric

Table 5-1 Possible invariant points in the system:
K-Fe-Si-Al-O-H

Invariant point	Phases present	Reciprocal notation
1.	st, da, al, mt	(mu, an, si)
2.	st, da, al, si	(mu, an, mt)
3.	st, da, mt, si	(mu, an, al)
4.	st, al, mt, si	(mu, an, da)
5.	al, da, mt, si	(mu, an, st)
6.	an, mu, st, da, al	(mt, si)
7.	an, mu, st, da, mt	(al, si)
8.	an, mu, st, da, si	(al, mt)
9.	an, mu, st, al, mt	(da, si)
10.	an, mu, st, an, si	(da, mt)
11.	an, mu, st, mt, si	(da, al)
12.	an, mu, da, al, mt	(st, si)
13.	an, mu, da, al, si	(at, mt)
14.	an, mu, da, mt, si	(st, al)
15.	an, mu, al, mt, si	(st, da)

invariant points, 5 of which are degenerate and contain only 4 phases plus quartz and fluid. These invariant points are listed in Table 5-1. The compositions of the ideal end-members are given in Table 5-2. There are 22 univariant equilibria possible and they are listed in Table 5-6. COMBAL, a FORTRAN IV program in Moore (1976), was used to balance the equilibria. For any equilibrium, the equilibrium constant (K) is written in terms of the fugacities of gas species and the activities of solids involved. The equilibrium constant for the reaction:

is written:

$$K = \frac{(a_C)^c \cdot (a_D)^d \cdot (fH_2O)^w \cdot (fH_2)^h}{(a_A)^a \cdot (a_B)^b} \quad (16)$$

In this chapter the standard state for solids is defined at 2 kb and the standard state for gases is taken at 1 bar. Thus, at equilibrium;

$$\Delta G = \Delta G^\circ + RT \ln K + \Delta V_S (P-2000) = 0 \quad (17)$$

and:

$$\Delta G = \Delta H^\circ - T \Delta S^\circ + V_S (P - 2000) \quad (18)$$

where ΔG° , ΔH° and ΔS° are the standard Gibbs free energy, enthalpy and entropy of reaction with standard states as defined above.

If the change in heat capacity and the thermal expansion and compressibility for reactants and products are assumed to be negligible (Thompson, 1955; Fisher and Zen, 1971) then ΔH° and ΔS° are virtually constant and $\ln K$ can be expressed in terms of ΔH° ,

$\Delta S''$ and ΔV_s as:

$$\ln K = -\frac{\Delta H''}{RT} + \frac{\Delta S''}{R} - \frac{\Delta V_s (P-2000)}{RT} \quad (19)$$

Skippen (1971) writes (5-4) as:

$$\log K = \frac{A}{T} + B + C \frac{(P-2000)}{RT} \quad (20)$$

$$\text{where: } A = -\frac{\Delta H''}{2.303R}; B = \frac{\Delta S''}{2.303R} \text{ and } C = -\frac{\Delta V_s}{2.303R} \quad (21)$$

If $\log K + \frac{V_s}{RT} (P-2000)$ is plotted against reciprocal temperature for a set of experimental data, then A and B can be determined from the resulting linear relationship and C can be calculated from the molar volume data in Table 5-3.

5-2 ACTIVITIES OF SOLID SPECIES

Many of the equilibria subsequently considered involve phases that do not have the pure end-member compositions listed in Table 5-2. The equilibrium constant, as expressed by equation 16, must then include terms for the activities of such species. The lack of experimentally measured activities for many of the phases considered in this study requires the use of solution models to account for the activities in the equilibrium constant.

The Temkin (1945) ideal ionic solution model has been used frequently in geology since Ringwood (1958) first applied it to the problem of Ni-Ge solid solution in spinel. An explanation of the model can be found in Oates (1969) or Froese (1975). The activity of a component is considered to be equal to the atomic fraction of the element being mixed, raised to a power equal to the number of sites on which mixing takes place. The details of

the activity calculation for annite, daphnite, almandine and Fe-stauroilite are given below:

Biotite

If activities are to be calculated from mineral analyses the following procedure has been used. A mineral formula is calculated on the basis of 21 anionic charges (assuming the potassium layer is stoichiometric). The tetrahedral layer is filled with Si and enough Al to complete the layer. Fe, Mg, Mn, Ti and the excess Al are included in the octahedral layer. Vacancies are added to account for the excess charge from Al^{3+} and Ti^{4+} in the octahedral layer. The mole fraction of Fe is calculated, including the vacancies with the elements assigned to the octahedral layer, and cubed to correspond to the number of sites in the unit formula. The tetrahedral layer is calculated so that the ideal 3 Si:Al stoichiometry of annite is maintained, and the mole fraction of Si on this site is also cubed and multiplied by the Fe mole fraction cubed. The result is then multiplied by the mole fraction of tetrahedral Al. The formula used to calculate the activity of annite in biotite is given below:

$$a_{\text{an}}^{\text{bi}} = \left(\frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Mg} + \text{Mn} + \text{Ti} + \text{Al}^{\text{VI}} + \square} \right)^3 \cdot \left(\frac{\text{Si}}{0.75(\text{Si} + \text{Al}^{\text{IV}})} \right)^3 \cdot \left(\frac{\text{Al}^{\text{IV}}}{.25(\text{Si} + \text{Al}^{\text{IV}})} \right)$$

If the amount of Fe^{3+} is known, or assumed, the biotite is "dehydrogenated" according to the suggestion of Wones (1967).

This maintains a charge balance, and the appropriate formula is:

$$a_{\text{an}}^{\text{bi}} = \left(\frac{\text{Fe}^{2+}}{\text{Fe}^{2+} + \text{Mg} + \text{Mn} + \text{Ti} + \text{Al}^{\text{VI}} + \square + \text{Fe}^{3+}} \right)^3 \cdot \left(\frac{\text{Si}}{0.75(\text{Si} + \text{Al}^{\text{IV}})} \right)^3 \cdot \left(\frac{\text{Al}^{\text{IV}}}{.25(\text{Si} + \text{Al}^{\text{VI}})} \right) \cdot \left(\frac{\text{H}}{\text{O} + \text{H}} \right)^2$$

where $\square$ represents the number of vacancies.

Chlorite

The same assumptions were adopted for chlorite as were used for biotite. The formula for the activity of daphnite end-member in chlorite is:

$$a_{da}^{ch} = \left(\frac{Fe^{2+}}{Fe^{2+} + Fe^{3+} + Mg + Mn + (Al^{VI} - 1) + Ti + \square} \right)^5 \cdot \left(\frac{Si}{0.75(Si + Al^{IV})} \right)^3 \cdot \left(\frac{Al^{IV}}{0.25(Si + Al^{IV})} \right) \cdot \left(\frac{H}{\square + H} \right)$$

Garnet

The activity of almandine in garnet is calculated as in Hutcheon et al (1974):

$$a_{al}^{gt} = \left(\frac{Fe^{2+}}{Fe^{2+} + Mg + Mn + Ca} \right)^3$$

Staurolite

The ideal stoichiometry of most phases, except staurolite is well known and structural formulae can be readily calculated from mineral analyses. Deer et al (1966) and Hollister (1970) accept the formula:

with one mole of H_2O per formula unit. Rutherford (1968) gives the proportions of Fe:Al:Si as 4:18:7.5 for the synthetically prepared staurolites used in his experiments and the experiments of Richardson (1968). Griffen and Ribbe (1973) verify approximately the stoichiometry of Richardson and Rutherford and report

two moles of H_2O formula unit, on the basis of a detailed crystal chemical study of X-ray data and published anhydrous analyses.

Smith (1968) also reports two moles of H_2O per formula unit. The stoichiometry of Rutherford is accepted with the water content proposed by Griffen and Ribbe (1973). The total formula is doubled to give a formula free of fractions to facilitate matrix manipulations. The formula for staurolite accepted in this work is:

To properly determine the equilibrium conditions of staurolite reactions the exact stoichiometry, possible solid substitutions and equilibrium water content must be determined. Such an investigation is beyond the scope of this thesis. Because of the difficulty in assigning elements to specific sites in staurolite it was assumed that Fe, Mg, Mn, Zn and Ti may substitute on the same site. The activity of Fe-staurolite is then calculated from the formula:

$$a_{Fe-St}^{st} = \left(\frac{Fe}{Fe + Zn + Mg + Mn + Ti} \right)^8$$

Ferric iron is not indicated in the above expression because Griffen and Ribbe (1973) report that no Fe^{3+} can be detected in Mossbauer spectra of staurolite.

5-3 EXTRACTION OF INDEPENDENT EQUILIBRIA

Experiments with iron-bearing phases employ either solid-phase oxygen to control the fugacity of oxygen (Eugster and Wones, 1962; Hsu, 1968) or the Shaw membrane (Wones *et al.*, 1971) to control the fugacity of hydrogen. If solid phase oxygen buffers

Table 5-2 Compositions of ideal end-members

End-Member	Composition
Daphnite	$\text{Fe}_5 \text{Al}_2 \text{Si}_3 \text{O}_{10} (\text{OH})_8$
Staurolite	$\text{Fe}_8 \text{Al}_{36} \text{Si}_{15} \text{O}_{96} \text{H}_8$
Annite	$\text{K Fe}_3 \text{Al Si}_3 \text{O}_{10} (\text{OH})_2$
Almandine	$\text{Fe}_3 \text{Al}_2 \text{Si}_3 \text{O}_{12}$

Table 5-3 Molar Volumes of Pure Phases

PHASE	VOLUME (cal/bar)	SOURCE
almandine	2.754	Hsu, 1968
annite	3.688	Robie <u>et al</u> , 1967
cordierite	5.577	Deer <u>et al</u> , 1962
daphnite	5.1396	McOnie <u>et al</u> , 1975
hercynite	0.974	Robie and Waldbaum, 1968
sanidine	2.605	Robie and Waldbaum, 1968
magnetite	1.064	Robie and Waldbaum, 1968
muscovite	3.361	Robie and Waldbaum, 1968
quartz	0.542	Robie and Waldbaum, 1968
sillimanite	1.192	Robie and Waldbaum, 1968
staurolite	21.406	Rutherford, 1968

Table 5-4 Constants for Solid Phase Oxygen Buffers
Standard state for solids is 1 bar.

BUFFER	A	B	C	SOURCE
NNO	-24930.	9.36	.046	Huebner & Sato (1970)
QFM	-24770.	8.47	.092	Hewitt (pers. comm.)
QFM	-25287.	8.95	.110	Hewitt (1976)
MW	-34667.	14.45	.083	Skippen (1967)
HM	-25773.	14.75	.091	Beane (pers. comm.)
MI	-29260.	8.99	.061	Norton (1955)
WI	-27480.	6.64	.056	Robie and Waldbaum (1968)

are used the following expression is used to calculate the oxygen fugacity, fO_2 :

$$\log fO_2 = \frac{A}{T} + B + \frac{C(P-1)}{T}$$

where (P-1) indicates that the solid phases of the buffer are referred to unit pressure standard state. Table 5-4 gives the A, B and C constants for various buffers and the sources of the data.

Fugacity coefficients for water were taken from Burnham et al (1969) and fugacity coefficients for hydrogen below 3 kb were taken from Shaw and Wones (1964) and Ryzhenko and Volkov (1971) for pressures above 3 kb. The methods used to extract each independent equilibrium are described below. The numbers for equilibria are the same as the appropriate number in Table 5-6.

Daphnite

The reaction used to introduce daphnite into calculated phase relations is:

James (written comm.) gives the following brackets for an equilibrium among cordierite, chlorite, magnetite and quartz.

$$p\text{H}_2\text{O} = 2 \text{ kb} \quad T = 538 \pm 12 \text{ c}$$

$$p\text{H}_2\text{O} = 4 \text{ kb} \quad T = 575 \pm 12 \text{ c}$$

on the NNO buffer. The coexistence of these minerals implies the equilibrium:

and

$$K_{1a} = \frac{f\text{H}_2\text{O}^{16} \cdot f\text{H}_2^8 \cdot a_{\text{mt}}^8}{a_{\text{da}}^6 \cdot a_{\text{ch}}^6}$$

Figure 5-1 $\log K$ for equilibrium data measured by James (written comm.) vs $1/T$. The equilibrium constant includes the activity of daphnite calculated from an ideal solution model for the compositions reported by James et al (1976).

Figure 5-2 $\log K$ vs $1/T$ for the cordierite-hercynite-sillimanite equilibrium. (Richardson, 1968). The activities of the spinels are calculated from compositions given by Richardson according to the solution model of Froese (1973).

James et al (1976) give the composition of the chlorite phase as:

Using the previously described Temkin model:

$$a_{\text{da}}^{\text{ch}} = 0.1833$$

James et al (1976) do not give the composition of the spinel phase in the experiments, but the magnetite must be less aluminous than magnetite coexisting with hercynite. At the maximum temperature of the experiments, magnetite coexisting with hercynite would have a composition of 0.85 magnetite (Turnock and Eugster, 1962).

Including the activity of magnetite with this composition, calculated as in Froese (1973), in the equilibrium constant would decrease $\log K_{1a}$ by approximately 0.4 log units; this adjustment is considered negligible when compared to log k values 55 to 62 for this reaction. The spinel phase is accordingly treated as pure magnetite, and $\log K_{1a}$ is shown in Figure 5-1.

