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Oxygen-Isotope Geochemistry and Metamorphism of Massive Sulfide Deposits of the Flin Flon - Snow Lake Belt, Manitoba

by

Pradeep Kumar Aggarwal

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
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PRADEEP KUMAR AGGARWAL

OXYGEN-ISOTOPE GEOCHEMISTRY AND METAMORPHISM OF MASSIVE
SULFIDE DEPOSITS OF THE FLIN FLON - SNOW LAKE BELT, MANITOBA

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled Oxygen-Isotope Geochemistry and Metamorphism of Massive Sulfide Deposits of the Flin Flon - Snow Lake Belt, Manitoba submitted by Pradeep Kumar Aggarwal in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Date December 19, 1985

Dedication

This dissertation is dedicated to

my parents who made it all possible for me.

Abstract

Estimates of temperature and pressure conditions of metamorphism in the Flin Flon - Snow Lake, Manitoba greenstone belt have been obtained using the mineral assemblages in mafic and felsic, metavolcanic rocks. The Flin Flon area around the Centennial deposit, in the western part of the belt, was metamorphosed at temperatures of less than 450 °C and pressure less than 3.8 kb. Metamorphic grade increases at Spruce Point, in the central part of the belt, where the temperature was 475 ± 50 °C at 2.6 ± 1.2 kb pressure. In the Snow Lake area to the east, the grade of metamorphism varies from low-greenschist facies in the south (chlorite-biotite zone) to amphibolite facies in the north (biotite-sillimanite-almandine zone). Pressure and temperature conditions in the amphibolite facies terrane, near the Anderson Lake deposit, have been estimated using several, calibrated silicate equilibria. In the staurolite - biotite - sillimanite zone, the temperature and pressure conditions were: 575 ± 50 °C at 5.25 ± 0.5 kb. In the biotite - sillimanite - almandine zone, the temperature was 620 ± 40 °C at 5.8 ± 0.5 kb pressure. Based on the temperature and pressure estimates from the Snow Lake area, the stability of the staurolite - quartz - almandine and biotie - almandine - muscovite - ilmenite equilibria are calibrated. It is suggested that experimental studies of the upper stability of staurolite and quartz at low pressures indicate unusually high temperatures. Further, it is proposed that the biotite - almandine - muscovite assemblage may be used as a geothermo-barometer.

Oxygen isotopic compositions of country rocks and hydrothermally altered rocks associated with three ore deposits in the Flin Flon - Snow Lake belt, Centennial (CL), Spruce Point (SP), and Anderson Lake (AL), have been measured. Whole-rock δ^{18}O values of felsic metavolcanic, country rocks range from +9.1 to + 16.1. Rocks from the "alteration pipe" at the three deposits have lower δ^{18}O values compared with the country rocks. The δ^{18}O values in the chlorite zone and muscovite zone-I (CL = +5.3; SP = +5.2 to +7.1; AL = +3.7 to +6.1) are lower than those in the gradational zone (CL = +9.0 to +11.1; SP = +8.0 to +10.8; AL = +6.6 to +7.7). An envelope of muscovite schist (Muscovite Zone-II) surrounds the Anderson Lake ore body and has δ^{18}O values higher than those of other altered rocks but lower than those of the country rocks. Quartz, biotite, muscovite, and chlorite

separates from the altered rocks have lower $\delta^{18}O$ values compared with those of minerals separated from the country rocks. However, fractionation between mineral-pairs is generally similar in both country and altered rocks.

It is interpreted that differences in the oxygen isotopic compositions of the altered and country rocks were produced prior to metamorphism, during hydrothermal alteration related to ore-deposition. Isotopic homogenization during metamorphism was on a grain to grain scale and no more than a scale of meters. The whole-rock, $\delta^{18}O$ values did not change significantly during metamorphism. The generally lower $\delta^{18}O$ values of the rocks and Cu-rich nature of the ore at Anderson Lake compared with the Centennial and Spruce Point deposits are consistent with a higher temperature of the hydrothermal fluids at Anderson Lake. It is suggested in this study that oxygen-isotope analyses are most useful for exploration for ore deposits in a previously known, mineralized district.

Metamorphic volatile and solid phase equilibria at Anderson Lake and Spruce Point were studied in detail in order to understand the fluid-rock interaction during metamorphism. The composition of the metamorphic fluid phase has been estimated from mineral equilibria. Calculations indicate that the fluid phase at Anderson Lake and Spruce Point consisted essentially of H_2O with minor contents of other species in the system H-O-S. Algebraic analysis of silicate equilibria indicates that μH_2O during metamorphism was not equal in all the rocks at Anderson Lake. Based on a simultaneous consideration of sulfide - silicate - oxide equilibria, it is suggested that local variations in μH_2O may be due to differences of approximately 750 bars in *Pfluid* such that *Pfluid* was nearly equal to or less than *Ptotal.*

An analysis of the phase equilibria is presented by means of activity - activity diagrams of two components, Al_2SiO_5 and FeO. In the country rocks and altered rocks, the activity of Al_2SiO_5 varied from that at sillimanite-saturation to approximately 0.1 log units below sillimanite-saturation. Variations in the activity of FeO were much greater. As a result of variations in component activities and *Pfluid*, the assemblage and compositions of Fe-Mg silicate minerals varied in different rocks. The composition of the metamorphic fluid phase was buffered internally by local mineral equilibria. Consequently, chemical interaction between the ore and the adjoining rocks was not significant.

Acknowledgements

I am thankful to Drs. Bruce Nesbitt and Fred Longstaffe for their continued interest in the completion of this work. I also express my thanks to Dr. Bill Gunter for many fruitful discussions on various aspects of the thesis; to Alex Stelmach, Peter Black, Steve Launspach, and Diane Caird for their expert technical asssistance; and to the geological staff of the Hudson's Bay Mining and Smelting Company at Flin Flon and Snow Lake, in particular Alaistair Walker, Dave Price, Murray Smith, Frank Bill, John Sullivan, Tom Fleming, and Neil Provins, for their kind assistance during field work. Many thanks are due the members of my examining committee, Drs. Hiroshi Ohmoto, Loren Hepler, Bill Gunter, Chris Scarfe, Fred Longstaffe, and Bruce Nesbitt, for their critical comments on the thesis.

I am deeply indebted to Garth Milvain for his friendship. But for Garths's help in money matters, I may not have been able to see the completion of this work. I also wish to thank my colleagues and friends in Edmonton, particularly Bob and Terry St. Louis, Gord McClymont, Al Crowe, and Pratap Sahay who provided much needed support when progress seemed to be less than desirable.

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I. Introduction

Since the general acceptance of the syngenetic origin of volcanogenic massive sulfide deposits, the effects of metamorphism on these deposits have been studied by many workers. Earlier studies of metamorphosed ore deposits focussed on the physical effects of metamorphism, such as: (1) an increase in grain size of the ore, (2) mobilization of the ore to stress-free regions, and (3) development of metamorphic textures due to re-equilibration of the ore and gangue minerals (see Vokes (1969), Sangster (1972) and Mookerjee (1975) for extensive reviews). More recent studies of metamorphosed ore deposits have identified several mineralogical and chemical effects of metamorphism, such as: (1) zonations of sulfide, oxide, and silicate minerals around the ore body, (2) systematic variations in the compositions of the Fe-Mg silicate minerals, and (3) development of certain diagnostic minerals (e.g., gahnite, cordierite, and anthophyllite) around ore deposits (Nesbitt, 1982; Craig, 1983; Spry, 1984). These mineralogical and chemical changes around an ore deposit could be a result of the migration of sulfur and other volatile species during metamorphism (Nesbitt, 1982; Spry, 1984). Alternatively, the zoning in mineral and chemical composition could be a result of the metamorphism of rocks with different bulk compositions. Thus metamorphism may preserve or destroy the mineralogical, chemical, and oxygen isotopic gradients that are known to be associated with unmetamorphosed, massive sulfide deposits (see Franklin et al. (1981) for a review). Because a number of economically important ore deposits worldwide occur in metamorphic terranes, it is necessary that the effects of metamorphism on ore deposits be studied in detail. Such studies serve a two-fold objective: (1) they contribute to developing a model for the metamorphism of ore deposits in different geological environments and, perhaps, to developing criteria for exploration; and (2) they contribute to the understanding of fluid-rock interaction during metamorphism in the presence of significant chemical-potential gradients due to chemical differences between the ore and the host rocks.

The present study was undertaken to characterize and examine the effects of progressive metamorphism on the mineralogical and oxygen isotopic compositions of country rocks and altered rocks associated with massive sulfide deposits in the Flin Flon - Snow Lake belt, Manitoba. These deposits provide an excellent opportunity for such a study because all the deposits occur in similar host rocks and have been metamorphosed at varying grades. Three ore deposits, Centennial, Spruce Point, and Anderson Lake, which have been metamorphosed at low-greenschist, upper greenschist, and amphibolite facies conditions, were selected for a detailed study. The specific objectives of this project were: (1) to estimate the pressure - temperature conditions of metamorphism; (2) to measure the oxygen-isotope compositions of rocks and minerals associated with the deposits and to study the nature and extent of isotopic equilibration during metamorphism; (3) to determine the variations, if present, in mineralogy, mineral chemistry, and the composition of the metamorphic fluid phase around the deposits; and (4) to develop a model for the metamorphism of these deposits. The results of this investigation are reported in Chapters II to IV and are summarized in Chapter V. Each chapter addresses one or more of the objectives outlined above.

The pressure and temperature conditions of metamorphism in the Flin Flon - Snow Lake belt are estimated in Chapter II. Assemblages in mafic and felsic metavolcanic rocks are used to put limits on the temperature of metamorphism in the Flin Flon and Spruce Point areas. Quantitative estimates of P and T are obtained from several well calibrated, silicate equilibria and the measured compositions of minerals.

The oxygen-isotope geochemistry of the Anderson Lake, Spruce Point, and Centennial deposits is presented in Chapter III. Isotopic compositions of the altered and country rocks have been measured in whole-rock and monomineralic samples. The origin of differences in isotopic compositions of the various rock units is discussed and the effects of metamorphism on these compositions are evaluated. Finally, the significance of the isotopic compositions in understanding the nature of hydrothermal alteration at these deposits is described.

Chapter IV deals with the metamorphic petrology of these deposits. The composition of the fluid phase in the altered and country rocks of the deposits has been estimated from calibrated silicate equilibria and from calculated species distribution in a gas phase. An analysis of the mineral equilibria is presented with the help of $a\mathrm{Al_2SiO_5}$ - $a\mathrm{FeO}$ diagrams. The volatile and solid phase equilibria are used to evaluate the relationship between the fluid pressure and lithostatic pressure and to characterize the fluid-rock interaction during metamorphism.

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II. Pressure and Temperature Conditions of Metamorphism in the Flin Flon - Snow Lake, Manitoba Greenstone Belt

A. Introduction

The Flin Flon - Snow Lake, Manitoba greenstone belt hosts a number of economically important ore deposits. The greenstone belt and the enclosed ore deposits have been metamorphosed at varying conditions ranging from greenschist to amphibolite facies. In order to fully understand the effects of metamorphism on the ore deposits and on the ore-host rock interaction during metamorphism, it is necessary to have accurate estimates of the pressure and temperature at which the rocks were metamorphosed. Such estimates are also required for calculating the composition of the metamorphic fluid phase and for understanding the metamorphic history of the area.

Estimates of metamorphic temperature and pressure have previously been reported for some parts of the Flin Flon - Snow Lake greenstone belt. Koo and Mossman (1975) inferred on the basis of the assemblage phengite-paragonite-calcite that rocks in the Flin Flon area were metamorphosed to low-greenschist facies. Bristol (1974; 1979), using the sphalerite geobarometer, suggested that metamorphic pressures in the Flin Flon area were in the range of 4 to 7 kb. Similar application of the sphalerite geobarometer in the Snow Lake area indicates pressures of 7±1 kb (Scott,1976; Hutcheon, 1978). Froese and Gasparrini (1975) and Froese and Moore (1980) studied the metamorphism at Snow Lake and suggested that peak metamorphic temperature in the northern part of the area was approximately 600 °C at pressures less than 6 kb.

As part of a study on the metamorphism of ore deposits in the Flin Flon - Snow Lake greenstone belt, the conditions of metamorphism in this belt have been re-evaluated to derive a consistent set of pressure - temperature conditions of metamorphism. Estimates of pressure and temperature presented in this study have been made by comparing the compositon and assemblages of minerals in mafic and felsic metavolcanic rocks with those from experimental studies on mineral systems.

B. Methods

Samples for this study were collected in the vicinity of three ore deposits in the Flin Flon - Snow Lake belt: Centennial deposit in the Flin Flon area to the west, Spruce Point deposit in the center, and Anderson Lake deposit in the Snow Lake area to the east (Fig 1). In addition, samples were collected from underground exposures and diamond-drill cores at the three deposits. Some 250 polished thin-sections were studied using transmitted- and reflected-light microscopes and electron microprobe.

Mineral Analyses

All mineral analyses were obtained by the energy-dispersive technique using an ARL-SEMQ electron microprobe. An accelerating voltage of 15.0 KV and an aperture current of 220 to 240 nano-amperes were used. Counting times for both the standards and the samples were 240 seconds at a rate of approximately 5000 counts per second. Natural silicate standards were used for all elements and the data were processed by the program EDATA2 (Smith and Gold, 1979). The statistical error at 99% confidence level is ±1% of the amount present for the major elements and may be as high as ±10% for minor elements.

Thermodynamic Calculations

In all thermodynamic calculations reported in this study, the standard state for the solid phases is defined as the stable form of the pure phase at the temperature and pressure of calculation. For gaseous phases, the standard state is a hypothetical ideal gas at one bar and temperature of calculation.

Thermodynamic data for mineral reactions are reported here as:

$$\log K = A/T + B + C(P-1)/T$$

The constants A, B, and C are related to the enthalpy, entropy, and volume change in the reaction. With the standard states described as above, it follows that at equilibrium:

$$0 = \Delta Gr(P,T) = -RT \ln K =$$

$$\Delta H^{\circ}f - T\,\Delta S^{\circ}f + \Delta Vs(P-1) + \int \Delta Cp\,dt - T\int \Delta Cp \ln T\,dt + RT\overset{\rho}{}(\Delta \ln fi - \Delta \ln fj) \qquad (1)$$

where ΔVs is the volume change due to solids, ΔCp is the heat capacity change in the reaction,

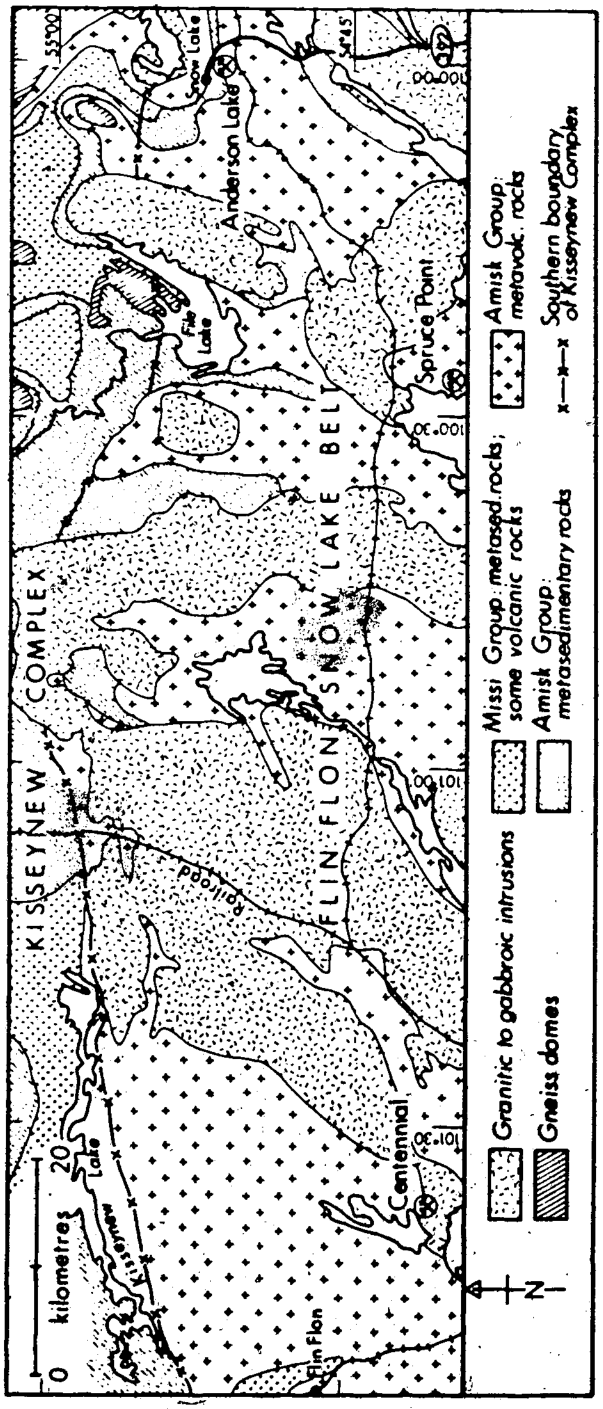

Figure 1. Regional geology of the Flin Flon - Snow Lake belt (after Froese and Moore, 1980) and the location of the present study areas.

and fi and fj are, respectively, the fugacities of the product and reactant fluid species. Assuming that the ΔVs is constant with T and P and that ΔCp is equal to zero, re-arranging equation (1) gives:

$$\ln K = -\Delta H^{o}f / RT + \Delta S^{o}f / R - \Delta Vs^{o}(P-1) \qquad (2)$$

The volume, enthalpy, and entropy terms in the above equations can be calculated from the data of Helgeson et al. (1978) or Robie et al. (1979) or can be derived from experimental studies of mineral equilibria. When tabulated data are used, the heat capacity term in equation (1) can be easily evaluated and therefore included in the calculations. In deriving data from experimental studies, the $\ln K + \Delta Vs^{o}(P-1)$ term of the reaction is plotted against $1/T$. The slope and intercept of the resulting linear relationship give the enthalpy and entropy terms in equation (2). The errors introduced due to this procedure, i.e. by assuming $\Delta Cp = 0$, are insignificant for extrapolations over a small range of temperature beyond that of the experiments.

Thermodynamic calculations involving solid-solutions were corrected for the activity of end-member phases. The activity models used for various phases are given below.

garnet: The solid solution of Ca and Mg in Fe-Mg garnets is non-ideal (Ganguly and Kennedy, 1974; Ganguly and Saxena, 1984). Free-energy interaction parameters for binary joins, Wij, derived by Ganguly and Saxena (1984) were used to calculate the activity coeficients of the endmembers in garnet solid-solution. These parameters are given in Table 1.

biotite: In addition to Fe and Mg, metamorphic biotites contain significant amounts of Na, Ti, and excess Al compared to biotites on the annite - phlogopite join (Holdaway, 1980). The solid solution of Mg and Fe in biotite has been considered to be ideal by many workers (Mueller, 1972; Ganguly and Kennedy, 1974). Experimental studies of fluid - mineral exchange equilibria (Schulien, 1980) also indicate that Fe and Mg mix ideally in biotite along the annite - phlogopite join. Owing to the lack of any activity-composition data, the mixing of Na, Ti, and Al in the biotite solid solution is also considered to be ideal which results in:

$a(ann) = XK\,(XFe)^3\,(XSi)^4$ (Holdaway, 1980; Zen, 1985).

Table 1. Mixing Data for the Garnet and Muscovite Solid Solutions
(in cal/mole cation)

Garnets	
W(Fe-Mg)	200
W(Mg-Fe)	2500
W(Ca-Mg)	4050 - 1.5T(K)
W(Mg-Ca)	1000 - 1.5T(K)
W(Ca-Fe)	-630 - 1.5T(K)
W(Fe-Ca)	4620 - 1.5T(K)
W(Mg-Ca)-W(Fe-Ca)	3000
W(Mg-Mn)-W(Fe-Mn)	3000
Muscovites	
W(Par)	2923.1 + 0.16P(bars) + 0.17T(K)
W(Mus)	4650 - 0.11P(bars) + 0.39T(K)

where X is the mole fraction of the ith element, given as: Ni/R; N is the number of atoms of the ith element on a site containing a total of R atoms.

paragonite: the solid-solution of muscovite and paragonite is non-ideal (Chatterjee and Froese, 1975; Eugster et al., 1972). The activity coefficient of paragonite can be calculated by assuming a binary solution between muscovite and paragonite components and using the two-parameter Margules equation of Chatterjee and Froese (1975). Free-energy interaction parameters based on this model are given in Table 1.

plagioclase: based on the experimental study of Orville (1972), analytical expressions for the activity coefficient of anorthite (γan) and albite (γab) in plagioclase solid solution have been presented by Saxena and Ribbe (1972) and Blencoe et al. (1982). Blencoe et al. (1982) argue that Saxena and Ribbe's (1972) model indicates a maximum in the value of γan at $Xan = 0.3$ and that it is inconsistent with the experimental results. To avoid this inconsistency, Blencoe et al. (1982) proposed a new expression for γan which gives essentially the same results as that of Saxena and Ribbe (1972) for plagioclase compositions of $Xan > 0.3$. In this paper, the model proposed by Blencoe et al. (1982) is used.

staurolite: there has been considerable controversy regarding the chemical formula of staurolite (Richardson, 1968; Ganguly, 1972; Griffen and Ribbe, 1973; Ribbe, 1982). Most workers now favor a chemical formula containing two hydroxyl ions. Using this formula, the activity of Fe-endmember staurolite has been modeled as an ideal ionic solution on the Fe site, resulting in:

$a(stau) = (XFe)^2$ in staurolite of the compositon $Fe_2Al_9Si_{3\ 75}O_{22}(OH)_2$.

C. Regional Geological Setting

The Flin Flon - Snow Lake greenstone belt is approximately 250 kilometers long and has an exposed width of nearly 40 kilometers. It is bounded to the north by the Kisseynew gneiss complex and is overlain to the south by Paleozoic limestones (Fig. 1). The Flin Flon -

Snow Lake belt and the Kisseynew gneisses together are part of the Churchill structural province of the Canadian Shield (Stockwell, 1964).

The greenstone belt consists of two major groups of rocks of Aphebian age (~ 1800 m.y.) and a number of intrusive granite bodies (Price, 1978). The older, Amisk Group rocks are the dominant lithology and consist mainly of volcanic rocks with minor metasedimentry members. The volcanic rocks are of tholeiitic and calc-alkalic affinity and range in composition from basalt to dacite-rhyolite (Stauffer et al., 1975). Metasedimentary rocks of the Amisk Group are principally of greywacke composition (Froese and Moore, 1980). The younger, Missi Group consists largely of metasandstones and metagreywackes.

Structure and Metamorphism

Rocks in the Flin Flon - Snow Lake belt were structurally deformed and metamorphosed during the Hudsonian Orogeny. The degree of deformation and metamorphism varies throughout the belt. In general, three phases of deformation have been identified (Stauffer and Mukherjee, 1971; Froese and Moore, 1980).

The earliest deformation, P1, resulted in east-west trending tight folds. The second, P2 event, produced the dominant northeasterly trend in the area. The P2 folds are generally open and have steep axial foliation and lineation. The third, P3 event was relatively minor and generally refolded the P2 folds along a northerly axis.

Metamorphism was generally coincidental with the P2 event when the peak of metamorphism was reached (Froese and Moore, 1980). The metamorphic event was largely over in the waning stages of the P2 event. The P3 event was characterized by minor, retrogressive metamorphism. Metamorphic grades of low-greenschist facies were reached in the Flin Flon area. In the Spruce Point area, the metamorphism was of the upper greenschist facies. The Snow Lake area shows a complete spectrum of metamorphic conditions from low greenschist facies in the south to middle-amphibolite facies in the north and northeast (Froese and Moore, 1980).

D. Temperature and Pressure Conditions in the Flin Flon and Spruce Point Areas

The Amisk Group in Flin Flon and Spruce Point areas consists dominantly of mafic metavolcanic rocks with subsidiary amounts of felsic metavolcanic rocks. At Flin Flon, the mafic rocks are generally composed of chlorite, plagioclase, quartz, and sphene with minor actinolite, zoisite, and calcite. The felsic rocks are composed dominantly of quartz and muscovite with minor plagioclase. At Spruce Point, the mafic rocks contain actinolite, plagioclase, quartz, hornblende, and zoisite with minor chlorite and sphene. Felsic rocks at Spruce Point contain quartz, biotite, and muscovite with minor ilmenite and rutile. These assemblages can be used to constrain temperature and pressure conditions during metamorphism.

Estimates Based on Assemblages in Mafic Rocks

In recent years, a number of experimental and empirical studies have been carried out to calibrate the compositon of minerals in mafic rocks with respect to temperature and pressure. The experimental studies of Liou et al. (1974), Moody et al. (1983), Apted and Liou (1983) indicate that the greenschist facies assemblage of chlorite + albite + quartz ± zoisite(epidote) ± sphene ± actinolite changes through a transition zone to the epidote-amphibolite or amphibolite facies assemblage of hornblende + plagioclase + quartz ± epidote. The onset of the transition zone is marked by the appearance of actinolite and a decrease in the modal amount of chlorite. The upper limit of the transition zone or the beginning of the amphibolite facies is marked by the appearance of hornblende and a lack of chlorite. Sphene breaks down to form ilmenite within the transitional zone (Moody et al., 1983).

The lower temperature limit of the transition zone (i.e. the actinolite-in curve in Fig. 2) has been placed at 475 °C and 510 °C at 2 and 4 kb pressure, respectively, with the fugacity of oxygen defined by the quartz - fayalite - magnetite (QFM) buffer (Liou et al., 1974; Moody et al., 1983). With an increase in the fO_2 to the hematite - magnetite (HM) buffer, the lower boundary of the transition zone shifts to approximately 500 °C at 2 and 4 kb pressure. The upper boundary of the transition zone (i.e. the chlorite-out curve in Fig. 2) is rather insensitive to changes in fO_2. It has been located at 550 ± 10 °C at 2 and 4 kb with fO_2 varying from the QFM buffer to HM buffer (Moody et al., 1983).

In spite of the experimental studies, pressure - temperature calibrations of the compositions of minerals in mafic rocks have been difficult due to the complex nature of substitutions and mineral reactions (Laird and Albee, 1981). Based on the geothermometers and geobarometers in intercalated pelitic rocks, Laird and Albee (1981) estimated the pressure - temperature conditions of compositional groups of amphiboles and plagioclase from a mafic schist in various metamorphic zones. These empirical calibrations are useful in the higher grade rocks but provide only qualitative estimates for low grade rocks because of a paucity of calibrated geothermo-barometers in lower grade pelites.

Mafic assemblages in the Flin Flon area show abundant chlorite and albite with minor sphene, actinolite, and zoisite. The minor development of actinolite and zoisite suggest that conditions for the lower boundary of the transition zone were not reached, i.e., T = 500 °C if P = 4 kb (Moody et al., 1983). In the Spruce Point area, the mafic assemblages are characterized by abundant actinolite, plagioclase, hornblende, and zoisite with minor chlorite and sphene. This suggests that the conditions of metamorphism were similar to those in the transition zone of the experimental studies. Thus the maximum temperature of metamorphism at Flin Flon, depending on the fO_2, would be less than approximately 500 °C and at Spruce Point, less than 550 °C (Liou et al., 1974; Moody et al., 1983).

Estimates Based on Assemblages in Felsic Rocks

At Flin Flon, muscovite and quartz are the dominant minerals in felsic rocks. In the Spruce Point area, biotite is commonly present together with muscovite and quartz. This suggests that the metamorphic conditions at Flin Flon were probably below, and at Spruce Point above, that of the biotite isograd.

The mechanism of the first appearance of biotite in pelitic rocks is not well understood (Turner, 1981; Winkler, 1979). Winkler (1979) suggests that the presence of biotite together with muscovite indicates that the upper stability of stilpnomelane according to the reaction:

Stilpnomelane + Muscovite = Biotite + Chlorite + Quartz + Water has been reached. This reaction has an upper stability between 430 °C and 460 °C at 1 to 7 kb pressure (Winkler, 1979). Ferry (1984) has recently analyzed various reactions responsible for the first appearance of biotite in pelitic rocks and has suggested a temperature of 400 °C at 3.5 kb for the biotite isograd. Thus the location of the biotite isograd can be reasonably placed at approximately 400 °C to 450 °C at 1 to 7 kb pressure. Consequently, the temperature of metamorphism at Flin Flon, where the biotite isograd was probably not reached, was less than 450 °C and at Spruce Point, greater than 400 °C

The pressure and temperature conditions at Spruce Point can be further constrained by considering mineral assemblages in altered rocks associated with the Spruce Point deposit. These rocks contain the assemblages chlorite - corundum - andalusite and muscovite - andalusite - plagioclase - quartz, respectively (Chapter IV). The presence of andalusite indicates that the pressure was less than 3.8 kb (Holdaway, 1971) and that the temperature was above the stability of pyrophyllite. The upper stability of pyrophyllite is given by the reaction:

Pyrophyllite = Andalusite + 3 Quartz + H_2O (1)

According to the data of Chatterjee et al. (1984), the equilibrium conditions for reaction (1) are: 430 °C at 4 kb and 375 °C at $PH_2O = 2$ kb. If PH_2O was less than the total pressure, the stability of pyrophyllite would shift to lower temperatures. The coexistence of muscovite, andalusite, plagioclase, and quartz in the muscovite zone rocks implies the reaction:

Paragonite (in muscovite) + quartz = andalusite + albite (in plagioclase) + H_2O (2)

The end-member equilibrium for this reaction has been studied by Chatterjee (1972) and the results of this study are consistent with:

$$\log K\ (2) = -4638/T + 8.7 + 0.014(P-1)/T \qquad (2)$$

where T is in K, P is is in bars, and K = a (albite) * fH_2O / a (paragonite).

The activities of paragonite and albite can be calculated using the compositions of these minerals from Table 2 and the activity models discussed earlier. At given values of the activities of albite and paragonite, reaction (2) is divariant with respect to T, P, and fH_2O. The equilibrium curve for reaction (2) has been plotted on a P - T diagram (Fig 2). The effect of variations in fH_2O is shown by plotting this curve at a range of fH_2O values corresponding[1]

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[1] according to the Lewis and Randall rule (Denbigh, 1981)

Table 2. Composition* of Minerals from Spruce Point used in Temperature Calculations

Sample	115-1307		115-1323	
	Plag	Musc	Plag	Musc
Si	2.44	6.08	2.52	6.01
Al	1.54	5.64	1.49	5.44
Na	0.45	0.21	0.52	0.27
Ca	0.54		0.47	
Mg		0.21		0.24
Fe		0.24		0.42
Ti		0.00		0.08
O	8.00	22.00	8.00	22.00

* complete analyses are given in Appendix I

Table 3. Calculated Speciation in the H-O-S Gas phase at Several Temperatures and Pressures

	1.5 kb			2.0 kb			2.5 kb		
	400°C	450°C	500°C	400°C	450°C	500°C	400°C	450°C	500°C
logfO_2	-24.9	-22.38	-20.18	-24.85	-22.33	-20.14	-24.8	-22.29	-20.10
logfS_2	-6.78	-5.50	-3.71	-6.78	-5.50	-3.71	-6.78	-5.50	-3.71
fH_2O	345	480	614	400	559	719	500	690	887
fSO_2	**	0.003	0.017	**	0.004	0.02	**	0.004	0.02
fH_2S	0.05	0.07	0.1	0.05	0.08	0.12	0.06	0.10	0.14
XH_2O	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999

** less than 0.0001

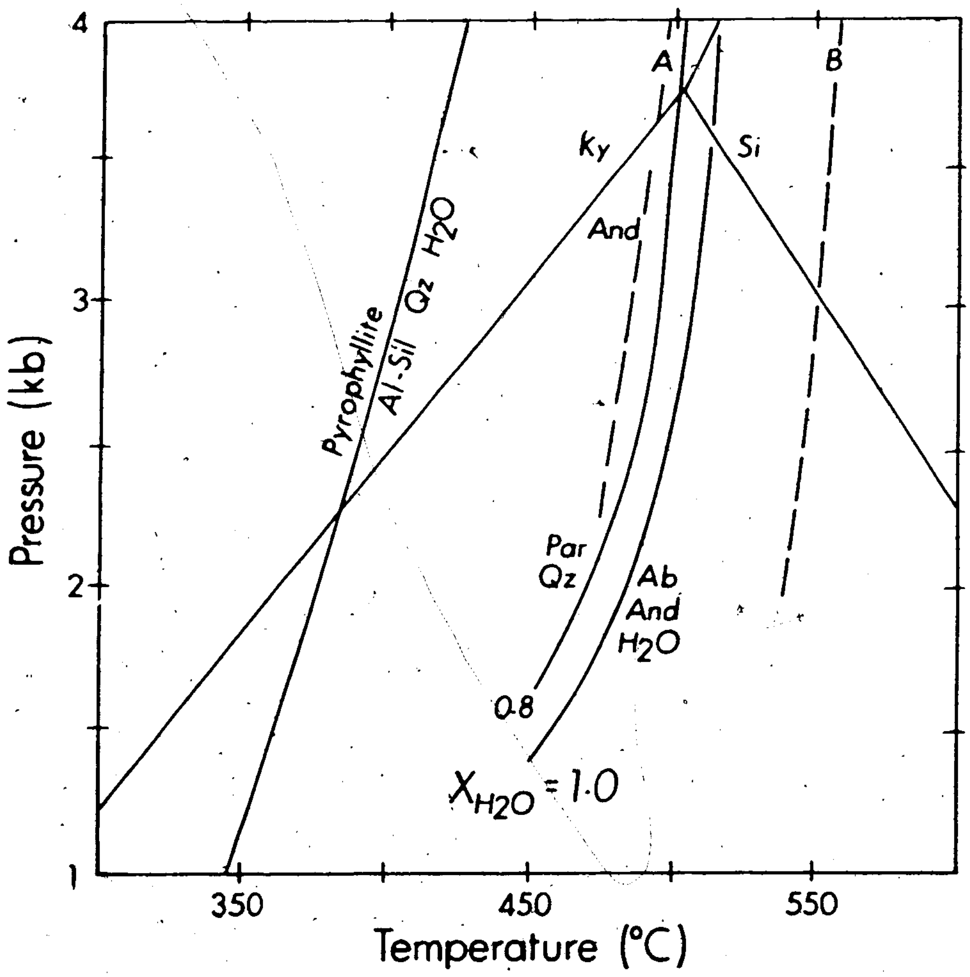

Figure 2. Pressure-temperature diagram for estimating the conditions of metamorphism at Spruce Point and Centennial. Stability curves for the Al_2SiO_5 polymorphs, andalusite (And), kyanite (Ky), and sillimanite (Si) are from Holdaway (1971). The pyrophyllite and paragonite (par) curves are calculated from the data of Chatterjee et al. (1984). Curve A = actinolite-in, chlorite-decreasing curve; Curve B = chlorite-out curve (Liou et al., 1974 and Moody et al., 1983). Other abbreviations: Al-Sil = Alumino-silicate (And/Ky); Qz = quartz; Ab = albite; X = mole fraction.

to XH_2O = 0.9±0.1. At these values of XH_2O, the P-T conditions for Spruce Point are: 490±20 °C at 2.6±1.2 kb.

