PYRRHOTITE COMPOSITION AND ITS RELATIONSHIP TO ACID DRAINAGE POTENTIAL IN THE HALIFAX FORMATION, MEGUMA GROUP, NOVA SCOTIA

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Submitted in Partial Fulfilment of the Requirements
for the Degree of Bachelor of Science, Honours
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March, 1996

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DATE April 9, 1996

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TITLE Pyrrhotite Composition and its Relationship to Acid Drainage Potential in the Halifax Formation, Meguma Group, Nova Scotia

Degree BSc Convocation ________ Year 1996

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Abstract

The physical disruption of sulphidic slates of the Halifax Formation of the Meguma Group in Nova Scotia, leads to oxidation of sulphides and the generation of acid rock drainage (ARD). Acid runoff has been a serious problem at the Halifax International Airport (HIA) since the early 1960's, resulting in fish kills, as well as severely degraded water quality and aquatic habitat in receiving streams. The seriousness of these accidents and the high cost of abatement and remediation procedures have lead to revised guidelines by the Nova Scotia Department of Environment (1995) which require strict predictive test procedures before allowing physical disruption of Halifax Formation slates.

Previous ARD studies in Nova Scotia have not considered in detail the mineralogy, texture, distribution and mode of occurrence of sulphides nor how these factors may influence the potential for ARD. Recently, research at the Department of Earth Sciences, Dalhousie University, Halifax, N.S., has shown that the most abundant sulphide from the problem area of the HIA is monoclinic pyrrhotite (Fe_7S_8) which is the most iron-deficient and magnetic form of pyrrhotite. It also oxidizes substantially faster than pyrite, and thus generates damaging pulses of ARD.

Due to the widespread distribution of the Halifax Formation throughout southwestern Nova Scotia, it is important to determine the type and composition of sulphides in other areas. Representative samples of sulphidic slates from the Halifax Formation were collected in the field and from drillcore at four locations throughout southwestern Nova Scotia, in areas with different geological settings, such as proximal to distal from granitic intrusions and contrasting in trace element lithochemistry, to obtain a variety of mineralogical assemblages.

Petrographic, microprobe and X-ray diffraction work confirm that pyrrhotite composition is consistent and relatively homogeneous regardless of geological environment and is of the monoclinic type, thus posing the worst risk in terms of ARD pulses when the sulphidic rocks are exposed to air and water. Two widely accepted acid drainage static tests, the BC Research Initial Test and the US Environmental Protection Agency's Acid-Base-Accounting procedure, were performed on samples from the four field areas. The two tests yield slightly different results of the samples, but confirm that these rocks are potential net acid producers, even though some contain carbonates.

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Acknowledgements

I especially wish to thank my thesis advisor, Dr. Marcos Zentilli for his kindness, supervision and the constant encouragement he extends to all of his students; and Don Fox for his patience, understanding and guidance throughout the preparation of this thesis. I am quite amazed they were able to guide me through the horrors of chemistry and instill in me the desire to learn more. I truly appreciate the confidence they both had in me.

I thank our thesis class professor Dr. Martin Gibling for his time and dedication; Gordon Brown for the thin section preparation; Robert MacKay, for his assistance with the microprobe and Nick Wilson, for his help in taking the photomicrographs.

I would like to thank my family for their love and support. Finally, I wish to thank my classmates, who inspire me to work hard and to do my best. I would especially like to mention Vanessa Gale, whose friendship has made my time at Dalhousie pleasant and memorable; and my friend Lara MacLean, who convinced me I could accomplish anything with a little bit of confidence and a great deal of determination.

CHAPTER 1: INTRODUCTION

1.1 General Statement

Disruption of sulphidic slates of the Halifax Formation, Meguma Group of Nova Scotia has created a serious and costly environmental problem in the province (King, 1985; Manchester, 1986; Worgan, 1987) . Acid rock drainage (ARD), resulting from acid generation and metal liberation from oxidation of sulphides contained in the slates, has created toxic run-off that is poisoning streams, lakes and drinking water sources. Once started, ARD can persist for many years and it is very difficult and costly to mitigate. The severity of ARD depends on many factors including the type, abundance, texture and grain size of the sulphides present, the availability of oxygen and water, local climatic conditions and the nature of the rock unit disruption (ie. construction, tailings pile). This thesis examines the composition and texture of sulphide minerals in relation to ARD in four selected areas within the Halifax Formation. Particular emphasis is on pyrrhotite compositions and textures.

Accurate prediction of ARD potential prior to development is a very important component of landuse planning. Two widely accepted tests, the BC Research Initial Test and the US Environmental Protection Agency's Acid-Base Accounting procedure, are static analyses used to predict whether or not a sample has the potential to produce ARD. This study also examines mineralogy and lithologic variation in the four selected representative areas within the Halifax Formation, and how these factors may influence the results of the two static ARD prediction procedures.

1.2 **Acid Rock Drainage - Definition**

ARD results from the oxidation of sulphide minerals. For example, sulphuric acid is generated when pyrite is exposed to oxygen and water. This is described in the following equation (Bruynesteyn and Duncan, 1979):

$$4FeS_2 + 15O_2 + 14H_2O \Longrightarrow 4Fe(OH)_3 + 8H_2SO_4 \qquad (1.1)$$

This equation represents the production of two moles of sulfuric acid per mole of pyrite and the complete hydrolysis of ferric iron. Oxidation can proceed inorganically, but the rate is greatly accelerated by acidophilic bacteria such as *Thiobacillus ferrooxidans*. In nature, ARD is more complicated than this simplified formula. The complete chemical reaction involved in acid generation from pyrite is a multi-staged process that can be characterized by the following four reactions (Stumm and Morgan, 1981):

Reactions:

$$FeS_2(s) + 7/2\ O_2 + H_2O \Longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1.2)$$

$$Fe^{2+} + 1/4\ O_2 + H^+ \Longrightarrow Fe^{3+} + 1/2\ H_2O \qquad (1.3)$$

$$Fe^{3+} + 3H_2O \Longrightarrow Fe(OH)_3(s) + 3H^+ \qquad (1.4)$$

$$FeS_2(s) + 14\ Fe^{3+} + 8H_2O \Longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (1.5)$$

The oxidation of sulphide to sulphate releases dissolved ferrous iron and acidity into the water (equation 1.2). Subsequently, the dissolved ferrous iron is oxidized to ferric iron (equation 1.3). Ferric iron hydrolyses to form insoluble "ferric hydroxide", releasing more acidity into the water (equation 1.4). Ferric iron can also be reduced by pyrite itself (equation 1.5), where sulphide is again oxidized and hydrogen ions are released along with additional ferrous iron which may re-enter the reaction cycle via the reaction in equation 1.3.

Pyrite oxidation has been the focus of research because of its prevalence in rocks associated with coal deposits (Paine, 1987; diPretoro and Rauch, 1988; Erickson and Hedin, 1988). However, the proportion of pyrrhotite to pyrite at many base and precious metal mines is relatively high and in some instances, pyrrhotite is the only significant waste sulphide present (Nicholson and Scharer, 1994). The overall oxidation of pyrrhotite by oxygen can be shown by the general equation (Nicholson, 1994):

$$Fe_{(1-x)}S + (2-x/2)\ O_2 + (x)\ H_2O = (1-x)\ Fe^{2+} + SO_4^{2-} + (2x)\ H^+ \qquad (1.6)$$

In equation 1.6, x represents the iron-deficiency in pyrrhotite and can vary from 0.0 to 0.125. At the end member where x=0 (troilite - FeS) no H^+ ions are produced. However, the end-member where x=0.125 (monoclinic pyrrhotite - Fe_7S_8) leads to the maximum amount of H^+ ions produced. In this case, one mole of Fe_7S_8 leads to 1/4 moles of H^+ ions produced. Therefore, for pyrrhotite, the amount of H^+ ions released into solution depends on its composition. Table 1.1 lists the different structures and chemical compositional ranges of pyrrhotite.

Typically, ARD has a pH of < 3.0 and high concentrations of sulphate (SO_4^{2-}) and ferrous iron (Fe^{2+}). Due to low pH conditions, ARD may also contain high concentrations of Al and Mn, as well as trace elements such as Cu, Zn, Ni, and Pb, if these are present in the host rock. Because of these conditions, ARD is responsible for the degradation of water quality in many

Table 1.1: Main pyrrhotite phases, chemical composition and structure type (Craig and Scott, 1982).

Troilite	FeS	Hexagonal
Hexagonal Pyrrhotite	$Fe_{1-x}S$	Hexagonal
MC-type Pyrrhotite	$Fe_{1-x}S$	Hexagonal ?
NA-type Pyrrhotite	$Fe_{1-x}S$	Hexagonal ?
NC-type Pyrrhotite	$Fe_{1-x}S$	Hexagonal ?
5C Pyrrhotite	Fe_9S_{10}	Hexagonal
11C Pyrrhotite	$Fe_{10}S_{11}$	Orthorhombic
6C Pyrrhotite	$Fe_{11}S_{12}$	Orthorhombic?
Anomalous	Fe_7S_8	Triclinic ?
4C Monoclinic	Fe_7S_8	Monoclinic

surface and groundwater sources. Most river and lake life cannot survive in pH levels of less than 5.0, therefore the destruction of ecosystems may be attributed to ARD in areas where sulphide-bearing rocks are disrupted (Paine, 1987). Table 1.2 shows some chemical parameters of ARD seepage from a sulphidic slate waste rock pile at the Halifax International Airport. The high values indicate ARD will likely have adverse affects on the surrounding environment. If sulphide-mineralized rocks are left undisturbed, they are less likely to produce ARD. However, activities such as mining and construction of highways expose sulphides to oxygen and water. Problems are intensified when these rocks are crushed during aggregate production and ore beneficiation, greatly increasing the surface area of exposed sulphides.

Table 1.2: An example of ARD from the waste rock pile from the Halifax International Airport before it has been treated (Lund, 1987), compared with the acceptable limits for freshwater aquatic life (Canadian Water Quality Guidelines, 1987). Note: ARD exceeds the acceptable limits for freshwater aquatic life by several orders of magnitude.

HALIFAX INTERNATIONAL AIRPORT	LIMITS FOR FRESHWATER AQUATIC LIFE
Fe = 3 800 mg/L	Fe = 0.3 mg/L
Al = 3 247 mg/L	Al = 0.005 - 0.1 mg/L
SO_4 = 27 000 mg/L	SO_4 = (?)
pH 2.4 - 3.2	pH 6.5 - 9.0

1.3 ARD in Nova Scotia

Geological units with significant sulphide mineralization are present within the Cambro/Ordovician metasedimentary rocks of the Meguma Group, in Nova Scotia. In particular, the sulphidic black slates of the Halifax Formation and the Goldenville-Halifax transition zone (GHT) are a source of ARD. These rock units are geographically widespread in the southwestern mainland of Nova Scotia, thus it is difficult to avoid their disruption (Fig 1.1).

In the past, Halifax Formation rocks have been exposed and redistributed for highway construction, industrial and urban development, and quarrying in various places throughout the province. It is easily mined as a cheap and convenient aggregate. Furthermore, slate is often preferred for quarrying over quartzite because of its inherent lesser hardness and cost of crushing. Environmental impacts documented in Nova Scotia include fish kills, closure of at least one fish hatchery, disruption of public water supplies, contamination of private wells (Table 1.3) and damage to engineering works (Hennigar & Gibb, 1987). The problem came to public attention during the building of the Halifax International Airport (HIA) in September of 1960. The sulphidic slates of the Halifax Formation were disturbed during construction, resulting in high acid run-off and adverse affects on water quality in the Shubenacadie and Salmon River systems. It was not until 1976, when a new hangar was constructed, that a study by the Environmental Protection Service linked fish kills in the Shubenacadie River to the slate disturbances at the HIA (Table 1.4, Environmental Protection Service, 1976).

A great deal of research has been done at the HIA on the general impact of ARD (Lund et al., 1987; King and Hart, 1990; Thompson 1978). Other cases in the province include a study done at Petpeswick Lake, Halifax County, where highway construction through the Halifax

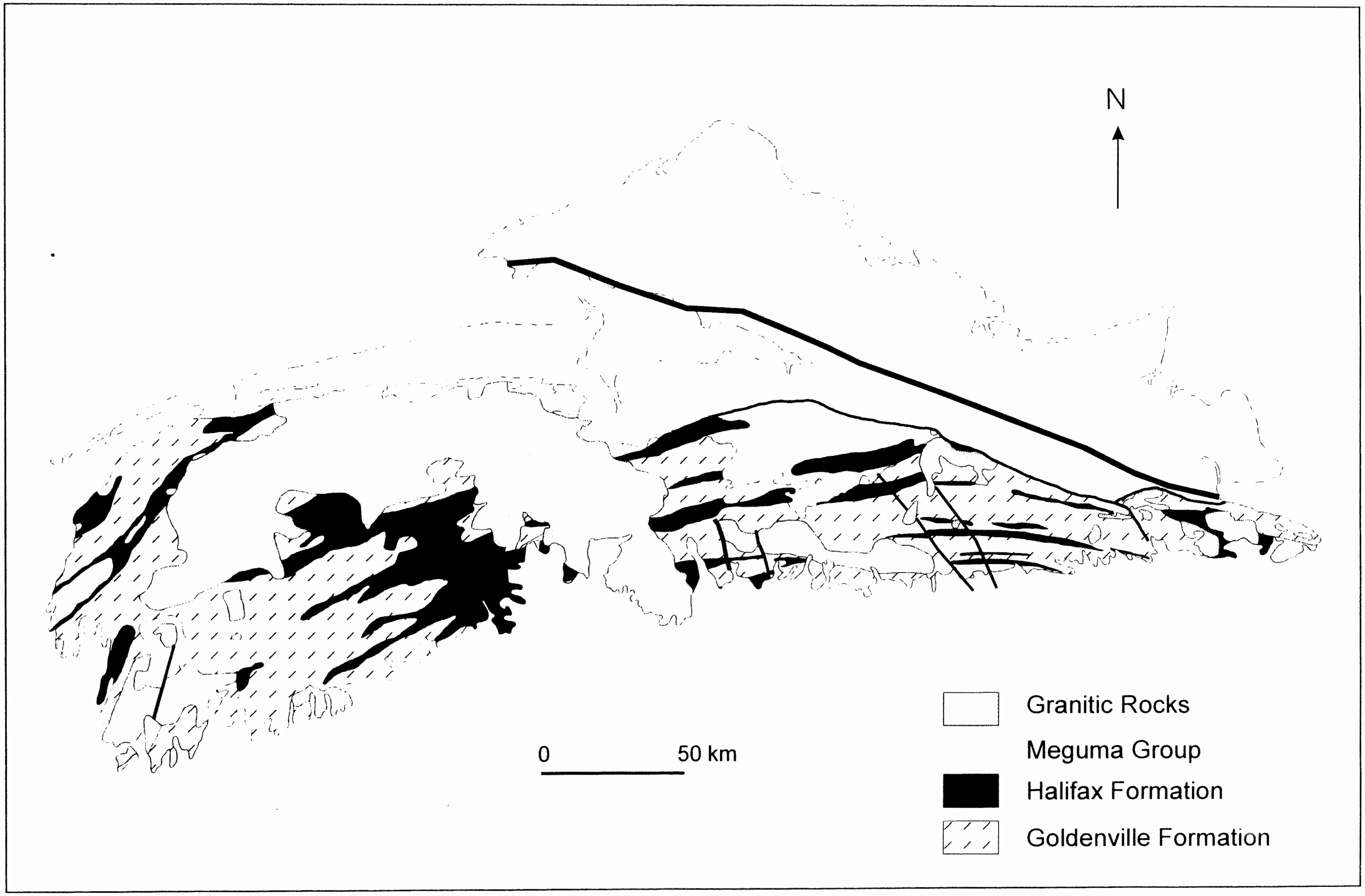

Figure 1.1: Geological map of the Meguma Group in Nova Scotia (modified from the Geological Map of Nova Scotia (1979), NS Department of Mines and Energy.

Table 1.3: pH units of wellwater samples collected at various locations in Halifax County by the Nova Scotia Department of Environment. Note: low pH values and probable causes. In each instance it appears that the wells are contaminated by surface water (Thompson, 1978).

LOCATION	Fall River	Timberlea	Birch Cove
DATE	12/11/76	31/01/76	14/03/74
pH	3.4	3.3	4.2
PROBABLE CAUSE	acid drainage	slate roadbed	slate roadbed

Table 1.4: Fish Kill History and Slate Disturbances at the Halifax International Airport (Environmental Protection Service, 1976).

Slate Disturbances (construction)	Date	Major Fish Kills
Terminal and runways	1957-1960	September, 1960
Imperial Oil	1959-1960	
IMP Hangar (large)	1959	
IMP Hangar (small)	1961	
Air Canada Hangar	1961	
Air Halifax Hangar	1961	October, 1961
Highway slate needs	1965	October, 1965
Avis Service Station	1966	September, 1966
Highway slate needs	1968	November, 1968
Halifax Flying Club	1970	
Mobil Oil Hangar	1972	
Highway Overpass	1974	August, 1974
Aircon Tank Farm	1975	October, 1975
EPA Hangar	1976	September, 1976

Formation lead to ARD problems (Jaques, Whitford and Associates Ltd., 1990). Another study was done to evaluate the effect of acid leachate on water quality near Union Square in Lunenburg County, where sulphidic slates from the Halifax Formation were used to resurface a road (Pettipas, 1979). Studies have also been undertaken concerning the treatment of ARD (Roberts, 1986; Silver, 1988; Kerekes et al., 1984).

Previous geological work has been performed in order to gain an understanding of where the Halifax Formation slates occur and the nature and degree of mineralization in the units. Zentilli et al. (1986) and Graves et al. (1988) studied the lithochemistry of the Goldenville-Halifax transition zone, an area that has been particularly critical with regard to the ARD problem. In other studies, pyrrhotite has been identified as the principle magnetic mineral in the Halifax Formation and its abundance enables the unit to be identified as an area with high readings on aeromagnetic maps for the region (Fig 1.2) (Schwartz and Broome, 1994; King, 1994). Pasava et al. (1995) examined the sulphide mineralogy at the Halifax International Airport and determined the main sulphide mineral is monoclinic pyrrhotite, and that mineralogical investigations are crucial in the risk assessment of ARD. MacInnis et al. (1994) studied the oxidation rates of pyrrhotite and pyrite from drill-core samples taken at the HIA. Pyrrhotite was found to oxidize much more quickly than pyrite, and may therefore be just as harmful (or more so) to the environment as pyrite, even though pyrite contains higher concentrations of sulphur.

Halifax Formation slates that have been affected by intrusion of the South Mountain Batholith (and related granitoid rocks) have also been mentioned in several studies. Schwartz and Broome (1994) consider that magnetic anomalies in the Halifax Formation near granite contacts likely result from magnetite. Samostie (1994) stated that pyrite is less abundant in the slates near

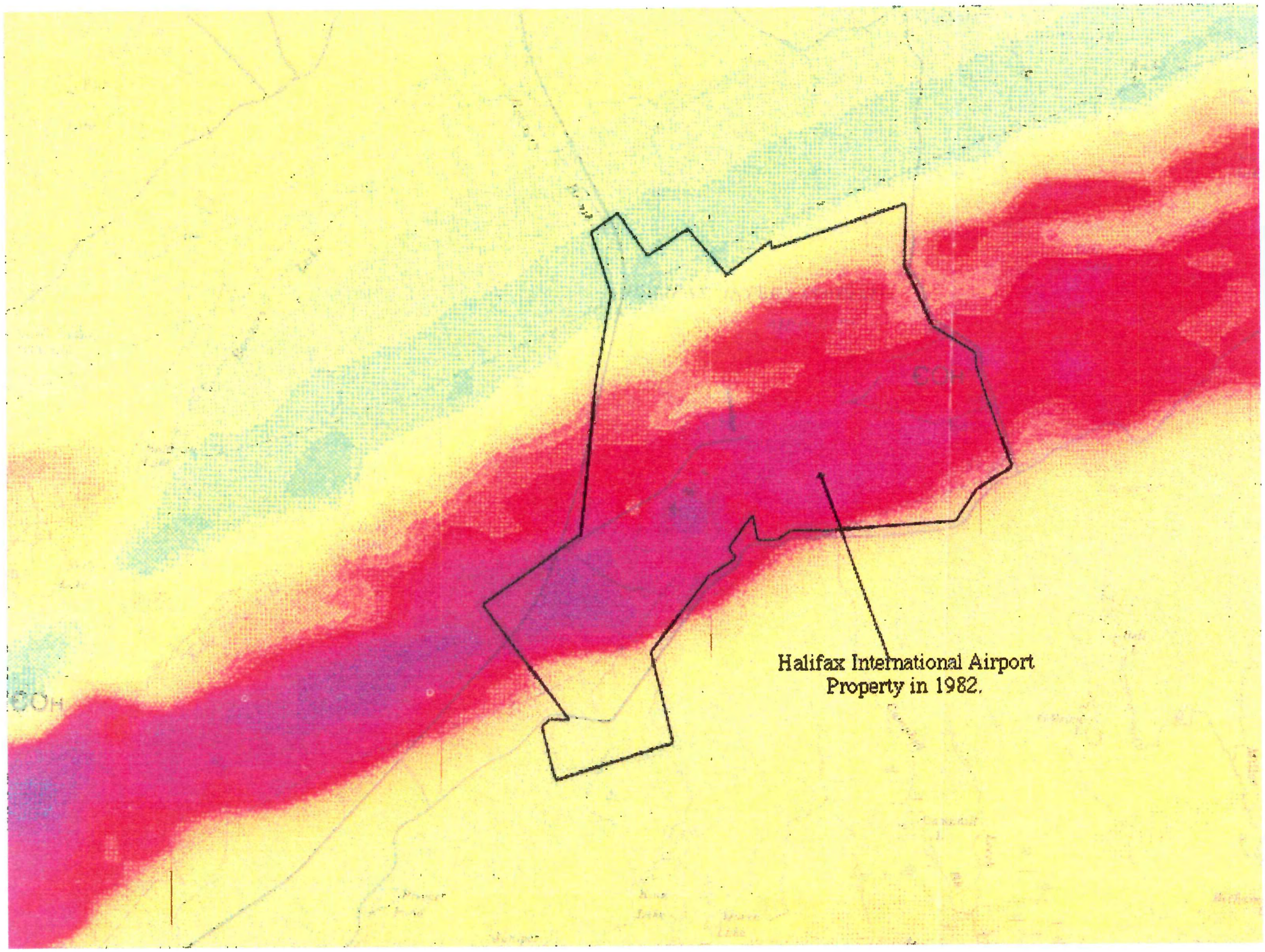

Figure 1.2: High resolution aeromagnetic residual total field map of an area within the Meguma Group near the Halifax International Airport. The red and purple zones indicate magnetically high areas within the Halifax Formation (GSC Map C20, 335G, 1982). Purple areas = 1000 gammas, red areas = 200 gammas, yellow areas = 0 gammas.

granite contacts and therefore these rocks are likely to be much less acid producing than slates away from granite contacts. Clearly these two hypotheses are important for the assessment of ARD.