Fe-cordierite contains structural water, and the water content is a function of temperature and $f\text{H}_2\text{O}$ (A. E. Gunter, pers. comm.). Richardson (1968) gives data for the stability of cordierite, sillimanite, hercynite and quartz, which imply the equilibrium:

Equilibrium (1b) will be used to subtract cordierite from the experiments performed by James, assuming that the cordierites have the same water content. The equilibrium constant for (1b) is:

$$K_{1b} = \frac{a_{\text{mt}}^{\text{sp}} \cdot a_{\text{hc}}^{\text{sp}} \cdot f\text{H}_2}{f\text{H}_2\text{O}}$$

Figure 5-3 $\log K$ vs $1/T$ for equilibrium (1) in Table 5-6.

The activities of magnetite and hercynite were determined from compositions given by Richardson (1968), using the Margules parameters in Froese (1973). Figure 5-2 shows $\log K_{1b}$ vs $1/T$. Equilibrium (1a) can be added to $1.5 \times (1b)$ to give:

The data in Table 5-5 may be used to calculate ΔH and ΔS for equilibrium (1d).

from the relationships:

$$\Delta H'' = \Delta H^0(298,1) + \int_{298}^T C_{pd}T + \Delta V_s (P-1)$$

$$\Delta S'' = \Delta S^0(298,1) + \int_{298}^T \frac{\Delta C_p}{T} dT$$

Using $\Delta H''$ and $\Delta S''$ and the calculated value of V_s , $\log K_{1d}$ can be calculated from (19). To obtain $\log K_{1a}$, equilibrium (1d) can be divided by 2, added to (1c) and the result divided by 2 to obtain equilibrium (1) (Table 5-6).

Staurolite

Two staurolite equilibria have been considered in this study. Equilibrium (2) in Table 5-6, ie.,

has been studied by Rutherford (1970) and $\log K_2$ is plotted against $1/T$ in Figure 5-4.

Table 5-5 Thermodynamic data for phases in the equilibrium: $3hc + 3qz = mt + 3si + H_2$

Component	ΔH_f^0	ΔS^0	ΔS_f^0	a	b	c	V_{cm}^3
hc	-475420 ¹	25.4 ²	-92.652 ³	11.63 ⁴	26.8	0.00	40.75 ²
αqz	-217650 ²	9.88 ²	-43.616 ³	11.22 ⁴	8.2	-2.7	22.69 ²
βqz	-217730 ⁵	9.00 ²	-44.496 ³	14.41 ⁴	1.94	0.00	23.72 ²
αmt	-267250 ⁶	34.83 ⁶	-82.722 ³	25.06 ⁷	43.11	-1.45	44.52 ²
βmt	-271720 ⁵	20.51 ⁵	-97.042 ³	42.24 ⁷	2.28	38.66	44.52 ²
si	-613145 ⁸	23.13 ⁸	-117.4 ³	40.02 ⁸	7.39	-11.67	49.9
H ₂ O	-57796 ²	45.104 ²	-10.602 ³	7.3 ⁴	2.46	0.00	0.00
H ₂	0.00	31.208 ²	0.00	6.52 ⁴	0.78	0.12	0.00
Al	0.00	6.77	0.00	4.94 ⁴	2.96	0.00	0.00
αFe	0.00	6.52	0.00	3.04	7.58	0.60	0.00
Si	0.00	4.50	0.00	5.70	0.70	-1.04	0.00
O ₂	0.00	48.996	0.00	7.16	1.00	-0.40	0.00

Sources of data: 1. Zen (1973) 2. Robie and Wauldbaum (1968) 3. calculated 4. Kelly (1960) 5. Beane (written communication to G.B. Skippen) 6. Haas and Robie (1973) 7. Haas (written communication to Beane) 8. Nesbitt (written communication).

Figure 5-4 $\log K$ vs $1/T$ for the stauroilite reaction of Rutherford (1970).

Figure 5-5 $\log K$ vs $1/T$ for the staurolite-almandine equilibrium (Richardson, 1968).

Equilibrium (12) in Table 5-7 was studied experimentally by Richardson (1968) and may also be used to introduce staurolite to calculated phase relations. The equilibrium is:

Figure 5-5 shows $\log K_{12}$ vs $1/T$.

Garnet (Equilibrium (3), Table 5-6)

Hsu (1968) gives brackets for the equilibrium:

$$K_{3a} = \frac{a_{\text{hc}}^3 \cdot a_{\text{mt}}^2 \cdot f_{\text{H}_2}^2}{f_{\text{H}_2\text{O}}^2}$$

if quartz and almandine are pure phases with unit activity, for Hsu's runs in which the product assemblage is stable and magnetite and hercynite coexist. Froese (1973) has fitted the data of Turnock and Eugster (1962) for the spinel solvus to a Margules solution model. For the temperature of each run in which Hsu reports coexisting magnetite and hercynite, the mole fractions and activities of hercynite and magnetite in the spinel phase can be calculated using the model reported by Froese (1973). Figure 5-6 shows $\log K_{3a}$ vs $1/T$ for equilibrium (3a).

To obtain $\log K_3$, hercynite must be removed from equilibrium (3a). This has been accomplished by subtracting equilibrium data for (1d) from (3a) as described for chlorite phase relations. The result can be divided by 3 to give equilibrium (3) (Table 5-6):

Figure 5-6 The experimental runs of Hsu (1968) for equilibrium (3a). The equilibrium constant contains terms for the activities of the spinels.

Figure 5-7 The experimental points of Hsu (1968) after hercynite has been removed from the equilibrium using the thermochemical data in Table 5-5.

Figure 5-8 Equilibrium (3), Table 5-6, derived by linear combination of equilibria (3a) (Hsu, 1968) and (1d) thermodynamic data, Table 5-5. The B constant, calculated from thermochemical data fits the most constraining brackets for equilibrium (3), Table 5-6.

The entropies in Table 5-5 can be combined with an estimated entropy of 67.7 for almandine (Nesbitt, pers. comm.) to obtain an entropy for reaction (3). Dividing ΔS° by $2.303R$ (see equation 21) gives the "B" term for equilibrium (3), Table 5-6 as 3.12, slightly larger than 2.346 estimated from Hsu's experimental data. The plot of $\log K_3$ vs $1/T$ with the estimated "B" term (Figure 5-8) fits the experimental data of Hsu (1968). The experimentally determined "B" constant is used for subsequent calculations.

Annite (Equilibrium (4), Table 5-6)

Wones et al (1971) give three brackets for the breakdown of biotite according to the reaction (Table 5-6)

Zen (1973) reports the biotite composition in Wones et al (1971) as:

Using a Temkin model $a_{\text{an}}^{\text{bi}} = 0.527$ for a biotite of the given composition. A Shaw hydrogen membrane (Shaw, 1967) was used in the experiments and $f\text{H}_2$ is obtained directly from a measured pH_2 and known values of γ_{H_2} (Shaw and Wones, 1965). Figure 5-9 shows $\log K_4$ vs $1/T$ for Wones et al (1971). Using the entropy of formation of sanidine = -177.554 (Robie and Waldbaum, 1968) in addition to the entropies of other phases in Table 5-4, a value can be calculated for the "B" constant of equilibrium (4). The entropy of annite is from Beane (1974). Figure 5-10 shows the two values of "B" plotted on a $\log K$ vs $1/T$ diagram. The ΔS° calculated from

Figure 5-9 The experimental brackets of Wones et al (1971). The equilibrium constant includes the activity of annite in biotite calculated from the stoichiometry in Zen (1973).

Figure 5-10. $\log K_4$ vs $1/T$ from Wones et al (1971). The solid curve is the fit chosen to Wones data and its intercept at $1/T = 0$ is the 'B' constant. The dashed curve has been plotted using estimated entropies for sanidine (Nesbitt, pers. comm.) and annite (Beane, 1974).

Table 5-6 Calculated equilibrium data for an equation of the type: $\log K = A/T + B + C(P_{\text{total}} = 2000 \text{ bars})/T$, for the staurolite reaction from Rutherford.

Reaction	A	B	C
1: $3\text{da} = 5\text{mt} + 3\text{si} + 6\text{qz} + 7\text{H}_2\text{O} + 5\text{H}_2$	-75720.	113.761	.7181
2: $3\text{st} + 9\text{qz} = 8\text{mt} + 54\text{si} + 4\text{H}_2\text{O} + 8\text{H}_2$	-99650.	118.240	-.8280
3: $\text{al} + \text{H}_2\text{O} = \text{mt} + \text{si} + 2\text{qz} + \text{H}_2$	-5631.	2.346	-.1280
4: $\text{an} = \text{kf} + \text{mt} + \text{H}_2$	-5314.	7.248	.0038
5: $\text{mu} + \text{qz} = \text{kf} + \text{si} + \text{H}_2\text{O}$	-4565.	8.245	.0232
6: $\text{an} + \text{si} + \text{H}_2\text{O} = \text{mu} + \text{mt} + \text{qz} + \text{H}_2$	-749.	-.997	-.0194
7: $3\text{da} = 3\text{al} + 2\text{mt} + 10\text{H}_2\text{O} + 2\text{H}_2$	-58827.	106.723	1.1021
8: $54\text{al} + 58\text{H}_2\text{O} = 3\text{st} + 46\text{mt} + 117\text{qz} + 46\text{H}_2$	-204424.	8.444	-6.0840
9: $54\text{da} = 3\text{st} + 82\text{mt} + 117\text{qz} + 122\text{H}_2\text{O} + 82\text{H}_2$	-1263310.	1929.458	13.7538
10: $\text{st} + 23\text{da} + 39\text{qz} = 4\text{al} + 96\text{H}_2\text{O}$	-382858.	815.394	10.4779
11: $3\text{da} + 2\text{si} + 4\text{qz} = 5\text{al} + 12\text{H}_2\text{O}$	-47465.	102.031	1.3581
12: $3\text{st} + 25\text{qz} = 8\text{al} + 46\text{si} + 12\text{H}_2\text{O}$	-54602.	99.472	.1960
13: $8\text{da} + 82\text{si} = 5\text{st} + 31\text{qz} + 12\text{H}_2\text{O}$	-35829.	106.295	3.2954
14: $\text{mu} + 3\text{da} + 3\text{qz} = \text{an} + 4\text{al} + 12\text{H}_2\text{O}$	-52447.	105.374	1.2495
15: $23\text{an} + 3\text{st} + 48\text{qz} = 23\text{mu} + 31\text{al} + 12\text{H}_2\text{O}$	57684.	22.583	2.6938
16: $31\text{da} + 41\text{mu} = 41\text{an} + 4\text{st} + 33\text{qz} + 108\text{H}_2\text{O}$	-618872.	1058.755	9.3193
17: $3\text{da} + 3\text{an} = 3\text{mu} + 8\text{mt} + 9\text{qz} + 8\text{H}_2 + 4\text{H}_2\text{O}$	-77967.	110.770	.6599
18: $3\text{st} + 54\text{an} + 50\text{H}_2\text{O} = 54\text{mu} + 62\text{mt} + 45\text{qz} + 62\text{H}_2$	-140096.	64.402	-1.8756
19: $3\text{da} + 5\text{mu} = 5\text{an} + 8\text{si} + \text{qz} + 12\text{H}_2\text{O}$	-71975.	118.746	.8151
20: $8\text{mu} + 3\text{st} + 17\text{qz} = 8\text{an} + 62\text{si} + 12\text{H}_2\text{O}$	-93658.	126.216	-.6728
21: $\text{an} + \text{al} + 2\text{H}_2\text{O} = \text{mu} + 2\text{mt} + 3\text{qz} + 2\text{H}_2$	-6380.	1.349	-.1474
22: $\text{mu} + \text{al} = \text{an} + 2\text{si} + \text{qz}$	-4882.	3.343	-.1086
23: $\text{si} = \text{ky}$	371.	-.553	.0303

Table 5-7 Calculated equilibrium data for an equation of the type: $\log K = A/T + B + C(P \text{ total} - 2000 \text{ bars})/T$, for the stauroilite reaction from Richardson 1968.

REACTION	A	B	C
1: $3da = 5mt + 3st + 6qz + 7H_2O + 5H_2$	-75720.	113.761	.7181
2: $3st + 9qz = 8mt + 54st + 4H_2O + 8H_2$	-376174.	410.308	-.8280
3: $a1 + H_2O = mt + st + 2qz + H_2$	-5631.	2.346	-.1280
4: $an = kf + mt + H_2$	-5314.	7.248	.0038
5: $mu + qz = kf + st + H_2O$	-4565.	8.245	.0232
6: $an + st + H_2O = mu + mt + qz + H_2$	-749.	-.997	-.0194
7: $3da = 3a1 + 2mt + 10H_2O + 2H_2$	-58827.	106.723	1.1021
8: $54a1 + 58H_2O = 3st + 46mt + 117qz + 46H_2$	72100.	-283.624	-6.0840
9: $54da = 3st + 82mt + 117qz + 122H_2O + 82H_2$	-986786.	1637.390	13.7538
10: $st + 23da + 39qz = 41a1 + 96H_2O$	-474957.	912.659	10.4776
11: $3da + 2st + 4qz = 5a1 + 12H_2O$	-47565.	102.031	1.3581
12: $3st + 25qz = 8a1 + 46st + 12H_2O$	-331126.	391.540	.1960
13: $8da + 32st = 5st + 31qz + 12H_2O$	425120.	-380.576	3.2951
14: $mu + 3da + 3qz = an + 4a1 + 12H_2O$	-52447.	105.374	1.2495
15: $23an + 3st + 48qz = 23mu + 31a1 + 12H_2O$	-218840.	314.651	2.6938
16: $31da + 41mu = 41an + 4st + 33qz + 108H_2O$	-250249.	669.422	9.3196
17: $3da + 3an = 3mu + 8mt + 9qz + 8H_2 + 4H_2O$	-77967.	110.770	.6599
18: $3st + 54an + 50H_2O = 54mu + 62mt + 45qz + 62H_2$	-416620.	356.470	-1.8756
19: $3da + 5mu = 5an + 8st + qz + 12H_2O$	-71975.	118.746	.8151
20: $8mu + 3st + 17qz = 8an + 62st + 12H_2O$	-370182.	418.284	-.6728
21: $an + a1 + 2H_2O = mu + 2mt + 3qz + 2H_2$	-6380.	1.349	-.1474
22: $mu + a1 = an + 2st + qz$	-4882.	3.343	-.1086
23: $st = ky$	371.	-.553	.0303

the entropy of formation of the solid phases fits the experimental data of Wones et al.