The value of XH_2O can be constrained by calculating XH_2O from the opaque mineral assemblages. In all rocks containing andalusite - muscovite, the assemblage ilmenite - rutile - pyrite - pyrrhotite is also present. This assemblage allows the calculation of fO_2 and fS_2 from the following equilibria:

$$\text{Pyrite} + \text{Rutile} + O_2 = \text{Ilmenite} + S_2 \quad (3)$$

$$\text{Pyrrhotite} + 0.5\ S_2 = \text{Pyrite} \quad (4)$$

Using these values of fO_2 and fS_2, the composition of the fluid phase can be calculated by the method of French (1966). Such calculations were performed for an H-O-S fluid at 400 to 500 °C and 1.5 to 2.5 kb pressure. Carbon species were not included as carbonaceous phases are not commonly present at Spruce Point. Thermodynamic data were taken from Robie et al. (1979). Fugacity coefficients of water were taken from Burnham et al. (1969) and those for all other species were calculated by the Redlich-Kwong equation of state using the program SUPCRT (Helgeson et al., 1978).

Calculated values of XH_2O are nearly equal to 1.0 (Table 3). These values provide an upper limit for XH_2O because no carbon bearing species were considered. However, a detailed analysis of sulfide - siliate - oxide equilibria (Chapter IV) also indicates that the fluid phase at Spruce Point consisted essentially of H_2O.

To summarize, the pressure - temperature conditions of metamorphism at Spruce Point are estimated to be 475 ± 50 °C at 2.6 ±1.2 kb. Accurate values of temperature and pressure are difficult to estimate for the Flin Flon area. An upper limit for temperature is calculated to be 450 °C at pressures less than 3.8 kb.

E. Pressure and Temperature Conditions in the Snow Lake Area

The Amisk Group in the Snow Lake area is composed of nearly equal amounts of felsic and mafic metavolcanic rocks with minor metasedimentary rocks (Froese and Moore, 1980). The mafic rocks consist of the greenschist facies assemblage chlorite - albite - actinolite - sphene - zoisite in the south and grade northwards into the amphibolite facies assemblage of hornblende - plagioclase - zoisite - sphene. The felsic rocks consist of quartz and plagioclase (An30 - An40) with subordinate biotite, almandine, and hornblende. In the vicinity of the Anderson Lake deposit (Fig. 3), the felsic rocks were hydrothermally altered prior to metamorphism. The altered rocks are characterized by the common presence of staurolite and kyanite/sillimanite (Walford and Franklin, 1982). Based on assemblages in the felsic metvolcanic and metasedimentary rocks of the Amisk Group, Froese and Gasparrini (1975) have divided the Snow Lake area into four metamorphic zones. From south to north, these zones are (Fig. 3): (1) chlorite - biotite zone, (2)biotite - staurolite zone, (3)staurolite - sillimanite zone, and (4) garnet - sillimanite - biotite zone.

Mineral assemblages in the felsic rocks at Snow Lake can be used to determine the pressure - temperature conditions during metamorphism by considering the following equilibria:

garnet - biotite, kyanite - sillimanite, anorthite - garnet - sillimanite - quartz, and garnet - rutile - ilmenite - sillimanite - quartz.

Estimation of Temperature

The partitioning of Mg and Fe between coexisting garnet and biotite is sensitive to temperature and, to some extent, pressure. The temperature dependence of the distribution coefficient (Kd) of the reaction:

Annite + Pyrope = Phlogopite + Almandine (5)

has been calibrated by empirical analysis of field data (Thompson, 1976; Goldman and Albee, 1977; Perchuk, 1977) and by experimental studies (Ferry and Spear, 1978; Perchuk and Lavrent'eva, 1982). These calibrations all provide different estimates of temperature for a given value of Kd. However, calibrations based on field studies are generally less reliable

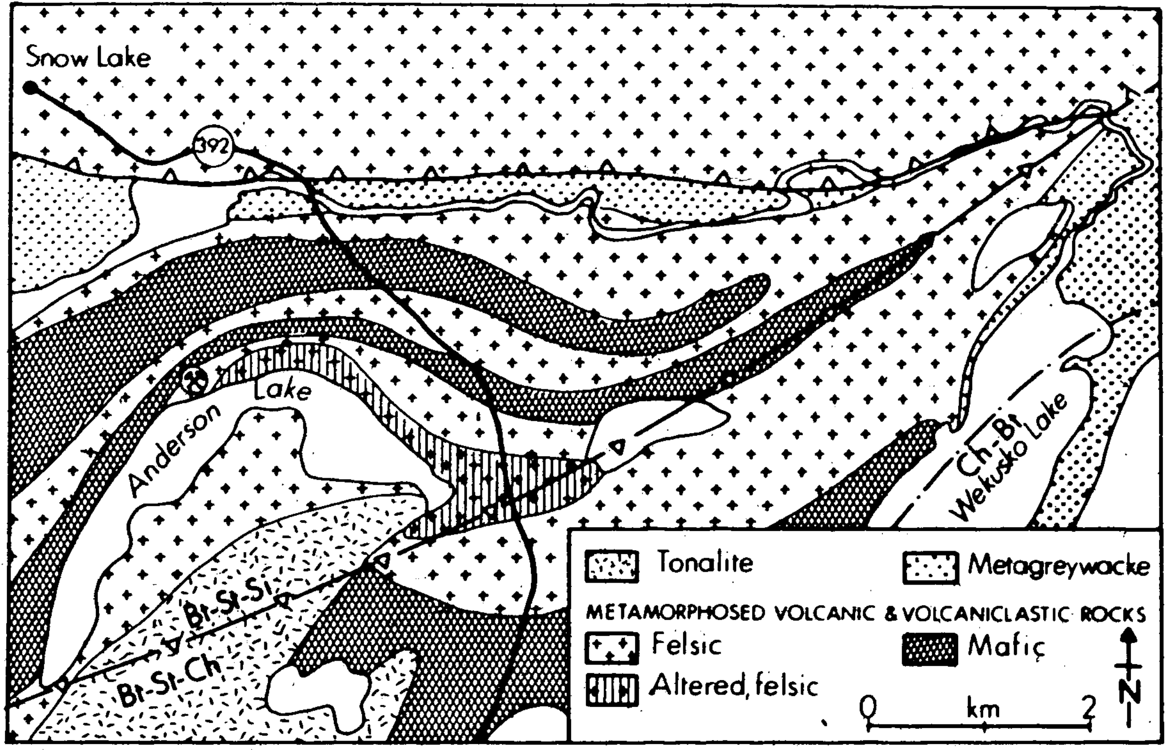

Figure 3. Generalized geological map of the Snow Lake area. Plotted on this map are isograds delineating the chlorite-biotite (Ch-Bt), chlorite-biotite-staurolite (Bt-St-Ch), and biotite-staurolite-sillimanite (Bt-St-Si) zones. Geology and isograds were taken from Froese and Moore (1980).

because they incorporate errors in other geothermometers with which they were compared.

The experiments of Ferry and Spear (1978) were done at 2.07 kb pressure over a temperature range of 550 - 800 °C using garnets and biotites on the pyrope - almandine and annite - phlogopite joins, respectively. Natural garnets and biotite contain significant amounts of other cations and deviate from the Fe - Mg joins. Extrapolation of Ferry and Spear's (1978) calibration beyond the experimental conditions, therefore, requires corrections for the effects of pressure and of reduced activities of Fe - Mg endmembers in garnet and biotite solid solutions.

The effect of pressure is relatively insignificant and can be calculated using the relation:

$(\partial G/\partial P)T = \int \Delta Vr\ dP$ and the volume data from Helgeson et al. (1978), assuming that ΔVs is constant with T and P. Activities of Fe and Mg end-member garnets and biotite can be calculated using the activity models discussed earlier. These corrections result in the following formulation of the garnet-biotite geothermometer (Ganguly and Saxena, 1984):

$$T(K) = (A + 9.45\ P(kb) + B) / C \qquad (6)$$

where:

$A = 2089 - 0.8\ W(Fe\text{-}Mg) / R$

$B = W(Fe\text{-}Mg) * (XFe - XMg) + (W(Mg\text{-}Ca) - W(Fe\text{-}Ca)) * XCa + (W(Mg\text{-}Mn) - W(Fe\text{-}Mn)) * XMn$

$C = \ln Kd - 0.782$

In the above equations, W(i-j) are the free-energy interaction parameteres for the respective binary joins (Table 1); Xi is the mole fraction of the ith element; and R is the gas constant.

Perchuk and Lavrent'eva (1982) have also experimentally studied the garnet - biotite exchange equilibrium at 6 kb pressure and 600 to 900 °C temperature. Their data are consistent with the following expression for T:

$$T = (7843.7 - 0.057(P-6000))/(R \ln Kd + 5.699) \qquad (7)$$

where T is in K, P is in bars, and $\ln Kd = (Fe/Mg)gt * (Mg/Fe)bt$

Perchuk and Lavrent'eva (1982) used natural and synthetic garnet and biotite as starting materials. Garnets used in their study contained 2 to 5 wt% CaO + MnO with XMg less than

0.44. The biotite contained 1 to 3 wt% TiO_2 and nearly 20 wt% Al_2O_3. These compositions are very similar to those of garnets and biotites from Snow Lake (Table 5). Therefore, the Perchuk and Lavrent'eva's (1982) calibration can be used in the present calculations without any correction for the composition of garnets and biotites.

Temperatures calculated using equations (6) and (7) are in good agreement (Table 5). However, temperatures calculated using equation (7) will be used in the rest of this paper. This is because equation (7) does not require corrections for compositional variations and is considered here to be more reliable than the calibration based on Ferry and Spear's (1978) experiments. In addition, eqation (7) can be plotted on a P-T diagram as curves of constant ln Kd which facilitates the calculation of pressure as discussed later.

Calculated temperatures using equation (7) range between 550 - 600 °C at 5 kb for the staurolite - biotite zone. For the biotite - sillimanite zone, the temperatures are slightly higher, 610 - 630 °C. Most of the samples analyzed did not show any significant compositional zoning in garnets. Some samples contain garnets with an Mn-rich core. Using garnet-core compositions gives temperatures which are approximately 20 °C lower. However, the garnet-core compositions may not represent peak metamorphic conditions and thus were neglected in temperature calculations (Essene, 1982). Perchuk and Lavrent'eva (1982) did not provide any error limits for their calibration. However, if an uncertainty of ± 0.01 in the calculation of lnKd is considered, it results in an uncertainty of ±30 °C in the temperature calculations. The temperatures calculated above are plotted on a P-T diagram as curves of constant Kd (Fig. 4).

Estimation of Pressure

Kyanite - Sillimanite Equilibrium

The stability of the Al_2SiO_5 polymorphs has been experimentally determined by Richardson et al. (1968) and by Holdaway (1971). The phase diagram given by Richardson et al. (1968) differs from that given by Holdaway (1971) mainly in the location of the andalusite - sillimanite boundary. Holdaway (1971) suggests that the sillimanite used by Richardson et al. (1968) contained significant fibrolite which, together with the small entropy change of the

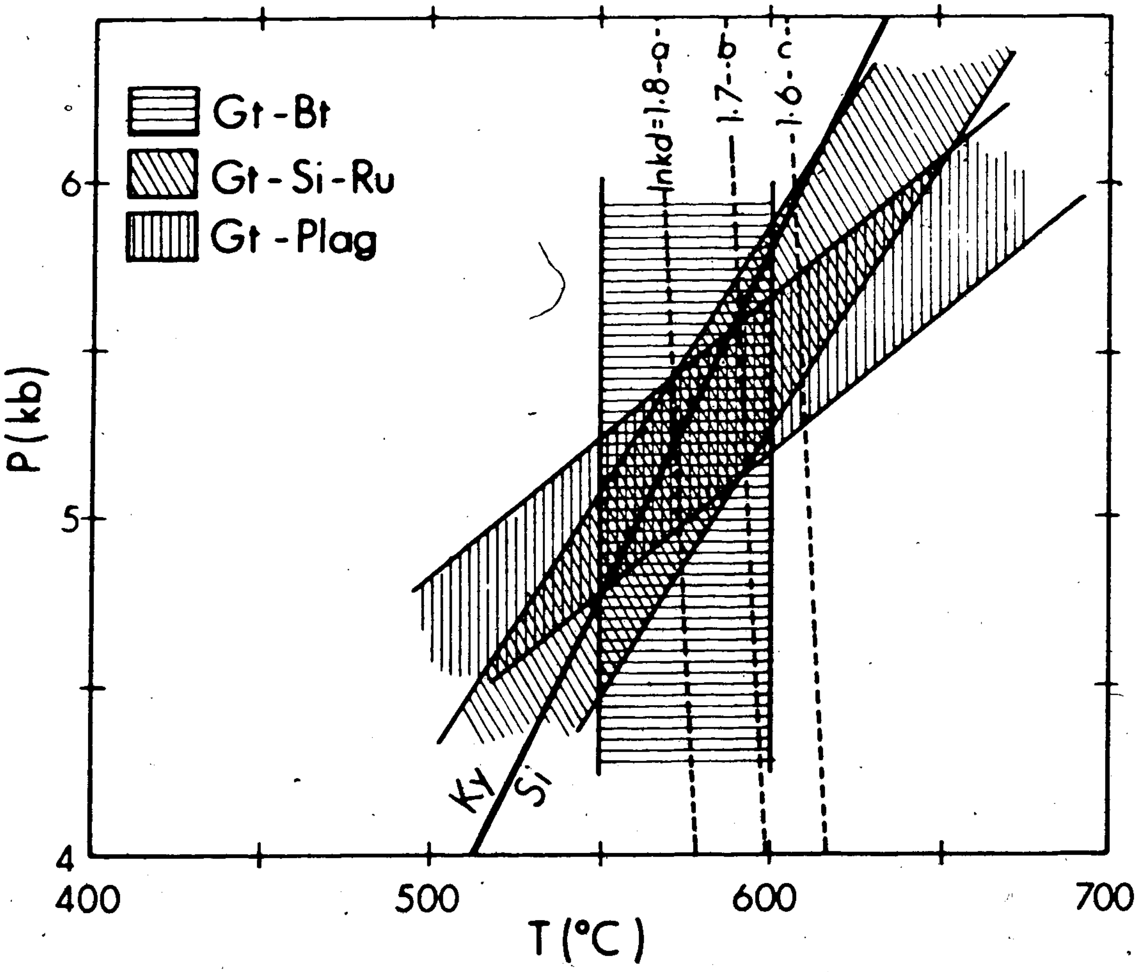

Figure 4. Pressure-temperature diagram for the Snow Lake area. Stability curves for the Al_2SiO_5 polymorphs, andalusite (And), kyanite (Ky), and sillimanite (Si) are from Holdaway (1971). The ranges of pressure and temperature indicated by various geothermo-barometers are plotted. Curves a, b, and c are the lnKd curves for the garnet-biotite geothermometer of Perchuk and Lavarenteva (1983). Abbreviations: Gt = garnet; Bt = biotite; St = staurolite; Plag = plagioclase; Ru = rutile.

Table 4. Estimates of Temperature at Snow Lake Using the Garnet - Biotite Geothermometer

		Biotite				Garnet					
				X						T(6)*	T(7)**
Sample		XFe	XMg	Al+Ti	Fe	Mg	XMn	XCa	lnKd	°C	°C
Staurolite-Biotite Zone											
SL-6A		0.43	0.39	0.17	2.18	0.37	0.09	0.06	1.67	573	603
SL-10	R	.57	.29	0.13	1.98	0.15	0.11	0.17	1.88	598	563
	C				1.83	0.12	0.13	0.21	2.04	580	536
SL-13	R	0.58	0.24	0.18	2.10	0.16	0.08	0.17	1.74	660	589
	C				1.91	0.12	0.13	0.22	1.91	632	558
SL-24	R	0.53	0.29	0.18	1.86	0.15	0.05	0.29	1.91	610	558
	C				1.91	0.15	0.07	0.23	1.96	588	549
SL-37		0.41	0.38	0.21	2.24	0.28	0.06	0.07	2.0	621	543
16-05		0.39	0.45	0.16	1.79	0.40	0.08	0.20	1.68	629	600
16-07		0.38	0.46	0.16	1.81	0.38	0.08	0.19	1.75	603	586
16-04		0.34	0.51	0.15	1.93	0.43	0.16	0.06	1.90	526	561
7-205		0.36	0.52	0.12	1.81	0.61	0.14	0.07	1.45	643	647
6-175		0.36	0.45	0.14	1.31	0.30	0.35	0.13	1.70	683	596
182-35		0.43	0.39	0.18	2.25	0.39	0.08	0.03	1.69	576	601
182-235	R	0.37	0.46	0.16	2.27	0.49	0.06	0.01	1.76	535	585
	C				2.22	0.45	0.08	0.03	1.83	531	572

....continued

		Biotite			Garnet						
				X						T(6)*	T(7)**
Sample		XFe	XMg	Al + Ti	Fe	Mg	XMn	XCa	lnKd	°C	°C
182-425	R	0.38	0.47	0.15	2.12	0.48	0.06	0.05	1.72	556	593
	C				2.01	0.36	0.08	0.11	1.94	517	555
182-620		0.41	0.42	0.16	2.23	0.37	0.07	0.07	1.80	561	578
182-785	R	0.42	0.45	0.13	2.14	0.33	0.11	0.08	1.91	541	558
	C				1.93	0.25	0.15	0.14	2.16	509	517
182-1040	R	0.63	0.20	0.17	2.04	0.10	0.15	0.11	1.72	631	593
	C				2.10	0.09	0.18	0.11	1.92	606	556
Biotite-Sillimanite-Almandine Zone											
SL-17		0.48	0.38	0.14	2.10	0.34	0.15	0.05	1.57	651	626
SL-18		0.42	0.46	0.12	2.13	0.31	0.15	0.05	1.53	635	624
SL-22		0.50	0.36	0.14	2.10	0.29	0.15	0.07	1.63	630	610

R=garnet rim; C=garnet core

* Ganguly and Saxena (1984)

** Perchuk and Lavrenteva (1982)

reaction, may be responsible for the large discrepancy in the two studies. Calorimetric measurements of heats of solution and low-temperature heat capacities of andalusite and sillimanite (Anderson,et al., 1977; Hemingway and Robie, 1984) and thermodynamic data derived from experimental studies in the system CaO - SiO_2 - Al_2O_3 - H_2O (Halbach and Chatterjee, 1984) also are consistent with Holdaway's (1971) phase diagram.

Sillimanite and kyanite are commonly present in the felsic rocks associated with the Anderson Lake deposit at Snow Lake. The two minerals are in apparent textural equilibrium and occur as sub-idioblastic to idioblastic, coarse grained crystals. This suggests that the pressure - temperature conditions were at or close to the kyanite - sillimanite transition. Therefore, the intersection of the lnKd curves for the garnet-biotite geothermometer and the kyanite-sillimanite boundary allows the estimation of pressure of metamorphism. The range of biotite - garnet Kd curves for the staurolite - biotite zone intersect the kyanite sillimanite boundary at 5.4 ± 0.2 kb (Fig. 4). Kd curve for the biotite - sillimanite zone intersects the kyanite - sillimanite boundary at 5.8 kb.

Ilmenite - Sillimanite - Garnet - Rutile barometry

Bohlen et al. (1983) have proposed a geobarometer based on the Fe content of almandine in the reaction:

3 Ilmenite + Sillimanite + 2 Quartz = Almandine + 3 Rutile (8)

This reaction was calibrated using experimental reversals obtained over a temperature range of 750 °C to 1100 °C at 11.0 to 16.0 kb. The results of these experiments can be represented by the equation:

$$\log K(8) = 174/T - 1.3 + 0.0975\,(P-1)/T \qquad (9)$$

where T is in Kelvin, P is in bars, and K = a(almandine)/a^3 (ilmenite).

The garnet - sillimanite - ilmenite - rutile - quartz assemblage is present in samples from the staurolite - biotite zone at Snow Lake. Using the garnet compositions from these samples and activity corrections as discussed earlier, metamorphic pressures were calculated (Table 6). These calculations indicate a pressure of 5.1±0.3 kb. The uncertainty of calculation, corresponding to an error of 0.02 in the XFe of garnet, is ±0.4 kb.

Table 5. Estimates of Pressure at Snow Lake Using Silicate Equilibria

	Garnet				Plagioclase		P (kb)	
Sample	XFe	γ	XCa	γ	XCa	γ	(9)*	(11)**
30-11	0.63	1.11	0.06	1.15	0.33	1.63	5.5	5.6
30-80	0.61	1.11	0.07	1.14	0.46	1.44	5.1	5.3
26-10	0.55	1.2	0.08	1.12	0.51	1.39	4.8	5.5

* almandine - sillimanite - rutile - ilmenite barometer
** anorthite - grossular - sillimanite barometer

Anorthite - garnet - sillimanite - quartz barometry

A third estimate of pressure at Snow Lake can be obtained by using the pressure dependence of the partitioning of Ca between anorthite and grossular according to the reaction:

Anorthite = Grossular + Sillimanite/Kyanite + Quartz (10)

(Kretz, 1959; Ghent, 1976). The endmember reaction with kyanite as the Al_2SiO_5 phase has been experimentally calibrated by many workers (Hariya and Kennedy, 1968; Hays, 1966; Goldsmith, 1980). Using the results of Goldsmith (1980), together with those of Holdaway (1971) for the kyanite - sillimanite equilibrium, gives:

$\log K\ (10) = 711/T - 5.42 + 0.287\,(P-1)/T$ (11)

where $K = (a\ \text{grossular}/a^3\ \text{anorthite})$.

In addition to the assumption that ΔVs (reaction) is independent of pressure and temperature, the above procedure of calculation assumes that the volume of mixing in the garnet or plagioclase solid-solutions does not show any deviations from ideality. This assumption is valid for the plagioclase solid-solution (Saxena and Ribbe, 1972), but may not be valid for the garnet solid-solution. The volume of mixing on the almandine - grossular and pyrope - grossular joins shows a strong, negative deviation from ideality at garnet compositions of $0.1 < Xgr < 0.3$ (Ganguly and Saxena, 1984). However, garnets from Snow Lake all have grossular contents less than 10 mole percent. Therefore, the volume correction can be neglected in the present calculations.

Using the temperature estimate from the garnet - biotite equilibrium and garnet and plagioclase compositions from Snow Lake, pressures were calculated for the staurolite - biotite zone. Activities of grossular and plagioclase were calculated using the activity models discussed earlier. The calculated pressures range from 6.3 to 6.6 kb (Table 6). The uncertainty of calculation, corresponding to an error of ± 5% in the estimation of XCa in garnet and of ± 0.01 in the estimation of XCa in plagioclase, is ± 0.5 kb.

The temperature and pressure estimates calculated above are plotted on the P-T diagram in Figure 4. The common intersection of these estimates indicates metamorphic temperatures of 575±50 °C at 5.25±0.5 kb pressure for the staurolite - biotite zone. For the biotite - sillimanite zone, the P-T conditions are: 620±40 °C at 5.8±0.5 kb.

F. Discussion

The estimates of pressure - temperature conditions during metamorphism in the Flin Flon - Snow Lake greenstone belt obtained in this study generally agree well with previous studies for the most part. However, previous estimates of pressure based on sphalerite geobarometry are considerably higher (4 - 7 kb in Flin Flon, and 7 - 8 kb in Snow Lake) than those of this study. It has been suggested by many workers that sphalerite, co-existing with pyrite and pyrrhotite, re-equilibrates at lower temperatures (see Essene, 1982 for a review). This results in lower contents of FeS in sphalerite and, therefore, higher estimates of pressure. Bristol (1979) suggested that re-equilibration of sphalerite at low temperatures probably caused the wide range in estimates of pressure in the Flin Flon area. In view of the close agreement in pressure estimates from mineralogical barometers used in this study, it is concluded that estimates of pressure in the Flin Flon - Snow Lake area based on sphalerite geobarometry are in error.

The pressure and temperature conditions for the Flin Flon - Snow Lake belt allow estimation of the geothermal gradients during metamorphism. Assuming a rock density of 2.6 gm/cm^3, the geothermal gradient in the Snow Lake area would be approximately 27 °C/Km. In the Flin Flon and Spruce Point areas, the geothermal gradient would be much shallower, 33 °C/Km at the upper limit and 83 °C/Km at the lower limit of temperature and pressure. The geothermal gradient in the Snow Lake area is similar to the Barrovian-type and that in the Flin Flon and Spruce Point areas, to the Buchan-type (Turner, 1981). This indicates that the P-T regime was not homogeneous throughout the belt. Further, the eastern parts of the Flin Flon - Snow Lake belt were subjected to a relatively lower heat flow during metamorphism.

Calibration of Silicate Equilibria

The pressure - temperature condition for metamorphism in the Snow Lake area derived above can be used to evaluate other mineral equilibria for which either the experimental data are not available or the available experimental data are not in agreement. Two such reactions are:

$$\text{6 Rutile + Almandine + Annite = Muscovite + 3 Quartz + 6 Ilmenite} \quad (12)$$

6 Staurolite + 3.75 Quartz = 4 Almandine + 23 Sillimanite + 6 H_2O (13)

Garnet - annite - muscovite - quartz - ilmenite - rutile equilibrium

This six phase assemblage is commonly present in the Snow Lake area. If the reaction is balanced as in equation (12), it has a dP/dT slope of 45 bars/K and, therfore, it may provide a reliable geobarometer together with the garnet-biotite geothermometer. Reaction (12) has not been studied experimentally and reliable thermodynamic data are not available for all the phases. A pressure - temperature calibration for this reaction can be derived by a combination of reaction (8) and the following equilibria:

Annite = K-feldspar + Magnetite + H_2 (14)

Muscovite + Quartz = K-feldspar + Sillimanite + H_2O (15)

Magnetite + 3 Rutile = 3 Ilmenite + 0.5 O_2 (16)

$H_2 + 0.5\, O_2 = H_2O$ (17)

Reactions (14) and (15) have been experimentally studied by many workers. The most recent calibration of reaction (14) is given by Hewitt and Wones (1981):

$$\log K(14) = -6758 + 8.58 + 0.0042(P-1)/T \qquad (18)$$

The upper stability of muscovite and quartz according to reaction (15) has been determined by Chatterjee and Johannes (1974) who give:

$$\log K(15) = -5285/T + 8.92 + 0.0248(P-1)/T \qquad (19)$$

The equilibrium conditions for reactions (16) and (17) can be calculated from thermodynamic data tabulated by Robie et al. (1979). Combining the pressure - temperature dependence of the equilibrium constants of reactions (8) and (14) to (17), the log K of reaction (12) can be expressed as:

$$\log K(12) = -1040/T + 4.02 - 0.0872(P-1)/T \qquad (20)$$

Using the composition of biotite and garnet from Table 6 and the activity corrections discussed earlier, equation (20) gives a pressure estimate of 11.7 ± 0.3 kb for the Snow Lake area. These pressures are significantly higher than those calculated by using other, experimentally calibrated, mineralogical geobarometers. To achieve consistency between the compositions of biotite and garnet and the pressure - temperature estimates for Snow Lake, the log K equation for reaction (12) should be given as:

$$\log K(12) = -1040/T + 3.88 - 0.0872(P-1)/T \qquad (21)$$

This equation is different from (20) in having a slightly lower value for the entropy of the reaction. Considering that several different equilibria were used to derive the calibration in equation (20), the minor change required to achieve consistency with field data is not very significant.

Upper stability of staurolite at low pressures

Staurolite is a common mineral in rocks from the Anderson Lake mine area. It usually occurs with biotite, muscovite, quartz, and sillimanite or garnet. In some samples, staurolite co-exists with garnet, sillimanite, and quartz, indicating that the equilibrium expressed by reaction (13) was achieved. Reaction (13) has been experimentally studied by many workers (Richardson, 1968; Ganguly, 1972; Rao and Johannes, 1979; Dutrow and Holdaway, 1983). In a detailed analysis by linear programming methods, Pigage and Greenwood (1982) concluded that the experimental data of only Ganguly (1972) and Rao and Johannes (1979) were compatible with each other and with estimates of the entropy of staurolite of composition $Fe_2Al_9Si_{3.75}O_{22}(OH)_2$. They also concluded that calculated activity of water, using the experimental results of Ganguly (1972) and Rao and Johannes (1979), was too low compared to that calculated from paragonite - albite - sillimanite equilibrium and gas speciation in the system C - O - H. With a simultaneous consideration of garnet - biotite, kyanite - sillimanite, staurolite - quartz, and paragonite - albite equilibria, Pigage and Greenwood (1982) suggested that the staurolite - quartz equilibrium should be located at 610 °C at 5700 bars, approximately 100 °C lower than that determined by experimental studies.

Dutrow and Holdaway (1983) have redetermined the low pressure stability of staurolite + quartz and have obtained reversals at 654 ± 12 °C, 3.25 kb, and 684 ± 12 °C, 5.25 kb. These data are consistent with those of Richardson (1968) at 5 kb and, therefore, inconsistent with those of Ganguly (1972) and Rao and Johannes (1979). Calculated entropy of staurolite from the data of Dutrow and Holdaway (1983) is lower than that based on summation estimates and calorimetric measurements of the heat-capacity of staurolite (Helgeson et al., 1978; Hemingway and Robie, 1984). Using Dutrow and Holdaway's (1983) data, at the pressure - temperature conditions (575 °C, 5.25 kb) and the compositions of staurolite and garnet from Snow Lake (XFe(stau) = 0.75 - 0.77; Table 5), the mole fraction of water in equilibrium with the staurolite - quartz - sillimanite - garnet assemblage will be 0.3 to 0.4. These values of XH_2O are extremely low compared with those (0.9 - 0.98) calculated by using opaque mineral assemblages and paragonite - albite - sillimanite - quartz equilibrium (Chapter IV).

To achieve consistency between the temperature, pressure, and XH_2O values at Snow Lake determined from other equilibria, the staurolite - quartz equilibrium for pure phases and $XH_2O = 1$ should pass through a point at 600 °C and 5.25 kb pressure. This temperature is 84 °C lower than that obtained by Dutrow and Holdaway (1983).

The staurolite - quartz equilibrium was extrapolated from a point at 600 °C and 5.25 kb using the relation:

$0 = dGr = SdT + VdP + RT \ln fH_2O$.

and entropy and volume data from Helgeson et al. (1978) and Hemingway and Robie (1984). At 5700 bars, the extrapolated curve has a temperature of 615 °C, which is in excellent agreement with that (610 °C, 5700 bars) suggested by Pigage and Greenwood (1982). The equilibrium conditions of equation (13) derived above are consistent with an analysis of solid and volatile phase equilibria in the Snow Lake area (Chapter IV). This lends further support to the argument that experimental studies of the staurolite - quartz equilibrium indicate unusually high temperatures for this assemblage.

In their detailed analysis of the studies of staurolite equilibrium, Pigage and Greenwood (1982) could not identify any systematic errors in the experimental data. While the data presented in this study is consitent with other field studies, it does not provide any evidence to further evaluate the experimental data.

G. Conclusions

Metamorphic conditions in the Flin Flon - Snow Lake greenstone belt varied from low-greenschist facies to middle-amphibolite facies. At Flin Flon, the temperature of metamorphism was less than approximately 450 °C and the pressure was less than 3.8 kb. In the Spruce Point area, the metamorphic temperature was 475 ± 50 °C at 2.6 ± 1.2 kb pressure. At Snow Lake, the grade of metamorphism was of low-greenschist facies in the south (chlorite - biotite zone). The grade of metamorphism increased to the north in the chlorite - biotite - staurolite, staurolite - biotite, and biotite - sillimanite - garnet zones. In the staurolite - biotite and biotite - sillimanite zones, the metamorphic conditions were, respectively, 575 ± 50 °C at 5.25 ± 0.5 kb and 620 ± 40 °C at 5.8 ± 0.5 kb. The metamorphic fluid phase at Spruce Point and Snow Lake consisted essentially of water, with minor proportions of other species of oxygen and sulfur.

Using the temperature and pressure estimates for the staurolite - biotite zone at Snow Lake, a P - T calibration of the almandine - annite - muscovite - ilmenite - rutile assemblage is derived. A simultaneous consideration of the estimates of pressure, temerature, and XH_2O in the metamorphic fluid and the staurolite + quartz equilibrium, suggests that experimental studies of the upper stability of staurolite + quartz may indicate unusually high temperatures.

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III. Oxygen-Isotope Geochemistry of Metamorphosed, Massive Sulfide Deposits of the Flin Flon - Snow Lake Belt, Manitoba

A. Introduction

It is now well known that significant differences exist in the oxygen isotopic compositions of the host rocks and altered rocks associated with many volcanogenic massive sulfide deposits (Beaty and Taylor, 1982; Green et al., 1983; Urabe et al., 1983). These differences are produced during fluid-rock interaction attending ore-deposition. The deposits examined in the above studies are either unmetamorphosed or metamorphosed to low grades. However, numerous economically important deposits worldwide occur in medium- to high-grade, regionally metamorphosed terranes. The effects of metamorphism on oxygen isotopic gradients associated with massive sulfide deposits have not been well established. Depending upon the nature of fluid-rock interaction, these gradients may or may not survive the metamorphism (Shieh and Schwarcz, 1974; Magaritz and Taylor, 1976; Rumble, 1978; Rumble et al., 1982). Further, fluid-rock interaction during metamorphism may result in the development of secondary isotopic gradients around an ore-deposit. Thus the oxygen isotopic relationships at a metamorphosed deposit would be a function of the fluid-rock interaction during both ore deposition and metamorphism.