1.4 Prediction of Acid Drainage Potential

The 1994-95 Nova Scotia Environmental Act defines Sulphide Bearing Material Disposal Regulations under Section 66. These regulations state that prior to developing land that contains sulphide-bearing rock, samples must be collected and analysed to determine the total sulphur and sulphate sulphur content. Test results must be given to an Administrator representing the Department of Environment prior to the start of any work (Environmental Act, 1995).

The B.C. Research Initial Test and the US Environmental Agency's Acid-Base Accounting procedure are predictive static test procedures used to quantitatively measure net acid production potential of the test sample. Acid producing potential is compared to the ability of the sample to neutralize the acid it generates. Both techniques base the maximum acid producing potential on the stoichiometric conversion of the total sulphur content to H_2SO_4. The techniques differ in the method used to determine the neutralizing potential of the sample (Calow et al., 1995). Chapter 4 presents a more detailed discussion of the ARD prediction techniques.

1.5 Purpose and Scope

The purpose of this thesis is to determine if samples selected from four locations within the Halifax Formation are net acid producers. Two of the four sites were chosen close to granite intrusions to see if the degree of metamorphism has an influence on sulphide mineralization and distribution. First, this thesis examines the minerals responsible for ARD, with a focus on pyrrhotite, which is considered to be one of the main acid producers in the Halifax Formation. Pyrrhotite compositions and the role they play in the ARD problem are studied. Secondly, two tests for acid drainage prediction are used to determine if the selected samples are likely to be net acid producers. The influences that mineralogy and different lithologies have on the ARD prediction techniques is evaluated. Results from the two acid drainage predictive techniques are compared to determine whether or not they are in fact accurate and appropriate for assessing ARD potential in the sulphidic slates of the Meguma Group.

1.6 Methodology

Rock samples containing sulphides were collected in the field in September and October, 1995 from selected areas in the Halifax Formation. Seven samples were taken from drillcore from the Eastville lead-zinc deposit. Pyrrhotite was located visually and with the aid of a magnetic susceptibility meter. Polished thin sections were made from these samples and minerals were studied using petrographic and ore microscopic techniques.

The microprobe was used to preform chemical analyses on the minerals and confirm their identification. A JEOL 733 electron microprobe was used to analyse the mineral chemistry of the selected grains. It is equipped with four wavelength dispersive spectrometers and an Oxford Link eXL energy dispersive system which was used for all elements. Resolution of the energy dispersive detector was 137ev at 5.9Kev. Each spectrum was acquired for 40 seconds with an accelerating voltage of 15 Kv and a beam current of 15nA. Probe spot size was approximately 1 micron. The raw data was corrected using Link's ZAF matrix correction program. Instrument calibration was performed on cobalt metal. Instrument precision on cobalt metal (x=10) was +/- 0.5% at one standard deviation. Accuracy for major elements was +/- 1.5 to 2.0% relative. Geological standards for sulphides were used as controls. These included arsenopyrite, chalcopyrite, pyrrhotite, sphalerite and metals.

Powders were made from 17 samples and analysed for total sulphur at the Technical University of Nova Scotia (Cyril Cole - analyst). Six of these samples were selected for assessment of net acid producing potential by two standard tests (outlined in Chapter 4). X-ray diffraction analyses on sulphides were performed on four selected samples.

1.7 Organization

Chapter two of this thesis discusses background information concerning the geology of the study area. Chapter three examines the mineralogy of the samples that were chosen. Results of the ARD predictive tests are given in Chapter four. Discussion, conclusions and recommendations for future work are included in Chapter five.

CHAPTER 2: SULPHIDIC ROCKS IN THE MEGUMA GROUP

2.1 The Meguma Group

The following paragraphs present an overview of the Meguma Group. The material was taken from the following references: Schenk, 1983, 1995 [1]; Graves and Zentilli, 1988; Binney et al., 1986; Henderson et al., 1986; O'Brien, 1985, 1986 and Waldron and Graves, 1987.

The Cambro-Ordovician Meguma Group crops out throughout southern Nova Scotia (Fig 1.1) and it consists of a 12-14 km thick, interstratified assemblage of clastic metasedimentary rock. During the Acadian Orogeny, the Meguma Group was intruded by granitoid plutons, such as the South Mountain Batholith. The unit is regionally metamorphosed from greenschist to amphibolite facies. Major kilometre scale, polydeformed, upright east-west trending folds occur, with anticlinal and synclinal fold axis parallel to the coastline of southwest Nova Scotia. Cleavage is well-developed throughout much of the group. The Meguma Group comprises two main parts: a lower unit of thickly layered metawacke interbedded with slate (Goldenville Formation) and an upper unit of slate interbedded with thinly layered metasiltstone (Halifax Formation). Between these two units is the Goldenville-Halifax Transition zone. All of these units are discussed in more detail below.

2.1.1 Goldenville Formation

The Goldenville Formation underlies the Halifax slates. It is the basal member of the Meguma Group and mainly consists of massive structureless quartz metawacke with minor

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[1] New nomenclature has recently been proposed by Schenk (1995) for these units, but it is not incorporated in this thesis.

interbedded slate. This formation is not the focus of this study although locally sulphide mineralization is known to be abundant.

2.1.2 Halifax Formation

The Halifax Formation is the younger of the two units that form the Meguma Group and it consists mainly of black graphitic slate with minor interbedded greywacke. The slate has a well-developed cleavage with sulphides concentrated in the cleavage planes. Pyrrhotite and pyrite are locally abundant in both the slate and the greywacke. Approximately 125 000 km^2 of the Halifax Formation is exposed in southern Nova Scotia, due to the folding pattern of the Meguma Group.

2.1.3 Goldenville - Halifax Transition Zone (GHT)

The Goldenville and Halifax formations occur as long alternating bands striking nearly parallel to the southern coast of Nova Scotia (Fig 1.1). The contact between the two formations is fairly sharp in the east and gradational in the central and western part of the Meguma Group outcrop. This transition zone is marked by a finely laminated, manganiferous unit, locally rich in calcareous or calc-silicate nodules and coticules (spessartine quartzite). It contains abundant sulphides and a relatively high concentration of metals. These are mostly syngenetic deposits that represent a decrease in the supply of dissolved oxygen at the sediment-water interface during deposition, which resulted in an increased amount of sulphides formed during diagenesis.

2.1.4 Mineralogy and Geochemistry

Sulphides and oxides are both present in the Meguma Group. Sulphides are predominant in the Halifax Formation and include pyrrhotite, pyrite, sphalerite, galena, chalcopyrite and arsenopyrite. Oxides occur as discrete crystals and include ilmenite and rutile. At Eastville, sphalerite and galena occur in significant amounts, deposited from metal-rich brines during the deposition of the sediments. Most iron sulphides were probably formed by early diagenetic reduction of iron in the carbonaceous sediment and were altered and deformed during later periods of metamorphism.

Metals occurring in the GHT include gold, tungsten, arsenic, antimony, manganese, lead and zinc. They are concentrated within less than 10% of the apparent stratigraphic thickness of the Meguma Group and are thus considered indicators of the actual transition zone (Table 2.1). The potential for water contamination from the GHT rocks is serious, not only from acid drainage, but by contamination by a variety of toxic elements. Cases of arsenic poisoning of wells in the Waverley area have been linked to past mining operations (Gibb et al., 1977). Areas of As and Sb enrichment have been identified around Lunenburg as well (Rogers and Ogden, 1992).

Abundant sulphide mineralization and above average metal concentrations in the Goldenville-Halifax transition zone make these areas especially susceptible to ARD problems. However, sulphide mineralization occurs locally throughout the Halifax Formation, therefore problems are not only restricted to areas in the transition zone.

2.1.5 Metamorphism

The metamorphic history of the Meguma Group is extremely complicated. The rocks have been subjected to both contact and regional metamorphism. Pyrrhotite possibly formed from pyrite during metamorphism (eg. Ferry, 1981) in the carbonaceous sediments and many sulphides were redistributed into veins and fractures during subsequent deformation. Metamorphic minerals such as spessartine garnet and calcite are common in areas with higher concentrations of

Table 2.1: Contents of selected environmentally important elements in rocks from the Goldenville-Halifax transition zone (from Graves and Zentilli, 1988). Note: n represents the number of samples analysed in each unit.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Fe_2O_3*	10.40	9.32	13.44	9.94	11.78	6.51	5.43	6.15	6.80	7.32
MnO	4.63	3.17	11.03	2.93	3.68	0.27	0.25	0.22	0.64	0.12
S	0.13	0.54	1.66	0.20	4.61	1.27	0.04	2.96	1.81	0.24
CO_2	0.21	2.04	7.36	2.20	2.61	0.04	0.03	0.00	2.80	trace
C	0.07	0.18	0.05	0.30	5.32	1.12	0.65	0.11	0.74	trace
Ba	1260	1081	1024	897	1009	1205	871	499	603	580
Pb	81	28	10	22	21	12	20	25	13	20
Zn	102	114	137	115	112	96	85	134	83	95
Cu	54	45	94	33	69	23	3	45	32	45
Ni	51	54	103	62	57	24	12	25	21	68
Co	34	31	88	58	78	25	11	82	27	19
As	134.9	58.8	93.0	48.9	18.9	5.3	trace	42.0	52.2	13.0
Sb	0.7	1.4	1.2	0.8	2.9	1.9	0.8	4.3	0.9	1.5
U	4.2	2.8	3.5	2.4	4.9	6.0	3.5	2.7	2.5	3.7
n	43	11	9	20	7	8	2	2	9	-

1 = Moshers Island Mbr, Bells Cove, Lunenburg Co, NS
2 = Moshers Island Mbr, Caribou drillcore LL81-5A, Halifax Co, NS
3 = Moshers Island Mbr, upper portion Lake Charlotte drillcore LC-86-1, Halifax Co, NS
4 = Moshers Island Mbr, lower portion Lake Charlotte drillcore LC-86-1, Halifax Co, NS
5 = Cunard Mbr slate, Lake Charlotte drillcore LC-86-1, Halifax Co, NS
6 = Cunard Mbr slate, Caribou drillcore LL81-5A, Halifax Co, NS
7 = Cunard Mbr slate, Bells Cove, Lunenburg Co, NS
8 = Cunard Mbr wacke, Bells Cove, Lunenburg Co, NS
9 = Cunard Mbr wacke, Caribou drillcore LL81-5A, Halifax Co, NS
10 = average slate[1]

Major Elements: in weight per cent recalculated volatile-free
- * total Fe as Fe_2O_3
- all analyses by standard atomic absorption analyses except FeO, S, CO_2 and C (wet chemical titration) at Dalhousie University, Halifax, Nova Scotia

Trace Elements: in parts per million (ppm)
- all analyses by X-ray fluorescence, Regional XRF Facility, St. Mary's University, Halifax, Nova Scotia

Trace Metals: in ppm
- all analyses by instrumental neutron activation (INAA) by Bondar Clegg and Company, Ltd, Ottawa, Ontario

[1] Mason, B and Moore, B. 1982. Principles of Geochemistry, 4th edition. John Wiley & Sons.

manganese and calcium, in conjunction with ilmenite (Binney et al., 1986).

2.2 Sample Sites

Samples were taken from selected areas in the Halifax Formation (Fig 2.1). Ten samples were collected from outcrops and seven more from a drill core from Eastville. The samples are described further in Chapter 3 and in Appendix A.

2.2.1 Halifax Site

Three samples (CR-95-001 to 003) were taken near the Halifax Industrial Park, off the Bicentennial Highway (Fig 2.2). These samples are near the contact with the South Mountain Batholith (SMB). Andalusite (Fig 2.3) and cordierite-rich layers are present in the outcrop. The rock is a massive, folded and jointed fine-grained hornfels, with disseminated sulphides (Fig 2.4).

2.2.2 Mount Uniacke Site

Two samples (CR-95-004 and 005) were collected from a quarry and another from a roadside outcrop (CR-95-006) in the Mount Uniacke area near the contact with the SMB (Fig 2.5). These rocks are slates with layers containing cordierite, andalusite and thin pyrite veinlets and they represent rocks that have undergone contact metamorphism.

2.2.3 Beaverbank Highway Site

Four more samples (CR-95-007 to 010) were taken near the Beaverbank Highway (Fig 2.6). Ryan (1993) determined the transition beds in this area to be approximately 390 m thick and divided the beds into two units: the lower beds (GHTlb) and the manganese-rich beds (GHTmn). The GHTlb units are composed of alternating metaquartzarenite and silty slate with tight pressure-solution cleavage (Fig 2.7). The Mn-rich beds of the upper transition zone are dark to

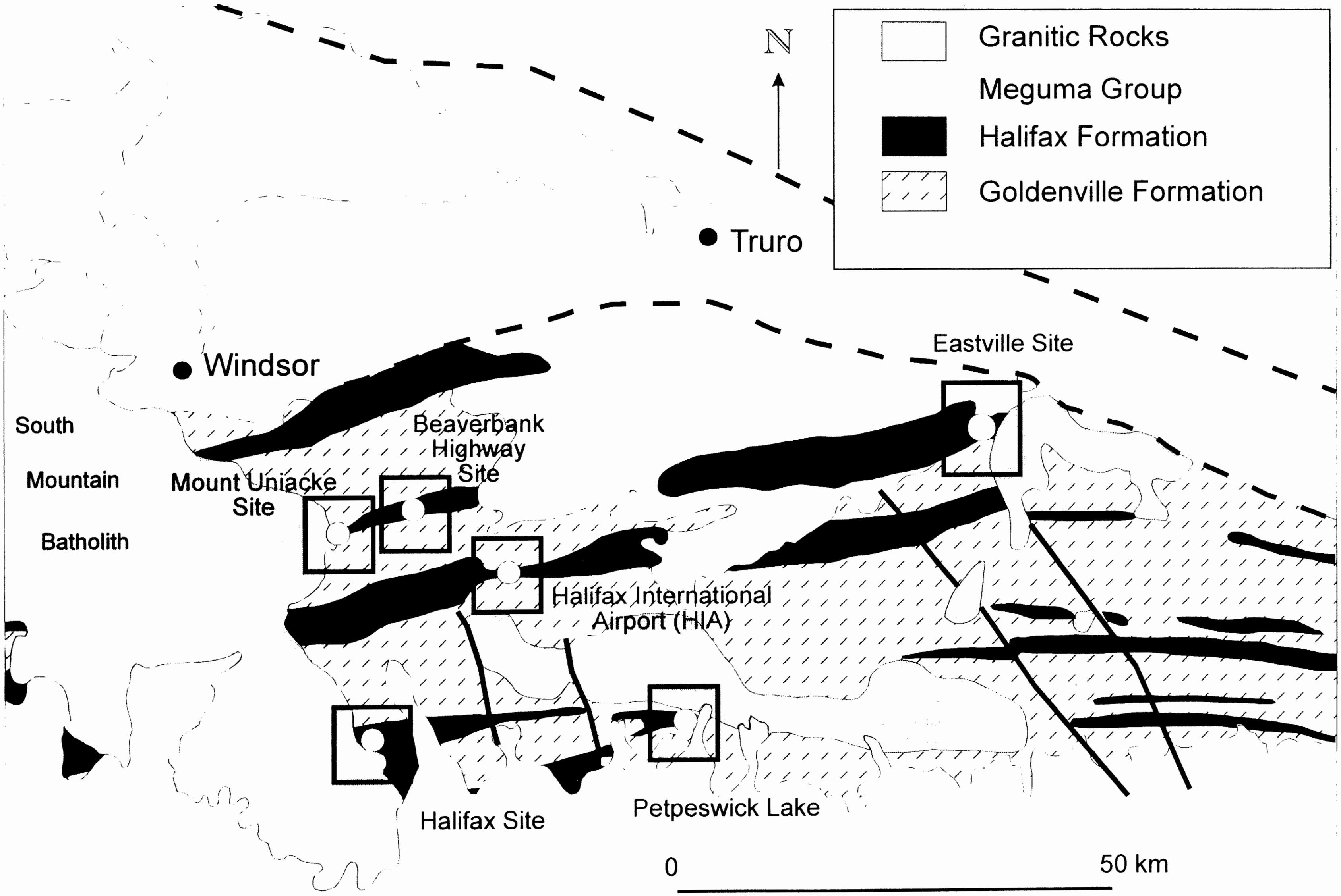


Figure 2.1: Location map of sample sites. Also shown is the location of the Halifax International Airport (HIA) and Petpeswick Lake, two sites of ongoing, active mitigation efforts for the abatement of ARD.

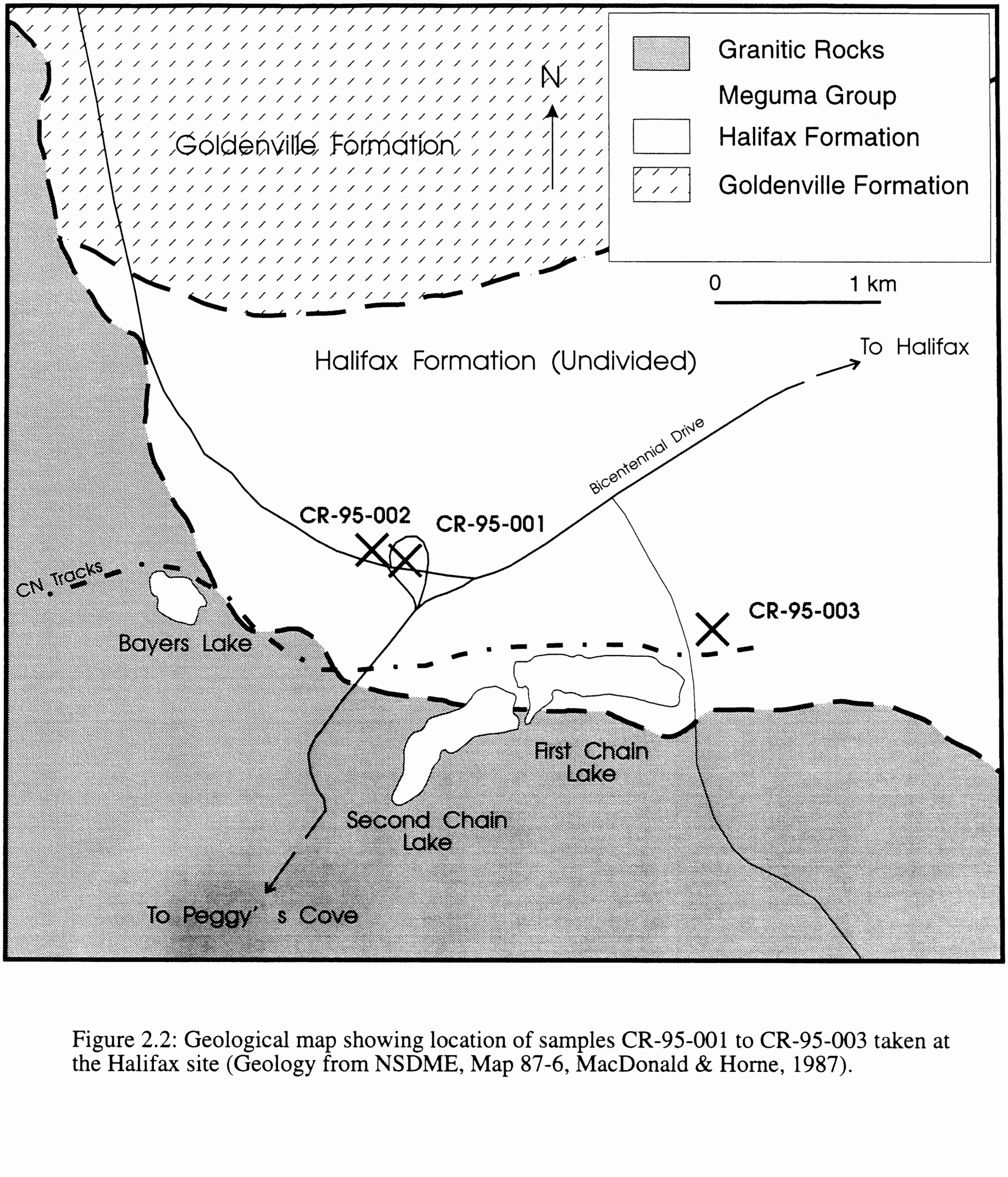


Figure 2.2: Geological map showing location of samples CR-95-001 to CR-95-003 taken at the Halifax site (Geology from NSDME, Map 87-6, MacDonald & Horne, 1987).

Figure 2.3: Andalusite crystals in hornfels of the Halifax Formation. Sample CR-95-001 came from this sample site. Pencil rests on a fracture plane. Note Fe-oxide staining.

Figure 2.4: Secondary minerals form dark red/yellow coloration both along fracture and bedding surfaces at the location of sample CR-95-003. Bedding is well defined here even though individual beds may have hornfels textures. Slaty cleavage is not well-developed, possibly lost to metamorphism. This section of the rock face is approximately 5.0 meters in height.