Muscovite

Moore (1976) gives the A, B and C constants in Table 5-6 for equilibrium (5), Table 5-6;

calculated from the experiments of Chatterjee and Johannes (1974). This equilibrium met the constraint that ΔH° be constant with temperature change and was selected by Moore as the set of muscovite breakdown experiments, in which the phases were best characterized.

Kyanite

Moore (1976) gives A, B and C for the equilibrium:

$$\text{si} = \text{ky} \quad (23) \text{ (Table 5-6)}$$

$$\text{as } A = 371. \quad B = -0.553 \quad C = 0.0303$$

In Tables 5-6 and 5-7 the equilibrium data for all possible reactions among daphnite, almandine, staurolite, annite, muscovite, quartz and magnetite are presented. The data for equilibria (6) to (22), Table 5-6, are obtained from linear combinations of equilibria (1) to (5) according to the method of Skippen (1971).

5-4 LOG FUGACITY DIAGRAMS

An equilibrium model for the phases of interest in this study is adequately represented by the list of equilibrium constants given in Tables 5-6 and 5-7. It is possible to apply such a

listing of equilibrium constants directly to equilibria observed in natural assemblages. It is also useful to express equilibrium data in graphical form to give some understanding of the implications of the data and to facilitate comparison of two sets of data such as that given in Tables 5-6 and 5-7. Isobaric, isothermal log fugacity diagrams provide one such graphical treatment of the data. These diagrams show the effect of independent variation of two gaseous species and are particularly meaningful when phase relations involve a gaseous phase that contains more than two species. They are also a convenient method for the evaluation of phase relations on more widely used T-X sections as discussed in the subsequent section.

Skippen (1975) has described in detail the calculations necessary to obtain log fugacity diagrams from equilibrium constants. Schreinemaker's rules may be used to determine the sequence of stable equilibria around the invariant point and the method of Korzhinskii (1959) may be used to determine the relative stability of invariant points. Because magnetite is the only phase capable of producing oxygen, and each invariant point has one magnetite absent reaction, then each invariant point contains at least one dehydration equilibrium. At a specific pressure and temperature an invariant point such as (2) or (13) (Table 5-1), which involves only dehydration reactions may occur. No invariant points of this type were found to be stable between 300 - 800 C and 2 - 5 kb.

To prepare T-XH₂ sections for Fe end-member minerals, log fugacity diagrams were prepared at 400, 600 and 800 C at 2 and 5 kb.

Figure 5-11 The projection, through muscovite on to the A-F face of the AKF triangle. Oxygen is added so magnetite can be shown explicitly.

Figure 5-12 $\log f_{H_2}$ vs $\log f_{H_2O}$ at 400 C and 2 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data of Richardson (1968).

Figure 5-13 $\log f_{H_2}$ vs $\log f_{H_2O}$ at 600 C and 2 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data of Richardson (1968).

Figure 5-14 log f_{H_2O} vs log f_{H_2} at 800 C and 2 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data from Richardson (1968).

Figure 5-15 $\log f_{H_2}$ vs $\log f_{H_2O}$ at 400 C and 5 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data of Richardson (1968).

Figure 5-16 $\log f_{H_2}$ vs $\log f_{H_2O}$ at 600 C and 5 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data from Richardson (1968).

Figure 5-17 log f_{H_2O} vs log f_{H_2} at 800 C and 5 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data of Richardson (1968).

Figure 5-18 $\log f_{H_2O}$ vs. $\log f_{H_2}$ at 400 C and 2 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data of Rutherford (1970).

Figure 5-19 $\log f_{H_2O}$ vs $\log f_{H_2}$ at 600 C and 2 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data of Rutherford (1970).

Figure 5-20 log f_{H_2O} vs log f_{H_2} at 800 C and 2 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data of Rutherford (1970).

Figure 5-21 $\log f_{H_2O}$ vs $\log f_{H_2}$ at 400 C and 5 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data from Rutherford (1970).

Figure 5-22 $\log f_{H_2O}$ vs $\log f_{H_2}$ at 600 C and 5 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data from Rutherford (1970).

Figure 5-23 log f_{H_2O} vs log f_{H_2} at 800 C and 5 kb for phases in the system K-Fe-Al-Si-O-H with the staurolite data of Rutherford (1970).

As no thermodynamic test could be used to pick a suitable staurolite equilibrium, $T-XH_2$ sections were prepared for the staurolite data from both Richardson (1968) and Rutherford (1970). The topologies of the diagrams for the two sets of input data are different, but for each set of data the topology does not change from 2 to 5 kb. By examining both sets of diagrams it can be observed that daphnite is replaced by almandine between 400 and 600 C, at both 2 and 5 kb.

Figure 5-11 shows the position of phases on the projection used to portray mineral assemblages in the K-Al-Fe-Si-O-H system. To show magnetite-oxygen tie lines, a projection was made through muscovite on to the A-F side of the A-K-F triangle, and oxygen was added. Figures 5-12 to 5-23 are log fugacity diagrams at 400, 600 and 800 C and 2 and 5 kb based on staurolite phase relations as determined by Rutherford (1970; Table 5-6) and Richardson (1968; Table 5-7).

5-5 ISOBARIC TEMPERATURE - FLUID COMPOSITION DIAGRAMS

Isobaric temperature-fluid composition diagrams can be constructed from the A, B and C constants and the $\log fH_2$ vs $\log fH_2O$ diagrams. The position, at fixed pressure, of each equilibrium can be calculated in $T-XH_2$ using XCDFOR (Skippen and Yzerdraat, 1973). Magnetite is the only iron oxide considered in the phase relations and so hematite, wustite and iron (below approximately 560 C) restrict the stability of all equilibria. These boundaries are plotted on the $T-XH_2$ sections (Figures 5-24 to 5-27).

All types of reactions described by Greenwood (1962) for

$\text{CO}_2\text{-H}_2\text{O}$ mixtures may take place in $\text{H}_2\text{-H}_2\text{O}$ mixtures; however only the water-rich portion of the X_{H_2} sections can be considered because of the magnetite stability restriction. The phase relations presented in these diagrams do not include cordierite, hercynite, chloritoid or fayalite and may be metastable with respect to equilibria involving these phases. Two sets of phase relations at 2000 and 5000 bars have been calculated. Figures 5-24 and 5-25 show the stability of annite, almandine, staurolite, daphnite, muscovite, sillimanite and magnetite at 2000 and 5000 bars for the staurolite equilibria measured by Rutherford (1968) as an independent equilibrium (ie. data from Table 5-6). Figures 5-26 and 5-27 show the stability of the same phases, except daphnite, at 2000 and 5000 bars if the staurolite data of Richardson (1968) (Table 5-7) are used.

The same general sequence of appearance and disappearance of minerals observed by Barrow (1893, 1912), Chinner (1960), Guidotti (1974) and Froese and Gasparri (1975) can be observed on the T-XH_2 diagrams. The stable phase relations determined using each staurolite equilibrium will be discussed in turn.

Using the staurolite data from Rutherford (1970), the end-member minerals daphnite, muscovite and biotite are stable below 450 C at 2 kb and 460 C at 5 kb. These temperatures give the upper stability of daphnite, at which muscovite and daphnite react to form annite and almandine (equilibrium (14), Table 5-6). Within the stability field of magnetite, at approximately 510 C at 2 kb or 600 C at 5 kb, staurolite forms from almandine. Staurolite, almandine, sillimanite and magnetite are stable, in the presence,

Figure 5-24: Isobaric temperature vs. gas composition diagram for equilibria in the system K-F. The equilibrium are from Rutherford (1970).

composition diagram for equilibria in the system K-Fe-Al-Si-O-H. The data for the staurolite
 ord (1970).

Figure 5-25. Isobaric temperature vs. gas composition diagram for equilibria in the system K-F. Equilibrium are from Rutherford (1970).

$$P_{H_2} + P_{H_2O} = 5000 \text{ bars}$$

 X_{H_2}

Position diagram for equilibria in the system K-Fe-Al-Si-O-H. The data for the staurolite (1970).

12.1

Figure 5-26. Isobaric temperature vs. gas composition diagram for equilibria in the system K-Fe-A. Data for the staurolite equilibrium are from Richardson (1968).

$P_{H_2} + P_{H_2O} = 2000 \text{ bars}$

composition diagram for equilibria in the system K-Fe-Al-Si-O-H.

Equilibrium data are from Richardson (1968).

Figure 5-27. Isobaric temperature vs. gas composition diagram for equilibria in the system. Data for the staurolite equilibrium are from Richardson (1968).

isobaric temperature vs. gas composition diagram for equilibria in the system K-Fe-Al-Si-O-H.
 Data for the staurolite equilibrium are from Richardson (1968).

of annite and muscovite in potassium-rich rocks, up to 590 C at 2 kb and 675 C at 5 kb. This is the upper stability of staurolite which reacts to form almandine and sillimanite. Above this temperature almandine, magnetite and sillimanite are stable.

If staurolite is introduced using the data of Richardson (1968) (Equilibrium (12), Table 5-7). Daphnite disappears at 325 C at 2 kb and 370 C at 5 kb by reaction (16) in which daphnite and muscovite react with increase in temperature to form annite and staurolite. Almandine only appears as a stable phase at 510 C at 2 kb and 490 C at 5 kb at which point annite and staurolite react to form almandine and muscovite according to equilibrium (15) (Table 5-7). Almandine, staurolite, annite, muscovite and magnetite are then stable up to 660 C at 2 kb and 675 C at 5 kb where staurolite reacts to form almandine and sillimanite.

It should be emphasized that the mineral compositions used to calculate the phase relations are not the exact minerals observed in the field, and in the case of daphnite and annite, they are not identical to the minerals in the experimentally studied reactions on which the phase relations are based. By using the "pure" phases, or ideal end-members, and correcting the equilibrium constants in the experimentally studied reactions for the activities of these phases, the useful standard state of the pure phase with unit activity at any pressure and temperature has been maintained.

In apparent contradiction to the work of Richardson (1968), staurolite is not restricted to high pressures in the phase relations calculated in this work. However cordierite and chloritoid, included in the experiments of Richardson, are not present in the

calculated phase relations. Cordierite has a variable and unknown water content and neither cordierite nor chloritoid have been identified in well-located samples from the Stall Lake or Anderson Lake mines.

Naturally occurring pelitic rocks contain more components than K-Fe Al-Si-O-H and therefore contain more phases. All the equilibria implied by the stable phases in a rock must be satisfied at equilibrium, and for a sample such as S7, which has staurolite, chlorite, biotite, muscovite, magnetite, sillimanite and quartz there must be a point in P - T - X_{H_2} where all equilibria implied in the stable assemblage are simultaneously satisfied. Nearly all the iron-bearing phases will be diluted with other components (eg. Mg, Zn, Ti, Mn, Ca etc.) and will not have unit activity. From mineral analyses and solution models the activity of the ideal end-member component can be estimated and applied to the equilibrium constant.

The equilibrium constants for all the implied simultaneous equilibria may then be solved on isobaric T - X_{H_2} diagrams to give an estimate of T and X_{H_2} at an assigned pressure.

All the rocks in this study contain sulfides, indicating the H-O-S vapor phase consists of more than H_2 and H_2O . The change in H-O-S vapor composition should affect the stability of end-member equilibria by decreasing the sum of $p_{H_2} + p_{H_2O}$. Chapter 6 describes an approach to dealing with the problem of solid solution in minerals and the effect of H-O-S gases on the stability of equilibria.

CHAPTER 6 APPLICATION OF END-MEMBER EQUILIBRIA TO ASSEMBLAGES OBSERVED IN THE FIELD

6-1 INTRODUCTION

Mineral assemblages and isograds observed in the field can be successfully compared to experimentally determined phase relations if the minerals observed in the field approach the ideal compositions of the minerals in the experiments. This technique has been successful for siliceous carbonate rocks and Rice (1977) has used solution models or calibrated activities to adjust carbonate equilibria for Mg-calcite and fluor silicates. Moore (1976) has applied solution models to calcsilicate rocks, in an area where the distribution of mineral assemblages does not justify the drawing of isograds, to estimate meta morphic conditions. In pelitic rocks, experimentally determined equilibria may not be directly applied to natural assemblages because:

- (1) The minerals rarely have ideal compositions;
- (2) Sulfides are often present, indicating the vapor phase consists of H-O-S gases, but experiments are conducted in O-H mixtures.

