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" Mineralogy, Petrology and Geochemistry of the Banded Iron Formation, Gairloch, N.W. Scotland"

A THESIS SUBMITTED

FOR THE M.So. (GEOLOGY) DEGREE

BY

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ABSTRACT

The Gairloch area lies at the southern end of the Lewisian outcrops in the N.W. of Scotland. The rocks of the Gairloch area are metasediments and belong to the Loch Maree Group. In these rocks lenses of Iron Formation facies occur. This Iron Formation is divided into two facies, the oxide facies (consisting of magnetite and quartz) and the silicate facies (consisting of garnet and amphibole). These minerals are coarsely crystalline and form a banded texture in the oxide facies, and a granoblastic or porphyroblastic texture in the silicate facies. In the associated metasediments, the textures are either lepidoblastic (biotite-muscovite schist) or nematoblastic (hornblende schist).

Grunerites, garnets, magnetites and rocks from the Gairloch

Iron Formation and the associated metasediments have been analysed
using X-ray fluorescence, X-ray diffraction, the electron microprobe
and wet chemical methods for both major and trace elements. The cell
parameters have been determined for the minerals. The analyses show
that the amphiboles are grunerite and manganoan grunerite, and the
garnets are either almandine or spessartite-almandine. These coexisting minerals are interpreted as being in equilibrium and the
Fe²⁺ and Mg²⁺ are preferentially incorporated into the grunerite
structure whilst the Mn²⁺ and Ca²⁺ are partitioned into the garnet
structure. The origin of these silicate minerals in the Gairloch
Iron Formation is assumed to be from the original hydrous iron silicates
and clay minerals. The trace elements Cr, V and Y are concentrated in
the garnet. Nb, Ni, Sc, Sr and Zr have approximately equal proportions
in the garnet and grunerite. Ba, Pb and Rb do not occur in these

minerals but they occur in minerals from the associated
metasediments. The magnetite from the oxide facies of the Gairloch
Iron Formation seems to be free of trace elements.

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CONTENTS

	Page
Abstract	i
Acknowledgments	iii
Contents	iv.
List of figures	xii
List of plates	xvi
List of tables	xix
CHAPTER ONE	
INTRODUCTION	
1 - 1 History of research in the Gairloch area	1
1 - 2 Aim of the study	2
1 - 3 Methods of study	2
1 - 3 - 1 Mapping	2
1 - 3 - 2 Sampling	2
1-3-3 Petrography	3
1 - 3 - 4 Mineral separation	3
1-3-5 Geochemistry	3
1 - 4 Contents of the thesis	3
CHAPTER TWO	
THE LEWISIAN	
2 - 1 The Lewisian Complex	5

				Page
2	-	2	The Lewisian of the Mainland of Scotland	6
			1) Northern region	
			2) Central region	
			3) Southern region	
2	_	3	The Scourian Complex	7
2	-	4	The Scourie dykes	8
2	-	5	The Laxfordian Complex	9
2	-	6	Position of Loch Maree Group (Gairloch) in the Lewisian	10
2	-	6 -	1 Isotopic evidence	11
2	-	6 -	2 Structural evidence	11
2	-	7	Stratigraphy of Loch Maree Group at Gairloch	12
T)	HE	BAN	CHAPTER THREE DED IRON FORMATION	
3	-	1	Introduction	14
3	_	2	The stability relationships of iron minerals	15
3	_	3	Origin of the Banded Iron Formation	15
3	-	4	Environment of deposition of the Banded Iron Formation	16
3	-	5	The Iron Formation in the Gairloch area	19
3	_	5 -	1 The oxide facies	19
3		5 -	2 The silicate facies	20
3	_	5 -	3 The mixed oxide - silicate facies	20
3	_	6	Manganese association with Banded Iron Formation	21
			CHAPTER FOUR	
P	ET	ROGE	АРНҮ	
4		. 1	Description of the Iron Formation rocks	23
			A) A silicate facies rocks	
			B) The oxide facies rocks	

		######################################
4 - 2	Description of the metasediments	24
	A) Hornblende schist	24
	B) Biotite-muscovite schist	24
	C) Quartzite	24
	D) Graphite schist	24
4 - 3	Description of the minerals	25
	1) Magnetite	25
	2) Quartz	26
	3) Grunerite	26
	4) Garnet	27
	5) Hornblende	28
	6) Chlorite	. 29
	7) Biotite	29
	8) Muscovite	29
	9) Calcite	30
	10) Siderite	30
	11) Graphite	30
	12) Plagioclase	30
	13) Sphene	30
	14) Epidote	31
	15) Zircon	31
	16) Zoisite	31
	17) Pyrite	31
	18) Hematite	31

Page

CHAPTER FIVE	
MINERALOGY	
5 - 1 Amphibole Group of minerals	32
5-1-1 General formula of the amphibole	32
5 - 1 - 2 Cation distribution between crystalographic sites	32
5 - 1 - 3 Chemistry and nomenclature of the amphibole group	33
1) Anthophyllite series	34
2) Cummingtonite - grunerite series	34
3) Tremolite - actinolite series	34
4) Hornblende series	35
5) Alkali amphiboles series	35
5 - 1 - 4 Chemistry of the amphiboles in the Iron Formation from	
the Gairloch area	35
5 - 1 - 4 - 1 Major elements concentration in the amphiboles	35
5 - 1 - 4 - 2 Comparison of grunerite from other Iron Formations	
with those from the Gairloch area	36
5 - 1 - 4 - 3 Zoning in the grunerite from the Gairloch area	37
5 - 1 - 4 - 4 The relationship between the major elements in gruner	rite
from the Gairloch area	37
5 - 1 - 4 - 5 Trace element concentrations in the amphiboles	38
5 - 1 - 4 - 6 Relationships between the trace elements in the	
grunerite	39
1) Positive correlation	39
2) Negative correlation	39
3) No correlation	39
5 - 1 - 4 - 7 Relationships of the trace elements with the major	
elements in the grunerite from the Gairloch area	
(correlations with the iron, manganese and magnesium	
ions) .	39

viii

						-	Page
5	-	1	_	5		X-ray diffraction pattern of grunerite	40
5	-	1	-	6		Variation of density with iron content in grunerite	40
5.	_	2		Ga	ırı	nets	42
5	_	2	_	1		General formula of the garnet group	42
5	-	2	_	2		Chemistry of the garnet group and its nomenclature	42
				1)	Pyralspite series	42
				2)	Ugrandite series	43
5	_	2	-	3		Chemistry of garnet in the Iron Formation of the	
						Gairloch area	43
5	-	2	_	3	-	1 Major element chemistry	44
5	-	2	-	3	-	2 Comparison between garnets from the Gairloch area	
						and thoes from other Iron Formations	44
5	-	2	-	3	-	3 Relationships between the major elements in the	
						garnet	45
5	-	2	-	3	-	4 Trace element chemistry	45
5	-	2	-	3	-	5 Trace element relationships in the garnet	46
5	-	2	-	3	-	6 Relationships between the trace elements and the	
						major elements in the garnet	46
						1) Positive relationships	47
						2) Negative relationships	47
						3) No relationships	47
5	-	2	-	4		X - ray diffraction patterns of garnet	47
5	-	2	-	5		Relationship between density and the unit cell	
						dimensions of the garnets	48
5	-	2	-	6		Use of garnet as indicator of the grade of metamorphism	48
5	_	2	-	7		Chemical zoning in garnet	49

	Page
5 - 3 Partition of element between garnet and grunerite	51
5 - 3 - 1 Relationships between elements in the garnet and	
grunerite from the Gairloch Iron Formation	52
5 - 4 Magnetite	54
5 - 4 - 1 General formula of magnetite	54
5 - 4 - 2 Chemistry and nomenclature of magnetite	54
5-4-3 Chemistry of magnetite in the Iron Formation from the	n e
Gairloch area	54
5-4-3-1 Major element chemistry	55
5-4-3-2 Trace element chemistry	55
5 - 4 - 4 X - ray diffraction pattern	55
CHAPTER SIX	
GEOCHEMISTRY	
	<i>F</i> 7
6-1 Type of rocks	57 57
6 - 2 Distribution of the major elements in the rocks	57
6 - 2 - 1 Silicon	58
6 - 2 - 2 Titanium	58
6-2-3 Aluminium	58
6 - 2 - 4 Iron	59
a) FeO	59 50
b) Fe ₂ 0 ₃	59
6 - 2 - 5 Manganese	59
6-2-6 Calcium	60

					Page
6 •	-	2	_	7 Magnesium	60
6 •	-	2	_	8 Sodium	61
6 -	-	2	_	9 Potassium	61
6 -	-	2	_	10 Phosphorus	61
6 •	-	2	_	11 Water	62
6 •	-	2	-	12 Carbon dioxide	62
6 -	-	3		Comparison between the major element constituents of the	•
				Iron Formation rocks in the Gairloch area and those in	
				the other Iron Formations	62
6 .	-	4		A C F diagram for the metasediments, silicate and oxide	
				facies rocks from the Gairloch area	64
6 .	_	5		Relationship between the major elements in the oxide ar	nd
				silicate facies rocks from the Gairloch Iron Formation	65
6 .	-	6		Relationships between the major element distribution in	
				the rocks and minerals	66
6	-	7		Trace element cocentration in the rocks of the Gairloch	
				area	66
6		8		Comparison between the trace element concentration in	
				different Iron Formations	68
6	-	9		Relationships between the major and trace elements in the	ne
				rocks from the Gairloch area	68
				CHAPTER SEVEN	

APPENDICES

			Page
APPENDIX I	***	Techniques used during investigation	78
APPENDIX II	-	The working condition for the instruments used during the investigation	83
APPENDIX III	-	Chemical analyses of rocks and minerals from the Gairloch Iron Formation	85
APPENDIX IV	•	Photomicrograph from the Gairloch area rocks	133
REFERENCES			157

Xii

LIST OF FIGURES

- 1. The Lewisian outcrops in Highlands of N. W. Scotland.
- 2. Map of the southern region showing generalised structural and subdivision into structural belts.
- 3. Map of Gairloch area showing sample locations.
- 4. Map showing distribution and nomenclature of principle rock unit.
- 5. The Eh-pH diagram for the stability of the iron minerals.
- 6. The Fe and Mn Eh-pH diagram.
- 7. Composition of grunerites and their suggested nomenclature.
- 8. Relationship between the major elements in the grunerite.
- 9. Relationship between the trace elements in grunerite.

 Positive correlation.
- 10. Relationship between the trace elements in grunerite.

 Negative correlation.
- 11. Relationship between the trace and major elements in grunerite. Positive correlation.

xiii

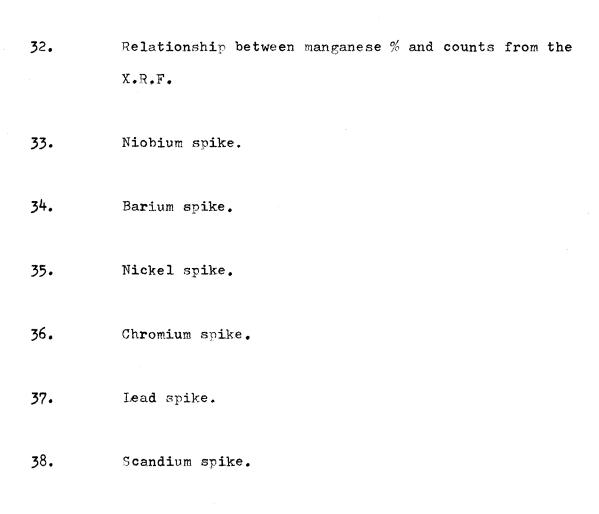
- 12. Relationship between the major and trace elements in grunerite. Negative correlations.
- 13. Variation of the X-ray pattern with composition ranging from 9° 60° 20 Cuk α_{1} for the grunerite.
- 14. Variation in specific gravity as a function of Fe and

 Mg in grunerite.
- 15. Compositions of the garnets and their suggested nomenclature.
- 16. Relationship between the major elements in the garnet.
- 17. Relationship between the trace elements in garnet.

 Positive correlation.
- 18. Relationship between the trace elements and major elements in the garnet. Positive correlation and negative correlations.
- 19. Relationship between the trace elements and Fe + Mn in garnet.
- 20. Core and rim molecular composition of garnets.
- 21. Relationship between the unit cell and density of the garnet.

χiν

- 22. Partition of Fe, Mn, Si, Ti and Cr between co-existing garnet and grunerite.
- 23. Fe, Mn and Mg molecular proportion in grunerite and garnet for each analysis from the microprobe.
- 24. Molecular proportions of Fe, Mg and Mn for the garnetgrunerite pairs.
- 25. Partition of Fe, Mn and Mg between co-existing garnet and grunerite.
- 26. A.C.F. Diagram for the metasediments and the Iron Formation rocks from Gairloch area
- 27. Relationships between the major elements in the silicate and oxide facies rocks, from the Gairloch Iron Formation.
- 28. Silica and aluminium in wt% in the silicate facies rocks of the Iron Formation.
- 29. Relationships between the major element distribution in the rocks and minerals.
- Relationships between the major and trace elements in the rocks from the Gairloch area.
- Relationship between total iron % (wet chemistry and X.R.F.) and counts from the X.R.F.



39.

Vanadium spike.

LIST OF PLATES

- Inter digitation of garnet and grunerite (Sample No. 11B) in the silicate facies rocks from the Iron Formation.
- 2. Porphyroblastic texture in the silicate facies rocks (Sample No. 21). It also shows anhedral crystals of garnet.
- Porphyroblastic texture and the sharp boundary to the core of the garnet crystals (Sample No. 14). It also shows the carbonate, quartz and grunerite inclusions in the garnet. from the silicate facies rocks.
- 4. Granoblastic texture in the silicate facies rocks

 (Sample No. 17). It also shows the sharp boundary to
 the core of some garnet crystals, full of inclusion of
 carbonate, quartz, and a clay mineral. Some crystals of
 grunerite show an inter digitating relationship with the
 garnet crystals.
- 5. Inter digitating of garnet and grunerite crystals in the silicate facies rocks (Sample No. 1(4)). It also shows grunerite crystals as inclusions within the garnet.
- 6. Sample No. 12 shows minor fault in alternating magnetite and quartz bands in the oxide facies rocks.

- 7. The porphyroblastic texture of the silicate facies rocks. It also shows the high concentration of magnetite, quartz and grunerite as inclusions in the garnet crystals.
- 8. Alternation between the quartz rich band and the magnetite rich band in the ferruginous quartzite.

 Sample No. 2(2).
- 9. Sample No. 5 shows minor chevron folds in alternating magnetite and quartz bands in the oxide facies rocks.
- 10. Magnetite inclusions in the grunerite in the silicate facies rocks. Sample No. 3.
- 11. Siderite concentration in a quartz rich band from the oxide facies rocks. Sample No. 12 (M).
- 12. Alteration of hornblende to biotite and chlorite in hornblende schist (Sample No. 5), also shows quartz inclusions in the hornblende.
- 13. Iepidoblastic texture in the metasediment sample No. (13).
- 14. Ribbon structure of the quartzite rock. Sample No. 15.
- 15. Magnetite inclusions in the granoblastic quartz in the quartzite. Sample No. (4).

XViii

- 16. Idioblastic crystal of garnet containing quartz inclusions in the hornblende schist. Sample No. 19.
- 17. Poikiloblastic texture of garnet in the biotite garnet schist. Sample No. 20.

LIST OF TABLES

- 1. Summary of the history and structure of the Lewisian Complex.
- 2. Approximate percentages of the mineral constituents in the rocks.
- 3. X-ray fluorescence analyses of grunerites in the Gairloch Iron Formation.
- 4. Microprobe analyses of the grunerites.
- 5. Mean chemical analyses of the garnet and grunerite by the electron microprobe.
- 6. X-ray diffraction patterns of the grunerite mineral between 9°- 60° 20 Cuk.
- 7A. Trace element concentrations of the grunerite (p.p.m).
- 7B. Trace element concentrations of the garnet (p.p.m).
- 8. Major constituents of grunerite from different Iron Formations.
- 9. X-ray diffraction, X-ray fluorescence and microprobe

 molecular proportions of iron with calculated and measured

 density of grunerites.

- 10. X-ray fluorescence analyses of garnets in Gairloch Iron Formation.
- 11. Core and rim compositions of garnet.
- 12. X-ray diffraction pattern of the garnet mineral between 19° 60° 20 Cuk \propto ₁.
- Major constituents of the garnet from different Iron Formations.
- 14. Unit cell dimensions, cell volume and density of the garnets.
- 15. X-ray fluorescence analyses of magnetite in the Gairloch Iron Formation.
 - a) Major elements
 - b) Trace elements
- 16. X-ray diffraction pattern of the magnetite mineral.
- 17. List of samples taken for analysis.
- 18. Molecular ratio of XFe, XMn, XMg in the grunerite and garnet.
- 19. Major element chemical analyses for the silicate and oxide facies rocks from the Gairloch Iron Formation.
- 20. Major element chemical analyses for the metasediments from Gairloch.

- 21. Trace element chemistry (P.P.M.) of the silicate and oxide facies rocks of the Gairloch Iron Formation.
- 22. Trace element chemistry (P.P.M.) of the metasediments from the Gairloch area.
- 23. The average chemical composition of oxide-facies rocks from different Iron Formations.
- 24. The chemical composition of silicate facies rocks from different Iron Formations.
- 25. Variations in the concentration of trace elements (P.P.M.) in the metasediments, and rocks of the silicate and oxide facies from the Gairloch area.
- 26. Comparison between the trace element concentration

 (P.P.M.) in the Iron Formation rocks from the Gairloch

 area and the other Iron Formations.
- 27. X-ray fluorescence standard values (P.P.M.) for garnets, grunerites, magnetite and rocks.
- 28. Working conditions of the X-ray diffractometer.
- 29. Working conditions for the X-ray fluorescence spectrometer.

- The detection limits for major and trace elements (X.R.F.).
 - a) Major elements (wt.%)
 - b) Trace elements (P.P.M.)
- Precision determination (X.R.F.) of Banded Iron

 Formation and the metasediments for the major and

 trace elements.
 - a) Major elements (wt.%)
 - b) Trace elements (P.P.M.)

CHAPTER ONE

INTRODUCTION

Introduction

1 - 1 History of research in the Gairloch area:

The area of study lies towards the southern end of the Lewisian outcrop in the north west Highlands of Scotland (Fig. No. 1). The first map of the Lewisian outcrops was published by Clough et.al in a memoir of the Geological Survey (1907). In 1930, Peach and Horne gave a different interpretation of the relationships between the rocks in the Gairloch area to that originally proposed by Clough et. al. (ibid). In 1950 Sutton and Watson re-studied the Lewisian rocks in more detail and included a fuller description of the Loch Maree Group of the Gairloch area. Park (1963,1964) studied structural history of the Lewisian Complex in the Gairloch area.

H. Hick (1880) was the first to recognize grunerite in the rocks of the Gairloch area but he thought it to be sillimanite, so the rocks were given the name sillimanite garnet - schist, and published the Annual Report of the Geological survey in 1895. Peach in Clough et.al (op.cit.) analysed these rocks, separated the garnet and the amphibole minerals, and analysed them. He found the garnet to be spessartite and the amphibole cummingtonite, so he was the first to give the name cummingtonite - garnet - schist to these rocks. (1938) also described these rocks and gave the name cummingtonite or grunerite to the amphibole mineral. He also published several analyses of these rocks. Finally Park (1963,1964) gave the name Iron Formation to these rocks and gave the name grunerite to the amphibole rather than cummingtonite as given by Peach and Tilley. No chemical analyses of either the rocks or the minerals have been published by Park or other workers on the Gairloch Iron Formation since Tilley (1938) until the present work for this thesis.

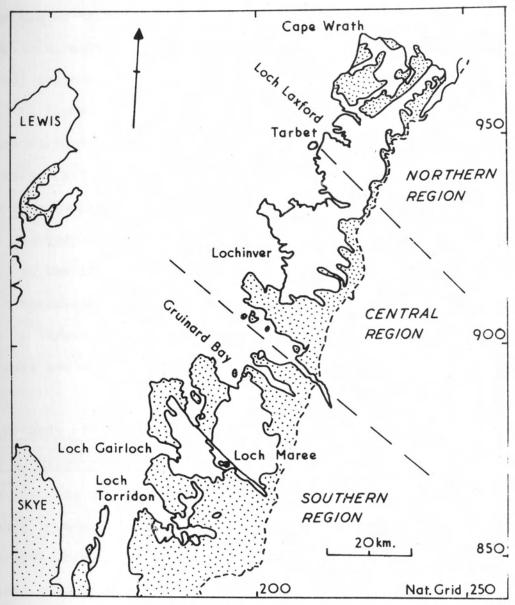


Fig. 1. Map of part of the North-West Highlands of Scotland showing the location of the Gairloch area and the regional sub-division of the mainland Lewisian. (after Park, 1973)

1 - 2 Aim of the study:

The aim of this work was to study the Iron Formation in the Gairloch area, north west Scotland.

This study includes:

- 1) An investigation into patterns of distribution of the major and trace elements in the Iron Formation rocks (oxide and silicate facies rocks), and some associated metasediments (hornblende schist, biotite muscovite schist).
- 2) A study of the relationships between the major and trace elements in the iron minerals (magnetite, garnet and grunerite) from the Iron Formation rocks.
- 3) A correlation of these rock and mineral analyses with the other rocks and minerals from different Iron Formations.

1 - 3 Methods of study:-

1 - 3 - 1 Mapping:

The mapping of the Iron Formation rocks within the area is based upon the 6 inch/mile maps No. NG 87 SW, SE, NW and NE, which include the Gairloch area. This map has been enlarged a little more than four times to a scale of 1 cm to 25 metres to emphasise the detail of the outcrops. Despite the large scale of the map the outcrops plot as points because they are very small, they vary in length from 0.5 to 15 metres and from 0.5 to 3 metres in width, with the exception of the outcrop G12 in which the length is approximately 250 metres and the width approximately 15 metres.

1 - 3 - 2 Sampling:

Thirty two samples were collected from the Iron Formation rocks and the associated metasediments. In some outcrops more than one

sample has been collected due to the rapidly changing mineralogical constituents.

1 - 3 - 3 Petrography:

Fifty two thin sections from the Iron Formation rocks and associated metasediments from the Gairloch area were made by the technical staff in the department. These thin sections were studied and helped to relate the geochemical results with the mineral occurrence or absence in the rocks.

1 - 3 - 4 Mineral separation:

The iron minerals from the Gairloch Iron Formation rocks were separated; magnetite from the oxide facies rocks, and garnet and grunerite from the silicate facies rocks.

1 - 3 - 5 Geochemical study:

The X-ray fluorescence (X.R.F.)was used to analyse the major and trace elements for both rocks and minerals, also wet chemistry was used to analyse some major elements (FeO, Fe2O3, MnO, H2O⁺ and CO₂). The X-ray diffractometer was also used to determine the cell parameters of the separated minerals. The electron microprobe of Manchester University was utilised for chemical analysis of the minerals. The full details of the analyses can be found in appendix No. 3.

1 - 4 Contents of the thesis:

This thesis contains seven chapters in which chapter one is an introduction, which includes both the previous geological work on the area, and also the methods of analysis used in the study. Chapter two shows the general geological history of the Lewisian rocks and its divisions in the Gairloch area. Chapter three discusses the Iron

Formations in general, and also the Gairloch Iron Formation and the main rock facies present. Chapter four, entitled "Petrography" is a petrographic description of the mineral assemblages in the Iron Formation rocks and the associated metasediments. Chapter five, Mineralogy, includes chemical analysis (major and trace elements) and chemical variation within grunerite, garnet and magnetite and the cell parameters of these minerals. Chapter six, the Geochemistry in which the complete analyses for the Iron Formation rocks and associated metasediments have been performed using X-ray fluorescence techniques to determine the major and trace elements of those rocks. Also wet chemical techniques were employed to determine some major elements. Chapter seven is the Conclusions. Appendix No. 1 shows the procedures of sample preparation. Appendix No. 2 shows the working conditions for the X-ray fluorescence and X-ray diffraction methods during the analyses. Appendix No. 3 shows the chemical results from both the rocks and minerals. Appendix No. 4 shows the photomicrograph for the rocks from the Gairloch area .

CHAPTER TWO

THE LEWISIAN

The Lewisian

2 - 1 The Lewisian Complex:

The Lewisian Complex consists of basic to acid gneisses, mainly of igneous origin but occasionally of sedimentary origin. The whole of the Lewisian Complex is of Precambrian age (2800 - 1700 m.y.) and is found in the north western part of Scotland adjacent to the Caledonian Mountains (Fig. No. 1). The name of the Lewisian originates from the Isle of Lewis in the Outer Hebrides where these Precambrian Complex outcrops in many areas, including the Outer Hebrides, certain of the Inner Hebrides, such as Iona, Coll, Tiree and also on the mainland of Scotland, in Wester Ross, and Sutherland from Glenelg in the south to Loch Eiroboll in the north.

The first detailed study of the Lewisian was carried out by Peach, Horne, Clough and Hinxman (1907) and published in a memoir of the Geological Survey entitled "North West Highlands of Scotland". This study was extremely detailed and wasthe last for nearly half a century until Sutton and Watson (1951), renewed interest in more detailed studies of the Lewisian Complex. From 1951 to the present day, many workers on the Lewisian Complex have concentrated on either the detailed structural history (e.g. Sutton and Watson (1951,1969), Bowes (1964,1965,1968b), Park (1964,1966,1973,1978), Coward (1969,1970), Cresswell (1969)......etc.), the geochemistry (e.g. Holland and Lambert (1973), Taylor (1975).....etc.), or the geochronology (e.g. Moorbath (1969,1975), Evans (1965), Giletti (1961).....etc.).

The Lewisian can be subdivided into two major units:

- (1) The Scourian Complex which is the earlier of the two (2800 2200 m.y.). This complex consists of highly metamorphosed igneous and sedimentary rocks which are now found as banded gneisses.
- (2) The Laxfordian Complex, which is the younger of the two (2200 1700 m.y.). This complex consists of reworked Scourian and Pre-Scourian rocks which had already been affected by several episodes of deformation.

The Scourian and the Laxfordian are distinguished from each other by a set of basic dykes, now called Scourie dykes, which cut through the Scourian Complex and were affected by the later Laxfordian events, (Sutton and Watson, 1951).

2 - 2 The Lewisian of the Mainland of Scotland:

The Lewisian Complex on the mainland has been geographically divided into three regions (Fig. No. 1) by Peach et.al (1907), these regions are:

- (1) The Northern region from Cape Wrath to mid-way between Laxford and Scourie (mainly Laxfordian).
- (2) The Central region from Scourie to Loch Broom (dominantly Scourian).
- (3) The Southern region, from Gruinard Bay to Loch Torridon including the island of Raasay (Laxfordian).

The central region is characterised by the development of pyroxene - bearing gneisses with an earlier set of basic rocks including both pyroxenites and amphibolites. The later intrusion of the basic dykes (Scourian) can be traced easily through the complex.

In the Northern region, where biotite gneisses and granular hornblende gneisses are predominant and pyroxene gneisses absent, the basic dykes are easily traceable, but further toward Cape Wrath these can only be traced for short distances. The Southern region differs from both the Central and Northern regions, in that there are no pyroxene gneisses as in the former (Central region), nor are basic dykes as common as in the latter (Northern region) in addition there is a development of biotite bearing augen gneisses. The Scourian rocks are at a high grade of metamorphism, i.e. in the granulite facies, whilst the Laxfordian are at a lower grade, in the amphibolite facies.

2 - 3 The Scourian Complex:

The Scourian rocks are mainly concentrated in the Central region of the Lewisian outcrop in the North West Highlands. This central block is 55 km in width. However, in some other places, the Scourian rock outcrops are occasionally less than one kilometre in width.

The most abundant rock types in the Scourian Complex are banded gneisses, which are characterised by having both ortho - and clino - pyroxene, together with garnet, quartz, oligoclase-andesine feldspar. Locally there are significant amounts of potash feldspar and sometimes brown hornblende, (Watson, 1975).

The earliest phase of deformation in the Scourian is accompanied by a granulite facies metamorphism, as revealed by the presence of orthopyroxene. This was then followed by a further period of deformation, igneous activity and metamorphism which shows a partial retrogression to the amphibolite facies. This retrogression is most clearly developed in the Southern region and in most of the Outer

Hebrides. In these early Scourian episodes, the metamorphism has affected the whole Lewisian outcrop. The high grade of metamorphism and the complicated structures which have been formed during the deformation make it difficult to determine the original nature of the rocks which now form the Scourian Complex. Evans (1965) and Evans and Lambert (1974) give the name Inverian to the latest stages of deformation and metamorphism during the Scourian. The effect of these Inverian deformations is irregularly distributed and more restricted in effect. The oldest structural patterns and mineral assemblages in the Lewisian Complex are those which formed during the gneiss forming episode. Park (1970) has given the name Badcallian to the earliest episode which has been dated by the Pb - Pb, U - Pb and Rb - Sr isochron data at 2900 - 2700 m.y ago (table No. 1).

2 - 4 Scourie dykes:

These are a suite of basic dykes intruded through the Scourian gneisses at the end of the Scourian. The dykes were affected by the later Laxfordian metamorphism. They are both widespread and well preserved, and have commonly a west - north - west trend. The thickness of the dykes varies between less than a metre and approximately 250 metres (Sutton and Watson, 1951). Most of these dykes are steep-sided and discordant, and occasionally show chilled margins to the country rocks. Sutton and Watson (1951) used these Scourian dykes as a time indicator, to separate events occurring prior to the intrusion of these dykes from events affecting the dykes themselves. The dykes show primary igneous textures ranging from gabbroic to basaltic, and show partial amphibolisation of the original igneous pyroxenes; a development of garnet rims around the

ferromagnesian minerals; and a clouding in the primary feldspars. Such factors indicate an incomplete metamorphic reaction, whereas those dykes which cross the Scourian gneisses in the Outer Hebrides show complete recrystalisation of the original mineralogy to hypersthene - clinopyroxene - plagioclase assemblages, i.e. the granulite facies. Dearnley (1962) interprets the difference between these two sets of dykes as a variation in metamorphic grade of the early Laxfordian metamorphism. However, O'Hara (1961), Bowes (1965, 1968 and 1969), and others suggest that there is more than one phase of intrusion. The first phase was at the end of the Scourian, when the dykes were intruded into the deeply buried and relatively hot country rocks. The later dykes cut across these earlier dykes. Both sets of dykes are then affected by a later amphibolite facies metamorphism.

Evans and Tarney (1964) used the K - Ar and Rb - Sr isotopic methods to suggest that the age of intrusion of the Scourie dykes is about 2000 m.y. Park and Moorbath (1972) obtained the same age from the Scourie dykes of the Southern region.

2 - 5 The Laxfordian Complex:

The Laxfordian Complex consists of regenerated Scourian gneisses. The Laxfordian was marked by polyphase deformation and metamorphism which affected most of the Lewisian outcrop on the mainland of north west Scotland. Events in the Laxfordian have been divided according to the several phases of the deformation and metamorphism, in which the early episodes are characterised by a high degree of deformation and high grade of metamorphism (granulite - amphibolite facies), while the later episodes are characterised by local deformation and a lower grade

of metamorphism (amphibolite-facies) - (Watson, 1975).

Injection of acidic intrusives is associated with this late stage of Laxfordian activity and the Rb - Sr isochron method gives an age of approximately 1700 m.y., (Van Breemen (1971), Lyon (1973). Ages up to 1850 m.y. have been proposed for the Northern mainland by Lambert and Holland (1972), and by using the K - Ar method for the Southern part of the mainland, Moorbath and Park (1972) have obtained an age of 1450 m.y.

Finally after the Laxfordian events were completed, the Lewisian formed the basement of the new sediments of the Torridonian and Moinian.

2 - 6 Position of Loch Maree Group (Gairloch) in the Lewisian:

The Gairloch area lies in the Southern region of the mainland Lewisian (Fig. No. 1). The rocks of both the Gairloch schist belt and Loch Maree schists are of a sedimentary origin. These metasediments are interbanded with amphibolites and form two belts which strike NW - SE, and are approximately 5 Km and 3 Km in width at Loch Maree and Gairloch respectively and have collectively been called the Loch Maree Group. These metasediments consist of semipelitic schists, with narrow bands or lenses of Banded Iron Formation, marble, quartzite and graphite schist.

The stratigraphic position of the Loch Maree Group has been studied and discussed by many authors (Peach and Horne (1930), Sutton and Watson (1951, 1969), Park (1964, 1970) and Bowes (1968, 1969). There is no direct indication of the absence of Scourie dykes cutting these metasediments and also there is a lack of the strong deformation and metamorphism associated with Laxfordian events.

Bowes (1968) and Park (1970) suggest that the stratigraphical age of these metasediments lies between the Bacallian and Inverian (table No. 1) because it does not show evidence either of the structures or granulite facies metamorphism of the former. They are therefore interpreted as being of post-Badcallian age, but their relationship with the Inverian is uncertain.

2 - 6 - 1 Isotopic evidence:

Bickerman, Bowes and Van Breeman (1975), obtained a Rb 87/Sr 86 isochron from the Gairloch metasediments, which gave an age around 2200 m.y. From this evidence it would appear that the Loch Maree Group represents the surviving part of the Lower Proterozoic supracrustal succession which was deformed and metamorphosed during the Laxfordian. But the significance of this data is doubtful according to Park (pers. comm). The metasediment sample localities of Bickerman et.al (op.cit.) lie in a belt of sheared Ard gneisses which Park interprets as reworked Archean basement.

2 - 6 - 2 Structural evidence:

The metasedimentary rocks occupying the NW - SE belt, which is about 3 Km in width in the Gairloch area, are bounded on both sides by acid gneisses (Fig No. 2). These metasediments and gneisses have been affected by at least three phases of deformation (Table No. 1). The early deformation, a schistosity (S1), is associated with an upper amphibolite facies metamorphism. This S1 schistosity is deformed by two sets of minor folds, F2 which is assymetric and plunges towards the SE, and F3 which is of chevron type. The F1 folds are of Inverian age and of isoclinal type, whereas F2 and F3 folds are Laxfordian

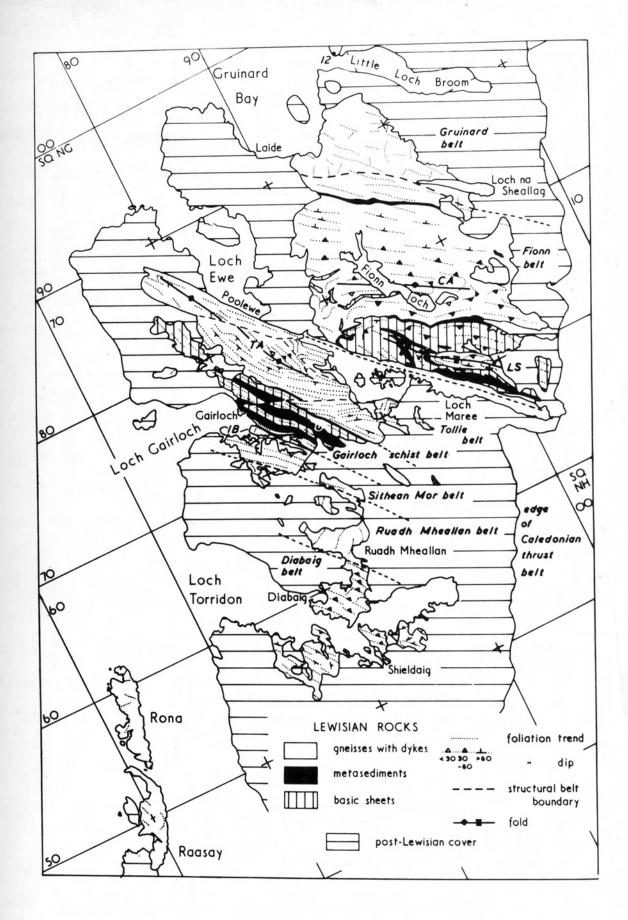


Fig. 2. Map of the southern region showing generalised structural trends and subdivision into structural belts. (after Park, 1973)



(table No. 1). Many large scale isoclinal folds (F1) are known in the Gairloch area. The Iron Formation at Kerrysdale (Fig. No. 3) has an S1 schistosity together with F1 isoclinal folds. Therefore from structural evidence, the age of the Loch Maree Group (Gairloch) is interpreted as being Pre-Inverian.