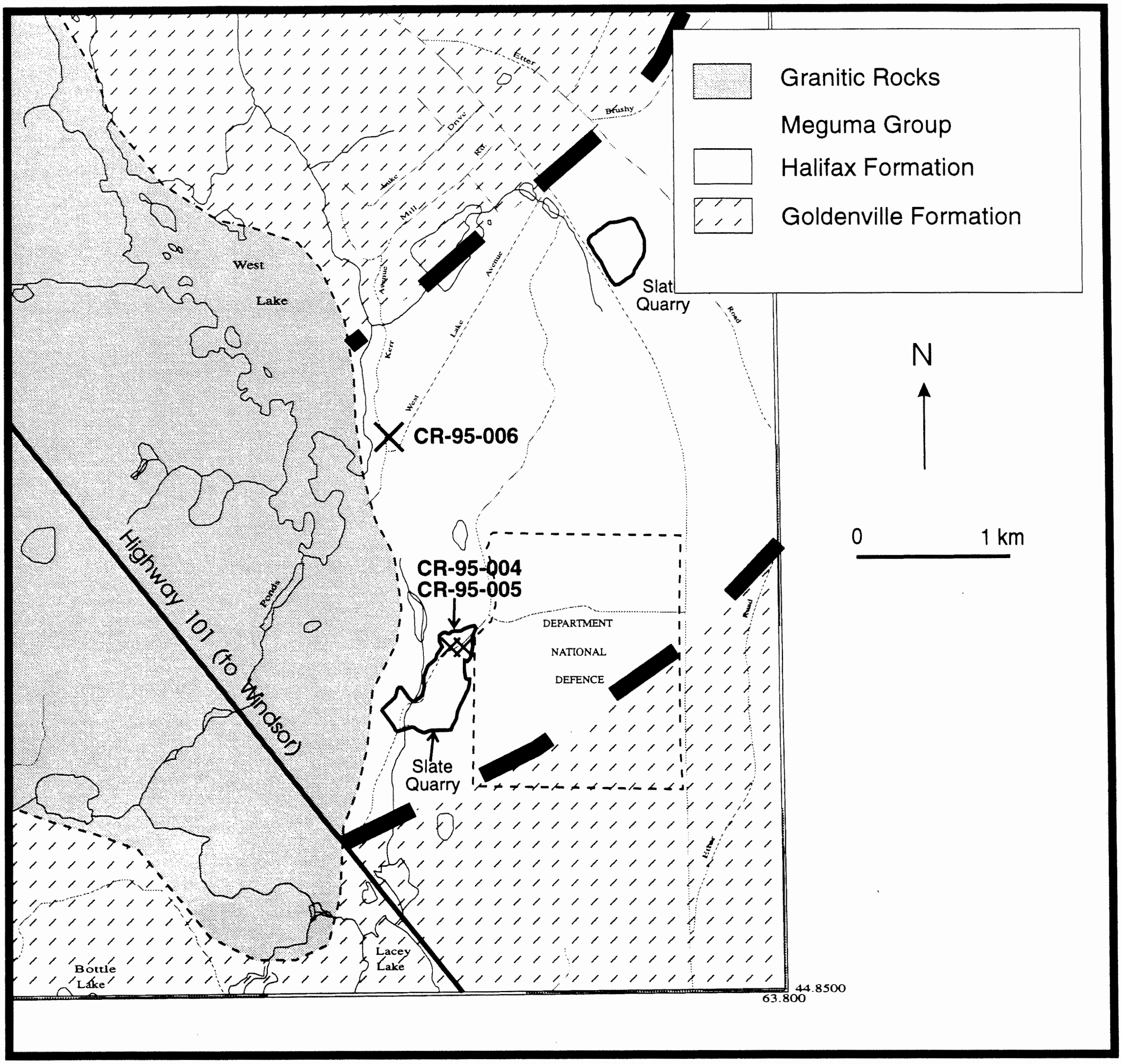


Figure 2.5: Geological map of the Mount Uniacke Site showing the location of samples CR-95-004 to CR-95-006. (Geology modified from M.C. Corey, 1987)

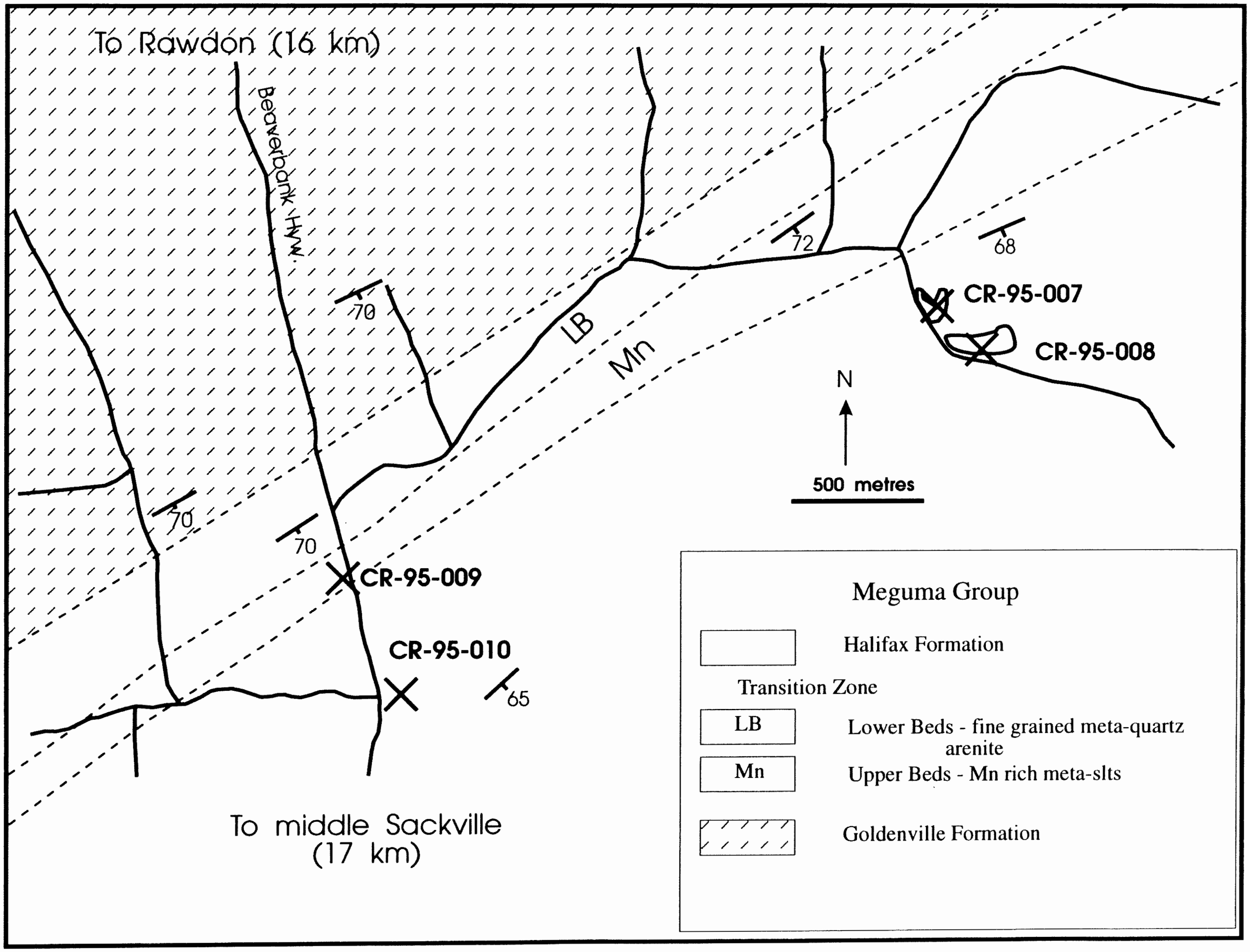


Figure 2.6: Geological map showing the location of samples CR-95-007 to CR-95-010, from the Beaverbank Highway Site. (Geology modified from Ryan, 1994)

Figure 2.7: Typical well-cleaved, black slate of the Halifax Formation. Photo taken at Beaverbank Highway site at the location of sample CR-95-008.

medium-grey, silty slate and metasiltstone. Garnets are present in this unit as well as tight chevron folds and parasitic folds occurring in the regional cleavage planes. This unit is similar to the calcareous quartzite unit in the transition zone described at Eastville (Ryan, 1993).

2.2.4 Eastville

Seven samples were taken from core drilled at Eastville. The samples were chosen for sulphide and carbonate content. Visual inspection and a magnetic susceptibility meter were used to locate sections of the core containing sulphides, in particular pyrrhotite, which is a magnetic mineral. Seven samples (CR-95-011 to 017) were taken from five different holes (Holes 224-6,12,13,18 and 24) (Fig 2.8). The samples are of quartz metawacke, calcareous quartz metawacke and slate and are representative of typical GHT lithologies in this area. The rocks at Eastville are folded and the sulphides have collected in fold hinges and fractures. The carbonate content of the samples from this site is very important, as rocks with elevated carbonate concentrations should not be very acid producing.

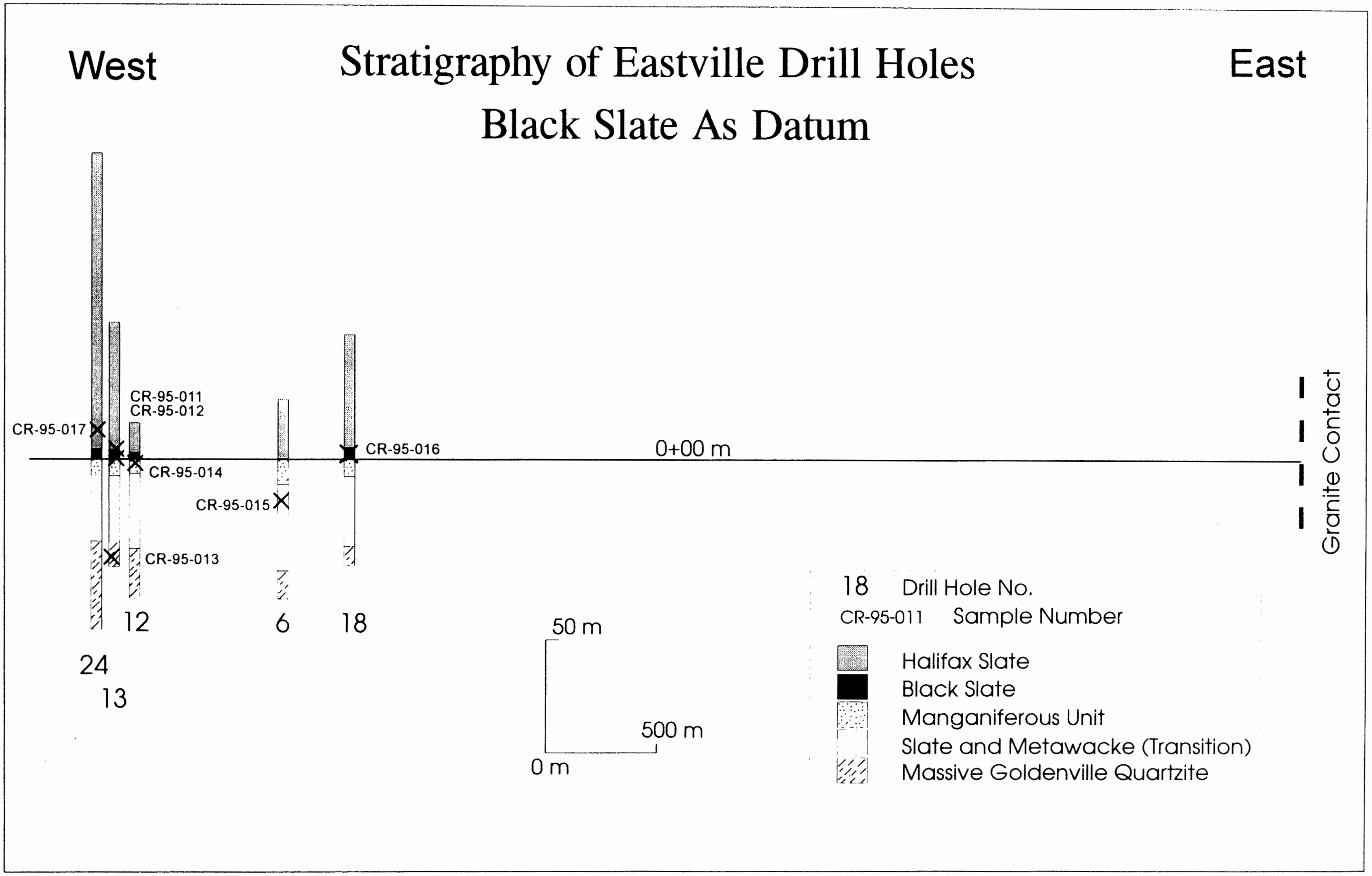


Figure 2.8: Stratigraphy of Eastville drill holes sampled for this study (modified from MacInnis, 1986). Note: Location of black slate in relation to other units and distance of holes from the granite contact.

CHAPTER 3: MINERALOGY OF PYRRHOTITE

3.1 Introduction

The purpose of this chapter is to describe the mineralogy of the samples and discuss the significance of mineral compositions and textures relating to acid rock drainage. Mineralogy was studied in hand samples and in polished thin sections under reflected light using a petrographic microscope. Microprobe and X-ray diffraction (XRD) analysis were performed on selected samples. More detailed descriptions and all microprobe data are located in Appendix A. These analyses are important in determining the types of sulphides present and the nature of their mineralization. Because this study is concerned with acid drainage potential, particular attention is paid to pyrrhotite and pyrite.

3.2 Petrographic Summary

Textures and mineralogy vary among samples from different locations. Table 3.1 provides a summary of the main mineralogical features of the samples. Samples are generally grey to black, sulphide-rich slates or fine grained quartzites. Pyrrhotite is the most abundant sulphide mineral present and varies from approximately 1 to 15% by volume. Grains are elongate and range in size from <1.0 mm to 1.0 cm in length. They are generally concentrated parallel to cleavage and/or bedding planes. In other cases they are randomly disseminated throughout the sample. Some pyrrhotite grains are unaltered, whereas others in the same thin section are partially or entirely replaced by other sulphide and oxide minerals. Pyrite is the next most abundant sulphide, comprising <1 to 5% of many samples. It commonly occurs as euhedral, cubic grains or it rims

Table 3.1: Summary of mineralogical characteristics of samples CR-95-001 to CR-95-017. Significant minerals are those that are present in concentrations ≥ 10%, not including the groundmass.

SAMPLE #	SAMPLE SITES	LITHOLOGY	SIGNIFICANT MINERALS
CR-95-001	Halifax	slate (hornfels)	andalusite, pyrrhotite
CR-95-002	Halifax	slate (hornfels)	andalusite, pyrrhotite
CR-95-003	Halifax	slate (hornfels)	andalusite
CR-95-004	Mount Uniacke	slate (hornfels)	pyrrhotite, cordierite(?)
CR-95-005	Mount Uniacke	slate (hornfels)	cordierite(?), pyrrhotite
CR-95-006	Mount Uniacke	slate	pyrrhotite
CR-95-007	Beaverbank Hwy.	slate	pyrrhotite
CR-95-008	Beaverbank Hwy.	slate	pyrrhotite
CR-95-009	Beaverbank Hwy.	slate	garnet, ilmenite
CR-95-010	Beaverbank Hwy.	slate	pyrrhotite
CR-95-011	Eastville	calcareous quartzite	pyrrhotite, garnet, calcite
CR-95-012	Eastville	calcareous quartzite	garnet, pyrrhotite, calcite
CR-95-013	Eastville	quartzite	none
CR-95-014	Eastville	slate	pyrrhotite, calcite
CR-95-015	Eastville	calcareous sandy slate	calcite, garnet, ilmenite
CR-95-016	Eastville	sandy slate	pyrrhotite, garnet
CR-95-017	Eastville	slate	garnet, pyrrhotite, pyrite, calcite

and replaces pyrrhotite. Anhedral pyrite grains also show replacement in some samples. Other sulphides present in minor concentrations ($\leq$ 1%) include chalcopyrite, sphalerite and arsenopyrite. In general, these minerals occur as inclusions in pyrrhotite. Two types of oxide minerals, ilmenite and rutile, occur as individual grains and as replacement minerals in some of the samples. Euhedral and subhedral garnets also occur in a few samples.

3.2.1 Halifax Site

Samples CR-95-001, CR-95-002 and CR-95-003 were taken <1 km from the contact with the South Mountain Batholith (Fig 2.2). The rocks are pelitic, fine-grained, medium-grey and massive. They have a granoblastic texture. Cleavage that may have existed has been destroyed by contact metamorphism. The predominant sulphide from this location is pyrrhotite. Most grains are < 2.0 mm in size, anhedral, and occur either as large, elongate grains or as smaller grains disseminated throughout the sample. Pyrrhotite may contain inclusions of pyrite, chalcopyrite and silicate minerals and is commonly associated with ilmenite and/or rutile (Fig 3.1). Cordierite and andalusite crystals occur in discrete beds. The andalusite crystals are subhedral to anhedral chiastolites and are up to 1.5 mm in length (Fig 3.2).

3.2.2 Mount Uniacke Site

Two samples were collected from a slate quarry in the Mount Uniacke area (CR-95-004 and CR-95-005) and one from a road-side outcrop (CR-95-006) (Fig 2.5). These sites are located <1 km from the contact with the South Mountain Batholith. The rocks are fine-grained, medium grey and massive. They contain well-developed bedding visible in both hand sample and thin section. Cleavage sub-parallel to bedding is present, but is not well developed. Pyrrhotite is the predominant sulphide mineral present. In samples CR-95-004 and 006, pyrrhotite grains are

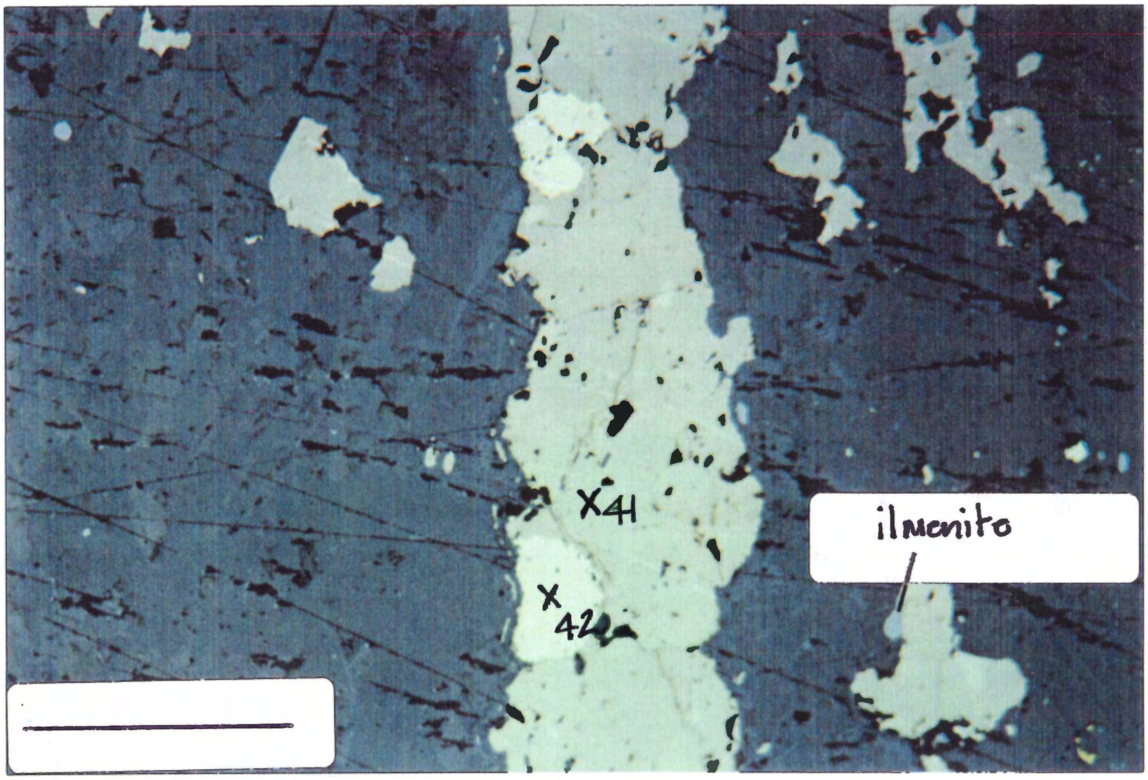


Figure 3.1: Photomicrograph of elongate pyrrhotite grain (beige) with pyrite inclusions (white/yellow) in sample CR-95-002. Numbers on photograph correspond to probe data presented in Appendix A. Reflected light. Scale bar = 190 μm.

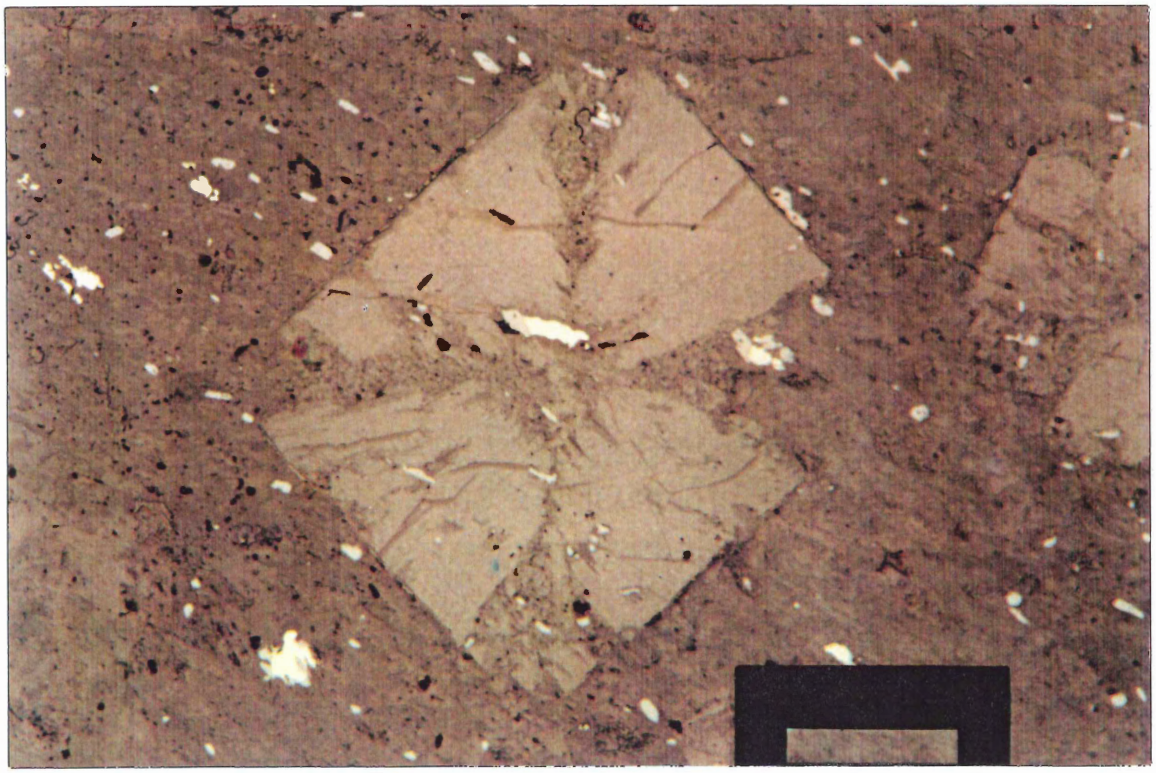


Figure 3.2: Photomicrograph of subhedral andalusite crystal in sample CR-95-003. Reflected light. Scale bar = 190 μm.

elongate, anhedral and range in size from <1.0 mm to 5.0 mm. They contain inclusions of silicates and other sulphide minerals. Pyrite displays well-developed replacement textures (Fig 3.3). Sample CR-95-005 contains a well-developed fabric interpreted to result from high strain. Quartz ribbons and thin sulphide veins are present in this sample. Andalusite is present in sample CR-95-004. It is found at the other two sample sites but its distribution is controlled by bedding and occurs only in aluminum-rich layers. Traces of altered cordierite are present in samples CR-95-004 and 005.