Therefore, the activities of ideal end-members in minerals and the composition of the vapor phase must be considered in any attempt to apply phase relations for the system K-Fe-Al-Si-O-H to rocks in the field.

Froese and Gasparrini (1975) report an isograd defined by the mineral reaction:

and the sillimanite-kyanite transition, near the Anderson and Stall Lake mines. From the coincidence of these reactions they estimate the metamorphic conditions: $P = 5.5 \text{ kb}$; $T = 600 \text{ C.}$ In Chapter 4, the sphalerite geobarometer and an equilibrium among biotite-muscovite-sillimanite-magnetite-pyrite-pyrrhotite provided similar estimates of the metamorphic conditions. Sample S7, used for the estimates in Chapter 4, provides a unique opportunity to test the experimental data for the system K-Fe-Al-Si-O-H, derived in Chapter 5, against a geological situation in which the temperature and pressure are well known.

The equations expressing the equilibrium constants for the independent equilibria (1), (2) and (6) (Tables 5-6 and 5-7) provide three equations in four unknown quantities; P , T , f_{H_2} and f_{H_2O} . In petrologic applications a fourth equation in which the partial pressures of the gas species sum to the total pressure is also used (Rice, 1977; Moore, 1976). For sulfide bearing rocks a binary gas phase cannot be assumed, since sulfur-bearing species must be present in addition to H_2 and H_2O , and, as discussed in Eugster and Skippen (1967),

$$P_{\text{gas}} = \frac{f_{H_2O}}{\gamma_{H_2O}} + \frac{f_{H_2}}{\gamma_{H_2}} + \frac{f_{H_2S}}{\gamma_{H_2S}} + \frac{f_{SO_2}}{\gamma_{SO_2}} + \frac{f_{S_2}}{\gamma_{S_2}} \quad (22)$$

Of the four additional unknown quantities introduced by the above equation, only three are independent since,

Rocks, such as S7, with coexisting pyrite-pyrrhotite-magnetite have buffered values of f_{O_2} and f_{S_2} at specified P and T (Eugster

and Skippen, 1967; Froese, 1971, 1975). The pyrite-pyrrhotite equilibrium is given by Froese and Gunter (1976) and the formation of magnetite is given by Haas and Robie (1973). Thus, for S7, if total pressure is specified each of the independent silicate equilibria can be used in conjunction with the buffering assemblage and the equilibrium constants for the formation of H_2O (Zen, 1973), H_2S and SO_2 (Kubachewski et al, 1967), to calculate all the remaining unknown quantities; fO_2 , fS_2 , fH_2O , fH_2 , fH_2S , fSO_2 and T . Using mineral analyses and Temkin solution models (described in Chapter 5) each of the independent equilibria for daphnite (1), staurolite (2) and biotite-muscovite (6) (all from Tables 5-6 and 5-7) can be tested against the known metamorphic conditions and each other.

6-2 FERRIC IRON IN NATURAL MINERALS

As many naturally occurring iron silicates contain ferric iron, the activities of ferrous end-member components, necessary for subsequent calculations, cannot be obtained directly from microprobe analyses which do not account for Fe^{3+} . Griffen and Ribbe (1973) report no Fe^{3+} in staurolite Mossbauer spectra, but Hounslow and Moore (1967) and Wones et al (1971) report up to 20% of the total iron in biotite as ferric iron. Deer et al (1966) indicate ferric iron in chlorite analyses. Table 6-1 shows the activities of annite and daphnite in biotite and chlorite for different assumed values of $Fe^{3+}/\Sigma Fe$. Hounslow and Moore (1967) report 7 biotite analyses from sulfide bearing pelitic rocks, with an average $Fe^{3+}/\Sigma Fe$ of 0.13, and ranging from 0.08 to 0.18. The

Table 6-1 Activities of Ideal End-Members in Minerals in
Samples S7 and A7 ($\text{Fe}^{3+}/\Sigma\text{Fe}$ assumed).

SAMPLE	MINERAL	ACTIVITY	$\text{Fe}^{3+}/\Sigma\text{Fe}$
S7	st	.0811	0.0
	bi	.0303	0.1
	bi	.0200	0.2
	bi	.0127	0.3
	ch	.0028	0.1
	ch	.0014	0.2
	ch	.0007	0.3
A7	st	.0804	0.0
	bi	.0489	0.1
	bi	.0318	0.2
	bi	.0198	0.3
	ch	.0032	0.1
	ch	.0016	0.2
	ch	.0008	0.3

hematite-rutile assemblages in their work indicate more oxidizing conditions than S7 and accordingly $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.1$ seems a reasonable estimate of ferric iron content. Most of the subsequent calculations have been performed assuming $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.0, 0.1$ and 0.2 , to display the effect of varying ferric iron content.

6-3 METAMORPHIC CONDITIONS CALCULATED FROM SILICATE EQUILIBRIA

Two independent reactions (Richardson, 1968; Rutherford, 1970) are available to introduce staurolite to phase relations. Since equilibria (1), (2) and (6) can be written in three unknowns; $f\text{H}_2$, $f\text{H}_2\text{O}$ and T , if P is specified they can be solved simultaneously at 5 kb to evaluate the silicate equilibria.

Staurolite from the work of Rutherford (1970) and Richardson (1968)

The equilibrium constants for equilibria (1), (2) and (6); (Tables 5-6 and 5-7) can be written in the form:

$$\log (f\text{H}_2\text{O}^w \cdot f\text{H}_2^h) = \frac{A}{T} + B$$

where w and h are the stoichiometric coefficients of water and hydrogen. A is calculated at 5000 bars, using the C constants in Tables 5-6 and 5-7, and B is calculated including the activities of the appropriate end-members. This provides three equations (one each for equilibria 1, 2 and 6) in three unknowns; $f\text{H}_2$, $f\text{H}_2\text{O}$ and T which can be solved simultaneously for various values of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in chlorite and biotite and the staurolite data reported by Richardson (1968) and Rutherford (1970). The results are recorded in Table 6-2 and suggest that the data of Richardson are more compatible with the known metamorphic conditions at Snow Lake than

Table 6-2 Simultaneous solutions of silicate equilibria for the staurolite data obtained from Rutherford (1970) and Richardson (1968) for various $\text{Fe}^{3+}/\Sigma\text{Fe}$ at 5 kb total pressure.

$\text{Fe}^{3+}/\Sigma\text{Fe}$	Rutherford (1970) T	$\text{Fe}^{3+}/\Sigma\text{Fe}$	Richardson (1968) T
0.0	1318 C	0.0	708 C
0.1	1190 C	0.1	703 C
0.2	1071 C	0.2	699 C

are the data of Rutherford. Compensating errors in the daphnite or biotite-muscovite equilibria could cause an incorrect result which may be unrelated to the staurolite data. In the next section each equilibrium (1, 2 and 6 from Tables 5-6 and 5-7) is tested separately using the pyrite-pyrrhotite-magnetite buffer, as described in the introduction.

6-4 SIMULTANEOUS SOLUTION OF SULFIDE-OXIDE-SILICATE EQUILIBRIA

In the introduction to this chapter a method for testing each independent silicate equilibrium against the known metamorphic conditions was outlined. The assemblage, magnetite-pyrite-pyrrhotite, fixes fO_2 and fS_2 at a specified P and T. For the total pressure of 5000 bars the gas composition can be calculated at any temperature, providing fH_2O , fH_2 , fS_2 , fH_2S and fSO_2 . Figure 6-1 shows the simultaneous solutions of the buffer assemblage and equilibrium (1) (Table 5-6) for various $Fe^{3+}/\Sigma Fe$ values. The temperatures 615 C ($0.0=Fe^{3+}/\Sigma Fe$), 630 C ($0.1=Fe^{3+}/\Sigma Fe$) and 650 C ($0.2=Fe^{3+}/\Sigma Fe$) at 5 kb are in close agreement with estimates in Chapter 4, indicating the daphnite equilibrium (1), derived from the data of James (pers. comm.) and James *et al* (1976), is compatible with the known metamorphic conditions at Snow Lake.

Figure 6-2 shows the simultaneous solutions of the buffer assemblage and the staurolite equilibrium (2), Tables 5-6 and 5-7, as obtained from the data of Rutherford (1970) and Richardson (1968). The Rutherford data give an equilibration temperature of approximately 705 C and the data of Richardson give 680 C. As in the previous section the data of Richardson are closer to the

Figure 6-1 The simultaneous solution of the pyrite-pyrrhotite-magnetite buffer (py-po-mt, dashed line) and the daphnite equilibrium ((1), Table 5-6) at 5 kb. The numbers on the daphnite curves are assumed $Fe^{3+}/\Sigma Fe$ ratios.

Figure 6-2 The simultaneous solution of the pyrite-pyrrhotite-magnetite buffer (py-po-mt, dashed line) and the staurolite equilibrium of Rutherford ((2), Table 5-6) and Richardson ((2), Table 5-7) at 5 kb.

other estimates than the data of Rutherford, but both sets of data indicate temperatures significantly higher than temperatures obtained using other equilibria.

Figure 6-3 shows the simultaneous solutions of the buffer assemblage and the biotite-muscovite equilibrium (6) (Table 5-6), obtained from the experiments of Chatterjee and Johannes (1974) and Wones *et al* (1971). The temperatures 540 C ($\text{Fe}^{3+}/\Sigma\text{Fe}=0.0$), 580 C ($\text{Fe}^{3+}/\Sigma\text{Fe}=0.1$) and 630 C ($\text{Fe}^{3+}/\Sigma\text{Fe}=0.2$) change rapidly with changes in the estimated ferric iron content, but are in general agreement with the other estimates.

The simultaneous solutions of each of the equilibria (1), (2) and (6), in Tables 5-6 and 5-7, with the buffer assemblage pyrite-magnetite-pyrrhotite indicate that the daphnite ((1), Table 5-6) and biotite-muscovite ((6), Table 5-6) can be tested successfully against a known geological situation, but the staurolite data (Richardson, 1968; Rutherford, 1970) are not as dependable.

6-5 H-O-S GAS COMPOSITIONS COEXISTING WITH PYRITE-PYRRHOTITE-MAGNETITE

Studies by Eugster and Skippen (1967), LeCheminant (1973) and Bachinski (1975) show that H_2O , H_2 , S_2 , H_2S and SO_2 are the major constituents of the H-O-S gas coexisting with pyrite, pyrrhotite and magnetite. Equation (22) can be solved using the equilibria for the formation of H_2O , H_2S and SO_2 in conjunction with fugacity coefficients from Ryzhenko and Volkov (1971) for γ_{H_2} , Burnham *et al* (1969) for $\gamma_{\text{H}_2\text{O}}$, Holloway (pers. comm.) for $\gamma_{\text{H}_2\text{S}}$ and γ_{SO_2} , from the revised Redlich-Kwong-Ngo equation of state (Redlich and Ngo, 1970)

Figure 6-3 The simultaneous solution of the pyrite-pyrrhotite-magnetite buffer (py-po-mt, dashed line) and the annite-muscovite equilibrium (6), Table 5-6) at 5 kb. The numbered curves correspond to assumed $Fe^{3+}/\Sigma Fe$ ratios.

and S_2 calculated from the Redlich-Kwong equation (Redlich and Kwong, 1949).

Substituting the relationships:

$$K_{H_2O} = \frac{f_{H_2O}}{f_{H_2} \cdot f_{O_2}^{1/2}} \quad (23)$$

$$K_{H_2S} = \frac{f_{H_2S}}{f_{H_2} \cdot f_{S_2}^{1/2}} \quad (24)$$

$$K_{SO_2} = \frac{f_{SO_2}}{f_{S_2}^{1/2} \cdot f_{O_2}} \quad (25)$$

obtained from Kubachewski, et al (1967), into equation (22) gives (26):

$$P_{total} = f_{H_2} \frac{K_{H_2O} \cdot f_{O_2}^{1/2}}{\gamma_{H_2O}} + \frac{1}{\gamma_{H_2}} + \frac{K_{H_2S} \cdot f_{S_2}^{1/2}}{\gamma_{H_2S}} + \frac{K_{SO_2} \cdot f_{S_2}^{1/2} \cdot f_{O_2}}{\gamma_{SO_2}} + \frac{f_{S_2}}{\gamma_{S_2}} \quad (26)$$

Figures 6-4, 6-5 and 6-6 show the composition of H-O-S gases coexisting with pyrite-pyrrhotite-magnetite at 4, 6 and 8 kb. For all the pressures considered the vapor phase is dominantly H_2O up to 700 C, and can be represented adequately by a binary gas.

Rocks from Anderson Lake and Stall Lake mines also coexist with pyrite-magnetite, pyrite-pyrrhotite and pyrrhotite-magnetite. For these assemblages f_{O_2} and f_{S_2} are not fixed at a specified P and T. To evaluate which assemblages are most likely to affect the stability of the coexisting silicates, the surface $p_{H_2} + p_{H_2O}$ was calculated at 600, 650 and 700 C and 5 kb for each of the

Figure 6-4 H-O-S gas compositions coexisting with the pyrite-pyrrhotite-magnetite buffer at 4000 bars.