2 - 7 Stratigraphy of the Loch Maree Group at Gairloch:

The Lewisian rocks in the Gairloch area vary in both lithology and metamorphic grade. They occur in elongated structures trending NW - SE (Fig. No. 4) and they are subdivided into thirteen outcrop units (Park 1964).

- (1) In the NE, the Buainichean gneiss occurs, these are acid gneisses with amphibolite sheets (Scourie dyke).
- (2) The central part is bounded on the NE by the thick Aundrary basite, which is an amphibolite with several metasedimentary bands, to the SW by Ialltaig gneiss (which is a complex of both acid and basic gneisses), and to the SE by acid gneisses with amphibolite sheets the Mill na Claise gneiss. Between the Aundrary basite and Mill na Claise group there are a number of narrow belts of schists namely:
 - a) The Flowerdale semipelitic schist.
 - b) The Kerrysdale siliceous schist.
 - c) The Charlestown semipelitic schist and sheared gneisses.
 - d) The Ard gneiss group which are acid gneisses with amphibolite sheets.

The Kerrysdale schists include highly siliceous material together with the Iron Formation and the graphite schists. The Kerrysdale basite group contains bands of marble, Iron Formation, chlorite schists and

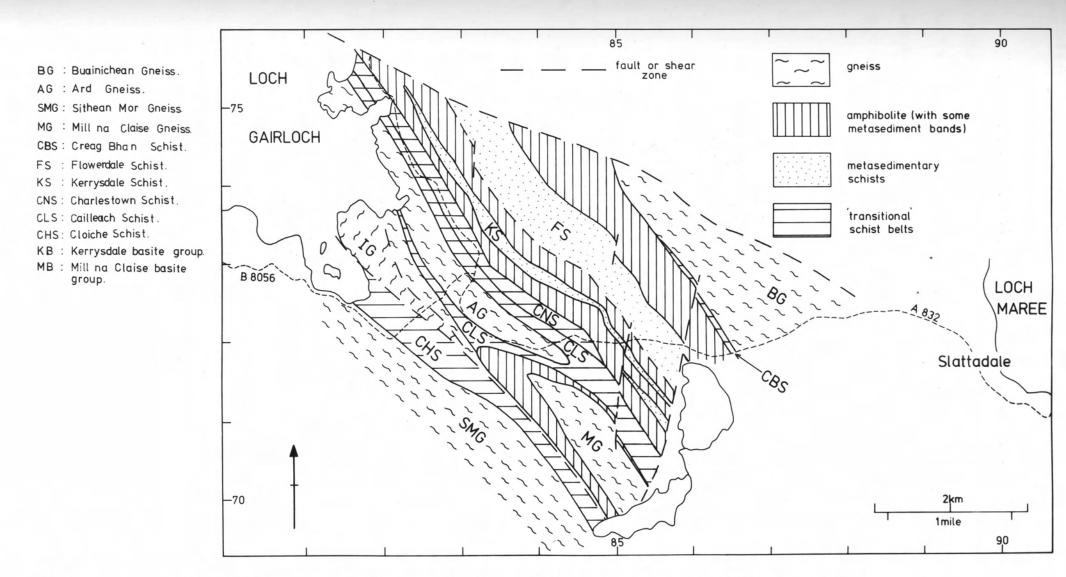


Fig.No. 4 Map showing distribution and nomenclature of principal rock unit (the map after Park unpublished)

graphite schists. In the SW of the Central area the Cloic schist belt has thin marble bands and contains siliceous gneisses. These are followed by the Sithean Mor gneiss, a group of gneisses with amphibolite sheets (Scourie dykes).

CHAPTER THREE

THE BANDED IRON FORMATION

The Banded Iron Formation

3 - 1 Introduction:

The name Banded Iron Formation (B.I.F.) has been given to rocks which contain more than 15% of iron oxides. The most acceptable definition for the B.I.F. is that given by James (1954), and by Lepp and Goldich (1964):- "The Iron Formation is a set of sedimentary rocks mainly chemical in origin, commonly, but not necessarily containing layers of chert." These chert layers alternate with iron rich bands and vary in thickness from one millimetre to a few centimetres. There is little or no clastic sediment associated with the Iron Formation rocks.

James (1954) subdivides the B.I.F. into four facies, each facies being characterized by a specific mineral assemblage which depends upon the environment of deposition. The four facies are oxide, carbonate, silicate and sulphide. The chief controls of the chemical precipitation process of these iron minerals are the hydrogen ion concentration (pH) and the redox potential (Eh), both of which change from shallow to deep water. In the oxide facies the predominant minerals are either magnetite or hematite, where the Eh value is relatively high, and the partial pressure of CO₂ is low. In the carbonate facies the main mineral is siderite. Garrels (1960) suggests that the occurrence of siderite is due to a reducing environment. He also proposes that the alteration of deposition of siderite and magnetite is due to the fluctuation of both pH and Eh values. In the

silicate facies the main minerals are iron silicates, such as grunerite (Fe7 Si8 O₂₂ (OH)₂), almandine (Fe3 Al₂ (SiO₄)₃), greenalite (Fe₆ Si₄ O₁₀ (OH)₈), minnesotaite ((Fe,Mg)₃ (Si,Al)₄ O₁₀ (OH)₂)...etc. The pH and Eh values for the silicate facies are similar to those for the iron oxide facies (illustrated later). In the sulphide facies the main mineral is pyrite which formed in a reducing environment.

3 - 2 The stability relationships of iron minerals:

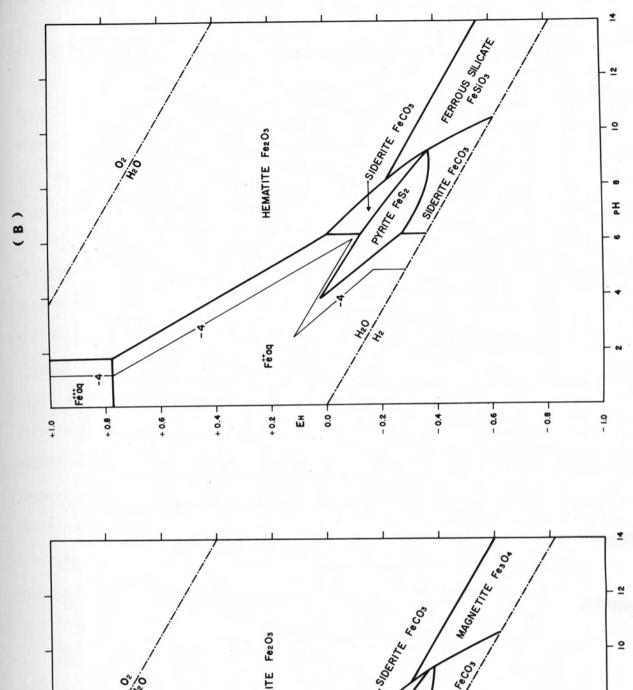
The relative stability of the iron minerals in a sedimentary environment is due to variation in pH and Eh (Garrels 1960). Using these variables (Figs. No. 5A and 5B) it can be seen that hematite is stable in a moderate to strongly oxidizing environment. In a reducing environment the stable minerals are pyrite, siderite or magnetite, and additionally the specific mineral depends upon the concentration of dissolved sulphur and the carbon dioxide. In figure 5A, silica is absent. Magnetite may co-exist with either hematite, pyrite or siderite. In figure 5B iron silicate takes the place of magnetite. Garrels (1960) shows that when the system becomes saturated in silica, i.e. when there is enough silica to combine with all the iron in the system, magnetite becomes unstable relative to iron metasilicate, and iron silicate will form preferentially. This suggests that the general conditions for silicate precipitation are similar to those of magnetite. (Garrels (1960), and Stanton (1972)).

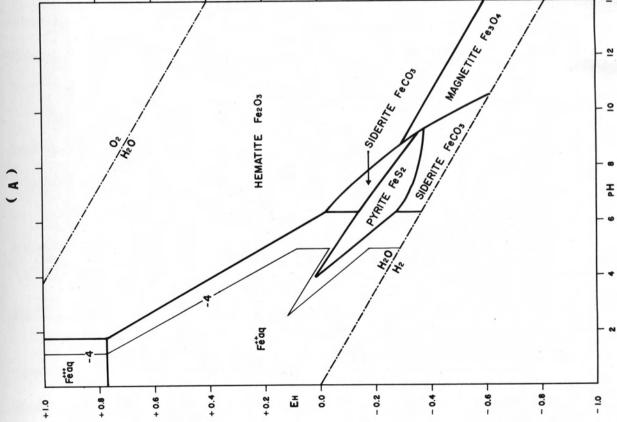
3 - 3 Origin of the Banded Iron Formations:

The genesis of the Iron Formation has been ascribed to an alternation in precipitation of iron oxide and silica, the latter

Fig.No. 5 A . Stability relations of iron oxids, sulfides, and carbonate in water at 25 C and 1 atmosphere total pressure . Total dissolved sulfur = 10^{-6} . Total dissolved carbonate = 10° . Note elimination of FeS field by FeCO₃ under strongly reducing conditions , and remarkable stability of pyrite in presence of small amount dissolved sulfur . (after Garrels 1960)

Fig.No. 5 B . Stability relations among iron oxides, carbonates, sulfides and silicates at 25 C , and 1 atmosphere total pressure in the presence of water . Other conditions: Total $\rm CO_2=10$; total sulfur = 10^{-6} ; amorphous silica is present . This diagram is intended to suggest the innumerable components that can be considered in pH - Eh representation, if arbitrary values are selected for constituent . (after Garrels 1960)





originally being deposited as an amorphous phase Drever, (1974) and Eichler (1976). There is no general agreement for the source of the iron or the silica. Among many suggestions, Hise and Leith (1911) suggest two possible origins of the iron, firstly weathering of the host rocks, and secondly a volcanic or magmatic origin. Gruner (1922) argues that the Iron Formation involves the chemical precipitation of silica and that the source of the iron is a weathering process. Sakamoto (1950) suggests that the rhythmic banding could be due to seasonal climatic fluctuations, where iron is supplied by surface run off during the wet season, and silica is precipitated during the dry season. Alexandrov (1955) speculates that both the iron and silica could be concentrated from basic igneous rocks, which are rich in these constituents, by processes such as leaching and weathering to give solutions rich in silica in warm seasons, and iron rich in cool seasons. Hough (1958) explains the rhythmic deposition of silica and iron as deposits in fresh water basins. On the other hand, Beukes (1973) claims that the source of the silica could be the weathering of acid volcanic rocks, while the iron oxide could have originated from pre-existing ironrich rocks.

It can be generally concluded that the main source of both the iron and the silica is from continental rocks, which are rich in both iron and silica. By processes such as weathering, the iron and silica is transported to the basin of deposition where it is precipitated under suitable conditions of pH - Eh.

3 - 4 Environment of deposition of the Banded Iron Formation:

There is no doubt that the Banded Iron Formation in the Gairloch area is of sedimentary origin, because of the associated metasediments, such as marble, quartzite and graphite schist. Some of the

metasediments have relict sedimentary structures such as graded bedding and layering Park, (1964).

Many workers e.g. Brown (1952), Cloud (1965), Holland (1962), Lepp and Goldich (1964), Oparin (1941), Rubey (1955) and White (1954) have agreed that the early stage of the Precambrian atmosphere was an-oxygenic or reducing. Evidence from stratigraphy and palaeontology indicate that the potential for the evolution of oxygen existed at least between 1.7 to 2.1 billion years ago. Cloud (1965) and Eugster and Ghou (1973) suggest that during the period when carbon dioxide was predominant in the earth's atmosphere, weathering of ferrous silicates such as olivines, pyroxenes, amphiboles and micas would release much ferrous iron and silica into the solution. Once oxygen began to accumulate, therefore, the partial pressure of the carbon dioxide would be decreased both in the atmosphere and the hydrosphere, leading to an acceleration of precipitation of the carbonate. authors have tried to give a model for the depositional environment of the Iron Formation. Hise and Leith (1911) suggest that the iron and the silica precipitated as a chemical sediment. Moore and Maynard (1929) prove that the carbonate water (during Precambrian times) can dissolve more iron and silica from basic igneous rocks. Also they explain the banding between iron and silica as due to different rates of precipitation of iron and silica, dependant on the concentration of these materials in the basin of deposition which reflects in turn a seasonal change. Woolnough (1941) proposed that the Iron Formation was deposited in an environment separated from the sea, most probably, because the marine environment could not give a condition for alterdeposition between iron and silica. Sakamoto (1950) suggests that the iron and silica are precipitated in the dry and the wet

seasons respectively in the basin of deposition, which are shallow and wide and were separated from the open sea. Tyler and Twenhofel (1952) noted that the deposits of the carbonate Iron Formation contain very little or no calcium or magnesium carbonate. From this they suggest that the basin of deposition can have bad or very restricted connection with the open sea. Thus the water in the basin of deposition must have had a composition similar to that of the indraining streams, which would mean that the iron and the silica are precipitated from fresh water and are not of marine origin.

It is now clear that the Iron Formation was precipitated from fresh water (i.e. Lake deposit). When the waters of the lake are hot, a convection cycle for the water will be in progress, and in this case the waters in the upper and lower zones of the lake become mixed together, oxygen can be brought down from the upper zone and oxidizing conditions exist throughout the basin. Another factor like pH, may be varying considerably toward the lower zone of the lake water.

Iron in nature is present in both ferrous and ferric ionic states, in general the ferrous iron compounds are highly soluble, while those of ferric iron are highly insoluble. Hough (1958) suggests that during the summer period stability of the lake water, the oxygen content in the lower zone is nearly zero, in which case conditions for reducing the iron occurs. Also in the summer period, the iron content in the lower zone of the lake waters increases and rises to a high concentration. As soon as circulation of the water begins in the autumn, oxygen is brought to the lower zone, so the iron will oxidize and ferric iron must be precipitated. When the next stagnation period begins, oxygen disappears from the bottom of the lake waters, and

reducing conditions enable the change from ferric iron to ferrous iron to start again. If the lower zone of the lake waters contains hydrogen sulphide dissolved in it, a ferrous iron sulphide is precipitated. In general the particular iron mineral which occurs is dependent on the Eh - pH of the environment (Fig. No. 5A and B).

3 - 5 The Iron Formation of the Gairloch area:

In the Gairloch area the Iron Formation crops out within the Kerrysdale basite group and Kerrysdale siliceous schists (Park 1964) (see Fig. No. 3 and 4). These outcrops occur as lenses in schist and can not be traced far along strike. Most of the outcrops vary in length from 0.5 to 15 metres, and in width from 0.5 to 3 metres. One major exception is the outcrop south-east of Flowerdale Mains (point G12). This outcrop can be traced along strike for about 250 metres. It varies in width from 0.5 to 15 metres. (Fig. No. 3).

The Iron Formation in the Kerrysdale siliceous schists occurs only as the silicate facies. The main mineral assemblage is grunerite and garnet with minor amounts of magnetite and quartz. The Iron Formation in the Kerrysdale basite group occurs as either silicate or as mixed silicate - oxide facies. The main mineral assemblages in these rocks are magnetite, quartz and grunerite with very minor garnet. In the Flowerdale marble belt the Iron Formation occurs as the oxide facies. The main mineral assemblage in these rocks is of magnetite and quartz with minor amounts of grunerite.

3 - 5 - 1 The oxide facies:

The iron mineral in this facies is magnetite. The rocks are dark in colour, the quartz and magnetite are concentrated into discrete bands.

The banding is often folded with chevron type folds (samples G5 and G12). These bands vary in thickness from one millimetre to a few centimetres. Occasionally, between these layers, fine prismatic crystals of grunerite develop, and some time they form a thin band of amphibolite. The quartz and the grunerite show a parallel lineation within the banding. The modal proportion of magnetite to quartz in the iron ore-rich bands is approximately 60: 40

3 - 5 - 2 The silicate facies:

The dominant iron minerals in the silicate facies are grunerite and garnet, with minor amounts of quartz and magnetite. Many of the rocks in this facies are quite coarse-grained, with the prismatic grunerite crystals up to five millimetres in length. Such crystals show alineation within the schistosity. Porphyroblastic garnets occur up to 3 millimetres in diameter. These garnet crystals are often concentrated into separate bands, and in one sample (G16) it is found concentrated with pyrite rich layers.

3 - 5 - 3 The mixed oxide-silicate facies:

In this mixed facies the iron is present in both oxide and silicate minerals. The main mineral assemblage of these rocks is of grunerite, magnetite and quartz, with minor amounts of garnet. There is quite a variation in modal proportions between individual bands. The thickness of individual bands changes from a fraction of a millimetre up to 15 centimetres.

From the preceding description of the mineralogical assemblages for the oxide facies rocks of the Banded Iron Formation in the Gairloch area, magnetite and quartz are the only two minerals, with some minor

amounts of grunerite in these rocks. There is no trace of hematite compared with other Banded Iron Formations distributed throughout the world, which often consist of hematite and magnetite and quartz, e.g. the North Michigan Iron Formation (James 1955), the Biwabik Iron Formation (French, 1968) the Wabush Iron Formation Labrador (Klein 1966), the Itabiri of Minas Gerais (Dorr, 1969), Sokoman Iron Formation (West Labrador) and the Singhbhum (India).

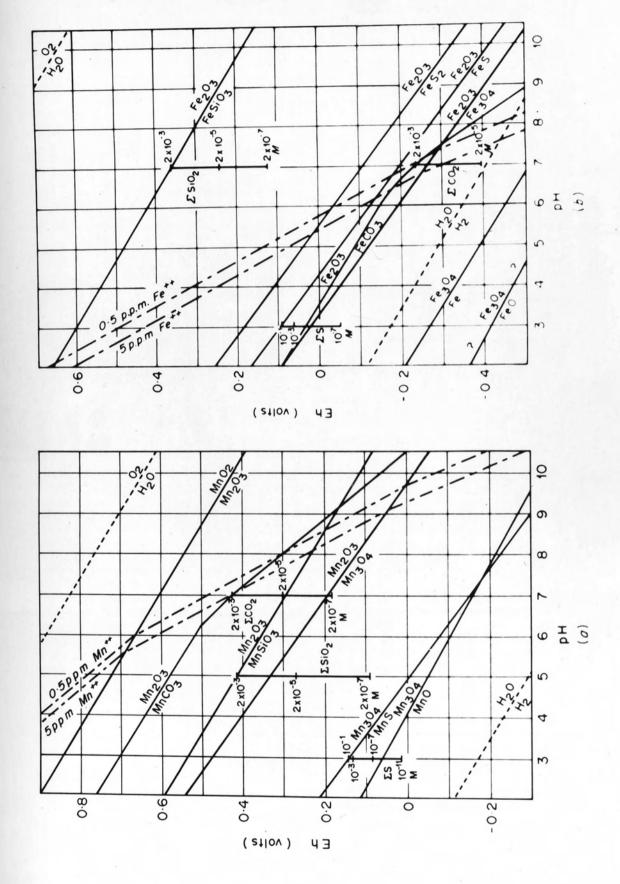
3 - 6 Manganese association with the Banded Iron Formation:

Manganese can be associated with the Iron Formation, such association can occur as oxide, as in the Iron Formation in Brazil. In the Guguna in Minnesota, manganese forms above 20% of the Iron Formation, and in the Gairloch Iron Formation the manganese reaches up to 13% and occurs in the silicate minerals. In some other iron formation like the Lake Superior region where the Mn/Fe ratio is 0.009, and the Biwabik Iron Formation where the Mn/Fe ratio is 0.016, while in the silicate facies rocks in the Gairloch Iron Formation the Mn/Fe ratio is 0.229 and in the oxide facies rocks the Mn/Fe ratio is 0.039. Krauskopf's (1957) interpretation is that the solutions which carry the iron and manganese ions have some similarity and some differences in oxidation and solubility. iron and manganese ions can pass through either oxidation or reduction under the conditions existing today. Garrels (1965) and Krauskopf (1957) demonstrated that iron compounds in nature are less soluble than the corresponding manganese compounds. Ferrous iron is more easily oxidized than the manganous ion under the same Eh-pH conditions. so the manganese compounds will enter solution more easily and will remain longer than the equivalent iron compounds, which means that the iron will be precipitated before the manganese from a solution

containing both Fe and Mn ions. This leads the relative separation in the sedimentary environment.

When iron and manganese are delivered to the basin of deposition they may be precipitated as oxide, silicate, carbonate or sulphide, depending on the pH-Eh condition of the sedimentary environment. Fig. No. 6 A & B shows the stability of the anhydrous iron and manganese, bearing in mind the limitation of the diagram when comparing with more complex conditions in nature. When both diagrams are studied carefully a wide stability field for Fe₂O₃ (hematite) can be seen which covers the whole manganese field down to Mn₃O₄. This means that the Fe₂O₃ is stable with any manganese oxide if they occur together, down to manganosite. Therefore, whenever the iron oxide is precipitated manganese will be precipitated as well. In fact however, in nature each is precipitated without the other. In Fig. No. 6 for a fixed pH, the iron compounds will precipitate at a lower Eh than their manganese counterparts. Alternatively for a fixed Eh the iron will precipitate at lower pH than the counterpart of manganese Krauskopf (1957). This means that the more basic the solution is, which contains both the iron and manganese ions, this leads to precipitation of iron before the manganese. This applies under the present day conditions.

Fig . No . 6 Eh - pH digram for anhydrous (a) manganese, and (b) iron compounds . (after Krauskoph , 1957)



CHAPTER FOUR

PETROGRAPHY

Petrography

4 - 1 Description of the iron formation rocks:

Eighteen samples were collected from the Gairloch Iron Formation, these rocks are characterized by two types:

- A) The silicate facies rocks:- the main mineralogical constituents are garnet, grunerite, and sometimes quartz. These rocks are yellowish grey in colour. Many are quite coarse grained with prismatic grunerite crystals up to 5mm in length, and porphyroblastic garnets up to 3mm in diameter. The garnet crystals are often concentrated into separate bands. These rocks have both a granoblastic texture (plates No. 1,4 and 5) and a porphyroblastic texture (plates No. 2,3 and 7)
- B) The oxide facies rocks:- The main mineralogical constituents are quartz and magnetite. The rocks are dark in colour and show an alternation between quartz and magnetite rich bands, which vary in thickness from a fraction of a millimetre to a few centimetres. The modal proportion of magnetite to quartz in the iron ore bands is approximately 2: 1. Some rocks are coarsely crystalline while others contain fine crystals.

 These oxide facies rocks have a banded texture (plates No. 6, 8 and 9). In all the oxide facies rocks, minor fold and fault structures occur, varying in size from a few millimetres to about 30 centimetres (plate No. 6 and 9).

4 - 2 Description of the metasediments:

Thirteen samples were collected from the rocks adjacent to the Iron Formation outcrop. These rocks vary in both texture, and mineralogical assemblage. They are:

- A) Hornblende schist: The main mineralogical constituents of these rocks are hornblende and quartz. Sometimes chlorite occurs as an alteration product of hornblende. The rocks are dark in colour and coarsely crystalline. They have a lepidoblastic texture.
- B) Biotite Muscovite schist: The main mineralogical constituents of these rocks are biotite, muscovite, and quartz. The rocks contain fine to medium sized crystals and also have a lepidoblastic texture.
- C) Quartzite:- The main mineral constituent of these rocks is quartz. The rocks are full of magnetite inclusions (plate No. 15). Occasionally samples have a banded texture (sample 2(2)) with magnetite rich bands (plate No. 8). Others (sample No. 4) have granoblastic texture (plate No. 15)
- D) Graphite schist: This rock is dark in colour (black). The main mineralogical constituents are quartz, graphite, and muscovite. This rock has a small scale folded structure, (few millimetres to a few centimetres). The approximate volume percentages of the mineral constituents in these rocks are shown in table No. 2. They are only approximate, because in the oxide facies rocks, the banded texture varies in thickness, so it is not possible to estimate the actual percentage contents of these minerals. Also in the silicate facies rocks, the distribution of garnet is not homogeneous through the rocks.

It is concentrated in one or two bands, and disseminated in small amounts through the rest of the rock. In the metasediments, some rocks also show a banded texture the same as the oxide facies rocks. The rest of the rocks (hornblende schist, and biotite - muscovite schist). The mineral distribution in these rocks are homogeneous, and the mineral percentages are merely rough estimates because it is outside the field of this study.

4 - 3 Description of the minerals:

1) Magnetite:-

Magnetite occurs in all the rock samples, varying in concentration from a trace amount up to 45%, in this latter concentration it forms one of the main mineralogical assemblages in the oxide facies rocks of the Iron Formation in the Gairloch area (plate No. 9). The magnetite varies in size from very small grains up to one millimetre in diameter, but the average size is 0.15mm. Some magnetites have irregular shapes due to the irregular intergrowth between the crystals, but others are subhedral crystals. Most magnetites are elongated and show a parallelism with the banding, with schistosity or with the long axis of the host mineral.

Magnetite also occurs as fine inclusions in garnets. Sometimes it forms about 50% of the garnet crystals (sample No. 1(3)C), (plate No. 7). Magnetite can also occur as fine inclusions in quartz in the quartzite rock (sample No. 4) (plate No. 15).

2) Quartz:-

Quartz occurs in abundant amounts in most of the rocks, varying in concentration from trace amounts in some silicate facies rocks in the Iron Formation up to 95% in the metasediments (quartzite rock). Also the grain size is variable from about 0.05 to 0.45mm. The quartz in the oxide facies rocks contains magnetite inclusions and occurs usually as lenses or bands of variable lengths and thicknesses. The crystals are subhedral and interlocking, and show ribbon structures (plate No. 14). Such ribbons are parallel to the banding of the rocks. In the silicate facies rocks, quartz usually occurs as fine idioblastic (polygonized) crystals, and always occurs beside the garnet crystals. Also quartz occurs as inclusions in most of the silicate minerals (plates No. 4,7,10,12,16 and 17).

3) Grunerite:-

The grunerite occurs only in the Iron Formation rocks, forming one of the major minerals in the silicate facies rocks, where it varies in concentration from 30% up to 80%. In the oxide facies rocks the grunerite occurs as a minor mineral phase, and varies from 1% up to 15% of the rock by volume. In these oxide facies rocks the grunerite occurs in both magnetite and quartz rich bands. In the former the grunerites are coarser and reach to 0.3mm in diameter, while in the latter, it occurs as fine prismatic crystals. Also the grunerite in these rocks occurs as very fine grains and forms thin bands of grunerite which attain 0.4mm in thickness. In the silicate facies rocks

the grunerite usually occurs as coarse crystals which reach up to 5mm in length, but is also found as inclusions in the associated garnet crystals, (plates No. 4, 5 and 7). Grunerite occasionally interfingers with garnet crystals (plates No. 1,4 and 5), indicating that the garnet and the grunerite might have formed simultaneously. Most of the grunerite crystals in the silicate facies rocks have magnetite inclusions and occasionally quartz inclusions (plate No. 10). The extinction angle $(Z \wedge C)$ varies from 16° to 19° and is dependent on the iron content in the grunerite. All the crystals show a parallelism with the schistosity or the banding of the rocks.

4) Garnet:-

The garnet forms one of the major minerals in the silicate facies rocks. Also it occurs in the metasediments as an accessory mineral. Most of the garnets in the Iron Formation rocks occur as very good idioblastic crystals, but some are subhedral and very occasionally anhedral crystals occur (plates No. 1 to 5 and 7). These garnets are highly fractured and some are in filled with the quartz, grunerite, magnetite, and carbonate inclusions (plates No. 4,5, and 7). The garnet in the oxide facies rocks usually occurs in magnetite rich bands. The average size is 0.25mm. Sometimes many crystals form a cluster-aggregate of garnets. The garnet in the silicate facies rocks is usually concentrated in separate bands, where the average size is 2mm in diameter. Some of these garnets, particularly in sample No. 7, have a dusty centre, which is

full of carbonate, quartz, and some inclusions which show alteration to a clay (plate No. 4). Other garnets show a concentric centre but have few inclusions, mainly quartz, and a few grains of carbonate (plate No. 3). Most of the garnets in the silicate facies rocks have interfingering margins with the grunerite minerals. The garnets in the metasediments are idioblastic crystals and show very sharp edges with the associated minerals. (Plates No. 16 and 17). Most of the garnet in sample No. 20 has a poikiloblastic texture in which the quartz and the magnetite minerals increase toward the centre of the crystals, (plate No. 17), the garnets in sample No. 19 have less inclusions, these being distributed randomly through the crystals (plate No. 16). Some of the garnets in the metasediments, show alteration to chlorite and biotite.

5) Hornblende:-

The mineral hornblende occurs in the metasediments only, forming the main mineral in the hornblende schists. The concentration of hornblende varies in these rocks, but on average it forms 46% of the rock, it usually occurs as long prismatic crystals but some are of irregular shape. The average length of these crystals is 0.3mm. They form the schistosity in the rocks. Sometimes near crystal margins there is some alteration to chlorite and biotite, (plate No. 12). The common inclusions in the hornblende are quartz, magnetite and zircon. The extinction angle varies between 16° and 19° and the mineral is highly pleochroic in which X is yellowish green, Y is grass green and Z is dark green.

6) Chlorite:-

Chlorite occurs in the metasediments as an alteration product of some of the silicate minerals, e.g. hornblende, biotite and garnet. It is a minor or trace constituent of the rocks, except for sample No. 1(5), in which the chlorite forms 35% of the rock. Quartz, magnetite and zircon are the common inclusions in the chlorite. The crystal have a fibrous shape and sometimes are irregular. The average size of the chlorite in sample No. 1(5) is 0.15mm.

7) Biotite:-

The mineral biotite occurs in the metasediment as brown platy crystals, and forms one of the main mineralogical constituents in the biotite - muscovite schist, where it varies in concentration from 16 to 27% of the rock. The grain size varies from 0.1 to 0.5mm, quartz, magnetite, and zircon are the common inclusions in biotite.

8) Muscovite:-

Muscovite occurs in the metasediments, forming one of the main minerals in the biotite - muscovite schist, and in the graphite schist. It varies in concentration from 20 to 38% of the rocks, and has the form of long thin prismatic crystals with an average length of 0.3mm (plate No. 13). Magnetite is the common mineral inclusion in the muscovite in the biotite - muscovite schist, while graphite is the common mineral inclusion in muscovite in the graphite schist. Some muscovite crystals have a biotite centre as remnant mineral due to alteration of biotite to muscovite.

9) Calcite:-

Calcite occurs as a trace constituent in the metasediments. The crystals are idioblastic to subhedral and vary in size from 0.2 to 0.5mm. The calcite dominantly occurs in the hornblende schist rocks. Magnetite is the only inclusion occurring in the calcite.

10) Siderite:-

The mineral siderite occurs in one quartz rich band in the oxide facies rocks of the Iron Formation only, in sample No. 12 (M) B. These crystals are subhedral and vary in size from very fine crystals up to 0.5mm, the average crystal size is 0.15mm. Magnetite and quartz occur as inclusions in the siderite crystals (plate No. 11). In sample No. 12 (G), carbonate occurs but in just a few crystals, whose average size is 0.05mm. They may be siderite.

11) Graphite:-

Graphite occurs as the main mineral which forms the graphite schist. It occurs as a fine grain and may reach to approximately 50% of the rock. Also it occurs as inclusions in sample No. 17 (A).

12) Plagioclase: -

The plagioclase occurs as an accessory mineral in some metasediments only, in the form of andesine and oligoclase. The average size is 0.075mm. Some magnetite occurs as an inclusion in the feldspar which also shows alteration to zoisite in sample No. 19.

13) Sphene:-

The sphene mineral occurs in a few samples as accessory mineral. The crystal is less than 0.05mm. Sample No. 10 has approximately 1% of sphene.

14) Epidote:-

This mineral occurs as a few subhedral crystals in sample No. 4 only. The average size is O.lmm.

15) Zircon:-

This mineral occurs as inclusions only in hornblende, biotite, and chlorite.

16) Zoisite:-

This mineral occurs only in sample No. 19, as an alteration product of the plagioclase, which form about 5% of the rocks.

17) Pyrite:-

This mineral occurs only in sample No. 16. The crystals are irregular shapes but some are subhedral. The average size is 0.5mm. Pyrite forms about 6% of the rock.

18) Hematite:-

Hematite is found in nearly all the samples, but only as a stain in the fractures of the garnets and the cleavages of the amphiboles, except for sample No. 5 in which hematite forms about 3% of the rock, and sample No. 12 (M)B where it forms about 1%. Table No. 17 is illustrating the main mineralogical assemblages in the rocks, and the variety of these rocks.

CHAPTER FIVE

MINERALOGY

Mineralogy

5 - 1 Amphibole:-

Hauy (1801) first gave the name amphibole to this group of minerals. Originally it comes from the Greek word "amphibolos"; meaning ambiguous. Penfield (1890) discovered that water forms a part of the tremolite structure. Schaller (1916) was the first to derive the correct formula for tremolite.

The chemistry of amphiboles show a wide variety of atomic substitutions, ranging in ionic radii from 0.4A° to 1.4A°, which makes the arrangement of those cation sites more complex, owing to differences in size and charge. Because of this, many names have been given to differentiate the minerals with small differences in composition or optical properties.

5 - 1 - 1 General formula of amphiboles:

The general formula of the amphibole group is: $A_{O-1} \times_2 \times_5 \times_8 \times_{O_{22}} (OH)_2$ which represents the half unit cell of the amphibole. The 'A' site is occupied by K or Na and represents the twelve fold co-ordinated cations. The X sites contain Fe^{2+} , Mg, Mn, Ca, or Na, and represent the eight fold co-ordinated cations. The Y sites are occupied by Fe^{3+} , Mg, Fe^{2+} , Al, Mn or Ti and represent the octahedrally co-ordinated cations. The Z sites are occupied by tetrahedrally co-ordinated Si and Al ions.

5 - 1 - 2 Cation distribution between sites:

The cations in the amphibole can be distributed as follows: The X cations occupy the M(4) site, the Y cations occupy the M(1), M(2) and M(3) sites, the Z cations occupy the Tl and T2 sites. The Fe^{2+} , Ca and Mn have a strong preference for occupying the M(4) site Ghose (1965), but when they occur together as in actinolite and hornblende, the Ca will occupy the M(4) site preferentially while the Fe^{2+} will occupy the M(2) site preferentially Ghose (1962). Cations like Mg, Fe^{3+} and Al occupy the M(1), M(2) and M(3) sites and the proportions of these cations vary in proportion from one amphibole group to another. Ghose (1959) and Boncroft (1967) found that the M(4) site in the cummingtonite-grunerite series is occupied by Fe^{2+} , while the M(2) concentrates Mg. The M(1) and M(3) sites contain Mg and Fe^{2+} ions randomly distributed between them.

5 - 1 - 3 Chemistry and nomenclature of the amphibole group:

The great flexibility of the amphibole structure makes it possible to have a great deal of isomorphous replacement between ions of similar size and charge. This consequently gives a wide range of complex chemical compositions which give rise to a profuse nomenclature which has recently been rationalized by a sub-committee of the I.M.A. (Leake 1978). Amphiboles occur in both the monoclinic and orthorhombic systems, which depend on the mode of stacking of the neighbouring bands when the large ions, particularly Ca, Na and K are in very small concentration in the M(4) sites. In this case the smaller ions will occupy theM(4) site and can result in an orthorhombic cell. Deer, Howie and Zussman (1963).