Sample CR-95-006 contains the rare arsenic mineral löllingite ($FeAs_2$) (Fig 3.4). This is important because löllingite has a relatively high percentage of arsenic. If this mineral or arsenopyrite (FeAsS) were present in significant concentrations, leaching may introduce potentially dangerous concentrations of arsenic into the environment.

3.2.3 Beaverbank Highway Site

The sample site in the Beaverbank Highway area is approximately 10-15 km from the contact with the South Mountain Batholith (Fig 2.6). Primary features such as bedding, cross-bedding and folds are visible in hand specimen and thin section. Pyrrhotite is the dominant sulphide mineral in the four samples taken from this site and is concentrated along bedding and cleavage planes. Grains are predominantly large (1-5 mm) but some smaller disseminated grains are present. All pyrrhotite is anhedral and most is elongate, containing inclusions and replacement textures. Euhedral pyrite is present in samples CR-95-007 and 008. Sample CR-95-009 was collected from the Goldenville - Halifax transition zone and contains ilmenite, rutile and euhedral manganese-rich (spessartine) garnet in the matrix. Some pyrrhotite grains display a manganese-rich garnet (spessartine) rim (Fig 3.5). This indicates that the sulphides were present

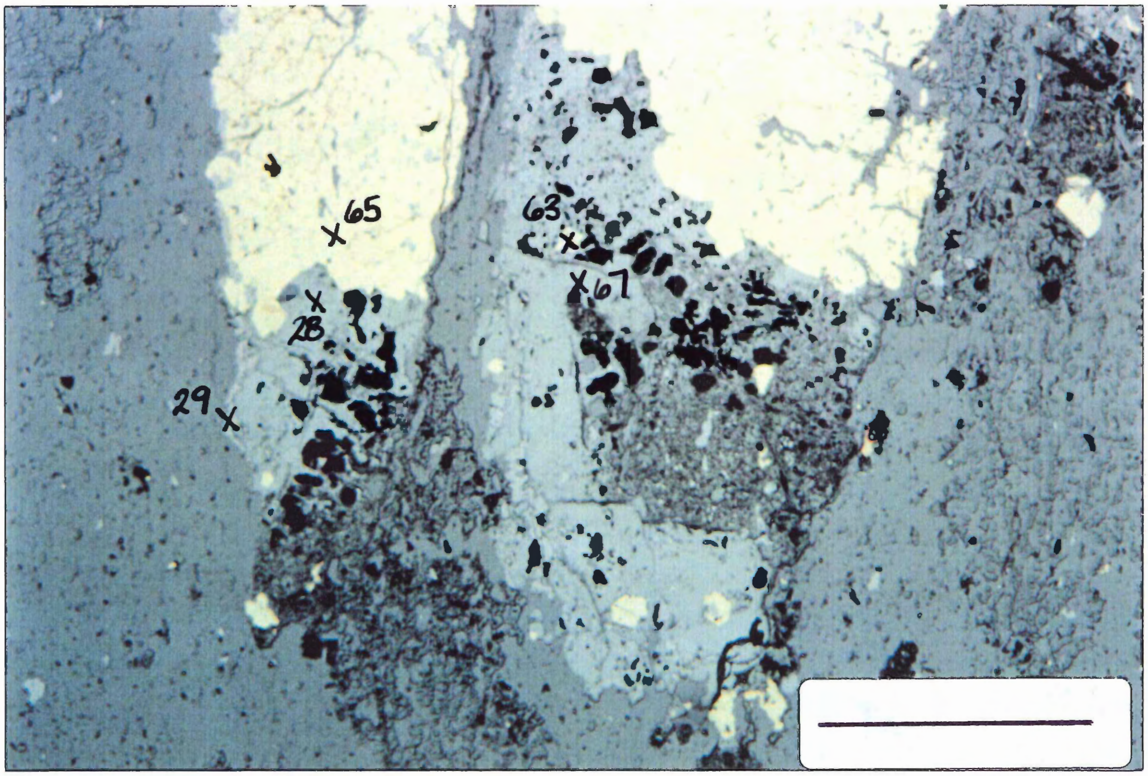
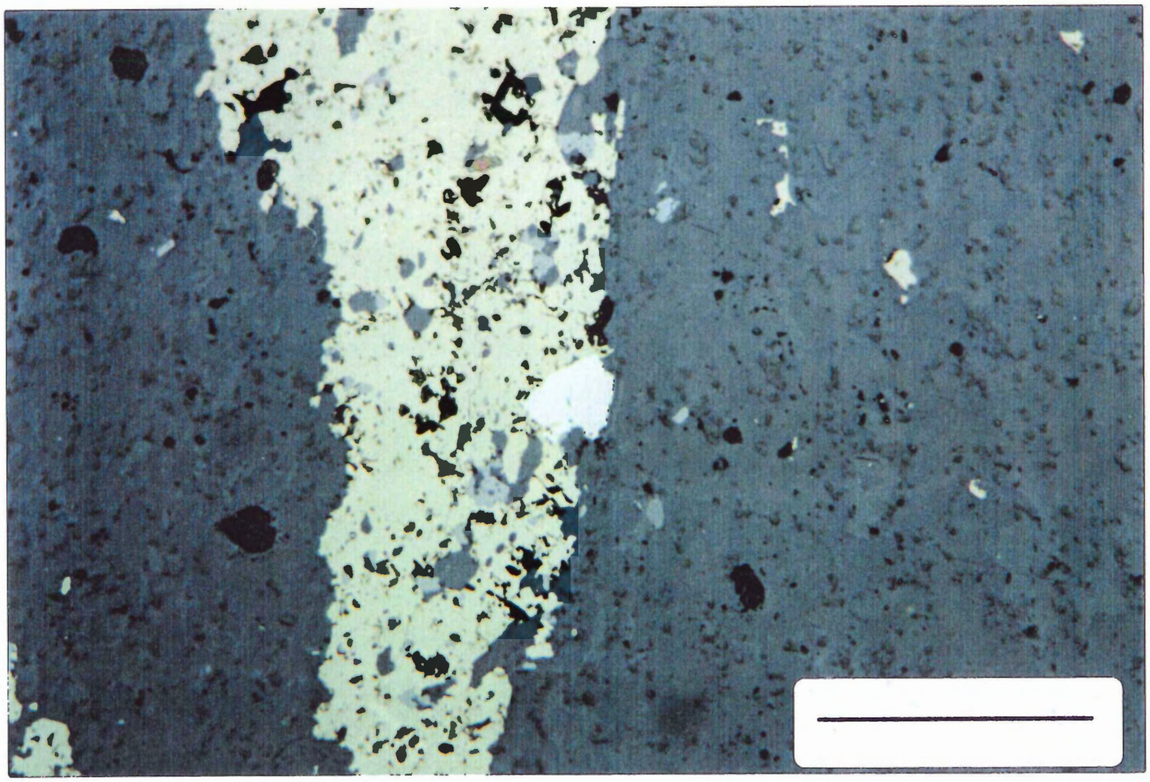


Figure 3.3: Photomicrograph of pyrite in sample CR-95-004. Pyrite (white/yellow) is partly replaced by rutile (dark grey) that is rimmed by ilmenite (light grey). Numbers on photograph correspond to probe data presented in Appendix A. Reflected light. Scale bar = 190 μm.



ELEMENT	ELEMENT %	ATOMIC %
Fe	23.051	28.342
As	68.910	63.160
S	1.270	2.721
Ni	1.733	2.027
Co	3.219	3.751
TOTAL	98.184	100

Figure 3.4: Photomicrograph and microprobe data for löllingite ($FeAs_2$) , an important arsenic mineral found in sample CR-95-006. Löllingite (white) occurs as an inclusion in pyrrhotite (beige). Scale bar = 190 μm.

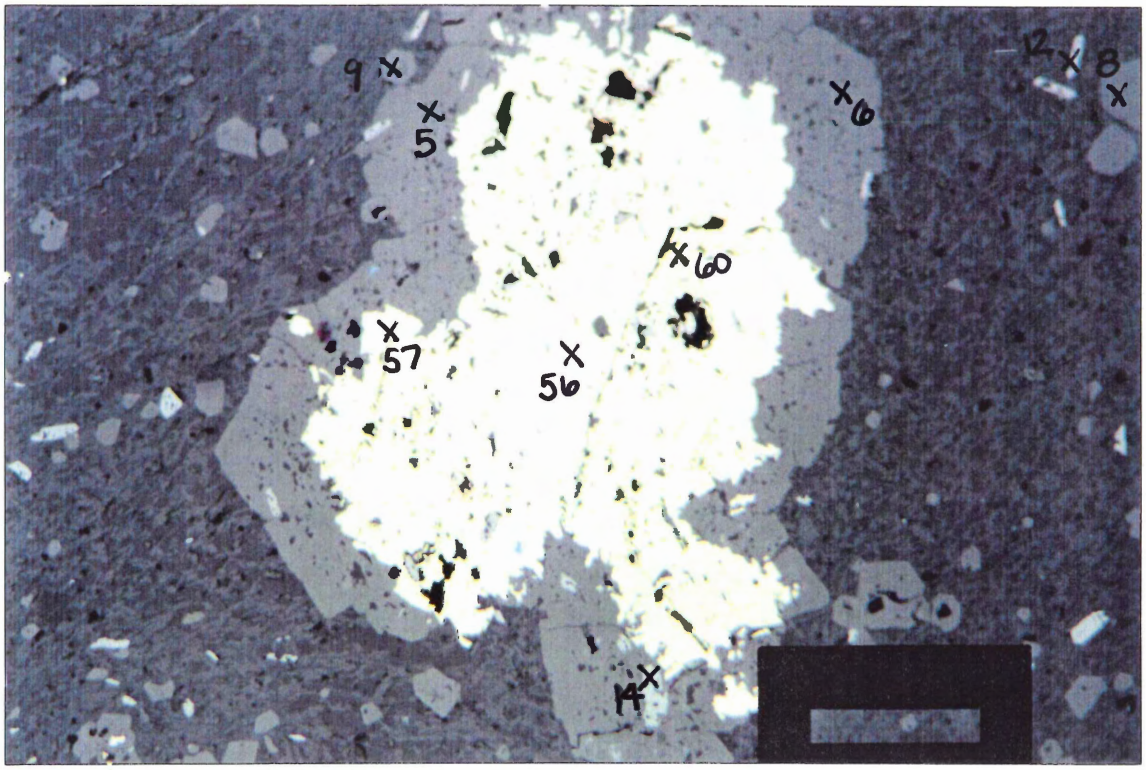


Figure 3.5: Photomicrograph of Mn-rich silicate rim (spessartine garnet) (grey) surrounding pyrrhotite (white) in sample CR-95-009. Chalcopyrite (light yellow) is present as an inclusion in the pyrrhotite. Numbers on photograph correspond to probe data in Appendix A. Reflected light. Scale bar = 190 μm.

in the layers before metamorphism, and suggests that the grains would not weather as easily. In CR-95-010, pyrrhotite is rimmed by pyrite (Fig 3.6).

3.2.4 Eastville

Tightly folded bedding planes are visible in drill core and thin section. Most samples are calcareous and range from fine-grained quartzite to pelitic slate. Significant concentrations of sulphides are present in five of the seven samples. Pyrrhotite is predominant and it is concentrated along bedding and cleavage planes. Disseminated grains occur as well as larger elongate grains. Pyrite and chalcopyrite are present in minor amounts. Sample CR-95-017 contains large anhedral pyrite grains (some >5.0 mm) and a pyrite vein. Calcite veins are present in most samples (Fig 3.7).

3.3 Mineral Chemistry

Microprobe data from all pyrrhotite grains analyzed in this study are presented in figures 3.8(a) and 3.8(b). Figure 3.8(a) shows a plot of atomic % Fe against atomic % S. Several forms of ideal pyrrhotite are also plotted. As indicated in the graph, the majority of the pyrrhotites analyzed for this study cluster around the monoclinic pyrrhotite end-member (Fe_7S_8), the most magnetic and iron-deficient phase. Smaller open circles represent pyrrhotite from samples close to the contact with the South Mountain Batholith (CR-95-001 to CR-95-006). Open squares represent pyrrhotite from all other samples (CR-95-007 to CR-95-017). The overlap in these points indicates the pyrrhotite composition is relatively uniform (monoclinic type) regardless of the specific geological environment, within the study area. Figure 3.8(b) is a frequency histogram indicating that the average composition of the grains probed lies between 45.5 and 47.5 atomic %

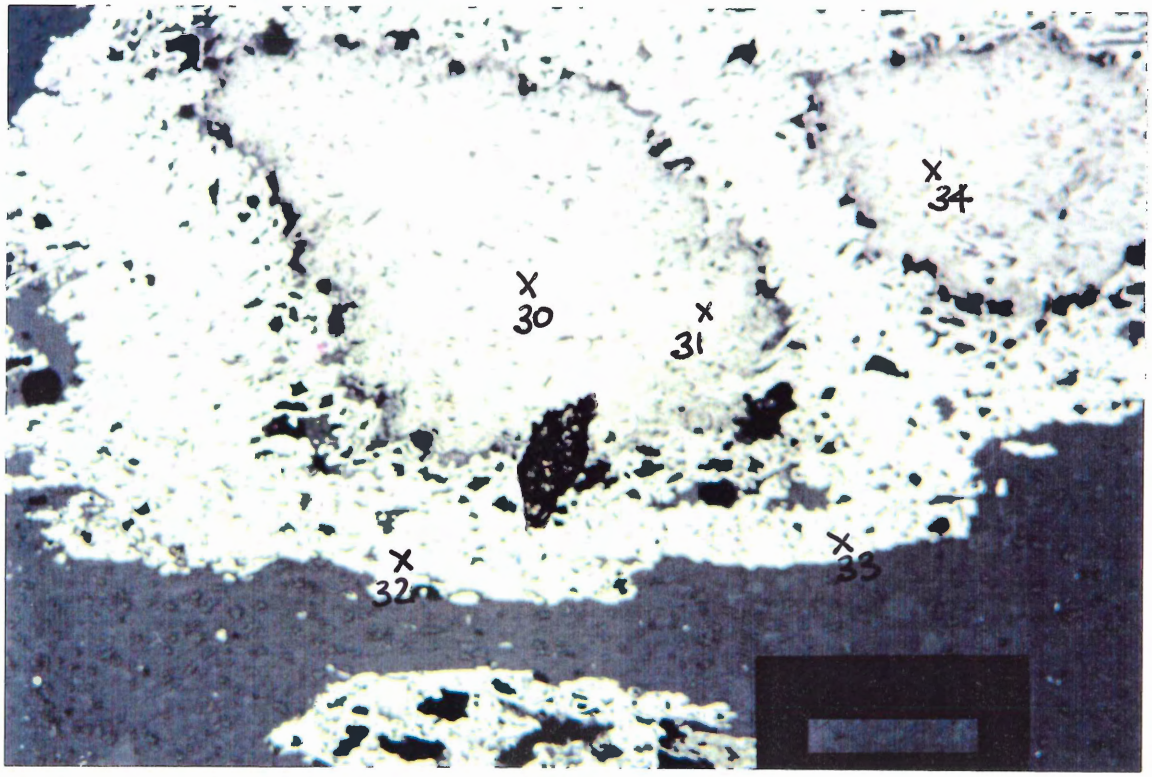


Figure 3.6: Photomicrograph of pyrite (outter - bright grey) rimming pyrrhotite (inner - light grey) in sample CR-95-010. Numbers on photograph correspond to probe data in Appendix A. Reflected light. Scale bar = 190 μm.

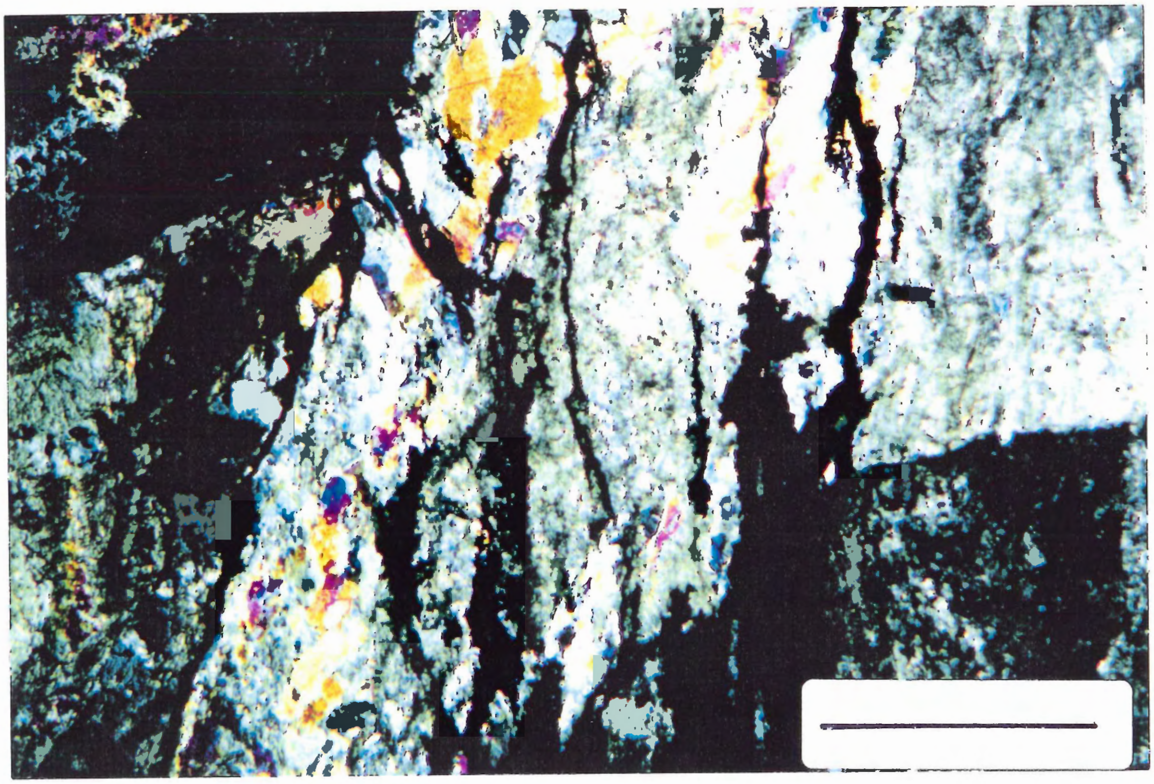


Figure 3.7: Photomicrograph of calcite vein present in sample CR-95-017. Eastville samples typically contain calcite. Note the thin opaque pyrite veins. Transmitted light. Scale bar = 190 μm.

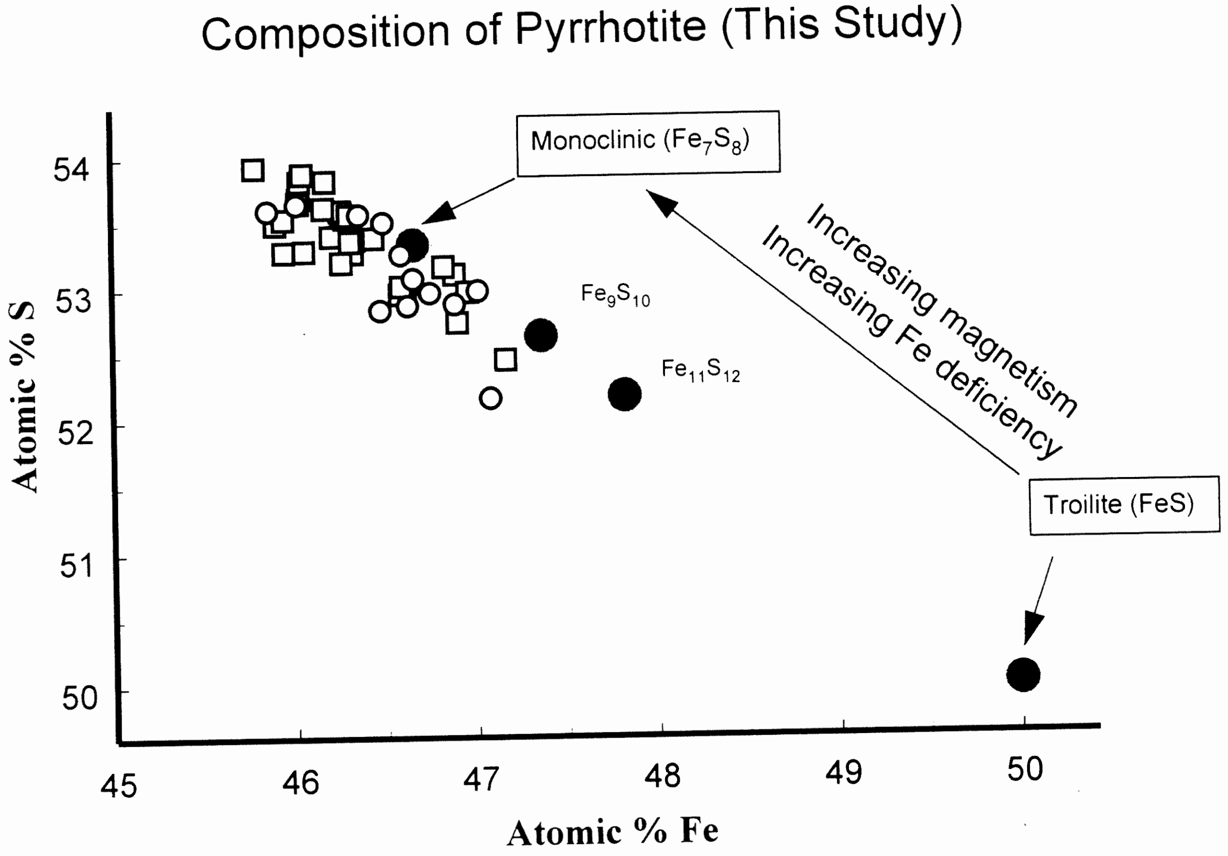


Figure 3.8(a): Graph of atomic % Fe vs atomic % S showing where pyrrhotite compositions from this study plot in relation to four ideal forms of pyrrhotite. The ideal forms are indicted by larger filled circles. Smaller open circles represent probe data from samples taken near the contact with the South Mountain Batholith (Halifax and Mount Uniacke Sites). Open squares represent probe data from all other samples. The overlap in these data indicate pyrrhotite composition is relatively uniform regardless of geological environment.