One of the common problems in identifying the effects of metamorphism on the isotopic gradients around an ore deposit is the lack of an equivalent deposit in the same terrane, metamorphosed at lower grades. In this paper, we report the oxygen-isotope compositions of rocks and minerals from three ore deposits, Anderson Lake, Spruce Point, and Centennial, in the Flin Flon - Snow Lake Belt, Manitoba. These deposits occur in similar host rocks and have been metamorphosed at low-greenschist to amphibolite facies. The objective of this paper is to evaluate the effects of metamorphism on the oxygen-isotope geochemistry of the host and altered rocks associated with the deposits. A second objective of this paper is to examine the significance of the isotopic data in understanding the nature of hydrothermal alteration during ore-deposition.

B. Regional Geological Setting

The Flin Flon - Snow Lake greenstone belt is approximately 250 kilometers long and has an exposed width of nearly 40 kilometers. It is bounded to the north by the Kisseynew gneiss complex and is overlain to the south by Paleozoic limestones (Fig. 1). The Flin Flon Snow Lake belt and the Kisseynew gneisses together are part of the Churchill structural province of the Canadian Shield (Stockwell, 1964).

The greenstone belt consists of two major groups of rocks of Aphebian age (approximately 1800 ± 50 m.y.) and a number of intrusive granite bodies (Price, 1978). The older, Amisk Group rocks are the dominant lithology and consist mainly of volcanic rocks with a minor, metasedimentary Member. The volcanic rocks are of tholeiitic and calc-alkalic affinity and range in composition from basalt to dacite-rhyolite (Stauffer et al., 1975). The metasedimentary Member of the Amisk Group is composed principally of metagreywackes (Froese and Moore, 1980). The Missi Group constitutes only a minor proportion of the Flin Flon - Snow Lake belt and is comprised largely of metasandstones and metagreywackes.

Structure and Metamorphism

Rocks in the Flin Flon - Snow Lake belt were structurally deformed and metamorphosed during the Hudsonian Orogeny. The degree of deformation and metamorphism varies throughout the belt. In general, three phases of deformation have been identified (Stauffer and Mukherjee, 1971; Froese and Moore, 1980).

The earliest deformation, P1, resulted in east-west trending tight folds. The P2 event, produced the dominant northeasterly trend in the area. The P2 folds are generally open and have steep axial foliation and lineation. The P3 event was relatively minor and generally refolded the P2 folds along a northerly axis.

Metamorphism was generally coincidental with the P2 event when the peak of metamorphism was reached (Froese and Moore, 1980). The metamorphic event was largely over in the waning stages of the P2 event. The P3 event was characterized by minor, retrogressive metamorphism. Metamorphic grades of low-greenschist facies were reached in the Flin Flon area. At Spruce Point, the metamorphism was of the upper greenschist facies.

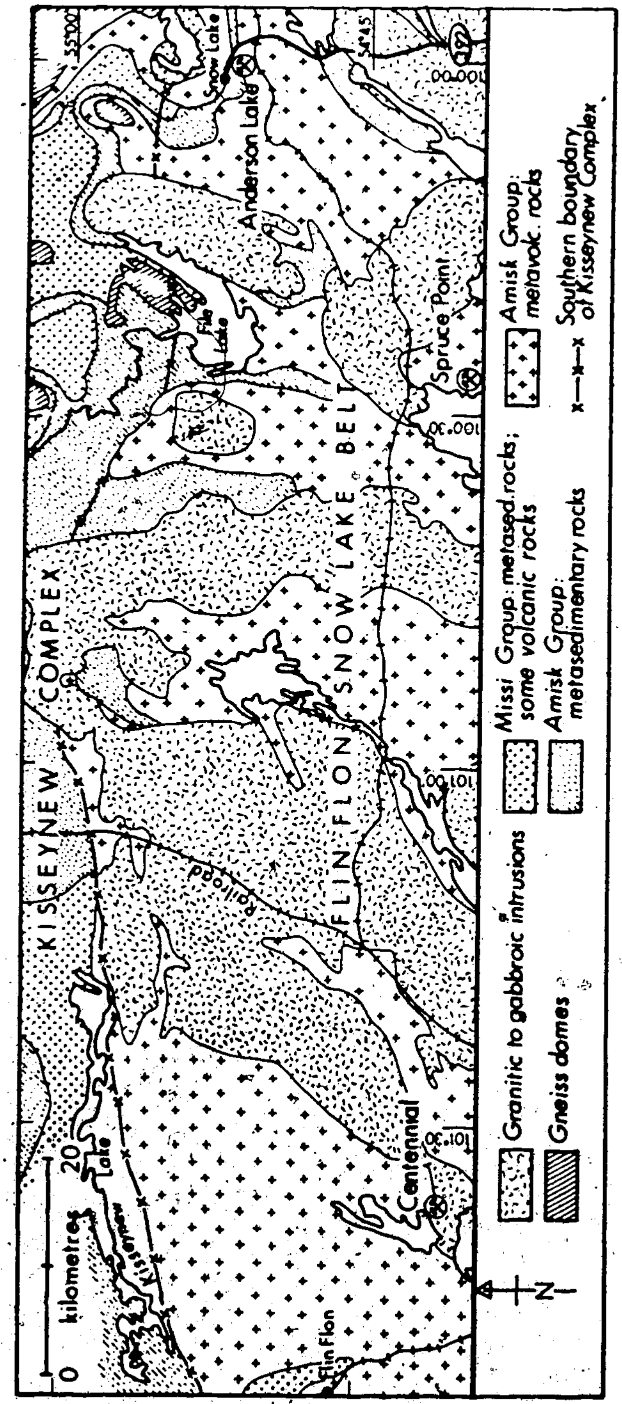

Figure 1. Regional geology of the Flin Flon - Snow Lake belt (after Froese and Moore, 1980) and the location of the present study areas.

The temperature of metamorphism was 475 ± 50 °C at 2.6 ± 1.2 kb pressure (Chapter II). The Anderson Lake area shows a complete spectrum of metamorphic conditions from low greenschist facies in the south to middle-amphibolite facies in the north and northeast (Froese and Moore, 1980). Based on mineral assemblages, Froese and Gasparrini (1975) have divided the Anderson Lake area into four metamorphic zones. From south to north, these zones are: (i) chlorite - biotite, (ii) biotite - staurolite, (iii) staurolite - sillimanite, and (iv) garnet - sillimanite - biotite. The temperature and pressure conditions in the staurolite - sillimanite and garnet - sillimanite zones have been estimated using the P-T calibrations of several silicate equilibria and compositions of minerals (Chapter II). Temperatures of 575 ± 30 °C at 5.25 ± 0.5 kilobar pressure are estimated for the staurolite - sillimanite zone; estimated temperature and pressure values are slightly higher for the garnet - sillimanite zone (620 ± 30°C at 5.4 ± 0.5 kb.).

C. Geology of the Ore Deposits

The felsic volcanic rocks of the Amisk Group host a number of Cu-Zn-Fe massive sulfide deposits in the Flin Flon - Snow Lake belt, including the Anderson Lake, Spruce Point, and Centennial deposits, selected for this study. These deposits constitute a major source of Cu and Zn in Canada. The tonnage and grades of the deposits vary from 0.1 million tonnes at 0.75 percent Cu and 9.4 percent Zn to 61.8 million tonnes at 2.2 percent Cu and 4.1 percent Zn. Total tonnage from past and producing mines in the entire belt is estimated at over 100 million tonnes (Walford and Franklin, 1982).

Anderson Lake deposit

The geology of the Anderson Lake deposit has been described by Price (1978) and Walford and Franklin (1982). The deposit consists of an elongated lens with a strike length of 90 meters, an average width of five meters, and a length of 800 meters along the plunge. The sulfide lens is composed primarily of pyrite, chalcopyrite, and pyrrhotite with minor sphalerite, quartz, staurolite, tourmaline, apatite, magnetite, ilmenite, and rutile.

The Anderson Lake deposit is contained in felsic metavolcanic rocks of the Amisk Group. These rocks are rhyolitic in composition and are composed of quartz, plagioclase, and biotite with minor amounts of hornblende, muscovite, and garnet.

In the vicinity of the Anderson Lake deposit, the footwall rocks were hydrothermally altered during ore-deposition. Based on their mineral assemblages, the altered rocks can be classified into four zones: (a) chlorite zone, (b) muscovite zone-I, (c) gradational zone, and (d) muscovite zone-II

The chlorite zone is similar to the "pipe" alteration of Archean, massive sulfide deposits (Franklin et al., 1981) and consists dominantly of chlorite with lesser amounts of biotite, kyanite, quartz, plagioclase, and rutile. At its lower end, the chlorite zone also occurs as a small, "semi-conformable" zone (Walford and Franklin, 1982). Here, the chlorite zone is relatively iron-rich and consists of chlorite, biotite, quartz, plagioclase, staurolite, garnet, and minor amounts of ilmenite.

Peripheral to the chlorite zone is a thin shell of muscovite zone-I. Rocks in this zone consist mainly of quartz, muscovite, sillimanite, plagioclase, and biotite. Outwards from the muscovite zone-I, the footwall rocks are pervasively altered in the gradational zone. Mineralogically, rocks in the gradational zone consist of quartz, plagioclase, and biotite with varying amounts of staurolite, muscovite, and sillimanite. Garnet occurs in some gradational zone rocks near the contact with the country rocks. In these rocks, sillimanite is absent except in one sample where thin needles of fibrolite are associated with garnet and staurolite.

In addition to the alteration zones described above, an envelope of muscovite schist surrounds the ore-body, both in the hangingwall and the footwall. This halo of muscovite schist, called here the muscovite zone-II, underlies the ore-body for the most part, except where the chlorite zone occurs in the footwall. Rocks in this zone are composed of quartz and muscovite with minor contents of biotite, plagioclase, staurolite, and sillimanite ± almandine. Mineralogically, these rocks are similar to those from the muscovite zone-I. However, a distinction is made between the two zones on the basis of thier locations with respect to the ore.

The altered rocks from the gradational zone and muscovite zones I and II contain minor amounts of ilmenite, rutile, pyrite, and pyrrhotite. Ilmenite-hematite solid solution is also present frequently. Rarely, magnetite has been observed in some gradational zone rocks which do not contain rutile.

Spruce Point deposit

The Spruce Point deposit consists of at least three separate, major lenses of massive sulfides. The deposit is still in the development stage and its geology has not been studied in detail. The sulfide bodies consist of pyrite, chalcopyrite, and sphalerite with minor arsenopyrite, pyrrhotite, magnetite, quartz, chlorite, ilmenite, and rutile.

The host felsic metavolcanic rocks are composed essentially of quartz, plagioclase, and muscovite with minor biotite, ilmenite, and pyrite. Footwall rocks at Spruce Point were also altered during ore-deposition. The alteration "pipe" is broadly similar to that at Anderson Lake. The central, chlorite zone consists of abundant chlorite with varying proportions of biotite, corundum, andalusite, and rutile. The adjoining, muscovite zone-I consists of quartz, muscovite, andalusite with minor plagioclase, biotite, ilmenite, rutile, pyrite, and pyrrhotite. Rocks in this zone have been variably affected by a minor phase of retrograde metamorphism. The retrograde metamorphism resulted in a partial or complete replacement of andalusite porphyroblasts by margarite, chloritoid, and chlorite.

The gradational zone at Spruce Point is more extensive than at Anderson Lake. Mineralogically, rocks in this zone contain an increased amount of biotite compared with the country rocks and consist of quartz, muscovite, biotite, plagioclase and minor ilmenite. The gradational zone underlies the ore body for the most part as the muscovite zone-II is absent at Spruce Point.

Centennial deposit

The geology of the Centennial deposit has been described by Provins (1980). The deposit consists of a single, massive sulfide lens enclosed in the felsic volcanic rocks of the Amisk Group. The sulfide body has a sharp contact with the hangingwall rocks and a relatively less distinct contact in the footwall. It is composed principally of pyrite, chalcopyrite, and sphalerite with minor galena, magnetite, quartz and calcite. Trace amounts of tetrahedrite-tennantite, arsenopyrite, and cobaltite are also present (Provins, 1980).

The host felsic volcanic and volcaniclastic rocks are composed essentially of quartz and muscovite with lesser amounts of ilmenite, magnetite, and pyrite. Rocks in the Centennial area are pervasively carbonatized. However, hydrothermal alteration related to ore depostion is less extensive at Centennial compared with that at the Anderson Lake and Spruce Point deposits. The chlorite zone, underlying the ore-body in the northern part, consists primarily of chlorite with minor quartz and trace amounts of rutile. The gradational zone underlies the ore-body in the south and is peripheral to the chlorite zone. This zone is characterized by slight Mg and K enrichment and Na and Ca depletion compared to the country rocks. Rocks in the gradational zone at Centennial are composed of quartz and muscovite with minor chlorite, ilmenite, and pyrite. Muscovite zones I and II are absent at the Centennial deposit.

D. Analytical Methods

Samples for isotopic analyses were collected from underground exposures and diamond-drill cores at the Anderson Lake, Spruce Point, and Centennial deposits. In addition, surface samples were collected in the vicinity of the Anderson Lake deposit. Co-existing minerals were separated by standard magnetic and density techniques. Purity of the mono-mineralic fractions was checked visually under a binocular microscope. Biotite, chlorite, and muscovite fractions were more than 95 percent pure. Quartz fractions were cleaned by treating with fluoboric acid for 24 hours at 50 °C. Whole-rock samples from Centennial deposit were treated with concentrated HCl to dissolve carbonates.

Oxygen was liberated from 15 to 20 milligrams of whole-rock or monomineralic samples by the BrF_5 method of Clayton and Mayeda (1963). The liberated oxygen was converted to CO_2 by passing over a heated graphite rod. Isotopic ratios were measured using a duel-inlet, VG602 mass spectrometer. The isotopic compositions are reported in the usual 'δ' notation, in parts per thousand (permill), with respect to Standard Mean Ocean Water (SMOW) using a CO_2-H_2O fractionation factor of 1.0412. The $\delta^{18}O$ value of a sample, x, is given as:

$$\delta^{18}Ox = ((Rx/Rs) - 1) \ast 1000$$

where R is the ^{18}O / ^{16}O ratio of the sample (x) or the standard (s). Replicate analyses of NBS 28 during the course of this study give a value of +9.61 ± 0.12.

E. Results

The oxygen isotopic compositions of rocks and minerals from the Anderson Lake, Spruce Point, and Centennial deposits are given in Tables 1, 2, and 3. The host, metarhyolitic rocks have a range of $\delta^{18}O$ values from +14.3 to +15.6 at Centennial, +10.2 to +13.0 at Spruce Point, and +8.6 to +11.6 at Anderson Lake. $\delta^{18}O$ values of metabasalts from the Centennial and Anderson Lake range from +6.7 to +9.4. Values for intrusive rocks from the Anderson Lake area, amphibolite dikes and tonalite, range from +5.8 to +6.6 and +5.9 to +6.2, respectively. Two samples of metasedimentary rocks from Anderson Lake have $\delta^{18}O$ values of +11.0 and +13.0.

The $\delta^{18}O$ values of metaigneous and metasedimentary rocks of the Flin Flon - Snow Lake belt presented above are similar to those of metaigneous and metasedimentary rocks form Archean greenstone belts in the Superior Province of the Canadian Shield (Longstaffe et al., 1980; Longstaffe et al., 1981). The isotopic values for metabasltic rocks from Anderson Lake and Centennial are also similar to those of submarine basalts (Muehlenbachs and Clayton, 1972). However, the felsic and mafic metavolcanic rocks of this study all have $\delta^{18}O$ values higher than those of fresh igneous rocks of rhyolitic (+6 to +8) and basaltic (+5.5 to +6.5) composition (Taylor, 1968). The higher $\delta^{18}O$ values of volcanic rocks can be attained during low-temperature, hydrothermal alteration (Garlick and Dymond, 1970; Muehlenbachs and Clayton, 1972). Differences in the temperature and water/rock ratio of such alteration can explain the range of $\delta^{18}O$ values in the felsic metavolcanic rocks of this study.

Although the oxygen-isotope compositions of the felsic and mafic volcanic rocks from Anderson Lake, Spruce Point, and Centennial indicate that they have been altered, these rocks are classified in this paper as "country rocks" and are not included in the category of "altered rocks" described below. This distinction is made based on the mineralogical composition of the rocks as discussed in the section on geology of the ore deposits.

Altered rocks associated with the three deposits have lower $\delta^{18}O$ values compared to the country rocks. In the gradational zone, the $\delta^{18}O$ values range from +9.9 to +11.7 at Centennial, from +8.4 to +9.7 at Spruce Point, and from +6.6 to +7.7 at Anderson Lake. $\delta^{18}O$ values in the chlorite zone are +5.3 at Centennial, +5.4 to +7.3 at Spruce Point, and

Table 1. Oxygen-Isotope Data from the Anderson Lake Deposit. (WR = whole rock; Qz = quartz, Mu = muscovite; Bt = biotite; Ch = chlorite

Sample			δ^{18}O					
	WR	Qz	Bt	Mu	Ch	ΔQz-Mu	ΔQz-Bt	ΔQz-Ch
Country Rocks (Felsic Metavolcanics)								
SL-11A	9.1							
SL-12A	9.6	10.7	4.6				6.1	
SL-13	10.5	11.7						
SL-17	10.4	13.0	5.5	5.4			7.5	7.6
SL-22	9.6	11.2						
SL-26	10.4	12.1						
SL-26-1	11.0	12.2						
SL-28	11.6	13.5	6.8	8.8			6.7	4.6
SL-34	9.5							
SL-34A	10.0							
SL-35	10.6							
SL-36	11.6							
26-14	8.7							
78-243	8.6							
182-425	9.4	10.9						
182-520	9.5							
251-1188	10.0							
251-1221	9.8							
Mafic Metavolcanics								
SL-3	8.2							
SL-10	7.6							
SL-35A	7.6							

Sample	$\delta^{18}O$							
	WR	Qz	Bt	Mu	Ch	ΔQz-Mu	ΔQz-Bt	ΔQz-Ch
Amphibolite								
SL-33	6.1							
26-09	5.8							
72-320	6.6							
Metasedimentary Rocks								
SL-29	13.0							
SL-37	11.0							
Tonalite								
24-16	5.9							
24-17	5.9							
30-01	6.2							
Chlorite Zone								
SL-14	5.9	6.5	1.8		1.5		4.7	5.0
16-01	5.9	8.3	2.7	5.6				
24-03	4.2							
182-235	3.7	6.7	1.1		1.2		5.6	5.5
Gradational Zone								
SL-6	7.7							
SL-30	7.6							
SL-31	7.1							
16-07	7.2	9.1			2.2			6.9
16-04	7.7							
16-03	7.0	8.9	2.9				6.0	
7-37	7.0							

Sample	δ^{18}O							
	WR	Qz	Bt	Mu	Ch	ΔQz-Mu	ΔQz-Bt	ΔQz-Ch
7-95	6.6	8.1	2.1				6.0	
24-04	7.1							
24-05	6.8							
24-07	7.2							
24-08	7.1	8.3	3.6				4.7	
24-10	6.9	8.8	3.7				5.1	
72-05	7.1							
72-70	6.7							
72-113	6.9							
72-220	6.7							
26-06	7.2							
78-30	7.5							
78-68	7.3							
Muscovite Zone-I								
SL-15	6.4							
24-01	4.7	6.3		-0.2				6.5
182-175	WR	5.2						
182-270	WR	5.8						
182-320	WR	6.1						

Sample	$\delta^{18}O$							
	WR	Qz	Bt	Mu	Ch	ΔQz-Mu	ΔQz-Bt	ΔQz-Ch
Muscovite Zone-II								
7-125	8.0	10.2	5.4	7.5		2.7	4.8	
7-190	8.0	9.4	2.9	6.7		2.7	6.5	
6-175		9.7	4.0	6.9		2.8	5.7	
16-05	8.3	9.3	4.3				5.0	
72-295		9.4	4.2	6.6		2.8	5.2	
72-330	8.3	10.3		7.4		2.9		
26-10	7.2							
78-103	7.8							
182-920	7.2							

Table 2. Oxygen-Isotope Data from the Spruce Point Deposit. (WR = whole rock; Qz = quartz. Mu = muscovite; Bt = biotite; Ch = chlorite

Sample	$\delta^{18}O$							
	WR	Qz	Bt	Mu	Ch	ΔQz-Mu	ΔQz-Bt	ΔQz-Ch
Country Rocks (Felsic Metavolcanics)								
115-235	13.0							
115-1373	10.2							
67-820	11.5							
67-920	12.0	14.3						
32-40	10.6							
32-80	10.9							
Chlorite Zone								
115-1308	5.4				5.2			
115-1303	6.9				6.1			
94-08	7.3							
Muscovite Zone-I								
115-1323	7.8	8.6		5.4		3.2		
115-1298	8.3							
115-1155	7.8							
Gradational Zone								
115-522	8.4							
115-1061	8.8							
68-702	9.7	11.2						
68-752	9.0	10.4		7.1		3.3		
68-768	9.2	10.5		7.2		3.3		
94-04		11.0		7.6		3.4		

32-182	8.9	10.6	7.2	3.4
32-232	8.8			

Table 3. Oxygen-Isotope Data from the Centennial Deposit (WR = whole rock; Qz = quartz, Mu = muscovite; Bt = biotite; Ch = chlorite

Sample	$\delta^{18}O$							
	WR	Qz	Bt	Mu	Ch	ΔQz-Mu	ΔQz-Bt	ΔQz-Ch
(Country Rocks								
(Felsic-metavolcanics)								
20-1145	15.3	17.2						
20-1174	15.6							
20-1198	14.5							
17-937	14.5							
Metabasalts								
20-W-330	9.4							
20-W-400	8.2							
20-W-773	6.7							
20-W-1025	8.3							
17-313	8.3							
Gradational Zone								
20-1025	11.7							
20-W-1273	10.7							
20-W-1288	10.5							
20-W-1293	11.3							
20-W-1324	11.3							
17-806	10.7	12.5						
17-785	11.2							
17-859	11.5							
17-866	9.9	13.8						
Chlorite Zone								

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17-829	5.3	13.0	5.3	7.7

+3.7 to +5.9 at Anderson Lake. The muscovite zone-I at Spruce Point and Anderson Lake has $\delta^{18}O$ values similar to those in the chlorite zone. Muscovite zone-II, present only at Anderson Lake, has $\delta^{18}O$ values ranging from +7.2 to +8.3. The compositions of altered and country rocks across the ore-body at Anderson Lake, Spruce Point, and Centennial deposits are shown in Figure 2.

Quartz, muscovite, biotite, and chlorite from country rocks and altered rocks show similar trends in their $\delta^{18}O$ values as the whole-rocks samples. Those separated from the country rocks have higher values than those from the altered rocks. Despite these differences in the composition of individual minerals, the fractionation between co-existing mineral pairs is generally similar in all rocks.

F. Origin of Differences in Isotopic Compositions

The lower $\delta^{18}O$ values of the altered rocks associated with the Anderson Lake, Spruce Point, and Centennial deposits could have been produced by equilibration with relatively ^{18}O-poor fluids. This fluid-rock interaction may have occurred (a) prior to, (b) during, or (c) after the greenschist to amphibolite facies metamorphism in the area.

Widescale fluid-rock interaction after the peak of metamorphism would produce disequilibrium mineral assemblages and isotopic relationships depending upon the capacity of the various minerals to re-equilibrate at lower temperatures. As described earlier, the metamorphic event in the Flin Flon - Snow Lake belt had a very minor retrogressive phase. In the Anderson Lake area, chlorite is the only mineral produced due to minor retrograde alteration of garnet, staurolite, and plagioclase. At Spruce Point, retrograde metamorphism has affected only the andalusite porphyroblasts which are now replaced by margarite and chloritoid. Other major minerals in the rocks, biotite and muscovite, do not show any visible retrograde alteration. Distribution of Fe and Mg between co-existing minerals at Anderson Lake and Spruce Point is consistent with their equilibration at the peak of metamorphism (Chapter IV). Because of the low grade of metamorphism in the Centennial area, no retrograde alteration is evident.

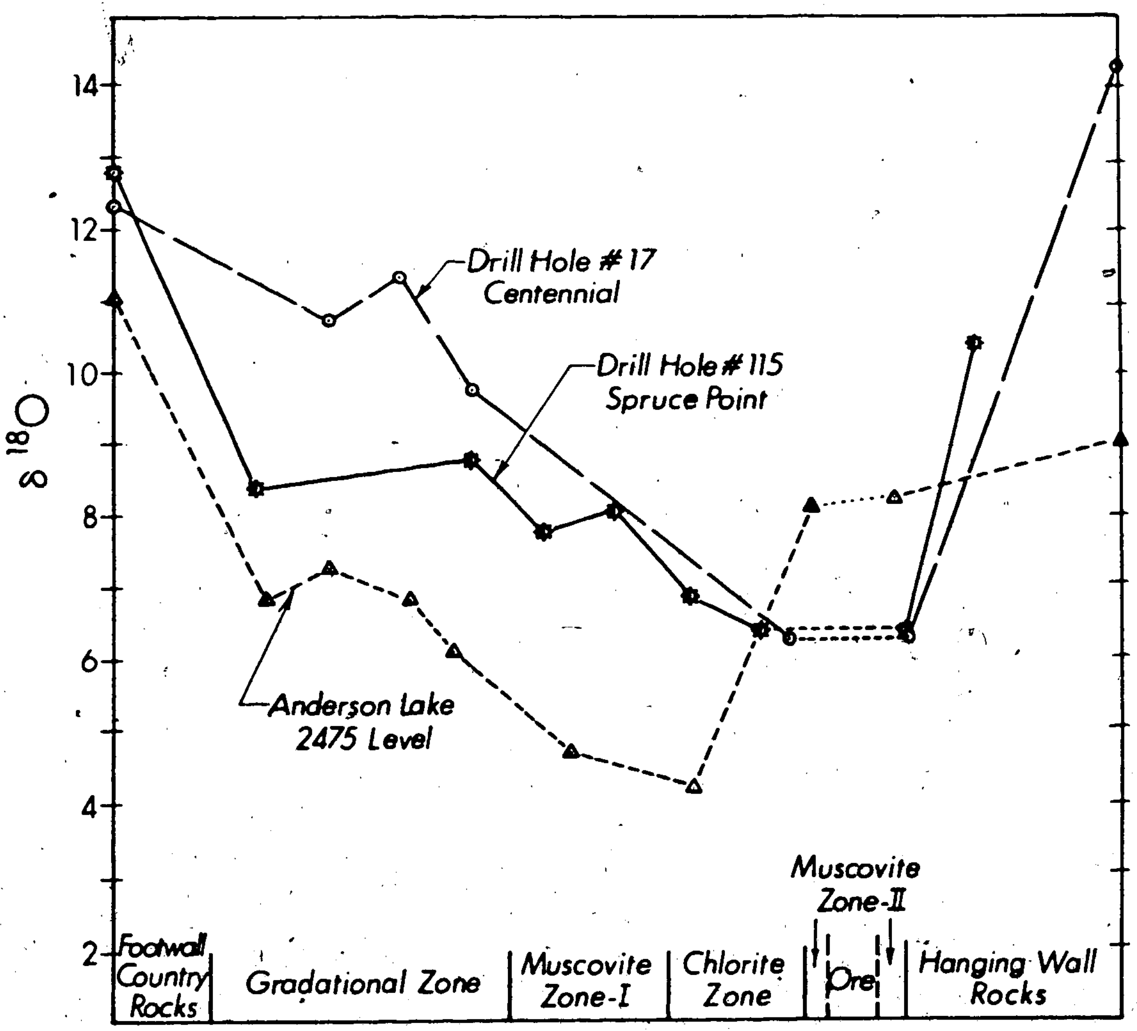

Figure 2. Whole rock, $\delta^{18}O$ values across the ore body at Anderson Lake, Spruce Point, and Centennial deposits. Horizontal scale is schematic; typical widths of the alteration zones are: Chlorite zone = 10 to 50 meters, Muscovite zone-I = 5 to 15 meters, Muscovite zone-II = 5 to 25 meters. The width of the gradational zone is not well established but is suggested in this study to be from 10 to 150 meters.

The isotopic compositions of minerals from Anderson Lake, Spruce Point, and Centennial areas also do not show evidence of major, retrograde exchange. The $\delta^{18}O$ values of coexisting minerals decrease in the order quartz > muscovite > biotite > chlorite, characteristic of minerals in rocks from regional metamorphic terranes (Garlick and Epstein, 1967). Isotopic fractionation between quartz and muscovite or chlorite is nearly constant in each area and decreases with increasing metamorphic grade (e.g., $\delta^{18}O_{quartz-muscovite} = 2.8 \pm 0.1$ at Anderson Lake and 3.3 ± 0.1 at Spruce Point). Even rocks with completely altered andalusite porphyroblasts from Spruce Point have the same quartz-muscovite fractionation as the other rocks (samples 67-768 and 32-182, Table 2).

Fluid-rock interaction during metamorphism can be evaluated by the mass-balance relationship given as:

$$W/R = (\delta^{18}O_{f,r} - \delta^{18}O_{i,r}) / (\delta^{18}O_{i,w} - (\delta^{18}O_{f,r} - \Delta_{r-w}) \qquad (1)$$

where the subscripts i and f refer to the initial and final isotopic compositions of rock (r) and water (w). Δ_{r-w} is the isotopic frationation between rock and water and can be adequately represented by the fractionation between plagioclase (anorthite 30) and water (Taylor, 1979). W/R is the water-rock ratio expressed in atom percent of oxygen in water (W) and rock (R). W/R in the above relationship is the minimum, integrated water to rock ratio over the life time of the hydrothermal system.

Because the $\delta^{18}O$ values of the altered rocks at all the three deposits in this study have been lowered compared to the country rocks, the numerator on the right hand side of equation (1) would always be negative. Given this constraint, an upper limit on the $\delta^{18}O$ value of the fluids involved in fluid-rock interaction during metamorphism is given by the factor ($\delta^{18}O_{f,r} - \Delta_{r-w}$); fluid $\delta^{18}O$ values lower than this factor will result in a negative value for W/R. Using the isotopic composition of rocks in the chlorite zone, the plagioclase-water fractionation curve of Matthews et al. (1983), and the temperatures of metamorphism estimated from silicate equilibria (Chapter II), upper limits for the $\delta^{18}O$ values of fluids at Anderson Lake, Spruce Point and Centennial are calculated to be between +2 and +4.

In order to investigate the possibility that $\delta^{18}O$ values of the altered rocks were lowered during metamorphism, the change in the isotopic composition of a rock, with an assumed initial composition, was calculated using equation (1). The calculations were performed at 575 °C, 475 °C, and 350 °C using three values of δ^{18}Oi,w : -6, 0, and +3. The temperatures used in the calculations correspond approximately to those estimated for metamorphism at Anderson Lake (575°C), Spruce Point (475°C), and Centennial (less than 450°C) using the chemical composition and stability relationships of silicate minerals (Chapter II). The δ^{18}O value of +3 for the fluid was chosen based on the upper limit of +2 to +4 calculated above. The other two values were chosen to be similar to that of seawater (0 permill) and a possible meteoric water (-6). Results of these calculations are shown in Figure 3. An inspection of the diagrams in Figuer 3 indicates that the observed isotopic compositions of altered rocks of this study (Tables 1 to 3) can be produced by water-rock interaction during metamorphism under following conditions: (1) the initial δ^{18}O values of the rocks were approximately +9, +10, and +14, respectively, at Anderson Lake, Spruce Point, and Centennial; (2) W/R varied between the different alteration zones; and (3) the δ^{18}O value of the fluids was less than approximately +3, as calculated earlier.

The isotopic composition of the intrusive rocks from Anderson Lake, however, do not indicate interaction with low-^{18}O fluids during metamorphism. The δ^{18}O values of metamorphosed, amphibolite dikes cross-cutting the ore-body, altered rocks, and the country rocks at Anderson Lake range from +5.8 to +6.6 (Table 1). These values are similar to those of fresh, igneous rocks of gabbroic composition (+5.5 to +6.5, Taylor, 1968). Calculations using equation (1) indicate that alteration of the amphibolites during metamorphism at Anderson Lake by fluids with δ^{18}O values of +3 or less would result in the δ^{18}O values of the amphibolites being much lower than +6. Thus, it appears that the isotopic exchange in the altered rocks took place prior to metamorphism, during or before ore-deposition.

Alteration by ore-depositing, hydrothermal solutions at Anderson Lake, Spruce Point, and Centennial is considered to have produced the chemical and mineralogical differences in the altered and country rocks at these deposits (Walford and Franklin, 1982; Chapter IV). It is likely that these fluids were also responsible for the lower δ^{18}O values of the altered rocks. In hydrothermal systems associated with volcanogenic massive sulfide deposits, fluid-rock interaction results in variable oxygen-isotope and chemical compositions of the altered rocks.