From the general amphibole formula, substitution of the ions can be summarized according to Mason (1959) and these are:

- (1) Na, Ca and K ions in the amphibole, may be absent or in very small amount, or may vary from 2-3 atoms per formula unit.
- (2) Mg and Fe²⁺ can completely replace each other.

- (3) Al can replace up to one Si in any (Si40]] formula unit.
- (4) F can replace the (OH).

Deer, Howie and Zussman (1963) based their classification for this group on the occupancy in the X position in the amphibole structure.

In general there are five series in the amphibole group. These are:

- (1) Anthophyllite series: These are orthorhombic and have the formula (Mg,Fe)₇ Si₈ O₂₂ (OH)₂, in which Mg is greater than Fe²⁺. In this series Fe²⁺ and Mg occupy the M(4) site. The ratio of Mg/(Fe+Mg) varies between 1 and 0.4. Two varieties occur in this series, an aluminium-poor variety (anthophyllite), and an aluminium-rich variety (gedrite). Aluminium can replace one silicon atom in the formula unit to make (Al Si₃ O₁₁), when this substitution takes place, an accompanying replacement of Mg by Al also takes place to balance the charge.
- (2) <u>Cummingtonite-Grunerite series:</u> These belong to the monoclinic system and have the formula (Fe, Mg)₇ Si₈ O₂₂ (OH)₂. In this series also the Fe²⁺ and Mg occupy the X position and the ratio of Fe/(Fe+Mg) varies from 1 to 0.4. The name grunerite is given to those members which have more than 50% Fe²⁺, whilst cummingtonite is given to those which have more than 50% Mg.
- (3) Tremolite-Actinolite series: The tremolite composition is Ca₂ Mg₅ Si₈ O₂₂ (OH)₂ and the actinolite is Ca₂ (Mg,Fe)₅ Si₈ O₂₂ (OH)₂. In this series Ca occupies the X position, Mg is replaced by Fe²⁺ to form ferroactinolite, also Mg may be replaced by small amounts of Al and Fe³⁺, and AL can replace silicon up to 0.5 atoms per formula unit.

- (4) <u>Hornblende series:</u> Hornblende minerals have a very wide range of composition. This series originated by the addition of one sodium ion for each $(Si_4 \ 0_{11})$ to the structure of the tremolite-actinolite series, this addition is accompanied by aluminium substitution for the silicon to balance the charge. There is another type of hornblende which is normally found in volcanic rocks, and has a high Fe^{3+}/Fe^{2+} ratio and a low hydroxyl content.
- (5) Alkali amphibole series: In summary this series may be considered to be derived from the hornblende series by the partial or complete replacement of calcium by sodium glaucophane (Na₂ Mg₃ Al₂ Si₈ O₂₂ (OH)₂) and riebeckite (Na₂ Fe²⁺₃ Fe³⁺₂ Si₈ O₂₂ (OH)₂) are well known alkali amphiboles.

5 - 1 - 4 Chemistry of the amphiboles in the Iron Formation from the Gairloch area:

All the analysed amphibole minerals were separated from silicate facies rocks from the Gairloch area. Seven amphiboles were analysed using the X-ray fluorescence method for both major elements (table No. 3) and trace elements (table No. 7A). Three samples have been analysed for major elements using the electron microprobe (table No. 4 and 5) to detect the presence or absence of any chemical zoning in the grunerite. Eight X-ray diffraction patterns were determined for the amphibole (table No. 6) to elucidate the type of amphibole and to calculate the mole percentage of iron (Klein, 1964, Klein and Waldbaum, 1967).

5 - 1 - 4 - 1 Major element concentration in the amphiboles:

The major constituents of the amphibole minerals which have been analysed are FeO, MgO, MnO and SiO_2 . All the iron is in the ferrous state (Fe²⁺), which varies between 30.4 and 39.6 wt% FeO. The

and 6.00 wt%, except for sample No. 7 which contains only 0.47 wt% MnO. Silica varies between 49.43 and 52.02 wt%. The other oxides only occur in minor amounts: TiO₂ (0.11 - 0.67)%, Al₂O₃ (0.2 - 0.82)%, CaO (0.15 - 0.6)%, Na₂O (0.03 - 0.05)%, P₂O₅ (0.02 - 0.17)%.

Potassium was analysed for but not detected. The silica content is quite constant therefore the three oxides (FeO, MgO, and MnO) can represent three end members of these amphiboles. From the petrographic study and the X-ray diffraction patterns, the amphibole is grunerite. The molecular proportion of the oxides FeO, MgO, and MnO have been recalculated to 100% and plotted on Fig. No. 7, which shows that the amphiboles in samples No. 1(3)A, 14 and 17A are manganoan grunerites, while samples No. 1(4), 3, 7 and 11 are grunerite, according to the nomenclature of Klein (1964) for the cummingtonite-grunerite series.

magnesium varies between 4.77 and 9.43 wt%, and manganese between 3.1

5 - 1 - 4 - 2 Comparison of grunerite from Gairloch with grunerite from other Iron Formations:

The mineral grunerite appears in many metamorphosed Iron Formations. A comparison may be made between the mineral composition of grunerites from the Gairloch area with those from other Iron Formations (table No. 8). The concentration of iron (Fe²⁺) in the grunerite of the Gairloch area varies between 3.9 and 5.31 atoms per formula unit, which is directly comparable to the range of iron content in grunerite (4.01 to 6.41 atoms per formula unit) from the Wabush Iron Formation (south western Labrador). The magnesium (Mg) content in the grunerite from the Gairloch area varies between 1.14 and 2.17 atoms per formula unit, which again lies within the range of the magnesium contents in grunerite (0.77 to 2.46 atoms per formula unit) from the Wabush Iron Formation. However the concentration of

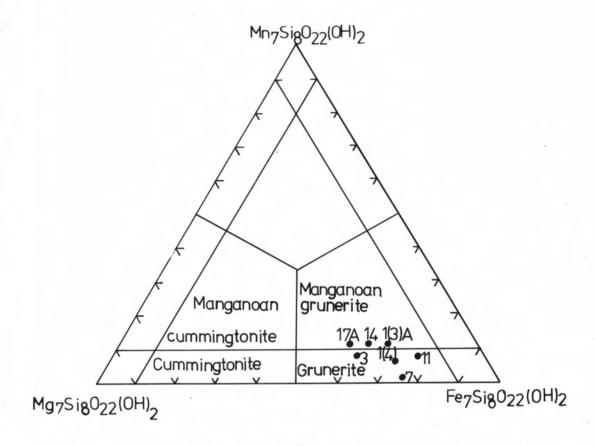


Fig. No. 7 Compositions of grunerites & their suggested nomenclature (after Klein, 1964).

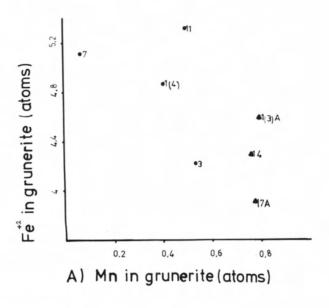
manganese in the Gairloch grunerites is much higher (0.07 to 0.8 atoms per formula unit), than manganese in the grunerite in the Wabush Iron Formation (0.03 to 0.13 atoms). It is similar in a way, to the manganese contents in the grunerite from the Gagnon Region (Canada) which have Mn values which overlap with those of the Gairloch area (0.07 to 0.53 atoms) but are much higher in magnesium (1.54to 3.52 atoms) and lower in iron (2.9 to 4.71 atoms).

5-1-4-3 Zoning in the grunerite from the Gairloch area:

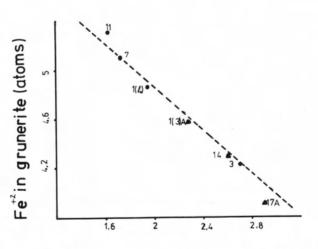
Eleven analyses on sample No. 11 and four analyses each on sample No. 14 and 17 have been made on grunerite using the electron microprobe. From the analyses, no chemical zoning in the grunerite has been detected in either transverse or longitudinal sections of the minerals.

5 - 1 - 4 - 4 The relationship between the major elements in grunerite from the Gairloch area:

When Fe²⁺ in the grunerite is plotted against Mn²⁺ (Fig. 8A), it does not show any correlation. However when Fe²⁺ is plotted against Mg²⁺ (Fig. 8B), it shows clearly a negative correlation which explains the mutual substitution between these two elements in grunerite. When Fe²⁺ is plotted against Mg²⁺ + Mn²⁺ together (Fig. 8C), it shows a much better negative correlation, the points more or less lie on a straight line which indicates that the iron is capable of being replaced by both Mg and Mn. Also the occurrence of the other major oxides in the grunerite may explain the deviation of these analyses from a straight line relationship.



1.3 1.5 1.7 1.9



B) Mg in grunerite(atoms)

- C) Mn+Mg in grunerite (atoms)
- Grunerite
- ▲ Manganoan grunerite

Fig.No. 8 Relationship between the major elements in the grunerite.

5 - 1 - 4 - 5 Trace element concentrations in the amphiboles:

Eleven trace elements have been analysed from the grunerite (Table No. 7Λ). These are:

Trace element	range	in	p.p.m
Ва	12	to	38
Cr	111	to	175
Nb	5	to	18
Ni	26	to	64
Pb	0	t o	4
Rb	0	to	5
Sc	20	to	68
Sr	0	to	10
V	48	to	167
Y	0	to	6
$Z\mathbf{r}$	26	to	96

From the above mentioned trace elements, it can be seen that they are quite variable in concentration compared to many other rock types, the overall concentration of trace elements is small. Some trace elements like Ba, Pb, Rb, Sr and Y although analysed for, the values show that they lie close to or below the detection limit of the instrument.

Interference from contaminating elements in the X-ray tube target has been found, and these include Cr and Ni. A blank disc made from cellulose measured 48 p.p.m Cr and 21 p.p.m Ni. Tests have been run on a variety of blank materials i.e. cellulose, spectrosil (SiO₂), sucrose and distilled water for both Ni and Cr. The results obtained from the cellulose, sucrose and distilled water samples were very similar, but the spectrosil (SiO₂) gave results 30 p.p.m higher for both Ni and Cr. The reason for this is not known but may be due

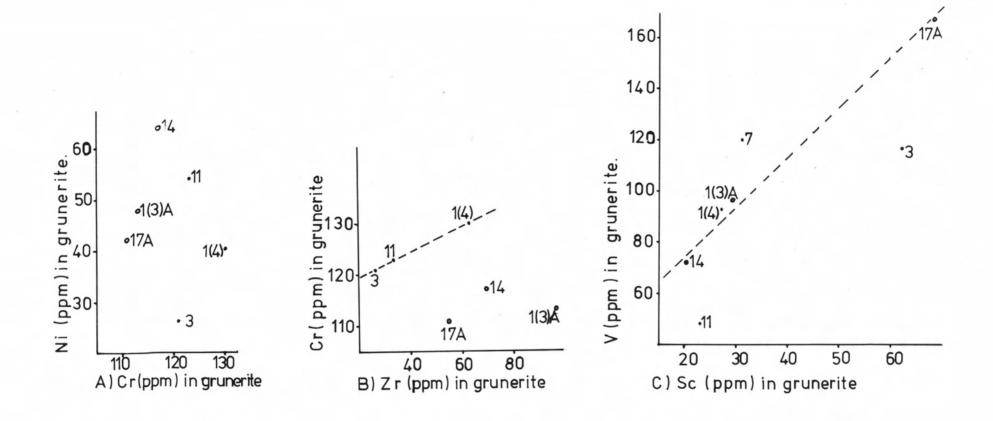
to a diffraction effect of the crystalline SiO₂. (G. J. Lees pers. comm.) For this reason no correction for the Ni and Cr contamination in the target tube has been made, therefore the values for these elements are thought to be too high.

5 - 1 - 4 - 6 Relationships between the trace elements in the grunerite:

- (1) <u>Positive correlation:</u> There appears to be a positive correlation between Ni and Cr, and V and Sc in the manganoan grunerites and between Zr and Cr in the grunerites although any conclusion must be rather tenuous as only limited data is available. (Fig. No. 9 A, B & C)
- (2) <u>Negative correlation:</u> There appears to be a negative correlation between Sc and Cr, and V and Cr in the manganoan grunerite and between Ni and V is seen only in the grunerite (Fig. No. 10 A,B and C). This conclusion must also be rather tenuous because of the limited data.
- (3) No correlation: No correlation seems to be apparent between the other pairs of trace elements.

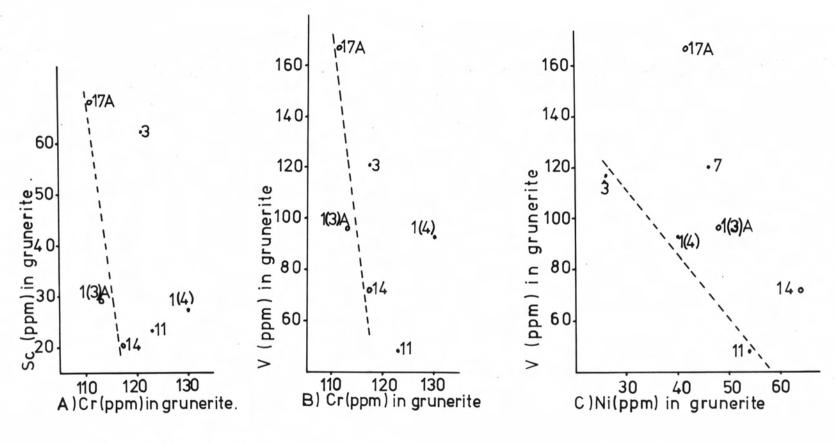
5 - 1 - 4 - 7 Relationships of the trace elements with the major elements in the grunerite from the Gairloch area:

As mentioned before the three main elements in the grunerite are Fe²⁺, Mg²⁺ and Mn²⁺, so the relationships between the major and trace elements will be restricted to those three oxides. Some trace elements appear to give positive or negative correlation, whilst others appear not to give any correlation (Figs. 11 and 12).



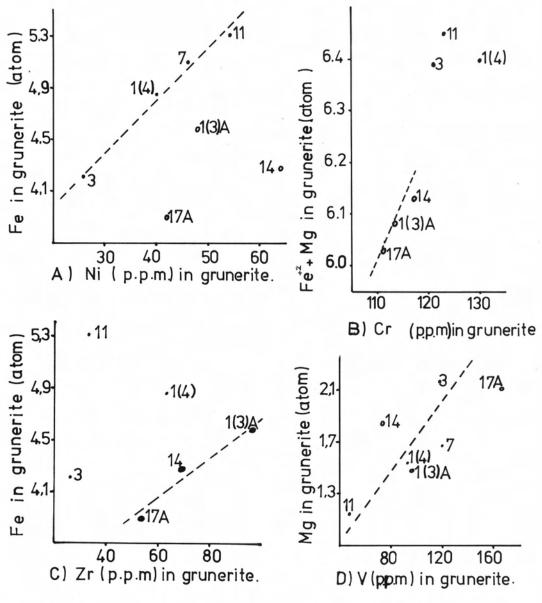
- grunerite
- ° manganoan grunerite

Fig. No. 9 Relationship between the trace elements in grunerite. Positive Correlation



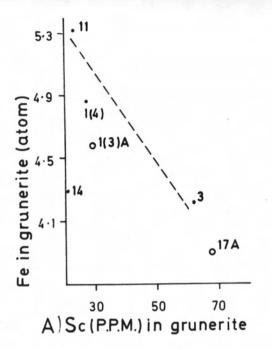
gruneritemanganoan grunerite

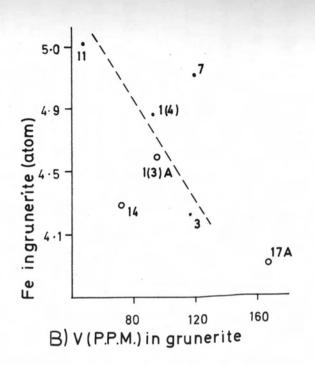
Fig. No. 10 Relationship between the trace elements in grunerite . Negative Correlation.

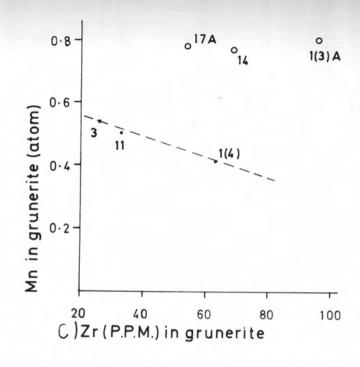


- grunerite.
- manganoan grunerite.

Fig. No.11 Relationship between the trace and major elements in the grunerite: Positive correlations.







- Grunerite
- o Manganoan grunerite.

Fig. No. 12 Relationship between the major and trace elements in grunerite: Negative Correlations.

Correlation	Relation with Fe ²⁺	Relation with Mn ²⁺	Relation with Mg ²⁺
positive)	Ni (grunerite) Zr (manganoan grunerite)		V (grunerite)
negative)	Sc (grunerite) V (grunerite)	Zr (grunerite) Cr (manganoan grunerite)	Ni (grunerite) Zr (manganoan grunerite)
no) correl-) ation)	Cr Nb	Ni Nb V Sc	Sc Cr Nb

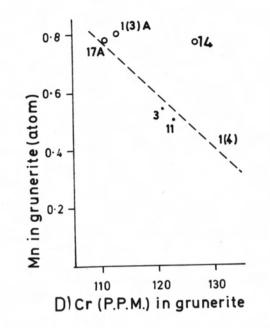
There is no correlation between the trace elements and the combination of either Fe + Mg or Fe + Mn in the grunerite, except for Cr, which shows no correlation with the iron alone, and no correlation with the magnesium alone, but it appears to have a positive correlation with a combination of both iron and manganese in the case of manganoan grunerite only. (Fig. No. 11D)

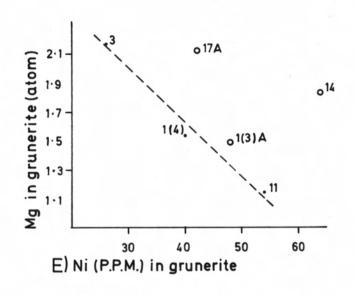
5-1-5 X-ray diffraction pattern of grunerite:

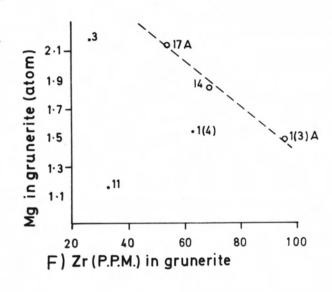
Eight X-ray diffraction patterns of grunerite have been obtained (table No. 6). The observed reflections are indexed by comparison with the A.S.T.M. file Borg (1969). The molecular percentages of iron in the grunerite were calculated from these patterns using equations derived by Klein and Waldbaum (1967). Variation in the iron content using this X-ray method in the grunerite from the Gairloch area lies approximately between 64 and 84 mole %. The 29 position of the (hkl) reflections is a function of the iron substitution for magnesium in grunerite (Fig. 13), so from the 29 angle position for any particular reflection one can estimate the amount of iron in the grunerite.

5 - 1 - 6 Variation of density with iron content in the grunerite:

The density of the grunerite has been measured directly using a pycnometer. Also it has been calculated from the chemical composition of the grunerite determined from both X-ray fluorescence and the

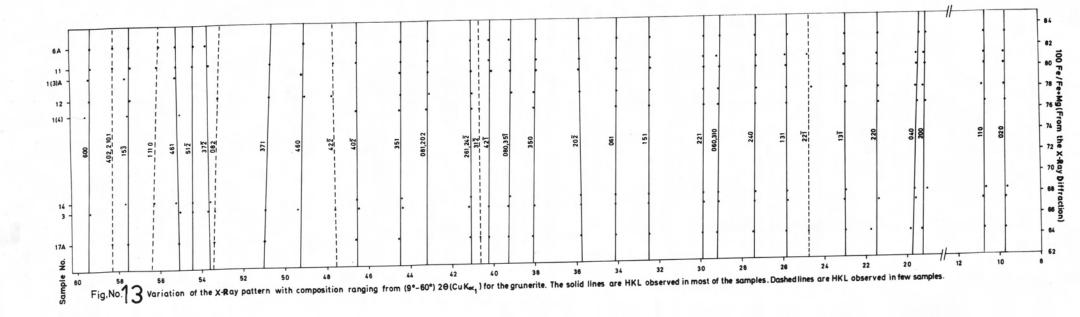






- Grunerite
- o Manganoan grunerite.

Fig. No.12 cont. Relationship between the major and trace elements in grunerite: Negative Correlations.



electron microprobe techniques using the equation given by Zussman (1977):

$$D = \frac{\text{(atomic weight per formula)} \times Z \times Z}{\text{(V)}}$$

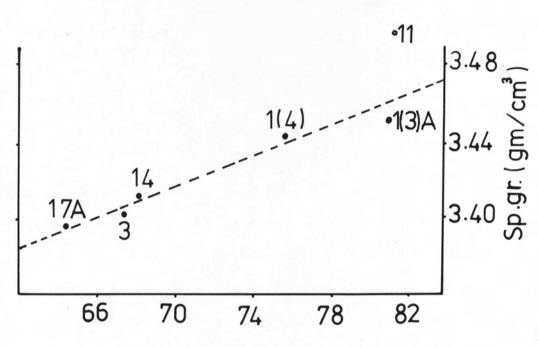
in which D is the density, V is the volume of the unit cell, Z is number of formula units in the unit cell. V is obtained from the equation given by Klein and Waldbaum (1967) using the X-ray diffraction pattern:

$$V = 8.77.790 + 46.916 \times Fe + 0.917 (XFe)^2 + 0.0003$$
 A

V is the volume of the unit cell and XFe is the mole percentage of iron in the grunerite (XFe = $\frac{Fe}{Fe + Mg}$).

The density measured using the pycnometer is different from the calculated density (Table No. 9), the reason probably being due to the inherently lower accuracy of the pycnometer method.

The mole percentages of the iron XFe = Fe/Fe+Mg for grunerite has been measured by three analytical methods (X-ray diffraction, X-ray fluorescence and the electron microprobe) table No. 9. Although the three different methods for the analyses have been done they give more or less similar values. The density of the grunerite is plotted against the mole percentage of the iron, calculated from the X-ray diffraction data in Fig. No. 14. From diagram No. 14 and No. 13, the mole percentages of the iron in the grunerite can be estimated if the density or the position of the (hkl) reflections are known.



Fe/Fe+Mg % of the grunerite.

Fig. No.14 Variation in specific gravity as a function of Fe&Mg in grunerite.

5 - 2 Garnet:

The name garnet comes from the Latin name - Granatus - which means similar to the fruit of the pomegranate. Garnets are characteristic minerals in metamorphic rocks, but are also found in some igneous rocks and rarely in sediments as an authigenic phase.

Menzer (1926-1928) was the first to study the crystal structure of garnet. Abrahams and Geller (1958) studied the structure of grossular garnet in more detail and reported accurate interatomic distances between the Si-O, Al-O and Ca-O ions. Different names have been given to garnet minerals depending on the molecular composition.

5 - 2 - 1 General formula of the garnet group:

The general formula for this group of minerals is X_3 Y_2 (SiO₄)₃, in which X can either be one or a combination of the following: Ca, Mg, Fe²⁺ and Mn ions. The usual co-ordination number of Fe²⁺ and Mg in silicates is six, but in the garnet structure, these ions occur in eight fold co-ordination. The Y sites also accommodate either one or a combination of Al, Fe³⁺ and Cr ions and occasionally Ti⁴⁺ or Mn³⁺.

5 - 2 - 2 Chemistry of the garnet group and its nomenclature:

The garnet group has six main end-member compositions, which depend on the cations occupying the sites in the structure. These six minerals can be divided into two series, each of which has complete isomorphism between the end members, these are:

- (A) Pyralspite series: (sometimes called the Almandite series).
- (Mg, Fe, Mn) $_3$ Al $_2$ (SiO $_4$) $_3$ which contain three end members
- (1) Pyrope Mg_3 Al₂ (SiO₄)₃
- (2) Almandite Fe_3 Al_2 $(SiO_4)_3$
- (3) Spessartite Mn₃ Al₂ (SiO₄)₃

- (B) <u>Ugrandite series</u>: (sometimes called the Andradite series), with a formula of Ca₃ (Al, Fe, Cr)₂ (SiO₄)₃, containing the three end members
- (1) Uvarovite $Ca_3 Cr_2 (SiO_4)_3$
- (2) Grossularite Ca₃ Al₂ (SiO₄)₃
- (3) Andradite $Ca_3 Fe_2 (SiO_4)_3$

Mg²⁺ and Fe²⁺, and Mn²⁺ and Fe²⁺, in the pyralspite series may freely substitute for each other in any ratio, which implies that there are all intermediate compositions between pyrope and almandite, and all intermediate compositions between spessartite and almandite. However substitution between Mn²⁺ and Mg²⁺ is very rare because of the ionic size difference. Among the trivalent elements there is also a large amount of substitution between ions like Al and Fe³⁺, and Cr and Al. However substitution between Ca and Fe²⁺ or Mg²⁺ in the garnet is very rare because of the ionic size difference. It is thought that phosphorus can replace the silicon atom in very small proportions. Titanium may replace aluminium. The name given to the garnet mineral, depends on the predominant element present.

5 - 2 - 3 Chemistry of garnet in the Iron Formation of the Gairloch area:

All the analysed garnets have been separated from the silicate facies rocks. Six garnets have been analysed for both major elements (table No. 10 and 5) and trace elements (table No. 7B) using X-ray fluorescence techniques. Three samples have been analysed using the electron microprobe to determine the presence or absence of any chemical zoning (table No. 11). X-ray diffraction data were obtained for the garnets (table No. 12) to determine both the garnet type and to measure the unit cell dimensions in order to calculate the density.

5-2-3-1 Major element chemistry:

The major constituents of the garnets are FeO, CaO, Al₂O₃, and All the iron is in the ferrous state. The FeO content varies between 19.14 and 34.81 wt%; MnO between 2.18 and 19.82 wt%; CaO between 3.77 and 4.71 wt% (except sample 1(3)A in which the CaO is 0.85 wt%); Al₂O₃ between 18.80 to 18.53 wt%, and silica between 36.08 and 37.96 wt%. Other oxides occur in minor amounts, such as TiO2 (between 0.27 and 0.77 wt%) and P_2O_5 (between 0.07 and 0.23 wt%). Potassium and sodium have been analysed for but not detected. In the pyralspite series alumina and the silica are constant, so the three oxides, FeO, MnO, and CaO can represent the three end members of the garnet composition. The molecular proportions of the three oxides have been recalculated to 100% and plotted on a triangular diagram (Fig. No. 15). From this diagram it may be seen that sample No. 1(3)A, 1(4), 11 and 14 are spessartite - almandine garnets, Vermaas (1952) while samples No. 7 and 21 are almandine garnets containing approximately 5% of the spessartite end member. The amount of the Fe, Mn, Mg and Ca contents in the garnet reflect the concentration of the garnet end-member minerals, in which almandine varies from 44.34 to 79.21%, spessartite from 5.02 to 48.79%, pyrope from 1.29 to 3.01% and the grossularite from 2.42 to 13.73% (table No. 10).

<u>5-2-3-2</u> Comparison between garnets from the Gairloch Iron Formation and other Iron Formations:

Members of the garnet group of minerals appear in few Iron Formations. They occur in the Lower Wabush Iron Formation (Klein. 1966) as almandine garnet, and in the Upper Wabush Iron Formation (Klein. 1966) as spessartite garnet. Garnet also occurs as almandine in the Itchen (Canada) Iron Formation (Bostock, 1977) which is of Archean age.

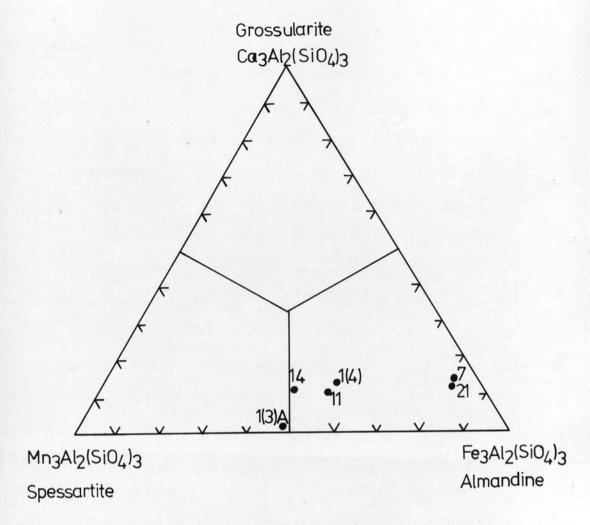


Fig. No.15 Compositions of the garnets & their suggested nomenclature

The garnet in the Lower Wabush Iron Formation contains 0.54 wt% $\text{Fe}_{2}\text{O}_{3}$ (table No. 13), and 1.89 wt% MgO. In the Upper Wabush Iron Formation, all the iron in the garnet is in the ferric state (14.9 wt%), and there is no MgO. The garnet from the Archean Iron Formation contains a very small amount of MnO up to 0.46 wt%, and a little MgO up to 1.44 wt%, (iron occurs in both Fe^{2+} and Fe^{3+} states together up to 38.15%). Calcium as the oxide appears to be of similar concentration in garnet in all these Iron Formations. In the Upper Wabush Iron Formation it is 5%, in the Lower Wabush Iron Formation it is 3.5%, in the Archean Iron Formation it ranges from 3.65 to 4.92% and in the Gairloch Iron Formation it varies from 3.77 to 4.71%, with the exception of sample 1(3)A which contains only 0.85% CaO. Although all the analysed garnets from Iron Formations are either almandite or spessartite they occupy compositional fields separate from each other, probably reflecting differences in parental bulk rock composition.

5 - 2 - 3 - 3 Relationships between the major elements in the garnet:

There is a negative correlation between the iron and the manganese, and manganese and calcium in the spessartite rich garnet (Fig. No. 16A and B) indicating substitution for each other. There is also a positive correlation between Fe and Ca, and Si and Ti in the spessartite rich garnet (Fig. No. 16 C and D). No correlation has been found with the other combinations of different pairs of the oxides.

5-2-3-4 Trace element chemistry:

Eleven trace elements have been analysed for in the garnets (table No. 7B). These trace elements vary very much in concentration. It seems that there is no Rb or Pb because these elements have a large ionic size and would not readily substitute for the major elements.

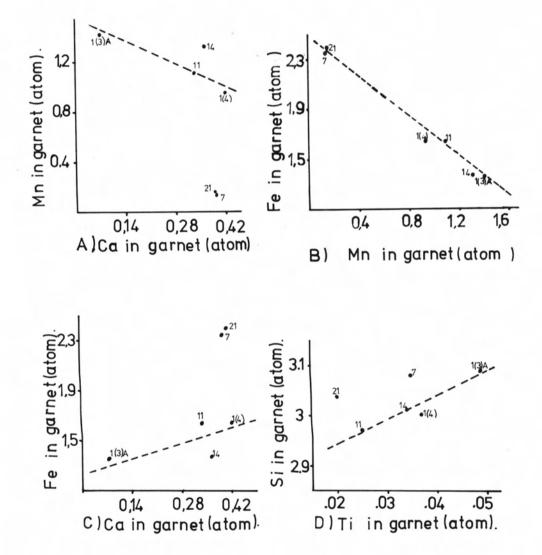


Fig. No.16 Relationship between the major elements in the garnet.

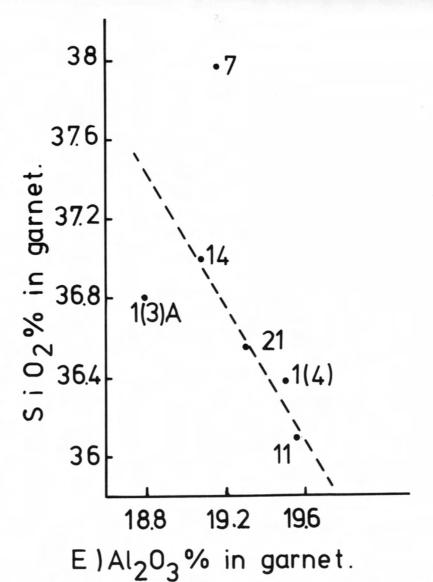


Fig. No.16 cont. Relationship between major oxides in garnet.

Nickel is thought to be below the detection limit because the blank cellulose disc values are higher than those determined for garnet. The barium values are also very low but in two samples (No. 1(4) and 11) they are slightly above the detection limit. The Sr values are also low, which is slightly above the detection limit. The main concentration of the trace elements in the garnet are Cr which varies between 140 to 302 p.p.m, V between 97 and 229 p.p.m, Y between 119 to 193 p.p.m and Zr between 7 and 71. Scandium (21 to 38 p.p.m) and niobium (11 to 56 p.p.m) also occur but in lower concentrations than the other trace elements.

5 - 2 - 3 - 5 Trace element relationships in the garnet:

It appears to be that there is a positive correlation between the following pairs of the trace elements: Nb and Cr, Y and V, Sc and V, Nb and Zr, Sc and Y (Fig. 17 A to F). Other combinations of these trace elements do not show any correlation.

5-2-3-6 Relationships between the trace elements and the major elements in the garnet:

The trace element behaviour seems to be different in the spessartite - and almandine - rich garnets, when correlated with the major elements (Fig. 18 A to E, and Fig. 19A to C). In these figures samples 7 and 21 are almandine and the others are spessartite-almandine garnets.

Yttrium values are high in the spessartite garnet, because of the great similarity between the ionic size of yttrium and manganese. Yttrium can replace manganese and occupy the manganese position in the garnet structure Jaffe (1951). Although there is a strong theoretical correlation between these two elements in spessartite (Goldschmidt, 1945), no correlation has been found between yttrium and manganese, nor with iron and yttrium, in garnets from the Gairloch area. However, yttrium

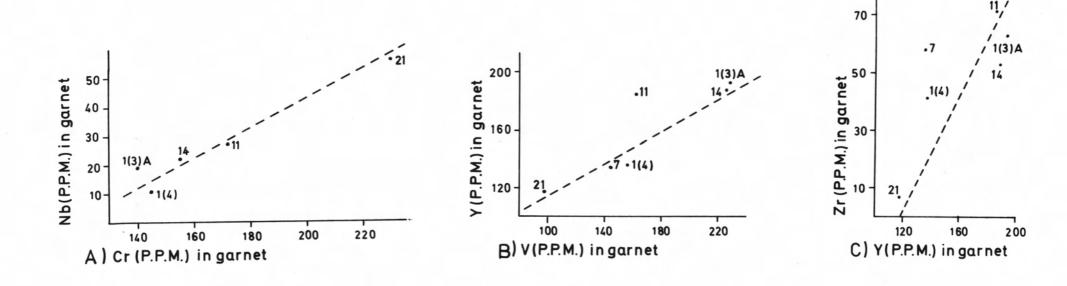


Fig. No. 17 Relationship between the trace elements in garnet. Positive Correlation.