Figure 6-5 H₂O-S gas compositions coexisting with the pyrite-pyrrhotite-magnetite buffer at 6000 bars.

Figure 6-6 H-O-S gas compositions coexisting with the pyrite-pyrrhotite-magnetite buffer at 8000 bars.

sulfide-oxide assemblages listed above. Figure 6-7 shows the $p_{H_2} + p_{H_2O}$ surfaces. The diagram is bounded by the surface $p_{H_2} + p_{H_2O} = P$ total. The assemblage pyrrhotite-magnetite is only stable until the appearance of wustite, at low oxygen fugacities (Figure 6-7). None of the analyzed pyrrhotite-magnetite bearing rocks from Snow Lake are constrained by sufficient silicate equilibria from Tables 5-6 or 5-7 to permit a unique solution for metamorphic conditions. However, Figure 6-7 indicates that such rocks can be treated, to a good approximation, as coexisting with a binary $H_2 - H_2O$ gas phase.

Some of the rocks from the mines coexist with pyrite-magnetite and, as Figure 6-7 shows, the $p_{H_2} + p_{H_2O}$ surface for this assemblage deviates significantly from the P total surface. The surface $p_{H_2} + p_{H_2O}$ terminates where hematite (ht) becomes stable. Above 600 C pyrite-hematite-magnetite is not a stable assemblage (LeCheminant, 1973). No analyzed pyrite-magnetite rocks have sufficient equilibria from Tables 5-6 or 5-7 to warrant further study.

The assemblage pyrite-pyrrhotite fixes fS_2 at a specified P total and T , but fO_2 may have any value below the stability of magnetite. Figure 6-7 shows that the $p_{H_2} + p_{H_2O}$ surface for rocks coexisting with pyrite-pyrrhotite deviates significantly from the P total = $p_{H_2} + p_{H_2O}$ surface. It is clear from Figure 6-7 that pyrrhotite-magnetite or pyrite-pyrrhotite magnetite rocks can be considered to coexist with a binary $H_2 - H_2O$ gas below 700 C. However, rocks which coexist with pyrite-magnetite or pyrite-pyrrhotite may contain appreciable amounts of sulfur bearing

Figure 6-7 The $\text{pH}_2 + \text{pH}_2\text{O}$ surfaces coexisting with all the possible two mineral combinations of pyrite-pyrrhotite-magnetite at 600, 650 and 700 C and 5000 bars total pressure. The closed black circles indicate pyrite-pyrrhotite-magnetite is stable (ht=hematite, wu=wustite). Note the X-axis is a log scale and the Y-axis is in real numbers.

species. Sample A7, from the Anderson Lake mine, contains staurolite-chlorite-biotite-muscovite-sillimanite-quartz-pyrite and pyrrhotite. By replacing the magnetite in equilibrium (6) with pyrite, using thermodynamic data, sufficient independent equilibria can be obtained to calculate metamorphic conditions.

6-6 METAMORPHIC CONDITIONS USING SILICATE-SULFIDE EQUILIBRIA

If the dissociation of water (Zen, 1973) is added to equilibrium (6), Table 5-6, the oxidation of annite to muscovite and magnetite is obtained.

To obtain an equilibrium which can be applied to A7, the magnetite in (27) can be replaced by pyrite by adding the reaction:

to equilibrium (27).

The free energy of formation of pyrite is given by equation (13) in Chapter 4. This can be combined with the free energy of formation of magnetite from equation (14), Chapter 4. Equilibria (27) and (28) can be added to obtain (29).

and

$$K_{29} = \frac{f_{\text{O}_2}^{3/2}}{a_{\text{an}} \cdot f_{\text{S}_2}^3}$$

The activity of annite can be obtained from Table 6-1, and $\log K_{29}$ is known. The fugacity of S_2 for coexisting pyrite-pyrrhotite can be calculated from the data of Froese and Gunter.

Figure 6-8 The simultaneous solutions of daphnite dehydration equilibrium (19), from Table 5-6 and the sulfide-silicate equilibrium (29) from Chapter 6 (open circles) for sample A-7 at various total pressures. The "convex up" curves are p_{H_2O} at each pressure calculated from (29). The "convex down" curves are p_{SO_2}

(1976). If values are specified for P total and T , equilibrium (29) can be used to calculate fO_2 and the H-O-S gas composition.

Equilibrium (29) can then be solved simultaneously with a dehydration reaction such as (19) from Table 5-6. Figure 6-8 shows the simultaneous solution of equilibrium (29) and (19) (from Table 5-6) at 4, 5, 6, 7 and 8 kb. The activities of daphnite and annite for $Fe^{3+}/\Sigma Fe = 0.1$ were taken from Table 6-1. The temperature obtained at 5 kb is 620 C, in good agreement with the estimates from sample S7 and previous estimates in Chapter 4. Figure 6-8 also shows that above 650 C, for sample A7, H_2O is no longer the dominant gas species, because the amount of SO_2 in the vapor phase increases rapidly above this temperature.

SUMMARY AND CONCLUSIONS

Proterozoic Amisk Group volcanic rocks associated with pelites and massive sulfide deposits have been mapped at an approximate scale of 1:8000. Figure 1-1 (in pocket) presents the geology of the Amisk group as seen in outcrops near the Anderson Lake and Stall Lake mines, near Snow Lake, Manitoba. Figure 1-2 shows sample locations.

Massive sulfide deposits occur in pelitic metasedimentary rocks approximately 500 m thick, within felsic pyroclastic rocks, suggesting the sulfides were deposited during a period of little or no extrusive volcanic activity. Chemical analyses of the meta-volcanic rocks indicate they are sub-alkaline, tholeiitic rocks and their areal distribution does not indicate any differentiation trend. The juxtaposition of volcanics of different compositions over the whole area indicates that lavas of very different compositions, possibly from different sources, were deposited over a short period of time in a volcanic arc which was probably close to the margin of an Archean craton (Moore and Froese, 1972; Bell et al, 1975). Two periods of deformation can be recognized in mica bearing rocks. The F_1 foliation trends approximately east-west and is folded by gentle, upright northeast plunging F_2 folds, with poorly developed axial plane cleavage. Lineations are parallel to F_2 fold axes. The top determinations, and other evidence, indicate the sequence mapped is monoclinial with "tops" to the north and the F_1 anticline proposed in Moore and Froese (1972) cannot be substantiated.

Drill core samples were examined from the massive sulfide orebodies near Stall and Anderson Lakes, both of which are close to the mineral reaction:

defined by Froese and Gasparrini (1975). Garnet-chlorite-biotite are stable south of the isograd defined by the above reaction and staurolite-biotite-garnet and biotite-sillimanite-staurolite are observed to the north. Samples from the Stall and Anderson Lake mines contain chlorite-biotite-staurolite, with or without sillimanite and may contain muscovite if sufficiently potassic. Garnet appears as a stable phase in biotite-chlorite or staurolite-biotite assemblages, but as mantled relicts from lower grade in staurolite-chlorite-biotite rocks. Microprobe analyses of coexisting biotite-chlorite-staurolite, from muscovite-bearing and non-muscovite bearing rocks, indicate these minerals are more iron-poor when they coexist with more oxidizing or more sulfurizing opaque assemblages. Significant amounts (up to 5.2 wt %) of ZnO were found in staurolite and, contrary to the findings of Guidotti (1974), increasing ZnO in staurolite is directly related to decreasing Fe/Mg of coexisting biotite and chlorite in muscovite-bearing rocks.

To further examine the observed silicate-sulfide equilibria, theoretical studies of the metamorphism of sulfides and silicates were undertaken. To determine the total pressure of metamorphism in the study area the thermodynamic properties of (Zn, Fe)S solid solutions were studied. To estimate the temperature, solution

models were used with the simultaneous solution of silicate and sulfide equilibria.

In Chapter 4, the thermodynamic properties of (Zn,Fe)S solid solutions have been derived from a two-constant Margules solution model, fitted to the data of Barton and Toulmin (1966). Assuming a linear temperature dependence of the partial molar free energy of mixing at infinite dilution:

$$\bar{G}_{\text{FeS}}^{\text{ex}} = -212. + 1.377 T$$

$$\bar{G}_{\text{ZnS}}^{\text{ex}} = -3235. + 4.006 T$$

and the free energy change of the equilibrium between pure FeS pyrrhotite and FeS sphalerite is:

$$\Delta G^0 = 1166. - 0.125 T$$

These data indicate that the activity of FeS in sphalerite is a function of temperature, contrary to the assumptions of Barton and Toulmin (1966), Scott (1973) and Fleet (1975). The P-T-X relations of sphalerite-pyrite-pyrrhotite were calculated using data on the pyrite-pyrrhotite equilibrium from Froese and Gunter (1976) and thermal expansions and compressibilities estimated by Scott (1973). Compositions of sphalerite from the Stall Lake mine give total pressures between 5 and 6 kb, in agreement with 5.5 kb estimated by Froese and Gasparri (1975) from pelitic assemblages, and at variance with 7 kb estimated by Scott (1976) using the experimentally calibrated sphalerite geobarometer. To obtain an estimate of the temperature, the equilibria:

were solved simultaneously for T and $f\text{O}_2$ at the estimated total pressure of 5 kb. The activity of annite in biotite ($a_{\text{an}}^{\text{bi}}$) was estimated using a Temkin (1945) solution model. The low angle of intersection of the biotite-muscovite and pyrite-magnetite equilibria listed above make the $f\text{O}_2$ - T estimate very sensitive to $a_{\text{an}}^{\text{bi}}$ and the assumed ferric to ferrous ratio. The temperature estimate, based on a sample with the appropriate coexisting minerals, ranges from 565 to 630 C, depending on the ferric iron content. At the estimated metamorphic conditions 600 C and 5 kb, a phase diagram for Fe-Mg-Al solid solutions in biotite was constructed, which confirms the observation that biotite becomes Fe-poor (Mg, Al-rich) with increasing $f\text{O}_2$ at fixed P and T.

To model pelitic reactions among the minerals observed at Snow Lake, a theoretical study of the system K-Fe-Al-Si-O-H was conducted. Using the additivity of the equilibrium constant, independent equilibria were combined to obtain one equilibrium for each mineral of interest. The equilibria used were adjusted to remove unwanted minerals and to pure ferrous end-member components. The equilibria and the sources of data used were (number of each equilibrium from Table 5-6 or 5-7):

(Hsu, 1968; Turnock and Eugster, 1962)

(Wones et al., 1971)

(Chatterjee and Johannes, 1974).

A reaction studied by Richardson (1968) was also used to introduce staurolite to the phase relations:

The five independent equilibria were used to generate 17 dependent equilibria. The end-member equilibria have been graphically presented on T vs $\text{pH}_2/(\text{pH}_2 + \text{pH}_2\text{O})$ diagrams at 2 and 5 kb.

Pelitic rocks generally contain more oxides than the ideal end-member system and therefore minerals in the field are not pure end-members and the end-member phase relations are only superficially similar to observed mineral assemblages. In Chapter 6 the activities of end-members dissolved in minerals are included in the equilibrium constants derived in Chapter 5. The simultaneous solution of three independent silicate equilibria in a staurolite-chlorite-biotite-muscovite-sillimanite-quartz-magnetite-pyrite-pyrrhotite rock (S7) indicates that the staurolite data from Richardson (1968) gives temperatures more in accord with the known metamorphic conditions than the staurolite data of Rutherford (1970). The simultaneous solution of each independent silicate equilibrium with the pyrite-pyrrhotite-magnetite buffering

assemblage shows the daphnite and annite-muscovite equilibria are consistent with the metamorphic conditions, but that both staurolite equilibria give temperatures approximately 100 C higher than the 600 C from all other estimates.

In a second rock, A7, with the same assemblage but without magnetite, the simultaneous solution of equilibria gives approximately the same equilibration temperatures.

The calculation of H-O-S gases coexisting with sulfides and oxides indicates that the gas can be considered an H_2 - H_2O binary phase up to 700 C at 5 kb for the assemblages pyrite-pyrrhotite-magnetite or pyrrhotite-magnetite but that sulfur species can be significant in rocks with pyrite-magnetite or pyrite-pyrrhotite. Sulfide-silicate equilibria in A7 have been used to calculate H-O-S gas compositions and show that for pyrite-pyrrhotite bearing rocks below approximately 650 C, the gas phase is dominantly H_2O .

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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

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Appendix I Mineral Assemblages in Pelitic Rocks from the Anderson Lake and Stall Lake Mines.
 x indicates minerals in mutual contact
 t indicates trace amount of mineral present
 - mineral present, but not in mutual contact
 r retrograde mineral
 nop opaques not determined (slide not polished)

Sample Number	Text Number	at	bt	ch	cp	gt	il	kf	ky	mu	pc	po	py	qz	sl	sp	st	to	other
A6-36	A-1	x	x	x	x	x	x	t			t	x	x	x	t		x		
A6-113	A-2	x	x	x	x				x	x	x	x	x	x		x	x	t	
A6-159		x					x		x	x	x		x	x			x	t	
A7-162		x	x	x			x			x	x	x	x	x			x	t	
A9-80	A-3	x	x	x	x					x			x	x		x	x		
A16-14		x	x	x	x		x		x		x	x	x	x					
A17-12	A-4	x	x	x	x				x			x	x	x		x	x		
A17-21		x	x	x	x		x	t	x	x	x	x	x	x			x		
A23-15		x	x	x	x				x			x	x	x			x		
A23-36	A-5	x	t	x							x	x	x	x					
A25-0	A-6	x	x	x	x				x		x	x	x	x					
A31-64	A-7	x	x	x	x			t		x		x	x	x			x		

Appendix I (cont.)