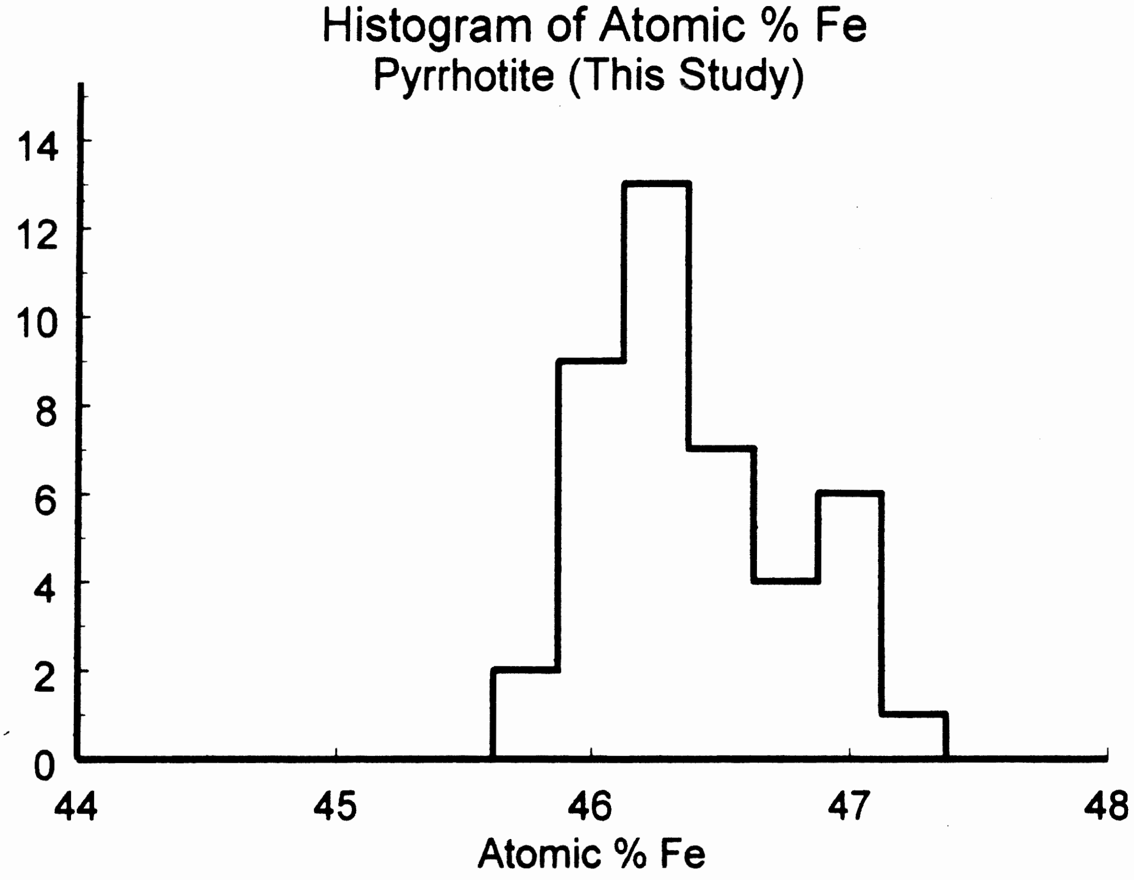


Figure 3.8(b): A frequency histogram showing that the average composition of pyrrhotite grains probed in this study is between 45.6 and 47. 4 atomic % Fe, which is characteristic of monoclinic pyrrhotite.

Fe, in the ideal monoclinic pyrrhotite range. Figures 3.9(a) and (b) show that data from analyses of pyrrhotite in drill-core samples from the Halifax International Airport (Knee, 1995) overlap with data from this study. The average stoichiometry of pyrrhotite grains in samples from the Airport was calculated to be $Fe_{7.058}S_{8.000}$, indicative of monoclinic pyrrhotite (Pasava et al., 1995), compatible with the results of this study.

3.4 X-ray Diffraction (XRD) Analysis

Ideal, stoichiometric pyrrhotite has the composition FeS but generally, naturally occurring pyrrhotite contains less iron than is indicated by this formula (Table 1.1). Stoichiometric FeS, known as troilite, is non-magnetic and occurs almost exclusively in meteorites. The structure for this "ideal" form of pyrrhotite is hexagonal (Fig 3.10), but minor deviations from this ideal structure occur for most compositions within the range Fe_7S_8-FeS, leading to larger hexagonal or monoclinic unit cells (Deer et al., 1985).

A decrease in cell dimensions as the Fe:S ratio decreases and density measurements indicate that the non-stoichiometric formula of ferrous sulphide is a result of missing iron atoms rather than the replacement of some iron atoms by sulphur (Deer et al., 1985). The structure of Fe_7S_8 has a regular arrangement of vacant metal sites giving rise to lower symmetry and specific magnetic properties. The decrease in the cell parameters of pyrrhotite as iron deficiency increases can be used for the determination of the compositions of homogeneous pyrrhotites (Deer et al., 1984).

X-ray diffraction (XRD) analysis is useful for identification and semiquantitative analysis of minerals in a rock and it is used to interpret which variety of pyrrhotite is present. X-ray

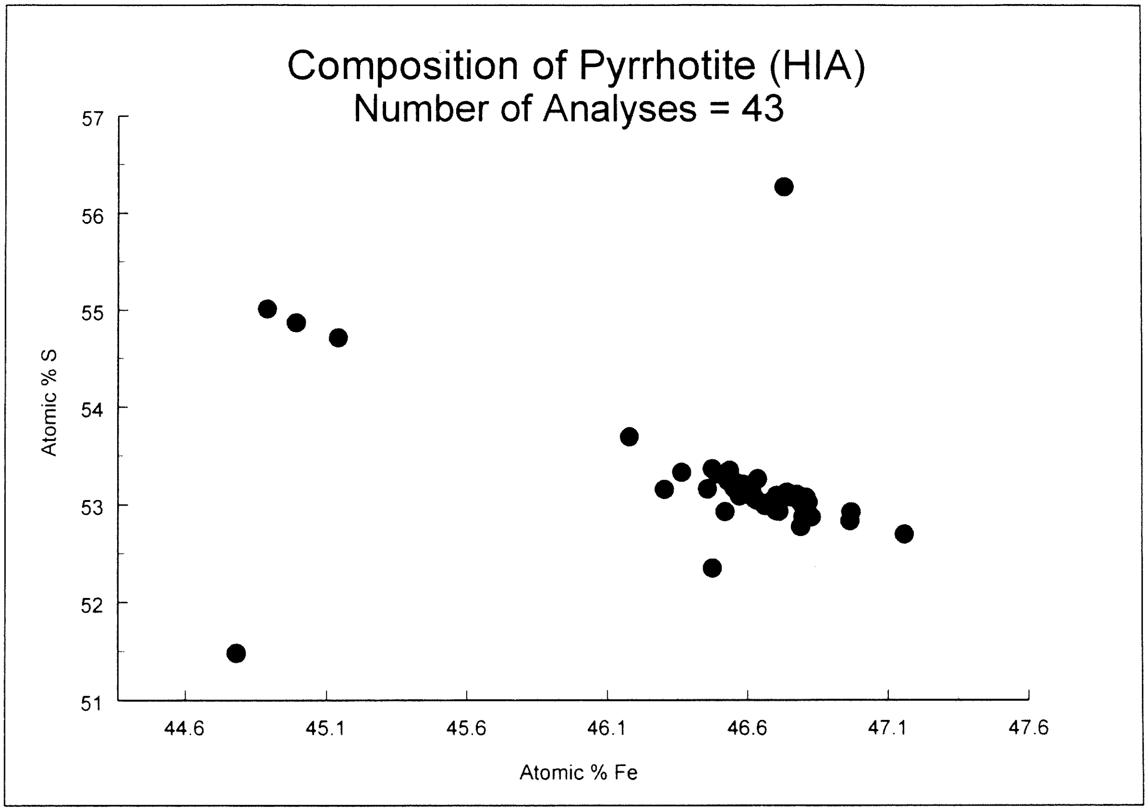


Figure 3.9(a): Graph of atomic % Fe vs atomic % S displaying microprobe data from pyrrhotite in drill-core from the Halifax International Airport (data taken from Knee, 1995). Note that the majority of the points fall between 46 and 47 atomic % Fe. This overlaps with analyses of pyrrhotite in this study.

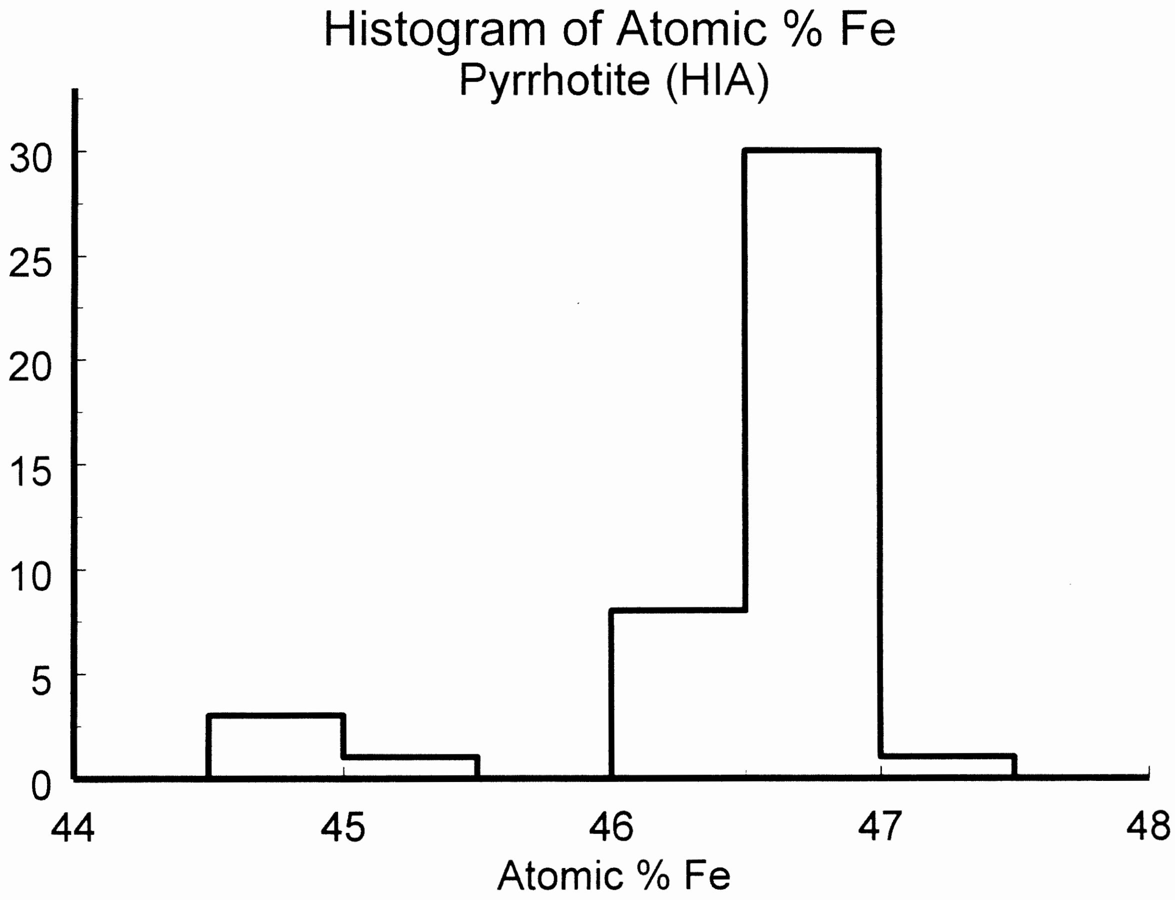


Figure 3.9(b): A frequency histogram showing that the average composition of pyrrhotite in drill-core from the Halifax International Airport is between 46 and 47 atomic % Fe (Knee, 1995). This overlaps with analyses of pyrrhotite in this study.

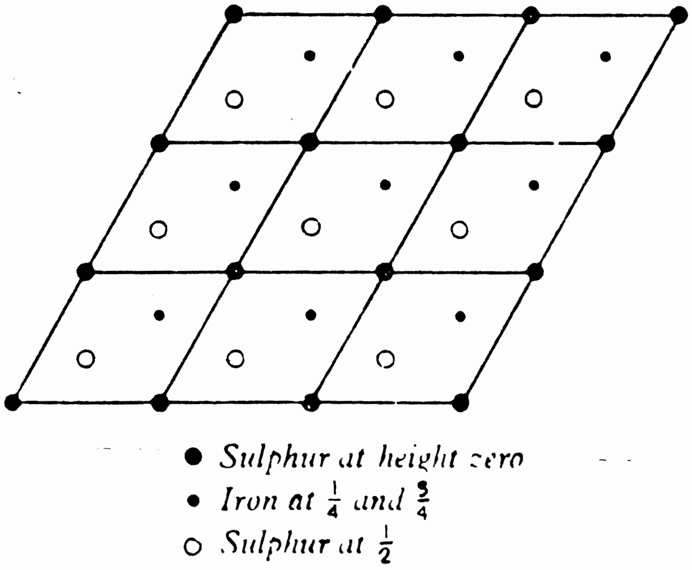


Figure 3.10: Idealized hexagonal structure of pyrrhotite (NiAs type) projected on (0001) (Deer et al., 1985).

diffraction involves examining inner electrons of minerals with X-rays and the use of Bragg's Law (Ragland, 1989):

$$n\lambda = 2d\sin\theta \tag{3.1}$$

where λ is the wavelength of incident X-radiation; d is distance between lattice planes of a crystal; θ is the angle of incidence, which equals the diffraction angle; and n is order. In terms of Bragg's Law for XRD, λ is constant (the specific wavelength of the X-ray tube), whereas d is a function of sin θ. A powdered sample is bombarded with primary X-rays from the tube. Different minerals in the sample diffract the X-rays according to Bragg's Law. The number of *d-spacings* are determined from a *diffractogram*, and collectively serve as a "fingerprint" for a particular mineral (Ragland, 1989).

Two closely spaced reflections of approximately equal intensity are indicative of monoclinic pyrrhotite (Arnold, 1969). Four samples from the four different locations in this study were analyzed using X-ray diffraction. The data is displayed is figures 3.11(a-d). Figure 3.11(a) shows the analysis of a hand-picked pyrrhotite grain from sample CR-95-003. The data shown in figures 3.11(b-d) represent grains that were separated with a magnet from samples CR-95-006, CR-95-007 and CR-95-011. All four analyses show relatively equal intensity double peaks, indicating the pyrrhotite is monoclinic. This is consistent with results from microprobe analyses presented above.

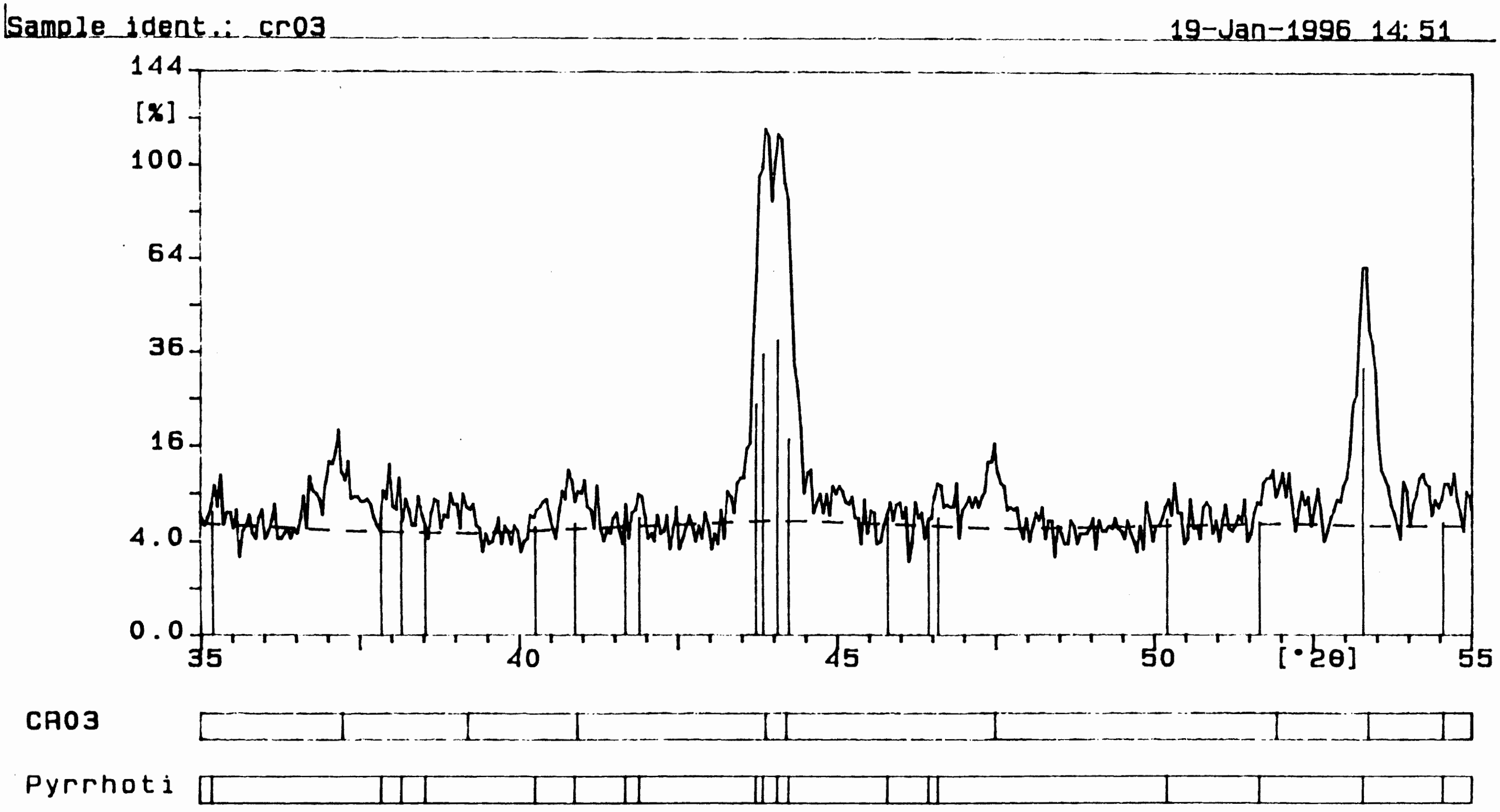


Figure 3.11(a): Results of X-ray diffraction analysis of pyrrhotite from sample CR-95-003 (Halifax Site). Pyrrhotite hand-picked from sample. Note the closely spaced, equal intensity double peaks indicative of monoclinic pyrrhotite.

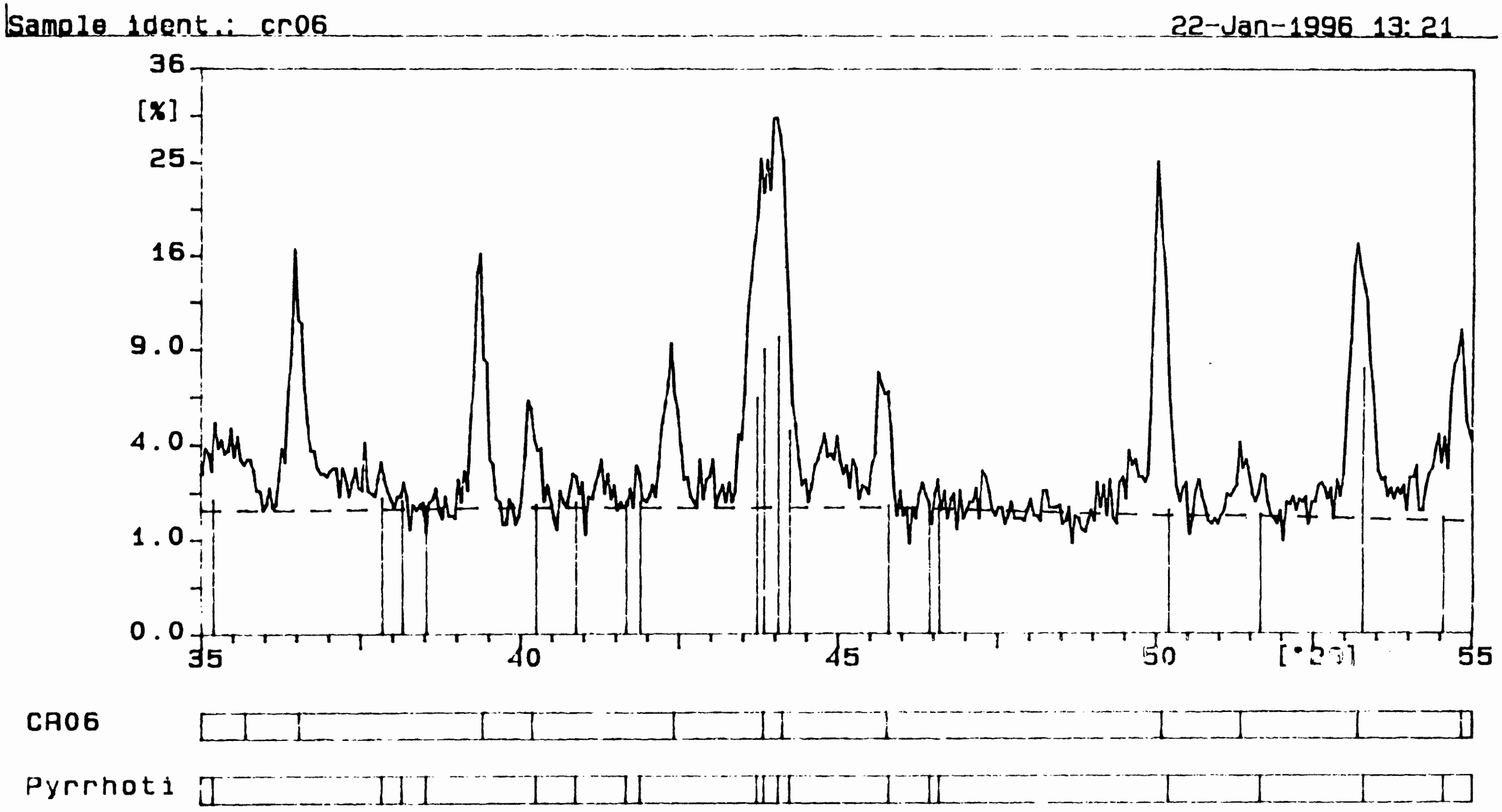


Figure 3.11(b): Results of X-ray diffraction analysis of pyrrhotite from sample CR-96-006 (Mount Uniacke Site). Pyrrhotite separated with magnet. Note the closely spaced, equal intensity double peaks, indicative of monoclinic pyrrhotite.