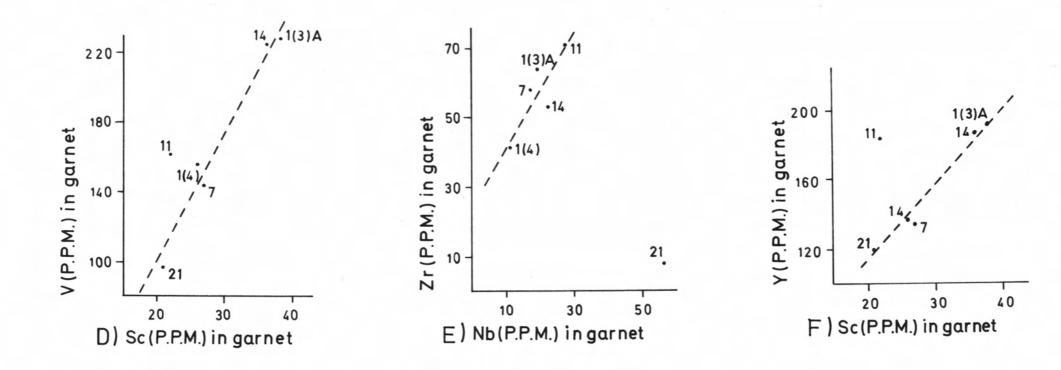


Fig. No.17 cont. Relationship between the trace elements in garnet. Positive Correlation.

has a good positive correlation with combined iron and manganese (Fig. No. 19 A). Scandium is a common trace element in the magnesium rich garnet, pyrope, and substitutes for either magnesium or ferrous iron in the garnet. Because the garnet from Gairloch area is poor in magnesium, scandium may substitute for iron and manganese as shown in Fig. No. 18 C and D. To summarise the following correlations between the major and the trace elements is as follows:-

(1) Positive correlation:

There appears to be a positive correlation between Cr and Fe, V and Mn, and Sc and Mn (Fig. No. 18 A, B and C respectively).

(2) Negative correlation:

There is a negative correlation between the following trace elements and major elements: Sc and Fe, V and Fe, and Al and V (Fig. No. 18 D, E and F respectively).

(3) No correlations have been found between the other trace and major elements. Neither Fe²⁺ nor Mn²⁺ has any correlation with Zr, Nb or Y. However the combination of Fe²⁺+ Mn²⁺ in the garnet gives a good positive correlation with those trace elements (Fig. No. 19 A, B and C).

5 - 2 - 4 X-ray diffraction data for garnets from the Gairloch Iron Formation:

Seven X-ray diffraction patterns for the garnets have been determined (table No. 12). From these patterns the unit cell dimensions have been calculated using the equation: $a = d\sqrt{h^2 + k^2 + 1^2}$, in which (a) is the unit cell dimension, h,k and l Miller indices of each reflection, and (d) the interplanar spacing. The unit cell volume: $V = (a)^3$.

From the cell dimensions, the garnets are interpreted as almandine-spessartite because the values of the unit cell all lie

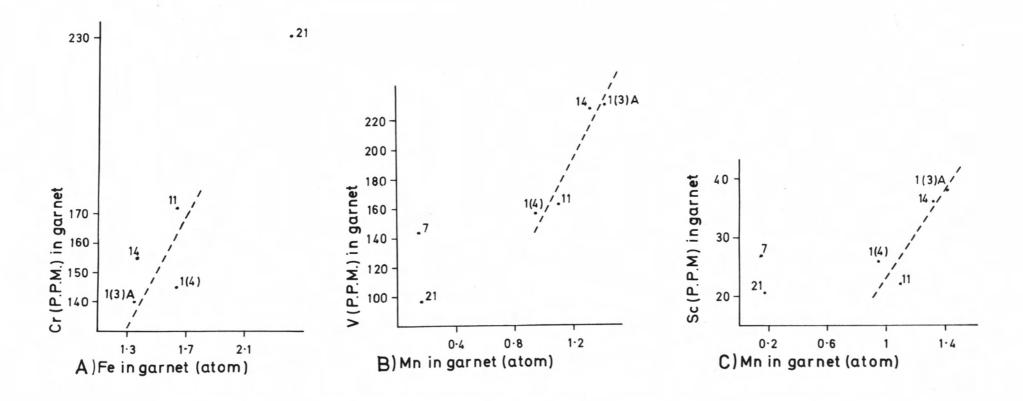
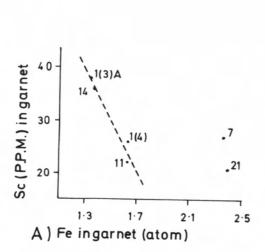
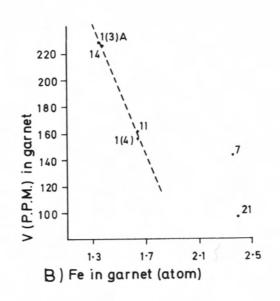


Fig. No. 18 Relationship between the trace and major elements in the garnet: Positive Correlations.





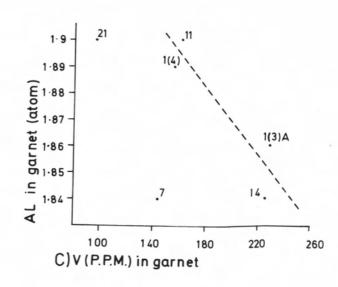
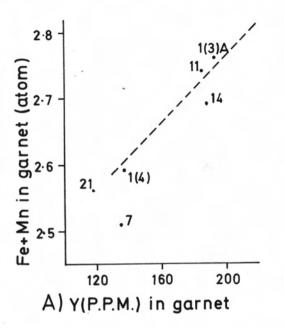
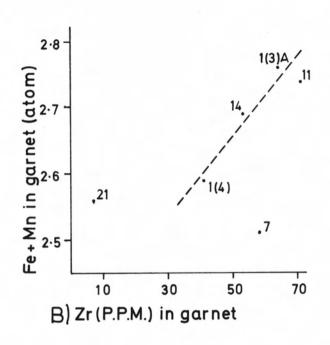


Fig. No.18cont Relationship between the trace and major elements in the garnet: Negative Correlations.





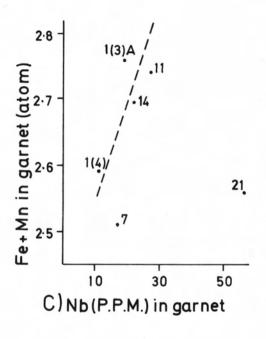


Fig. No.19 Relationship between the trace elements and

Fe+Mn in garnet.

between those for the spessartite unit cell and those for the almandine unit cell, so from the unit-cell dimension of the garnet we can estimate the type of the garnet by comparison with the diagrams produced by Winchell (1958).

<u>5-2-5</u> Relationship between density and the unit cell dimension of garnets from the Gairloch Iron Formation:

The density of the garnets was measured directly by using a pycnometer and indirectly from a combination of the unit cell dimension obtained from the X-ray diffraction data and the chemical composition of the garnet (see section 5 - 1 - 6 for grunerite density). The density and unit cell dimension of garnet are shown in table 14. The density has been plotted against the unit cell dimension (Fig. 21), and it appears to show a negative correlation which indicates that the more almandine rich the garnet the smaller the unit cell edge Dahl (1972).

5-2-6 Use of garnet as an indicator of the grade of metamorphism:

The variation of Mn²⁺ and Ca²⁺ contents in the garnet, (Tracy, 1976) particularly the Mn²⁺ have been used as a function for the determination of metamorphic grade. Miyashiro (1953) suggested that Mn²⁺ is preferentially incorporated into the garnet structure at low grade, because the X position of the garnet structure can accommodate eightfold co-ordinated ions, which requires a large ion like Mn²⁺ and Ca²⁺ to give stability to the garnet structure, while a small ion like Mg²⁺ has only six-fold co-ordination. Also the interatomic distance between the magnesium and the oxygen is large, which may give a low stability to the garnet structure under low temperature and pressure conditions (Miyashiro, 1953). At a higher metamorphic grade, the structure of the garnet preferentially incorporates Mg²⁺ and Fe²⁺. Hence, an increase in the metamorphic grade will be accompanied by a decrease in the Mn²⁺ content in the

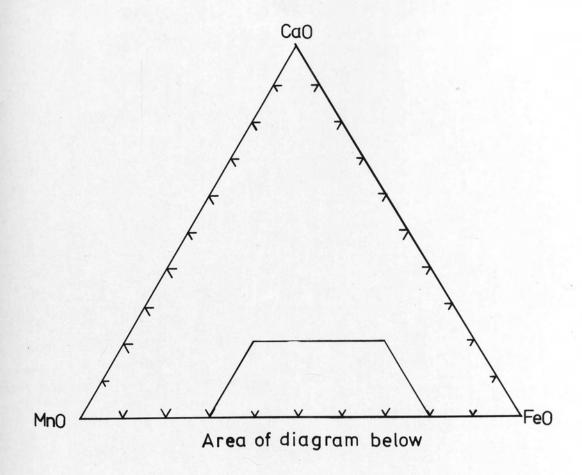
garnet. Hart and Henley (1966) examined garnets from the Caledonides of Scotland and Norway; they found that in garnet, Mn²⁺ and Ca²⁺ increase toward the core, and Mg²⁺ and Fe²⁺ are higher at the rim of the crystals. This may be due to the growth of the garnet during prograde metamorphism. Grant and Weibin (1971) found that the garnet in the gneisses from the Minnesota River valley is the reverse of the case given by Hart and Henley (1966). They found that Mn²⁺ and Ca²⁺ increase toward the rim, and Fe²⁺ and Mg²⁺ increase toward the core. This phenomenon they attributed to a retrogressive effect on the initially homogeneous garnet. Garnet analyses from the Iron Formation of Broken Hill Australia (Stanton and Williams, 1978) remain the same composition within individual beds but they found differences in composition between different beds even those found within centimeters of each other.

The grade of metamorphism in the Gairloch area is in the lower amphibolite facies, and variation of the composition of the garnet is not ascribed to change in the grade of metamorphism, but is interpreted as being related to the various compositions of the parental rocks.

5 - 2 - 7 Chemical zoning in garnets:

Both core and rim compositions have been determined on three specimens (Sample Nos. 11, 14 and 17) to detect any chemical variation in major element concentration. (Table No. 11).

The molecular compositions of Fe^{2+} , Mn^{2+} and Ca^{2+} of the core and rim of the analysed garnet crystals are recalculated to 100%, and plotted on a triangular diagram (Fig. 20) and show that the amount of Fe^{2+} increases toward the rim of the crystals up to a maximum value of 11%, and also Ca^{2+} increases toward the rim of the crystal. In contrast the Mn^{2+} is concentrated in the core of the garnets (maximum value 12% Mn^{2+}). The concentration of Mg^{2+} in the garnet is so low, that any systematic relationship involving Mg^{2+} is obscured.



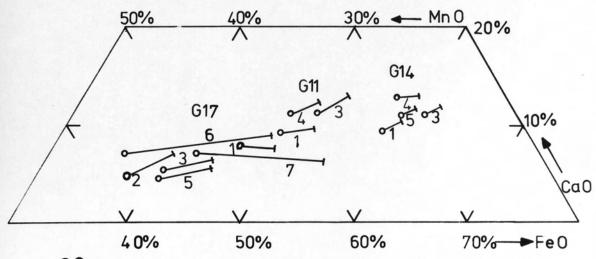


Fig. No. 20 Core & rim molecular composition of garnets.

o. Core of the crystal .

I. Rim " " "

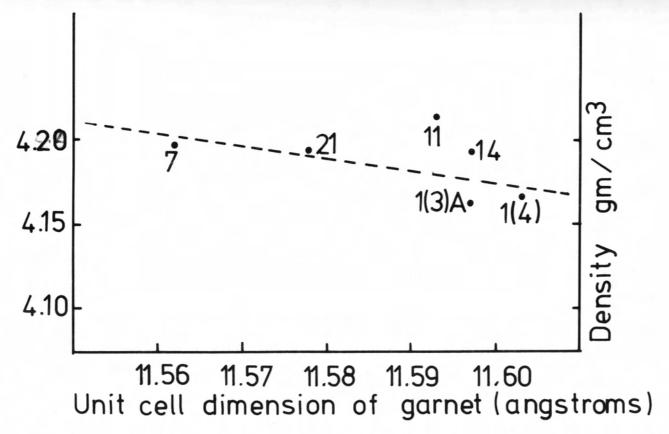


Fig. No. 21 Relationship between the unit cell and density of the garnet

Atherton & Edmunds (1966), Banno (1965), Brown (1969) and Leake (1967) generally suggested cation substitution in the zoning of garnet is:

$$\operatorname{Mn}^{2+}$$
 + Ca^{2+} \longrightarrow Fe^{2+} + Mg^{2+} rim

which implies that Fe²⁺ and Mg²⁺ increase, and Mn²⁺ and Ca²⁺ decrease toward the rim of the garnet crystal. This type of zoning in garnets has been interpreted as reflecting an increase or decrease of metamorphic grade during the growth of the garnet crystals. Other factors such as original bulk rock chemistry may cause zoning without a change in metamorphic grade. An additional factor may cause the zoning, when another mineral is involved in the production of the mineral assemblage within the rock (Harte and Henley 1966). This may be exemplified by the presence of plagioclase and other calcium bearing minerals such as calcite, hornblende and clinozoisite.

The magnesium values (table No. 11) are very low and there appears to be little difference between core and rim compositions, therefore in these garnets from Gairloch the cation substitution is:

$$\operatorname{Mn}^{2+}$$
 \longrightarrow Fe^{2+} + Ca^{2+} core

From the petrographic study for those garnets in samples 11, 14 and 17 the garnet seems to be homogenous in samples 11 and 14, but in sample 17, most of the garnets show a sharp cloudy dusty core (plate No. 4) which could be due to a possible discontinuity in the growth of the garnet crystal. This may explain the big differences in the composition of the core and rim (see Fig. No. 20), in which the garnet crystal begins to grow first and for some reason this growth is stopped, then the garnet and grunerite start to grow together later. While in sample 14 the differences in the composition are very small, in sample 11 the differences in composition between the core and the rim of the crystal are considerable, but optically the crystals look

homogeneous. In fact it seems that two types of garnet occur, a garnet with no apparent discontinuity in growth Fediukova and Vejnar (1971) (in which the variation in composition is small), and garnet with an apparent discontinuity in growth (which shows a large variation in the composition).

5 - 3 Partition of elements between garnet and grunerite:

From the petrographic study (chapter 4), garnet and grunerite are often intergrown, therefore the main supply of cations from the parental rock will be shared between garnet and grunerite during the growth of these two minerals. Most of the manganese cations in the rocks appear to be preferentially incorporated into the garnet, because the (X) position of the garnet can accommodate a large ion which has an eight fold co-ordination number , like Mn^{2+} and Ca^{2+} . The (X) position in the grunerite structure can accommodate ions which enter 6 - 8 co-ordinated sites, but smaller cations such as Fe²⁺ are preferred, the smaller cations like Mg²⁺ appear to be incorporated preferentially into grunerite. whilst larger cations such as Mn²⁺ and Ca²⁺ are incorporated into the garnet structure. Ferrous iron is intermediate in ionic size between Mn²⁺ and Mg²⁺. so Fe²⁺ can be substituted with equal facility into both the garnet and grunerite structures . When the garnet started to grow first as in case of sample 17, most of the large ions like Ca^{2+} and Mn^{2+} enter the (X) position in the garnet structure, but the Mn^{2+} is preferred. When the grunerite began to grow later, simultaneously with later garnet growth , some of the Mn^{2+} enters the grunerite (X) or M(4) site which means that the Mn²⁺ will be partitioned between garnet and grunerite and consequently the Mn²⁺will decrease in the garnet. Because the calcium ion is too large to be accommodated in the grunerite structure to any extent, then calcium will increase continuously and enter the

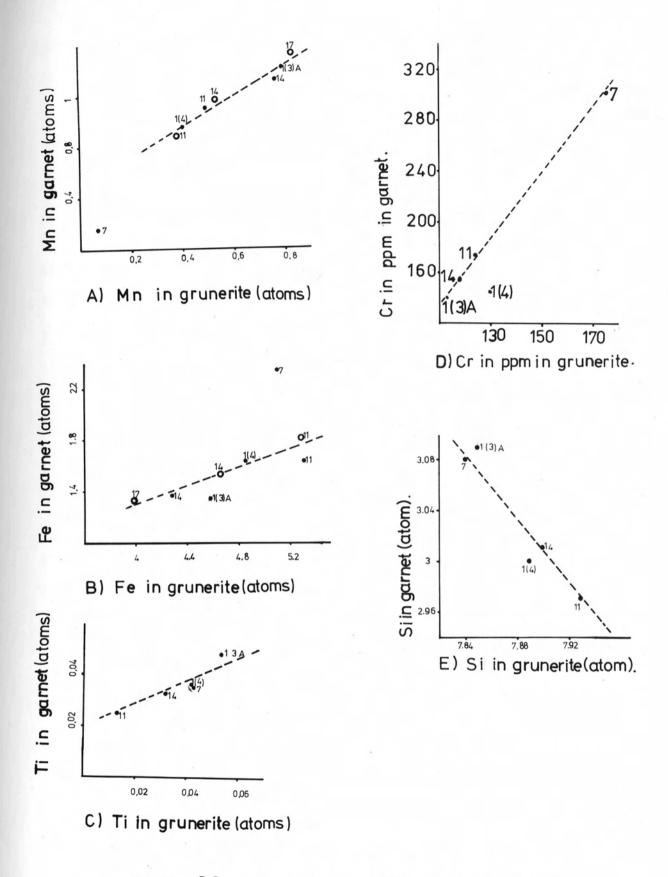


Fig.No. 22 Partition of Fe. Mn.Si.Ti & Cr between Co-existing garnet & grunerite.

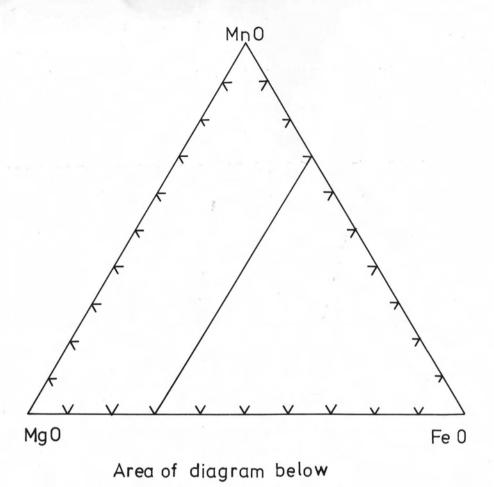
garnet. This is interpreted as explaining the behaviour of Ca²⁺ in the garnets, which increases toward the rim of the crystal.

Yoder and Keith (1951) have synthesized Mn²⁺ rich garnet at atmospheric pressure. Also Pabst (1938) has found an Mn²⁺ rich garnet which formed at low pressure, thus Mn²⁺ rich garnets can be stable under low pressure. The zoning in the garnet (spessartite) from the Gairloch area may therefore not be due to change in metamorphism grade but could be regarded as fractionation of Mn²⁺ into the early stages of growth of the garnet crystals.

5-3-1 Relationships between elements in the garnet and grunerite from the Gairloch Iron Formation:

The main major element constituents in the garnet and grunerite are Mn. Fe. Ca. Al and Si, and Fe, Mn, Mg and Si respectively. There is a positive correlation between the pairs for Ti, Mn, and Fe (Fig. No. 22A. B and C) and there is a negative correlation between pairs for Si (Fig. No. 22 D). Also there appears to be a positive correlation between the Cr partition between garnet and grunerite. The trace elements such as vanadium are concentrated into the garnet much more than the grunerite in fact up to 2 to 4 times more. In addition all the yttrium occurs in the garnet and very little in the co-existing grunerite. This may either be due to the large ionic size of the yttrium ion or the lack of a large ion like Ca in the amphibole. The other trace elements such as Sc, Zr and Cr are equally concentrated in both the garnet and grunerite. Barium, lead, rubidium and strontium occur slightly above the detection limit of the instrument and no preference is demonstrated for either mineral phase.

From the electron microprobe analyses, Mn, Mg and Fe for both the garnet (core and rim) and the grunerite have been recalculated to 100% and plotted on to a triangular diagram (fig. No. 23), and



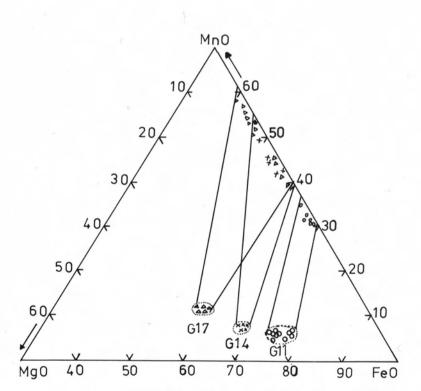


Fig.No.23 Fe,Mn &Mg molecular proportion in grunerite & garnet for each analysis from the microprobe.

it shows that there is only a small variation (up to $\frac{1}{7}$ 2%) in the grunerite composition, while the garnet shows a large variation (up to $\frac{1}{7}$ 10%) particularly in samples 14 and 17.

The mean analyses from the electron microprobe (table No. 5) of each garnet (core and rim together) and grunerite (dashed lines) are shown on figure 24. In addition the X-ray fluorescence analyses are present on the diagram for both garnet and grunerite pairs (solid lines). The mineral pairs analysed by the electron microprobe appear to exhibit equilibrium behaviour, because of the parallel lines (Crank, 1961), while the same pairs when analysed by the X-ray fluorescence show crossed die-lines. However the variation in the compositions are not too great, and this apparently may be due merely to the different methods of analysis.

The molecular ratios of Fe^{2+} and Mn^{2+} in the system Fe^{2+} $+ Mn^{2+}$ + Mg^{2+} (table No. 18) have a regular trend which may show equilibrium behaviour for Fe^{2+} and Mn^{2+} (Fig. No. 25 A and B). However the molecular ratio of the Mg^{2+} in the system does not apparently show equilibrium behaviour (Fig. No. 25C) which may be due to the ion concentration of magnesium in the garnets.

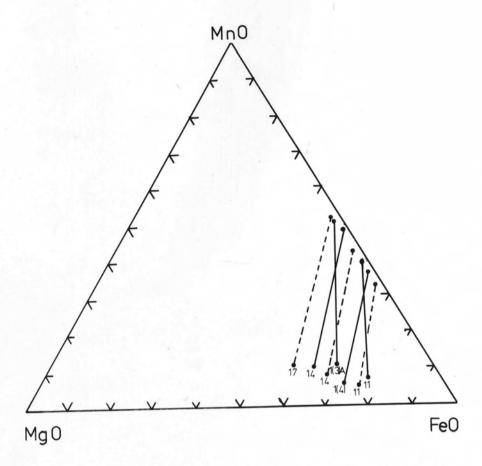
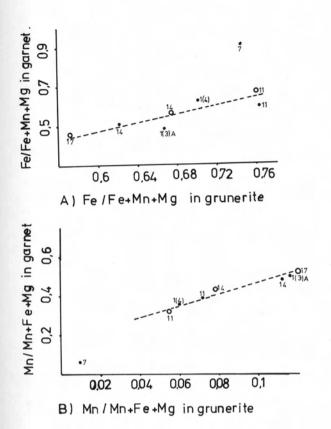
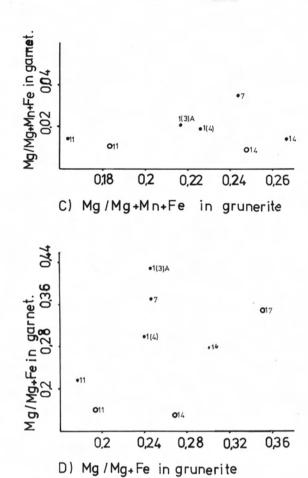


Fig. No. 24 Molecular proportions of Fe, Mg & Mn (recalculated to 100%) for the garnet-grunerite pairs.

Solid lines are from the X.R.F analyses.

Dashed lines are the mean of the microprobe analyses





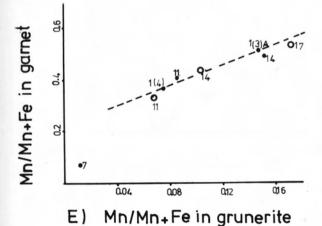


Fig. No.25 Partition of Fe. Mn & Mg between Co-existing garnet & grunerite.

- ·X.R.F analyses
- Electron microprobe analyses

5 - 4 Magnetite:

The mineral magnetite belongs to the spinel group. The magnetite series is one of the three series in this group. The origin of the name magnetite is vague, but it is thought to be derived either from the locality Magnesia or from the name of shepherd Magnes who (in ancient times) discovered the magnetic stone.

5 - 4 - 1 General formula of magnetite:

The general formula of the magnetite series is X Y_2 O_4 , in which X is mainly Fe²⁺, but some other cations may occur as well, e.g. Mg, Mn, Zn, Ni and occasionally Ca. While the Y cation is chiefly Fe³⁺, some trivalant cations like Al, Cr, Mn³⁺ and V can also occur.

5 - 4 - 2 Chemistry and nomenclature of the magnetite:

The theoretical end member composition of magnetite is Fe_2O_3 68.97% and FeO 31.03 wt%, Deer, Howie and Zussman (1962). Some divalent cations like Mg, Zn, Ni, Mn, and Ca can occur in small amounts, replacing the divalent iron. Also a continuous replacement of Fe^{2+} by some of these cations can occur, to form magnesio-ferrite (Mg Fe_2^{3+} O_4). Ti can enter the structure of magnetite in considerable amounts to form ulvöspinel (Fe_2^{2+} Ti O_4), so a continuous relationship between the magnetite and the ulvöspinel can occur. The trivalent iron (Fe_2^{3+}) can also be replaced by Cr and V up to the level of a few percent.

5 - 4 - 3 Chemistry of the magnetite from the B.I.F. from the Gairloch area:

Two samples have been analysed by X-ray fluorescence to determine both the major and the trace element compositions. Four X-ray diffraction patterns using the powder camera method, have been produced to determine the cell parameters of the magnetite crystals.

Unfortunately it was very difficult, if not impossible, to separate pure magnetite from the quartz and some silicate minerals (like grunerite and garnet), due to the high magnetic susceptibility of magnetite which occurred as inclusions in these minerals. Many attempts were made using both a hand magnet and heavy liquid.

5-4-3-1 Major elements chemistry:

Table No. 15A shows the major element concentrations in the magnetite. In sample No. 12, total iron is 76.1% in which Fe²⁺ is 32.17% and

Fe³⁺ is 43.93%. The other oxides

(TiO₂, Al₂O₃, MnO, MgO, CaO, Na₂O, K₂O and P₂O₅) only form 1.5% of the total, and SiO₂ 21.62%. In sample No. 5, total iron is 83.95% in which Fe²⁺ is 36.76% and Fe³⁺ is 47.19%. The other oxides

(TiO₂, Al₂O₃, MnO, MgO, CaO, Na₂O and P₂O₅) represent 2.65%, and SiO₂ 12.28%. Most of this high amount of mixed oxide is MnO, MgO and CaO, which may be due to some contamination by garnet and grunerite of the magnetite which was not separated during preparation of the sample.

5 - 4 - 3 - 2 Trace element chemistry:

It may be noted that the concentration of trace elements (Table No. 14B) in both analysed samples are very similar. However it does not show, as expected, a high concentration of Cr, Ni or V. Most of the trace element concentrations in the magnetite lie slightly above the instrumental detection limit. Cr and Ni concentrations lie below those of the blank cellulose disc. Thus it looks as if the magnetite is free of the trace elements which were analysed for.

5 - 4 - 4 X-ray diffraction patterns of the magnetite:

Four X-ray diffraction patterns of magnetite (table No. 16) have been determined using the powder camera method. Table No. 16 shows the possible observed (hkl) reflections for magnetite from which the unit cell dimensions have been calculated. These show that samples No. 5, 6A and 12 have the same unit cell edge which is 8.388 A°, 8.389 A° and 8.387 A° respectively which give an average of 8.388 A°, while sample No. 4 shows a smaller unit cell, which is 8.351 A°. The reason for this result is obscure.

CHAPTER SIX

GEOCHEMISTRY

Geochemistry

6 - 1 Type of rocks:

Three different type of rocks from the Gairloch area have been collected and studied. These divisions depend on the mineralogical constituents of the rocks (table No. 17). These are

- (1) Silicate facies rocks from the Iron Formation in the Gairloch area. The main mineralogical constituents are garnet and grunerite. Sometimes quartz and magnetite are associated but in small amounts.
- (2) Oxide bearing rocks from the Iron Formation in the Gairloch area. The main mineralogical constituents are quartz and magnetite. Grunerite is always associated in these rocks but in small amounts. Garnet sometimes occurs as a very minor phase.
- (3) Metasedimentary rocks which have been collected from the neighbouring rocks to the Iron Formation. These are hornblende schists, biotite-muscovite schists, quartzites, and graphite schists.

6 - 2 Distribution of the major elements in the rocks:

Twenty eight samples from the Iron Formation and the associated metasedimentary rocks in the Gairloch area have been analysed by X-ray fluorescence techniques for both major elements (table No. 19 and 20) and trace elements (table No. 21 and 22). Wet chemical methods were used to determine ferrous iron, carbon dioxide and water.

The major elements vary in concentration from one rock to the other depending on the kind of rock. These elements are:

6 - 2 - 1 SiO2: SiO2 forms the main constituent of the rocks, with the concentration varying from 46.21 to 64.08% in the silicate facies rocks. This silica occurs dominantly in the silicate minerals and sometimes as quartz. In the oxide facies rocks it varies from 42.45% to 64.1%. This SiO, occurs dominantly as quartz and in the silicate minerals. In the metasediment, SiO, varies from 49.36% to 93.65% and occurs in both the quartz and silicate minerals. 6 - 2 - 2 TiO2: The TiO2 varies in concentration in different types of rock. It varies from 0.25% to 0.79% in the silicate facies rocks, with the exception of sample 17A which contains 1.99% TiO2. In the oxide facies rocks there is a very low concentration (0.02% to 0.03%) of TiO2 except for samples 12M and 12G which contain 0.2% and 0.16% respectively. In the metasediments TiO2 increases from 0.42% to 1.59%, except for samples 2(2) and 15 which contain much smaller (0.02% and 0.01%) concentrations, both these rocks being quartzite. Most of the TiO, occurs in the metasediments in sphene. 6-2-3 Al₂0₃: The range of concentration of Al₂0₃ in the silicate facies rocks increases from 0.55% to 7.06% depending on the amount of garnet in the rocks, because it is the only phase which contains any appreciable aluminium. In the oxide facies rocks it varies from 0.15 to 0.3% except for sample 12G, which contains 3.38% Al₂O₃, due to the high content of garnet in the sample. Al203 occurs in the silicate minerals in these rocks. In the metasediments, the level of Al₂O₃ content is much higher (12.07% to 18.43%), except for samples 2(2) and 15, which contain only 0.22% in the former and has not been detected in the latter. The Al₂O₃ occurs in hornblende, chlorite,

muscovite, biotite, and garnet.

- 6-2-4 Iron oxides: The iron oxides represent one of the major constituents in the rocks. The average total iron oxide content of the sixteen samples from the Iron Formation in the Gairloch area is 28.33%, which is similar to the total iron content in the Biwabik Iron Formation (28.39%), and also close to the total iron content from the Itchen Iron Formation of the Canadian Shield (26.7%).
 - A) FeO: The iron in the silicate facies rocks is concentrated in the garnet and grunerite and occurs only as ferrous iron. This varies from 19.35 to 31.35%, except for two samples (16 and 21), which contain both ferric and ferrous iron because they contain magnetite. In the oxide facies rocks ferrous iron varies from 14.59 to 27.64%. In the metasediments the ferrous iron varies from 0.87 to 12.70%. This iron is concentrated in magnetite and silicate minerals such as hornblende, chlorite and biotite.
 - B) Fe₂O₃: Ferric iron is concentrated in the oxide facies rocks in magnetite, and varies from 14.89% to 29.91% except for sample No. 12G which contains only 3.43% Fe₂O₃ due to the low content of magnetite. Fe₂O₃ also occurs in the metasediments but in small amounts (O to 2.78%), and mostly in magnetite. It is uncertain how much of the ferric iron in these rocks is original, because of oxidation-reduction reactions taking place during metamorphism.
- 6-2-5 MmO: The MmO occurs in the silicate facies rocks in high concentrations, which represents one of the major constituents of these rocks. It varies from 4.06% to 13.28% except for samples (7 and 21) which contain 0.68% and 0.81% MmO respectively. Most of

the manganese is concentrated in the garnet and this may explain the low values obtained for the manganese in samples 7 and 21 as they contain only small amounts of garnet. In the oxide facies rocks, MnO occurs in low concentrations (0.6 - 1.08%) compared to the rocks of the silicate facies, except for sample 12G which contains an appreciable concentration (4.07% MnO), this is due to the occurrence of garnet in that sample. Most of the manganese in these rocks is concentrated in silicate minerals like garnet and grunerite. The MnO in the metasediments, on the other hand, is present in very small amounts with a range from 0.02% to 0.6% and even the higher value can be correlated with the presence of garnet. 6-2-6 CaO: The calcium in both the oxide and silicate facies rocks is present in only small quantities, which vary from 0.15 to 1.7% in the silicate facies rocks and from 0.32 to 1.5% in the oxide facies rocks. The calcium in the silicate facies rocks is concentrated in the mineral garnet because it is the only mineral present which can accommodate calcium in its structure in these rocks. In the oxide facies rocks there is a small amount of CaO which occurs either in the silicate minerals or as a carbonate phase. In sample 12(G)B which contains a considerable amount of CaO (3.79%) occurs in the garnet. In the metasediments CaO has a range of concentration from 0 to 10.06%, this calcium is present in either calcite or silicate minerals or both.

6-2-7 MgO: Magnesium also represents one of the major constituents of the silicate facies rocks in the Iron Formation, where it varies from 1.75% up to 8.33%. This magnesium is concentrated in grunerite, because the analyses do not show more than small amounts of magnesium in garnet (0.4% as an average). In the oxide facies rocks MgO varies from 0.05 to 0.98%, except sample 12G

which contains 3.38% MgO because of the presence of grunerite. There is a high level of MgO in the metasediments (1.28 to 7.68%) and again this is concentrated in the silicate minerals.

6 - 2 - 8 Na₂0: The concentration of alkalis in the Iron Formation rocks is very low and Na₂0 increases from below detection limit to a maximum of 0.1% in both the silicate and oxide facies rocks, this is probably due to a fresh water environment for the deposition of the original rocks. However the concentration of Na₂0 in the metasediments is much higher (0.56-3.08%), except the quartzites which contain very small amounts (0.1 - 0.2%). The sodium in the metasediments is concentrated in silicate minerals such as hornblende, muscovite and biotite.

6-2-9 Potassium: K₂O has not been detected in most of the Iron Formation rocks, only samples 1(4) and 12 M show even small amounts (0.04 and 0.01%). Potassium occurs in the metasediments and the level of concentration depends upon whether they are calc pelites (0.02-0.4%) or pelites (2.01-4.67%) in composition.

6-2-10 P_2O_5 : Phosphorus occurs in the silicate facies rocks in small amounts, varying from 0.02 to 0.35%, and in the oxide facies rocks it varies from 0.3 to 0.87%. From the petrographic study no phase has been found which would contain phosphorus in their structure (e.g. apatite). However phosphorus is thought to replace up to 4% SiO_2 in spessartite garnet (Manson and Berygen, 1941), but although the garnet in the silicate facies rocks are spessartites they contain smaller amounts of phosphorus (0.07 to 0.23%) than the rocks, so it is possible that some of this phosphorus in the silicate facies rocks enters the garnet structure. There is also a low concentration of P_2O_5 (0.02 - 0.29%) in the metasediments, and no phase has been found which would contain phosphorus.

6-2-11 H_20^+ : In the silicate facies rocks, water occurs in the grunerite, and therefore the water concentration (0.97 to 1.63%) will depend upon the proportion of this mineral in the rock. Again in the oxide facies rocks water content appears to depend upon amphibole content and H_20^+ varies from 0.39 to 1.14%. On the contrary, in the metasediments, water is found in chlorite, the micas and hornblende, and therefore the range of concentration is greater (0.33 to 3.58%).

6-2-12 Carbon dioxide: Carbon dioxide has been detected in the silicate facies rocks in very small amounts, increasing from 0.07 to 0.24% except for sample 16 in which the carbon dioxide reaches to 0.99%. In the oxide facies rocks carbon dioxide varies from 0.07 to 0.36% except for sample 12M and 12G in which the CO₂ occurs in relatively high concentrations (4.21% and 4.38% respectively). This is because of the presence of siderite in the samples. In the metasediments the carbon dioxide varies from 0.07 to 1.95% this variation probably depends on the amount of calcite in the sample.