Sample Number	Text Number	at	bi	ch	cp	gt	tl	kf	ky	mt	mu	pc	po	py	qz	si	sp	st	to	other
A46-45		x	x	x	x					x	x	x	x	x	x				t	
A47-25		x		x	x				x	x	x	x	x	x	x				x	t
A51-31	A-8	x	x	x	x					x	x	x	x	x	x				x	
A51-70		x	x	x	x		x		x	x	t	x	x	x	x				x	
A76-130		x					x		x	x	x			x	x				x	
A77-213				x	x	-	x			x	t	x	x	x	x				x	
A78-62	A-11	x	x	x	x		x		x	x	x	x	x	x	x				x	
A78-223		x	x	x	x		x		x	x	x	x	t	x	x				x	t
A86-90	A-10	x	x	x	x			x	x	x	x	x	x	x	x				x	
A101-17		x	x	x	x				x	x	t	x	x	x	x				x	
ATH62-40		x	x	x	x				x			x	x	x	x				x	x
ATH87-20				x					x		x	x		x	x				x	
ATH88-40	A-9	x	x	x	x		x			x	x	x	x	x	x				x	
ATH89-45		x	x	x						x				x	x				x	x
ATH93-67	A-12	x	x	x	x	-	x			x	x	x		x	x				x	

Appendix I (cont.)

Sample Number	Text Number	at	bi	ch	cp	gt	il	kf	ky	mt	mu	pc	po	py	qz	si	sp	st	to	other
ATH110-90	A-13	x	x	x	x	-	x		t	x		x		x	x					
ATH111-43		x	x	x	x		x			x	x	x	x	x	x			x		
S94-115		x	x	x						x		x	x	x	x	x		x		
S95-28	S-1	x	x	x	x		x			x		x	x	x	x			x	t	
S96-40		x	x	x		-					x				x			x		
ST114-45	S-2	x	x	x	x		x			x		x	x	x	x		x	x		
ST115-70	S-3	x	x	x	x	-					x	x	x	x	x		x			
ST116-5		x	x	x		-					x				x			x	nop	
ST117-85		x	x	x	x		x			x	x	x	x	x	x		x	x		
ST118-100		x	x	x							x			x	x			t		
ST129-5		x	x	x		-					x				x				nop	
ST131-75		x	x	x	x		x			x			x		x			x		
S132-95		x	x	x	x		x			x			x	x	x			x		
S133-20	S-4	x	x	x	x		x			x			x	x	x			x		
S135-80	S-11	x		x	x	x	x			x	x	x	x	x	x			x		

Appendix I (cont.)

Sample Number	Text Number	at	bl	ch	cp	gt	il	kf	ky	mt	mu	pc	po	py	qz	si	sp	st	to	other
S136-80		x	x												x			x		nop
S139-25		x	x	x	x		x		x			x	x	x	x			x		
S142-100	S-5	x	x	x	x		x		x			x	x	x	x			x		
S143-105		x	x	x	x	x	x		x			x	x		x					
S144-5		x	x	x	x		x		x			x	x	x	x			x		
S145-105		x	x	x	x	x	x		x			x	x	x	x					
S146-195		x	x						x			x	x		x			x		nop
S147-39		x	x	x	x		x		x			x	x	x	x			x		
S158-202		x	x	x					x			x			x			x		nop
S160-20		x	x	x			x		x			x	x		x			x		
S180-296	S-6	x	x	x	x				x			x	x	x	x			x		
S181-130		x	x	x	x		x		x				x		x			x		
S182-145		x	x	x	x				x				x		x					
S215-15	S-12	x	x						x			x	x	x	x			x		
S216-20		x	x						x			x	x	x	x			x		

Appendix I (cont.)

Sample Number	Text Number	at	bi	ch	cp	gt	il	kf	ky	mt	mu	pc	pq	py	qz	sf	sp	st	to	other
S218-35		x	x	x	x		x		x			x	x		x			x		
S263-75	S-7	x	x	x	x		x		x	x	x	x	x	x	x	x		x		
S265-45		x	x	x	x				x	x		x		x	x		x			
S266-40		x	x	x	x		x		x	x		x	x		x			x		
S267-55	S-8	x	x	x	x	-	x		x	x		x	x		x			x		
S269-65		x	t	x	x	x	x					x		x	x			x		
S271-80		x	x	x	x	x	x			x		x	x	x	x			x		
S308-5		x	x	x	x	x			x	x		x	x	x	x		-	x		
S385-67			x	x	x	x	x		x	x		x	x	x	x				hb	
S385-107		x										x			x				hb	
S387-55			x	x	x				x	x			x	x	x			x		
S388-122			x	x	x	x			x	x			x	x	x	x	x	x		
S393-104			x	x	x								x	x	x			x		
S394-123		x	x									x			x			x		
S404-100		x	x	x	x				x		x	x	x	x	x			x		

Appendix I (cont.)

Sample Number	Text Number	at	bi	ch	cp	gt	il	kf	ky	mt	mu	pc	po	py	qz	si	sp	st	to	other
S405-60		x	x											x	x			x		ga
S406-44			x	x	x	x			x				x	x	x	x		x		
S407-15		x	x	x	x				x	x	x	x	x	x	x	x		x		
S408-142		x	x	x					x	x	x	x	x	x	x	x		x		
S409-2		x	x	x	x	x			x		x	x	x	x	x	x		x		
S409-95		x	x	x		x			x			x	x		x	x		x		
S410-46		x	x	x	x				x	x	x	x	x	x	x	x		x		
S411-35		x	x	x	x	x			x	x	x	x	x	x	x	x		x		
S412-132		x	x	x	x	x	x		x	x	x	x	x	x	x	x		x		
S419-20		x	x	x	x	x			x	x	x	x	x	x	x	x		x		
S420-16		x	x	t	x	x			x	x	x	x	x	x	x	x		x		
S421-10	S-9	x	x	x	x	x			x			x	x	x	x	x		x		
STH222-25		x	x	x	x			x		x		x	x	x	x	x		x		
STH223-25		x	x	x	x						x		x	x	x	x		x		
STH330-40	S-10	x	x	x	x	x						x	x	x	x	x		x		hb

Appendix I (cont.)

Metavolcanic mineral assemblages

Sample Number	ap	bf	ca	cc	ch	cu	ep	gt	hb	kf	mu	pc	qz	op	others
FQH 9	x				x		x	x	x	x		x	x	x	
FQH 10												x			mt
FQH 14	x			x			x	x			x	x	x		mt
FQH 16		x						x	x			x	x	x	
FQH 18			x				x		x			x	x		
FQH 27	x	x					x	x			x	x	x		
FQH 35		x						x	x			x	x		
FQH 36	x	x	x		x	x		x	x			x	x	x	
FQH 49									x			x	x	x	
FQH 50						x			x			x	x	x	
FQH 52B						x	x	x	x			x	x		mt
FQH 53						x		x	x			x		x	
FQH 56		x	x		x		x	x		x	x		x	x	
FQH 58		x					x	x		x	x	x	x	x	

Appendix I (cont.)

Sample Number	ap	bf	ca	cc	ch	cu	ep	gt	hb	kf	mu	pc	qz	qp	others
FQH 63		x			x		x		x			x	x		
FQH 69		x			x	x		x				x	x		mt
FQH 75				x	x		x		x			x	x		mt,py
FQH 76		x		x			x	x				x	x		mt,py
FQH 81	x	x		x	x		x	x				x	x		
FQH 91		x		x			x	x				x	x		
FQH 91A		x				x	x		x			x	x		
FQH 92		x		x								x	x		
FQH 97	x	x		x	x	x						x	x		
FQH 102									x			x	x		
FQH 104							x		x			x	x		
FQH 115				x	x			x				x	x		
FQH 119	x					x			x			x	x		
FQH 120		x			x			x				x	x		

Appendix I (cont.)

Sample Number	ap	bf	ca	cc	ch	cu	ep	gt	hb	kf	mu	pc	qz	op	others
FQH 122					x			x				x	x		
FQH 123	x	x		x	x	x		x	x			x	x	x	
FQH 128		x					x	x	x			x	x		
FQH 129						x			x		x				
FQH 132		x			x	x		x	x		x	x	x		
FQH 134							x		x			x	x	x	
FQH 135		x			x		x		x			x	x		
FQH 141A		x						x	x			x	x		
FQH 150							x	x	x		x	x	x		
FQH 155									x			x	x	x	
FQH 156		x							x			x	x	x	
FQH 158								x	x			x		x	
FQH 166								x	x			x			mt
FQH 170				x				x	x		x	x			mt

Appendix I (cont.)

Sample Number	ap	bf	ca	cc	ch	cu	ep	gt	hb	kf	mu	pc	qz	op	others
FQH 171	x				x			x			x				
FQH 180	x				x		x		x		x	x	x		
FQH 182					x		x	x		x	x	x	x		
FQH 183															
FQH 186	x				x		x		x		x	x	x	mt	
FQH 188	x			x	x			x		x	x	x	x		
FQH 189	x			x				x	x	x	x	x	x		
FQH 196				x	x		x		x			x	x	x	
FQH 198	x				x					x		x	x		

Appendix I (cont..)

Mineral assemblages in pelitic rocks from surface outcrops.

Sample Number	bt	ch	gt	ky	mu	pc	qz	st	to others
FQH 24	x	x		x	x		x		
FQH 25	x	x		x	x		x		mt
FQH 25A	x	x		x	x		x		
FQH 32	x		x		x	x	x	x	mt,py
FQH 71	x	x			x	x	x	x	mt
FQH 72	x	x	x		x		x		mt
FQH 108	x	x	x		x		x	x	

Appendix II

Table A-1 Whole rock chemical analyses of metavolcanic rocks from Snow Lake, in oxide weight per cent. Analyses by The Geological Survey of Canada.

	H9	H16	H18	H36	H49	H50	H53	H56	H58	H75
SiO ₂	75.20	52.20	43.10	64.90	47.70	48.60	49.10	71.80	73.50	50.40
Al ₂ O ₃	10.60	19.30	16.60	13.70	19.50	17.90	19.70	13.10	11.90	17.00
TiO ₂	0.21	0.58	0.29	0.54	0.40	0.31	0.48	0.44	0.22	0.54
FeO	4.50	9.70	9.60	7.60	10.70	10.30	9.10	4.90	3.20	8.10
Fe ₂ O ₃	0.00	1.40	3.10	1.00	1.60	1.80	1.10	0.30	0.30	4.80
MgO	0.41	2.82	4.56	2.22	4.90	5.50	4.07	0.61	0.40	4.67
MnO	0.15	0.22	0.21	0.17	0.24	0.20	0.18	0.13	0.06	0.26
CaO	2.56	7.54	15.60	3.56	11.40	12.80	11.30	2.10	1.07	8.66
Na ₂ O	3.50	4.10	1.20	3.90	2.00	0.92	1.60	3.40	3.50	3.33
K ₂ O	0.98	0.70	0.31	1.45	0.28	0.25	0.31	2.10	3.42	0.24
P ₂ O ₅	0.09	0.09	0.06	0.16	0.08	0.06	0.08	0.13	0.06	0.11
CO ₂	1.00	0.10	2.90	0.20	0.10	0.10	0.00	0.10	0.10	0.50
H ₂ O ^T	0.70	1.10	1.60	1.20	1.20	2.40	1.20	0.80	0.60	1.50
Total	99.90	99.85	99.13	100.60	100.10	101.14	98.22	100.51	98.33	100.08

Table A-1 (cont.)

	H76	H81	H91	H91A	H97	H102	H115	H119	H120	H122
SiO ₂	68.70	72.30	78.40	52.10	71.80	57.00	51.40	56.90	73.80	65.50
Al ₂ O ₃	12.30	12.70	11.10	17.70	11.80	13.90	14.50	10.70	11.50	14.50
TiO ₂	0.50	0.27	0.20	0.62	0.28	0.72	0.70	0.25	0.32	0.44
FeO	4.60	3.00	1.60	1.10	3.60	11.20	12.50	7.40	3.90	6.70
Fe ₂ O ₃	3.00	0.50	0.00	9.10	0.50	0.80	2.00	1.50	0.60	1.30
MgO	1.02	1.96	0.52	6.09	1.57	4.20	4.93	9.81	2.01	2.06
MnO	0.21	0.09	0.04	0.21	0.07	0.17	0.24	0.17	0.09	0.17
CaO	2.80	2.67	1.73	9.16	2.87	7.54	8.35	10.70	2.79	1.74
Na ₂ O	2.00	3.20	2.00	2.30	2.80	2.00	1.90	1.30	1.60	3.60
K ₂ O	2.71	2.24	2.20	0.26	1.93	0.64	0.65	0.38	1.91	2.11
P ₂ O ₅	0.22	0.07	0.06	0.09	0.09	0.08	0.06	0.05	0.12	0.12
CO ₂	0.40	0.80	0.00	0.00	0.90	0.00	0.20	0.00	0.00	0.00
H ₂ OT	1.40	1.00	1.20	1.20	1.30	2.00	1.80	1.50	1.20	1.80
Total	99.86	100.80	99.05	99.93	99.51	100.25	99.23	100.69	99.84	100.04

Table A-1 (cont.)