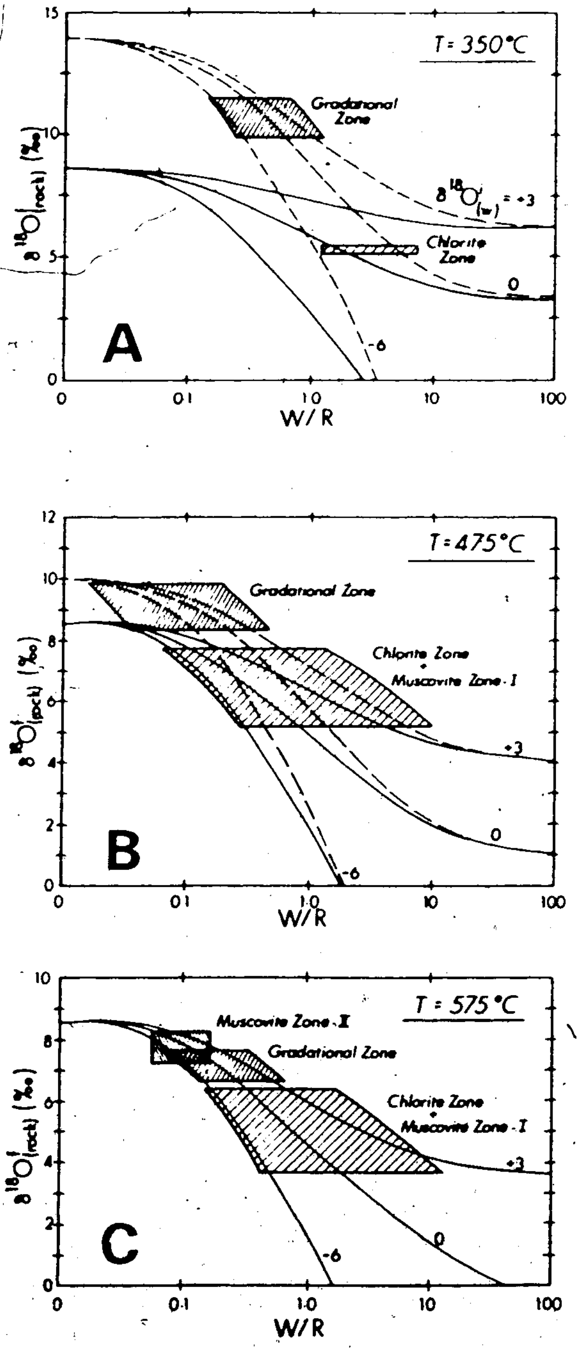

Figure 3. $\delta^{18}O$ - Water-rock ratio (W/R) diagram showing the change in $\delta^{18}O$ value of a rock as a function of W/R (atom % oxygen) during equilibrium isotope exchange at constant temperature. The solid curves are for $\delta^{18}O_{i,r}$ = +8.6 and the dashed curves for $\delta^{18}O_{i,r}$ value of +11 (3A) and +14 (3B). The range of isotopic values of the altered rocks plotted above correspond to the values at Centennial (3A), Spruce Point (3B), and Anderson Lake (3C). See text for the procedure of calculation.

The extent of the compositional change depends on the temperature and degree of equilibration between the rocks and the fluid (Cathles, 1983). Rocks near the vent of the solutions, in the "pipe" zone, suffer maximum alteration at the highest temperature. These rocks are characterized by a significant increase in their magnesium content and development of abundant chlorite. Outwards from this zone, the degree of alteration decreases gradually through a zone of less-altered rocks to the country rocks. Consequently, rocks in the "pipe" or chlorite zone show maximum lowering in their $\delta^{18}O$ values (Cathles, 1983; Beaty and Taylor, 1982; Green et al., 1983) because chlorite concentrates ^{16}O relative to most other silicate minerals and because of a higher temperature of alteration near the vents. Thus, the most altered rocks have high MgO and low $\delta^{18}O$ values (Franklin et al., 1981; Beaty and Taylor, 1982; Green et al., 1983).

The chlorite zone rocks from the three deposits in this study all have the lowest $\delta^{18}O$ values compared with rocks from other alteration zones. The $\delta^{18}O$ values of rocks in gradational zone and muscovite zones I and II vary between those of the chlorite zone and the country rocks. Whole-rock, MgO contents and $\delta^{18}O$ values of typical country rocks and altered rocks from the Anderson Lake and Spruce Point deposits are plotted in Figure 4. The country rocks have high $\delta^{18}O$ values with low values for MgO. On the opposite end, the chlorite zone rocks have high MgO content and low $\delta^{18}O$ values. The chlorite zone and the country rocks define a linear trend of negative correlation between the MgO and $\delta^{18}O$ values (Fig. 4). This correlation indicates that the extent of fluid-rock interaction decreased from the inner to the outer areas of the chlorite zone. The muscovite zones I and II have low values for both $\delta^{18}O$ and MgO relative to the country rocks. In the gradational zone, the MgO values are slightly higher and the $\delta^{18}O$ values lower than those of the country rocks. Rocks in the gradational zone and muscovite zones I and II from Anderson Lake plot below the linear trend between country rocks and chlorite zone. This may be due to a change in the composition of fluids or due to different temperature and water/rock ratio during alteration in these zones.

On the basis of the preceding discussion, it can be concluded that differences in the oxygen isotopic compositions of altered and country rocks at Anderson Lake, Spruce Point, and Centennial were most likely produced during ore-deposition, prior to metamorphism. This

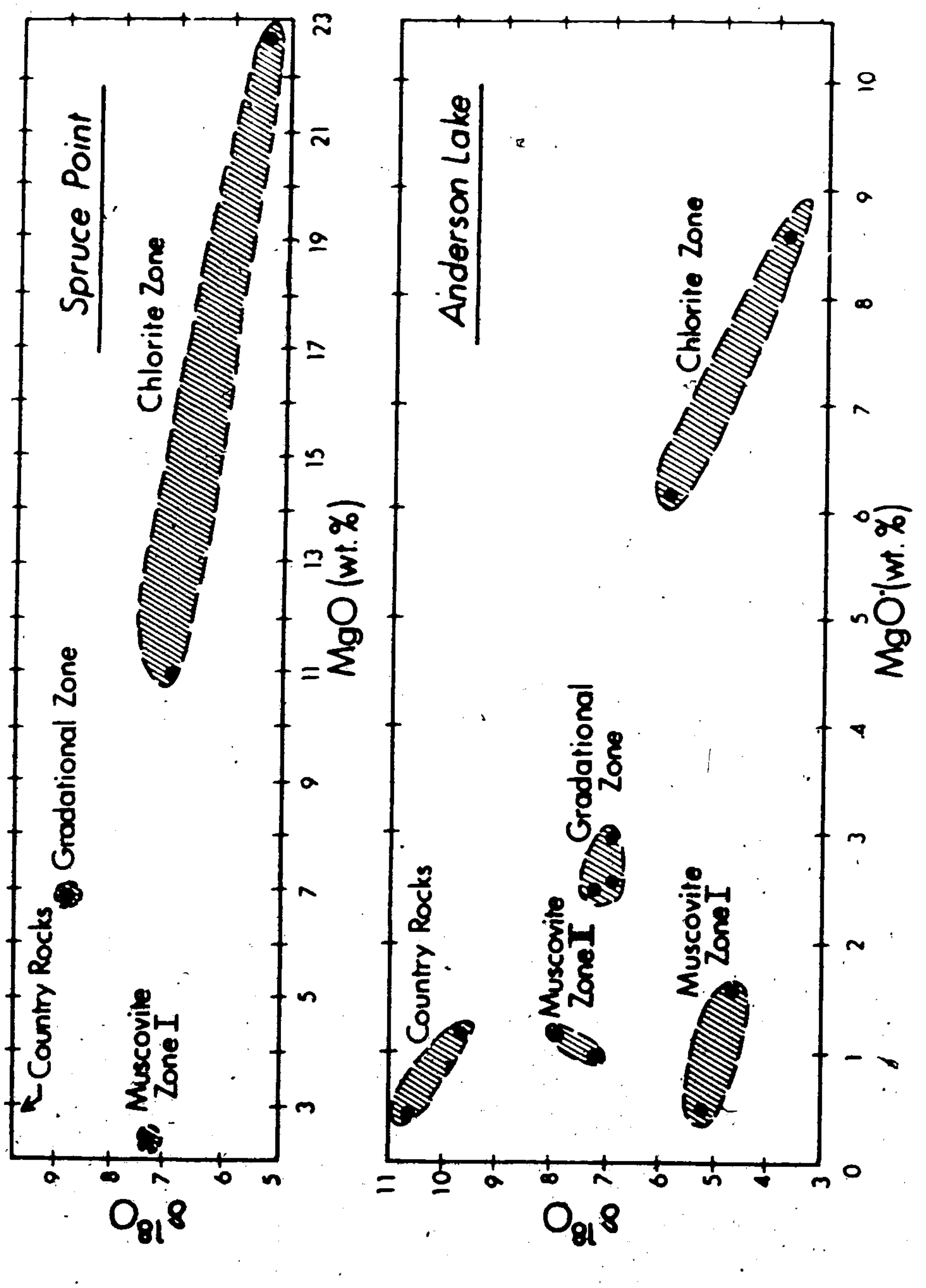

Figure 4. Whole rock, $\delta^{18}O$ versus MgO (wt %) diagram for altered rocks from Anderson Lake and Spruce Point. The chemical analyses were performed by the X-ray fluorosence technique (see Aggarwal et al., 1984, for details of the technique).

conclusion is consistent with the proposed origin of differences in the oxygen-isotope composition of rocks associated with massive sulfide deposits in other areas of varying metamorphic grade and age. Altered rocks at the unmetamorphosed, Fukazawa, Japan, and Cyprus deposits of Phanerozoic age have δ^{18}O values (+5 to +9 and +1.4 to +4.1) that are significantly lower than those of the country rocks (+15 to +21 and +8 to +13; Green et al., 1983; Heaton and Sheppard, 1976). Similar relationships are seen in massive sulfide deposits in low-grade metamorphic terranes of Archean age (South Bay and Corbet deposits, Canada; Urabe et al., 1983) At the Amulet "A" deposit of Archean age subjected to medium temperature contact metamorphism, the altered rocks have δ^{18}O values of +3.7 to +4.2, lower than those of the andesitic host rocks (+5.2 to +6.7; Beaty and Taylor, 1982). The lower δ^{18}O values of altered rocks at the above deposits are attributed to isotopic exchange with hydrothermal, ore-forming fluids.

In the only detailed oxygen-isotope study of a massive sulfide deposit subjected to medium-grade regional metamorphism, Addy and Ypma (1977) observed a lowering of upto 2 permill in the δ^{18}O values of wall-rocks relative to country rocks at the Ducktown, Tennessee deposits. They suggested that the deposit was in part syn-metamorphic and ascribed the lowering of isotopic compositions of the wall rocks to equilibration with ^{18}O-depleted, ore-forming solutions during metamorphism. However, petrologic and sulfur isotopic studies (Nesbitt and Kelly, 1980; Mauger, 1972) do not indicate any massive influx of fluids during metamorphism and suggest that the ores are pre-metamorphic. More recently, Woodruff et al. (1984) have suggested that the oxygen isotopic gradients associated with other ore deposits in the same geological province as Ducktown have probably survived the medium- to high-grade regional metamorphism in this terrane.

G. Effects of Metamorphism

The effects of metamorphism on the oxygen-isotope compositions of rocks depend on the nature of fluid-rock interaction. As has been discussed above, the rocks of this study did not equilibrate with a pervasive, externally derived fluid during metamorphism. Thus the isotopic exchange during metamorphism was attained by interaction with local pore fluids.

Under such conditions, the fluid-rock interaction can be described by a model of Raleigh distillation with chemical reaction between minerals (Rumble, 1982). In this model, the effects of metamorphism on the oxygen-isotope systematics are two fold. First, recrystallization homogenizes the isotopic compositions on a grain to grain scale. Second, the pre-metamorphic $\delta^{18}O$ value of the whole-rock changes as a result of devolatilization.

Isotopic Homogenization during Metamorphism

The oxygen isotopic compositions of rocks at the Anderson Lake, Spruce Point, and Centennial deposits all have been homogenized at least on a granular scale, as indicated by generally similar fractionation between co-existing mineral pairs and a decrease in quartz - muscovite or quartz - chlorite fractionation with increasing metamorphic grade (Tables 1, 2, and 3). Variations in the $\delta^{18}O$ values of minerals from rocks only a few meters apart in the same alteration zone or from different alteration zones suggest that isotopic homogenization beyond a granular scale was not extensive.

Isotopic fractionation between co-existing, metamorphic minerals together with calibrated mineral-water fractionation curves can be used to calculate metamorphic temperatures. Oxygen-isotope fractionation curves for muscovite-water and biotite-water have been determined by O'Neil and Taylor (1969) and Bertenrath and Friedrichsen (1975). The chlorite-water curve has been empirically calibrated by Wenner and Taylor (1971). Calibrations for the quartz-water fractionation have been proposed on the basis of theoretical and empirical studies (Bottinga and Javoy, 1973; Blattner, 1975) and experimental studies (Clayton et al., 1972; Matsuhisa et al., 1979). Depending upon the quartz-water fractionation used, calculated isotopic temperatures at Anderson Lake (Table 4) vary from 320 °C - 600 °C (quartz-muscovite), 400 °C - 540 °C (quartz-biotite), and 400 °C - 560 °C (quartz-chlorite). Quartz-muscovite fractionations at Spruce Point indicate temperatures of 300 °C - 500 °C. A single analyzed pair of quartz-chlorite from Centennial indicates temperatures of approximately 200°C - 300 °C.

Temperatures obtained by using empirical curves of quartz-water, oxygen-isotope fractionation are similar to the temperature of metamorphism at Anderson Lake and Spruce

Table 4. Oxygen-Isotope Temperatures for Anderson Lake, Spruce Point, and Centennial using empirical and experimental, mineral-water fractionation curves.

	Δ-	Temperature (°C)				
	Qtz-Min	1*	2*	3*	4*	5**
Anderson Lake						
Qz-Ms	2.9 – 2.7	520 – 540	540 – 655	440 – 490	320 – 370	545 – 605
Qz-Bt	6.7 – 4.7	400 – 575	420 – 565	400 – 540	390 – 490	
Qz-Ch	6.9 – 4.7	380 – 575	430 – 588	330 – 500	340 – 480	
Spruce Point						
Qz-Ms	3.4 – 3.2	470 – 490	485 – 520	380 – 400	290 – 320	425 – 525
Centennial						
Qz-Ch	7.6	350	350	290	280	<450

· the range of values in this column are the minimum and maximum values from Tables 1 and 2.

* temperatures calculated from the data of O'Neil and Taylor (1969) and the quartz-water data of (1) Bottinga and Javoy, 1973; (2) Blattner, 1975; (3) Clayton et al., 1972; and (4) Matsuhisa et al., 1979.

** estimated temperatures of metamorphism based on silicate equilibria (Chapter II).

Point estimated from silicate mineral equilibria (Table 4). However, experimentally determined quartz-water fractionation curves give much lower temperatures. This discrepency is probably due to errors in the calibration of either the experimental or empirical mineral-water fractionation curves and is as yet unresolved.

Another significant factor that affects temperature calculations is the chemical composition of minerals (Taylor and Epstein, 1962). The experimental determinations of oxygen-isotope, muscovite- and biotite-water fractionations are based on the end-member compositions of these minerals (muscovite = $KAl_3Si_3O_{10}(OH)_2$, biotite = $K(Fe,Mg)_3AlSi_3O_{10}(OH)_2$) However, muscovite and biotite from rocks of this study contain significant substitutions in the octahedral and/or tetrahedral sites. An approximate magnitude of the effect of these substitutions on the isotopic compositon of a mineral can be estimated from isotopic fractionations between diopside-jadeite and albite-anorthite. The isotopic fractionation between albite and anorthite gives the magnitude of the isotopic shift due to the replacement of Si in a tetrahedral site as the effect of Ca-Na substitutions is negligible (Taylor and Epstein, 1962). Similarly, the magnitude of the isotopic shift due to the replacement of Al in a octahedral site is given by the fractionation between diopside and jadeite. Albite-anorthite and jadeite-diopside have a permill fractionation, respectively, of 1.61 and 1.46 at 550 °C (Matthews et al., 1983). At 500 °C, the corresponding fractionations are 1.82 and 1.66 permill. Thus at 550 °C, the substitution of Si by Al on one tetrahedral site decreases the $\delta^{18}O$ value of the mineral by 1.61 permill whereas the substitution of Mg/Fe by Al on one octahedral site increases the $\delta^{18}O$ value of the mineral by 1.46 permill.

Electron microprobe analyses of muscovites from Anderson Lake and Spruce Point indicate that 0.2 to 0.3 of the octahedral aluminum sites per formula unit have been replaced by Mg and/or Fe (Chapter IV). If the isotopic effects of substitutions in muscovite are similar to those in the pyroxenes, the $\delta^{18}O$ value of muscovites in this study could be lower by 0.3 to 0.5 permill compared with the value for end-member muscovite at temperatures of 550 °C to 450 °C.

In the case of biotite and chlorite, Al substitutes for approximately 0.4 of the octahedral Mg/Fe site and 0.25 of the tetrahedral Si site. The effects of these two substitutions are opposite to each other. Consequently, the $\delta^{18}O$ values of biotites and chlorites analyzed from Anderson Lake could be approximately 0.1 to 0.2 permill lower than those of the end-member annite/phlogopite and Fe/Mg-chlorite.

In order to estimate the errors in temperature calculations due to errors in the calibration of mineral-water curves and due to compostional effects, quartz-muscovite fractionations from Anderson Lake and Spruce Point have been plotted in Figure 5. After corrections for compositional effects as discussed above, quartz-muscovite fractionations from Anderson Lake indicate temperatures in excess of 700 °C based on the quartz-water curve of Blattner (1975) and 575 °C to 600 °C based on the curves of Bottinga and Javoy (1973). Quartz and muscovite data from Spruce Point indicate temperatures of 575 °C to 600 °C, using Blattner's (1975) curve and 500 °C to 575 °C, using the curve of Bottinga and Javoy (1973). Quartz-muscovite curve based on the experimental, quartz-water curve of Matsuhisa et al. (1979) indicates a reversal in the sign of the fractionation between quartz and muscovite above 500 °C. This reversal in the sign of mineral-mineral fractionation is rather unlikely (Matthews et al., 1983) and indicates errors in the experimental calibration of quartz-water or muscovite-water fractionation. The temperatures indicated by the curves of Bottinga and Javoy are in excellent agreement with the estimated temperatures of metamorphism at Anderson Lake and Spruce Point. However, Matthews et al. (1983) suggest that the theoretical basis used by Bottinga and Javoy in deriving their equations is not consistent with experimental data for many mineral-water systems. The above discussion underscores the fact that the reasons for the discrepency in calculated temperatures using the oxygen-isotope data may be far from understood (see also Clayton, 1981).

Effects of Devolatilization

The change in $\delta^{18}O$ value of the whole-rock due to devolatilization is a result of the loss of oxygen-bearing species to the fluid phase. In general, devolatilization at high temperatures lowers the $\delta^{18}O$ value of a rock as H_2O and CO_2 are the major species in most metamorphic fluids. The extent of lowering of the $\delta^{18}O$ value varies with the atomic proportion of the total oxygen in the rock that is lost to the fluid. Thus an increase in the proportion of CO_2 in the

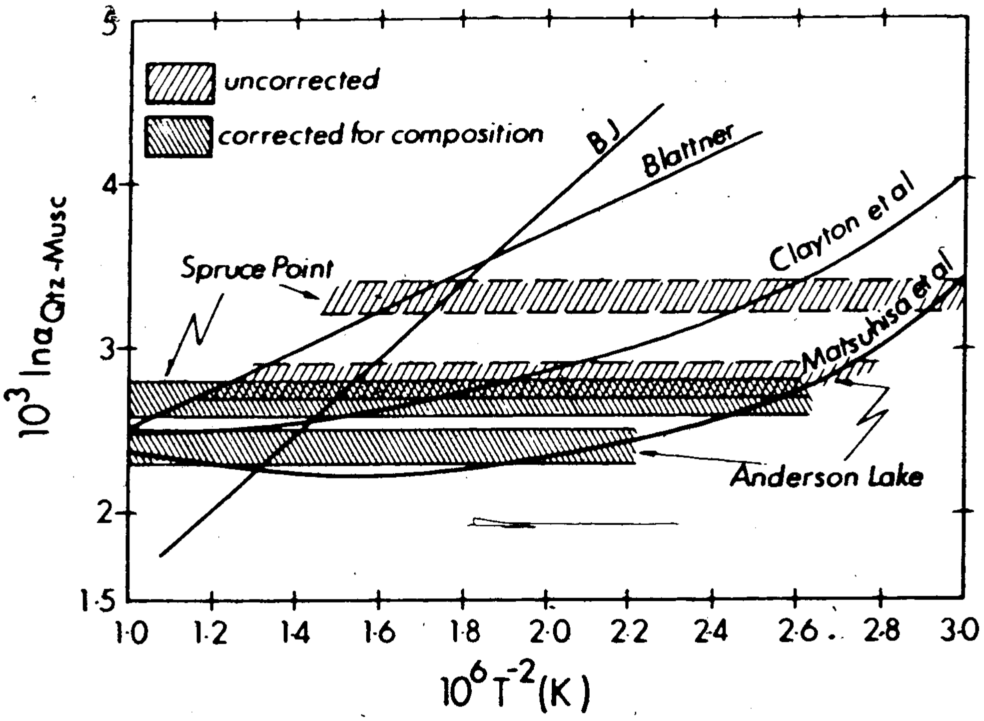

Figure 5. Oxygen isotopic fractionation curves for the quartz (qtz) - muscovite (msuc) pair derived by combining the muscovite-water data of O'Neil and Taylor (1969) and the quartz-water data of Bottinga and Javoy, 1973 (BJ); Blattner, 1975 (Blattner); Clayton et al., 1972 (Clayton e al); and Matsuhisa et al., 1979 (Matsuhisa et al). The hatched area, show the range of quartz-muscovite fractionaitons at Anderson Lake and Spruce Point, before and after the corrections for compositonal effects. See text for details of the corrections.

fluid has a greater effect on the $\delta^{18}O$ value of the rock.

Model calculations of the change in the isotopic composition of a zoisite - calcite - garnet - quartz rock have been reported by Rumble (1982). Devolatilization in this rock was modeled according to the reaction:

$$2\ \text{Zoisite} + 5\ \text{Calcite} + 3\ \text{Quartz} = 3\ \text{Grossular} + 5\ CO_2 + H_2O$$

in which approximately 20 atomic percent of the total oxygen in the rock are lost to the fluid, mainly in CO_2. Calculations show that even a complete devolatilization according to the above reactions would change the whole-rock $\delta^{18}O$ value by less than two permill. Consequently, devolatilization of rocks with little or no carbonaceous constituent would produce even lower change in the $\delta^{18}O$ value. The metamorphic fluid in equilibrium with the rocks of this study consisted essentially of H_2O (Chapter IV). Thus it is likely that the pre-metamorphic whole-rock $\delta^{18}O$ values of these rocks did not change significantly.

H. Nature of Hydrothermal Alteration at Anderson Lake, Spruce Point, and Centennial

The isotopic compositions of altered rocks associated with massive sulfide deposits are a function of the $\delta^{18}O$ values of the rocks before alteration, the $\delta^{18}O$ value of the fluids, the temperature of alteration, and the water-rock ratios (W/R) during alteration. In order to study the nature of the hydrothermal system at Anderson Lake, Spruce Point, and Centennial, the change in the isotopic composition of a rock was calculated as a function of temperature and W/R using the mass-balance relationship given by equation (1). The initial $\delta^{18}O$ value of the rock was assumed to be +8, in the normal range of values for igneous rocks of rhyolitic composition (Taylor, 1968). Calculations were performed at several temperatures with three initial $\delta^{18}O$ values of the fluid, -3, 0, and +3. These values are within the range of $\delta^{18}O$ values for hydrothermal fluids at massive sulfide deposits and at the present-day hydrothermal systems on the sea floor (Ohmoto et al., 1983). Results of these calculations are shown in the diagrams in Figure 6. Also plotted on these diagrams are the range of $\delta^{18}O$ values of the altered rocks of this study.

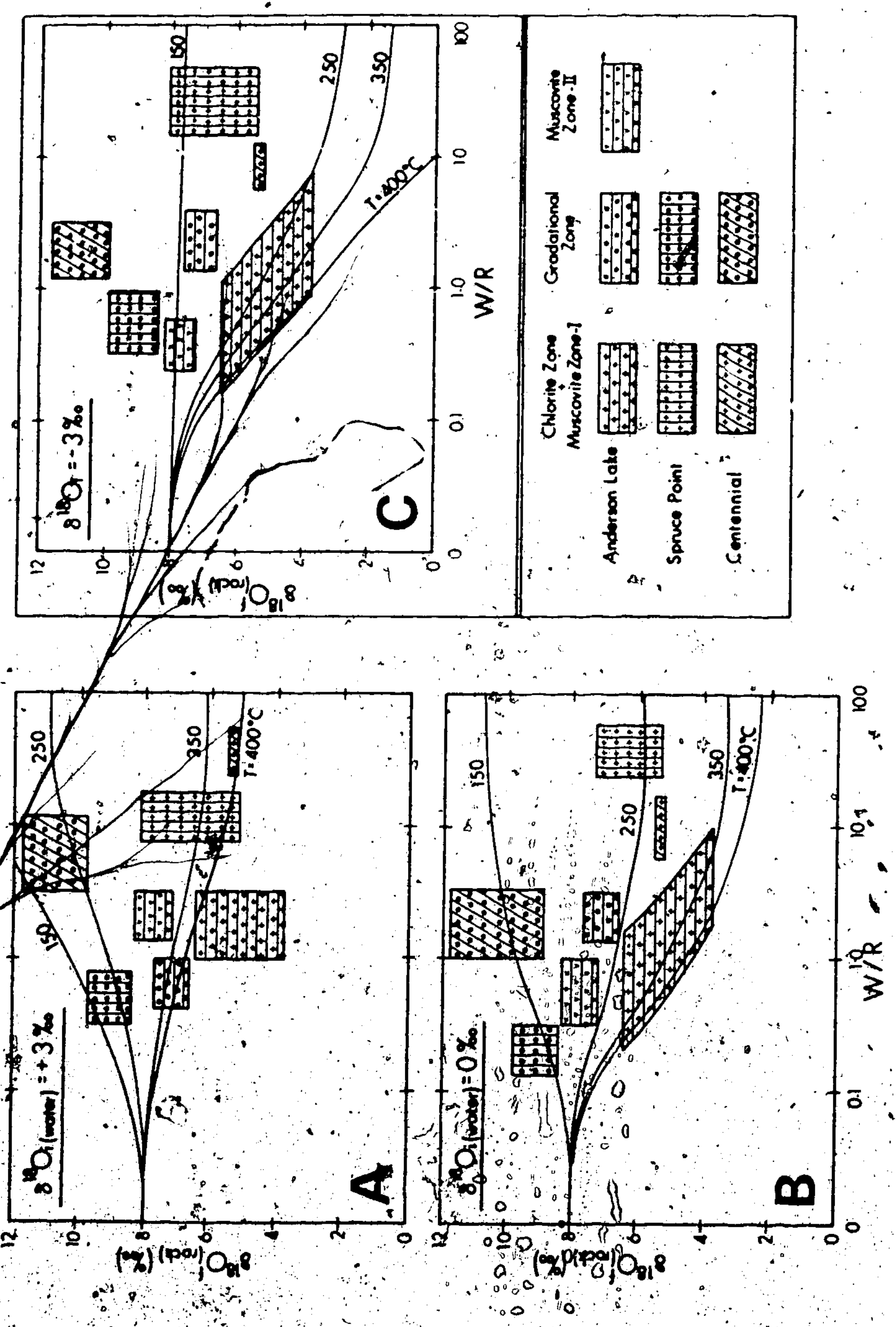

Figure 6. $\delta^{18}O$ - Water-rock ratio (W/R) diagram showing the change in $\delta^{18}O$ value of a rock as a function of W/R (atom % oxygen) during equilibrium isotope exchange at constant temperature. The range of isotopic values of the altered rocks at Centennial, Spruce Point, and Anderson Lake are plotted. See text for discussion and the procedure of calculation.

Temperature and Isotopic Composition of the Fluids

It can be seen on Figure 6 that in order to produce the observed $\delta^{18}O$ values of the altered rocks at Anderson Lake, Spruce Point, and Centennial, the hydrothermal fluids would have a temperature of between 200 °C and 400 °C with $\delta^{18}O$ values of approximately -3 to +3. These limits on temperature are consistent with those observed in present-day hydrothermal systems on the sea-floor (~300 ± 100 °C) and with the temperatures calculated for hydrothermal alteration in the chlorite zone at other ore deposits (Franklin et. al., 1981; Green et al., 1983). A lower temperature limit of 200 °C is also consistent with the studies of solubility of Cu and Zn (Barnes, 1979). The solubility of Cu and Zn decreases sharply at temperatures below 200 °C. Therefore, these metals are unlikely to be transported in sufficient quantities at lower temperatures to form an ore deposit..

$\delta^{18}O$ values of fluids significantly beyond the range of 0 ± 3 would require very low values of W/R (<1) for alteration even in the chlorite zone (Fig. 6). As mentioned earlier, the chlorite zone represents the venting area of the hydrothermal fluids and rocks in the zone must have interacted with large quantities of the fluids, i.e. high W/R. In addition, mass-balance on other elements, for example Mg, do not support low values of W/R in the chlorite zone.

The relationship for mass-balance on Mg can be formulated as:

$$W/R = (Mg(f) - Mg(i))_{rock} / (Mg(i) - Mg(f))_{water} \qquad (2)$$

where Mg is the Mg content (by weight) of the rock and water before (i) and after (f) alteration. W/R is the water-rock ratio in mass units and is approximately equal to twice the W/R given by equation (1). The initial Mg value for water is the Mg content of water in the reservoir feeding the hydrothermal system. This water undergoes water-rock interaction prior to entering venting area (i.e. the chlorite zone) and loses most of its Mg. Thus the Mg(f) value of water in equation (2) refers to the Mg content of water at the time it entered the venting area. If we consider that the hydrothermal fluids involved in alteration and ore-depositon at the ore deposits of this study were similar to the present-day seawater (Mg=0.13 wt%) then the maximum value for the factor (Mg(i) - Mg(f)) water in equation (2) would be 0.13. Substitution of this value for calculations using equation (2) would only give a minimum value for W/R.

Using the MgO content of rocks from Anderson Lake (Fig. 3), equation (2) gives a minimum W/R of approximately 30 for the chlorite zone and approximately 9 for the gradational zone.

The above calculations indiate high W/R for the altered rocks; it is likely that the $\delta^{18}O$ values of the hydrothermal fluids were approximately 0±3. Because of the high W/R, a change in the assumed initial $\delta^{18}O$ value of the rocks (+8) would not significantly affect the calculated range of 0±3 for the $\delta^{18}O$ value of the hydrothermal fluids.

Chlorite Zone and Gradational Zone

The chlorite zone rocks have $\delta^{18}O$ values of +5.3 at Centennial and +5.4 to +7.3 at Spruce Point. The gradational zone at Centennial and Spruce Point deposits has $\delta^{18}O$ values of +9.9 to +11.7 and +8.4 to +9.7, respectively. The chlorite and gradational zone rocks from Anderson Lake (+3.7 to +5.9 and +6.6 to +7.7, respectively) have lower values compared with those of rocks from Spruce Point and Centennial. These differences in the $\delta^{18}O$ values of rocks could be produced due to variations in temperature and/or the $\delta^{18}O$ of the fluids (Pisutha-Arnold and Ohmoto, 1983). The effect of variations in W/R would be negligible because of the high values for W/R in these zones (see earlier discussion).

An insight into the reasons for lower $\delta^{18}O$ values at Anderson Lake is provided by the relative concentrations of Cu and Zn at the three deposits. The Anderson Lake deposit consits of 3.4% Cu and 0.1% Zn (Price, 1978) with a Zn/Cu ratio of much less than 1. On the other hand, the Centennial (Cu = 2.2%, Zn = 4.1%) and Spruce Point (Cu = 2.7%, 4.3%) deposits both have Zn/Cu ratio of around 2 (Walford and Franklin, 1982).

The relative solubilities of Cu and Zn are significantly influenced by the temperature of the hydrothermal solutions. Cu is generally more soluble than Zn at higher temperatures (Barnes, 1979). The Zn/Cu ratio in the ore body also reflects the temperature of the hydrothermal solutions. Ohmoto et al. (1983) have calculated the relative concentrations of Cu and Zn in the precipitate from solutions of compositions similar to those from the Kuroko deposits. These calculations indicate that the Zn/Cu ratio of the precipitate increases with a decrease in the temperature of the hydrothermal solutions at the time of the begining of precipitation. Thus the higher Zn/Cu ratio in the Centennial and Spruce Point deposits may reflect a lower temperature of the hydrothermal solutions at these deposits compared with the temperature of the solutions at the Zn-poor, Anderson Lake deposit. These differences in temperature may be responsible for the generally lower δ^{18}O values of the altered rocks at Anderson Lake.

Muscovite Zone-I

At the Anderson Lake and Spruce Point deposit, a thin shell of muscovite zone-I infrequently occurs between the chlorite zone and the gradational Zone. Rocks in the muscovite zone-I have δ^{18}O values of +7.8 to +8.1 at Spruce Point and +4.7 to +6.4 at Anderson Lake. These values are similar to or slightly higher than those of the chlorite zone at these deposits (Spruce Point= +5.3 to +7.3; Anderson Lake = +3.7 to +6.2), despite significant mineralogical differences in the two zones. The MgO content of rocks in the muscovite zone-I are very low (0.5 to 1%, Fig. 3) as opposed to the Mg-rich rocks of the chlorite zone.

δ^{18}O values of the altered rocks are buffered by those of the fluids at very high W/R, regardless of the chemical compositon of the alteration product, as long as the initial composition of the rocks were the same (Fig. 4). As the W/R in the chlorite zone were likely very high (>30), the similar δ^{18}O values of rocks in the muscovite zone-I and chlorite zone suggest that the temperature and δ^{18}O values of the fluids during alteration in these zones were virtually the same.

The occurrence of muscovite zone surrounding the chlorite zone at several other massive sulfide deposits has been considered to be due to hydrogen metasomatism of the early formed chlorite or the wall rocks (Riverin and Hodgson, 1980; Urabe et al., 1983). Hydrogen ions required for this metasomatism are thought to be contributed by the precipitation of chlorite by reactions of the type:

$$5\ Mg^{2+} + 2\ Al^{3+} + 3\ SiO^{2} + 6\ H^{2}O = \text{Clinochlore} + 12\ H^{+}$$

The hydrogen ions released in such reactions will significantly decrease the pH of the fluids.

With a decrease in pH, chlorite becomes unstable and muscovite may be produced by hydrogen metasomatism either of early formed chlorite or of plagioclase in the wall rocks (Bowers et al., 1984). Thus the temperature and isotopic composition of the fluids in the muscovite zone-I could nearly be the same as in the chlorite zone. This is consistent with the isotopic and chemical compositons of the muscovite zone rocks from Anderson Lake and Spruce Point.