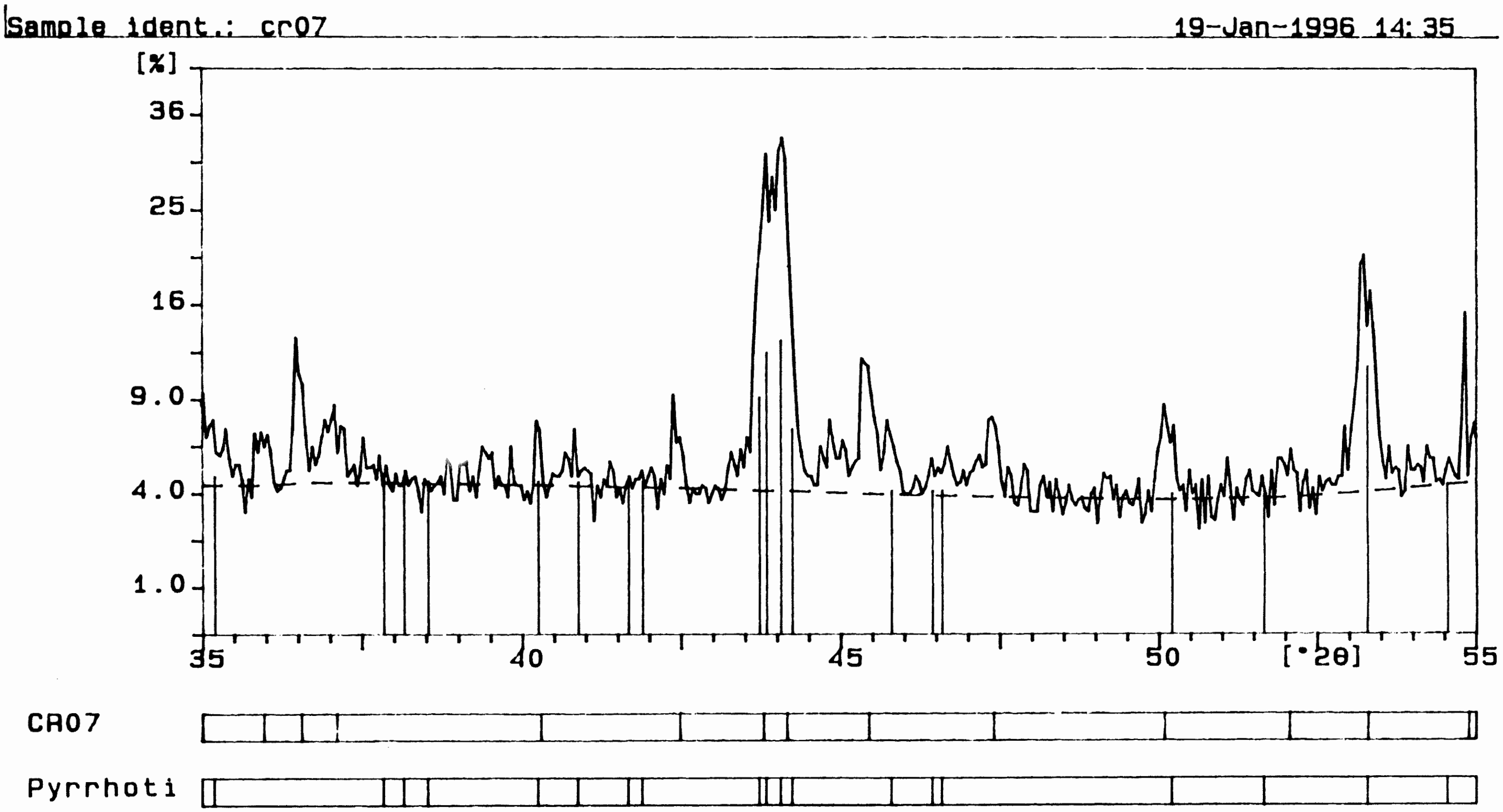


Figure 3.11(c): Results of X-ray diffraction analysis of pyrrhotite from sample CR-96-007 (Beaverbank Highway Site). Pyrrhotite separated with magnet Note the closely spaced, equal intensity double peaks, indicative of monoclinic pyrrhotite.

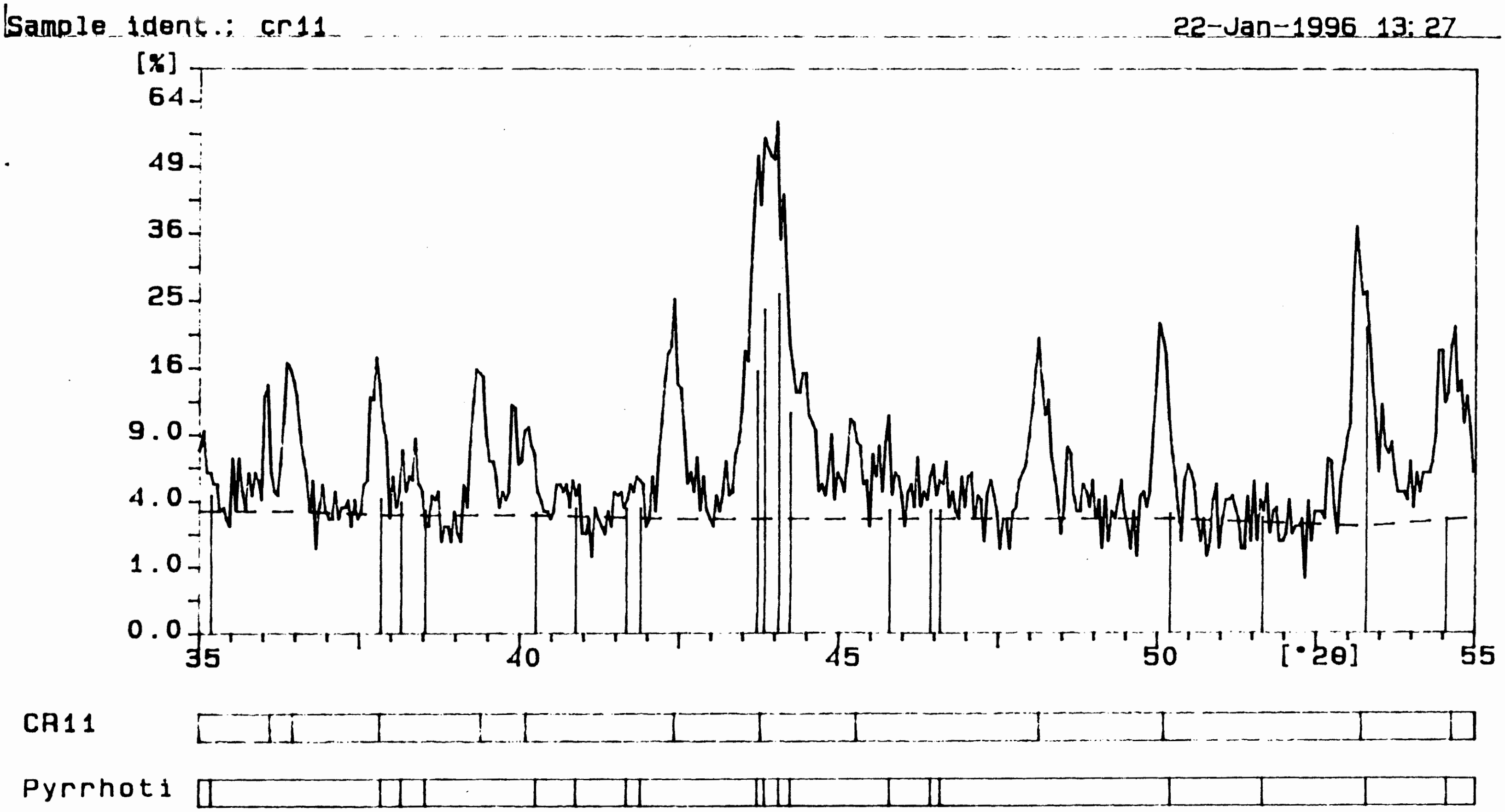


Figure 3.11(d): Results of X-ray diffraction analysis of pyrrhotite from sample CR-96-011 (Eastville Site). Pyrrhotite separated with magnet Note the closely spaced, equal intensity double peaks, indicative of monoclinic pyrrhotite.

3.5 Discussion and Conclusions

This study indicates that monoclinic pyrrhotite is the main sulphide mineral present within the Halifax Formation. As discussed in Chapter 1, pyrite produces more H^+ ions per mole than pyrrhotite when exposed to oxidizing conditions. However, pyrrhotite is considered to be much less stable at the surface than pyrite and oxidizes substantially faster. Figure 3.12 shows mineral stability fields for iron oxides and sulphides in terms of Eh and pH. The stability field of pyrite is in a reducing environment and extends from acidic to basic conditions. Pyrrhotite is stable only in extreme reducing environments (more reducing than for pyrite) with high pH and has a much narrower stability range than that of pyrite. Figure 3.13 shows Eh - pH stability fields of various types of water-dominated environments. ARD waters occur in low pH - high Eh (oxidizing) conditions. If these waters are brought into contact with pyrrhotite, as opposed to pyrite, the oxidizing reaction is likely to be more severe because of the more limited stability conditions of pyrrhotite. The faster oxidation of pyrrhotite vs pyrite has been investigated previously (Nicholson & Scharer, 1994; Nicholson, 1994) and has been confirmed for sulphide samples from the Halifax Formation taken at the Halifax International Airport (MacInnis et al., 1994). Therefore, although pyrrhotite produces quantitatively less acid than pyrite, it may produce it much more rapidly, resulting in more severe environmental effects. The pulses of acid that are generated could be enough to overload the neutralizing capacity of an environment, creating acidic conditions and affecting aquatic wildlife.

The analysis of pyrrhotite compositions is also an important step in the assessment of ARD. As outlined in Chapter 1, monoclinic pyrrhotite will produce more acid than other types of pyrrhotite when oxygen is the main oxidant. From the present study, pyrrhotite compositions

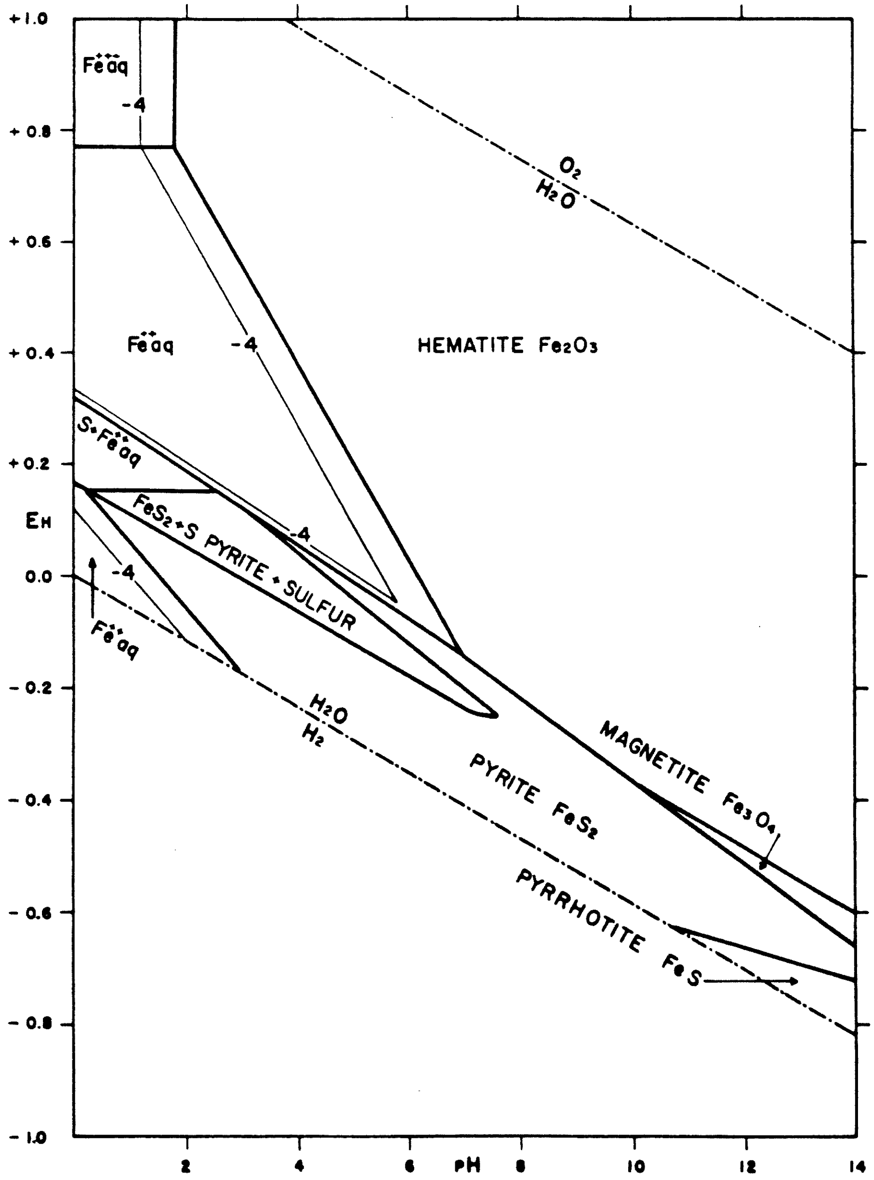


Figure 3.12: Stability relations of iron oxides and sulphides in water at 25°C and 1 atmosphere total pressure at an activity of dissolved sulphur of 10^{-1} (Garrels, 1960). Pyrite is stable under mainly reducing conditions in basic to acidic environments. Pyrrhotite is stable under lower Eh conditions than pyrite and only in basic environments.

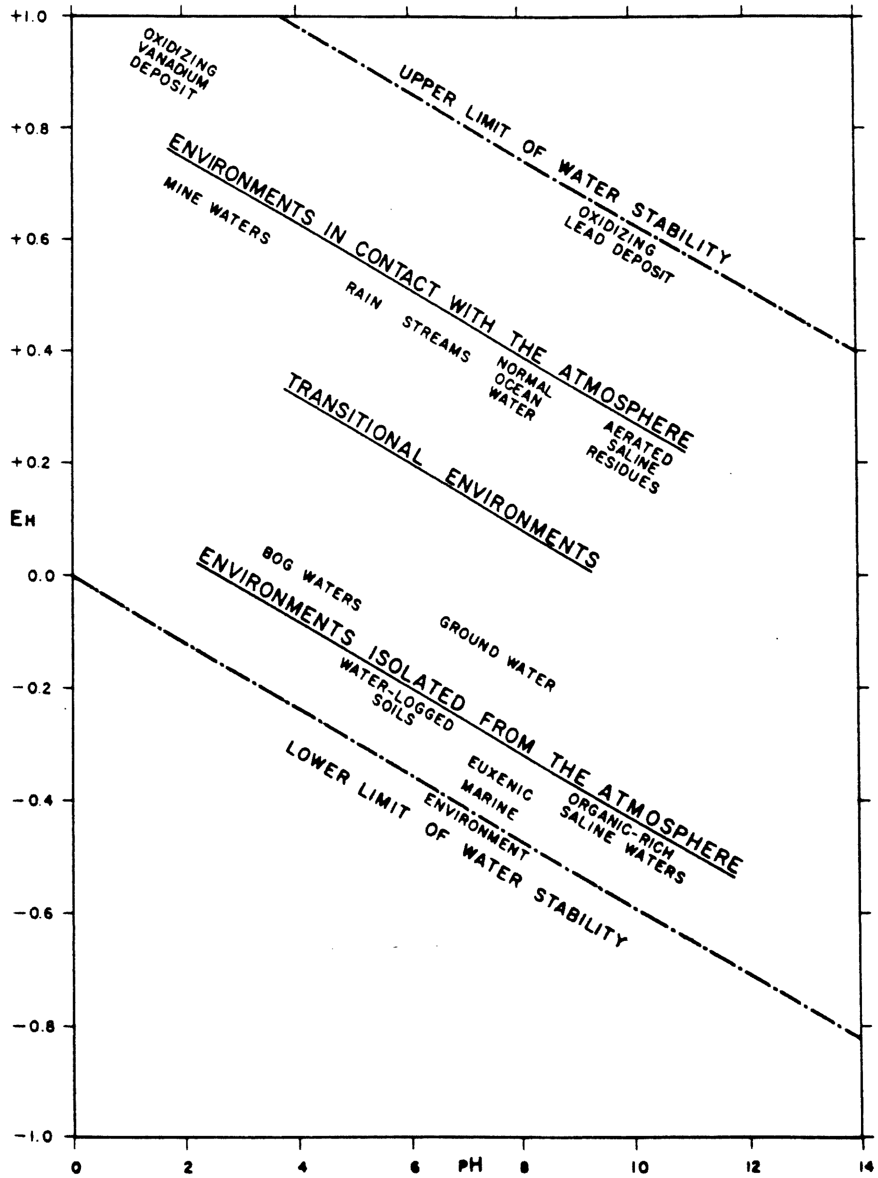


Figure 3.13: Stability fields in terms of Eh and pH for various types of water environments (Garrels, 1960). ARD waters occur in highly oxidizing (high Eh) and acidic (low pH) conditions.

appear to be relatively consistent and homogeneous regardless of geological environment and are the monoclinic type. These data suggest pyrrhotite compositions found in the Halifax Formation will lead to the maximum amount of H^+ ions produced for that mineral, confirming the potential for serious acid drainage problems.

CHAPTER 4: PREDICTIVE STATIC TESTS FOR ACID ROCK DRAINAGE

4.1 Introduction

Mineralogical investigations presented in Chapter 3 of this study confirm that samples taken from the four field areas in the Halifax Formation contain sulphide minerals. The main sulphides identified are monoclinic pyrrhotite and pyrite, the former being the maximum acid producing form of pyrrhotite and possibly the most significant contributor to the ARD problem. However, because rocks contain sulphide minerals does not necessarily mean they are net acid producers. The oxidation of sulphide minerals produces acid, but the acid-consuming ability (or neutralizing potential) of a rock plays an important role in terms of its net acid-producing ability. Therefore, it is necessary to test both the acid-producing and acid-consuming potential of a rock to determine whether or not it is a net acid producer. ARD predictive static tests are designed to measure the net acid producing ability (or net acid-consuming ability) of the test sample.

The two most widely accepted ARD static tests are the B.C. Research Initial Test (BC RIT) (Bruynesteyn & Duncan, 1979) and the U.S. Environmental Protection Agency's Acid-Base-Accounting procedure (EPA ABA) (Sobek et al., 1978; CANMET, 1990). Considerable controversy exists over which of these two tests provides the best results for predicting ARD (Calow, et al., 1995). The BC RIT is the preferred method in Nova Scotia (Lund, 1987; Albright, 1987; C. Cole, personal communication), however, the EPA ABA test procedure is used in most other locations (diPretoro & Rauch, 1988; Erickson & Hedin, 1988).

Tables 4.1 and 4.2 outline the methods used to calculate the acid producing, acid consuming, and net acid producing ability for the BC RIT and the EPA ABA procedures

Table 4.1: Summary of the procedure for the BC RIT (Department of Environment - Project Report 1499, 1972). See Appendix B for a more detailed procedure.

BC RESEARCH INITIAL TEST
Acid Producing Ability (AP) = % Sulphur × 30.6
Acid Consuming Ability (AC) = mL(H_2SO_4) × 4.5
Net Acid Consumption = AC - AP
* *all units are kg (H_2SO_4) / tonne*

Table 4.2: Summary of the procedure for the EPA ABA (CANMET - ARD Prediction Manual, 1990). See Appendix C for a more detailed procedure.

US ENVIRONMENTAL PROTECTION AGENCY'S **ACID BASE ACCOUNTING**
Acid Producing Ability (AP) = % Sulphur × 31.35
Acid Consuming Ability (AC) = % Sulphur × $\frac{50\,a\,[x - (b/a)\,y]}{c}$ a = normality of HCL b = normality of NaOH c = sample weight in grams x = volume of HCL add (in mL) y = volume of NaOH added to pH = 7 (in mL)
Net Acid Consumption = AC - AP
* *all units are tonnes* $CaCO_3$ *equivalents / 1000 tonnes*

respectively. It is important to note that the tests vary in method, but are designed for the same purpose; to determine net acid producing ability of the sample. Appendix B outlines the procedure for the BC RIT in more detail and Appendix C describes the EPA ABA procedure.

4.2 Sulphur Analyses

Total sulphur analyses were performed for all seventeen samples in this study. Six samples considered to be lithologically representative of all four sites, containing variable sulphur and carbonate content, were selected for predictive static test analysis. Samples were prepared by crushing the rocks to powders using a jaw crusher, disk mill and shatterbox mill. Sulphur analyses for this study were done at the Technical University of Nova Scotia (Cyril Cole - analyst). Results are presented in Table 4.3. Total sulphur ranges from 0.011 % (Eastville sample) to 6.12 % (Eastville sample). Most samples contain in the range of 1 to 2 % total sulphur.