	H123	H129	H132	H135	H141A	H150	H155	H156	H158	H166
SiO ₂	57.10	58.00	65.10	51.00	51.50	54.20	54.40	48.00	52.50	51.80
Al ₂ O ₃	14.70	16.20	13.60	20.50	17.70	15.60	19.10	18.70	18.10	16.30
TiO ₂	0.75	0.75	0.51	0.54	0.56	0.49	0.50	0.52	0.69	0.95
FeO	9.70	8.40	7.50	6.70	7.80	7.60	6.40	8.50	7.90	9.70
Fe ₂ O ₃	1.80	1.60	1.50	3.60	2.90	3.50	1.50	4.00	2.60	3.50
MgO	3.95	3.95	2.44	3.60	4.86	4.72	3.65	3.76	3.97	3.77
MnO	0.18	0.14	0.18	0.17	0.20	0.19	0.15	0.23	0.24	0.23
CaO	6.55	6.78	3.82	9.87	10.10	9.29	10.50	11.60	8.52	8.51
Na ₂ O	3.00	3.80	3.40	2.40	1.60	1.70	1.80	3.30	3.70	2.20
K ₂ O	0.51	0.34	1.07	1.12	0.52	0.54	0.29	0.36	0.40	0.48
P ₂ O ₅	0.08	0.11	0.16	0.24	0.23	0.07	0.10	0.09	0.08	0.08
CO ₂	0.10	0.00	0.40	0.00	0.00	0.00	0.00	0.60	0.00	0.00
H ₂ O	1.40	1.00	1.20	1.10	1.30	1.50	1.00	1.20	1.10	1.10
Total	99.82	101.07	100.88	100.60	99.27	99.40	99.39	100.86	99.80	98.62

Table A-1 (cont.)

	H171	H182	H186	H188	H189	H196	H198
SiO ₂	66.40	80.90	52.60	69.40	67.70	47.90	71.60
Al ₂ O ₃	13.30	10.60	15.90	13.00	12.80	21.30	12.50
TiO ₂	0.36	0.08	0.63	0.44	0.36	0.58	0.34
FeO	6.40	1.20	7.40	5.20	3.70	5.70	3.00
Fe ₂ O ₃	2.20	0.10	3.30	1.90	2.10	2.70	2.30
MgO	2.85	0.37	2.88	0.83	1.61	4.39	2.96
MnO	0.21	0.04	0.22	0.21	0.11	0.16	0.09
CaO	5.65	1.29	9.94	4.01	6.19	11.70	2.12
Na ₂ O	0.71	2.70	0.86	2.60	2.50	2.70	2.60
K ₂ O	0.50	2.92	0.99	1.63	0.60	0.58	1.30
P ₂ O ₅	0.08	0.03	0.15	0.16	0.09	0.13	0.11
CO ₂	0.10	0.00	0.30	0.80	0.70	0.50	0.00
H ₂ O ^T	1.20	0.60	1.40	0.90	1.00	1.60	1.60
Total	99.61	100.83	96.57	101.08	99.46	99.94	100.52

Table A-2 Calculated normative mineralogy for metamorphosed volcanic rocks from Snow Lake, Manitoba.

	H9	H16	H18	H36	H49	H50	H53
quartz	41.702	0.000	0.000	20.751	0.000	3.128	3.810
corundum	0.000	0.000	0.000	0.000	0.000	0.000	0.000
orthoclase	5.769	4.187	1.814	8.606	1.672	1.496	1.890
albite	29.472	35.082	6.230	33.111	17.087	7.873	13.953
anorthite	10.270	32.558	38.576	15.646	43.831	44.478	47.059
nepheline	0.000	0.000	2.066	0.000	0.000	0.000	0.000
diopside	0.195	1.326	13.185	0.293	4.661	7.684	3.683
hedenbergite	1.368	2.652	18.427	0.579	6.032	8.456	4.861
enstatite	0.926	5.538	0.000	5.412	6.939	10.291	8.739
ferrosillite	7.430	12.701	0.000	12.290	10.299	12.988	13.230
forsterite	0.000	0.666	3.589	0.000	2.258	0.000	0.000
fayalite	0.000	1.682	6.339	0.000	3.694	0.000	0.000
magnetite	0.000	2.053	2.567	1.455	2.343	2.640	1.644
ilmenite	0.000	1.114	0.545	1.029	0.767	0.595	0.940
hematite	0.000	0.000	0.000	0.000	0.000	0.000	0.191
apatite	0.208	0.211	0.138	0.372	0.187	0.141	0.000
calcite	2.263	0.230	6.525	0.456	0.230	0.230	0.000

Table A-2 (cont.)

	H56	H58	H75	H76	H81	H91	H91A
quartz	35.443	35.635	0.000	36.562	34.187	53.964	6.022
corundum	1.739	0.650	0.000	1.529	0.321	2.479	0.000
orthoclase	12.517	20.672	1.435	16.214	13.142	13.299	1.570
albite	28.987	30.261	28.226	17.116	26.854	17.293	19.864
anorthite	9.641	5.023	31.206	12.594	12.684	8.370	37.980
diopside	0.000	0.000	4.200	0.000	0.000	0.000	3.911
hedenbergite	0.000	0.000	5.445	0.000	0.000	0.000	2.482
enstatite	1.531	1.018	9.275	2.569	4.841	1.323	13.668
ferrosilite	8.329	5.494	13.789	8.086	4.778	2.741	9.950
forsterite	0.000	0.000	0.375	0.000	0.000	0.000	0.000
fayalite	0.000	0.000	0.615	0.000	0.000	0.000	0.000
magnetite	0.438	0.444	2.990	2.933	0.719	0.000	3.138
ilmenite	0.842	0.427	1.037	0.961	0.509	0.388	1.202
apatite	0.304	0.142	0.258	0.516	0.161	0.142	0.213
calcite	0.229	0.232	1.150	0.920	1.805	0.000	0.000

Table A-2 (cont.)

	H97	H102	H115	H119	H120	H122	H123
quartz	37.454	14.429	6.150	11.582	46.299	25.540	12.636
corundum	0.102	0.000	0.000	0.000	2.042	3.478	0.000
orthoclase	11.490	3.853	3.952	2.267	11.453	12.704	3.061
albite	23.843	17.222	16.525	11.092	13.724	31.004	25.756
anorthite	13.738	27.542	29.932	22.427	13.236	7.987	25.510
diopside	0.000	3.263	4.189	17.339	0.000	0.000	2.461
hedenbergite	0.000	5.178	6.126	7.583	0.000	0.000	3.364
enstatite	3.935	9.133	10.679	16.598	5.075	5.222	8.841
ferrosillite	5.903	16.619	17.911	8.325	6.392	11.013	13.860
magnetite	0.730	1.181	2.981	2.193	0.882	1.919	2.648
ilmenite	0.535	1.392	1.367	0.479	0.616	0.851	1.445
apatite	0.210	0.189	0.143	0.117	0.282	0.283	0.188
calcite	2.060	0.000	0.047	0.000	0.000	0.000	0.231

Table A-2 (cont.)

	H129	H132	H135	H141A	H150	H155	H156
quartz	9.968	24.332	2.384	7.961	11.899	12.608	0.000
corundum	0.000	0.286	0.000	0.000	0.000	0.000	0.000
orthoclase	2.010	6.317	6.653	3.142	3.268	1.743	2.125
albite	32.128	28.711	20.393	13.830	14.716	15.478	24.734
anorthite	26.126	17.870	42.036	40.437	34.114	43.888	35.078
nepheline	0.000	0.000	0.000	0.000	0.000	0.000	1.695
diopside	2.614	0.000	2.093	3.889	5.078	3.560	7.176
hedenbergite	3.041	0.000	2.564	3.765	5.396	3.404	11.188
enstatite	8.618	6.065	8.033	10.562	9.672	7.588	0.000
ferrosillite	11.499	12.003	11.283	11.730	11.786	8.320	0.000
forsterite	0.000	0.000	0.000	0.000	0.000	0.000	4.217
fayalite	0.000	0.000	0.000	0.000	0.000	0.000	8.310
magnetite	2.318	2.171	2.971	3.051	2.952	2.210	2.923
ilmenite	1.423	0.967	1.030	1.087	0.952	0.965	0.986
apatite	0.255	0.370	0.559	0.545	0.166	0.236	0.208
calcite	0.000	0.908	0.000	0.000	0.000	0.000	1.362

Table A-2 (cont.)

	H158	H166	H171	H182	H186	H188	H189
quartz	1.944	8.133	39.851	49.724	15.927	34.756	35.059
corundum	0.000	0.000	1.527	0.720	0.000	0.050	0.000
orthoclase	2.398	2.915	2.992	17.232	6.136	9.527	3.573
albite	31.731	19.109	6.076	22.792	7.625	21.737	21.295
anorthite	32.031	34.068	27.823	6.189	38.354	18.623	22.082
diopside	4.051	2.924	0.000	0.000	4.003	0.000	3.211
hedenbergite	4.529	4.443	0.000	0.000	6.379	0.000	3.673
enstatite	8.143	8.283	7.204	0.919	5.660	2.042	2.548
ferrosilite	10.439	14.436	10.689	2.059	10.346	7.552	3.343
magnetite	3.218	3.647	2.728	0.145	8.236	2.722	2.715
ilmenite	1.328	1.852	0.692	0.152	1.254	0.826	0.688
apatite	0.188	0.191	0.188	0.069	0.365	0.367	0.210
calcite	0.000	0.000	0.230	0.000	0.715	1.798	1.603

Table A-2 (cont.)

	H158	H166	H171	H182	H186	H188	H189
quartz	1.944	8.133	39.851	49.724	15.927	34.756	35.059
corundum	0.000	0.000	1.527	0.720	0.000	0.050	0.000
orthoclase	2.398	2.915	2.992	17.232	6.136	9.527	3.573
albite	31.731	19.109	6.076	22.792	7.625	21.737	21.295
anorthite	32.031	34.068	27.823	6.189	38.354	18.623	22.082
diopside	4.051	2.924	0.000	0.000	4.003	0.000	3.211
hedenbergite	4.529	4.443	0.000	0.000	6.379	0.000	3.673
enstatite	8.143	8.283	7.204	0.919	5.660	2.042	2.548
ferrosillite	10.439	14.436	10.689	2.059	10.346	7.552	3.343
magnetite	3.218	3.647	2.728	0.145	3.236	2.722	2.715
ilmenite	1.328	1.852	0.692	0.152	1.254	0.826	0.688
apatite	0.188	0.191	0.188	0.069	0.365	0.367	0.210
calcite	0.000	0.000	0.230	0.000	0.715	1.798	1.603

Table A-2 (cont.)

	H196	H198
quartz	0.000	41.399
corundum	0.000	3.260
orthoclase	3.468	7.774
albite	23.095	22.239
anorthite	44.776	9.905
diopside	6.218	0.000
hedenbergite	4.513	0.000
enstatite	2.727	7.452
ferrosillite	2.270	4.228
forsterite	3.815	0.000
fayalite	3.500	0.000
magnetite	3.049	2.756
ilmenite	1.114	0.730
hematite	0.000	0.000
apatite	0.305	0.258
calcite	1.150	0.000

Appendix III

Table AIII-1 Chlorite microprobe analyses from Anderson Lake and Stall Lake Mines.

	A1	A2	A3	A4	A6	A7	A8	S1	S2	S4
SiO ₂	24.99	25.14	24.91	24.53	24.55	25.03	25.16	25.79	25.14	25.43
Al ₂ O ₃	23.14	22.60	23.18	22.81	23.02	23.98	23.18	22.30	23.09	23.00
FeO	19.63	22.02	15.66	22.52	22.94	19.08	19.88	18.99	17.32	19.71
MgO	19.57	17.57	22.45	17.04	16.38	19.27	18.75	19.51	21.23	20.01
MnO	0.06	0.17	0.30	0.18	0.04	0.38	0.45	0.25	0.20	0.21
TiO ₂	0.08	0.06	0.09	0.07	0.07	0.08	0.07	0.07	0.10	0.07
CaO	0.00	0.01	0.00	0.02	0.04	0.00	0.00	0.02	0.00	0.00
Na ₂ O	0.00	0.01	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00
Total	87.47	87.57	86.59	87.17	87.04	87.82	87.49	86.93	87.08	88.43

Table AIIr-1 (cont.)

	S5	S6	S7	S8	S9	S10
SiO ₂	25.22	25.21	24.97	25.11	25.17	25.15
Al ₂ O ₃	23.15	23.20	23.40	22.81	23.21	22.83
FeO	19.94	18.01	18.25	19.69	17.27	19.77
MgO	19.80	20.26	19.60	19.16	20.61	19.23
MnO	0.13	0.24	0.17	0.25	0.27	0.22
TiO ₂	0.06	0.06	0.09	0.08	0.13	0.18
CaO	0.00	0.00	0.01	0.01	0.01	0.02
Na ₂ O	0.00	0.00	0.00	0.01	0.00	0.01
Total	88.30	86.98	86.49	87.11	86.67	87.40

Table AIII-1 Staurolite microprobe analyses from Anderson Lake and Stall Lake Mines.