Muscovite Zone-II

This zone occurs only at the Anderson Lake deposit where it forms an envelope around the ore-body (Figs. 7, 8). It is overlain in the hangingwall by country rocks. In the footwall, it overlies rocks of the gradational zone. Away from the ore-body, the muscovite zone-II defines the ore-horizon. Walford and Franklin (1982) suggest that rocks in this zone are of epiclastic origin and have not been altered during ore-deposition. The oxygen-isotope compositions of rocks, however, do not support a lack of alteration in this zone.

The muscovite zone-II has a narrow range of $\delta^{18}O$ values (+7.2 to +8.3), both laterally and vertically. This is indicated by samples collected from 2650 and 1600 levels in the Anderson Lake mine (Figs. 7, 8). These values are higher than those of other altered rocks and are lower than those of metavolcanic, country rocks. The $\delta^{18}O$ values of the muscovite zone-II are also lower than those of clastic rocks in the area (+11.0 to +13.0).

The $\delta^{18}O$ values of clastic sedimentary rocks vary between those of the clay minerals and the precursor rocks. Clastic metasedimentary rocks analyzed from Archean, greenstone belts have $\delta^{18}O$ values that are nearly the same or higher than those of the felsic metavolcanic rocks (Longstaffe and Schwarcz, 1977; Longstaffe et al., 1981). Lowest $\delta^{18}O$ values are found in rocks which consist mostly of volcanic rock fragments. Thus the lower $\delta^{18}O$ values of the muscovite zone-II at Anderson Lake, compared with those of the metavolcanic rocks, indicate that they have been hydrothermally altered. Whether they were of clastic sedimentary or volcanic origin can not be determined from the oxygen isotopic compositions alone.

The mineralogical and chemical compositions of rocks in the muscovite zone-II are similar to those of muscovite zone-I rocks. Thus, the muscovite zone-II may also have originated, at least in part, by hydrogen metasomatism. Higher $\delta^{18}O$ values of muscovite zone-II rocks may be due to lower temperatures of alteration in this zone compared with the muscovite zone-I. The extensive development of this zone requires a large source of hydrogen ions late in the history of ore-deposition. One such source is the ore-body itself. Sulfide and silicate minerals in the ore-zone are deposited due to cooling of the ore-bearing solutions and mixing with fresh, cooler fluids (Ohmoto et al., 1983; Aggarwal and Nesbitt, 1984). The deposition of pyrite and chalcopyrite can be represented by the following reactions:

$$Fe^{2+} + 0.5\ O_2 + H_2S = FeS_2 + 2\ H^+ + H_2O$$

$$Cu^+ + Fe^{2+} + 2\ H_2S = CuFeS_2 + 3\ H^+$$

For every mole of pyrite or chalcopyrite deposited, 2 or 3 moles of hydrogen ions will be released. The sharp decrease in pH brought about by the deposition of the ore-body would shift the solution composition in the muscovite field, as discussed earlier. However, if the temperature of the ore-bearing solutions is not sufficiently high, the decrease in temperature due to mixing with cooler fluids may prevent the shift of the solution composition to the muscovite field as the stability of muscovite decreases with a decrease in temperature (Bowers et al., 1984). This may inhibit the development of the muscovite zone-II.

Rocks in the muscovite zone-II at Anderson Lake commonly contain pyrite and chalcopyrite and indicate significant grades of ore (Walford and Franklin, 1982). This suggests that the ore-forming solutions had not been cooled below approximately 200 °C during the formation of this zone, (see the earlier discussion on temperatures of the ore fluids). The absence of the muscovite zone-II at Spruce Point and Centennial deposits may indicate a lower temperature of the hydrothermal solutions at these deposits, consistent with the generally higher $\delta^{18}O$ values of rocks from these deposits.

The metasomatic origin of the muscovite zone-II proposed above can only be applicable to the development of this zone in the footwall, close to the ore body. The occurrence of the muscovite zone-II adjacent to and in the hangingwall of the ore body may be due to a continuation of the hydrothermal activity after ore deposition. A similar origin has been proposed for the existence of the muscovite zone overlying the Fukazawa deposit in Japan (Green et al., 1983).

I. Applications to Exploration for Cu-Zn-Fe Massive sulfide deposits 7

A major effort in exploration for volcanogenic, Cu-Zn-Fe massive sulfide deposits is concentrated in locating the "pipe" alteration characterized by Mg-rich, chlorite zone. The potential of using the isotopic compositions in locating such alteration zones, indicated by the low $\delta^{18}O$ values of altered rocks, has been emphasized by many workers (Beaty and Taylor, 1982; Green et al., 1983; Urabe et al., 1983). The presence of these compositional and isotopic gradients after low- to medium-grade, regional metamorphism, as exemplified by this study, is significant for exploration for massive sulfide deposits in metamorphosed terranes. However, a good correlation between mineralogical and isotopic signatures of ore-related alteration makes the expensive, oxygen-isotope technique rather unattractive for regional exploration. But for exploration in an existing mineralized district, the oxygen-isotope analyses may prove to be very effective in identifying weakly altered rocks from unaltered rocks. Isotopic relationships at Anderson Lake can be used to illustrate this point.

Figures 7 and 8 are horizontal sections of the Anderson Lake mine at, respectively, 1600 and 2650 levels. At the 2650 level, the lower end of the chlorite zone is intersected which appears in part as a "semi-conformable" zone. The ore-body pinches out to the east and west where the ore-horizon is represented by the muscovite zone-II.

The gradational zone rocks immediately below the ore-body on 1600 level show significant mineralogical differences compared with the country rocks. These rocks have $\delta^{18}O$ values of +6.6 to +7.0, characteristic of gradational zone rocks elsewhere in the deposit. On the 2650 Level, the rocks between the muscovite zone-II and chlorite zone have fairly uniform mineralogical composition. The MgO-contents of these rocks also do not show a distinct trend of variation. Thus the mineralogical and chemical criteria cannot be used to classify these rocks as altered and country rocks. However, the isotopic compositions can be used to easily identify the altered rocks. Samples 26-06, 78-30, and 78-68, collected from below the ore body, have $\delta^{18}O$ values ranging from +7.2 to +7.5. These values are towards the upper end of the range for values in the gradational zone (+6.6 to +7.7). This indicates only minor hydrothermal alteration of these rocks, consistent with the absence of significant mineralogical characteristics of alteration. In contrast, samples collected only 30 to 40 meters above the muscovite zone-I in

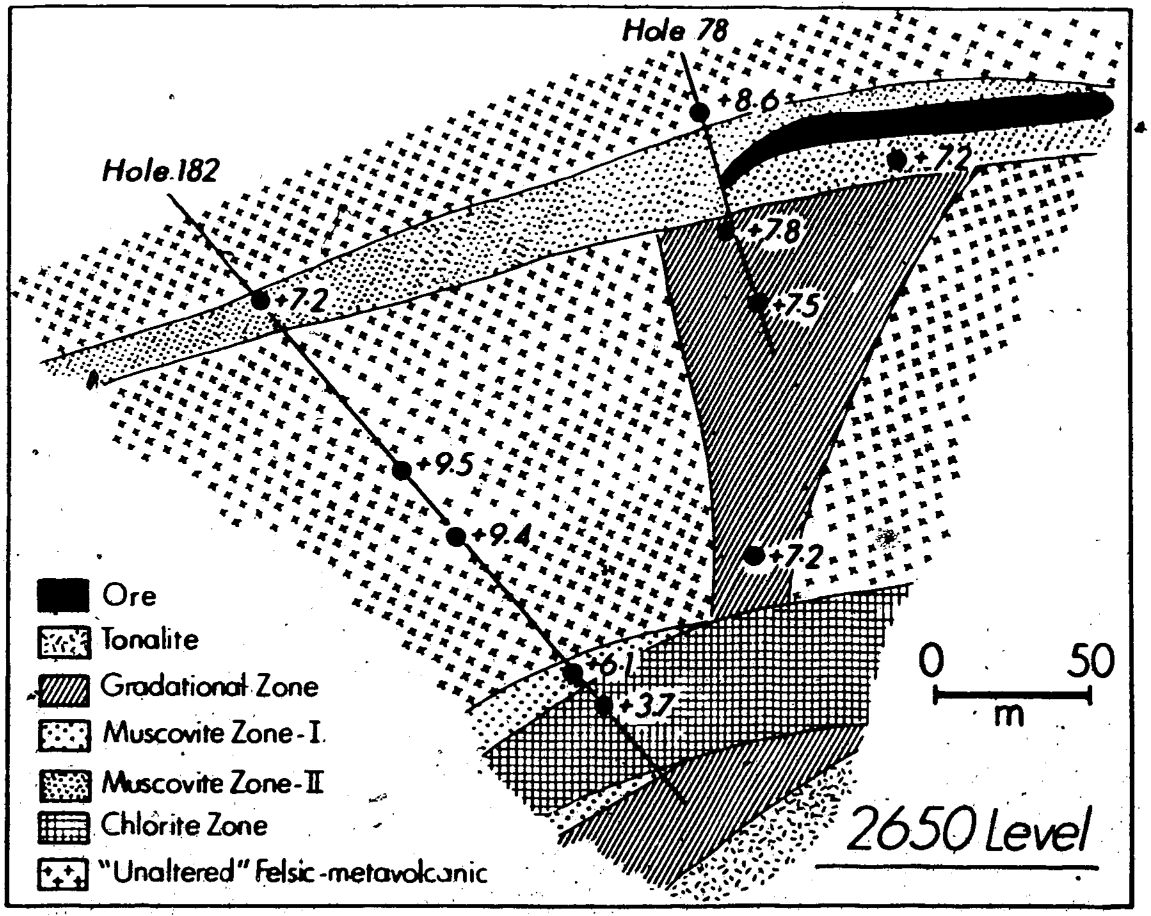

Figure 7. Horizontal section of the Anderson Lake ore body at 2650 Level. Oxygen isotopic composititions of samples from subsurface exposures and drill holes are plotted. Limits of the gradational zone are only schematic, based on the isotopic data.

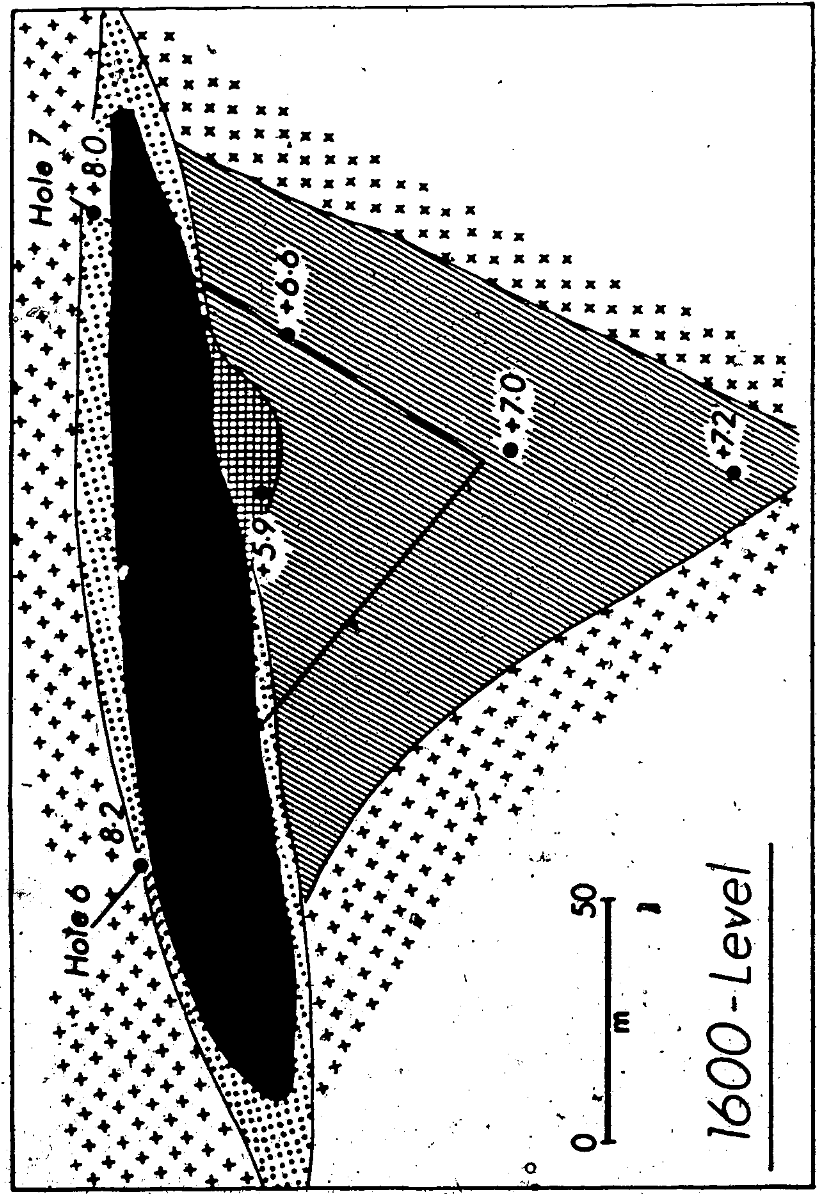

Figure 8. Horizontal section of the Anderson Lake ore body at 1600 Level. Oxygen isotopic composititions of samples from subsurface exposures and drill holes are plotted. Limits of the gradational zone are only schematic, based on the isotopic data. The symbols are the same as in Figure 7.

drill-hole 182 (samples 182-425 and -520) have much higher δ^{18}O values (+10.9 to +11.0) that are similar to those of country rocks. It is interesting to note that hole 182, or holes drilled further east of it, did not intersect the ore-zone that had pinched out further west. Thus the oxygen isotopic analyses can be very effective in delineating the extent of the hydrothermal system in a mineralized area.

J. Conclusions

Altered rocks associated with metamorphosed massive sulfide deposits of the Flin Flon - Snow Lake belt, Manitoba have significantly lower δ^{18}O values compared with the country rocks. These low values were produced by isotopic exchange with low-^{18}O, hydrothermal solutions during ore-formation, prior to metamorphism. The hydrothermal solutions had a temperature of 200 °C to 400 °C and δ^{18}O values of approximately -3 to +3. The solutions at Anderson Lake were probably hotter than those at Centennial and Spruce Point. Differences in the isotopic compositions of the altered and country rocks survived the low-greenschist to amphibolite-facies metamorphism. During metamorphism, the isotopic compositions were homogenized at least ~~on a~~ granular scale and to a maximum of a scale of meters. Whereas the isotopic analyses are significant in regional exploration, it is suggested that this technique may be more effective for exploration in an existing mineralized terrane.

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IV. Metamorphism of Massive Sulfide Deposits of the Flin Flon - Snow Lake Belt, Manitoba

A. Introduction

It has long been recognized that the presence of sulfide and oxide minerals has a significant impact on the composition of silicate minerals and the fluid phase in metamorphic rocks (Chinner, 1960; Thompson, 1972; Hounslow and Moore, 1967). However, an examination of such effects around ore deposits has received relatively less attention (Froese, 1969; Bachinski, 1976; Hutcheon, 1979; Nesbitt, 1982, Petersen, 1984). Detailed studies of sulfide-oxide-silicate equilibria in sulfide ore deposits (Nesbitt, 1982; Petersen, 1984) indicate that ore-host rock interaction during metamorphism results in systematic variations in the mineral assemblages and the compositions of ferro-magnesian silicate minerals. The mineralogical and mineral-chemical effects of ore-host rock interaction are a product of variations in the activities of components, principally oxygen and sulfur, of the metamorphic fluid phase. These variations in the activities of the volatile components are considered to be a result of the migration of species produced by sulfidation/desulfidation reactions during metamorphism. Thus depending on the buffering capacity of the rocks with respect to the volatile species, the effects of ore-host rock interaction may vary from deposit to deposit. In addition, the nature of fluid-rock interaction is dependent upon the relationship between the lithostatic pressure (P total) and fluid pressure (P fluid) (Bruton and Helgeson, 1983). Consequently, to develop a generalized model of the metamorphism of ore deposits and sulfide-bearing rocks, it is first necessary to understand the diverse effects of metamorphism on ore deposits with varying conditions of fluid-rock interaction.

In this paper, we report the results of a petrological study of three ore-deposits from the Flin Flon - Snow Lake belt, Manitoba. These deposits occur in similar host rocks and have been metamorphosed at low-greenschist to low-amphibolite facies. The objective of the paper is to determine the nature of fluid-rock interaction during metamorphism and its effect on the mineralogy and mineral compositions of the ore and the host rocks.

B. Methods

Samples for this study were collected in the vicinity of three ore deposits in the Flin Flon - Snow Lake belt: Centennial in the west, Spruce Point in the center, and Anderson Lake in the east (Fig 1). In addition, samples were collected from underground exposures and diamond-drill cores at the three deposits. Some 250 polished thin-sections were studied using transmitted- and reflected-light microscopes and electron microprobe.

Mineral Analyses

All mineral analyses were obtained by the energy-dispersive technique using an ARL-SEMQ electron microprobe. An accelerating voltage of 15.0 KV and an aperture current of 220 to 240 nano-amperes were used. Counting times for both the standards and the samples were 240 seconds at a rate of approximately 5000 counts per second. Natural silicate standards were used for all elements and the data were processed by the program EDATA2 (Smith and Gold, 1979). The statistical error at 99% confidence level is ±1% of the amount present for the major elements and may be as high as ±10% for minor elements.

Thermodynamic Calculations

In all thermodynamic calculations reported in this study, the standard state for the solid phases is defined as the stable form of the pure phase at the temperature and pressure of calculation. For gaseous phases, the standard state is a hypothetical ideal gas at one bar and temperature of calculation. Calculations involving solid-solutions were corrected for the activity of end-member phases. The activity models used for various phases are as follows:

garnet: natural garnets contain significant amounts of Mn and Ca in their structure. The solid solution of these cations is non-ideal in Fe-Mg garnets (Ganguly and Kennedy, 1974; Ganguly and Saxena, 1984). The free-energy interaction parameters, Wij, derived by Ganguly and Saxena (1984) are given in Table 1.

biotite: in addition to Fe and Mg, metamorphic biotites contain significant amounts of Na, Ti,

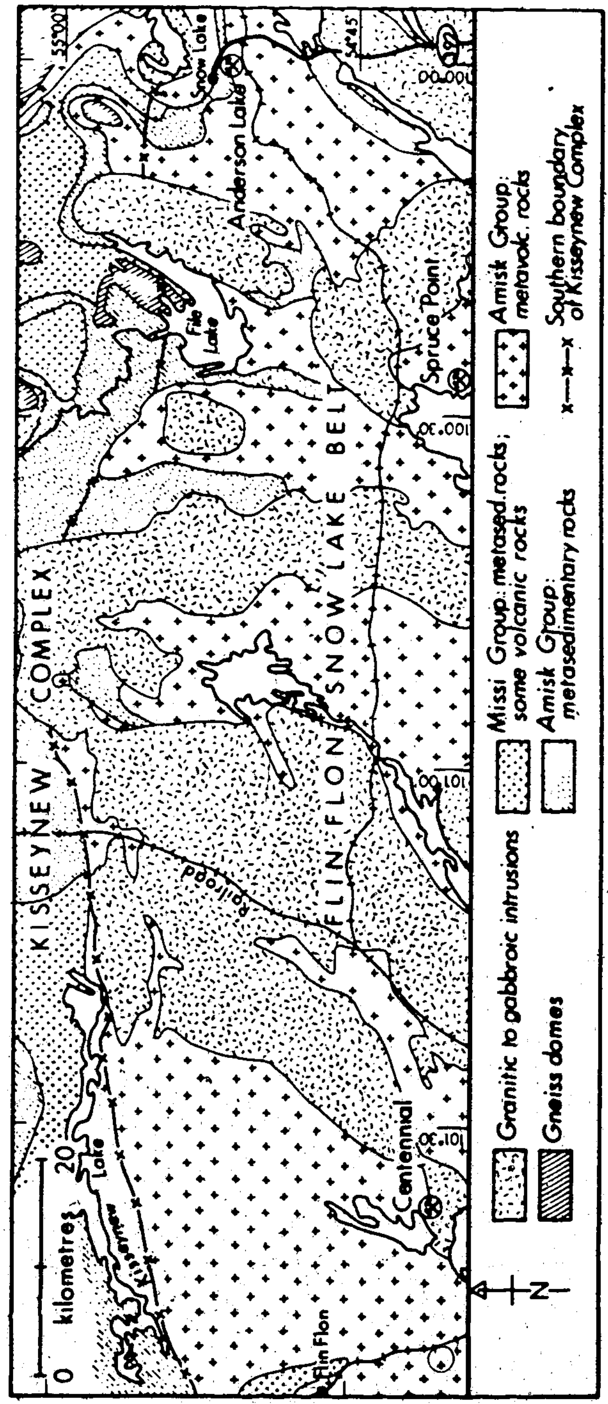

Figure 1. Regional geology of the Flin Flon - Snow Lake belt (after Froese and Moore, 1980) and the location of the present study areas.

Table 1. Mixing Data for the Garnet and Muscovite Solid Solutions
(in cal/mole cation)

Garnets	
W(Fe-Mg)	200
W(Mg-Fe)	2500
W(Ca-Mg)	4050 - 1.5T(K)
W(Mg-Ca)	1000 - 1.5T(K)
W(Ca-Fe)	-630 - 1.5T(K)
W(Fe-Ca)	4620 - 1.5T(K)
W(Mg-Ca)-W(Fe-Ca)	3000
W(Mg-Mn)-W(Fe-Mn)	3000
Muscovites	
W(Par)	2923.1 + 0.16P(bars) + 0.17T(K)
W(Mus)	4650 - 0.11P(bars) + 0.39T(K)

and excess Al compared to biotites along the annite - phlogopite join (Holdaway, 1980). The solid solution of Mg and Fe in biotite has been considered to be ideal by many workers (Muller, 1972; Ganguly and Kennedy, 1974). Experimental studies of fluid - mineral exchange equilibria (Schulien, 1980) also indicate that Fe and Mg mix ideally in biotite along the annite - phlogopite join. However, if a significant amount of Fe^{3+} is present, the biotite solid solution becomes non-ideal (Beane, 1974; Schulien, 1980). The Fe^{3+} content in most biotites from Anderson Lake and Spruce Point is between 3 to 8 mole% and, therefore, the solid solution of Fe and Mg is considered to be ideal. Owing to the lack of any activity composition data, the mixing of Na, Ti, and Al in the biotite solid solution is also considered to be ideal which results in:

$a(ann) = XK\,(XFe)^3\,(XSi)^4$ (Holdaway, 1980; Zen, 1985).

Xi, the mole fraction of the ith cation, is defined as:

$Xi = Ni / \Sigma R$ where Ni is the number of ith cations on a site containing a total of R cations.

Using the above expression for the activity of annite, the mole fraction of annite in biotite is given as:

$\log Xann = \log a(ann)/3$

paragonite: the solid-solution of muscovite and paragonite is non-ideal (Chatterjee and Froese, 1975; Eugster et al., 1972). The activity coefficient of paragonite in muscovite can be calculated by assuming a binary solution between muscovite and paragonite components or a quaternary solution with K-celadonite and Na-celadonite as additional components. Results based on the two models, however, do not differ significantly (Pigage and Greenwood, 1982). For the ease of calculations, I have used the two-parameter margules equation of Chatterjee and Froese (1975), assuming a binary solution between muscovite and paragonite. Free-energy interaction parameters based on this model are given in Table 1.

plagioclase: activity-composition relations in the plagioclase solid-solution have been experimentally studied at 700 °C and 2 kb (Orville, 1972) and at 600 - 800 °C at 2 kb (Seil and Blencoe, 1979). Saxena and Ribbe (1972) presented an analytical expression for the activity coefficient (γan) of anorthite in plagioclase using a regular soltion model based on Orville's (1972) data. Blencoe et al. (1982) argue that Saxena and Ribbe's (1972) model indicates a maximum in the value of γan at $Xan = .3$ and that it is inconsistent with the experimental results. To avoid this inconsistency, Blencoe et al. (1982) proposed a new expression for γan which gives essentially the same results as that of Saxena and Ribbe (1972) for plagioclase compositions of $Xan > 0.3$. In the present calculations, the activity of anorthite in the plagioclase solid-solution was calculated using the model proposed by Blencoe et al. (1982).

zoisite: an ideal ionic solution model was used assuming the mixing only of Fe and Al in the octahedral site (Bird and Helgeson, 1981). This results in the following expression for the activity of zoisite:

$a(\text{zoisite}) = (XAl)^3$

staurolite: there has been considerable controversy regarding the chemical formula of staurolite (Richardson, 1968; Ganguly, 1972; Griffen and Ribbe, 1973; Ribbe, 1982). Most workers now favor a chemical formula containing two hydroxyl ions (Ribbe, 1982). Using this formula, the activity of Fe-end member staurolite (St) has been modeled as an ideal ionic solution, with mixing only on the Fe site, resulting in:

$a(St) = (XFe)^2$ in staurolite of the composito $Fe_2Al_9Si_{3.75}O_{22}(OH)_2$.

C. Regional Geological Setting

The Flin Flon - Snow Lake greenstone belt is approximately 250 kilometers long and has an exposed width of nearly 40 kilometers. It is bounded to the north by the Kisseynew gneiss complex and is overlain to the south by Paleozoic limestones (Fig. 1). The Flin Flon - Snow Lake belt and the Kisseynew gneisses together are part of the Churchill structural province of the Canadian Shield (Stockwell, 1964).

The greenstone belt consists of two major groups of rocks of Aphebian age and a number of intrusive granite bodies (Price, 1978). The older, Amisk Group rocks are the dominant lithology and consist mainly of volcanic rocks with minor metasedimentry members.

The volcanic rocks are of tholeiitic and calc-alkalic affinity and range in composition from basalt to dacite-rhyolite (Stauffer et al., 1975). Metasedimentary rocks of the Amisk Group are principally of greywacke composition (Froese and Moore, 1980). The younger, Missi Group consists largely of metasandstones and metagreywackes.

Structure and Metamorphism

Rocks in the Flin Flon - Snow Lake belt were structurally deformed and metamorphosed during the Hudsonian Orogeny. The degree of deformation and metamorphism varies throughout the belt. In general, three phases of deformation have been identified (Stauffer and Mukherjee, 1971; Froese and Moore, 1980).

The earliest deformation, P1, resulted in east-west trending tight folds. The second, P2 event, produced the dominant northeasterly trend in the area. The P2 folds are generally open and have steep axial foliation and lineation. The third, P3 event was relatively minor and generally refolded the P2 folds along a northerly axis.

Metamorphism was generally coincidental with the P2 event when the peak of metamorphism was reached (Froese and Moore, 1980). The metamorphic event was largely over in the waning stages of the P2 event. The P3 event was characterized by minor, retrogressive metamorphism. Metamorphic grades of low-greenschist facies were reached in the Flin Flon area. At Spruce Point, the metamorphism was of the upper greenschist facies. The temperature of metamorphism was 475 ± 50 °C at 2.6 ± 1.2 kb pressure (Chapter II). The Anderson Lake area shows a complete spectrum of metamorphic conditions from low greenschist facies in the south to middle-amphibolite facies in the north and northeast (Froese and Moore, 1980). Based on mineral assemblages, Froese and Gasparrini (1975) have divided the Anderson Lake area into four metamorphic zones. From south to north, these zones are: (i) chlorite - biotite zone, (ii) biotite - staurolite zone, (iii) staurolite - sillimanite zone, and (iv) garnet - sillimanite - biotite zone.

The temperature and pressure conditions in the staurolite - sillimanite zone and garnet - sillimanite zone have been determined from the following equilibria: garnet - biotite, kyanite - sillimanite, anorthite - garnet - sillimanite - quartz, and garnet -

rutile - ilmenite - sillimanite - quartz.

Using the experimental calibrations of the above equilibria and compositions of minerals from Snow Lake, temperatures of 575±50 °C at 5.25±0.5 kilobar pressure are estimated for the staurolite - sillimanite zone (Chapter II). In the garnet - sillimanite zone, the temperature and pressure conditions were slightly higher (620±40°C at 5.8±0.5 kb.).

D. Geology of the Ore Deposits

The massive sulfide deposits of the Flin Flon - Snow Lake belt all are similar to typical volcanogenic massive sulfide deposits of the Canadian Shield (Franklin et al., 1981). The most common features of these deposits are:

1. The massive sulfide bodies occur at or near the top of felsic rocks in a volcanic pile of mafic and felsic rocks.
2. The footwall rocks contain a "pipe" shaped zone of alteration produced during interaction with the ore-forming solutions. The core of this alteration zone is characterized by intense Mg-enrichment and is represented by a chlorite-rich rock.

The geology and mineralogical composition of the host and altered rocks associated with the deposits selected for this study are presented in this section.

Anderson Lake deposit

The geology of the Anderson Lake deposit has been described by Price (1978) and Walford and Franklin (1982). The deposit consists of an elongated lens which strikes 245°, dips 60° to north and plunges 55° north. It has a strike length of 90 meters with an average width of five meters and a length of 800 meters along the plunge. The sulfide lens is composed primarily of pyrite, chalcopyrite, and pyrrhotite with minor sphalerite, quartz, staurolite, tourmaline, apatite, and magnetite, ilmenite, and rutile.

The Anderson Lake deposit is contained in the felsic metavolcanic rocks of the Amisk Group. These rocks are of rhyolitic composition and are composed of quartz, plagioclase, and biotite with minor amounts of hornblende, muscovite, and almandine. In rocks where muscovite occurs in significant proportions, hornblende is absent. In one rock, staurolite is present in trace amounts. However, garnet and staurolite do not occur in contact with each other indicating that the two phases may not be in equilibrium.

The metasedimentary rocks of the Amisk Group consist of quartz, muscovite, biotite, staurolite, garnet, and plagioclase. Staurolite and garnet in these rocks are in apparent textural equilibrium and staurolite occurs as porphyroblasts upto five centimeters long.

The metavolcanic and metasedimentary rocks at Anderson Lake contain minor quantities of opaque minerals (less than 1%). Traces of pyrite and, rarely, chalcopyrite are the common sulfide minerals. Ilmenite is the most abundant opaque mineral and is present in nearly all rocks.

In the vicinity of the Anderson Lake deposit, the footwall rocks were hydrothermally altered during ore-deposition. Based on their mineral assemblages, the altered rocks can be classified into four zones: (a) chlorite zone, (b) muscovite zone-I, (c) gradational zone, and (d) muscovite zone-II.

The chlorite zone forms the core of the alteration and is similar to the "pipe" alteration of Archean, massive sulfide deposits (Franklin et al., 1981). It consists dominantly of chlorite with lesser amounts of biotite , kyanite, quartz, plagioclase, and rutile. At its lower end, the chlorite zone also occurs as a small, "semi-conformable" zone (Walford and Franklin, 1982). Here, the chlorite zone consists of chlorite, biotite, quartz, plagioclase, staurolite, garnet, and minor amounts of ilmenite.

Peripheral to the chlorite zone is a thin shell of muscovite zone-I. Rocks in this zone consist mainly of quartz, muscovite, sillimanite plagioclase, and biotite. Outwards from the muscovite zone-I, the footwall rocks are pervasively altered in the gradational zone. Mineralogically, rocks in the gradational zone consist of quartz, plagioclase, and biotite with varying amounts of staurolite, muscovite, and sillimanite. Garnet occurs in some gradational zone rocks near the contact with the country rocks. In these rocks, sillimanite is absent except in one sample where thin needles of fibrolite are associated with garnet and staurolite.

In addition to the alteration zones described above, an envelope of muscovite schist surrounds the ore-body, both in the hangingwall and the footwall. This halo of muscovite schist, called here the muscovite zone-II, underlies the ore-body for the most part, except where the chlorite zone occurs in the footwall. Rocks in this zone are composed of quartz and muscovite with minor contents of biotite, plagioclase, staurolite, and sillimanite with or without almandine.

Altered rocks from all the zones described above contain minor amounts of ilmenite, rutile, pyrite, and pyrrhotite (IRPP). Ilmenite-hematite solid solution is also commonly present. Rarely, magnetite has been observed in some gradational zone rocks which do not contain rutile. Distribution of sulfide, silicate, and oxide minerals across the ore body in the Anderson Lake mine is shown in Figure 2.

Spruce Point deposit

The Spruce Point deposit consists of at least three separate, major lenses of massive sulfides delineated through diamond drilling. The deposit is still in the development stage and, therefore, its geology has not been studied in detail. The sulfide bodies consist of pyrite, chalcopyrite, and sphalerite with minor arsenopyrite, pyrrhotite, magnetite, quartz, chlorite, ilmenite, and rutile.

The host felsic metavolcanic rocks are composed essentially of quartz, plagioclase, and muscovite with minor biotite, ilmenite, and pyrite. Footwall rocks at Spruce Point were also altered during ore-deposition. The alteration "pipe" is broadly similar to that at Anderson Lake. The central, chlorite zone consists of abundant chlorite with varying proportions of biotite, corundum, andalusite, and rutile. The adjoining, muscovite zone-1 consists of quartz, muscovite, andalusite and minor plagioclase, biotite with IRPP. Rocks in this zone show variable effects of retrograde metamorphism which has produced margarite, chloritoid, and chlorite pseudomorphs after andalusite.

The gradational zone at Spruce Point is more extensive than at Anderson Lake. Mineralogically, rocks in this zone contain an increased amount of biotite compared with the country rocks and consist of quartz, muscovite, biotite, plagioclase and minor ilmenite. The gradational zone underlies the ore body for the most part as the muscovite zone-II is absent at Spruce Point.

	Gradational Zone	Muscovite Zone - I	Chlorite Zone	ORE	Muscovite Zone - II
1600 Level	Ch + Bt + Ms + Qz + Plag + Mt + Ilm + Stau + Gt + Py + Po + Cpy		Ch + Bt + Qz + Plag + Ru + Py		Bt + Ms + Sil + Stau + Qz + Gt + Plag + Ilm + Ru + Py + Po + Cpy
2475 Level	Ch + Bt + Sil + Stau + Qz + Plag + Ilm + Ru + Py + Po + Tour	Ch + Bt + Ms + Sil + Stau + Qz + Plag + Ilm + Ru + Py + Po	Ch + Bt + Stau + Qz + Plag + Mt + Ilm + Py		Ch + Bt + Ms + Sil + Stau + Qz + Plag + Ilm + Ru + Py + Po + Cpy + Tour

Figure 2. Distribution of sulfide, silicate, and oxide minerals across the Anderson Lake ore body.