6 - 3 Comparison between the major element constituents of the Iron Formation rocks in the Gairloch area and those in other Iron Formations:

a) Oxide facies rocks:

The average chemical composition of the oxide facies rocks from different Iron Formations are shown in table 23. All these rocks are characterized by low and similar contents of TiO₂, P₂O₅, Na₂O, K₂O, CaO, Al₂O₃ and MnO. SiO₂ has an average content of 45% in these rocks, most of it occurring as quartz (chert), and to a lesser extent in the associated silicate minerals. The main oxides which are widely variable in these rocks are: ferrous and ferric iron oxides,

magnesium, water and carbon dioxide. The CO₂ reflects the amount of carbonate in these rocks, and the H₂O⁺ reflects the amount of hydrous silicate phases. Magnesium occurs in considerable amounts and mainly reflects the amount of silicate minerals. The ferrous and ferric iron occur in variable amounts, which depend on the oxidation ratio which probably arises firstly from different grades of metamorphism being reached in different Iron Formations and the original oxidation state of iron prior to metamorphism.

The oxide facies rocks in the Gairloch area contain a small amount of CO₂, H₂O⁺ and MgO compared to the oxide facies rocks from other areas which is indicative of the mineralogy. Also the iron mineral in the oxide facies rocks of the Gairloch area is magnetite only with no trace of hematite, while the other oxide facies Iron Formation rocks contain both magnetite and hematite together.

b) Silicate facies rocks:

The chemical composition of the silicate facies rocks from different Iron Formations are shown in table 24. All these contain on average 50% silica, and about 27% ferrous iron (table 24). The rest of the oxides occur in variable amounts, depending on the mineralogical assemblage of the rocks. The differences between the silicate facies rocks from the Gairloch area and those of other Iron Formations are that, in the former there are only two mineral phases in all the samples, these are garnet (spessartite-almandine) and amphibole (grunerite and manganoan grunerite). There is sometimes another phase such as magnetite, but it only occurs occasionally and then in small amounts. The other Iron Formation areas often contain more than two minerals, and may occur at lower or higher grades of metamorphism. They contain minerals like greenalite, ferrohypersthene, almandine or other iron silicate minerals in addition to oxide minerals

like magnetite. Thus it is very difficult to make a direct comparison between these rocks and those from Gairloch, because of these factors.

In conclusion the silicate facies rocks from the Gairloch area are not similar to any other silicate facies rocks from different Iron Formations, but the oxide facies rocks of the Gairloch area are similar to the oxide facies rocks of the lower cherty division of the Biwabik Iron Formation (see table No. 22 G and H).

6 - 4 A.C.F. diagram for the metasediments, silicate and oxide facies rocks from the Gairloch area:

The A.C.F. diagram (Fig. No. 26) has been drawn for all the rocks from the Gairloch area. It shows that the silicate facies rocks lie close to the FeO+MgO+MnO corner, while the oxide facies rocks lie along the join between the Al₂O₃+Fe₂O₃ - (K₂O+Na₂O) and FeO+MgO+MnO. This is due to the presence of ferric iron in the magnetite. In the metasediments two groupings occur, those which are the hornblende schists, and the others which are biotite-muscovite schists. An overlap between the areas of the biotite-muscovite schist and the oxide facies rocks is due to the presence of a large amount of aluminium in the former and to the presence of a high amount of ferric iron in the latter. The A.C.F. diagram does not apply to the rocks from the Iron Formation because they contain a high concentration of points in one corner of the diagram.

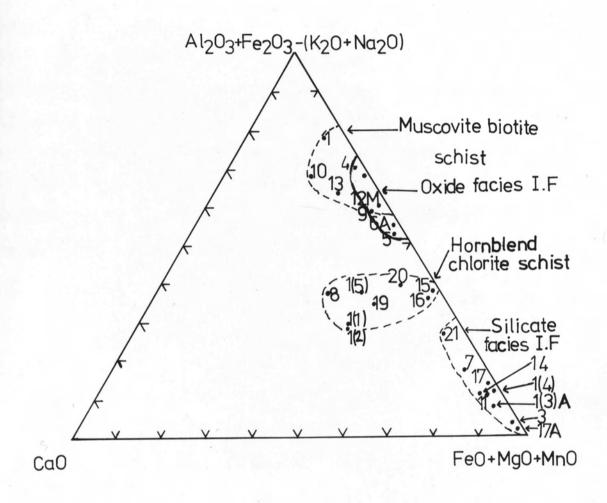


Fig. No. 26 ACF Diagram for the metasediments & the I.F rocks from Gairloch area.

6 - 5 Relationship between the major elements in the oxide and silicate facies rocks from the Gairloch Iron Formation:

A positive correlation occurs between the FeO and MnO (Fig. No. 27 A) and Al₂O₃ and SiO₂, in the silicate facies rocks (Fig.No.28). There is a negative correlation between the iron and magnesium in the oxide facies rocks (Fig.No. 27B), which reflects the same relationship between these two elements in the grunerite (Fig. No. 8B) where it occurs in these rocks. Grunerite is the only phase which carries the magnesium. There is a negative correlation between titanium and silica in the oxide facies rocks (Fig. No. 27C). The main source of the titanium in these rocks is garnet in which the amount of garnet reflects the level of titanium in the rocks. Magnetite and silica are the two main minerals in the oxide facies rocks and these minerals contain very low concentration of titanium.

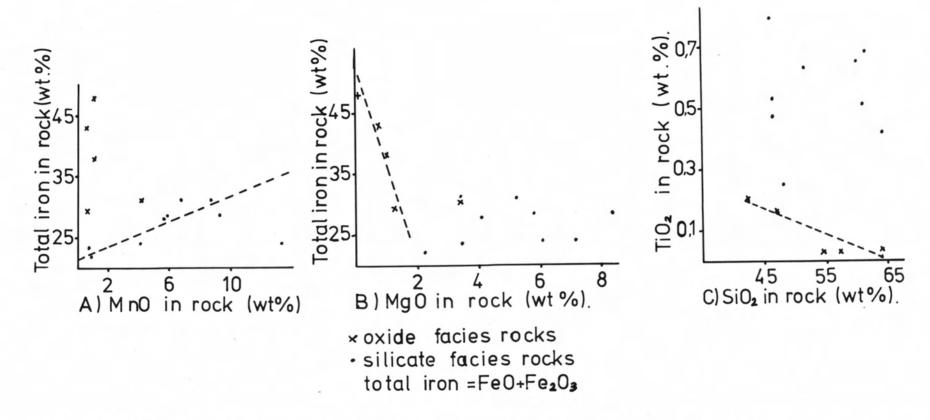


Fig.No.27 Relationships between the major elements in the silicate and oxide facies rocks from the Gairloch Iron Formation.

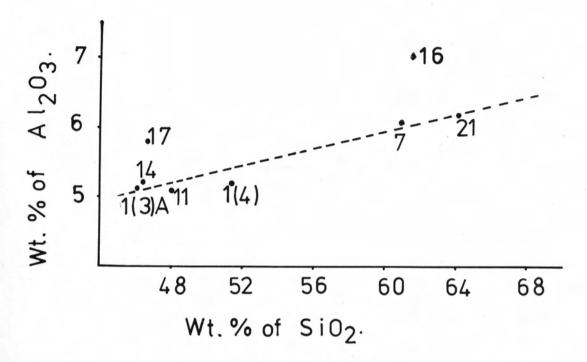


Fig. No. 28 Silica & aluminium in wt% in the silicate facies rocks of the bandediron formation.

6 - 6 Relationships between the major element distributions in the rocks and minerals:

On the one hand there is a positive relationship between the iron in the rocks and iron in the amphiboles (grunerite and manganoan grunerite) whilst on the other hand a negative correlation is found between the iron of the rock and the iron of the garnet (Fig. 29A) which indicates that the iron is preferentially incorporated in the grunerite rather than the garnet. Consequently a negative correlation has been found between iron in the rock and Mg in the amphibole. (Fig. 29 C). No relation with the Mg in the garnet has been found because there appears to be no Mg 2+ in the garnet. A positive correlation occurs between the MnO in the rock and manganese in the garnet (Fig. 29 D) while there is no correlation with the manganese in the amphibole which indicates that most of the MnO enters the garnet rather than the amphibole. Consequently the MnO in the garnet gives a negative correlation with the iron content of the rock (Fig. 29 B). These distributions can be explained by noting that manganese is very strongly partitioned into the garnet whereas iron appears to prefer the amphibole structure. Finally a positive correlation occurs between TiO, in the rock and TiO, in the garnet, while there is no such correlation between the rocks and the amphibole which again indicates that the TiO2 is partitioned into the garnet structure.

6 - 7 Trace element concentration in the rocks of the Gairloch area:

Eleven trace elements have been determined using X-ray fluorescence methods (table 21 and 22). Some of these trace elements belong to the transition element series and could be expected in the Iron Formation rocks when the behaviour of these elements are similar

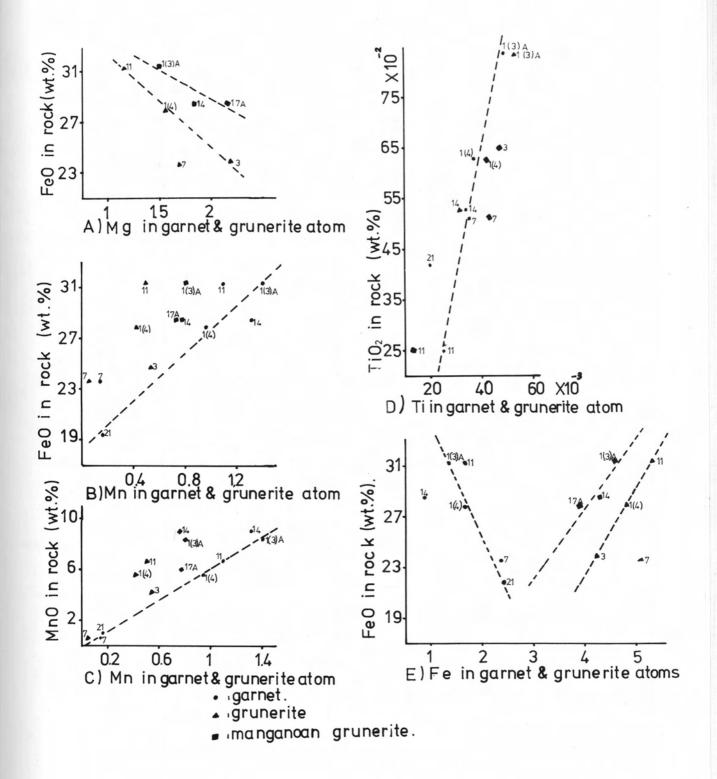


Fig.No.29 Relationships between the major element distribution in the rocks and minerals.

to iron. These elements are Sc. V. Cr and Ni (first transition series), and Y, Zr and Nb (second transition series). The other trace elements (Ba, Rb, Pb and Sr) do not belong to the transition series but may be expected in the metasediments associated with the Iron Formation. These trace elements vary in concentration as is summarized in table 25. In the silicate facies rocks, the main trace elements are Cr. Ni. V. Y and Zr which are partitioned between the garnet and grunerite. The Cr seems to be a little more concentrated in the garnet, whilst the Ni seems to be concentrated in the grunerite. The V appears to be strongly concentrated in the garnets, twice to four times more than in grunerite. All the Y in the rock is concentrated in the garnet because there is no Y in the grunerite, so the amount of the Y in the rocks reflects the concentration of garnet. Zr in the rocks is equally partitioned between the garnet and grunerite. The other trace elements in the silicate facies rocks occur in very small concentrations or below the detection limit of the instrument. In the oxide facies rocks all the trace elements occur in very small amounts, although some, like Cr, appear to be high in concentration. This is caused by the contamination of the X-ray tube target material. When this contamination is taken into account, the magnetite in these rocks has a very low concentration of chromium. In the metasediments, the trace elements having the highest concentration are Ba, Cr, Ni, Sr and V and Zr in which the Ba is thought to be concentrated in the mica minerals. Barium values are twice to twenty times higher in the biotite-muscovite schist than the hornblende schist. Cr, Ni, Sr, and V appear to have similar concentrations in both rock types. The Zr appears to be slightly more concentrated in the biotite-muscovite schist, than the hornblende The other trace elements have been detected but they are present in only small amounts.

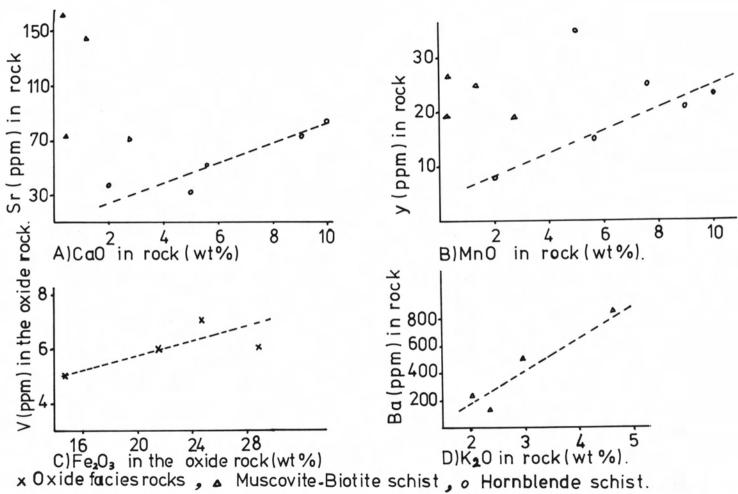
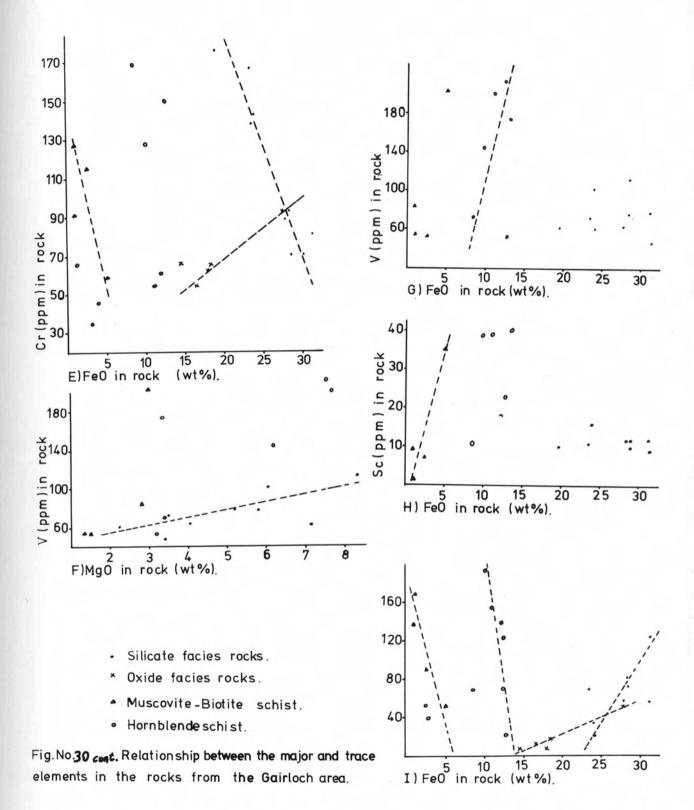


Fig. No. 30 Relationships between the major and trace elements in the rocks from the Gairloch area.



6 - 8 Comparison between the trace element concentrations in different Iron Formations:

There are a large number of chemical analyses available for major elements in Iron Formations, but analyses for trace elements in these rocks are relatively rare. Trace element concentrations from different Iron Formation rocks and minerals (magnetite and hematite) are shown in table 26. Among twelve trace element analyses from the Sokoman Iron Formation in Central Labrador, Cr and Sr have been determined and they occur in low concentration. Also, Ba, Ni and V have been determined in the oxide and silicate facies rocks from the Kursk Magnetic Anomaly Iron Formation by Plaksenko et. al. (1973), who found that these elements lie in the range between 28 and 110 p.p.m. Since there are not enough data for trace elements from the other Iron Formations it is difficult to make a comparison with the Gairloch Iron Formation. In general Cr. Ni, Sc and Y in the Gairloch Iron Formation seem more concentrated than in the other Iron Formations. However the concentration of Ba is higher in the Minais Gerais Iron Formation (Brazil). Also in the iron oxide minerals, V and Ni in the magnetite from the Gairloch area are lower than those which occur in the Grangesberg Iron Formation (Sweden) and the Minais Gerais Iron Formation (Brazil).

6 - 9 Relationships between the major and trace elements in the rocks from the Gairloch area:

The major element constituents of the rocks from the oxide facies rocks are ferric and ferrous iron, in the silicate facies rocks are ferrous iron, manganese and magnesium, and in the metasedimentary rocks are calcium, ferric and ferrous iron, magnesium, and the alkalies. Thus the main major element oxides in these rocks are FeO, Fe₂O₃,

MgO, MnO, CaO and K_2O which when correlated with the trace elements in the rocks appear to have positive and negative correlations as shown below:

a) Positive correlations

FeO	-	V	Hornblende schist	Fig.	30	A
FeO	-	Ni	Oxide facies rocks		11	В
FeO	-	Ni	Silicate facies rocks		11	В
FeO	-	Sc	Biotite-muscovite schist		11	C
FeO	-	Cr	Oxide facies rocks		11	D
Fe ₂ 03	-	ν	Oxide facies rocks		11	E
K20	-	Ba	Biotite-muscovite schist		11	F
MgO		V	Silicate facies rocks		tt	G
CaO	-	Sr	Hornblende schist		11	Н
Cao	-	Y	Hornblende schist		n	I

b) Negative correlations

FeO	-	Ni	Biotite-muscovite schist Fig.	. 30	В
FeO	-	Ni.	Hornblende schist	11	В
FeO	-	Cr	Biotite-muscovite schist	11	D
FeO	_	Cr	Silicate facies rocks	11	D

From the above mentioned relationships, it seems that iron is the most common element which can be replaced by V, Ni, Cr and Sc in the rocks (first transion element series), but although the behaviour of some trace element like Ni and Cr in the metasediment appears to show a negative correlation with the FeO, it has in fact no correlation because the range of the iron content in these rocks is low. In the oxide facies rocks the Cr, Ni and V increase with increasing iron content. Also the Sc and V in the biotite-muscovite schist and hornblende schist (respectively) show the same correlation. This is because all of these elements belong to the first transion

elements which can show a similar bahaviour. The MgO occur in the silicate facies rocks only in the grunerite. The increase of the MgO in the grunerite is accompanied by an increase in V which reflects the same correlation in the host rock. This is because of the similar ionic radius of these two elements. There is a positive correlation between K₂O and Ba, CaO and Sr in the metasediments, due to the similarity in the ionic radius of these elements. The Y in the silicate facies rocks occurs only in the garnet mineral occupying the same position as the Mn²⁺ ion, so the amount of Y will reflect the garnet concentration. In the hornblende schist Y and Ca are again strongly correlated. Yttrium may therefore substitute for the calcium in the hornblende.

CHAPTER SEVEN

DISCUSSION AND CONCLUSION

Discussion and Conclusions

The age of the Loch Maree Group (Gairloch) in which Banded Iron Formation facies is found is not clear because of the effect of strong deformation and metamorphism associated with the Laxfordian events. It appears, from the structural evidence in the Gairloch area, that the age is Pre-Inverian, however. The Iron Formation in the Gairloch area occurs in the Kerrysdale silicous schist as the silicate facies only, and in the Kerrysdale basite group as oxide facies or as mixed oxide - silicate rocks. Garnet and grunerite are the main mineral assemblages in the silicate facies rocks; these minerals appear to be growing together. These rocks have a granoblastic or porphyroblastic texture. Magnetite and quartz are the main mineralogical constituents in the oxide facies rocks; the rocks have a banded texture.

Generally, the main source for the iron and silica in the Iron Formation rocks is continental rocks which were rich in both iron and silica. By various weathering processes, iron and silica are transported to the basin of deposition (fresh-water lake deposits) where they are precipitated under suitable conditions of Eh - pH.

Manganese is associated with iron in the silicate facies rocks from the Gairloch Iron Formation. These elements tend to be separated in the sedimentary environment because they have different solubilities at any given pH (see section 3 - 6). Similarly, under a condition of fixed Eh, the iron will be precipitated as an oxide phase at a lower pH than the equivalent manganese oxide which could be the explanation

for the lower content of manganese in the oxide facies rocks. On the other hand, in a neutral to slightly reducing environment, the iron and manganese may precipitate together as a carbonate phase (Marchandise, 1956). Marchandise states that; "The solubilities of the iron and manganese carbonates are very similar and in addition their carbonates have overlapping stability fields. Under these conditions there is no reason at all for the two elements to separate. On the contrary there are good reasons why they should be intimately associated." It is not necessary, however, for the primary deposition to exist as a carbonate facies because, as Garrels (1960) states for the iron minerals; "All the facies (may) lie within a very narrow range of pH and Eh values". As a conclusion for the lack of separation between the iron and manganese, as Marchandise (1956), Garrels (1960), and Cloud (1965) have mentioned, in the Precambrian Iron Formation, iron and manganese could be precipitated due to the atmospheric conditions existing in the early Precambrian. At that time the atmosphere was enriched in carbon dioxide which could be reflected by precipitation under reducing conditions rather than under oxidizing conditions where these elements would have a tendency to separate.

The grunerite from the Gairloch Iron Formation occurs in the silicate and oxide facies rocks. It is of two types:

- 1) Grunerite;
- 2) Manganoan grunerite.

The iron content in the manganoan grunerite is less than that in the grunerite. This reflects the higher amount of other oxides (MgO and MnO) present in the former, and explains the two trends in the grunerite when correlation between these elements is made. A negative correlation occurs between iron and magnesium in the grunerite,

due to substitution between these elements.

The Mn^{2+} is probably present in the M(4) site of the amphibole because of its ionic size. The manganese replaces some of the ferrous iron in this site and magnesium concentration is similar for both the grunerite and manganoan grunerite, so the ferrous iron will be lower in the manganoan grunerite varieties. Magnesium is thought to prefer the M(2) site, while M(1) and M(2) have variable ratios of both Fe²⁺ and Mg^{2+} .

Trace elements in the grunerite vary in concentration but some occur in considerable amount (e.g. Cr, Nb, Ni, Sc, V and Zr).

Correlations occur between some of these trace elements because they belong to transition element series as illustrated in section 5 - 1 - 4 - 6. These trace elements, particularly Sc, V, Ni and Cr, might be expected in higher concentration than actually found in the grunerite because of the iron and manganese. Some elements like Cr and Ni show apparently high values due to some interference from X-ray tube target contamination. Because of the low contents of these trace elements on the one hand and the small number of samples on the other, any conclusions drawn from the limited data must be more or less tenuous.

Frost (1971) has calculated the stability of the iron end-member of the cummingtonite - grunerite series in the presence of sulphide and at oxygen partial pressures. He suggested that the grunerite is de-stabilized by the addition of sulphide. Popp, Gilbert and Craig (1977) demonstrated that the iron end-member of the cummingtonite - grunerite series is unstable in the presence of sulphide and also at elevated partial pressures of oxygen. These experiments may explain the small amount of grunerite (5%) in sample 16 from the Gairloch Iron Formation which contains the largest amount of sulphur (3.9%), present as pyrite. It is proposed that the reactions given by Popp et. al (1977)

could be applied to sample 16, namely:-

grunerite + 7/2 S₂ \longrightarrow 7 pyrite + 8 quartz + 7/2 O₂

3 grunerite + 7/2 0₂ 7 magnetite + 24 quartz + 6 water

The rock adjacent to sample 16 is a graphite schist which could be the source of the sulphide available during metamorphism.

The garnet from the Gairloch Iron Formation occurs both in the silicate and oxide facies rocks. They are of two types:

- 1) Almandine garnet;
- Spessartite-almandine garnet.

All the iron in the garnet is in the ferrous state and garnet is the main mineral which concentrates manganese in the silicate and oxide facies rocks. A negative correlation between calcium and manganese, indicates that substitution between these elements takes place.

The trace elements Cr, Nb, Sc, V, Y, and Zr occur in considerable amounts in the garnet. These trace elements show a positive correlation when combined as pairs, as illustrated in section 5-2-3-5. These correlations may arise because these elements belong to transition element series and they have similar properties. Yttrium values are very high in the garnet, replacing and occupying the Mn position, and show a positive correlation with the iron and manganese together.

The zoning in the garnet from the Gairloch Iron Formation reveals manganese rich cores and may be regarded as resulting from the fractionation of Mn²⁺ into the garnet during the early stages of growth of these crystals, rather than reflecting prograde metamorphic reactions.

The petrographic study of the Iron Formation rocks in the Gairloch area does not show any evidence for, or remnants of, the original mineral constituents of the rocks, unlike some other Iron Formations, which show a sequence of mineral assemblages from unmetamorphosed through low grade to high grades of metamorphism. Such sequences can help to formulate ideas about the formation of the minerals during

metamorphism. It is difficult to predict the original mineral assemblages of these rocks from the Iron Formation in the Gairloch area by looking at the minerals now found.

Several possible chemical reactions have been postulated for the occurrence of grunerite and garnet. These are:

- A) If the origin is by reaction of some silicate minerals and silica, the reaction could be of the form:
- B) If the origin is by reaction of silicate minerals together with iron oxide minerals and silica the reaction could be of the form:
 - greenalite + hematite + silica == grunerite + magnetite + water..5;
- C) If the origin is by reaction of silicate minerals, iron carbonate and silica, the reaction could be of the form:
- 6 siderite + greenalite + 12 silica 4 minnesotaite + 6 carbon dioxide..6

 This minnesotaite could react in the same manner as in equation No. 3 to form grunerite;
- D) If the origin is by reaction of carbonate mineral and silica in the presence of water, the reaction could be of the form:
 - 7 siderite + 8 silica + water grunerite + 7 carbon dioxide7.

These equations (1 - 7) have been postulated by Floran and Papike (1978), and could be reasonably applied to the Gairloch Iron Formation.

To form garnet in Iron Formation rocks it is necessary to have a source of aluminium. It is proposed that this source is the clay mineral kaolinite. When clay mineral such as kaolinite occurs in the parental rocks, on metamorphism garnet could form as in the proposed reaction:

 $\frac{1}{2}$ kaolinite + 4 greenalite = 3 grunerite + garnet + water

or:

½ kaolinite + 8 minnesotaite == 3 grunerite + garnet + water + 7 quartz.

The Iron Formation rocks are thought to have originally been precipitated in a fresh water environment. The clay mineral which can occur under such conditions is kaolinite. Evidence which has led to this conclusion comes from the analyses of silicate facies rocks from the Gairloch Iron Formation, which contain neither potassium nor sodium. These elements would be fixed originally in an illitic or smectitic clay mineral in sediments; these elements are essential components in these clay minerals. When this kaolinite mineral occurs in a considerable proportion together with the precurser hydrous iron silicate minerals, these react under suitable temperatures and pressures to form another aluminous phase, in this specific case, almandine or spessartite-almandine garnet.

The grade of metamorphism in the Gairloch area is the lower amphibolite facies, and it has been demonstrated from the analytical data that the Mn²⁺ and Ca²⁺ are preferentially incorporated into the garnet structure whilst the Fe²⁺ and Mg²⁺ enter the grunerite structure. Also it has been shown that all the Y is concentrated in the garnet mineral and the V and Cr occur in the garnet in greater proportions than in the grunerite, while the Zr, Nb, Sc, and Sr occur in both minerals but at lower levels of concentration. The amount of the iron in the oxide and silicate facies rocks from the Gairloch Iron Formation vary from 29.48 to 47.87% and from 21.87 to 31.35% respectively. This iron occurs only in the ferrous state in the silicate facies rocks, while it occurs in both ferric and ferrous states in the oxide facies rocks. The manganese is also concentrated in the silicate facies rocks, varying from 0.68 to 13.28%, and is concentrated in the garnet, so the silicate facies rocks of the Gairloch Iron Formation are manganiferous in their composition.

The trace elements in these silicate facies rocks reflect the

amount of the host mineral in each specific rock, but generally these elements are of low abundance. The main trace elements which occur are Cr, Ni, V, Zr, and Y. The relationship between these trace elements and the major elements seems to be dependant upon the iron content in the rocks.

The variation in the mineralogical constituents in metamorphosed Iron Formation rocks depends on the grade of metamorphism and the proportion and type of volatile material. The presence of water, sulphur and carbon dioxide is demonstrated by the occurrence of minerals such as grunerite, pyrite and siderite. In the Gairloch area the carbonate minerals in the Iron Formation rocks have not been found in any abundance except as inclusions in garnet crystals, and in the oxide facies rocks at sample locality G12. One part of this outcrop shows siderite associated with the quartz rich bands, while another part of the outcrop shows thin lamellae of small prismatic crystals of grunerite. This grunerite could have originated in a reaction between the silica and siderite caused by the presence of water. This reaction could have the form:

APPENDIX ONE

SAMPLE PREPARATION AND PURIFICATION

Appendix No. 1

(1) Sample preparation and purification for analysis:

All weathered and iron stained surfaces were removed from the specimens using a jaw splitter, after which the sample was crushed by a Sturtevant 2 x 5 inch jaw crusher and mixed well. By hand quartering, the sample was divided into four quarters, the opposite two were mixed together and quartered again until a quarter contained between 90 and 120 grams of sample. This aliquot was crushed in a Tema Disc Mill with a Widia (tungsten carbide) pot for 15 to 17 seconds, when approximately 15 grams was taken out for the determination of FeO. The rest of the sample was crushed for a further 15 to 25 seconds to produce a fine powder of 150 micron diameter. This sample was then mixed well for 30 to 40 minutes in a polythene mixing bottle on the Turbula Mixer/Shaker to make it more or less homogeneous. Finally 12 to 15 grams of the mixed powder was crushed again using a Glen Creston ball mill for 40 to 45 minutes in a tungsten carbide pot to make it very fine (5 μ diameter). This ball-milled sample was then put in the oven (105°C) overnight to dry. The powder sample was then ready for wet chemical analysis.

(2) Sample preparation for X-ray fluorescence analysis:

Twenty eight rock samples and fifteen mineral samples were prepared for X-ray fluorescence analysis of the major and trace elements. Major elements were determined on fused glass beads and trace elements on pressed powder pellets.

- a) The major element discs: One gram of the dried sample was ignited at 1000°C in an electric furnace for 30 minutes to determine the loss on ignition. Then 0.5 gram of the cooled ignited sample was mixed well with 2.5 gram of lithium metaborate flux and fused together. The liquid fusion was pressed into a mould to obtain a disc shaped glass bead. It had a copper wire rim to render it more robust. The disc bead was ready for analysis of the major elements.
- b) The trace element pellets: Six to seven grams of the dried sample was mixed with a few drops of a 2% solution of binding agent (usually organic matter). This mixture was then pressed in a die under 25 tons pressure for four minutes, to obtain a parallel-sided, disc-shaped pellet of the sample. The pellet was then dried in the oven (105°C) overnight to dry. The pellets were then ready for trace element analysis.

(3) Mineral separation:

About 120 grams of the crushed sample were taken from the jaw crusher and crushed again using the Tema Disc Mill for 5 to 6 seconds. This crushed sample was then sieved through nylon boulting cloths of various mesh size (60, 90, 120, 150 and 180) - British Standard mesh size. (The best size for separating the minerals in the rock was found to be between 90 and 120 mesh particle size, using the magnetic separator). The sample was washed well and dried in the oven (105°C). A hand magnet was used to separate the magnetite from the samples. A magnetic separator was used to separate the garnet and grunerite minerals. A binocular microscope was used to investigate the purity of the separated mineral samples. The heavy

liquids, Bromoform and Clerici's solution (Thallium malonate + Thallium formate), were used to purify the garnet of grunerite and vice versa for those grains which were not separated by use of the magnetic separator. Nine samples of the grunerite and eight samples of garnet were separated, but only seven of the grunerite and six of the garnet were analysed, due to the occurrence of a considerable amount of magnetite as inclusions in these minerals.

Two magnetite minerals were separated using ahand magnet and heavy liquids to separate the magnetite from the quartz and some silicate minerals, but unfortunately it was very difficult, if not impossible, to separate pure magnetite, due to the high magnetic susceptibility of the magnetite which occurred as inclusions in these minerals.

Other minerals from the associated metasedimentary rocks were separated, like chlorite, biotite, hornblende and garnet, but no analyses have been made on these separated minerals.

(4) Sample preparation for X-ray diffraction:

All the separated minerals were crushed to a very fine grain size using an agate hand mortar. Quartz was mixed with the grunerite and magnetite, and potassium bromate (KBrO3) was mixed with the garnet as an internal standard. The smear method on a glass slide was used for the garnet, while the powder camera (114.6mm diameter) method was used for the magnetite. The grunerite, with the quartz as internal standard and a small amount of cellulose were mixed and dissolved in acetone, after which it was smeared onto the glass slide using a spray gun to prevent the orientation of the grunerite crystals Bloss (1967).

(5) Spikes:

- 1) Fifteen spiking mixtures with a magnetite matrix were prepared to investigate the trace element distribution in magnetite minerals and the oxide facies rocks.
- 2) Fifteen spiking mixtures with a garnet matrix were made to investigate the trace element distribution in the garnet minerals.
- 3) Fifteen spiking mixtures having a rock matrix were made for investigating the trace element distribution in the silicate facies rocks.

The mixtures 1,2 and 3 were made up in three groups, each group containing certain specific elements and having five concentrations (table No. 27). These concentrations correspond to dilutions of 3:1, 1:1, 1:3 and 1:9 of the spiking concentration (top spike) and matrix.

- 4) Eight spike mixtures for iron (mixed with silica) of different concentrations were made, the values being: 10%, 15%, 25%, 40%, 50%, 60%, 70% and 80% Fe₂O₃.
- 5) Eight spike mixtures for manganese (mixed with silica) of different concentrations were made, the values being: 3%, 5%, 7%, 10%, 13%, 15%, 17% and 20% Mn₃O₄.

Spiking mixtures 4 and 5 were made because of the high concentration of iron and manganese in the rocks and minerals analysed.

(6) Wet chemical analysis:

1) Wet chemical analyses have been made for FeO, Fe₂O₃, CO₂ and $\rm H_2O^+$, on all the rock samples.

- 2) Wet chemical analyses have been made for seven rock samples containing high concentrations of MnO.
- 3) Complete major oxide wet chemical analyses for two samples have been made using the Atomic Absorption Spectrophotometer (Pyeu nicam SP 1900) for K_2O , Na_2O , M_gO and CaO; a (Pyeunicam SP 500) Spectrophotometer for TiO_2 , Fe (total), MnO and P_2O_5 ; and classical wet chemical methods for Al_2O_3 and SiO_2 .

All these analyses have been performed using the procedure detailed in Bennett and Reed (1971).

APPENDIX TWO

WORKING CONDITION FOR INSTRUMENTS

Appendix No. 2

(1) The working conditions for the X-ray diffractometer:

Monochromatic Cobalt-radiation (CoKel, $\lambda = 1.788965 A^{\circ}$) was used for the garnet. X-ray diffraction patterns for some garnets were produced between 32° to 74° 20 and for others between 32° to 57° 20. Each sample was run twice and the (hkl) reflections were obtained by comparison with the ASTM file.

Monochromatic Copper-radiation (CuK \propto 1, λ = 1.5405A°) was used for the determination of grunerite and garnet. The X-ray diffraction pattern was run for the grunerite between 9° to 60° 20 and between 19° to 60° 20 for the garnet. Each sample was run three times and the average taken. The (hkl) reflections were obtained by comparison with the ASTM file.

For both garnet and grunerite, the scan speed was $\frac{10}{2}$ /min. that is 2cm for 1^{0} 20, which gives a greater accuracy in measuring the 20 position.