4.3 Acid Producing Ability

The acid producing ability for the BC RIT is related to the sulphur content of the samples as shown by the following equation:

$$4FeS_2 + 15O_2 + 14H_2O = 4Fe(OH)_3 + 8H_2SO_4 \qquad (4.1)$$

In this equation, two moles of sulphuric acid are produced per mole of pyrite consumed. Total sulphur (atomic weight = 32) is converted to sulphuric acid (molecular weight = 98) assuming a 1:1 conversion factor. The acid producing ability is calculated by multiplying % total sulphur by 30.6 using units of kg H_2SO_4/ tonne. See Appendix B for a detailed outline of the procedure.

Table 4.3: Sulphur analysis for samples CR-95-001 to CR-95-017.

SAMPLE #	LOCATION	TOTAL SULPHUR (%)
CR-95-001	Halifax Area	1.25
CR-95-002	Halifax Area	2.34
CR-95-003	Halifax Area	0.93
CR-95-004	Mount Uniacke	2.41
CR-95-005	Mount Uniacke	1.38
CR-95-006	Mount Uniacke	1.91
CR-95-007	Beaverbank Road	1.53
CR-95-008	Beaverbank Road	2.30
CR-95-009	Beaverbank Road	0.42
CR-95-010	Beaverbank Road	2.75
CR-95-011	Eastville	4.04
CR-95-012	Eastville	6.12
CR-95-013	Eastville	0.011
CR-95-014	Eastville	4.5
CR-95-015	Eastville	0.017
CR-95-016	Eastville	2.54
CR-95-017	Eastville	2.52

The acid producing ability for the EPA ABA procedure is based on the following equation:

$$\mathbf{FeS_2 + 2CaCO_3 + 3.75O_2 + 1.5H_2O \leftrightarrow Fe(OH)_3 + 2SO_4^{-2} + 2Ca^{+2} + 2CO_2} \tag{4.2}$$

This reaction shows that one mole of pyrite (1 FeS_2 = 64g of sulphur) is neutralized by 2 moles of calcite ($2CaCO_3$ = 200g). This relates to a ratio of 1g sulphur to 3.125g of $CaCO_3$. Therefore, 31.25 tonnes of $CaCO_3$ equivalent is needed to neutralize 1000 tonnes of rock containing 1.0 wt. % pyritic sulphur. Therefore, the acid producing ability of the sample is calculated by multiplying the total % sulphur value by the 31.25. Appendix C contains a detailed outline of the procedure.

Table 4.4 displays the acid producing ability results for both tests. One sample from Eastville (CR-95-015) contains very little sulphide minerals and therefore has a low acid producing ability (0.5). For the BC RIT the values range from 71.6 to 187.3. Values for the EPA ABA are only slightly higher than those for the BC RIT allowing for different units and for slightly different theory for the acid producing ability.

4.4 Acid Consuming Ability

Data for the BC RIT acid consuming ability is presented as the kilograms of H_2SO_4 neutralized per tonne of the sample material. Data for the EPA acid consumption is expressed as tonnes of $CaCO_3$ equivalent per 1000 tonnes of the sample material. Even though these units are different, the molecular weights of H_2SO_4 (MW = 98) and $CaCO_3$ (MW = 100) are similar enough for the resulting values to be comparable.

Table 4.5 presents acid consuming ability of the BC RIT. This table shows the amount of H_2SO_4 added per sample and the acid consuming ability (kg / tonne). Acid consuming ability

Table 4.4: Acid producing potential results for both tests. Note: for BC Research Initial Test (BC RIT) the sulphur % is multiplied by 30.6 and for US Environmental Protection Agency's Acid-Base Accounting procedure (EPA ABA) the % sulphur is multiplied by 31.25. These calculations are based on the stoichiometric equations described above.

Sample Number	Location	% Sulphur	Acid Production (BC RIT) x 30.6	Acid Production (EPA ABA) x 31.5
CR-95-002	Hfx Site	2.3	71.6	73.1
CR-95-004	Mt. Uniacke	2.4	73.7	75.3
CR-95-010	BB Hwy	2.8	84.2	85.9
CR-95-012	Eastville	6.1	187.3	191.3
CR-95-014	Eastville	4.5	137.7	140.6
CR-95-015	Eastville	0.02	0.5	0.5

Table 4.5: Acid Consuming Ability results for the BC RIT.

Sample Number	Location	H_2SO_4 added (mL)	Acid Consuming Ability kg/tonne
CR-95-002	Hfx Site	0.3	1.35
CR-95-004	Mt. Uniacke	0.25	1.125
CR-95-010	BB Hwy	0.3	1.35
CR-95-012	Eastville	1.8	8.1
CR-95-014	Eastville	12	54
CR-95-015	Eastville	1.5	6.75

ranges from 1.1 to 54.0. The sample with 54.0 (Eastville) has the highest content of calcite. Table 4.6 indicates the results for the acid consuming ability of the EPA ABA. This table shows the results of the fizz test and the volume and concentration of HCl added to each sample. Also shown is the amount and concentration of NaOH used in the back titration to neutralize the sample. Acid consuming ability (tonnes $CaCO_3$ equivalent / 1000 tonnes) ranges from -11.5 to 65.0. The sample with 65.0 (Eastville) has the highest calcite content.

4.5 Net Acid Consuming Ability

The net acid consuming ability is determined by subtracting the acid producing ability from the acid consuming ability. Negative values indicate a net acid producing ability whereas positive values indicate a net acid consuming ability. Final results of the tests are presented in Table 4.7 showing that five of the six samples tested are net acid producers. The sample that is not net acid producing contains very little total sulphur and also contains calcite, therefore it is not expected to produce acid.

4.6 Discussion

All of the samples studied from the Halifax Formation that contain sulphur have the potential to produce acid. The overall sulphur content and acid consuming capabilities of the rock determine whether or not the sample will be a net acid producer or a net acid consumer. The samples from the Halifax, Mount Uniacke and Beaverbank Highway sites (CR-95-002, 004 and 010) have considerable total sulphur content and, according to the acid consuming tests are not adequate acid consumers. Therefore they are classed as net acid producers. Two samples from

Table 4.6: Acid Consuming Ability results for the EPA ABA procedure.

Sample #	Fizz	Vol. HCl mL	Conc. HCl	Conc. NaOH	Amt. NaOH mL	Acid Consuming Ability tonnes CaCO3 equiv. per 1000 tonnes
CR-95-002	none	20	0.1 N	0.1 N	23.8	-9.5
CR-95-004	none	20	0.1 N	0.1 N	24.6	-11.5
CR-95-010	none	20	0.1 N	0.1 N	23	-7.5
CR-95-012	slight	40	0.1 N	0.1 N	34	15
CR-95-014	moderate	40	0.5 N	0.5 N	34.8	65
CR-95-015	slight	40	0.1 N	0.1 N	34.3	14.3

Table 4.7: Net Acid Consumption results for both tests. "Yes means the sample is acid producing; "no" means it is not

Location	Sample #	% Sulphur	Acid Production (EPA ABA) tonnes CaCO3 equiv per 1000 tonnes	Acid Consumption tonnes CaCO3 equiv per 1000 tonnes	Net Acid Consumption tonnes CaCO3 equiv per 1000 tonnes	
Halifax	2	2.3	73.1	-9.5	-82.6	yes
M. Uniacke	4	2.4	75.3	-11.5	-86.8	yes
BB Highw	10	2.8	85.9	-7.5	-93.4	yes
Eastville	12	6.1	191.3	15.0	-176.3	yes
Eastville	14	4.5	140.6	65.0	-75.6	yes
Eastville	15	0.02	0.5	14.3	13.8	no
			Acid Production (BC RIT) kg(H2SO4)/tonne	Acid Consumption kg(H2SO4)/tonne	Net Acid Consumption kg(H2SO4)/tonne	
Halifax	2	2.3	71.6	1.4	-70.3	yes
M. Uniacke	4	2.4	73.7	1.1	-72.6	yes
BB Highw	10	2.8	84.2	1.4	-82.8	yes
Eastville	12	6.1	187.3	8.1	-179.2	yes
Eastville	14	4.5	137.7	54.0	-83.7	yes
Eastville	15	0.02	0.5	6.8	6.3	no

Eastville (CR-95-12 and 14) contain significant concentrations of sulphur and also have higher acid consuming abilities, due to their calcite content. However, they were still found to be net acid producers. The only sample that is not a net acid producer is CR-95-015, from Eastville. This is because it has a very low total sulphur content.

In a study comparing the BC RIT and the EPA ABA procedures, Calow, et al. (1995) has shown the EPA ABA procedure gives a higher number for the acid consuming ability of the sample as shown in Figure 4.1. With these discrepancies between the two procedures, samples with considerable total sulphur content could be ruled net acid consuming by the EPA procedure when the BC RIT would classify them as net acid producing. Such samples have not been found in the Halifax Formation as part of this study. Samples studied by Calow must have had considerable calcite content for the acid consuming ability to be so high. Within the Meguma Group of Nova Scotia, such samples would likely only be found within the transition zone if they occur at all.

4.7 Advantages And Disadvantages Of The Static Tests

Material for the following discussion is taken mainly from CANMET (1990) and Calow et al. (1995). Fundamental problems exist in several aspects of the BC RIT and the EPA ABA theory and procedures. Regarding the acid producing ability, both tests involve assumptions that (1) all sulphur occurs as pyrite; (2) that there is a total conversion of sulphur to sulphate; and (3) that all pyrite is consumed by the reaction. As presented in Chapter 3, all sulphur does not occur as pyrite. Assumptions 2 and 3 may or may not hold, depending on the environmental conditions existing at the specific site.

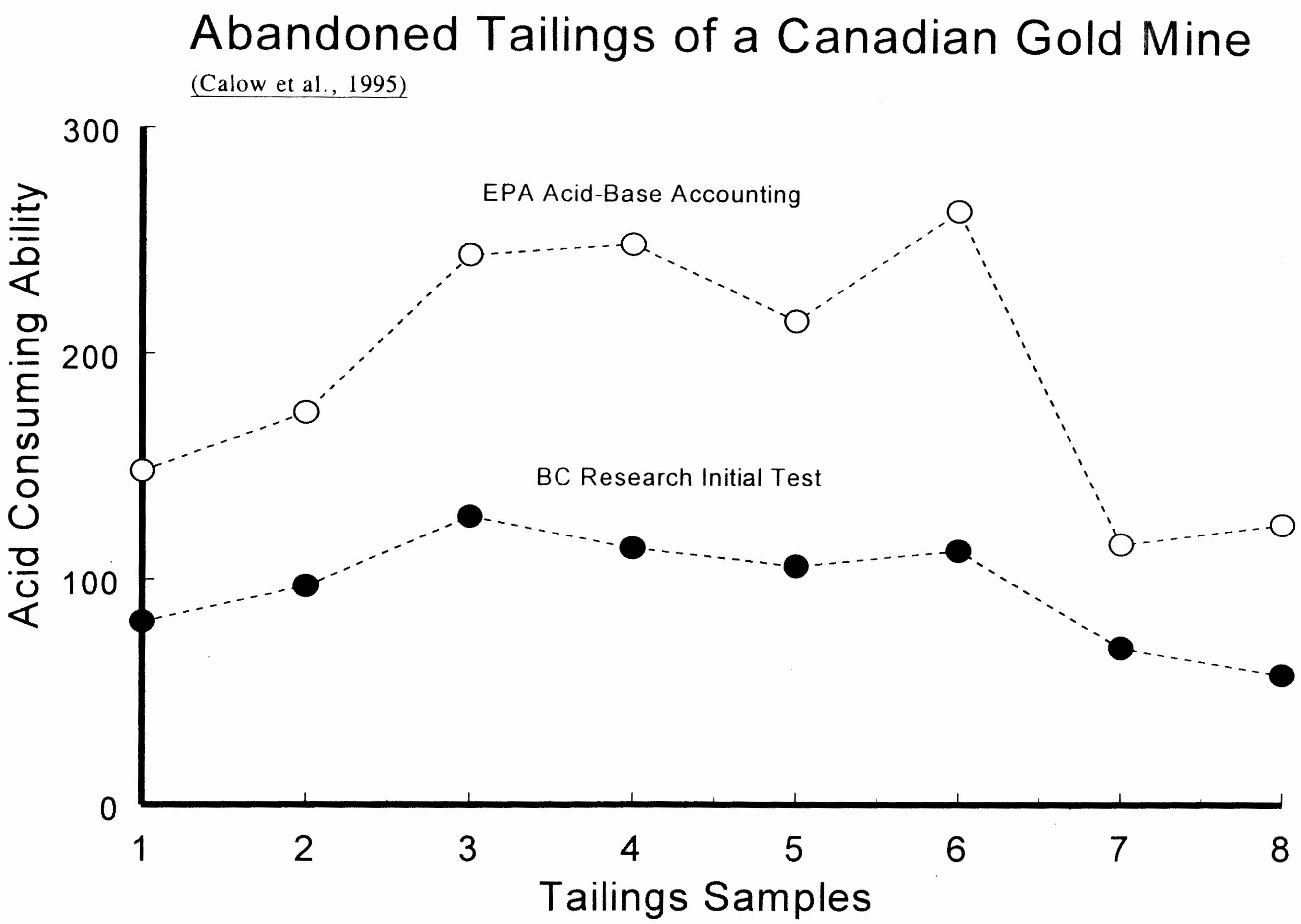


Figure 4.1: Comparison of acid consuming ability for the BC RIT and the EPA ABA procedures. Samples are from abandoned tailings of a Canadian gold mine. Data show a large discrepancy in results between the two tests (Calow et al., 1995).

In the acid consuming tests, advantages of the EPA ABA procedure include the fact that it is a much less labour intensive method of testing and is relatively quick. This method also enables the analyst to control the completion time of the test. The BC RIT procedure has excellent reproducibility and some consider it the most representative of the acid drainage problem in nature because it uses H_2SO_4, the main ARD component, as part of the titration process. This technique is less complicated and therefore less prone to operator error.

Disadvantages of the EPA ABA are that it requires the use of HCl which is a very strong acid. The heating of this acid creates a solution that attacks mineral phases that would not normally weather to produce H_2SO_4, and is therefore not very representative of acid drainage conditions in nature. This heating process also causes an acidic vapour to form. These problems combined lead to excessive consumption of HCl, creating a higher acid consuming ability. The fizz test used to determine the normality of HCl in this procedure may produce very arbitrary results. It is quite difficult for the analyst to distinguish between a slight and moderate fizzing leading to possible discrepancies in the calculations of the acid consuming ability of the samples (Appendix C). Further problems arise when trying to achieve a pH endpoint for 30 seconds, due to pH instrument drift.,

The BC RIT test can be quite long because the analyst has no control over the stop time of the experiments. More equipment and space is required to carry out the experiments than needed for the EPA ABA test.

4.8 Conclusions

In cases where rocks are well into the acid producing field it is irrelevant which test is used. However, for more borderline cases mineralogy, kinetic tests and metal analyses are necessary to obtain the most accurate prediction of acid drainage potential. Tests indicate that the five samples containing significant amounts of total sulphur from the Halifax Formation are well into the acid producing field. Variable silicate mineralogy apparently has little effect on the results of the acid consuming tests. The only mineral likely to affect these tests is calcite.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 Pyrrhotite

In the Halifax Formation, the predominant sulphide mineral in the samples examined in this study is pyrrhotite. Also present, in lesser amounts, are pyrite, chalcopyrite, löllingite, ilmenite, rutile and garnet. Microprobe data indicate that the pyrrhotite is the monoclinic variety (Fe_7S_8). The average composition of the grains probed lies between 45.5 and 47.5 atomic % Fe, in the ideal monoclinic pyrrhotite range. Data from analysis of pyrrhotite in drillcore samples from the Halifax International Airport overlap with the data from this study.

Pyrrhotite from four samples show typical, almost equal intensity XRD double peaks, indicative of monoclinic pyrrhotite. These data confirm the results from the microprobe work.

In comparing pyrrhotite composition between samples taken from different geological settings (proximal and distal from the granitic intrusions), these results suggest there is little to no regional variation in pyrrhotite composition. Samples close to granitic intrusions do contain significant sulphide minerals and are theoretically acid producing, contrary to reports in the literature for Nova Scotia.

5.1.2 Predictive Static Tests

Acid drainage predictive static testing on six of the samples show that rocks from the sites studied are overall net acid producers, indicating a definite risk of ARD, if these rocks are allowed to oxidize. Acid production results from the two static tests vary slightly. Results from the BC RIT range between 0.5 - 187.3 kg (H_2SO_4)/tonne of material and those from the EPA ABA are between 0.5 - 191.3 tonnes $CaCO_3$ equivalent per 1000 tonnes of material. Acid consumption results also vary between the two tests. The BC RIT is between 1.1 - 54.0 kg (H_2SO_4)/tonne of material and the EPA ABA is between -11.5 - 65.0 tonnes $CaCO_3$ equivalent per 1000 tonnes of material. Net acid consumption results, for both tests, show that all but one of the samples analyzed is classified as a net acid producer.

5.2 Recommendations

This study confirms that there is a risk of acid drainage in the Halifax Formation and proves that the risk is not just in certain areas. Therefore, all areas should be treated as potential ARD producers.

Results from the static ARD tests should be regarded carefully. First, the number of tests completed in this thesis, although positive, are insufficient to reach conclusions with statistical validity. Perhaps, tens to hundreds of similar tests should be completed to obtain a thorough representation of a site. Second, the variability in net acid producing results within a sample site indicate that thorough sampling techniques and detailed mineralogical studies be an essential step in landuse planning throughout the Halifax Formation.

Finally, since this study indicates that monoclinic pyrrhotite is the most abundant magnetic mineral in the Halifax Formation, magnetic maps may be useful in predicting potential ARD problem areas.

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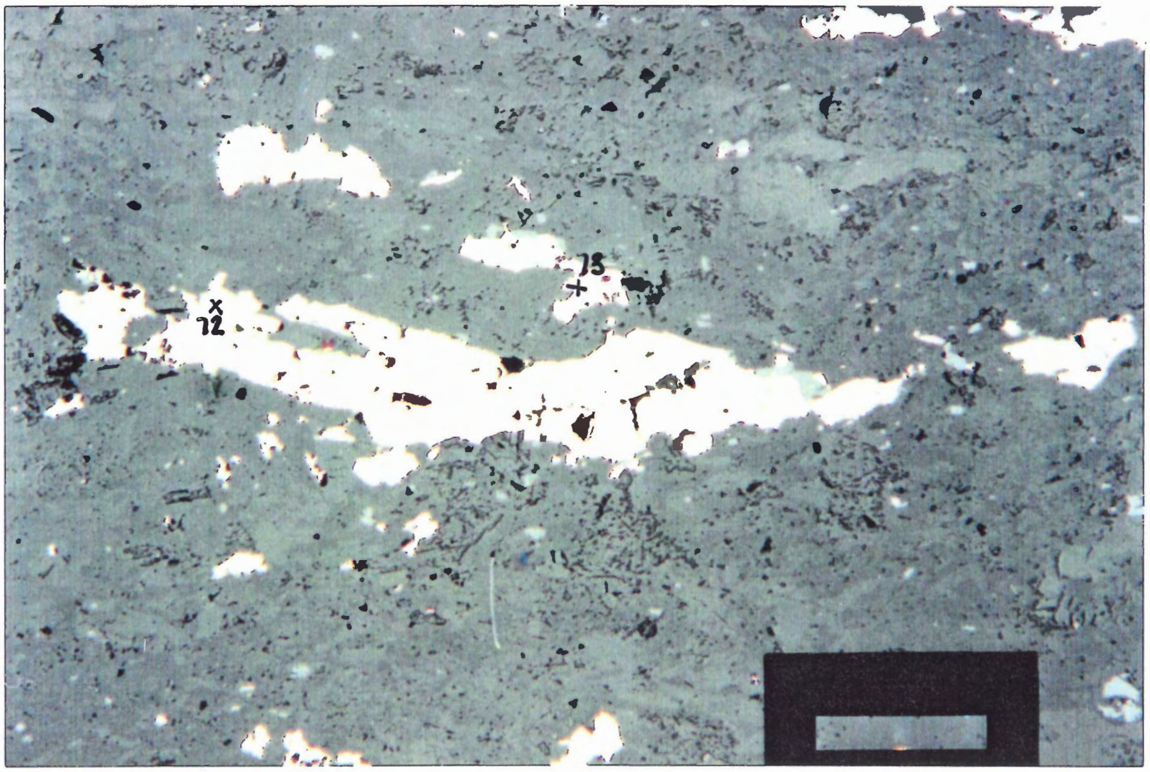
Appendix A

Petrographic Descriptions and Microprobe Data

CR-95-001	Halifax site	
Lithology:	pelitic slate (hornfels)	
Mineralogy:	fine-grained groundmass	70%
	andalusite (chiastolite; subhedral; 1-1.5 mm)	20%
	pyrrhotite (poikiloblastic)	10%
	chalocopyrite (inclusions)	minor
	ilmenite(?)/rutile(?) (inclusions)	minor

Massive (no slaty cleavage), fine-grained, medium-grey. Pyrrhotite is elongate (≤ 2.0 mm) and disseminated. The larger elongate grains contain inclusions of ilmenite(?)/rutile(?), chalcopyrite and silicate minerals. Ilmenite and rutile appear to be intergrown. The texture is granoblastic.