Centennial deposit

The geology of the Centennial deposit has been described by Provins (1980). The deposit consists of a single, massive sulfide lens enclosed in the felsic pyroclastic rocks of the Amisk Group. The sulfide body has a sharp contact with the hangingwall rocks and a relatively less distinct contact in the footwall. It is composed principally of pyrite, chalcopyrite, and sphalerite with minor galena, magnetite, quartz and calcite. Trace amounts of tetrahedrite-tennantite, arsenopyrite, and cobaltite are also present (Provins, 1980).

The host, felsic pyroclastic rocks are composed essentially of quartz and muscovite with lesser amounts of ilmenite, magnetite, and pyrite. In general, rocks in the hangingwall side contain much less and finer sized fragments than those in the footwall side. Rocks in the Centennial area are pervasively carbonatized (Provins, 1980).

Hydrothermal alteration related to ore depostion is less extensive at Centennial compared with the Anderson Lake and Spruce Point deposits. The chlorite zone, underlying the ore-body in the northern part, consists primarily of chlorite with very minor contents of quartz and rutile. The gradational zone underlies the ore-body in the south and is peripheral to the chlorite zone. This zone is characterized by slight Mg and K enrichment and Na and Ca depletion compared to the country rocks. Rocks in the gradational zone at Centennial are composed of quartz and muscovite with minor chlorite, ilmenite, and pyrite. The muscovite zones I and II are absent at the Centennial deposit.

E. Composition of the Fe-Mg Silicate Minerals

The presence and composition of ferro-magnesian silicate minerals are indicative of the metamorphic conditions. Assemblages and compositions of these minerals associated with metamorphosed sulfide deposits are found to show systematic variations with distance from ore and have been suggested as potential exploration guides (Nesbitt, 1982; Petersen, 1984; Spry, 1984). In addition, the composition of the ferromagnesian minerals can be used to estimate the composition of the metamorphic fluid phase and to examine the fluid-rock interaction during metamorphism. The composition of Fe-Mg silicate minerals in the country rocks and altered rocks from the Anderson Lake and Spruce Point deposits have been measured and are presented in this section. Rocks at the Centennial deposit are pervasively carbonatized. This together with the low grade of metamorphism in the area makes a detailed petrological analysis difficult. Therefore, the composition of chlorite, present only in the altered rocks at Centennial, was not measured.

Country Rocks

Biotite and garnet are common Fe-Mg silicate minerals in the metavolcanic and metasedimentary rocks from Anderson Lake. Staurolite occurs as a major phase in the metasedimentary rocks and is present in trace quantities in samples of metavolcanic rocks. Another common Fe-Mg silicate mineral in the metavolcanic rocks is hornblende. However, its composition has not been measured as it is absent in the altered rocks.

The Xann (see the section on Methods for the calculation of Xann) values of biotites in the country rocks at Anderson Lake range from 0.36 to 0.51 (Table 2). Biotite occurring with or without muscovite shows no systematic variation in its Xann content.

Garnet and staurolite in the country rocks are close to their Fe-end member composition. The XFe of garnet varies from 0.69 to 0.77. Staurolite has a nearly constant XFe value of 0.83. The compositions of garnet and staurolite do not show a significant variation between metavolcanic and metasedimentary rocks.

In the country rocks at Spruce Point, biotite is the only ferro-magnesian silicate mineral with an Xann value of 0.48 (Table 2).

Altered Rocks

Anderson Lake: Biotite, staurolite, and chlorite occur ubiquitously in the altered rocks at Anderson Lake. Garnet occurs in significant proportions in the lower chlorite zone and infrequently, as a minor phase in the gradational zone and muscovite zone II. The compositions of these minerals are given in Table 3.

Biotite in the altered rocks at Anderson Lake varies in composition from Xann = 0.21 to 0.33. It shows a consistent variation in different zones and mineral associations. In the lower chlorite zone and muscovite zone II, biotite is relatively iron rich, Xann = 0.32-0.33. It

Table 2. Composition of Fe-Mg Silicate Minerals in the Country Rocks from Anderson Lake and Spruce Point. Complete analyses are given in Appendix I.

	SL-22		SL-17		SL-13*		SL-37*			115-920*
	Bt	Gt	Bt	Gt	Bt	Gt	Bt	St	Gt	Bt
Si	5.46	3.00	5.49	3.00	5.45	2.98	5.48	3.78	3.04	5.47
Al	3.00	1.96	2.91	1.94	3.40	2.00	3.49	8.94	2.01	3.22
Mg	2.10	0.29	2.19	0.34	1.38	0.16	2.14	0.33	0.28	1.45
Fe	2.86	2.10	2.77	2.10	3.29	2.10	2.33	1.57	2.24	3.12
Ti	0.32		0.39		0.14		0.24	0.05		0.30
Mn	0.01	0.20	0.00	0.15	0.03	0.26	0.00	0.01	0.19	0.09
Ca		0.45		0.46		0.49			0.20	
Zn								0.02		
K	1.80		1.74		1.94		1.68			1.87
Na	0.01		0.00		0.00		0.00			0.05
XFe	0.50	0.69	0.48	0.69	0.58	0.70	0.41	0.83	0.77	0.55
XAnn	0.44		0.43		0.51		0.36			0.48

* muscovite-bearing

Table 3. Composition of Fe-Mg Silicate Minerals in the Altered Rocks from Anderson Lake and Spruce Point. Complete analyses are given in Appendix I.

	Gradational Zone								
	16-07*		7-25*		7-105*		72-220		67-702*
	Bt	Gt	Bt	St	Bt	St	Bt	St	Bt
Si	5.43	2.98	5.46	3.81	5.57	3.92	5.54	3.77	5.68
Al	3.30	1.99	3.27	8.61	3.22	8.51	3.33	8.80	3.00
Mg	2.69	0.38	2.91	0.63	2.77	0.65	3.20	0.71	3.38
Fe	2.21	1.81	1.85	1.51	1.86	1.51	1.59	1.35	1.49
Ti	0.18		0.17	0.05	0.21	0.04	0.12	0.04	0.18
Mn	0.01	0.58	0.01	0.09	0.00	0.05	0.00	0.03	0.00
Ca		0.25							
Zn				0.06		0.01		0.07	
K	1.76		1.78		1.73		1.63		1.75
Na	0.09		0.20		0.25		0.18		0.04
XFe	0.36	0.60	0.33	0.71	0.33	0.70	0.28	0.66	0.26
XAnn	0.30		0.28		0.29		0.24		0.24

* muscovite-bearing

Table 3. continued

	Muscovite Zone 1					115		Muscovite Zone 2			
	182-270			182-320		1323	72-295			72-330	
	Bt	St	Ch	Bt	St	Bt	Bt	St	Bt	St	Ch
Si	5.45	3.78	5.22	5.47	3.78	5.36	5.46	3.75	5.43	3.78	
Al	3.23	8.74	5.54	3.28	8.67	3.45	3.36	8.74	3.37	8.73	
Mg	3.01	0.64	6.10	2.86	0.72	2.63	2.64	0.59	2.68	0.56	
Fe	1.89	1.49	3.15	1.91	1.57	2.18	2.11	1.59	2.11	1.63	
Ti	0.19	0.04		0.19	0.06	0.17	0.18	0.05	0.16	0.04	
Mn	0.00	0.04	0.01	0.00	0.03	0.00	0.00	0.04	0.00	0.05	
Zn		0.04			0.01			0.02		0.02	
K	1.72			1.71		1.82	1.72		1.73		
Na	0.22			0.25		0.14		0.19			
XFe	0.33	0.70	0.26	0.33	0.69	0.38	0.37	0.73	0.37	0.74	0.30
XAnn	0.28			0.32	0.33		0.32				

Table 3. continued

	Chlorite Zone									
	182-235				SL-14		24-03		115-1303	
	Bt	St	Gt	Ch	Ch	Bt	St	Ch	Ch	Bt
Si	5.45	3.74	2.98	5.11	5.23	5.55	4.47	5.17	5.28	5.49
Al	3.32	8.73	2.02	5.74	5.68	3.29	7.98	5.73	5.61	3.24
Mg	2.68	0.61	0.49	5.33	6.60	3.40	0.51	5.48	6.48	3.61
Fe	2.13	1.67	2.27	3.84	2.43	1.37	1.46	3.56	2.58	1.36
Ti	0.19	0.06				0.15	0.05			0.13
Mn	0.00	0.12	0.03			0.00	0.02	0.01	0.00	0.00
Ca			0.19							
Zn		0.02					0.01			
K	1.75					1.63				1.74
Na	0.22					0.19				0.17
XFe	0.37	0.73	0.76	0.32	0.20	0.24	0.74	0.30	0.22	0.23
XAnn	0.33					0.21				0.20

shows no variation in the two zones despite different mineral assemblages, garnet - staurolite - chlorite - ilmenite in the chlorite zone and muscovite - sillimanite - staurolite and IRPP in the muscovite zone. Biotites in the upper chlorite zone and the muscovite zone-I have lower iron contents, Xann = 0.21 and 0.28, respectively. The Xann content of biotite shows the maximum variation in the gradational zone. It varies from 0.24, in association with sillimanite/kyanite and staurolite without muscovite, to 0.30 in muscovite - garnet - staurolite bearing rocks. With the assemblage muscovite - sillimanite - staurolite and IRPP in the gradational zone, similar to that in the muscovite zones I and II, the Xann value of biotite is fairly constant at 0.28 to 0.29.

The composition of staurolite varies from XFe = 0.69 to 0.76. It is Fe-rich in the lower chlorite zone and muscovite zone-II (0.74±0.1) and relatively iron-poor in muscovite zone-I and gradational zone (0.66 to 0.71). In addition to Fe and Mg, staurolites from Anderson Lake contain minor proportions of Zn, Ti, and Mn, generally less than 4.0 wt% ZnO + MnO + TiO_2. One sample from the gradational zone contains staurolite with 5.8 wt% ZnO. The Zn content of staurolite does not show significant variation within a single alteration zone and with different opaque mineral assemblages.

Chlorite is a common mineral in the muscovite zones I and II, in addition to the chlorite zones. In the gradational zone, chlorite occurs as a minor phase. Chlorite generally occurs in apparent textural equilibrium with other minerals and is considered in this study to be a prograde metamorphic mineral. In some rocks, chlorite occurs in trace amounts as a distinct alteration product of other minerals and is regarded as a retrograde mineral. Additional evidence for the prograde/retrograde nature of chlorite is provided by the oxygen isotopic compositions. The oxygen isotopic compositions of chlorite and quartz indicate that only chlorite separated from rocks where it occurs in apparent textural equilibrium shows isotopic equilibrium at the peak metamorphic conditions (Chapter III).

Qualitative analysis of the retrograde chlorite indicates that it is of nearly Fe-end member composition. The XFe of prograde chlorite varies from 0.24 to 0.29 in the gradational zone and muscovite zone-I. In the upper chlorite zone, chlorite is Fe-poor, XFe = 0.20. As in the case of biotite and staurolite, chlorite is slightly Fe-rich in the lower chlorite zone and muscovite zone-II (XFe = 0.30 to 0.32).

Garnet occurs as a major phase in the lower end of the chlorite zone and is relatively iron-rich (XFe=0.75). The XFe of garnet is significantly lower, XFe=0.55 to 0.63, in the gradational zone and muscovite zone-II. The lower iron content of garnet in these zones is compensated by an increased Mn content while Mg and Ca contents are nearly the same.

Spruce Point: At the Spruce Point deposit, biotite and/or chlorite are the only ferro-magnesian silicate minerals present in the altered rocks and the ore zone. Biotite has the lowest Xann (0.23) in the chlorite zone where it occurs with chlorite, corundum, andalusite, gahnite, pyrite, and rutile (Table 3). The Xann of biotite is highest (0.32-0.33) in the muscovite zone-I. Coexisting minerals in this zone include muscovite, andalusite, plagioclase, pyrite, pyrrhotite, rutile, and ilmenite. In the gradational zone, biotite coexists with muscovite and rutile and has a lower value of Xann (0.24).

Chlorite in the altered rocks at Spruce Point has a narrow range in XFe values (0.17-0.24). The lowest values occur in the ore zone. In the chlorite zone and the gradational zone, the XFe of chlorite ranges from 0.22 to 0.24. Chlorite is absent in the muscovite zone-I at Spruce Point.

To summarize, the ferromagnesian silicate minerals at Anderson Lake and Spruce Point show differences in their compositions in the country rocks and altered rocks. In the altered rocks, variations in the composition of these minerals do not have any apparent relationship with the opaque mineral assemblages or with distance from the ore. However, the compositions of all minerals show systematic variations in different alteration zones. These relationships are contrary to those observed at other metamorphosed deposits where the compositions of ferromagnesian minerals show a decrease in their iron content with decreasing distance from the ore (Nesbitt, 1982; Petersen, 1984).

F. Composition of the Metamorphic Fluid Phase

The composition of the metamorphic fluid phase can be determined by considering mineral equilibria involving one or more fluid species that are divariant in the P-T-X space (see Ferry and Burt, 1982 for a detailed discussion of the thermodynamic basis of calculations). The presence of hydrous and sulfide minerals at Anderson Lake and Spruce Point indicates that the metamorphic fluid contained species of hydrogen, oxygen, and sulfur. In addition to these species, minor contents of species of carbon are generally present in the metamorphic fluid, even in the absence of carbon-bearing phases. However, the concentration of the species of carbon in the metamorphic fluid at Anderson Lake and Spruce Point can not be calculated because of the lack of mineral assemblages that would describe an equilibrium involving these species. Thus the following calculations of the composition of the fluid phase are restricted to species in the system H-O-S. It will be shown later in this section that the species of carbon constituted an insignificant proportion of the fluid phase at Anderson Lake and Spruce Point.

Silicate mineral equilibria which can be used to estimate the composition of the fluid phase at Anderson Lake and Spruce Point are given by the following reactions:

1. Paragonite + Quartz = Albite + Andalusite/Sillimanite + H_2O(gas)
2. 4 Zoisite + Quartz = Grossular + 5 Anorthite + 2 H_2O(gas)
3. 3 Pyrite + 2 O_2(gas) = Magnetite + 3 S_2(gas)
4. Magnetite + 3 Rutile = 3 Ilmenite + 0.5 O_2(gas)
5. Pyrite = Pyrrhotite + 0.5 S_2(gas)

Thermodynamic data for reactions (1) to (4) are given in Table 4. The equilibrium conditions for reaction (1) with andalusite have been obtained by Chatterjee (1972). Results of these experiments were combined with those of Holdaway (1971) to obtain the log K for reaction (1) with sillimanite. Reaction (2) has been experimentally studied by Boettcher (1970) and by Chatterjee et al. (1984). Results of Chatterjee et al. (1984) were used in the present study. The equilibrium constants for reactions (3) and (4) were calculated from thermodynamic data tabulated in Robie et al. (1979) and those for reaction (5) were taken from Toulmin and Barton (1964).

Table 4. Thermodynamic data used in calculations of volatile and solid phase equilibria

	log K			
	850 K	850 K	750 K	
Reaction	5.25 Kb	4.5 Kb	2.5 Kb	Ref
1A: Par + Qz = Ab + And + Water	3.31	3.30	2.59	1
1B: And = Sil	-0.04	-0.05		4
2: 4Zo + Q = Gr + 5An + 2Water	5.51			3
3: 3Py + $2O_2$ = Mt + $3S_2$	28.11	27.99	32.36	7
4: Mt + 3Ru = 3Ilm + $0.5O_2$	-8.50	-8.53	-10.52	7
5: Alm = 3FeO + 2Sil + Q	-3.11			5,7
6: 6St + 3.75Qz = 4Alm + 23Sill + 6Water	20.34	20.29		9
7: Mt = 3FeO + $0.5O_2$	-12.10	-12.13	-13.22	7
8: Ann + Sill = Ms+Q + 3FeO	-2.06	-2.04		2,7,8
9: Ms = $0.5K_2O$ + 1.5Sill + 1.5Qz + Water	-23.14	-23.24		6,7
Kd values:				
Alm - Bt = 0.19				
Alm - St = 0.62				
St - Bt = 0.24				

Par=paragonite; Qz=quartz; Ab=albite And=andalusite Sil=sillimanite Zo=zoisite Gr=grossular An=anorthite Py=pyrite Mt=magnetite Ru=rutile Ilm=ilmenite Alm=almandine St=staurolite Ann=annite Ms=muscovite Bt=biotite

References: (1)Chatterjee (1972) (2)Chatterjee and Johannes (1974) (3)Chatterjee et al. (1984) (4) Holdaway (1971) (5) Bohlen et al. (1983) (6)Helgeson et al. (1978) (7) Robie et al. (1979) (8) Hewitt and Wones (1981) (9) Chapter II

To calculate the composition of the fluid phase, the above equilibria must be corrected for the effects of solid solution in muscovite, plagioclase, staurolite, garnet, and biotite. The activities of endmembers in these solid solutions can be calculated using activity models discussed in an earlier section. The composition of the fluid phase thus calculated is given in Table (5) and is discussed below.

Country Rocks

The country rocks at Anderson Lake and Spruce Point generally do not contain assemblages which allow the estimation of the composition of the fluid phase. In one sample of the country rocks from Anderson Lake (SL 26), the assemblage zoisite - garnet - plagioclase - quartz has been observed. The fugacity of H_2O in equilibrium with this assemblage has been calculated using data for reaction (2) and the compositions of garnet, zoisite, and plagioclase (Table 5) with the appropriate activity models. Calculated value of fH_2O (Table 5) has been converted to PH_2O and XH_2O using the Lewis and Randall rule (Denbigh, 1981):

$fi = fi^{\bullet} \times Xi^{\bullet}$ where $fi^{\bullet} = P \times \gamma i^{\bullet}$, assuming that $Pfluid = Ptotal$.

In the above equation, fi and Xi are the fugacity and mole fraction of the ith species in an ideal mixture of gaseous species. $fi^{\bullet}$ and $\gamma i^{\bullet}$ are the fugacity and fugacity coefficients of pure i at a total pressure P. Values of PH_2O and XH_2O for sample SL 26 are, respectively, 5020 bars and 0.96 (Table 5).

In addition to H_2O, an H-O-S fluid phase at the pressure and temperature conditions of metamorphism at Anderson Lake would contain minor quantities of O_2, S_2, H_2S, H_2, and SO_2 (Rice and Ferry, 1982). The concentrations of these species also are difficult to estimate because of a lack of any assemblage which would describe an equilibriam involving these species.

Altered Rocks

Anderson Lake: the altered rocks at Anderson Lake commonly contain assemblages which allow estimation of the composition of the fluid phase. Assemblages corresponding to the paragonite-albite equilibrium (reaction 1) are present in altered rocks from the gradational

Table 5. Calculated Composition of the Metamorphic Fluid Phase at Anderson Lake and Spruce Point Using Silicate Equilibria

Country Rocks, Anderson Lake

Zo - Plag - Gr Equilibrium (850 K, 5.25 kb)

X(Zo)	0.81	a(Zo)	0.53
X(Gr)	0.33	a(Gr)	0.05
X(An)	0.40	a(An)	0.54
log K	-1.41		
fH_2O	2866 bars		
PH_2O	5020 bars		
XH_2O	0.96		

Altered Rocks

	Anderson Lake (850 K, 5.25 Kb)					Spruce Point (750 K, 2.0 Kb)	
	7-25	7-140	182-320	24-10	72-295	115-1307	115-1323
XPar	0.20	0.16	0.20	0.14	0.15	0.11	0.13
XAb	0.70	0.63	0.65	0.39	0.46	0.45	0.54
logKs	0.10	0.11	0.12	0.20	0.18	0.13	0.14
fH_2O	2344	2399	2455	2951	2818	501	512
PH_2O	4105	4201	4299	5168	4836	1616	1654
XH_2O	0.78	0.80	0.82	0.98	0.94	0.81	0.83

zone, muscovite zone-I, and muscovite zone-II. Using the compositions of muscovite and plagioclase and data for reaction (1) (Table 4), fH_2O in equilibrium with these assemblages has been calculated and is given in Table (5). Calculated values of PH_2O and XH_2O are, respectively, 5000±60 bars and 0.94±0.02 in the muscovite zone-II. In the gradational zone and muscovite zone-I, PH_2O and XH_2O (4200±100 bars and 0.78±0.02 are similar but are lower than those in the muscovite zone-II.

Fugacities of oxygen and sulfur also are easily constrained in the altered rocks. The assemblage pyrite-pyrrhotite-ilmenite-rutile (IRPP) is present in the gradational zone and the muscovite zones I and II. Using data for reactions (3) to (5), the fugacity of O_2 and S_2 in these rocks are: $\log fO_2 = -17.0$, $\log fS_2 = -2.0$. These values are nearly constant in all rocks as ilmenite, the only mineral in the above assemblage which shows solid solution, is generally close to its endmember composition (Xilm = 0.97 to 0.98). Some samples from the gradational zone contain the assemblage pyrite-pyrrhotite-magnetite (PPM). Fugacities of oxygen and sulfur in equilibrium with this assemblage are: $\log fO_2 = -17.1$, $\log fS_2 = -2.0$ (reactions (3) and (5)). These values are virtually the same as those calculated from the assemblage IRPP. This is consistent with the occasional presence of magnetite in rocks from the muscovite zone-II and ore zone containing IRPP. The calculated value of fO_2 in the altered rocks is also consistent with the frequent presence of the ilmenite-hematite solid solution. According to the data of Spencer and Lindslay (1981), the value of $\log fO_2$ in equilibrium with ilmenite-hematite solid solution is approximately -17.0 at 575 °C, the temperature of metamorphism at Anderson Lake.

Using the values of fO_2 and fS_2 in equilibrium with IRPP, the distribution of H_2S, SO_2, and H_2 in the fluid phase has been calculated by a simultaneous solution of the following equations (French,1966):

$$P_{fluid} = P_{total} = \Sigma P_i = \Sigma f_i/\gamma_i \ (i = H_2O, O_2, S_2, H_2S, SO_2, H_2) \qquad (6)$$

$$K(H_2O) = 0.5\, fO_2 * fH_2 / fH_2O \qquad (7)$$

$$K(H_2S) = 0.5\, fS_2 * fH_2 / fH_2S \qquad (8)$$

$$K(SO_2) = 0.5\, fS_2 * fO_2 / fSO_2 \qquad (9)$$

Thermodynamic data used in the above calculations were taken from Robie et al. (1979).

Fugacity coefficients of H_2O were taken from Burnham et al. (1969) and that for all other species were calculated using the program SUPCRT (Helgeson et al., 1978). Results of these calculations are given in Table (6).

Spruce Point and Centennial: At Spruce Point, rocks from the muscovite zone-I contain the assemblage muscovite - andalusite - plagioclase and IRPP. In these rocks, fH_2O has been calculated using the compositions of muscovite and plagioclase and reaction (1) (Table 5). The fugacities of O_2 and S_2 have been calculated using equations (3) to (5). Distribution of minor gas species (Table 6) has been calculated using equations (6) to (9) as described earlier. Values of PH_2O calculated from reaction (1) (1710 ± 20 bars) are less than those calculated from the gas equation (2497 bars). These differences are due to the large uncertainity in the estimation of pressure (± 1.2 kb) at Spruce Point.

Altered rocks from the chlorite zone and gradational zone generally contain rutile and pyrite without ilmenite, pyrrhotite, or magnetite. The fugacities of O_2 and S_2 in these rocks would be higher than those in the muscovite zone-I.

Altered rocks from the Centennial deposit do not contain assemblages which allow estimation of the composition of the fluid phase.

Relationship between PH_2O, $Pfluid$, and $Ptotal$

Caluculations for the composition of the metamorphic fluid based on mineral equilibria presented above were performed with the assumption that $Pfluid = Ptotal$. Values of $Ptotal$ at Spruce Point were calculated with an additional assumption that $Pfluid \cong PH_2O$. However, $Ptotal$ at Anderson Lake was calculated from solid-solid equilibria and no assumptions with respect to the value of PH_2O were made. Thus the values of PH_2O calculated above can be used to evaluate the relationship between PH_2O, $Pfluid$, and $Ptotal$ and the validity of the assumption $Pfluid = Ptotal$.

Calculated values of PH_2O using silicate equilibria in the country rocks and the muscovite zone-II at Anderson Lake (assuming $Pfluid \cong Ptotal$) are, respectively, 5020 bars and 5000 ± 60 bars. The value of fH_2O in the muscovite zone-II calculated using the gas equation

Table 6. Calculated Distribution of Species in the H-O-S Gas Phase for the Temperature and Pressure Conditions at Anderson Lake and Spruce Point

	Anderson Lake		Spruce Point
	850 K	850 K	750 K
	5.25 kb	4.5 kb	2.0 kb
$\log fO_2$	-17.0	-17.03	-21.53
$\log fS_2$	-2.03	-2.05	-5.0
fH_2O	2977	2365	600
fSO_2	2.46	2.24	0.004
fH_2S	39.91	32.07	0.28
fH_2	0.44	35.96	0.08
PH_2O	5213	4469	1998
XH_2O	0.992	0.993	0.999
XSO_2	0.0002	0.0002	**
XH_2S	0.007	0.006	0.001

** less than 0.0001

(assuming Ptotal = Pfluid ≅ PH_2O) is 5213 bars, similar to that calculated from silicate equilibria. This indicates that in these rocks Ptotal, Pfluid, and PH_2O were approximately equal to each other and that the assumption of Pfluid = Ptotal is valid.

However, in the gradational zone and the muscovite zone-I, PH_2O calculated from silicate equilibria (4200 ± 100 bars) is much lower than that calculated from the gas equation (5213 bars) and the value of PH_2O in the muscovite zone-II. That this discrepency in the calculated values of PH_2O is not an artifact of errors in calculation is supported by the compositions and equilibria between all silicate minerals.

An algebraic analysis of equilibria in the assemblage staurolite - biotite - sillimanite - chlorite, present in the muscovite zones I and II, indicates that these minerals all become Mg-rich with decreasing values of the chemical potential (μ) of H_2O at constant P and T (Spear et al., 1982, pp 135-136), irrespecive of the associated sulfide and oxide minerals. The higher Mg content of staurolite, biotite, and chlorite in the muscovite zone-I than in muscovite zone-II (Table 3), therefore, suggests that μH_2O was lower in the muscovite zone-I. With the standard state at 1 bar and T, as used in this study, the chemical potential, μ, of a gaseous species is given as:

$$\mu(P,T) = \mu^0 + RT \ln f$$

where μ^0 is the chemical potential in the standard state and is a function only of T. f is the fugacity of the gas and is related to pressure by the Lewis and Randall rule, as discussed earlier. The above relationship indicates that the lower μH_2O in the muscovite zone-I reflects a lower PH_2O in these rocks compared with the muscovite zone-II, which is consistent with the calculated values of PH_2O.

The lower values of PH_2O calculated for the muscovite zone-I and gradational zone may be due to an increase in the proportion of other species (e.g., CO_2, CH_4) in the fluid phase. Alternatively, the fluid pressure may be less than Ptotal in these zones. The relationship between Pfluid, PH_2O, and Ptotal at Anderson Lake can be evaluated by considering sulfide-silicate-oxide equilibria that are independent of PH_2O and PCO_2.

The assemblage biotite-sillimanite-muscovite-quartz is commonly present with the IRPP assemblage in the gradational zone and muscovite zones I and II. These assemblages imply the following equilibria:

Biotite + Sillimanite + 3 S_2 = Muscovite + Quartz + 3 Pyrite + 1.5 O_2 (10)

Magnetite + 3 Rutile = 3 Ilmenite + 0.5 O_2 (11)

When fO_2 and fS_2 are defined by the IRPP (equation (11)), the equilibrium given by equation (10) is invariant at a given T, P, and the compostions of biotite and muscovite. Using the data in Table (4) and the composition of muscovite in Table (5), biotite in equilibrium with sillimanite, muscovite, quartz, and pyrite will have an Xann value of 0.31 at 850 K temperature and 5.25 Kb pressure. This value is the same as that of biotite in muscovite zone-II (0.31 - 0.32) but is higher than that of biotite in the gradational zone and muscovite zone-I (0.28-0.29). If we assume that *Ptotal* was equal to *Pfluid* and that the temperature was constant, any variation in the activity of biotite must be compensated by a corresponding variation in the activity of muscovite as these are the only minerals in the above assemblage which show significant solid solution. However, variations in the composition of muscovite are negligible and do not correlate with the variations in the composition of biotite (Tables 3 and 5). Differences in the composition of biotite, therefore, suggest that *Pfluid* in the muscovite zone-II was higher than that in the gradational zone and muscovite zone-I. Thus the assumption of *Pfluid* = *Ptotal* may be in error for rocks in the m[illegible]vite zone-I and the gradational zone.

The condition of *Pfluid* not equal to *Ptotal* would exert a non-hydrostatic stress and alter the normal equilibrium of a geologic system derived for a state of hydrostatic stress (Thompson, 1955). The thermodynamic behavior of rock-fluid systems under non-hydrostatic stress has been studied by many workers (Thompson, 1955; Kamb, 1961; Paterson, 1973, Bruton and Helgeson, 1983). A rigorous thermodynamic analysis of the effects of non-hydrostatic on the equilibrium between minerals and fluids in geologic systems has been presented by Bruton and Helgeson (1983). These authors demonstrate that while the thermodynamic properties of solids are nearly unaffected for crustal conditions, non-hydrostatic stress has a significant impact on the thermodynamic behavior of assemblages involving a fluid species. Bruton and Helgeson (1983) calculated that the free energy of a reaction between solid and fluid species at a fluid pressure *Pfluid* and total pressure *Ptotal* can be expressed as:

ΔGr (*Pfluid*,*Ptotal*,T) = ΔGr (*Pfluid*,T). Applying the above criterion for equilibrium to rocks in the gradational zone and the muscovite zone-I, *Pfluid* at which biotite with Xann = 0.28 - 0.29 is in equilibrium with the assemblage biotite - sillimanite - muscovite - quartz - pyrite and †RPP was calculated from the data in Tables 4 and 5. This value of *Pfluid* (4400 ± 200 bars) was then used to calculate PH_2O from equation (1) and the gas equation (equations 6 to 9) with the assumtion that *Pfluid* = *Ptotal*. Recalculated values of PH_2O from equation (1) (4500 ± 50 bars) and the gas equation (4469) are similar to each other. This suggests that the lower values of Xann in the gradational zone and the muscovite zone-I were produced by local variations in *Pfluid*, consistent with the calculated values of &ph2o> based on silicate equilibria.

In summary, the metamorphic fluid phase at Anderson Lake and Spruce Point consisted essentially of H_2O ($XH_2O = 0.96 \pm 0.03$). Other species in the system H-O-S, SO_2, H_2S, O_2, S_2, and H_2, were present in minor quantities. Calculated values of PH_2O using silicate equilibria are nearly equal to *Pfluid* in all rocks and are indicative of a negligible presence of non H-O-S species in the fluid phase.

G. Phase Equilibria

The relationship between coexisting minerals and their compositions in metamorphic rocks are conventionally represented by means of isothermal, isobaric, triangular diagrams (Thompson, 1957). Because the variations in the Fe/Mg ratio of ferromagnesian minerals are indicative of metamorphic conditions, the triangular diagrams are projected from three phases in the system K-Fe-Al-Si-Mg-O-H on to a plane whose two apices are FeO and MgO (Greenwood, 1975). The choice of the projection points depends on the non-Fe-Mg phases that are most commmonly present in all rocks. Generally, the points of projections are quartz and muscovite with kyanite or H_2O (Greenwood, 1975). These diagrams can be further modified to include phases in the system Fe-Ti-O-S (Rumble, 1978; Froese, 1969). Another common technique to represent sulfide-silicate-oxide equilibria is by means of log fO_2 - log fS_2 diagrams (Froese, 1971).

A common feature of the above diagrams is that they enable one to study the parameters responsible for variations in mineral assemblage and/or mineral composition in rocks that contain similar assemblages and have been metamorphosed at isothermal - isobaric conditions. In addition to the local variations in *Pfluid*, altered and country rocks at Anderson Lake do not always contain muscovite and sillimanite/kyanite which makes the choice of projection points difficult. Similarly, muscovite and/or andalusite is not present in all rocks from Spruce Point. In order to consider all rocks simultaneously, the phase equilibria in rocks from Anderson Lake and Spruce Point are represented by means of activity - activity diagrams of two components, Al_2SiO_5 and FeO. These diagrams are similar to the log fO_2 - log fS_2 diagrams and to the *u* - *u* diagrams of Ferry and Burt (1982). A detailed treatment of the construction and interpretation of these diagrams can be found in Nesbitt (in press).