For magnetite, the camera method was used for eight hours using monochromatic copper radiation. The working conditions of the instrument is shown table No. 28.

(2) Working conditions for the X-ray fluorescence spectrometer:

Analyses were made on a Phillips PW1212 automatic sequential X-ray fluorescence spectrometer operating procedure was similar to that outlined in Leake et al. 1968. The working conditions for the X-ray fluorescence spectrometer are summarized in table No. 29.

As Rb, Sr, Y and Zr were determined using a Mo target tube, the compton scatter peak Mok c was used to correct for matrix and mass absorption differences empirically (Reynolds 1963).

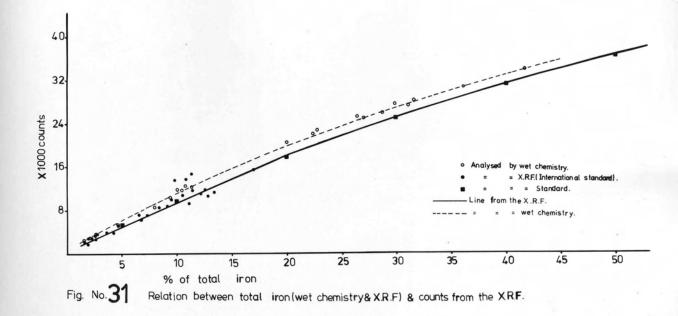
The detection limit for the instrument was taken to be equivalent to two standard deviations above mean background counts rate as in table No. 30, and the precision was taken as two standard deviations about the mean as summarized in table No. 31.

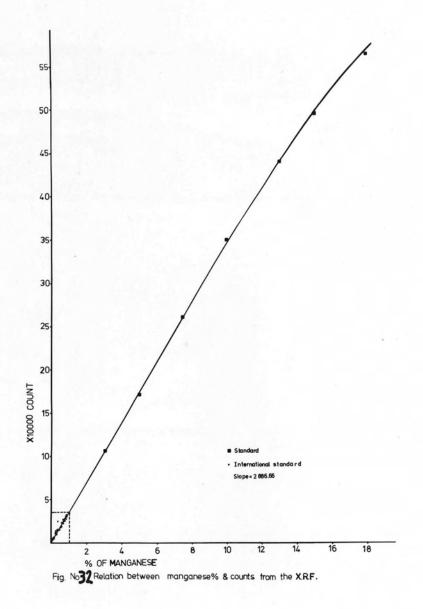
A dead time correction was made for the manganese and the iron determinations, and the right current used for the analyses.

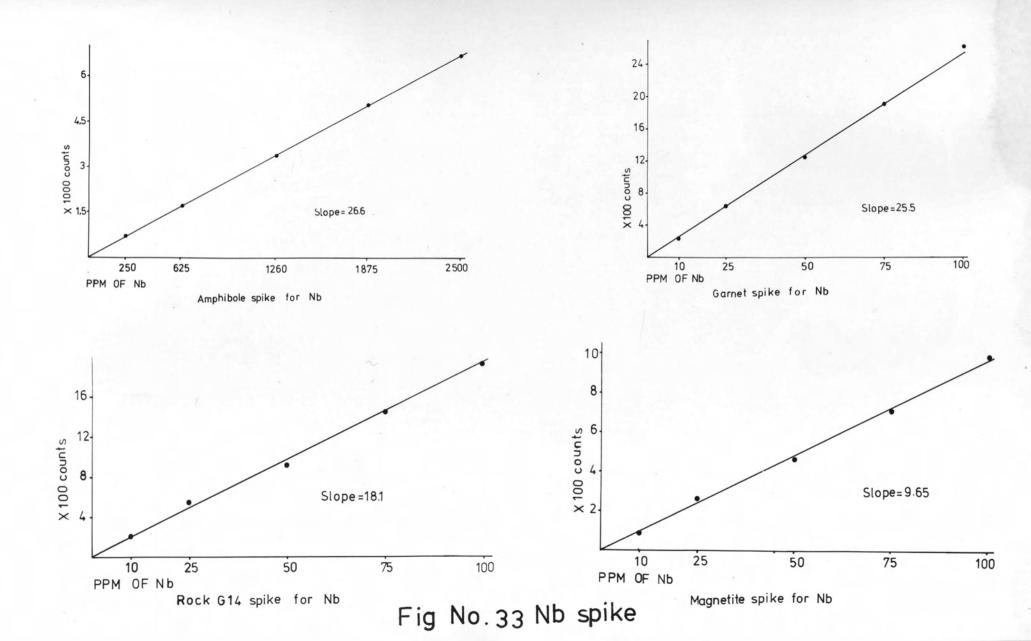
Also all the samples were analysed for iron by wet chemical methods. Fig. No. 31 shows the relation between the counts rate from the X-ray fluorescence and the concentration percentages of iron (for X-ray fluorescence and wet chemistry analyses). All the iron values in the minerals and the rocks are recalculated from the wet chemical analysis graph.

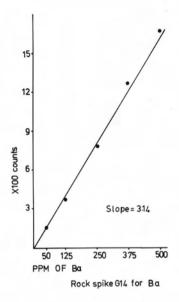
Also Fig. No. 32 shows the relation between the counts rates from the X-ray fluorescence and the concentration percentages of manganese in the samples.

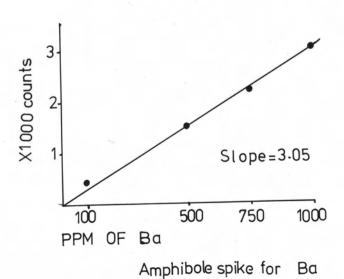
Figs. No. 33, 34, 35, 36, 37, 38 and 39 show the spike concentration in p.p.m. plotted against the counts rates from the X-ray fluorescence for Nb, Ba, Ni, Cr, Ph, Sc, and V respectively.

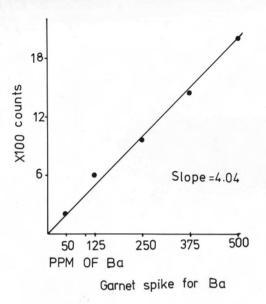












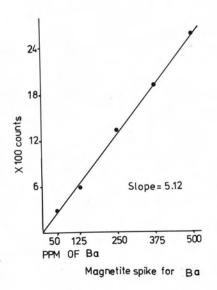
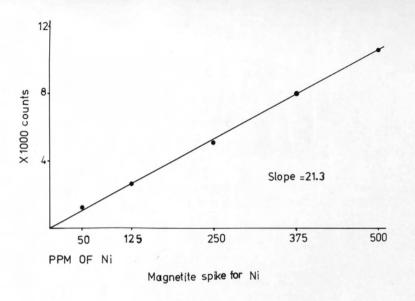
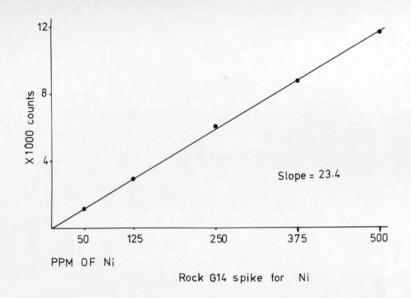
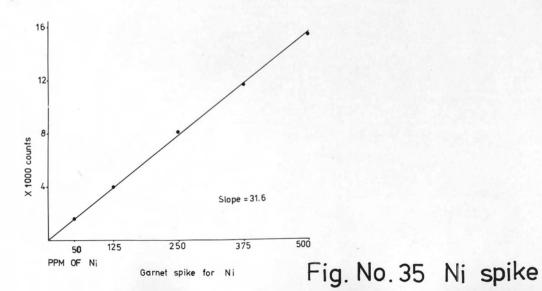
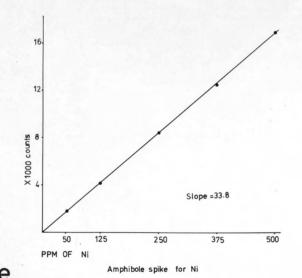


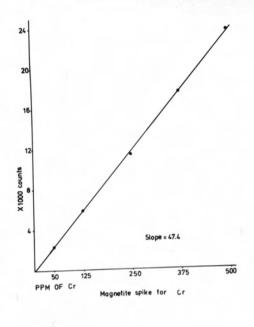
Fig.No 34 Ba spike

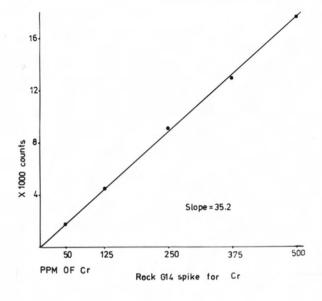


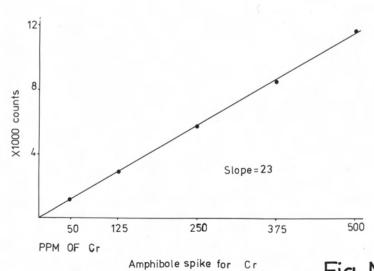


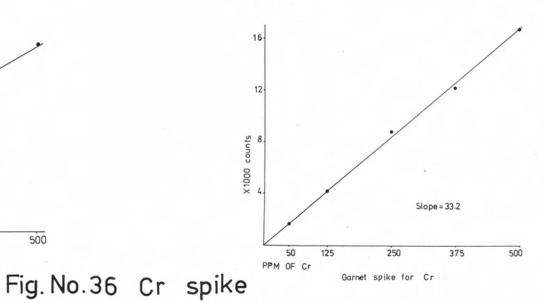


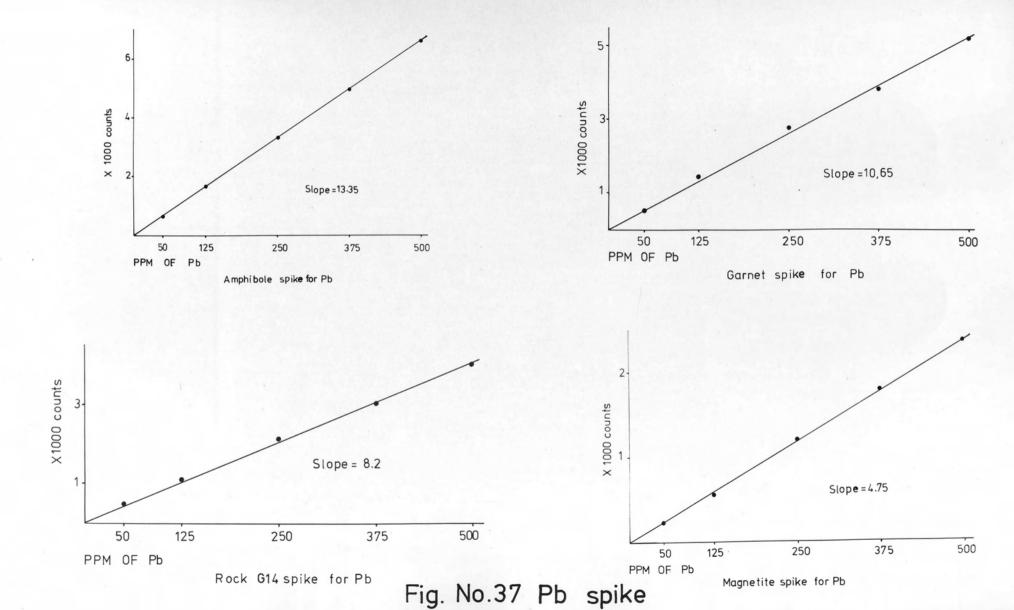


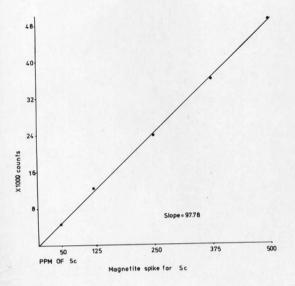


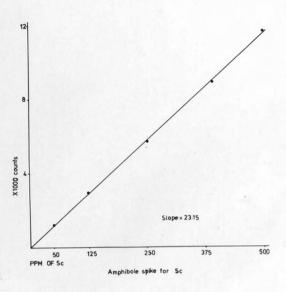


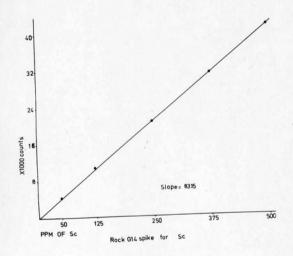












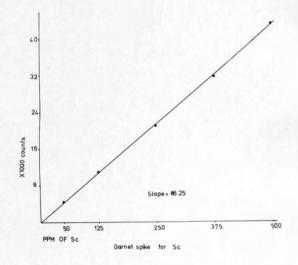
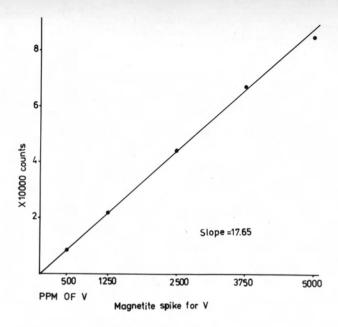
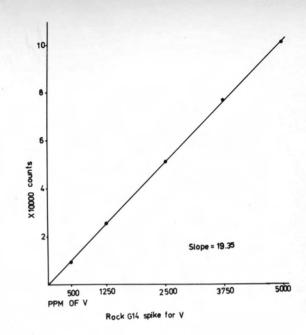
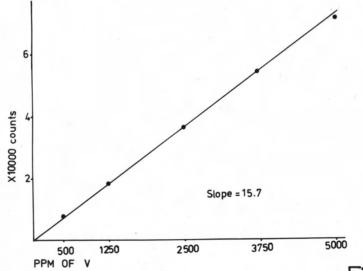


Fig. No.38 Sc spike







Garnet spike for V

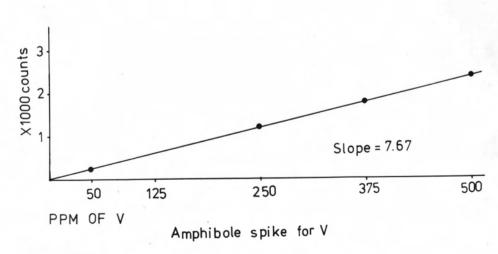


Fig. No. 39 V spike

APPENDIX THREE

RESULTS OF THE ANALYSES

Table No. 1

Summary of the history and structure of the Lewisian complex

Period	Events	Structural episode	Characteristic Structures	Metamorphic Facies			Date
	т.	PD1	Gneissose Banding	Amphibolite facies			2900 m.y
Scouria n	Pre-Inverian (Badcallian)	PD2	Steep NW-SE gneissose banding	or Granulite facies	Diorite dykes		2500 m .y
		PD3	NE-SW gneissose banding	with migmatisation	Loch Maree		
		ID1	NW-SE folding with foliation of variable dip	Almandine-amphibolite Facies	Group	F1	2200 m.y
	Inverian	ID2	Folds usually NW-SE without general foliation	Local migmatisation	,		
		S	COURIE DYKE INT	RUSION			
		LD1	First foliation in dykes	Almandine-amphibolite			1700 m.y
				Facies			1700 ш.у
Laxfordian		LD2	NW-SE folding in dykes, local foliation			F2	1500 m.y
Laxfordian		LD2		Facies Low amphibolite to		F2 F3	
Laxfordian Post-Laxfordian			dykes, local foliation Variable local folding without foliation	Low amphibolite to green-schist facies Retrogressive			1500 r

Approximate percentages of the minerals constituent in the rocks from the Gairloch area .

samples No.	1(1)	1(2)	1(3)A	1(3)B	1(4)	1(5)	2(1)	2(2)	3	4	5	6A	6B &C	7	8	9	10	11A	118	12M A	12M B	13	14	15	16	17	17A	19	20	21	12G
magnetite	45	< 5	< 5	8	_ 5	T	10	< 5	< 5	7	37	25	20	<5	<5	T	?	15	7	45	40	T	<5	T	т	8	9?	T	T	T	<5
quartz	25	25	<5	32	T	30	52	95	38	90	45	70	63	43	50	59	25	70	t	5/4	54	60	Т	84	49	T	T	40	39	40	10
grunerite			40	41	54				60		15	<5	15	30				15	50	T			51		<5	52	80			I	68
garnet			54	19	40						Т		<5	25					43				45		40	40	11	10	30.	30	15
hornblende	67	72				33				T					42									15				45			
chlorite	< 5	T			T	35				T		Т	Т	Т	т	T			т	T									< 5		
biotite						т						T			<5	16						20							27		T
muscovite							38									25	25					20									
calcite	T	т				Т				<5				T	T									T							T
siderite																					< 5										T
graphite																	49	T									?				
plagioclase		Т													<5													T	T		
sphene		T				T	T										Т														
zircon						T									т	T													T.		
zoisite																												<5			
pyrite										~															< 5						
hematite								T		~~	(5							T	T		T										

Table No.3 X-Ray Fluorescence analyses of Grunerites in Gairloch Iron Formation

Oxide %	1(3)A	1(4)	3	7	11	14	17A
SiO ₂	49.92	50.42	51.11	49.97	49.43	50.59	52.02
Tio2	0.45	0.36	0.40	0.36	0.11	0.27	0.67
Al ₂ O ₃ FeO MnO MgO CaO	0.70 34.80 6.00 6.34 0.33	0.81 37.11 3.10 6.61 0.36	0.30 32.58 4.11 9.43 0.20	0.82 38.98 0.47 7.13 0.60	0.30 39.60 3.66 4.77 0.42	0.40 32.90 5.82 7.91 0.42	0.20 30.40 5.95 9.30 0.15
Na ₂ O	0.03	0.04	0.05	0.05	0.05	0.04	0.03
K ₂ 0	-		_	-	-	-	-
H ² O,	•	•	•	•	•	•	i •
P ₂ 05	0.06	0 .1 0	0.11	0.16	0.06	0.17	0.02 *
Co2 L.O.I	-1. 05	-0.98	- 0.35	-0.32	-1.08	-0.58	-0.42
Total	98,63	98.91	98.29	98.54	98.40	98.52	98.74

Ions	1(3)A	1(4)	3	7	11	14	17A
Si	7.87	7.89	7.91	7.84	7.93	7.90	7.98
ĀĪ	0.13	0.11	0.06	0.15	0.06	0.08	0.02
A1		0.04		_	****	- [0.02
Ti	0.053	0.042	0.047	0.043	0.013	0.032	0.077
Fe	4.59	4.86	4.22	5.11	5.31	4.29	3.90
Mn	0.8	0.41	0.54	0.07	0.50	İ	0.78
Mg	1.49	1.54	2.17	1.67	1.14	1.84	2.13
Ca	0.06	0.06	0.03	0.10	0.07	0.06	0.03
Na	0.01	0.01	0.02	0.01	0.01	0.01	0.01
P	0.01	0.01	0.01	0.02	0.01	0.02	0.03
$\Sigma_{\rm R}^{2_{+}^{+}} {\rm R}^{3+}$	7	6.96	7.03	7.00	7.03	7.01	6.94

* less than 0.07% (Detection limit 0.07%) The range of water contents is from (1.45 to 1.92)%

⁻ Analysed but not detected

Table No. 4 i

Microprobe analyses of the Grunerites

G11

Oxide	1	2	3	4	5	6
SiO ₂	51.19	51.46	51.63	50.87	51.03	50.74
*FeO	40.39	39.46	40.26	40.10	41.40	41.24
MnO	3.1 6	2.89	2.93	2.95	2.86	2.81
MgO	5.60	6.05	5.87	5.68	4.91	5.00
Ca0		0.13				
Total	100.34	99•99	100.69	99.60	100.20	99•79

Ions	1	2	3	4	5	6
Si	7.992	8.024	8.015	8.001	8.016	8.004
Fe	5.274	5.146	5.227	5.275	5.439	5.441
Mn	0.418	0.382	0.386	0.393	0.381	0.376
Mg	1.326	1.405	1.359	1.333	1.150	1.177
Ca		0.022				
E R ²⁺	7.018	6.955	6.972	7.001	6.97	6.994

^{*} Total iron determined as FeO

TiO₂, Al₂O₃, Na₂O and K₂O were analysed but not detected.

Table No.4 cont. ii

Microprobe analyses of the Grunerites

Oxide	7	8	9	10	11
SiO ₂	51.33	50.87	51.14	51.83	51.32
*FeO	41.12	41.11	40.82	38.82	40.69
MnO	2.95	2.96	2.67	2.87	2.89
MgO	4.95	5.02	5.20	6.54	5•29
CaO		tino-tum	***	0.18	
Total	100.35	99.96	99.83	100.24	100.19

Ions	7	8	9	10	11
Si	8.036	8.009	8.033	8.028	8.030
Fe	5.384	5.412	5.362	5.029	5•324
Mn	0.392	0.394	0.356	0.377	0.384
Mg	1.155	1.178	1.219	1.511	1.235
Ca			**************************************	0.030	
Σ R ²⁺	6.931	6.984	6.937	6.947	6.943

^{*} Total iron determined as FeO

 ${\rm TiO}_2$, ${\rm Al}_2{\rm O}_3$, ${\rm Na}_2{\rm O}$ and ${\rm K}_2{\rm O}$ were analysed but not detected

Table No. 4 cont. iii

Microprobe analyses of the Grunerites

G14

Oxide	1	2	3	4
SiO ₂	51.23	51.52	51.34	51.55
*FeO	36.45	35.41	35.91	35.51
MnO	4.05	4.17	4.04	4.13
MgO	7.45	7.64	7.69	7.18
Ca0		0.18	0.17	
Total	99.18	98.92	99.15	98.37

Ions	1	2	3	4
Si	7•989	8.019	7.991	8.066
Fe	4.754	4.610	4.674	4.647
Mn	0.536	0.551	0.533	0.547
Mg	1.733	1.773	1.783	1.675
Ca		0.031	0.029	
∑R ²⁺	7.023	6.975	7.019	6.869

^{*} Total iron determined as FeO

TiO₂, Al₂O₃, Na₂O and K₂O were analysed but not detected.

Table No.4 cont. iv $\label{eq:microprobe} \mbox{ Microprobe analyses } \mbox{ of the Grunerites }$ $\mbox{ G17}$

0xide	1	2	3	4
si02	51.96	52.33	5 2 .76	6 2. 69
*Fe0	31. 40	31 。35	31.11	31.65
Mn0	6.52	6.65	6.43	6 .3 7
Mg0	9 . 0 2	9.27	9.78	9.41
Ca0	0.13	0.17		0.17
Total	99.03	99.77	100.08	100.29

Ions	1	2	3	4
Si	8.006	7.997	8.007	8.002
Fe	4.046	4.007	3. 948	4.020
Mn	0.851	0.861	0.827	0.819
Mg	2.071	2.112	2.213	2.131
Ca	0.022	0.028		0.027
\(\text{R}^{2+}	6.990	7.008	6.988	6.997

* Total iron determined as Fe0

TiO₂, Al₂O₃, Na₂O and K₂O were analysed but not detected

Table No.5

Mean chemical analyses of the Garnet and Grunerite by the electron microprobe.

Garnet

Grunerite

Oxide %	G11	G14	G17
SiO ₂	36.45	36.74	36.56
TiO ₂	_	_	-
Al ₂ 0 ₃ *Fe0	20.08 26.48	20 . 15 22 . 37	20.30 19.43
MnO	12.78	16.97	21.81
MgO CaO	0.22 3.96	0 .1 9 3 . 65	0.33\ 2.15
Total	99.97	100.07	100.58

Oxide %	G11	G14	G17
SiO ₂	51.20	51.41	52.49
TiO ₂	-	-	-
A1 ₂ 0 ₃		-	_
FeO MnO	40.47 2.90	35.82 4.09	31.32 6.46
MgO	5.49	7.41 0.08	9.45
0a 0		0.00	0.13
Total	100.06	98.81	99.85

Number of cations recalculated to the basis of 12 Oxygens

Number of cations recalculated to the basis of 23 Oxygens

Ions	G11	G14	G17
Si	2.997	3.01	2.993
Al	0.003	-	0.007
Al	1.942	1.95	1.953
Fe	1.821	1.534	1.331
Mn	0.889	1.178	1.513
Mg	0.029	0.024	0.048
Ca	0.351	0.321	0.189
∑ _R 2 _{+ R} 3+	3.09	3.06	3.08
A13+	1.94	1.95	1.95

İons	G11	G14	G17
Si Fe Mn Mg Ca	8.017 5.299 0.385 1.281	8.023 4.674 0.542 1.723 0.015	8.001 3.993 0.834 2.148 0.022
\(\sum_{\text{R}}^{2+} \text{R}^{3+}\)	6.97	6.95	7.00

 $^{\mathrm{Na}_{2}\mathrm{O}}$ + $^{\mathrm{K}_{2}\mathrm{O}}$ were analysed but not detected * Total iron determined as FeO

Table No. 6 i X-Ray diffraction patterns of the grunerite minerals between 9 - 60° 20Cuk \approx G1(3)A G1(4)

I(obs)	20Cuk≪	d(obs)	HKL		I(obs)	2θCuk⊶	d(obs)	HKL
6 0	9.70	9.11	020	9	15	9,66	9•15	020
100	10.65	8.30	110	rected of cops	100	10.65	8.30	110
50	19.00	4.668	2 00	Wacorrected d co	10	19.00	4.668	200
25	19.40	4.571	040	7 7	10	19.425	4.565	040
60	21.325	4.163	22 0		15	21.30	4.168	220
10	22.95	3.872	131		15	22。 90	3.88	131
20	25.72	3.462	131		15	25.74	3.459	131
90	27.20	3.27 6	24 0		25	27.266	3.268	240
100	28.98	3.078	060, 31	0	60	29.06	3.07 0	060, 310
25	29.725	3.0025	221		10	29.77	2.998	221
70	32,325	2.767	151		35	32.4	2.761	151
25	33.95	2.639	061	- [25	33 ,969	2.637	061
2 0	35.79	2.507	202		10	38,00	2.365	35 0
15	37.825	2.375	35 0		7	40.60	2.220	312
30	3 9.05	2.304	080, 35	ī	20	40,98	2.1995	261, 242
50	40.00	2.252	421		5	43.075	2.098	081, 202
30	40.98	2.200	261, 24	2	5	44.36	2.042	351
15	43.00	2.101	081, 20	2	7	46.45	1.9525	40 2
10	44.30	2.043	35 1		10	54.95	1.669	461
15	46.35	1.956	40 2		10	57.45	1.603	153
25	49,05	1.855	460		10	59,50	1.553	600
35	55.175	1.664	461		L	<u> </u>	<u> </u>	<u> </u>
15	57.56	1.600	153					
25	59.30	1.523	600					

Table No. 6 cont. ii X-Ray diffraction patterns of the Grunerite minerals between 9 - 60^{9} eCuk $^{\circ}$

I(obs)	20Cuk∝	d(obs)	HKL		(a)	I(obs)	20Cuk⊶	d(obs)	HKL
35	9.69	9.12	0 2 0		100 A	15	9,63	9.18	020
100	10.675	8.28	110	ı	Uncorrected	100	10.625	8,32	110
2 0	19.513	4.545	040		Unc	15	18.95	4.68	2 00
25	21.34	4.160	220		*	5	19.30	4.595	040
15	22. 99	3.862	131			15	21.275	4.172	220
10	25.715	3.462	131			10	22.875	3.884	131
65	27.362	3.257	2 40			10	25.65	3.47 0	131
100	29.11	3.065	060,	310		35	27.25	3.270	2 40
2 0	2 9.80	2 ,995	221			90	2 8•945	3.082	0 60, 31 0
60	32.5	2.753	151			10	29.73	3.002	221
25	34. 09	2.628	061			35	32.34	2 .7 66	151
20	35.775	2.508	202			25	33.945	2.639	061
20	37.985	2,366	35 0		'	15	35.75	2.510	202
10	39.233	2.294	080,	351		7	37.20	2.415	261
10	40.22	2.239	421			5	37.785	2.378	35 0
15	41.18	2.190	261,	$24\bar{2}$		7	39.14	2.299	080, 351
10	43.14	2.095	081,	202		5	40.10	2.246	421
20	44.3	2.043	35 1			15	40.98	2.200	261, 242
5	46.4	1.954	402			10	43.02	2.100	081, 202
5	47.5	1.912	422			10	44.22	2.046	351
5	49.333	1.8447	460			5	45.40	1.995	1 90 , 37 0
10	50,9	1.793	371			5	46.366	1.955	402
5	53.33	1.716	082			5	48.90	1.860	460
10	53.633	1.707	372			7	53.66	1.707	372
10	54.433	1.684	512			5	54.25	1.6895	512
30	55.00	1.668	461			20	55.1	1.666	461
10	59.35	1.556	600			10	55.9	1.642	1 11 0
I	-1					10	57.35	1.6055	153
						10	58.133	1.586	402,2 10 1
						7	59.20	1.559	600

Table No. 6 cont. iii X-Ray diffraction patterns of the Grunerite minerals between 9 - $60^{\circ}20$ Cuk \sim_1

I(obs)	20Cuk∝	d(obs)	нк L			I(obs)	20Cuk∝	d(obs)	HKL
40	9.70	9.11	0 2 0		Î,	30	9,69	9.12	0 2 0
100	10.675	8.28	110		d (obs)	100	10.77	8.21	11 0
3 0	19.05	4.656	2 00	!	مردو	25	19.125	4.637	2 00
25	19.413	4.568	040		- Choc	25	19.475	4.554	040
35	21.33	4.165	22 0			30	21.31	4.166	22 0
15	22.909	3,881	131			20	22,835	3.891	131
10	24.716	3.598	221			10	24.535	3.627	221
25	25.775	3,467	131			2 5	25.725	3.461	131
65	27.20	3.276	2 40			7 0	27.235	3.271	2 40
100	29.11	3.065	060,	31 0		100	29.05	3.071	060, 310
25	29.74	3.001	221			10	29.76	2. 999	221
60	32.33	2.766	151			50	32.36	2.764	151
40	33.97	2.637	061			35	34.00	2.635	061
25	35.75	2.509	202			15	35.76	2.509	202
10	37.816	2.376	35 0			10	37.365	2.405	261
15	39.085	2.302	080,	35 ī		10	37.965	2.367	35 0
10	40.07	2.248	421			30	39.033	2.305	080, 351
30	40.98	2.200	261,	$24\bar{2}$		35	40.96	2.201	261, 242
10	43.00	2.101	081,	202		10	42.92	2.105	081,202
2 0	44.25	2.045	351			10	44.28	2.044	351
10	45.52	1.990	190,	37 0		10	47.6	1.908	422
1 5	46.375	1.955	40 2			10	48 . 933	1.859	460
15	47.48	1.913	422			15	50.60	1.802	371
2 0	48.10	1.889	191			10	53.1	1.723	082
10	50.55	1.804	371			15	57.333	1.606	153
10	53.53	1.710	372			10	59.30	1.557	600
15	54.30	1.688	512			L	4	<u>L</u>	.T
3 0	55.10	1.666	461						
15	56.00	1.641	1 11	0					
1 5	57.30	1.607	153						

402,2 10 1

58.16

59。2

1.559

15

Table No. 6 cont. iv

X-Ray diffraction patterns of the Grunerite minerals between 9 - 60°2°Cuk~; G17A

I(obs)	d(obs)	20Cuk∝	HKL	5) (4)	I(obs)	20Cuk∝	D(obs)	HKL
20	9.2 050	9.6	0 2 0	uncerrested (d)	25	9.725	9.087	020
100	8 .3 095	10.64	110	ادورد	100	10.715	8 .2 5	110
10	4.679	18.95	20 0	3/	1 0	19,083	4.647	040
10	4.5250	19.59	040		10	19.425	4.565	200
10	3.8784	22.91	131		1 5	21.74	4.154	22 0
10	3.4568	25.75	131		15	22.96	3. 870	131
30	3,2639	27.3 0	240		5	24.75	3.592	221
75	3.0625	29.11	060, 310		25	25.824	3. 449	131
10	2 ,9966	2 9. 7 9	221		35	27。45	3,246	240
3 0	2.7568	32.45	151		60	29.21	3.055	060 , 31 0
15	2.6294	34.07	061		15	29.86	2.989	221
7	2.5088	35.76	202		40	32,475	2.755	151
10	2.2 9 7 0	39.19	080, 351		25	34.1	2.628	061
15	2.1 960	41.08	261,242		2 0	35.765	2.508	202
7	2.0407	44.35	351		5	37.065	2.423	261
7	1.9525	46.47	402		5	38.1	2.360	35 0
7	1.7098	53.55	372		15	3 9 ,2 66	2.292	080, 351
7	1.6850	54.40	512		2 5	40.22	2.23 9	421
10	1.6610	55.2 0	461		10	40.633	2.218	312
10	1.6340	56.25	1 11 0		2 5	41.1	2.194	261, 242
10	1.5986	57.61	153		15	44.5	2.034	351
		<u> </u>		4	5	46.55	1.949	402
					5	50.95	1.791	371
					5	53,4	1.714	082
					20	55.1	1.665	461
					10	57.55	1.600	153
					10	58.3	1.582	402,2 101

Sample No. element	1(3)A	1(4)	3	7	11	14	17A
Ва	33	2 9	12	(not measured)	24	12	38
Cr	113	130	121	175	123	117	111
Nb	18	11	8	17	5	10	10
Ni	48	40	26	46	54	64	42
Pb	x	2	4	2	x	2	х
Rb	. x	5	x	x	х	x	х
Sc	2 9	27	6 2	31	23	2 0	68
Sr	10	10	3	8	9	9	х
v	96	9 3	117	120	48	72	167
Y	6	x	х	x	2	x	2
Zr	96	63	2 6	33	33	69	54

B) Trace element concentration of the Garnets (P.P.M)

Sample No. element	1(3)A	1(4)	7	11	14	21
Ва	24	56	32	75	x	х
+ _{Cr}	140	145	302	172	155	230
Nb	1 9	11	17	27	22	56
+ _{Ni}	15	21	17	15	16	15
Pb	2	3	x	х	4	x
Rb	х	x	x	х	х	x
Sc	38	2 6	27	22	36	21
Sr	6	3	x	13	7	2
V	22 9	156	144	161	22 6	97
Y	1 9 3	137	135	185	188	119
Zr	64	41	58	71	53	7

- (+) Blank disc of cellulose measured 48 ppm Cr 💸 21 ppm Ni
- (x) Determined but not detected

 $\mbox{Table No.8} \label{eq:table No.8} \mbox{Major constituents of } \mbox{ } \mbox{grunerite from different iron formations} \mbox{}$

Locality of the Iron Formation	Fe ²⁺ atom	Mg ²⁺ atom	Mn ²⁺ atom
Wab ush I.F. Klein (1964)	4.42-6.41	0.77-2.46	0.03 -0.13
Wabush I.F. S.W. Labrador Klein (1966)	4.01 Fe ²⁺ 0.04 Fe ³⁺	2.77	0.06
Quebec I.F. Mueller (1960)	5.95-6.67	0.13-0.77	0.09 -0.1
Archean I.F. of Itchen Lake area (Canada) Bostock (1977)	4•73-6•54	0.27-1.99	0.001-0.097
I.F. of the Gagnon Region Butler (1969)	2.9 -4.71	1.54-3.52	0.07 -0.53
I.F. of the Gairloch area, N.W. Scotland	3 . 9 - 5 . 31	1.14-2.17	0.07 -0.8

Table No.9

X.R.D., X.R.F. and Microprobe molecular proportion of iron with calculated and measured density of grunerites.