	A1	A2	A3	A4	A5	A7	A8	A9	A10	A11
SiO ₂	27.34	27.60	27.67	27.46	26.94	28.60	27.14	27.50	28.43	29.43
Al ₂ O ₃	52.84	53.34	53.84	52.87	53.56	51.07	52.67	53.44	53.05	54.41
FeO	14.73	13.87	9.91	14.48	14.29	14.14	10.71	12.81	14.35	9.36
MgO	2.39	2.07	2.48	1.95	2.08	2.26	2.01	1.63	2.23	2.32
MnO	0.13	0.37	0.59	0.37	0.36	0.76	0.89	0.63	0.64	0.74
CaO	0.02	0.00	0.02	0.00	0.00	0.01	0.00	0.01	0.04	0.00
ZnO	0.16	1.27	4.30	0.27	0.73	0.06	3.21	2.20	0.05	n.d.
TiO ₂	0.50	0.39	0.47	0.41	0.43	0.42	0.45	0.45	0.53	0.42
Total	98.11	98.91	99.28	97.81	98.79	97.32	97.08	98.67	99.32	96.68

Table AIII-1 (cont.)

	S1	S2	S4	S5	S6	S7	S8	S9	S10
SiO ₂	28.08	27.46	28.02	28.07	27.63	27.56	27.41	27.36	27.38
Al ₂ O ₃	52.27	51.70	51.57	52.49	53.69	53.15	52.30	52.84	52.03
FeO	13.95	11.08	13.66	14.40	13.84	14.20	12.21	13.00	11.88
MgO	2.13	2.48	2.43	2.60	2.38	2.47	2.23	2.68	2.32
MnO	0.58	0.40	0.54	0.35	0.64	0.38	0.95	0.55	0.43
TiO ₂	0.36	0.44	0.51	0.44	0.33	0.29	0.46	0.54	0.42
ZnO	0.76	5.17	1.00	0.91	0.28	0.21	3.28	0.31	3.71
CaO	0.01	0.03	n.d.	n.d.	0.01	0.01	0.01	0.02	n.d.
Total	98.14	98.76	97.76	99.26	98.80	98.27	98.85	97.30	98.17

Table AIII-1 Biotite microprobe analyses from Anderson Lake and Stall Lake Mines.

	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
SiO ₂	36.97	36.66	37.80	36.44	36.23	36.19	36.89	36.58	36.83	36.95
Al ₂ O ₃	18.37	18.33	18.68	18.12	18.72	18.48	18.42	18.34	19.15	18.87
K ₂ O	9.11	9.44	9.29	9.63	9.18	9.19	9.49	9.43	8.97	8.65
Na ₂ O	0.57	0.35	0.39	0.25	0.29	0.43	0.22	0.27	0.45	0.29
FeO	15.83	17.97	12.36	18.47	18.82	15.75	17.85	15.20	15.71	17.69
MgO	13.43	12.17	15.80	11.73	11.32	12.45	11.85	13.27	13.02	12.28
MnO	0.02	0.10	0.17	0.11	0.01	0.08	0.18	0.22	0.21	0.19
TiO ₂	1.25	1.31	1.30	1.44	1.48	1.33	1.32	1.46	1.21	1.36
H ₂ O	4.03	4.01	4.11	3.99	3.94	3.93	4.01	3.95	4.04	4.04
Total	99.58	100.34	99.90	100.18	99.99	98.83	100.23	98.72	99.59	100.32

Table AIII-1 (cont.)

	A11	A12	A13	S1	S2	S4	S5	S6	S7	S8
SiO ₂	36.87	35.12	36.83	37.66	37.09	37.16	37.11	37.33	36.40	36.75
Al ₂ O ₃	18.12	17.79	17.84	18.27	18.27	19.26	18.87	19.44	20.17	17.87
K ₂ O	9.50	9.38	9.33	8.51	8.86	8.53	8.56	8.97	9.04	9.12
Na ₂ O	0.32	0.10	0.27	0.40	0.58	0.73	0.69	0.52	0.43	0.40
FeO	17.61	18.84	16.18	16.22	15.06	15.27	15.82	14.78	15.55	16.49
MgO	12.30	11.38	13.45	13.23	14.69	13.56	13.72	13.92	13.43	12.85
MnO	0.10	0.13	0.17	0.18	0.12	0.16	0.10	0.17	0.08	0.16
TiO ₂	1.37	1.69	1.43	1.22	1.66	1.49	1.37	1.03	0.94	1.54
H ₂ O	4.01	3.90	3.96	4.05	4.08	4.08	4.07	4.09	4.06	4.00
Total	100.20	98.33	99.46	99.74	100.41	100.24	100.31	100.25	100.10	99.18

Table AIII-1 (cont.)

	S9	S10	S11	S12
SiO ₂	37.15	37.00	35.92	36.73
Al ₂ O ₃	18.24	17.54	18.30	19.18
K ₂ O	8.94	8.73	9.29	9.21
Na ₂ O	0.50	0.28	0.58	0.36
FeO	14.33	16.77	16.99	17.34
MgO	14.00	13.92	12.57	12.15
MnO	0.17	0.14	0.12	0.19
TiO ₂	1.42	1.37	1.62	1.26
H ₂ O	4.03	4.03	3.98	4.04
Total	98.78	99.78	99.37	100.46

Table AIII-1 Garnet microprobe analyses from Anderson Lake and Stall Lake Mines.

	A6	S3(rim)	S3(core)	S8	S10
SiO ₂	37.03	36.38	36.68	37.20	37.39
Al ₂ O ₃	20.93	20.74	20.75	21.03	21.05
FeO	34.97	33.34	32.62	26.04	27.49
MgO	3.23	2.85	3.02	4.39	4.22
MnO	1.72	1.80	2.06	8.51	7.25
CaO	2.36	3.26	3.53	2.75	2.50
TiO ₂	0.01	n.d.	n.d.	0.02	n.d.
Total	100.25	98.10	98.66	99.94	99.90

Table AIII-1 Muscovite microprobe analysis from Anderson Lake and Stall Lake Mines.

	A10
SiO ₂	46.63
Al ₂ O ₃	34.42
K ₂ O	8.53
Na ₂ O	0.93
FeO	2.86
MgO	0.66
MnO	0.09
TiO ₂	0.37
Total	94.49

Table AIII-2 Structural formulae of biotite based on 12 oxygen atoms.

	A1	A2	A3	A4	A5	A6
Si	2.749	2.737	2.755	2.736	2.753	2.761
Al	1.251	1.263	1.245	1.264	1.247	1.239
Al	0.358	0.350	0.359	0.339	0.339	0.332
Mg	1.488	1.354	1.716	1.313	1.282	1.416
Fe	0.984	1.122	0.753	1.160	1.196	1.069
Ti	0.070	0.074	0.071	0.081	0.085	0.076
Mn	0.001	0.006	0.010	0.007	0.001	0.005
K	0.864	0.899	0.864	0.922	0.890	0.894
Na	0.082	0.051	0.055	0.036	0.043	0.064
H	2.000	2.000	2.000	2.000	2.000	2.000
O	12.000	12.000	12.000	12.000	12.000	12.000

Table AIII-2 (cont.)

	A7	A8	A9	A10	A11	A12
Si	2.754	2.776	2.733	2.739	2.752	2.699
Al	1.246	1.224	1.267	1.261	1.248	1.301
Al	0.374	0.326	0.408	0.388	0.346	0.310
Mg	1.319	1.501	1.440	1.357	1.369	1.303
Fe	1.114	0.965	0.975	1.097	1.099	1.211
Ti	0.074	0.083	0.068	0.076	0.077	0.098
Mn	0.011	0.014	0.013	0.012	0.006	0.008
K	0.904	0.913	0.849	0.818	0.905	0.919
Na	0.032	0.040	0.065	0.042	0.046	0.015
H	2.000	2.000	2.000	2.000	2.000	2.000
O	12.000	12.000	12.000	12.000	12.000	12.000

Table AIII-2 (cont.)

	A13	S1	S2	S4	S5	S6
Si	2.784	2.786	2.724	2.727	2.730	2.736
Al	1.216	1.214	1.276	1.273	1.270	1.264
AL	0.284	0.378	0.305	0.393	0.365	0.416
Mg	1.515	1.459	1.608	1.483	1.504	1.521
Fe	1.023	1.003	0.925	0.937	0.973	0.906
Ti	0.081	0.068	0.092	0.082	0.076	0.057
Mn	0.011	0.011	0.007	0.010	0.006	0.011
K	0.900	0.803	0.830	0.798	0.803	0.839
Na	0.040	0.057	0.083	0.104	0.098	0.074
H	2.000	2.000	2.000	2.000	2.000	2.000
O	12.000	12.000	12.000	12.000	12.000	12.000

Table AIII-2 (cont.)

	S7	S8	S9	S10	S11	S12
Si	2.684	2.756	2.764	2.754	2.703	2.725
Al	1.316	1.244	1.236	1.246	1.297	1.275
Al	0.437	0.335	0.362	0.292	0.326	0.402
Mg	1.476	1.436	1.552	1.544	1.410	1.344
Fe	0.959	1.034	0.891	1.044	1.069	1.076
Ti	0.052	0.087	0.079	0.077	0.092	0.070
Mn	0.005	0.010	0.011	0.009	0.008	0.012
K	0.850	0.872	0.848	0.829	0.892	0.872
Na	0.061	0.058	0.072	0.040	0.085	0.052
H	2.000	2.000	2.000	2.000	2.000	2.000
O	12.000	12.000	12.000	12.000	12.000	12.000

Table AIII-2 Structural formulae of chlorite based on 18 oxygen atoms.

	A1	A2	A3	A4	A6	A7
Si	2.560	2.605	2.532	2.565	2.573	2.547
Al	1.440	1.395	1.468	1.435	1.427	1.453
Al	1.354	1.365	1.308	1.375	1.416	1.422
Mg	2.988	2.714	3.401	2.655	2.559	2.923
Fe	1.682	1.908	1.331	1.969	2.011	1.624
Ti	0.006	0.005	0.007	0.006	0.006	0.006
Mn	0.005	0.015	0.026	0.016	0.004	0.033
Ca	0.000	0.001	0.000	0.002	0.004	0.000
H	8.000	8.000	8.000	8.000	8.000	8.000
O	18.000	18.000	18.000	18.000	18.000	18.000

Table AIII-2 (cont.)

	A8	S1	S2	S4	S5	S6
Si	2.583	2.649	2.559	2.578	2.563	2.576
Al	1.417	1.351	1.441	1.422	1.437	1.424
Al	1.387	1.348	1.328	1.325	1.335	1.370
Mg	2.869	2.987	3.221	3.023	2.999	3.086
Fe	1.707	1.631	1.474	1.671	1.695	1.539
Ti	0.005	0.005	0.008	0.005	0.005	0.005
Mn	0.039	0.022	0.017	0.018	0.011	0.021
Ca	0.000	0.002	0.000	0.000	0.000	0.000
H	8.000	8.000	8.000	8.000	8.000	8.000
O	18.000	18.000	18.000	18.000	18.000	18.000

Table AIII-2 (cont.)

	S7	S8	S9	S10
Si	2.569	2.586	2.573	2.582
Al	1.431	1.414	1.427	1.418
Al	1.406	1.355	1.368	1.345
Mg	3.006	2.942	3.140	2.943
Fe	1.570	1.696	1.476	1.698
Ti	0.007	0.006	0.010	0.014
Mn	0.015	0.022	0.023	0.019
Ca	0.001	0.001	0.001	0.002
H	8.000	8.000	8.000	8.000
O	18.000	18.000	18.000	18.000

SNOW
LAKE

54°52'

ANDERSON
LAKE

LEGEND

5

Intrusive hornbl

3c

Mafic tuffs co
and graded

3b

Mafic intrusive

3a

Mafic fragme

2b

Mafic pillow

2a

Felsic to in
tuffs and fr

2a

Felsic to int
fragmental r

50

Pelitic schist
and garnet.

50

Pelitic schist
and kyanite.

50

bedding, top

50

bedding, top

50

F₁ foliation

50

F₂ foliation

LEGEND

- 5 Intrusive hornblendite sills
- Mafic tuffs contain bedding, cross bedding and graded bedding.
- 3c Mafic intrusive rocks, massive.
- 3b Mafic fragmental rocks.
- 3a Mafic pillow lavas.
- 2b Felsic to intermediate "quartz eye" tuffs and fragmental rocks.
- 2a Felsic to intermediate tuffs and fragmental rocks.
- Pelitic schist with staurolite and garnet.
- Pelitic schist with chlorite and kyanite.
- bedding, top known.
- bedding, top unknown.
- F₁ foliation.
- F₂ foliation.

100°00'

STALL LAKE

99°55'

2a

Felsic to intermediate tuffs and fragmental rocks.

Pelitic schist with staurolite and garnet.

Pelitic schist with chlorite and kyanite.

bedding, top known.

bedding, top unknown.

F₁ foliation

F₂ foliation

lineation

geologic contact, known

geologic contact, assumed

outcrop boundary

mine shaft

gravel road

•69
•70

3.

34

CAB 75

TA :129

•128

CAB 49

TB 50
TD 9

✓ 16 CAB

48 NAB

44

48

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-45

43

41

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51.19

20

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0.29

30

74

26

27

67

65

-66-

-68-

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-62

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48

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22

25

24

-10

29

2.

2d

3 of 1

END

07 11 77

FIN