The a(Al_2SiO_5) - a(FeO) diagrams can be constructed by writing equations of the type:

Almandine = 3 FeO + Al_2SiO_5 + Quartz

Annite = 3 FeO + 0.5 Al_2SiO_5 + 0.5 K_2O + 2 Quartz + Water

Staurolite + 0.75 Quartz = 2 FeO + 4.5 Al_2SiO_5 + Water

The endmember reactions can be displaced for the effects of solid solution by choosing an appropriate activity model. Variations in the activities of two co-existing minerals can be monitored by contouring the lines of equilibrium Kd between the two phases. The locus of these lines can be determined by considering the phases, i and j, as binary solid solutions of Fe and Mg and the following relationships at a given value of Kd (Table 4):

$Kd(i\text{-}j) = Fe(i) * Mg(j) / Mg(i) * Fe(j)$

because $Mg(i \text{ or } j) = 1 - Fe(i \text{ or } j)$,

$$Fe(j) = Fe(i) / (Kd(i\text{-}j) * (1 - Fe(i)) + Fe(i)) \qquad (11)$$

Anderson Lake

In order to study the phase equilibria in the altered and country rocks at Anderson Lake, a(Al_2SiO_5) - a(FeO) diagrams have been constructed at 850 K temperature and 5.25 kb and 4.5 kb pressures (Figs. 3 & 4). These diagrams were constructed using the thermodynamic

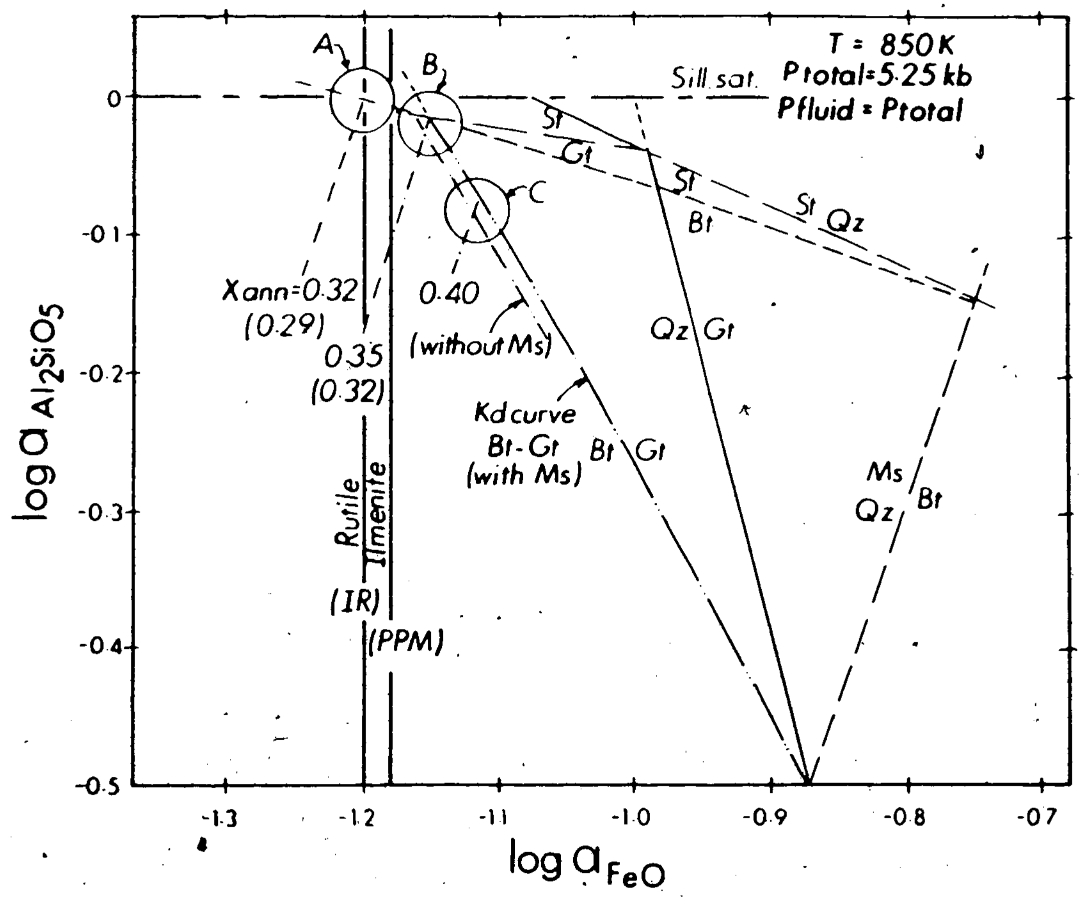

Figure 3. Activity - activity diagram at 850 K temperature and 5.25 Kb pressure (*Pfluid = Ptotal*) for the analysis of phase equilibria at Anderson Lake. The stabilities of biotite (Bt), staurolite (St), and almandine garnet (Gt) are shown by solid (stable region) and dashed (meta-stable region) curves. Dashed curves with two dots are the Kd-curves for Bt-Gt, Bt-St, and Gt-St. The Kd-curve for Bt-Gt is shown for assemblages with or without muscovite. Dashed lines with one dot indicate the mole fraction of annite (Xann) in equilibrium with the assemblages at locations A, B, and C. Xann values in parentheses are for muscovite-free assemblages.

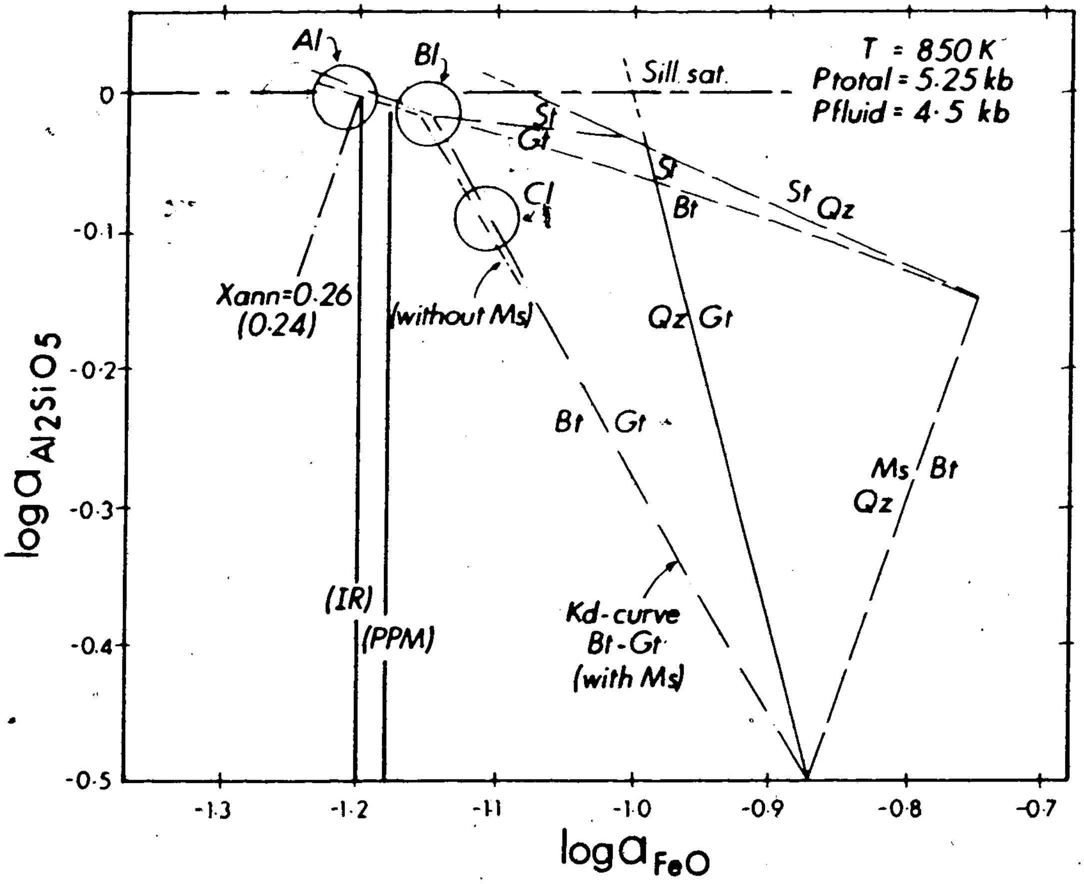

Figure 4. Activity - activity diagram at 850 K temperature and *Ptotal* = 5.25 Kb (*Pfluid* = 4.5 Kb) for the analysis of phase equilibria at Anderson Lake. The symbols are the same as in Figure 3.

data given in Table (4). The activity of K_2O required to plot the stability of biotite in muscovite-free assemblages was arbitrarily set at 0.2 log units below that necessary for muscovite saturation. Although chlorite is a common phase in the altered rocks at Anderson Lake, its stability has not been plotted on the diagrams in Figures 3 and 4 due to a lack of reliable thermodynamic data for this phase. An internally consistent set of data for chlorite will be derived later in this section.

The endmember reactions were displaced for solid solution in biotite, garnet, and staurolite using the activity models discussed in an earlier section. In these models, biotite and garnet are not binary solutions of Fe and Mg. Therefore, to calculate the Kd-curves as described above, the Xann and XFe of biotite and garnet must be converted to their respective Fe/(Fe+Mg) ratios.

There are no crystal-chemical constraints on the relationship between Fe/(Fe+Mg) ratio and Xann in biotite. This relationship is dependent on the Al/Si ratio and, therefore, may be quite consistent within one area (Holdaway, 1980). To determine the relationship between Fe/(Fe+Mg) and Xann in biotites at Anderson Lake, these two parameters were plotted against each other. A linear, least squares regression of these data gives a straight line with a correlation coefficient of 0.99. Similarly, a linear regression of Fe/(Fe+Mg) in garnet against XFe gives a straight line with a correlation coefficient of 0.97. Thus the Fe/(Fe+Mg) in biotites and garnets at Anderson Lake can be reliably converted to Xann or XFe using the equaitons of the regression lines. In order to calculate the loci of Kd-curves involving biotite and garnet in the diagrams in Figures 3 and 4, the Fe/(Fe+Mg) ratio estimated from equation (11) were converted to the Xann and XFe values as described above.

The opaque mineral assemblages are represented in Figures (3) and (4) by vertical lines. Of maximum interest to the following discussion is the location of the ilmenite-rutile line (IR). This line defines the activity of FeO in equilibrium with ilmenite and rutile given by the reaction:

Ilmenite = Rutile + FeO

All assemblages containing ilmenite and rutile, with or without any other oxide or sulfide mineral, must plot on this line. Assemblages with rutile only will plot to the left of this line and those with ilmenite only will plot to the right of this line. The pyrite-pyrrhotite-magnetite (PPM) assemblage plots very close to the IR line, slightly to its right.

An inspection of Figure 3 indicates that sillimanite - muscovite - ilmenite - rutile bearing rocks metamorphosed at *Pfluid = Ptotal* would also contain biotite and staurolite (location A). The composition of biotite and staurolite in this assemblage, assuming the Kd values given in Table (4), would be: Xann = 0.32, XFe (St) = 0.75. In slightly iron-rich rocks, biotite, garnet, and staurolite would coexist with ilmenite and muscovite without sillimanite (location B, Figure 3). The composition of biotite, staurolite, and garnet being: Xann=0.36, XFe(St)=0.77, XFe(garnet)=0.73.

In the absence of muscovite, biotite and staurolite coexisting with sillimanite - ilmenite - rutile would have slightly lower iron content (Xann=0.28, XFe(stau)=0.72) compared to those in muscovite-bearing rocks (location A, Figure 3). Similarly, in the absence of muscovite and sillimanite, biotite and staurolite coexisting with ilmenite would have the composition: Xann=0.32, XFe(St)=0.74 (location B).

Rocks metamorphosed at conditions of *Pfluid* < *Ptotal* would have similar assemblages,for corresponding activities of Al_2SiO_5 and FeO, as described above. The major effect of the lower fluid pressure is seen in the compositions of biotite and staurolite. As seen in Figure 4, these minerals are relatively iron-poor compared to those in similar assemblages in rocks metamorphosed at *Pfluid = Ptotal* (Fig. 3).

The assemblages and compositions of minerals predicted in the diagrams in Figures 3 and 4 are in excellent agreement with those observed at Anderson Lake. Biotite and staurolite coexist with sillimanite, muscovite and IRPP in the muscovite zones I and II and the gradational zone. The iron-content of biotite and staurolite is higher in the muscovite zone-II (Xann=0.31-0.32, XFe(stau)=0.74-0.75) where *Pfluid* is estimated to be equal to *Ptotal*. In the gradational zone and muscovite zone-I, metamorphosed at *Pfluid* < *Ptotal*, biotite and staurolite have a lower iron content. Muscovite-free rocks from the gradational zone contain biotite and staurolite with a still lower iron content (Xann=0.24, XFe(stau)=0.65-0.67).

Biotite, staurolite, and garnet coexist only with ilmenite, with or without muscovite, in the lower parts of the chlorite zone and in the metasedimentary country rocks. The iron content of all ferromagnesian minerals is lower in muscovite-free rocks (Table 3). The assemblages and compositions of minerals are again in excellent agreement with the predicted values in Figure 3.

In muscovite bearing rocks, garnet occurs as a minor phase with biotite and staurolite. In the gradational zone, sillimanite-free rocks contain muscovite, biotite and garnet with the PPM assemblage. In these rocks, biotite and staurolite have slightly higher iron content (Xann=0.3, XFe(stau=0.74), as predicted in Figure 4. However, the predicted relationships suggest that garnet will not be a stable phase in these rocks. Similarly, garnet is occasionally present in the muscovite zone-II in association with the IRPP assemblage. This is also contrary to the predicted relationships in Figure 3. The higher values of MnO in these garnets (Table 3) may be responsible for their presence. An increase in the stability field of garnets due to extensive solid solution of Mn has also been observed in other metamorphosed ore deposits (Nesbitt, 1982).

Spruce Point

Phase relations in the country rocks and altered rocks at Spruce Point can be studied by means of the diagram in Figure 5. This diagram was constructed at 750 K and 2.0 kb pressure using the data in Table (4) and the condition ***Pfluid = Ptotal***. Thermodynamic properties of andalusite were used for calculating the activity of Al_2SiO_5. Due to the lack of reliable thermodynamic data, chlorite was again excluded in the modeling calculations. Figure 5 indicates that biotite coexisting with andalusite, muscovite, and IRPP would have an Xann content of 0.33 (Point A, Fig. 5). Biotite in assemblages containing rutile without ilmenite would have a lower value of Xann. In assemblages containing only ilmenite, biotite would have a higher Xann content than 0.33.

The composition of biotite from the altered and country rocks at Spruce Point agree well with those predicted in Figure 5. In the country rocks, biotite occurs with muscovite and ilmenite and is iron-rich (Xann=0.48) compared with biotite in the gradational zone (Xann=0.24) which occurs with muscovite, rutile, and pyrite. In andalusite bearing rocks, biotite is iron-rich (Xann=0.32) when it occurs with IRPP (msucovite zone-I) compared with

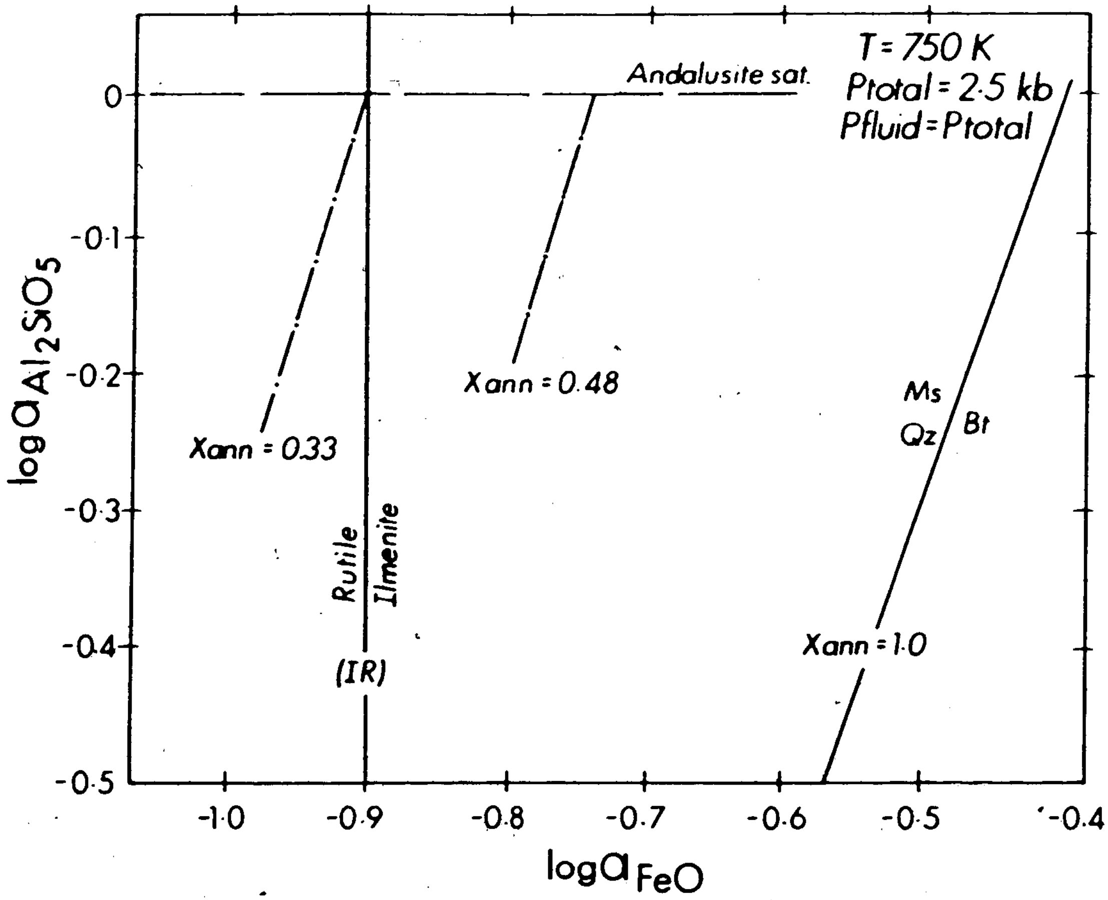

Figure 5. Activity - activity diagram at 750 K temperature and 2.5 Kb pressure (*Pfluid* = *Ptotal*) for the analysis of phase equilibria at Spruce Point. The symbols are the same as in Figure 3.

biotite coexisting with rutile (Xann = 0.22, chlorite zone).

Stability of Chlorite

As has been stated earlier, the stability of chlorite was not considered in the analysis of phase equilibria due to a lack of reliable thermodynamic data. Using the phase relations among biotite, garnet, and staurolite described above, an internally consistent set of themodynamic data can be derived for chlorite.

Experimental studies on the stability of Fe-end member chlorite, daphnite, have been reported by James ~~et al. (1976)~~ and Bryndzia (1984). Combining the data of James et al. (1976) with those from several other sources, Hutcheon (1979) derived an expression for the stability of chlorite according to the reaction:

$$\text{3 Daphnite} = \text{5 Magnetite} + \text{3 Sillimanite} + \text{6 Quartz} + 7\,H_2O + 5\,H_2 \tag{11}$$

Combining reaction (11) with reaction (12):

$$H_2 + 0.5\,O_2 = H_2O \tag{12}$$

gives the reaction:

$$\text{3 Daphnite} + 2.5\,O_2 = \text{5 Magnetite} + \text{3 Sillimanite} + \text{6 Quartz} + 7\,H_2O \tag{13}$$

Equilibrium conditions for raction (13) are obtained from the data of Hutcheon (1979) and Burnham et al. (1969). A direct, experimental calibration for reaction (13) is given by Bryndzia (1984).

Using Hutcheon's (1979) data for reaction (13), chlorite in equilibrium with rutile, ilmenite, pyrite, and pyrrhotite at 575 °C and 5.25 kb would have an XFe of 0.4. Data derived from the experiments of Bryndzia (1984) give similar values (0.43). These values of XFe for chlorite are much higher than those observed in the altered rocks at Anderson Lake (Table 3).

To achieve consistency between the composition of chlorite and other Fe-Mg silicate minerals at Anderson Lake, the endmember equilibrium for reaction (13) should have an fO_2 of $10^{-20.9}$ bars at 575 °C and 5.25 kb pressure. The values of equilibrium fO_2 based on the data of Hutcheon (1979) and Bryndzia (1984) are, respectively, 10^{-20} bars and $10^{-19.3}$ bars.

Using the value of $10^{-20.9}$ bars for fO_2 at 575 °C and 5.25 kb, the XFe value of chlorite in the presence of sillimanite and IRPP will be 0.29. At 475 °C and 2.0 kb, chlorite coexisting with andalusite and IRPP will have XFe = 0.35. In the presence of rutile without ilmenite, the XFe values of chlorite will be lower. These calculated compositions of chlorite are in excellent agreement with the observed values at Anderson Lake and Spruce Point (Table 3). This suggests that experimental determination of the stability of chlorite may be in error. The calibration for reaction (13) by Hutcheon (1979) is based on several different experimental studies and is subject to large errors. However, the experiments of Bryndzia (1984) are well reversed. It is possible that the excess aluminum present in metamorphic chlorites (compared with ideal daphnite) is responsible for the observed discrepency in field and laboratory data.

H. Fluid-Rock Interaction During Metamorphism

An important aspect of fluid-rock interaction is the degree of internal or external buffering of the metamorphic fluid phase (Ferry and Burt, 1982). Internal buffering by mineral equilibria refers to the case where the metamorphic fluid is derived from pre-metamorphic pore fluids and from devolatilization reactions (Greenwood, 1975). In the case of external buffering, the fluid phase in contact with the rock is derived at some other source and infiltrated during metamorphism. This infiltrated fluid buffers the mineral equilibria by imposing an externally controlled chemical potential of the fluid species (Rice and Ferry, 1982). The nature of fluid-rock interaction at Anderson Lake and Spruce Point can be characterized using the volatile and solid phase equilibria discussed above.

Analysis of mineral equilibria at Spruce Point and Anderson Lake suggests that variations in the assemblage and compositions of minerals were produced primarily due to differences in the bulk compositions of the altered rocks. Variations in the bulk compositions of the altered rocks are a result of the hydrothermal alteration during ore deposition, prior to metamorphism (Walford and Franklin, 1982; Chapter III). Thus the mineral assemblages at Spruce Point and Anderson Lake did not equilibrate with externally imposed conditions, indicating that the fluid phase was buffered internally.

A second factor responsible for variations in mineral composition at Anderson Lake was *Pfluid*. Local variations in *Pfluid* in the altered rocks suggest that the pore fluids in these rocks were not in communication with each other (Hanshaw and Zen, 1965). Consequently, the rocks were not infiltrated by externally derived fluids.

The oxygen isotopic compositions of rocks from the Anderson Lake and Spruce Point deposits also are consistent with internal buffering of the fluid phase during metamorphism. The isotopic compositions of rocks and minerals from these areas are given in Chapter III. The altered rocks have lower $\delta^{18}O$ values than the country rocks. Coexisting minerals from altered and country rocks, however, show isotopic equilibration at the peak of metamorphism although individual minerals differ in their isotopic composition by 3 to 6 permill. Based on the isotopic compositions of the altered rocks, country rocks, and intrusive rocks, it is concluded that the altered rocks equilibrated with ^{18}O depleted fluids prior to metamorphism (Chapter III). Isotopic homogenization during metamorphism took place on a grain to grain scale and, at most, on a scale of meters.

The preceding discussion suggests that during metamorphism, there was no significant chemical interaction between the ore and the adjoining rocks at Anderson Lake and Spruce Point. This is consistent with no apparent, systematic variations in the assemblage and compostions of minerals with distance from the ore. For example, the assemblage biotite - staurolite - sillimanite - chlorite is present in the muscovite zone-II, surrounding the ore, as well as in the gradational zone and muscovite zone-I. The iron content of silicate minerals in this assemblage is higher close to the ore and varies in other zones as a result of the variations in *Pfluid*.

This "closed system" behavior of the ore at Anderson Lake and Spruce Point is significantly different than that reported at the Ducktown, Tennessee and Geco, Manitowadge deposits (Nesbitt, 1982; Petersen, 1984). At these deposits, it is interpreted that sulfur and oxygen released in sulfidation/desulfidation reactions equilibrated with adjoining rocks. This migration of the volatile species produced systematic zonations in sulfide - silicate - oxide assemblages and the compositions of Fe-Mg silicate minerals. The reasons for the apparent differences in the nature of fluid - rock interaction at Ducktown, Geco, and the deposits of this study are not clear. One possible reason is the difference in the host rocks. At Ducktown, the deposits are contained in metasedimentary rocks with a significant proporiton of carbon-bearing phases. The presence of carbon-bearing phases generally facilitates fluid flow during metamorphism and may be responsible for the differences in fluid-rock interaction between Ducktown and the deposits of this study. However, this reason is not valid for the Geco deposit which is also contained in felsic metavolcanic rocks, similar to the deposits of the Flin Flon - Snow Lake belt. It is possible that data for the Geco deposit may be re-interpreted as a case of internal buffering in view of the results of this study.

I. Conclusions

The distribution of Fe-Mg silicate minerals at the Anderson Lake and Spruce Point deposits show distinct variations in the altered and country rocks. Biotite, staurolite, chlorite, and garnet are iron-poor in the altered rocks compared with those in the country rocks. Variations in the compositions of these minerals within the altered rocks do not show any apparent relationship to coexisting opaque minerals or to distance from ore. An analysis of the metamorphic phase eqilibria indicates that variations in the compositions of the Fe-Mg silicate minerals were produced due to variations in the bulk composition of the rocks and *Pfluid*. Chemical interaction between the ore and the host rocks was insignificant as the metamorphic fluid was buffered by local mineral equilibria.

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V. Summary

This dissertation reports the results of an investigation of the metamorphism of massive sulfide deposits in the Flin Flon - Snow Lake Belt, Manitoba. Three deposits in this belt, Anderson Lake, Spruce Point, and Centennial, were selected for a detailed study. The objective of the investigation was to characterize and understand the effects of metamorphism on the oxygen-isotope geochemistry, mineralogy, and mineral chemistry of the altered and country rocks associated with these deposits.

The pressure and temperature conditions of metamorphism at the Anderson Lake, Spruce Point, and Centennial deposits were estimated using the mineral assemblages in mafic and felsic metavolcanic rocks. The mafic rocks are composed of chlorite + plagioclase ± sphene ± actinolite ± zoisite in the Centennial area and of actinolite + plagioclase + hornblende + zoisite ± chlorite ± sphene in the Spruce Point area. The felsic rocks at Centennial are composed of quartz and muscovite and those at Spruce Point are composed of quartz, muscovite, and biotite. Altered rocks associated with the Spruce Point deposit contain andalusite, muscovite, and plagioclase. Comparisons with experimental studies of mineral systems in mafic rocks indicate metamorphic conditions of low greenschist facies at Centennial and of middle to upper greenschist facies at Spruce Point. A simultaneous consideration of the paragonite - albite - andalusite equilibrium and oxygen-isototpe fractionations between quartz, muscovite, and chlorite suggests that the conditions of metamorphism at Spruce Point were: 475±50°C at 2.0±0.5 kb pressure. In the Centennial area, the temperature of metamorphism was 330±30°C at less than 2.0 kb pressure.

Metamorphic grades of amphibolite facies were reached in the Snow Lake area, near the Anderson Lake deposit. The temperature and pressure conditions of metamorphism were estimated using the garnet - biotite, kyanite - sillimanite, ilmenite - almandine - sillimanite - rutile, and anorthite - grossular - sillimanite equilibria. Calculated values of temperature and pressure are: 575±30°C at 5.25±0.5 kb in the staurolite - biotite zone; and 625±30°C at 5.4±0.5 kb in the biotite - sillimanite - almandine zone.

The oxygen-isotope compositions of whole-rock and monomineralic samples from the Anderson Lake, Spruce Point, and Centennial deposits were measured. The altered rocks at the three deposits all have significantly lower $\delta^{18}O$ values compared with the associated country rocks. Quartz, biotite, muscovite, and chlorite separated from the altered rocks have lower $\delta^{18}O$ values than those separated from the country rocks. However, isotopic fractionations beween coexisting mineral pairs are generally similar in both altered and country rocks, indicating that these rocks did not re-equilibrate significantly after the peak of metamorphism. Based on mass-balance calculations of isopoic exchange by fluid-rock interaction and the $\delta^{18}O$ values of amphibolite dikes in the altered and country rocks, it is suggested that the lower isotopic compositions of the altered rocks were produced prior to metamorphism, during hydrothermal alteration related to ore deposition. The hydrothermal fluids are estimated to have a $\delta^{18}O$ value of 0 ± 3 permill and a temperature of 300 ± 100 °C. Hydrothermal fluids were probably hotter at Cu-rich, Anderson Lake deoposit relative to the Zn-rich, Spruce Point and Centennial deposits The higher temperature of the fluids is also considered to be responsible for the development of the muscovite-rich rocks around the Anderson Lake ore body.

The mineralogy of the altered rocks at the Anderson Lake and Spruce Point deposits differs from that of the country rocks mainly by the absence of hornblende and by a greater abundance of staurolite, sillimanite, muscovite, and chlorite. The Fe-Mg silicate minerals all are iron-poor in the altered rocks compared with those in the country rocks. Calculations of the composition of the fluid phase indicate that the fluid phase at the Anderson Lake and Spruce Point deposits consisted essentially of H_2O with minor contents of O_2, S_2, SO_2, H_2S, and H_2. PH_2O was nearly equal to *Pfluid* which latter was equal to *Ptotal* at Spruce Point. At Anderson Lake, *Pfluid* was equal to or up to 750 bars lower than *Ptotal.*

Altered rocks at the Anderson Lake and Spruce Point deposits had a higher activity of Al_2SiO_5 and a lower activity of FeO compared with the country rocks. The activities of Al_2SiO_5 and FeO varied also in altered rocks from different alteration zones. These variations in the bulk composition of the rocks, together with local variations in *Pfluid* at Anderson Lake, were responsible for the variations in the compositions of the Fe-Mg silicate minerals. The composition of the fluid phase was buffered by local mineral equilibria and consequently, chemical interaction between the ore and the adjoining rocks was insignificant.

VI. Appendix I

A. Sample Locations, Mineral Assemblages, and Mineral Analyses

The location of samples together with the assemblage and compositions of minerals in thin-section are tabulated in this appendix. The sample numbers are organized as follows:

Series	Location
Snow Lake	
SL-xx	Surface Sample
14-xxx	Sub-surface Sample, 1425 Level, Anderson Mine
16-xxx	Sub-surface Sample, 1600 Level, Anderson Mine
7-xxx	Drill Hole 7, xxx feet, 1600 Level, Anderson Mine
6-xxx	Drill Hole 6, xxx feet, 1600 Level, Anderson Mine
17-xxx	Sub-surface Sample, 1750 Level, Anderson Mine
19-xxx	Sub-surface Sample, 1950 Level, Anderson Mine
24-xxx	Sub-surface Sample, 2474 Level, Anderson Mine
72-xxx	Drill Hole 72, xxx feet, 2475 Level, Anderson Mine
26-xxx	Sub-surface Sample, 2650 Level, Anderson Mine
78-xxx	Drill Hole 78, xxx feet, 2475 Level, Anderson Mine
182-xxx	Drill Hole 182, xxx feet, 2475 Level, Anderson Mine
30-xxx	Sub-surface Sample, 3000 Level, Anderson Mine
Spruce Point	
115-xxx	Drill Hole 115, xxx feet
67-xxx	Drill Hole 67, xxx feet
32-xxx	Drill Hole 32, xxx feet
94-xx	Subsurface Sample, 94 meter level
Centennial	
17-xxx	Drill Hole 17, xxx feet
20-xxx	Drill Hole 20, xxx feet
20-W-xxx	wedge from Drill Hole 20, xxx feet

The abbreviations used in this section are as follows:

RT	Rock Type
	1 = chlorite zone
	2 = muscovite zone-I
	3 = gradational zone
	4 = muscovite zone-II
	5 = felsic metavolcanics
	6 = mafic metavolcanics
	7 = metasedimentary
	8 = Tonalite
Ch	Chlorite
Bt	Biotite
Ms	Muscovite
Gt	Garnet
As	Alumino-silicate (sillimanite, kyanite, andalusite)
St	Staurolite
Zo	Zoisite
Hb	Hornblende
Qz	Quartz
Fs	Plagioclase Feldspar
Mt	Magnetite
Im	Ilmenite
Ru	Rutile
Py	Pyrite
Po	Pyrrhotite
Cp	Chalcopyrite
Sp	Sphalerite
Ti	Titanite (Sphene)
To	Tourmaline

Mineral Assemblages

No.	RT	Ch	Bt	Ms	Gt	As	St	Zo	Hb	Qz	Fs	Mt	Im	Ru	Py	Po	Cp	Sp	Ti	To
Snow Lake area:																				
SL-5	3	x	x	x	x		x			x	x		x		x	x				
SL-6	3	x	x	x	x		x			x	x		x		x	x				
SL-6A	3	x	x	x	x		x			x	x		x		x	x				
SL-8	6																			
SL-9	6		x						x	x	x								x	
SL-10	6																			
SL-11	5									x										
SL-13	5	x	x	x	x					x	x	x	x							
SL-14	1	x	x			x				x			x	x						
SL-17	5		x		x				x	x	x		x		x					
SL-18	5		x		x				x	x	x		x		x					
SL-21	6		x						x	x	x								x	
SL-22	6		x		x				x	x	x									
SL-24	5	x	x	x	x				x	x	x		x		x					
SL-25	6								x	x			x	x					x	
SL-26	5	x	x	x	x															
SL-27	5		x							x	x		x	x			x			
SL-28	5	x	x	x	x		x			x	x		x		x					x
SL-29	7		x	x	x		x			x	x		x		x					
SL-30	3	x	x		x					x	x									
SL-31	3		x		x				x	x	x									
SL-33																				
SL-34	3	x	x		x		x			x	x									
SL-35	5		x		x				x	x	x		x							
SL-36																				
SL-37																				
Anderson Lake Mine:																				
1475 Level																				
-01	3	x	x				x			x	x	x	x	x	x	x				
-02	3		x				x			x	x	x	x		x	x				
1600 Level																				
-07	3	x	x	x	x		x			x	x	x	x	x	x	x	x			
-06	3	x	x							x	x	x	x	x	x	x	x			
-05	3	x	x	x	x		x			x	x	x	x	x	x	x	x			x
-04	3	x	x		x					x	x	x	x							
-03	3	x	x							x	x	x	x	x	x	x	x			
-01	1	x	x				x						x	x	x	x	x			
Drill Hole AS 7																				
-10	1	x								x	x									
-17	3		x	x		x	x			x	x	x	x		x	x	x			
-25	3		x	x		x	x			x	x		x	x	x	x	x			x
-85	3		x	x		x	x			x	x		x	x	x	x	x			
-95	3		x	x		x	x			x	x		x	x	x	x	x			
-105	3		x	x		x	x			x	x		x	x	x	x	x			
-112	3		x	x		x	x			x	x		x	x	x	x	x			x
-140	O		x	x		x	x			x	x		x	x	x	x	x			x
-172	O		x	x		x	x			x	x		x	x	x	x	x			x
-205	4	x	x	x	x					x	x	x	x		x	x	x			