Sample No.	X Fe	D(calc)	D(mes)
*1(3)A	0.8107	3.4510	3,45
⁺ 1(3)A	0.7550		
°1(4)	0.7581	3.4441	3.33
⁺ 1(4)	0.7590		
*3	0.6745	3.4014	3.30
+3	0.6600		
•6A	0.8310		
+7	0.7540		
•11	0.8119	3,4995	3.43
+11	0 .823 0		
°11	0.8050	3.4861	
•12	0.7815		3.18
•14	0.6832	3,4136	
+14	0.7000		
⁰ 14	0.7310	3.4352	
•17A	0.6449	3.3976	
⁺ 17A	0.6470		
⁰ 17A	0,6500	3.4060	

X Fe = Fe0/Fe0 + Mg0

X Fe = -45.441 + 16.731 d (151)

X Fe = -40.946 + 15.823 d (061)

X Fe = -52.275 + 25.963 d (351)

X Fe = -34.467 + 21.476 d (1 11 0)

Equations from C. Klein and D. Waldbaum (1967)

Calculated from the X-Ray diffraction pattern using (hkl) reflection (see below)

⁺ Calculated from X-Ray Fl .rescense analysis

 $^{^{}m o}$ Calculated from the Microprobe analysis

X-Ray-Fluorescence analyses of Garnets in Gairloch Iron Formation

Table No.10

Oxide %	1(3)A	1(4)	7	11	14	21
SiO ₂	36.81	36.37	37 . 96	36.08	36.99	36.55
TiO ₂	0.77	0.60	0.52	0.38	0.56	0.27
A1 ₂ 0 ₃	18.80	19.45	19.16	19.53	19.09	19.31
FeO MnO	19 . 14 19 . 82	23.87 13.58	34.81 2.18	23.96 15.79	20.13 19.16	34•43 2•32
MgO	0.46	0.43	0.78	0.32	0.41	0.61
CaO Na ₂ O	0.85	4.71	4•53	3.77	4.23	4.35
K ₂ 0	-	-		_	_	_
H ₂ O ⁺	_		_	_	_	_
P ₂ 05	0.20	0.22	0.09	0.23	0 .1 8	0.07
*Ĉo ₂	_	-	_	_	-	71000
L.O.I.	-0.86	-0.29	-2.33	-0.77	-0.81	- 2 . 87
Total	99.85	99.23	100.03	100.06	100.75	
Numbe:	Number of cation recalculated on the basis of 12 Oxygens					
Ions	1(3)A	1(4)	7	11	14	21
Si	3.09	3.00	3.08	2.97	3.01	3.04
A1 A1	- 1.86	- 1.89	1.84	0.03 1.87	- 1.84	1.90
Ti	0.049	0.037	0.035	0.025	0.034	0.02
Fe Mn	1•35 1•41	1.64 0.95	2.36 0.15	1.64 1.10	1.37 1.32	2.40 .0.16
Mg	0.06	0.05	0.09	0.04	0.04	10.08
Ca	0.07	0.42	0.39	0.33	0.36	0.39
P	0.01	0.01	0.01	0.01	0.01	0.01
Alm	46.71 48.79	53.59 31.05	78.93 5.02	52.73 35.37	44•34 42•72	79•21 5•28
Spess Pyr	2.08	1.63	3.01	1.29	1.29	2.64
Gross	2.42	13.73	13.04	10.61	11.65	12.87
$\sum_{R}^{2_{+}^{+}} R^{3+}$	2.89	3.06	2.99	3.11	3.09	3. 03
\(\sum_{\text{Ti}^{\dagger^4}\text{A1}^{\dagger^3}}\)	1.91	1.93	1.88	1.90	1.87	1.92

^{*} Co₂ not measured

Table No.11 i

Core and Rim compositions of Garnet

G11

Oxide	R ₁	^C 1
SiO ₂	36.64	36.2 8
TiO ₂		
A1203	19,96	20.19
*Fe0	26,46	25.80
Mn0	13,59	14.30
Mg0	0.22	0.21
C a 0	3.51	3,38
Total	100.38	100.16

G11

R ₃	с ₃
36.72	36,63
0.18	
20.07	20.02
27.08	27.03
11.77	11.88
0.34	0.20
4.36	4.07
100.52	99.83

G11

R ₅	С ₅
36.18	36.44
0.18	
20.14	2 0,05
26.72	2 6.09
12.40	12.59
0.20	0 .2 6
4.21	4.04
100.03	99.47

Number of cations recalculated to the basis of 12 Oxygens

Ions	R ₁	^c 1
Si	3.006	2. 985
Ti		
Al	1.930	1.958
Fe	1.816	1.775
Mn	0.945	0.997
Mg	0.027	0 . 0 2 6
Ca	0 .3 09	0 .2 99
$\sum R^{2+} + R^{3+}$	3,097	3.097

R ₃	c ₃
2.998	3.011
0.011	
1.932	1.940
1.849	1.859
0.814	0.827
0.042	0.025
0.382	0.359
3.087	3.070

R ₅	c ₅
2.976	3.005
0.012	
1.953	1.949
1.839	1.800
0.864	0.880
0 . 0 2 5	0.033
0.372	0.357
3.100	3.070

R = Rim%

C = Core%

* = Total iron determined as Fe0

 ${\rm Na_2^{\,0}}$, ${\rm K_2^{\,0}}$ were analysed but not detected

Table No.11 cont. ii Core and Rim compositions of Garnet

G14

36.44

20.26

23.18

17.25

3.30

100.43

0xide

 Si_{2}

TiO2

A1203

*Fe0

Mn0

Mg0

Ca0

Total

36.52 20.08 21.46 17.62 0.19

 c_1

3.06

98.93

G14

 c_2 37.01 36.71 0.17 19.97 20.30 22.25 21.99 16.00 17.67 0.33 0.25 4.39 3.59 99.95 100.68 G14

R ₃	c ₃
3 6.7 1	36.66
20.26	19.96
23.43	22.64
15.31	16.93
0.23	
4.48	3,40
100.42	99.59

Number of cations recalculated to the basis of 12 Oxygens

Ions	R ₁	с ₁
Si	2.991	3.023
Ti		
Al	1.960	1.959
Fe	1.591	1.486
Mn	1.200	1.236
Mg		0.024
Ca	0.291	0.272
$\Sigma R^{2+} + R^{3+}$	3.082	3.018

R ₂	c ₂
3.028	2.994
	0.011
1.926	1.952
1.522	1.500
1.109	1.221
0.041	0.031
0 .3 85	0.314
3,057	3. 066

R ₃	c ₃
2.999	3.024
1.950	1.940
1.601	1.562
1.060	1.083
0.028	
0.392	0.301
3.081	2.946

R = Rim%

C = Core%

* = Total iron determined as Fe0

 $\mathrm{Na_2^{\,0}}$, $\mathrm{K_2^{\,0}}$ were analysed but not detected

Table No.11 cont. iii Core and Rim compositions of Garnet

	G	1	/					
-				 _	7	_	 _	-

0xide	R	^C 1
Si ⁰ 2	36.94	36.78
$\mathtt{Ti0}_{2}$		
A1203	20.56	20.50
*Fe0	21.99	20.46
MnO	19.23	20.06
MgO	0,33	0.34
Ca0	2.32	2.44
Total	101.37	100.58

G17

R ₂	c ₂
36.68	99.97
20.32	20.27
18.24	16.95
23.41	24.72
0.30	0.23
2.24	1.46
101.19	99.97

G17

R ₃	c ₃
36.36	3 6 .3 5
0.19	
20.56	20.21
19.64	18.02
21.61	23.99
0.37	0 .2 5
2.41	1.79
101.14	100.61

Number: of cations recalculated to the basis of 12 Oxygens

Ions	R ₁	c ₁
Si	2,998	3.002
Ti		
A1	1.967	1.973
Fe	1.493	1.397
Mn	1.323	1.387
Mg	0.041	0.042
Ca	0.202	0.214
$\sum R^{2+} + R^{3+}$	3.059	3.040

R ₂	c ₂
2 。990	2. 997
1.953	1.970
1.244	1.169
1.616	1.727
0.037	0.028
0.196	0.130
3.093	3.054

R ₃	с ₃	
2,964	2.985	
0,012		
1.975	1.957	
1.339	1.238	
1.492	1.670	
0.046	0.031	
0.211	0.158	
3.088	3.097	

R = Rim%

C = Core%

* - Total iron determined as Fe0

 $\mathrm{Na_2^{0}}$, $\mathrm{K_2^{0}}$ were analysed but not detected

Table No.11 cont. iv

Core and Rim compositions of Garnet

G17

Oxide	R ₅	С ₅
SiO ₂	36,68	36.34
TiO ₂	0.18	
A1203	20.54	20.33
*Fe0	19.43	18.07
Mn0	21.54	23,55
MgO	0.36	0.24
Ca0	2.26	1.72
Total	100.99	100.25

G17

R ₆	c ₆
36.66	36.85
0.21	0.58
20.16	20.21
21.81	16.76
18.46	25.18
0 .3 9	0.26
2.73	2.15
100,42	101.99

G17

R ₇	c ₇
36.32	36.48
20.20	19.91
23.69	19.24
17.13	22.18
0.47	0.37
2.12	2.19
99 .93	100.37

Number of cations recalculated to the basis of 12 Oxygens

Ions	R ₅	C ₅
Si	2.987	2.990
Ti	0.011	
Al	1.972	1.972
Fe	1.323	1.244
Mn	1.486	1.641
Mg	0.044	0.029
Ca	0.198	0.152
$\sum R^{2+} + R^{3+}$	2 ,9 5 8	3.066

R ₆	с ₆
3.000	2.981
0.013	0.036
1.945	1.928
1.492	1.135
1.280	1.726
0.048	0.032
0.240	0.187
3. 060	3.080

R ₇	с ₇
2. 99 3	3.000
1.962	1.930
1.632	1.324
1.196	1.545
0.059	0.046
0.187	0.193
3.074	3.108

R = Rim%

C = Core%

* = Total iron determined as Fe0

 $^{\text{Na}}2^{0}$, $^{\text{K}}2^{0}$ were analysed but not detected

Core and Rim compositions of Garnet
(Crystals which do not show difference in composition)
G11
G11
G17

0xide	R ₂	c ₂
Si ⁰ 2	36.55	36.72
Ti02		
A1203	20.18	20,33
*Fe0	26.88	26,93
Mn0	13.00	13,27
Mg0	0.22	0.21
Ca0	3.47	3.39
Total	100.30	100.85

R ₅	c ₅
36.18	36.44
0.18	
20.14	20.05
26.72	26.09
12.40	12.59
0.20	0.26
4.21	4.04
100.03	99.47

R ₄	C ₄
36.61	36.51
20.38	20.14
19.14	18.64
22.44	21.91
0.38	0.37
2.18	2.10
101.13	99.67

Number of cations recalculated to the basis of 12 Oxygens

Ions	R ₂	C ₂
Si	2. 99 8	2. 996
Ti		
Al	1.951	1.956
Fe	1.845	1.838
Mn	0.904	0.917
Mg	0.027	0.026
Ca	0.305	0.297
$\sum_{R^{2+} + R^{3+}}$	3.081	3. 078

R ₅	c ₅
2.976	3.005
0.012	
1.953	1.949
1.839	1.800
0.864	0 .8 80
0.0 25	0.033
0.372	0.357
3.10	3.07

R ₄	c ₄
2. 986	3.010
1. 9 5 9	1.957
1.306	1.286
1.5 50	1.530
0.046	0.046
0.191	0.186
3.093	3.048

R = Rim%

C = Core%

* = Total iron determined as Fe0

 $\mathrm{Na_20}$, $\mathrm{K_20}$ were analysed but not detected

Table No.12 (i)

X-ray diffraction patterns of the garnet minerals

between 25°-60° 20 CuK%1

Gl (3) A

I (obs)	20 CuK≪l	d (obs)	HKL
90	30.838	2.897	400
100	34.561	2.593	420
60	37.948	2.369	42 2
50	39.544	2.277	431
50	42.673	2.117	521
15	44.139	2.050	440
50	48.346	1.881	532
40	54.790	1.674	444
60	57.242	1.608	640
70	59•637	1.549	642

G1 (4)

I (obs)	20 CuK≪I	d (obs)	HKL
90	30.827	2.898	400
100 -	34.520	2.596	420
30	3 6 . 280	2.474	332
60	37.948	2.369	422
50	39•562	2.276	431
60	42.630	2.119	521
50	48.318	1.882	532
50	54.862	1.672	444
80	59•5 95	1.550	642

Table No.12 cont. (ii)

X-ray diffraction patterns of the garnet minerals

between 25°-60° 20 CuK~1

G7

I (obs)	2 0 CuK≪l	d (obs)	HKL
90	30.904	2.891	400
100	34.561	2.593	420
20	36.341	2.470	3 22
35	39.634	2 .27 2	510
40	42 .7 36	2.114	521
60	48.428	1.878	6 1 1
30	54.933	1.670	444
50	57•398	1.604	640
90	59.807	1.545	642

Gll

I (obs)	20 CuK≪l	d (obs)	HKL
90	30.817	2.899	400
100	34.561	2.593	42 0
60	39.562	2.276	431
40	42.673	2.117	521
50	48.373	1.880	532
35	54.862	1 . 6 7 2	440
7 0	57.281	1.607	640
80	5 9.637	1.549	642
		and the second s	

Table No.12 cont. (iii)

X-ray diffraction patterns of the garnet minerals

between 25°- 60° 20 CuK∝1

G14

I (obs)	2 0 CuK≪l	d (obs)	HKL
90	30.806	2.900	400
100	34.547	2.594	420
20	36.295	2.473	332
40	37.964	2.368	422
35	39.580	2.275	431
35	42.630	2.119	521
25	54.862	1.672	444
50	57.281	1.607	640
60	59.637	1.549	642
			Company of the Compan

G21

I (obs)	20 CuK≪l	d (obs)	HKL
90	30.860	2.895	
100	34.658	2.586	
50	39.652	2.271	
40	42.715	2.115	
20	44.185	2.048	
60	48.428	1.878	
40	54.862	1.672	
70	57•357	1.605	
60	59.765	1.546	

 $\label{thm:constituents} \mbox{Table No.13}$ Major constituents of the Garnet from different iron formations

Locality of the Iron Formation	Fe ₂ 0 ₃ %	Fe0%	Mn0%	Mg0%	Ca0%
Archean I.F. of the Itchen Lake area (Canada) Bostock (1977)		94-38.15) al iron	0.06-0.46	0.67-1.44	3.65-4.92
Lower Wabush I.F. Klein C. (1966)	0.54	32.66	3 .3 6	1.89	3. 50
Upper Wabush I.F. Klein C. (1966)	14.90	-	35.60	_	5.00
I.F. of the Gairloch area NW Scotland	-	19.14-34.81	2.18-19.82	0.32-0.78	0.85-4.71

Table No.14
Unit cell dimensions, cell volume and density of the garnets

Sample No.	a(A) ⁰	V(A) ³	Density (Cal.)	Density (Mes.)
1(3)A	11.597	1559.685	4.1613	4.115
7	11.603	1562.107 1545.606	4. 1652 4. 1926	4.071 4.062
11	11.593 11.597	1558.072 1559.685	4.2139 4.1938	4.175 -
21	11.578	1552.032	4.1951	

X-Ray Fluorescence analyses of Magnetites in Gairloch Iron Formation

(a) Major elements

Oxide %	Sample No 5	Sample No 12
SiO ₂	12.28	21.62
TiO	0.03	0.02
A1 ₂ 0 ₃	0.2	0.2
Fe ₂ 0 ₃	47.19	43.93
FeO	36.76	32.17
MnO	0.59	0.37
MgO	0.56	0.08
Ca0	0.75	0.43
Na ₂ O	0.05	0.05
k ₂ 0	-	0.03
H ₂ O ⁺	-	
P ₂ 0 ₅	0.46	0.35
$\overline{\alpha}_2$	_	-
L.O.I.	0.1	0.58
⊕ Total	98.93	99.60

(b) Trace elements (p.p.m.)

Elements	Sample No 5	Sample No 12
Ba	32	22
*Cr	22	27
Nb	26	9
*Ni	17	32
Pb	12	12
Rb	x	x
Sc	1	1
Sr	5	5
V	10	11
Y	7	6
Zr	х	x

- Θ \geq of the oxide plus the L.O.I.
- * Blank disc of cellulose measure 21 p.p.m. Ni, and 48 p.p.m. Cr
- x Measured but not detected

Table No.16 (i)

X-Ray Diffraction pattern of the magnetite minerals

Sample No. 4 Sample No. 5

I(obs)	20Cok 🗷	d(obs)	HKT		I(obs)	20 C ok ∝ ₁	d(obs)	HKL
М	21.349	4.8290	111		W	21. 095	4.8865	111
W	35•142	2.9630	220		М	35•237	2.9552	220
V.W	41.619	2.5178	311		W	41.425	2.5291	311
W	43.734	2.4016	222		М	50.483	2.0976	400
W	50.977	2.0786	400		W	62.977	1.7125	422
М	63.556	1.6985	422		М	67.231	1.6157	333,511
W	67.831	1.6031	333,511		W	74 .1 11	1.4844	440
V.W	74.776	1.4731	440		M	90.510	1.2594	622
V.W	84.992	1.3241	620		V.W	95.147	1.2118	444
W	90.675	1.2576	622		M	109.666	1.0942	553,731
М	117.353	1.0471	800		M	117.120	1.0484	800
М	130.038	0.9868	660,822		M	129.347	0.9896	660,822
М	136.068	0.9645	555,751	NA CAMPANA AND AND AND AND AND AND AND AND AND	M	137.084	0.9611	555,751
М	145.113	0.9376	840					

Unit cell dimensions :

 $a = 8.351 \text{ A}^{\circ}$

 $a = 8.388 \text{ Å}^{\circ}$

Table No.16 cont. (ii)

X-Ray Diffraction pattern of the magnetite minerals

Sample No. 6A Sample No. 12M

I(obs)	20Cok ≪ ₁	d(obs)	HKL
7.7	24 205	l. 0.0a	111
М	21.207	4.861	111
M	35.129	2.964	220
W	41.409	2.530	311
W	50.472	2.098	400
W	63.038	1.711	422
W	67.359	1.613	333 , 5 11
W	74.310	1.481	<i>L</i> ₁ <i>I</i> ₁ O
W	88.839	1.278	53 3
V.W	90.731	1.257	622
М	109.696	1.094	553,731
W	117.013	1.049	800
W	129.322	0.9897	660,822
W	134.512	0.9699	555 ,7 51
W	144.307	0.9397	840

I(obs)	20Cok ≪ ,	d(obs)	HKL
М	21.2407	4.8534	111
М	35.139	2.9632	220
М	50.519	2.0962	400
М	62.985	1.7123	422
W	67.411	1.6119	333,511
W	74.234	1.4823	440
W.V	84.850	1.3259	620
W	95.209	1.2112	440
M	109.607	1.0946	553,731
М	116.853	1.0499	800
М	129.200	0.9902	660,822
M	134.597	0.9696	555,751

Unit cell dimensions:

a = 8.388 A

 $a = 8.387 \text{ A}^{\circ}$

Table No.17
List of samples taken for analysis

Sample No.	Type of Rock	Main Mineralogical Constituents
G1(1)	Hornblende schist	Hornblende, Quartz, Magnetite
G1(2)	11	Hornblende, Quartz
G1(3)A	Silicate I.F	Garnet, Grunerite, Quartz
G1(3)B	11	Garnet, Grunerite, Quartz, Magnetite
G1(4)	`11	Garnet, Grunerite, Magnetite
G1(5)	Hornblende Chlorite schist	Hornblende, Chlorite, Quartz
G2(1)	Muscovite schist	Muscovite, Quartz, Magnetite
G2(2)	Quartzite	Quartz, Magnetite
G3	Silicate I.F	Grunerite, Quartz
G4	Black Quartzite	Magnetite, Quartz
G5	Banded Oxide I.F	Magnetite, Quartz, Grunerite
G6A	11	Magnetite, Quartz, Grunerite
G6B & C	Mixed Oxide & Silicate I.F	Magnetite, Quartz, Grunerite
G7	Silicate I.F	Garnet, Grunerite, Quartz
G8	Hornblende schist	Hornblende, Quartz
G9	Biotite, Muscovite schist	Biotite, Muscovite, Quartz
G10	Graphite schist	Graphite, Muscovite, Quartz
G11(A)	Mixed Oxide & Silicate I.F	Magnetite, Grunerite, Quartz
G11(B)	Silicate I.F	Magnetite, Grunerite, Garnet
G12(M)A	Banded Oxide I.F	Magnetite, Quartz
G12(M)B	Mixed Oxide & Carbonate I.F	Magnetite, Quartz
G12(Gar)	Mixed Oxide & silicate I.F	Magnetite, Quartz, Grunerite, Garnet
G13	Muscovite, Biotite schist	Biotite, Muscovite, Quartz
G14	Silicate I.F	Grunerite, Garnet
G15	Quartzite	Hornblende, Quartz
G16	Sulphide I.F	Garnet, Grunerite, Pyrites, Quartz
G17(1)	Silicate I.F	Garnet, Grunerite, Magnetite
G17(2)	11	Garnet, Grunerite, Magnetite
G19	Hornblende, Ziosite, Garnet schist	Hornblende, Quartz, Ziosite
G20	Biotite, Garnet schist	Garnet, Biotite, Quartz
G21	Silicate I.F	Garnet, Grunerite, Quartz

Table No.18 i

Molecular ratio of XFe, XMn, XMg in the Grunerites

X-Ray-Fluorescence analyses

	1(3)A	1(4)	3	. 7	11	14	17A
Fe/Fe+Mn+Mg Mn/Fe+Mn+Mg Mg/Fe+Mn+Mg Mg/Fe+Mg Mn/Fe+Mn Fe/Fe+Mg	0.667	0.714	0.609	0.746	0.764	0.622	0.573
	0.116	0.060	0.078	0.010	0.072	0.112	0.115
	0.217	0.226	0.313	0.244	0.164	0.267	0.313
	0.245	0.241	0.340	0.246	0.177	0.300	0.353
	0.148	0.078	0.113	0.014	0.086	0.152	0.167
	0.7549	0.7594	0.6604	0.7537	0.8233	0.6998	0.6477

Molecular ratio of XFe, XMn, XMg in the Garnets

X-Ray-Fluorescence analyses

	1(3)A	1(4)	İ	7	11	14	21
Fe/Fe+Mn+Mg	0.479	0.621		0.907	0.590	0.502	0.909
Mn/Fe+Mn+Mg	0.500	0.360		0.058	0.396	0.484	0.061
Mg/Fe+Mn+Mg	0.021	0.019		0.035	0.014	0.014	0.030
Mg/Fe+Mg	0.043	0.030		0.037	0.024	0.028	0.032
Mn/Fe+Mn	0.511	0.367		0.060	0.401	0.491	0.063

Table No.18 cont. ii

Molecular ratio of XFe, XMn, XMg in the Grunerites (Microprob@analyses)

element ratio	11	14	17
Fe/Fe+Mn+Mg Mn/Fe+Mn+Mg Mg/Fe+Mn+Mg Mg/Fe+Mg Mn/Fe+Mn Fe/Fe+Mg	0.760	0.674	0.572
	0.055	0.078	0.120
	0.184	0.248	0.308
	0.195	0.269	0.350
	0.068	0.104	0.173
	0.805	0.731	0.650

Molecular ratio of XFe, XMn, XMg in the Garnets (Microprobanalyses)

element ratio	11	14	17
Fe/Fe+Mn+Mg	0.664	0.561	0.460
Mn/Fe+Mn+Mg	0.325	0.431	0.523
Mg/Fe+Mn+Mg	0.011	0.009	0.017
Mg/Fe+Mg	0.016	0.015	0.035
Mn/Fe+Mn	0.328	0.434	0.532

 $\label{thm:continuous} \begin{tabular}{ll} Table No.19 & i \\ \\ Major element chemical analyses for the silicate and oxide facies rocks \\ & from the I.F Gairloch \\ \end{tabular}$

Sample No. Oxide %	1(3)A	1(4)	3	4	5	6A	6C	7
S i 02	46.21	51.56	59.93	84.04	54.40	57.63	64.10	61.01
TiO2	0.79	0,63	0.65	0.03	0.02	0.02	0.03	0.51
A1203	4.47	5.17	0.95	0.4	0.25	0.26	0.3	6.08
Fe ₂ 0 ₃				8.7	21.58	24.7	14.89	
Fe0	31.20	27.82	23.92	3.83	16.63	18.36	14.59	23.50
Mn0	8.73	5.65	4.06	0.06	1.05	0.60	0.62	0.68
Mg0	5,20	4.03	7.15	0.02	0,98	0.73	1.22	3.46
Ca0	1.20	0.14	0.37	0.32	1.50	0.56	0.75	1.65
$^{\mathrm{Na_2^0}}$	0.04	0 .03	0.05	0.02	0.10	0.09	0.05	0.06
к ₂ 0		0.05						
H ₂ 0 ⁺	1.41	1.63	1.37	0,24	0.76	0.75	0.39	1.40
P ₂ 0 ₅	0.20	0.25	0.15	0.03	0.87	0.46	0.50	0.23
*c0 ₂	0.23	0,20	0.22	0.43	0.07	0.36	0.15	0.21
L.O.I	-0.45	0.51	-0.05	0.07	0.15	-1.08	-0.27	-0.34
<u> </u>	<u> </u>]	<u> </u>	<u> </u>	<u> </u>		<u> </u>	

^{*} Detection limit for $CO_2 = 0.07\%$

Table No.19 cont. ii

Major element chemical analyses for the silicate and oxide facies rocks from the I.F. Gairloch.

Sample No. Oxide %	11	12M	12G	14	16*	17	17A	21
SiO ₂	48.09	42.45	47.01	46.48	61.39	46,65	5 2,3 0	64.08
TiO ₂	0.25	0.20	0.16	0.53	0.68	0.47	1.99	0.42
A1 ₂ 0 ₃	5.07	0.15	3.38	5,25	7. 06	5.79	0.55	6.22
Fe ₂ 0 ₃		29.91	3.43		4.93			2.53
Fe0	31.35	17.96	27.64	28.46	6.86	23.88	28.56	19.34
MnO	6.74	1.08	4.07	9.13	11.04	13.28	5.91	0,81
MgO	3,41	0.05	3,38	5,78	1.75	6.06	8.33	2.23
Ca0	1.39	0.94	3,79	1.56	0.91	0.85	0.15	1.70
Na ₂ 0	0.04	0.03		0.03	0.01	0.07	0.03	0.02
к ₂ 0		0.01						
H ₂ 0	1.44	0.68	1.14	1.61	0.50	1.46	1.61	0.97
P ₂ 0 ₅	0.35	0.67	0.30	0 .2 9	0 ,23	0.17	0.02	0.32
°co ₂	0.23	4.21	4.38	0.24	0,99	0.07	0.07	0.10
L.O.I.	0.60	2.18	3,37	-0.61	4,23	0.57	0 .2 9	-0.20
Total	98.46	98 . 1 6	98.68	99.36	100.25	98.75	99.45	98.74

^{*} The sulphur in G16 = 3.9%

[°] Detection limit for $C0_2 = 0.07\%$

Sample No. Oxide %	1(1)	1(2)	1(5)	2(1)	2(2)	8	9	10
Si ⁰ 2	49.61	49.36	55.77	69 . 9 2	93,65	59 .13	61.76	56.86
Ti02	1.33	1.41	0.68	0.58	0.02	1.37	0.64	1.00
A1 ₂ 0 ₃	13.15	13.87	13.90	14.94	0.22	14.41	18.43	16.56
$^{\mathrm{Fe}}2^{0}3$		****	0.95	2.47	2.78		0.34	1.28
F e 0	10.9	12.6	9.95	0.97	1.14	8.5	5.05	0.87
Mn0	0.2	0.21	0.16	0.03	0.17	0.14	0.06	0.02
Mg0	7.68	7.59	6.18	1.51	0.08	3.44	2.97	2.80
Ca0	9.01	10.06	5.69	0.63		7.65	0.68	2.75
$^{ m Na_2^{0}}$	2.03	2.12	1.41	2.73	0.01	2.34	1.55	3.08
к ₂ 0	0.13	0.20	0.25	2. 94		0.40	4.67	2.01
H ₂ 0+	2.28	1.71	3,58	1.96	0.42	1.28	2.86	1.53
P ₂ 0 ₅	0.12	0.11	0.08	0.13	0.02	0.18	0.11	0.03
c0 ₂	1.95	0.33	1.09	0,22	0.07	0 . 93	0.21	0.10
L.0.I	3,3	0.89	3.17	4.22	1.04	1.29	2.74	11.44
Total	98,39	99.57	99.69	99 . 0 3	98.58	99.77	99.36	98.7*

^{*} of the total oxide + L.O.I (CO_2 & H_2O are not included) sample has free carbon present

Detection limit for CO_2 = 0.07%

Table No. 20 cont. i i

Major element chemical analyses of the metasediments from Gairloch.

Sample No. Oxide %	13	1 5	19	2 0
SiO ₂	75.16	92.55	61.52	62.67
TiO ₂	0.42	0.01	1.03	1.59
A1203	12.72		12.07	12.92
Fe ₂ 0 ₃		1.98		
Fe0	2.44	3.12	12.70	12.33
MnO	0.04	0.02	0.60	0.09
Mg0	1.28	0.02	3.18	3.35
Ca ^O	1.23	0.05	4.99	1.95
Na ₂ 0	2.28	0.02	0.56	1.49
к ₂ 0	2.37		0.20	0.02
H ₂ 0+	0,59	0.33	1.94	1.76
P ₂ O ₅	0.15	0.02	0 .2 9	0.11
•c0 ₂	0.11	0.26	0.21	0.31
L.O.I.	1.36	0.70	1.09	1.46
Total	98.79	98.38	99.29	98.59

[•] Detection limit for $CO_2 = 0.07\%$

Table No.21

Trace element chemistry (p.p.m.) of the silicate and oxide facies rocks of the I.F. Gairloch.

Elements	1(3)A	1(4)	3	4	5	6 A	6C	7
Ва	28	59	47	7	36	12	5	31
Cr	70	88	143	46	54	65	66	167
Nb	8	8	10	56	18	14	12	14
Ni	57	59	34	27	13	16	14	70
Pb	2	6	8	8	7	6	3	18
Rb		-		-	-	-	-	
Sc	12	12	16	1	2	1	1	11
Sr	4	4	-	2	5	4	2	2
ν	7 9	64	61	-	6	7	5	72
Y	28	20	11	_	7	3	3	25
Zr	90	47	22	_	-	-	-	46

Elements	11	12M	12G	14	16	17	17A	21
Ва	15	25	40	17	27	17	27	22
Cr	82	62	92	9 3	141	138	70	177
Nb	7	6	4	8	23	13	17	14
Ni	124	14	54	73	376	21	81	62
Pb	_	7	6	11	20	9	10	21
Rb	_	-	7	-				-
Sc	9	1	9	12	10	10	62	10
Sr	21	8	32	9	5	6	-	5
v	47	6	44	77	63	102	112	61
Y	42	10	17	33	32	33	19	22
Zr	99	_	17	87,	75	58	253	42

Table No. 22

Trace element—Chemistry (p.p.m.) of the metasediments from the Gairlock area.

Elements	1(1)	1(2)	1(5)	2(1)	2(2)	8
Ba	34	44	78	504	3 6	51
Cr	54	1 50	12 8	9 2	66	169
Nb	10	11	6	64	65	14
Ni	155	123	192	168	53	70
Pb	10	18	11	43	15	18
Rb			5	8	72	
Sc	3 9	40	3 9	9	1	11
Sr	73	84	5 2	156		2
v	2 00	212	144	54	6	72
Y	21	23	15	19		25
Zr	7 0	74	2 6	196		46

Elements	9	10	13	1 5	1 9	20
Ba	848	23 0	12 0		23	2 90
Cr	59	12 8	115	35	61	21 9
Nb	1 9	31	37	67	2 0	22
Ni	52	138	90	40	21	139
Pb	11	60	66	21	16	2 0
Rb	4	147	101		5	48
Sc	35	1	7		23	18
Sr	72	70	146		33	3 9
V	203	84	54		54	173
Y	27	19	25		35	8
Zr	102	109	255		132	102

The average chemical composition of oxide - facies rocks from different Iron Formations.

Oxide %	A	В	С	D	Е	F	G	Н
SiO ₂	46.12	44.45	40.15	42.89	41.24	40.78	48.28	54.65
TiO ₂	0.04	0.14	n.d	-	0.17	0.07	n.d	0.07
Al ₂ 0 ₃	0.86	2.1	0.8	0.42	0.87	0.71	0.23	0.24
Fe ₂ 0 ₃	19.47	26.42	50.1	51.69	40.45	16.09	22.47	22.77
FeO	19.26	18.79	1.6	2.10	12.95	24.77	17.79	16.89
MnO	0.66	0.10	0.13	0.30	0.12	0.08	n.d	0.84
MgO	2.88	2.27	1.4	~	1.35	3. 78	2.94	0.75
C aO	1. 79	1.65	2.0	0.1	0.84	4.12	1.46	0.94
Na ₂ 0	0.05	0.18	n.d	-))o•2	ಂ.1	n.d	0.07
к ₂ 0	0.14	0.50	n.d)	0.12	n.d	-
H ₂ 0+	1.68*	1.98	n.d	0.43	0.27	1.86	1.36	0.65
co ₂	6.79	1.24	2.6		0.19	2.63	5.05	0.20 ^x
P ₂ 0 ₅	0.07	0.17	0.03	0.03	0.06	2.82	0.07	0.63
Total	99.81	99•99	98.81	97.96	98.71	97•93	99.65	98.70

The CO2 is the average of three samples

- A = Average chemical composition of the Biwabik Iron Formation. Lepp (1966).
- B = Average chemical composition of the Russian Proterozoic ferruginous rocks. Ronov and Migdisov (1971).
- C = Average chemical composition of the Menominee district Michigan Iron Formation. James (1966).
- D = Average chemical composition of the Brazit Iron Formation. Minais Gerais Eichler (1970).
- E = Average chemical composition of the Bong Range Iron Formation. Liberia Thienhaus (1964).
- F = Average chemical composition of the Vayrylankyla Iron Formation. NE Finland. (Geological survey of Finland) (1973).
- G = Average chemical composition of six analyses of the Lower Cherty division of the Biwabik Iron Formation of the Mesabi Range Gruner (1946).
- H = Average chemical composition of four analyses of the banded Iron Formation from the Gairloch area NW Scotland.

n.d = Not determined

^{* =} Ignition

^{- =} Not detected

Table No.24

The chemical composition of silicate facies rocks from different Iron Formations.

Oxide %	A	В	С	D	E	F	G
SiO2	50.96	49.43	32.98	47.27	55.4	45.5	53•77
TiO ₂	n.d	8 844	0.06	0.28	0.18	0.06	0.69
Al ₂ 03	1.09		0.45	3.27	5.85	1.23	4.66.
Fe ₂ 0 ₃	5.01	8.16	26.25	5.1	3.36	21.40	0.75
Fe0	30•37	30.52	28.87	25.1	27.2	21.70	24.49
MnO		0.17	0.06	0.21	0.94	3.2 ¹ +	6.60
MgO	5.26	4.77	5.83	4.93	4.24	5.69	4.74
C a()	0.04	0.18	0.62	1.80	2.45	0.51	0.99
Na ₂ 0		-	0.05	0.08	0.01	0.04	0.04
K ^S O	-	-	0.02	0.92	0.03	0.007	
H ² O+	6.41	6.24	1.90	2.55	0.34	0.22	1.34
co ₂		0.43	0.64	3• 79	0.05	n.d	0.22
P ₂ 0 ₅	-		0.44	1.24	0.079	0.003	0.26
Total	99.14	99.90	98.17	96.54	100.12	99.6	98.55

n.d = not determined

^{- =} not detected

⁽A) and (B) are greenalite bearing rocks from the Iron Formation.

Mesabi range James (1954).

⁽C) Fe-silicate-magnetite rocks from the Vuorijarvi Iron Formation Finland. Geological Survey of Finland (1973).

⁽D) Chert meso banded grunerite bearing rocks from the Vuorijarvi Iron Formation. Finland (Geological Survey of Finland (1973).

⁽E) and (F) Iron silicate rocks from the Iron Formation in the SW Montana. Immega and Klein (1976).