No	RT	Ch	Bt	Ms	Gt	As	St	Zo	Hb	Qz	Fs	Mt	Im	Ru	Py	Po	Cp	Sp	Tt	To
1750 Level																				
01	3	x	x				x			x	x	x	x	x	x	x	x	x		
03	3	x	x	x		x	x			x	x	x	x	x	x	x				
-05	3		x	x			x			x	x	x	x	x						
2475 Level																				
01	2	x	x			x	x			x	x		x	x						
-03	1	x	x				x			x	x	x	x	x	x					
04	3	x	x				x			x	x	x	x	x	x		x			
05	3		x	x				x		x	x	x	x		x	x	x			
-07	3	x	x	x		x	x			x	x		x			x	x			x
-08	3	x	x	x		x	x			x	x		x	x	x					x
09	3	x	x			x	x			x	x	x	x	x	x	x				
10	4	x	x	x		x	x			x	x		x	x	x	x	x			
-13	4	x	x	x		x	x			x	x		x	x	x	x	x	x		
Drill Hole AS 72																				
-05	3	x	x	x			x	x		x	x		x	x	x	x				
-33	4		x	x		x	x			x	x		x	x	x	x				
-35	3	x	x			x	x			x	x		x	x	x	x	x			
-65	3	x	x			x	x			x	x		x	x	x	x				
-70	3	x	x			x	x			x	x				x	x	x			
-113	3	x	x			x	x			x	x		x	x	x					
-170	3	x	x	x		x	x			x	x				x	x	x			
-220	3	x	x			x	x			x	x		x	x			x			
-295	4	x	x	x		x	x			x	x		x	x	x	x	x			
-330	4	x	x	x		x	x			x	x		x	x	x	x	x			
Drill Hole AS 78																				
-243	5	x	x						x	x	x		x	x	x		x			
-238	4	x	x	x		x	x			x	x	x	x	x	x	x	x			
-186	4		x	x			x			x	x		x	x	x	x	x			x
-175	3		x	x			x			x	x		x		x	x	x			x
-68	3	x	x	x			x			x	x	x	x		x	x				
-51	3	x	x	x		x	x			x	x		x		x	x	x			
-30	3		x							x	x				x	x				
2650 Level																				
-10	4		x	x	x	x	x			x	x		x	x	x	x	x			
-06	1	x	x		x		x			x	x									
-02	3		x							x	x		x	x	x	x				
Drill Hole AS 182																				
-35	6		x		x			x		x	x									
-95	1	x	x				x			x	x		x	x			x			
-175	2		x	x		x	x			x	x		x	x						
-235	1	x	x		x		x			x	x		x			x	x			
-270	2	x	x	x		x	x			x	x		x	x	x	x	x			
-320	2	x	x	x		x	x			x	x		x	x	x	x	x			
-425	5	x	x		x					x	x		x	x						
-520	5	x	x		x		x			x	x	x	x				x			
-620	5		x		x					x	x	x	x	x						
-715	6	x	x						x	x	x	x	x							
-785	6		x		x				x	x	x									
-920	4		x	x				x		x2		x			x					
-1040	6		x		x				x	x	x			x						

No	RT	Ch	Bt	Ms	Gt	As	St	Zo	Hb	Qz	Fs	Mt	Im	Ru	Py	Po	Cp	Sp	Ti	To
Spruce Point																				
Drill Hole SP 32																				
-40	3		x	x				x	x											
-55	3	x	x	x				x	x											
-80	3	x	x	x		x		x	x		x	x	x	x				x		
-85	3	x		x				x	x				x	x		x			Ap	
-182	3	x		x				x	x	x	x		x	x					Ap	Mg
-205	3	x	x																	
		x						x	x										Gh	
210	3	x		x				x			x	x	x	x					Ap	
-232	3	x	x	x	x			x	x	x	x	x	x	x					Cd	Mg
Drill Hole 67																				
-702	3		x	[illegible]				x	x			x								
-752	3		x	[illegible]				x			x		x	x	x					Mg
-768	3	x		x						x	x		x		x				Cd	21Mg
-797	O	x				x				x			x	x	x	x				
-920	5		x	x				x	x		x				x					
Drill Hole 115																				
-235	5		x	x		x		x	x										Cc	
-325	6			x		x	x	x	x											
-1061	3	x	x	x				x	x			x	x	x	x				Cc	
-1307	1	x	x	x				x		x	x	x	x	x	x					
-1323	2	x	x	x	x					x	x	x	x	x						
-1394	6		x				x	x	x											

Ap = Arsenopyrite; Cd = Chloritoid; Mg = Margarite; Gh = Gahnite
Cc = Calcite

Composition of Minerals from Anderson Lake

Biotite

	24-04	24-13	24-09	24-07	24-08	24-01	72-05	72-33	72-70	72-113
SiO_2	35.57	35.56	36.40	37.24	36.80	36.56	36.42	35.97	36.90	37.12
Al_2O_3	18.15	18.77	18.47	18.47	20.11	18.16	18.17	18.38	19.29	19.42
MgO	12.00	11.68	12.12	15.38	11.69	13.76	12.71	12.24	12.90	14.03
FeO	16.05	16.55	16.89	12.24	14.10	13.39	15.90	16.41	15.24	12.63
TiO_2	1.55	1.44	1.31	1.10	1.37	1.61	1.63	1.46	1.06	1.14
MnO	0.08	0.00	0.00	0.11	0.08	0.00	0.36	0.00	0.00	0.0
K_2O	9.06	8.91	9.32	9.44	8.92	9.25	9.47	9.09	8.83	8.88
Na_2O	0.46	0.52	0.82	0.56	0.36	0.23	0.43	0.62	0.44	0.62
Total	92.94	93.45	95.32	94.63	93.50	93.00	95.16	94.21	94.66	93.83

No of Cations Based on 22 Oxygen

Si	5.47	5.44	5.47	5.52	5.53	5.53	5.47	5.46	5.50	5.52
Al	3.29	3.38	3.27	3.22	3.56	3.24	3.22	3.29	3.39	3.40
Mg	2.75	2.66	2.72	3.40	2.62	3.10	2.85	2.77	2.87	3.11
Fe	2.06	2.12	2.12	1.52	1.77	1.69	2.00	2.08	1.90	1.57
Ti	0.18	0.17	0.15	0.12	0.15	0.18	0.18	0.17	0.12	0.13
Mn	0.01	0.00	0.00	0.01	0.01	0.00	0.05	0.00	0.00	0.0
K	1.78	1.74	1.79	1.78	1.77	1.79	1.82	1.76	1.68	1.68
Na	0.14	0.16	0.24	0.16	0.10	0.07	0.12	0.18	0.13	0.18

	72-220	72-295	72-330	30-06	30-07	30-11	30-80	16-07	16-05	16-03
SiO_2	37.33	36.61	36.36	36.90	35.92	36.82	36.75	35.98	35.62	37.28
Al_2O_3	19.04	19.09	19.17	19.03	18.61	18.78	18.80	18.74	18.89	16.50
MgO	14.47	11.87	12.03	13.22	12.03	12.91	11.90	11.99	11.51	15.06
FeO	12.71	16.90	16.90	15.25	16.66	15.66	16.76	19.58	17.66	13.88
TiO_2	1.03	1.59	1.46	1.44	1.47	1.55	1.75	1.56	1.59	1.46
MnO	0.00	0.00	0.00	0.08	0.00	0.00	0.20	0.06	0.08	0.16
K_2O	8.59	9.04	9.06	9.49	8.93	9.19	9.55	9.15	9.11	8.68
Na_2O	0.62	0.49	0.65	0.28	0.45	0.70	0.43	0.30	0.35	0.23
Total	93.79	95.59	95.64	95.69	94.06	95.60	96.11	95.35	94.78	93.35

No of Cations based on 22 Oxygen

Si	5.54	5.46	5.43	5.47	5.45	5.47	5.47	5.43	5.41	5.63
Al	3.33	3.36	3.37	3.32	3.33	3.29	3.30	3.30	3.35	2.93
Mg	3.20	2.64	2.68	2.92	2.72	2.86	2.64	2.69	2.61	3.39
Fe	1.59	2.11	2.11	1.89	2.11	1.95	2.09	2.21	2.24	1.75
Ti	0.12	0.18	0.16	0.16	0.17	0.17	0.20	0.18	0.18	0.17
Mn	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.01	0.01	0.02
K	1.63	1.72	1.73	1.79	1.73	1.74	1.81	1.76	1.77	1.67
Na	0.18	0.14	0.19	0.08	0.13	0.20	0.12	0.09	0.10	0.07

	16-01	7-17	7-25	7-95	7-105	7-112	7-140	7-172	7-205	6-175
SiO_2	36.19	37.87	36.75	38.03	38.35	38.54	35.92	37.24	36.85	36.13
Al_2O_3	18.24	18.68	18.67	18..68	18.79	17.99	18.40	19.31	17.17	17.59
MgO	12.77	12.67	13.14	12.62	12.81	13.55	13.78	12.91	13.24	11.87
FeO	15.26	16.88	14.87	15.30	15.31	14.53	15.28	15.75	16.49	16.90
TiO_2	1.36	1.53	1.54	2.13	1.91	1.99	1.55	1.67	1.46	1.82
MnO	0.12	0.00	0.10	0.00	0.00	0.09	0.00	0.29	0.00	0.18
K_2O	9.65	9.54	9.37	10.16	9.33	10.03	9.08	8.49	9.78	9.46
Na_2O	0.00	0.69	0.87	0.24	0.88	0.33	0.30	0.17	0.31	0.29
Total	93.65	97.86	95.21	97.16	97.37	97.04	94.21	95.82	95.31	94.28

No of Cations Based on 22 Oxygen

	16-01	7-17	7-25	7-95	7-105	7-112	7-140	7-172	7-205	6-175
Si	5.50	5.52	5.46	5.53	5.57	5.60	5.41	5.48	5.52	5.50
Al	3.27	3.21	3.27	3.20	3.22	3.08	3.27	3.35	3.03	3.16
Mg	2.89	2.76	2.91	2.74	2.77	2.93	3.09	2.83	2.96	2.70
Fe	1.94	2.06	1.85	1.86	1.86	1.77	1.92	1.94	2.07	2.15
Ti	0.16	0.17	0.17	0.23	0.21	0.22	0.18	0.19	0.16	0.24
Mn	0.02	0.00	0.01	0.00	0.00	0.01	0.00	0.04	0.00	0.02
K	1.87	1.76	1.78	1.86	1.73	1.86	1.75	1.60	1.87	1.84
Na	0.00	0.20	0.20	0.06	0.25	0.11	0.09	0.05	0.09	0.09

	16-4	182-175	182-235	182-270	182-320	182-425	182-620	182-785	182-1040
SiO_2	37.13	36.83	36.12	36.40	36.29	36.73	35.57	36.28	34.80
Al_2O_3	18.08	18.58	18.89	18.30	18.44	17.98	18.63	16.63	17.22
MgO	8.33	13.19	11.92	14.48	12.72	12.22	10.45	11.64	4.74
FeO	12.88	14.58	16.92	15.11	15.16	17.73	19.30	19.47	27.19
TiO_2	1.51	1.76	1.67	1.69	1.70	1.64	1.59	1.58	2.81
MnO	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K_2O	9.08	9.25	9.05	9.01	8.88	8.71	8.95	8.89	9.34
Na_2O	0.37	0.92	0.80	0.74	0.86	0.00	0.00	0.00	0.00
Total	95.16	95.12	95.39	94.74	94.05	95.01	94.69	94.49	96.13

No of Cations Based on 22 Oxygen

	16-4	182-175	182-235	182-270	182-320	182-425	182-620	182-785	182-1040
Si	5.54	5.48	5.45	5.45	5.47	5.52	5.43	5.56	5.47
Al	3.18	3.26	3.32	3.23	3.28	3.16	3.35	3.00	3.16
Mg	2.93	2.93	2.68	3.01	2.86	2.74	2.42	2.66	1.11
Fe	1.97	1.81	2.13	1.89	1.91	2.23	2.46	2.49	3.57
Ti	0.17	0.20	0.19	0.19	0.19	0.19	0.18	0.18	0.33
Mn	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

K	1.73	1.76	1.75	1.72	1.71	1.67	1.74	1.74	1.87
Na	0.11	0.26	0.22	0.22	0.25	0.00	0.00	0.00	0.00

	78-51	78-68	78-175	78-238	26-10	SL-14	SL-28	SL-35	SL-37
SiO_2	37.20	36.86	37.15	36.66	36.97	38.11	34.78	35.22	36.26
Al_2O_3	19.49	18.31	18.91	19.28	18.47	19.17	18.54	18.90	19.60
MgO	11.80	12.14	12.28	12.50	12.28	15.69	8.97	5.18	9.50
FeO	16.86	16.79	16.55	16.01	17.13	11.24	21.02	24.29	18.43
TiO_2	1.70	1.35	1.34	1.66	1.43	1.35	1.69	2.05	2.14
MnO	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.30	0.00
K_2O	9.02	9.02	9.22	9.19		8.77	9.63	9.46	8.69
Na_2O	0.82	0.91	0.82	0.57	0.70	0.67	0.34	0.00	0.00
Total	97.04	95.47	96.06	96.02	96.34	94.98	94.98	95.40	94.63

No of Cations Based on 22 Oxygen

Si	5.47	5.53	5.51	5.43	5.49	5.55	5.38	5.49	5.48
Al	3.37	3.23	3.30	3.37	3.23	3.29	3.38	3.47	3.49
Mg	2.58	2.71	2.71	2.76	2.72	3.40	2.07	1.20	2.14
Fe	2.07	2.10	2.05	1.98	2.13	1.37	2.72	3.16	2.33
Ti	0.19	0.15	0.15	0.19	0.16	0.15	0.20	0.24	0.24
Mn	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.04	0.00
K	1.72	1.72	1.70	1.74	1.74	1.63	1.90	1.88	1.68
Na	0.23	0.26	0.24	0.16	0.20	0.19	0.10	0.00	0.00

	SL-17	SL-18	SL-13	SL-10	SL-22	SL-24
SiO_2	35.46	35.75	34.82	34.67	35.40	35.88
Al_2O_3	16.10	16.12	18.65	16.68	16.66	18.59
MgO	9.51	11.81	5.91	7.15	9.13	7.25
FeO	21.40	19.28	25.12	25.59	22.18	23.89
TiO_2	3.38	3.07	1.23	2.48	2.77	2.13
MnO	0.01	0.00	0.20	0.00	0.10	0.04
K_2O	8.83	8.29	9.73	8.31	9.13	9.29
Na_2O	0.02	0.05	0.00	0.31	0.07	0.00
Total	94.71	94.37	95.66	95.19	95.44	97.07

No. of Cations Based on 22 Oxygen

Si	5.49	5.47	5.45	5.44	5.46	5.46
Al	2.91	2.88	3.40	3.05	3.00	3.30
Mg	2.19	2.69	1.38	1.67	2.10	1.64
Fe	2.77	2.47	3.29	3.36	2.86	3.04
Ti	0.39	0.35	0.14	0.29	0.32	0.24
Mn	0.00	0.00	0.03	0.00	0.01	0.01

K	1.74	1.62	1.94	1.66	1.80	1.80
Na	0.00	0.01	0.00	0.11	0.01	0.00

Staurolite

	24-03	24-09	24-13	24-01	24-08	24-10	72-33	72-70	72-113	72-220
MgO	2.42	0.2.77	2.75	2.00	1.94	1.77	2.63	3.00	3.24	3.46
Al_2O_3	47.94	52.38	52.80	52.28	52.28	51.66	52.31	54.87	55.01	54.62
SiO_2	31.64	27.82	26.75	26.97	26.64	26.46	27.00	27.18	27.97	27.60
TiO_2	0.48	0.55	0.50	0.57	0.38	0.43	0.42	0.48	0.25	0.41
MnO	0.18	0.29	0.37	0.53	0.38	0.38	0.32	0.220	0.24	0.25
FeO	12.33	13.37	13.82	11.88	12.47	13.18	13.85	13.24	11.36	11.85
ZnO	0.09	0.14	0.07	0.37	0.22	0.44	0.00	0.52	1.34	0.70
Total	95.08	97.32	97.04	94.59	94.29	94.30	96.53	99.49	99.39	98.90

No. of Cations Based on 23 Oxygen

	24-03	24-09	24-13	24-01	24-08	24-10	72-33	72-70	72-113	72-220
Mg	0.51	0.57	0.58	0.43	0.41	0.38	0.55	0.61	0.66	0.71
Al	7.98	8.58	8.75	8.80	8.85	8.79	8.68	8.83	8.82	8.80
Si	4.47	3.87	3.76	3.85	3.83	3.82	3.80	3.71	3.80	3.77
Ti	0.05	0.06	0.05	0.06	0.04	0.05	0.04	0.05	0.03	0.04
Mn	0.02	0.03	0.04	0.06	0.05	0.05	0.04	0.02	0.03	0.03
Fe	1.46	1.55	1.63	1.42	1.50	1.59	1.63	1.51	1.29	1.35
Zn	0.01	0.01	0.01	0.04	0.02	0.05	0.00	0.05	0.13	0.07

	72-295	72-330	30-06	30-07	30-80	SL-28	SL-37	SL-5	SL-6A
MgO	2.90	2.72	2.69	2.74	2.10	1.01	1.59	1.75	1.84
Al_2O_3	53.61	53.51	54.54	54.27	52.76	54.80	55.23	51.73	53.35
SiO_2	27.15	27.29	27.53	27.40	27.29	28.84	27.52	29.33	28.19
TiO_2	0.48	0.42	0.51	0.42	0.46	0.36	0.46	0.49	0.46
MnO	0.35	0.39	0.63	0.45	0.84	0.22	0.13	0.29	0.23
FeO	13.79	14.09	11.82	13.80	13.07	12.63	13.67	13.15	14.18
ZnO	0.22	0.20	1.59	0.58	0.32	0.85	0.20	0.00	0.26
Total	98.47	98.62	99.31	99.66	96.85	98.71	98.80	96.84	98.49

No. of Cations Based on 23 Oxygen

	72-295	72-330	30-06	30-07	30-80	SL-28	SL-37	SL-5	SL-6A
Mg	0.59	0.56	0.55	0.56	0.44	0.21	0.33		0.38
Al	8.74	8.73	8.81	8.77	8.74	8.84	8.94		8.69
Si	3.75	3.78	3.77	3.76	3.84	3.95	3.78		3.89
Ti	0.05	0.04	0.05	0.04	0.05	0.04	0.05		0.05
Mn	0.04	0.05	0.07	0.05	0.10	0.02	0.01		0.03
Fe	1.59	1.63	1.35	1.52	1.54	1.45	1.57		1.64

Zn	0.02	0.02	0.16	0.04	0.03	0.09	0.02		0.03

	7-17	7-25	7-95	7-105	7-112	7-140	16-01	16-15	16-17
MgO	3.00	3.05	3.03	3.19	2.68	2.74	1.91	2.00	2.21
Al_2O_3	53.26	52.56	53.76	53.03	54.17	55.20	54.28	53.32	52.42
SiO_2	29.16	27.46	28.56	28.76	28.92	27.29	27.70	27.01	27.79
TiO_2	0.49	0.52	0.52	0.41	0.61	0.57	0.43	0.54	0.57
MnO	0.16	0.73	0.31	0.40	0.19	0.21	0.40	0.53	0.51
FeO	13.85	13.02	11.89	13.27	10.80	11.13	11.29	13.73	13.60
ZnO	0.00	0.57	0.82	0.12	1.39	1.19	2.88	1.18	0.98
Total	99.09	97.89	98.89	99.18	98.75	98.33	98.89	98.22	98.07

No. of Cations based on 23 Oxygen

Mg	0.60	0.63	0.62	0.65	0.54	0.56	0.39	0.42	0.46
Al	8.48	8.61	8.64	8.51	8.70	8.93	8.82	8.77	8.62
Si	3.94	3.81	3.89	3.92	3.94	3.75	3.82	3.77	3.88
Ti	0.05	0.05	0.05	0.04	0.06	0.06	0.04	0.11	0.12
Mn	0.02	0.09	0.04	0.05	0.02	0.02	0.05	0.13	0.12
Fe	1.57	1.51	1.36	1.51	1.23	1.28	1.30	1.60	1.59
Zn	0.00	0.06	0.08	0.01	0.14	0.12	0.29	0.12	0.10

	182-95	182-175	182-235	182-270	182-320	78-51	78-68	78-175	78-238	26-10
MgO	2.90	2.94	2.98	3.06	3.41	2.69	2.64	2.57	2.93	2.79
Al_2O_3	52.07	52.90	53.76	53.07	52.25	54.43	53.10	53.13	53.71	52.69
SiO_2	27.03	27.41	27.15	27.08	26.82	27.44	26.85	27.13	26.87	27.72
TiO_2	0.56	0.38	0.58	0.43	0.53	0.53	0.48	0.38	0.57	0.50
MnO	0.45	0.35	0.11	0.41	0.25	0.47	0.16	0.35	0.53	0.81
FeO	13.19	12.16	14.50	12.75	13.30	13.74	9.89	13.32	13.01	12.99
ZnO	0.32	0.81	0.15	0.40	0.10	0.23	5.78	1.11	0.17	1.31
Total	96.52	96.95	99.23	97.20	96.66	99.63	98.74	97.99	97.89	98.81

No. of Cations Based on 23 Oxygen

Mg	0.61	0.61	0.61	0.64	0.72	0.55	0.55	0.53	0.61	0.58
Al	8.66	8.72	8.73	8.74	8.67	8.76	8.73	8.74	8.80	8.60
Si	3.81	3.83	3.74	3.78	3.78	3.75	3.74	3.78	3.74	3.84
Ti	0.06	0.04	0.06	0.04	0.06	0.05	0.05	0.04	0.06	0.05
Mn	0.05	0.04	0.12	0.05	0.03	0.05	0.02	0.04	0.06	0.09
Fe	1.56	1.42	1.67	1.49	1.57	1.57	1.15	1.55	1.52	1.50
Zn	0.03	0.08	0.02	0.04	0.01	0.02	0.59	0.11	0.02	0.13

Garnet

	SL-5	SL-6A	SL-13		SL-10		SL-17	SL-18	SL-22	SL-37
			Core	Rim	Core	Rim				
MgO	3.04	3.10	1.04	1.33	1.03	1.27	2.89	3.89	2.44	2.35
Al_2O_3	21.01	21.16	21.26	21.40	21.33	21.49	20.87	21.31	21.09	21.29
SiO_2	39.40	37.90	37.44	37.31	37.86	37.78	37.61	37.98	37.81	37.99
CaO	2.25	0.92	7.66	5.76	7.35	5.84	5.33	4.99	5.26	2.28
MnO	4.67	4.00	5.19	3.85	6.26	4.94	2.21	2.70	3.01	2.74
FeO	31.47	32.38	28.60	31.44	27.61	29.77	31.51	29.83	31.54	33.41
Total	101.84	99.46	100.42	100.05	101.44	101.09	100.42	100.70	101.15	100.06

Cations Based on 12 Oxygen

Mg	0.35	0.37	0.12	0.16	0.12	0.15	0.34	0.46	0.29	0.28
Al	1.94	2.00	1.98	2.00	2.00	2.00	1.94	1.96	1.96	2.01
Si	3.09	3.05	2.98	2.98	3.00	3.01	3.00	3.00	3.00	3.04
Ca	0.19	0.08	0.65	0.49	0.63	0.50	0.46	0.42	0.45	0.20
Mn	0.31	0.27	0.35	0.26	0.42	0.33	0.15	0.18	0.20	0.19
Fe	2.06	2.18	1.91	2.10	1.83	1.98	2.10	1.97	2.10	2.24

	SL-24		182-235		182-425		182-620	182-785		182-35
	Core	Rim	Core	Rim	Core	Rim		Core	Rim	
MgO	1.28	1.28	3.78	4.16	3.02	4.11	3.11	2.11	2.77	3.26
Al_2O_3	21.90	21.94	21.70	21.71	21.92	22.15	20.96	20.82	20.79	21.66
SiO_2	38.38	38.51	37.73	37.45	38.07	38.13	37.40	37.43	37.44	37.56
CaO	8.08	10.39	2.96	2.23	2.73	2.07	2.34	5.09	3.88	2.73
MnO	3.26	2.24	1.30	0.42	5.04	2.25	3.19	6.04	3.40	1.52
FeO	29.24	28.58	33.55	34.12	30.48	32.27	33.20	28.80	31.78	33.84
Total	102.14	102.94	101.02	100.09	101.26	100.98	100.20	100.29	100.06	100.57

Cations Based on 12 Oxygen

Mg	0.15	0.15	0.45	0.49	0.36	0.48	0.37	0.25	0.33	0.39
Al	2.02	1.99	2.02	2.02	2.04	2.03	1.96	1.95	1.95	2.01
Si	3.01	2.99	2.98	2.98	3.00	3.00	3.00	3.00	3.01	2.99
Ca	0.68	0.86	0.25	0.19	0.23	0.17	0.20	0.44	0.33	0.23
Mn	0.22	0.15	0.09	0.03	0.34	0.15	0.22	0.41	0.23	0.10
Fe	1.91	1.86	2.22	2.27	2.01	2.12	2.23	1.93	2.14	2.25

	182-1040		16-04	16-07	16-05	6-175	30-80	30-11	26-10
	Rim	Core							
MgO	0.78	0.86	3.63	3.21	3.32	2.51	3.42	4.60	3.30
Al_2O_3	21.52	21.51	21.46	21.28	21.41	20.93	20.76	21.76	21.31
SiO_2	37.80	37.72	37.73	37.10	37.11	37.65	37.46	37.57	38.00
CaO	6.22	5.38	1.97	2.88	2.77	4.67	2.60	2.19	2.78
MnO	4.68	5.26	7.10	8.59	8.69	15.41	8.01	5.64	11.77
FeO	30.24	30.74	29.10	26.92	26.64	19.57	27.48	28.81	24.97
Total	101.23	101.46	100.99	99.997	99.94	100.74	99.73	100.56	102.13

Cations Based on 12 Oxygen

Mg	0.09	0.10	0.43	0.38	0.40	0.30	0.41	0.54	0.39
Al	2.00	2.02	2.01	1.99	2.00	1.95	1.97	2.03	1.98
Si	3.01	3.00	2.99	2.98	2.98	3.00	3.01	2.97	2.99
Ca	0.53	0.46	0.17	0.25	0.24	0.40	0.22	0.19	0.23
Mn	0.32	0.36	0.48	0.58	0.59	1.04	0.55	0.38	0.78
Fe	2.10	2.05	1.93	1.81	1.79	1.31	1.85	1.91	1.64

Chlorite

	SL-14	SL-28	16-01	16-03	7-172	182-95	182-235	182-270	78-51
MgO	22.71	13.45	19.01	20.84	17.69	18.76	17.53	19.63	17.23
Al_2O_3	24.74	22.38	23.08	21.38	24.05	22.60	23.87	22.55	24.23
SiO_2	26.81	23.52	24.97	25.37	25.39	24.89	25.07	25.03	25.14
MnO	0.00	0.13	0.18	0.16	0.51	0.19	0.00	0.08	0.25
FeO	14.91	26.63	18.56	16.10	20.44	18.75	22.52	18.08	21.03
Total	89.17	86.09	85.80	83.85	88.08	85.19	88.99	85.37	87.88

Cations Based on 28 Oxygen

Mg	6.60	4.35	5.91	6.53	5.38	5.87	5.33	6.10	5.26
Al	5.68	5.73	5.65	5.30	5.79	5.58	5.74	5.54	5.85
Si	5.23	5.11	5.19	5.34	5.18	5.22	5.11	5.22	5.15
Mn	0.00	0.02	0.03	0.03	0.09	0.03	0.00	0.01	0.04
Fe	2.43	4.83	3.22	2.83	3.49	3.30	3.84	3.15	3.61

	24-01	24-03	24-04	72-05	72-70	72-330	30-07	30-80
MgO	20.47	16.90	17.16	18.67	18.47	17.86	16.74	17.79
Al_2O_3	22.91	22.34	22.50	23.00	23.58	23.73	23.78	23.03
SiO_2	25.09	23.75	23.94	24.96	25.16	24.78	24.96	24.91
MnO	0.22	0.10	0.00	0.51	0.00	0.18	0.23	0.36
FeO	16.70	19.57	18.83	19.45	18.92	20.98	22.51	20.97
Total	85.39	82.66	82.43	86.59	86.13	87.53	88.22	87.06

Cations Based on 28 Oxygen

Mg	6.32	5.48	5.56	5.77	5.69	5.49	5.14	5.51
Al	5.59	5.73	5.76	5.62	5.74	5.77	5.77	5.64
Si	5.20	5.17	5.20	5.18	5.20	5.11	5.14	5.17
Mn	0.04	0.01	0.00	0.09	0.00	0.03	0.04	3.64
Fe	2.89	3.56	3.42	3.37	3.27	3.62	3.88	0.06

Plagioclase

	7-25	7-105	7-140	24-10	24-13	72-295	182-320	30-11	30-80
Na_2O	8.22	7.81	7.25	4.32	6.04	5.42	7.76	7.31	5.93
Al_2O_3	23.39	25.75	26.42	30.91	29.01	29.65	25.66	24.90	28.56
SiO_2	63.51	60.04	58.91	52.75	57.87	55.63	58.21	58.20	56.87
CaO	5.56	6.68	7.74	13.34	10.27	11.25	7.25	6.68	9.95
Total	100.61	100.28	100.32	101.32	103.19	101.95	98.87	97.08	99.31

Cations Based on 8 Oxygen

Na	0.70	0.67	0.63	0.38	0.51	0.46	0.66	0.65	0.53
Al	1.30	1.35	1.39	1.63	1.49	1.54	1.37	1.34	1.47
Si	2.71	2.66	2.62	2.36	2.52	2.46	2.63	2.66	2.52
Ca	0.29	0.32	0.37	0.64	0.48	0.53	0.35	0.33	0.46

Muscovite

	7-25	7-140	24-10	24-13	72-295	182-320	30-11
Na_2O	1.50	1.18	1.11	1.06	1.14	1.50	1.13
MgO	1.34	1.10	1.13	1.12	1.16	1.15	1.18
Al_2O_3	34.47	35.17	35.22	35.55	35.55	35.25	34.99
SiO_2	46.50	44.78	46.19	45.85	46.03	45.23	45.44
K_2O	9.15	9.49	9.87	9.22	9.23	8.88	9.87
FeO	2.01	2.18	2.91	2.52	2.61	2.03	2.74
TiO_2	0.00	1.01	0.18	0.41	0.50	0.49	0.43
Total	93.47	93.73	95.50	94.67	95.08	93.03	94.65

Cations Based on 22 Oxygen

Na	0.39	0.31	0.28	0.27	0.29	0.39	0.27
Mg	0.27	0.22	0.22	0.22	0.23	0.23	0.23
Al	5.42	5.56	5.49	5.56	5.53	5.58	5.48
Si	6.02	6.01	6.11	6.08	6.08	6.06	6.04
K	1.56	1.63	1.66	1.56	1.55	1.52	1.67
Fe	0.22	0.25	0.32	0.28	0.29	0.23	0.30
Ti	0.00	0.10	0.02	0.04	0.05	0.05	0.04

Composition of Minerals from Spruce Point
Biotites

	115-920	115-1323	115-1307	115-1303	67-702	94-08
SiO_2	34.67	35.63	36.51	36.80	38.60	38.15
Al_2O_3	17.34	19.46	19.88	18.42	17.32	16.83
FeO	23.69	17.35	17.63	10.87	12.14	13.91
MgO	6.18	11.75	12.61	16.23	15.43	14.99
K_2O	9.32	9.49	9.00	9.17	9.30	9.49
TiO_2	2.52	1.48	0.73	1.13	1.66	1.58
Na_2O	0.16	0.40	0.19	0.60	0.13	0.27
MnO	0.70	0.00	0.08	0.00	0.00	0.00
Total	94.58	95.56	96.63	93.22	94.58	95.22

Cations Based on 22 Oxygen

Si	5.47	5.36	5.40	5.49	5.68	5.64
Al	3.22	3.45	3.47	3.24	3.00	2.93
Fe	3.12	2.18	2.18	1.36	1.49	1.72
Mg	1.45	2.63	2.78	3.61	3.38	3.31
K	1.87	1.82	1.70	1.74	1.75	1.79
Ti	0.30	0.17	0.08	0.13	0.18	0.18
Na	0.05	0.12	0.05	0.17	0.04	0.08
Mn	0.09	0.00	0.01	0.00	0.00	0.00

Chlorites

	67-702	67-768	67-797	115-1303	94-08
SiO_2	26.58	24.27	26.87	25.74	27.14
Al_2O_3	22.52	22.51	23.71	23.20	21.64
MgO	21.29	10.97	24.52	21.20	21.49
FeO	14.97	29.62	11.63	15.02	16.75
K_2O	0.16	0.18	0.00	0.00	0.00
TiO_2	0.12	0.00	0.00	0.00	0.00
Total	85.54	87.55	86.73	85.16	87.02
	Cations Based on 28 Oxygen				
Si	5.42	5.24	5.30	5.28	5.48
Al	5.41	5.73	5.52	5.61	5.15
Mg	6.47	3.53	7.21	6.48	6.47
Fe	2.52	5.35	1.92	2.58	2.83
K	0.04	0.05	0.00	0.00	0.00
Ti	0.02	0.00	0.00	0.00	0.00

Muscovite and Plagioclase

	115-1323		115-1307	
	Musc	Plag	Musc	Plag
SiO_2	44.93	56.43	46.22	54.67
Al_2O_3	34.34	27.73	36.41	29.33
K_2O	10.23		9.93	
FeO	3.55		2.20	
TiO_2	0.93		0.00	
MgO	1.19		1.06	
Na_2O	0.98	6.25	0.83	5.93
CaO		9.46		11.30
Total	96.15	99.87	96.65	101.23
	Cations Based on 22 or 8 Oxygen			
Si	6.02	2.53	6.08	2.44
Al	5.42	1.47	5.64	1.54
K	1.75		1.66	
Fe	0.40		0.24	
Ti	0.09		0.00	
Mg	0.24		0.21	
Na	0.25	0.54	0.21	0.45
Ca		0.46		0.54