⁽G) Average analyses of the Iron Formation from the Gairlock area,

NW Scotland.

Table No.25

Variations in the concentration of trace elements (p.p.m.) in the metasediments, and rocks of the silicate and oxide facies from the Gairloch area.

Trace elements	Metasedimen	ts Average	Oxide facie	s rocks Average	Silicate facies rocks Average		
Ba	* o - 848	188.2	5 - 40	19•5	7 - 59	29	
Cr	35 - 219	106.3	54 - 92	61.8	46 - 177	116.9	
Nb	6 - 67	30.5	4 - 18	12.5	7 - 56	12.2	
Ni	21 - 192	103.4	14 - 54	14.3	21 - 376	64.6	
Pb	10 - 66	28.8	3 - 7	5.8	* 0 - 21	10.5	
Rb	* 0 - 147	32. 5	* 0 7		0	_	
Sc	* 0 - 40	18.6	1 - 9	1.3	1 - 62	16.4	
Sr	* 0 - 156	60.6	2 - 32	4.8	* 0 - 21	6.4	
V	* 0 - 203	104.7	5 - 44	6	* 0 - 112	73.8	
Y	* 0 - 35	18.1	3 - 17	5.8	* 0 - 42	26.5	
Zr	* 0 - 255	92.7	* 0 - 17	_	* 0 - 253	62.9	

^{*} The lower figure (o) indicates below detection limit.

Table No.26

Comparison between the trace element concentration (p.p.m.) in the Iron Formation rocks from the Gairloch area and the other Iron Formations.

Elements	А	В	C	D	E	F	G	Н	I
Ba	x	9 1	181	179	x	х	19.5	29	27
Cr	22	35	51	2 8.5	17.1	4.47	61.8	116.9	72.5
Nb	x	х	x	x	х	х	12.5	12.2	17.5
Ni	70	14.5	60	20.5	х	x	14.3	x 64.6	14.5
Pb	9	х	х	Х	х	х	5.8	10.5	12
Rb	х	x	х	х	x	х	-	-	-
Sc	x	x	х	х	0.25	0.05	1.3	16.4	1
Sr	х	x ·	х	х	х	х	4.8	6.4	5
V	1460	44.5	74	35	x	х	6	73.8	10.5
Y	х	х	х	х	Х	x	5.8	26.5	6.5
Zr	х	31	101.5	17.3	х	х	-	⁺ 62.9	

- x not determined
- not detected
- x exclude sample No. 16
- + exclude sample No. 17A
- A Magnetite mineral from the Grangesberg Iron Formation Sweden.
 Annersten and Ekstrom (1971)
- B Average trace element in Hematite
- C Average trace element in Mangano-ferruginous material
- D Average trace element in Itabirite

 B, C & D are from the Minais Gerais Iron Formation (Brazil)

 Barabosa and Grossi Sad (1973)
- E Average trace element in the oxide facies rocks
- F Average trace element in the silicate facies rocks E & F from the Sokoman Iron Foramtion Fryer (1977)
- G Average trace elements in the oxide facies rocks
- H Average trace elements in the silicate facies rocks G & H from the Iron Formation in the Gairloch area
- I Average trace elements in the Magnetite mineral from the Gairloch

Table No.27

X.R.F. Standard values (P.P.M.) for (Garnets (Grunerites (Magnetite (Rocks)))

Element	Top Value	3:1	1:1	1:3	1:9	Group
Sr	100	75	50	25	10	\uparrow
Y	100	75	5 0	2 5	10	
Zn	500	375	250	125	50	(A)
V	5000	3750	25 00	1250	500	
Pb	500	375	250	125	50	1
Zr	500	3 75	250	125	50	1
Rb	100	75	50	25	10	
Cr	500	375	250	125	50	(B)
Cu	200	1 50	100	50	2 0	
Ni	500	375	25 0	12 5	50	\downarrow
Sc	500	3 75	250	12 5	50	^
Ba	500	37 5	250	125	50	
Ga	100	75	50	25	10	(c)
Nb	100	75	50	25	10	\downarrow

Groups A.B&C. - Trace element combinations run together.

Table No. 28
Working conditions of the X-Ray Diffractometer

Variables	Cu k∝1 Rad.	Co kel Rad.
1-17	35	30
kV	33	30
mA.	20	16
Filter	Ni	Fe
2θ range	9 - 60° 20	32 - 74 ⁰ 2 0
Goniometer speed	½°/min.	½°/min.
Chart speed	2 cm/min.	2 cm/min.
Slit(divergence)	1 mm	1 mm
Slit(receiving)	O.1 mm	0.1 mm
Time constant	3 sec.	3 sec.
Proportional counter	1850 V	1920 V
Statistical error	5%	5%
Counter/min.	4X10 ³	4X10 ³
Method	Smear on glass	Smear on glass

Table No.29
Working condition for the X-Ray Fluorescence Spectrometer

Element	Atomic	Rad.	Tube	k.V	т.А	Crystal	Colli-	Counter	Vacuum/	hethod	Time	Counts	26peak	peak	pos.	38GD	(1)	P4600	(2)		[D e s .65
	No.	line	 				mator		Airnath	<u> </u>				6,550	: KOS+	chan	[40.Sa	chan	1056	(1)	
Х	19	Kα	Cr	40	8	PE	Coarse	Flow	Vacuum	ABS. RAT	F.C	3x10 ⁴	50.27	5	1	3	3	-~		32,20	
Ti	22	Kac	Cr	40	8	Li F ₂₀₀	Fine	Flow	Vacuum	ABS. RAT	F.C	3×104	86.02	4	10	5	15			88,50	
Si	14	You	Ct	40	16	PE	Coarse	Flow	Vacuum	ABS. RAT	F.C	3x10 ⁴	109.02	6	5	7	5			112.00	
Ca	20	Koc	Cr	40	8 .	LiF ₂₀₀	Fine	Flow	Vacuum	ABS. RAT	F.C	3x10 ⁴	112.99	8	9	9	7			115.50	
Al	13	K≪	Ĉr,	60	24	PE .	Coarse	Flow	Vacuum	ABS. RAT	F.C	3x10 ⁴	144.88	10	8	11	17			138.50	
'Mn	25	Κ∝	W	50	50	LiF ₂₂₀	Fine	Flow	Vacuum	ABS.	F.C	104	95,12	4	12	2	14			97.00	
гe	26	K≪	W	16	16	LiF ₂₂₀	Fine	Flow	Vacuum	APS. RAT	F.C	104	85.62	5	13	3	6			8 7. 50	
Ng	12	K≪	Cr	40	35	KAP	Coarse	F1ow	Vacuum	ABS.	F.C	104	43.45	10	10	11	12			46,50	
P	15 .	Κ≪	Cr	60	24	GE	Coarse	Flow	Vacuum	ABS. RAT	F.C	104	140.93	12	14	13	18			145.00	
Na	11	Χ∝	Cr	40	40	Teap	Coarse	Flow	Vacuum	ABS. RAT	F.C	104	54.81	14	11	15	13			36,50	
Pb	82	LB1	Мо	30	20	LiF ₂₂₀	Fine	Scin t.	Vacuum	ABS.	40 Sec	F.T	40.21	13	20	14	14	15	15	39,85	61.00
Şc	21	Κœ	Cr	60	24	LiF ₂₀₀	Fine	Flow	Vacuum	ABS.	40 Se c	F.T	97.60	3	5	4	6	7	17	95,50	82,34
v	23	K∝	Cr	60	24	LiF ₂₀₀	Fine	Flow	Vacuum	ABS. RAT	F.C	10 ⁴	76.83	5	7	6	15		-	75.50	
Cr	24	Χ∝	W	60	32	LiF ₂₀₀	Fine	Flow	Vacuum	ABS. RAT	F.C	10 ⁴	69.24	6	3	7	3			74,50	
::i	28	K∝	W	60	32	LiF ₂₂₀	Fine	Flow	Vacuum	ABS. RAT	F.C	104	71.13	8	4	9	7			73,000	
Rb	37	K∝	No	80	20	LiF ₂₂₀	Fine	Scint.	Vacuum	ABS.	40 Sec	F.T	37.78	7	7	2	1	3	3	38.50	36.70
Sr	38	κ∝	Мо	80	20	LiF ₂₂₀	Fine	Scint.	Vacuum	ABS.	40 Sec	F.T	35.66	8	8	3	3	4	4	36,70	34,70
Y	39	Χ×	No	80	20	LiF ₂₂₀	Fine	Scint.	Vacuum	ABS.	40 Sec	F.T	33.69	9	9	4	4	5	5	34,70	3 2. 90
Zr	40	K≪	Мо	80	20	LiF ₂₂₀	Fine	Scint.	Vacuum	ABS.	40 Sec	F.T	31.88	10	10	5	5	6	6	32.90	31.5
Mo kec		Кес	Мо	80	20	LiF220	Fine	Scint.	Vacuum	ABS.	40 Sec	F.T	29,90	11	11						
Ба	56	LB2	W	50	30	LiF ₂₂₀	Fine	Flow+	Vacuum	ABS.	40 Sec	F.T	115.10	10	21	11	19	12	20	113.90	117.00
NЬ	41	K∝	и	60	30	LiF ₂₂₀	Fine	Scint.	Vacuum	ABS.	40	F.T	30.23	13	2	14	13	15	14	29.80	3 0.80

Table No.30

The detection limits for major & trace elements (X.R.F.)

(a) Major Elements (Wt%)

Element	Rocks %	Garnet	Grunerite	Magnetite
к	0.002	mate days		***
Ti	0.003	**** *****		wee was
Si	0.03			
Ca	0.01			
A1	0.02			
Mn	0.001			
Fe	0.01			
Mg	0.12			
P	0.004			
Na	0.04	***		

(b) Trace Elements (P.P.M.)

Element	Rocks %	Garnet	Grunerite	Magnetite
Pb	6	5	4	11
Sc	1	1	3	1
v	3	3	7	3
Cr	2	2	2	1
Ni	4	3	2	4
Rb	3	2	2	
Sr	2	2	2	
Y	2	2	2	
Zr	8	10	8	
Ва	37	44	34	
Nb	55	50	55	

Table No.31

Precision determination (X.R.F.) of Banded Iron Formation and the metasediments for the major and trace elements.

(a)

Major Element contents									
Element	Rocks %	Garnet	Grunerite	Magnetite					
K	0.002								
Ti	0.01		1000 SHIP	and tipe					
Si	1.00		- -	***					
Ca	0.03								
A1 < 6%	0.02								
<12%	0.3								
Mn < 3%	9								
< 8%	0.02								
1	0.24								
Fe<10%	1								
<25%	0.43								
	0 .5 8								
Mg	0.14								
P	0.01	}							
Na	0.04								

(b) Trace Element (P.P.M.)

Element	Rocks %	Garnet	Grunerit e	Magnetite
Pb	9	7	5	1 5
Sc	1	1	4	1
V	6	8	1 6	7
Cr	4 .	4	6	3
Ni	5	6	4	7
Rb	3	3	3	T
Sr	2	2	2	not
Y	3	6	3	measured
Zr	10	18	11	
Nb	80			

APPENDIX FOUR

PHOTOMICROGRAPH

Legends of the photomicrographs

G = Garnet

A = Grunerite

H = Hornblende

Ma = Magnetite

Q = Quartz

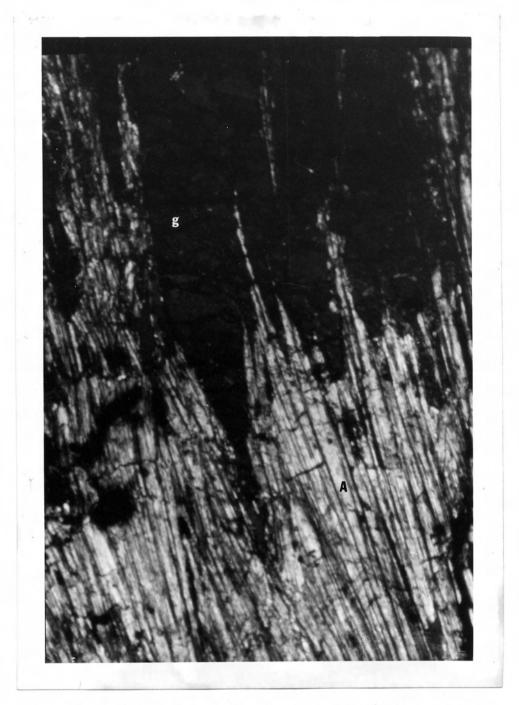
C = Chlorite

B = Biotite

Mu = Muscovite

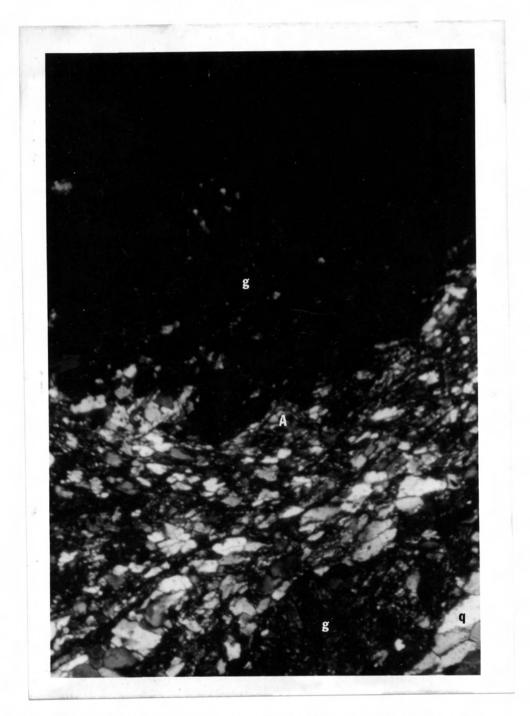
S = Siderite

Plate No. 1



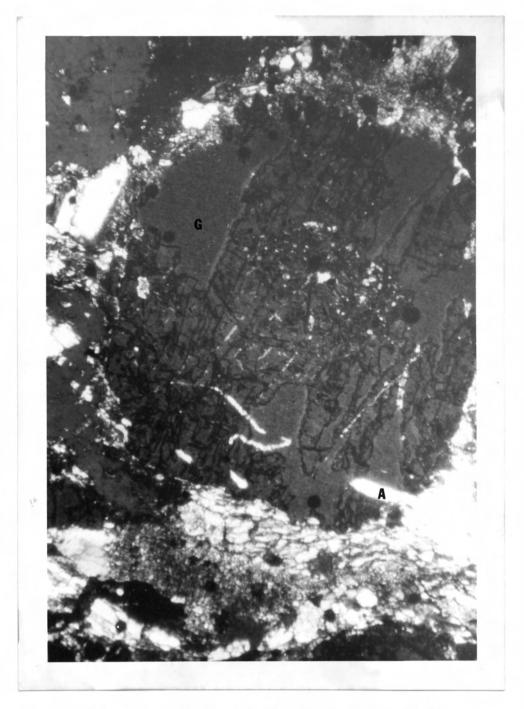
Inter digitation of garnet and grunerite (Sample No. 11B) in the silicate facies rocks from the Iron Formation (X50)

Plate No. 2



Porphyroblastic texture in the silicate facies rocks (Sample No. 21). It also shows anhedral crystals of garnet (X50).

Plate No. 3

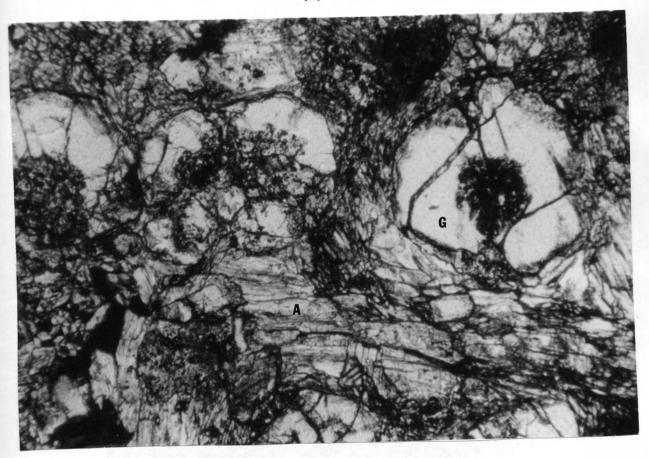


Porphyroblastic texture and the sharp boundary to the core of the garnet crystals (Sample No. 14). It also shows the carbonate, quartz and grunerite inclusions in the garnet. From the silicate facies rocks (50X).

Plate No. 4

Granoblastic texture in the silicate facies rocks (Sample No. 17). It also shows the sharp boundary to the core of some garnet crystals, full of inclusion of carbonate quartz, and a clay mineral. Some crystals of grunerite show an inter digitating relationship with the garnet crystals. (50X)

- A) Under polarized light
- B) Under cross nicols.





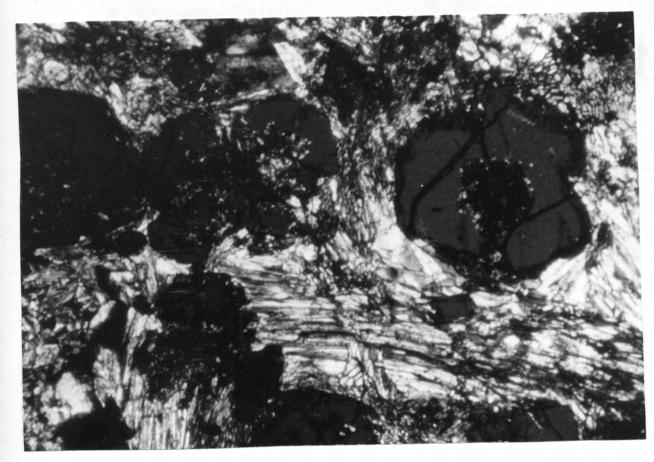
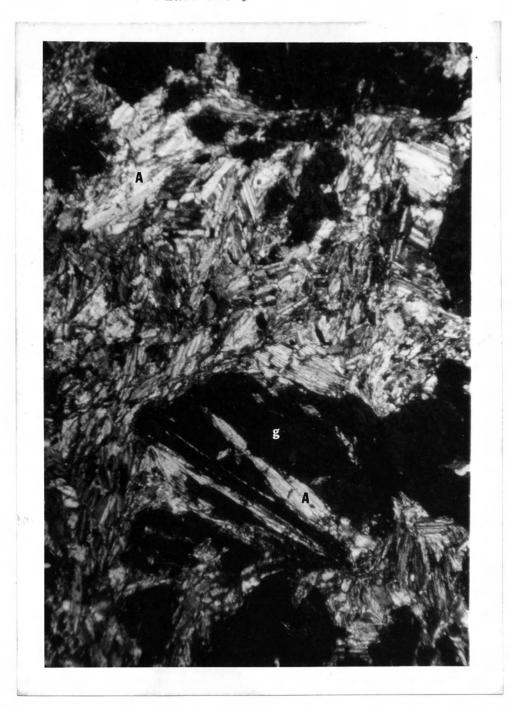
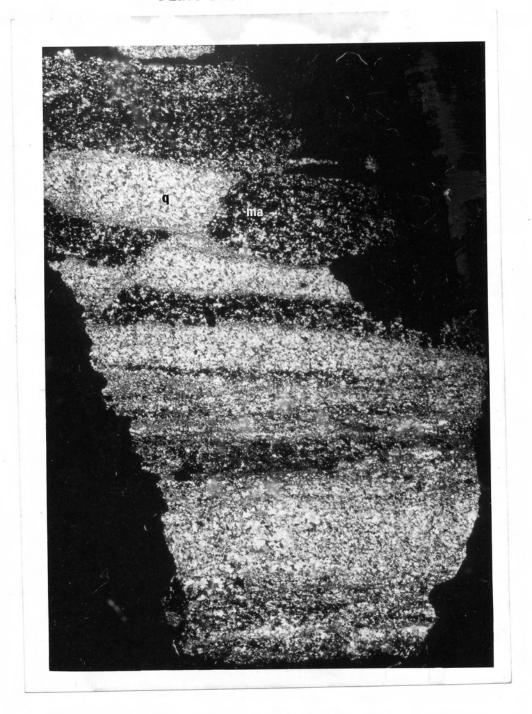


Plate No. 5



Inter digitating of garnet and grunerite crystals in the silicate facies rocks (Sample No. 1(4)). It also shows grunerite crystals as inclusions within the garnet. (X50).

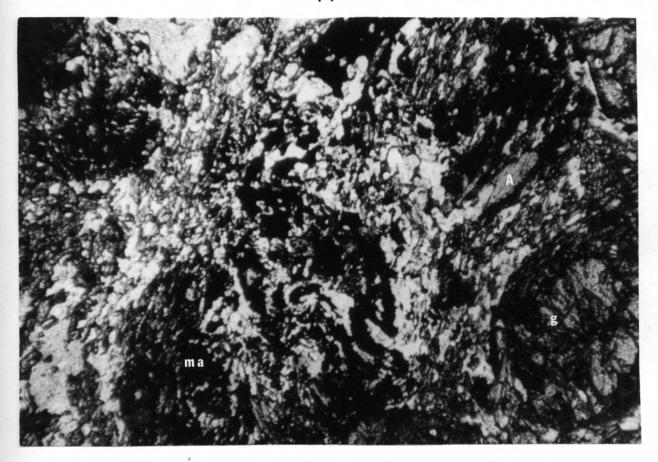
Plate No. 6

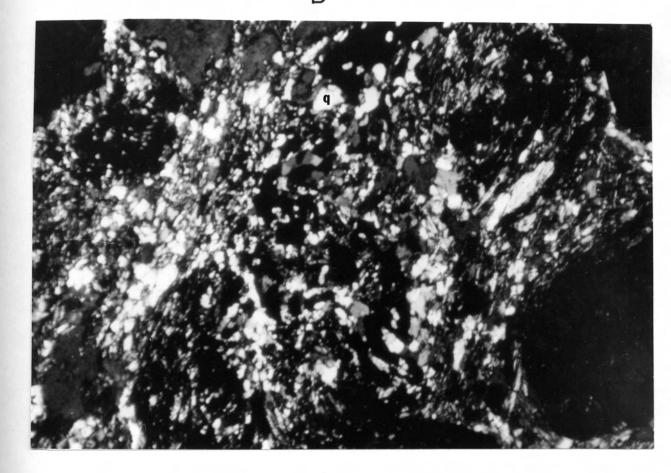


Sample No. 12 shows minor fault in alternating magnetite and quartz bands in the oxide facies rocks (X4).

The porphyroblastic texture of the silicate facies rocks. It also shows the high concentration of magnetite, quartz and grunerite as inclusions in the garnet crystals. (X50).

- A) Under polarized light
- B) Under cross nicols





Alternation between the quartz rich band and the magnetite rich bands in the ferroginous quartzite. (Sample No. 2(2), (X50)).

- A) Under polarized light
- B) Under cross nicols

Α

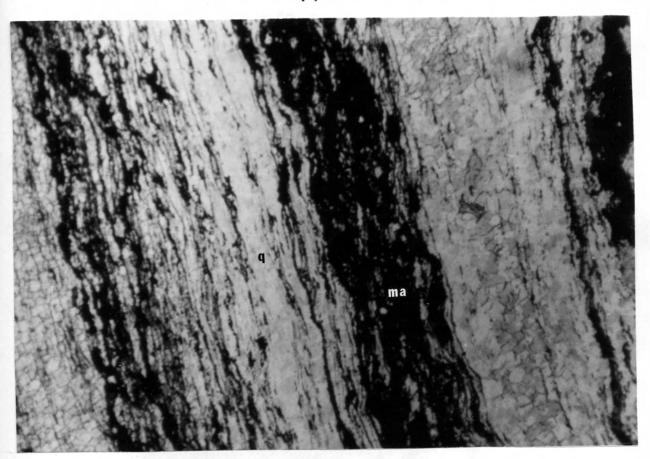




Plate No. 9

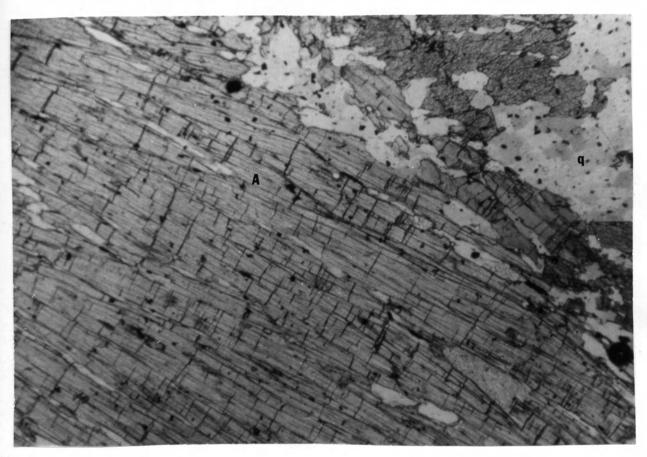


Sample No. 5 shows minor chevron folds in alternating magnetite and quartz bands in the oxide facies rocks (X4)

Magnetite inclusions in the grunerite in the silicate facies rocks. Sample No. 3, (X50).

- A) Under polarized light
- B) Under cross nicols.

Α

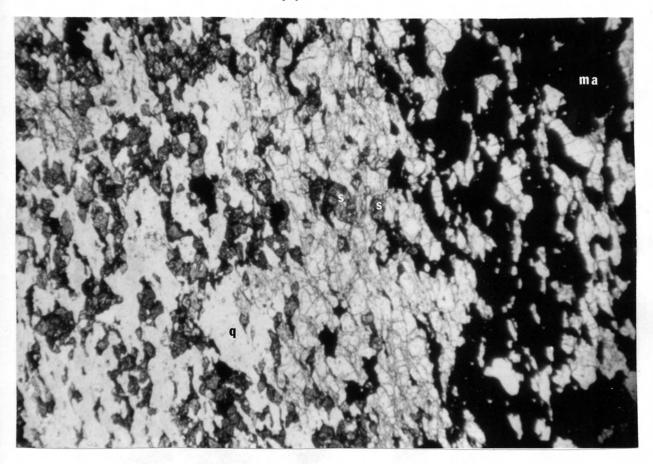




Siderite concentration in a quartz rich band from the oxide facies rocks. Sample No. 12 (M), (X50).

- A) Under polarized light
- B) Under cross nicols

A



B

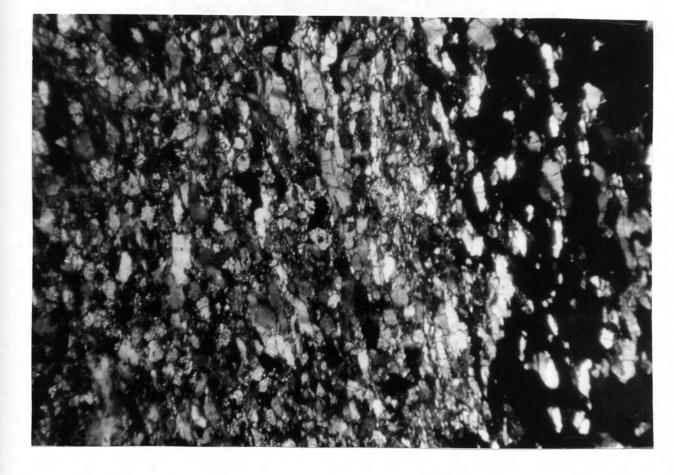
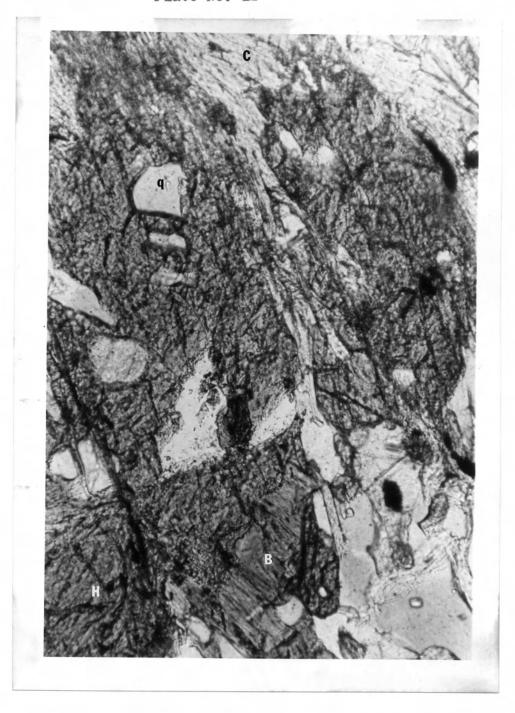


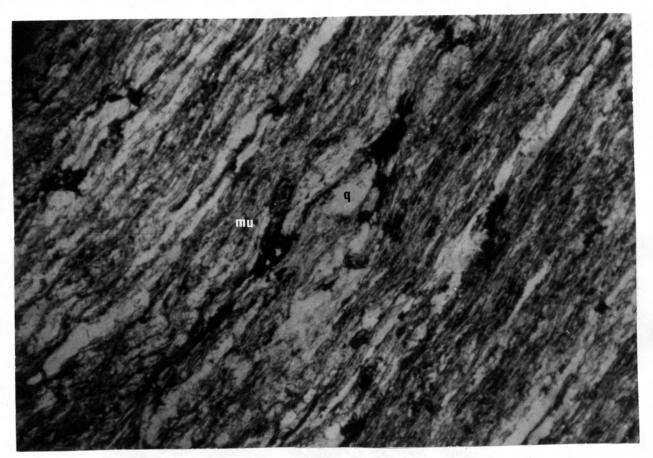
Plate No. 12



Alteration of hornblende to biotite and chlorite in hornblende schist (Sample No. 1(5)), also shows quartz inclusions in the hornblende (X100).

Iepidoblastic texture in biotite-muscovite schist.
Sample No. 2(1), (X50).

- A) Under polarized light
- B) Under cross nicols



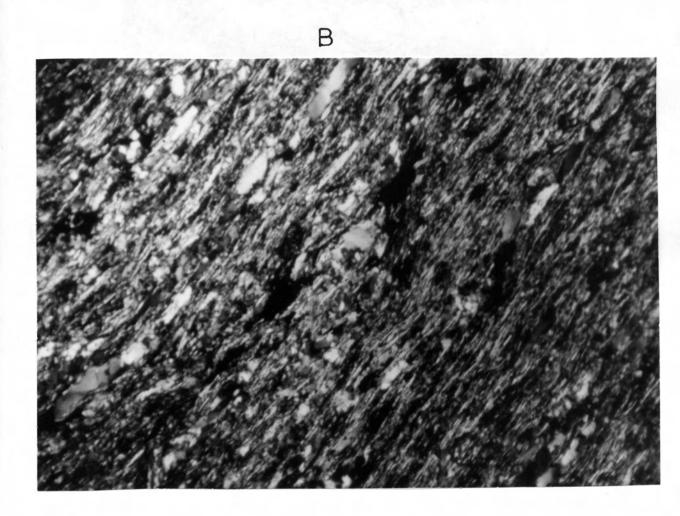
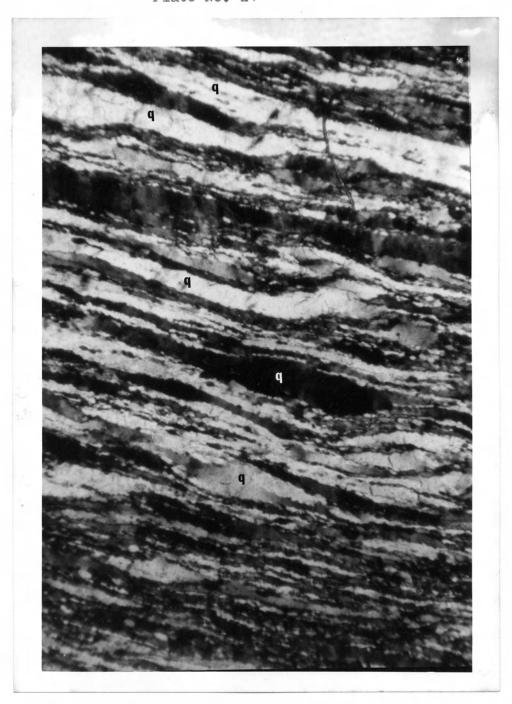


Plate No. 14

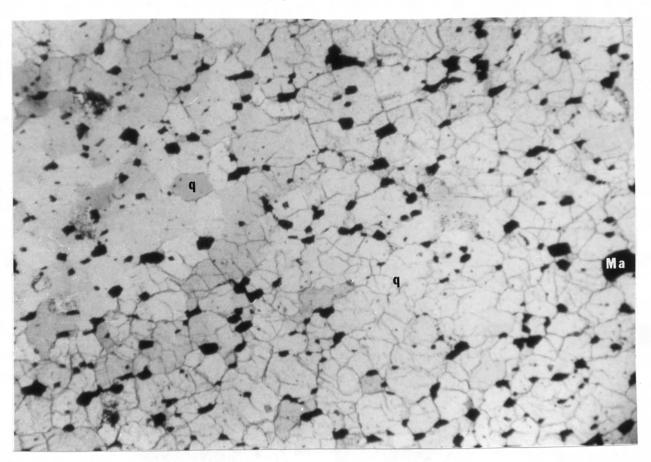


Ribbon structure of the quartz in the quartzite rock. Sample No. 15, (X50)

Magnetite inclusions in the granoblastic quartz in the quartzite. Sample No. 4,(X50).

- A) Under polarized light
- B) Under cross nicols

Α



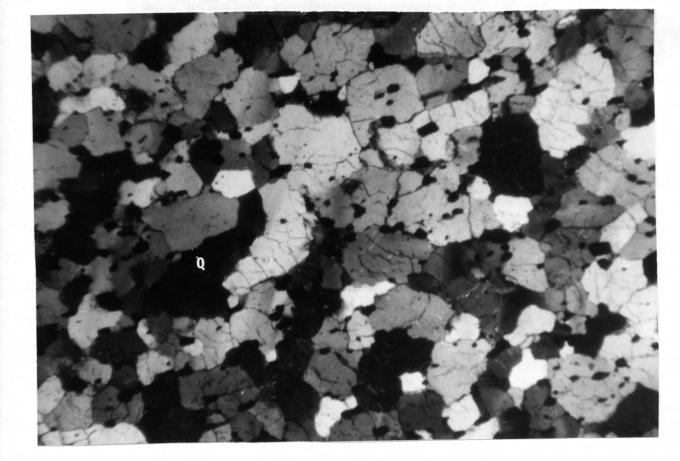
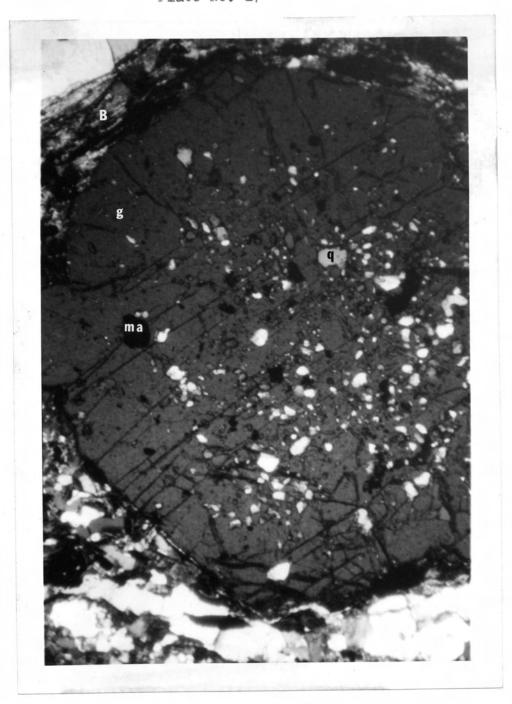


Plate No. 16



Idioblastic crystal of garnet containing quartz inclusions in the hornblende schist. Sample No. 19, (X50)

Plate No. 17



Poikiloblastic texture of garnet in the biotite garnet schist. Sample No. 20, (X50).

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