Mineral Sample # Point	Pyrrhotite CR-95-001 72	Pyrrhotite CR-95-001 73
Zn	0.47	0.02
Fe	59.30	59.68
As	0.31	0.16
S	38.59	38.80
Total	98.68	98.66

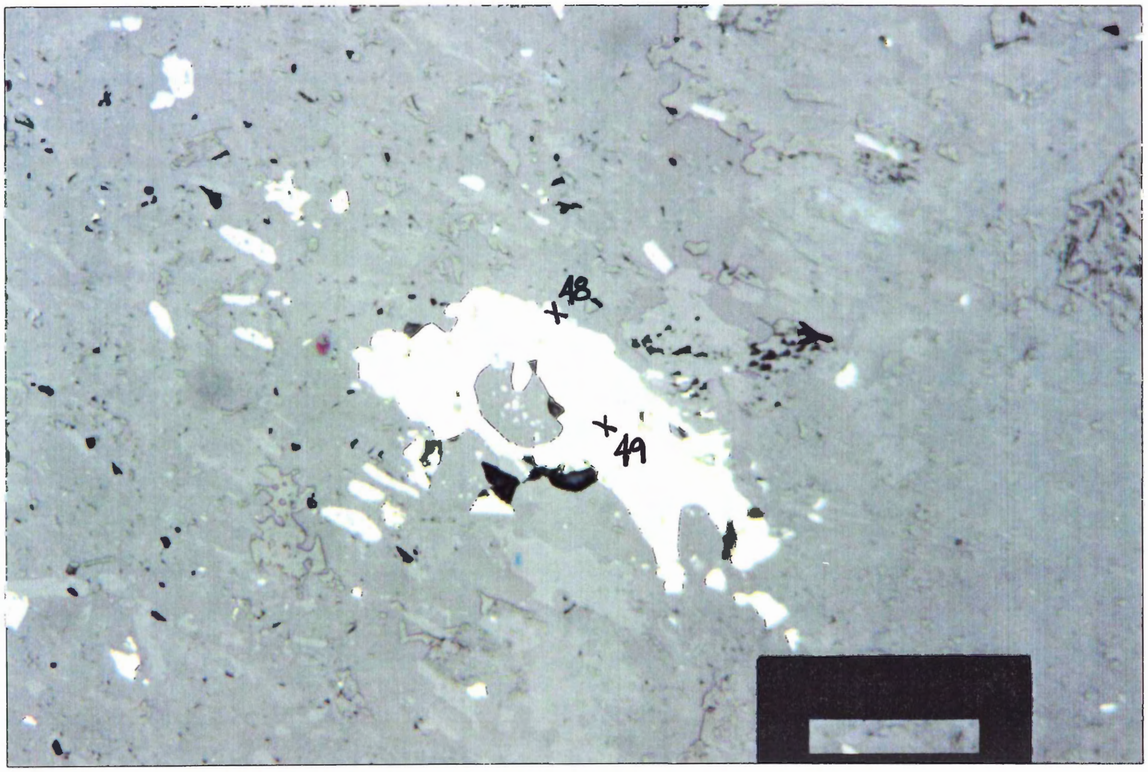
CR-95-002	Halifax site	
Lithology:	pelitic slate (hornfels)	
Mineralogy:	fine-grained groundmass	50%
	andalusite (chiastolite; subhedral; 1-1.5 mm)	35%
	pyrrhotite (poikiloblastic)	15%
	pyrite (inclusions)	minor
	chalcopyrite (inclusions)	minor
	ilmenite (inclusions)	minor
	rutile (inclusions)	minor

Massive (no slaty cleavage), fine-grained, medium-grey. Bedding is visible; layers rich in andalusite are separated by a pyrrhotite-rich layer. Pyrrhotite in the sulphide layer is elongate parallel to bedding (≤ 3.0 mm) and contains inclusions of ilmenite, rutile, pyrite, chalcopyrite and silicate minerals. Other pyrrhotite grains are smaller (≤ 1.0 mm) and are disseminated throughout the other layers. The texture is granoblastic.

Mineral Sample # Point	Pyrrhotite CR-95-002 41	Rutile CR-95-002 42	Ilmenite CR-95-002 43	Ilmenite CR-95-002 44
Fe	59.76	0.22	32.40	30.08
As	0.32	-	-	-
S	38.01	-	-	0.15
Ni	0.35	-	-	-
Mn	-	-	1.47	2.52
Co	0.40	-	-	-
Au	-	0.32	-	-
Cr	-	0.32	-	-
Si	-	0.16	0.10	0.18
Ti	-	51.67	27.92	28.55
Al	-	-	-	0.09
Mg	-	-	-	0.18
Total	98.84	52.68	61.89	61.75

CR-95-003	Halifax site	
Lithology:	pelitic slate (hornfels)	
Mineralogy:	fine-grained groundmass	60%
	andalusite (chiastolite; subhedral; 1-2 mm)	30%
	pyrrhotite (poikiloblastic)	5%
	cordierite? (highly altered)	< 5%
	chalcopyrite (inclusions)	minor
	ilmenite (inclusions)	minor

Massive (no slaty cleavage), fine-grained, medium-grey. Pyrrhotite grains are all elongated (< 1.0 mm) and disseminated. They contain small inclusions of ilmenite, chalcopyrite and silicate minerals. The texture is granoblastic.



Mineral Sample # Point	Pyrrhotite CR-95-003 46	Pyrrhotite CR-95-003 49	Ilmenite CR-95-003 48
Fe	59.36	58.91	31.79
S	38.76	38.44	-
Mn	-	-	1.67
Co	0.35	-	-
Si	-	0.11	-
Ti	-	0.56	28.19
Total	98.47	98.02	61.65

CR-95-004	Mount Uniacke site	
Lithology:	pelitic slate (hornfels)	
Mineralogy:	fine-grained groundmass	65%
	pyrrhotite (poikiloblastic)	15%
	cordierite? (highly altered)	10%
	andalusite (chiastolite; subhedral; 1-1.5 mm)	5%
	pyrite (anhedral)	5%
	chalcopyrite (inclusions)	minor
	ilmenite (inclusions and replacement)	minor
	rutile (inclusions and replacement)	minor

Massive (no slaty cleavage), very fine-grained, dark-grey. Pyrrhotite grains (≤ 2 mm) are both round and elongated. They contain inclusions of chalcopyrite and silicate minerals. Pyrite grains are larger (≤ 1 cm), elongate and contain fewer inclusions than pyrrhotite. In some cases, pyrite grains are partially or completely replaced by ilmenite and rutile. Sulphides appear to be concentrated along bedding planes.

Mineral Sample # Point	pyrite 004 63	pyrite 004 65	pyrite 004 4	pyrrho 004 6	pyrrho 004 7	pyrrho 004 8	pyrrho 004 9	pyrrho 004 10	ilmen 004 11	ilmen 004 67
Fe	46.38	45.86	47.34	61.02	60.01	59.30	59.46	60.20	30.04	29.96
As	0.32	-	0.29	-	-	-	-	-	-	-
S	51.45	51.94	53.23	40.03	39.64	39.78	39.79	39.92	-	-
Ni	-	0.40	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	-	-	3.46	2.29
Co	0.34	-	-	-	-	0.38	-	-	-	-
Sn	-	-	-	-	-	0.35	-	-	-	-
Cr	-	-	-	-	-	-	-	-	-	0.13
Ti	-	-	-	-	-	-	-	-	28.29	27.08
Mg	-	-	-	-	-	-	-	-	0.13	0.20
Total	98.50	98.20	100.85	101.05	99.65	99.82	99.25	100.12	61.93	59.66

Mineral Sample # Point	ilmenite 004 28	ilmenite 004 30	ilmenite 004 31	rutile 004 29
SiO_2	0.19	0.25	0.18	4.06
TiO_2	52.44	53.01	52.42	81.39
Al_2O_3	-	-	-	2.52
FeO	45.55	43.48	44.24	4.32
MnO	2.35	2.42	2.81	0.11
MgO	0.28	0.14	0.16	1.39
Total	100.81	99.30	99.80	93.80

CR-95-005	Mount Uniacke site	
Lithology:	pelitic slate (hornfels)	
Mineralogy:	fine-grained groundmass	65%
	cordierite? (highly altered)	20%
	pyrrhotite (poikiloblastic)	15%
	pyrite	minor
	chalcopyrite (inclusions)	minor
	ilmenite (inclusions and replacement)	minor
	rutile (inclusions and replacement)	minor

Massive (no slaty cleavage), very fine-grained, dark-grey. Pyrrhotite grains are small (≤ 1 mm), elongated and disseminated. They contain inclusions of chalcopyrite and silicate minerals. In some cases, pyrrhotite grains are partially or completely replaced and/or rimmed by ilmenite and rutile. Pyrrhotite also occurs in thin (< 0.5 mm thick) veins. Minor euhedral pyrite (< 0.5 mm) is present. A well developed fabric is visible, with quartz ribbons and pressure shadows occurring.

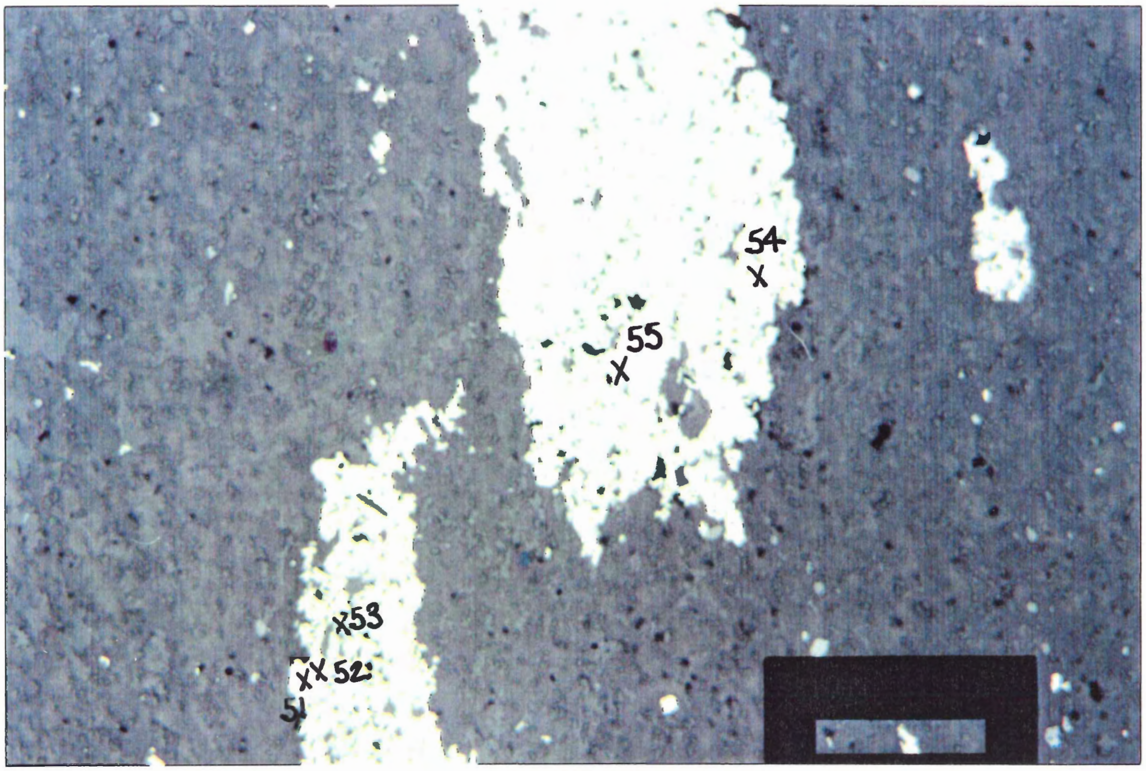
Mineral Sample # Point	pyrite CR-95-005 68	pyrite CR-95-005 69	ilmenite CR-95-005 71
Fe	46.48	46.53	30.04
As	-	0.24	-
S	52.02	53.28	-
Ni	-	-	-
Mn	-	-	3.24
Ti	0.18	-	27.72
Total	98.68	100.16	61.17

Mineral Sample # Point	ilmenite CR-95-005 24	ilmenite CR-95-005 25	rutile CR-95-005 26	rutile CR-95-005 27
SiO_2	0.18	0.13	0.21	0.19
TiO_2	52.99	51.99	99.18	98.65
FeO	42.85	43.44	0.62	1.22
MnO	4.10	4.57	-	-
MgO	0.16	0.19	-	-
Total	110.28	100.33	100.01	100.06

100.28

CR-95-006	Mount Uniacke site	
Lithology:	pelitic slate	
Mineralogy:	fine-grained groundmass	80%
	pyrrhotite (poikiloblastic)	15%
	ilmenite (inclusions and replacement)	5%
	chalcopyrite (inclusions)	minor
	Löllingite - $FeAs_2$ (inclusion)	minor

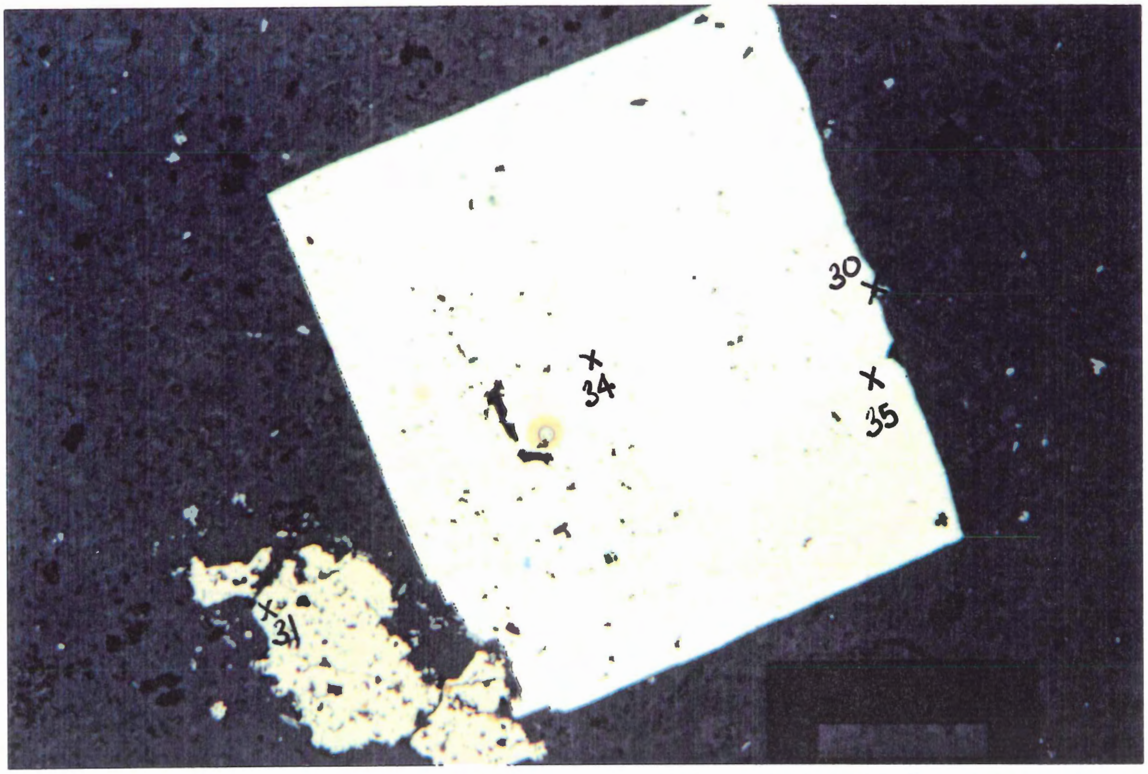
Massive (no slaty cleavage), fine-grained, dark-grey. Pyrrhotite grains vary in size (< 0.5 - 4 mm) and are disseminated throughout the slide. The larger grains are elongated and contain inclusions of ilmenite, chalcopyrite and silicate minerals. One pyrrhotite grain has an inclusion of an arsenic mineral (0.3 mm).



Mineral Sample # Point	pyrrhotite CR-95-006 50	pyyrrhotite CR-95-006 55	arsenopyrite CR-95-006 51	arsenopyrite CR-95-006 52	chalcopyrite CR-95-006 54	ilmenite CR-95-006 53
Cu	-	-	0.14	-	36.28	-
Fe	59.86	59.65	31.98	31.80	30.06	26.91
As	-	0.29	48.31	48.13	-	-
S	38.71	38.61	16.79	16.93	33.92	-
Mn	-	-	-	-	-	6.57
Co	-	-	1.42	1.73	-	-
Si	-	-	-	-	0.12	0.42
Ti	-	-	-	-	-	27.37
Total	98.57	98.54	98.64	98.59	100.37	61.28

CR-95-007	Beaverbank Highway site	
Lithology:	pelitic slate	
Mineralogy:	fine-grained groundmass	85%
	pyrrhotite (poikiloblastic)	10%
	pyrite (euhedral)	5%
	chalcopyrite (inclusions)	minor
	rutile (inclusions)	minor
	ilmenite (inclusions)	minor

Slaty cleavage, very fine-grained, dark-grey. Pyrrhotite grains (≤ 2 mm) are rounded and elongated. They contain inclusions of silicate minerals, rutile, ilmenite and chalcopyrite. Pyrite (≤ 1 mm) is mostly euhedral with few inclusions. Minor folding and cross-bedding are visible. Sulphides are concentrated along discrete bedding planes.



Min Samp # Pnt	py 007 28	py 007 29	py 007 34	py 007 35	py 007 37	po 007 31	po 007 32	po 007 38	rutile 007 30	rutile 007 33	rutile 007 39	aspy 007 36
Fe	47.11	47.21	46.44	46.41	46.25	60.71	60.69	59.70	0.38	0.58	0.47	34.79
As	0.45	0.36	0.40	0.78	0.40	-	-	-	-	-	-	44.34
S	53.25	53.78	52.26	52.58	51.87	39.47	39.29	38.96	-	-	-	20.34
Co	-	0.35	-	-	-	-	-	-	-	-	-	-
Ti	-	-	-	-	-	-	-	-	52.95	52.45	51.70	-
Total	100.81	101.70	99.09	99.77	98.52	100.18	99.98	98.66	53.33	53.03	52.18	99.47

CR-95-008	Beaverbank Highway site	
Lithology:	pelitic slate	
Mineralogy:	fine-grained groundmass	90%
	pyrrhotite (poikiloblastic)	5%
	pyrite (subhedral and euhedral)	5%
	sphalerite (inclusions and replacement)	minor
	chalcopyrite (inclusions)	minor
	rutile (inclusions and separate grains)	minor

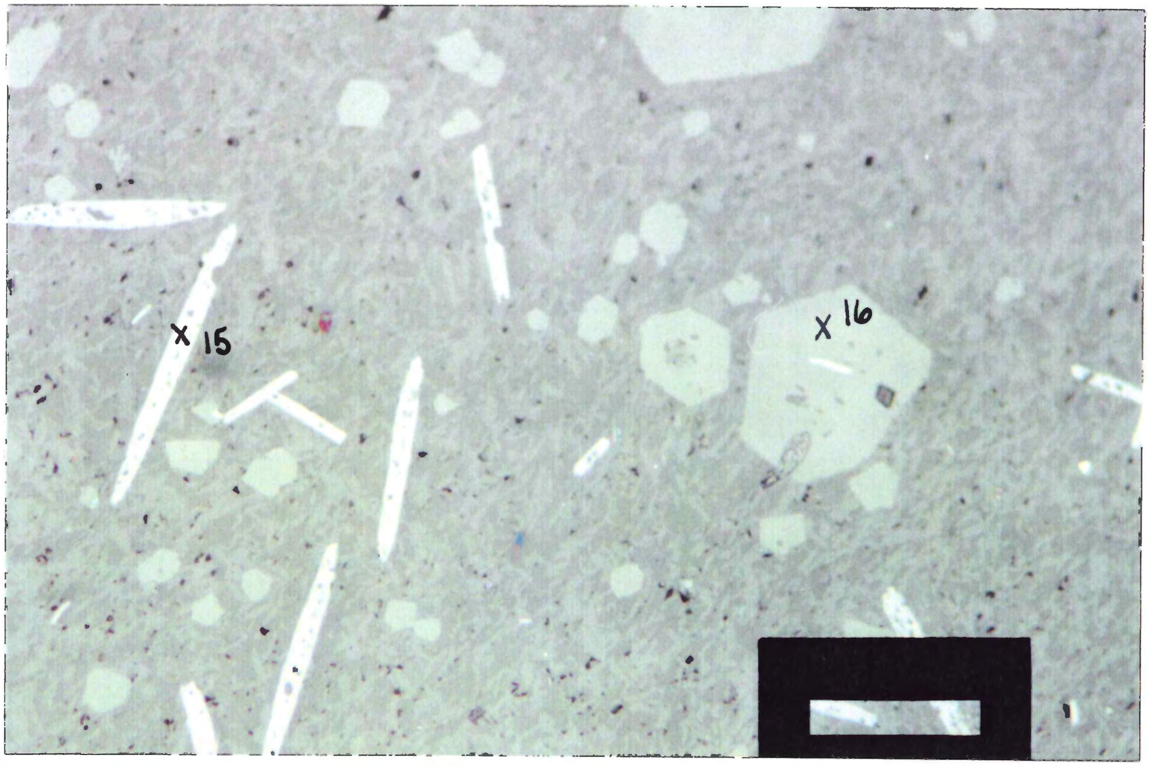
Slaty cleavage, fine-grained, dark-grey. Pyrrhotite grains (≤ 5 mm) are mostly elongated and are concentrated along cleavage planes. They contain inclusions of sphalerite, chalcopyrite, rutile and silicate minerals. Subhedral pyrite (≤ 2 mm) contains the same types of inclusions, but is not as poikiloblastic as pyrrhotite. Euhedral pyrite (≤ 1 mm) does not contain inclusions. Pyrite also rims and replaces pyrrhotite along fractures.

Min Samp # Pnt	po 008 3	po 008 9	cpy 008 4	cpy 008 5	cpy 008 8	sphl 008 6	sphl 008 7	sphl 008 14	rutile 008 13	py 008 10	py 008 11
Zn	-	-	-	-	-	56.09	56.29	59.15	-	-	-
Cu	-	-	36.64	36.80	36.53	0.63	0.38	0.46	-	-	-
Fe	60.86	61.30	30.99	30.60	30.84	5.31	4.81	6.83	0.34	47.04	47.38
As	-	-	-	-	-	-	-	-	-	0.71	0.61
S	39.28	39.13	34.27	34.36	34.70	28.39	27.06	32.45	-	53.41	53.63
Ti	-	-	-	-	-	6.25	7.00	-	48.49	-	-
Total	100.1	100.4	101.9	101.8	102.1	96.7	95.5	98.9	48.8	101.2	101.6

CR-95-009	Beaverbank Highway site	
Lithology:	pelitic slate	
Mineralogy:	fine-grained groundmass	65%
	garnet (subhedral and euhedral)	15%
	ilmenite (tabular)	15%
	pyrrhotite (poikiloblastic)	5%
	chalcopyrite (inclusions)	minor

Slaty cleavage, fine-grained, dark-grey. Pyrrhotite grains (≤ 1 mm) are rounded and contain inclusions of chalcopyrite and silicate minerals. A Mn-rich silicate mineral rims most grains. Pyrrhotite is concentrated along discrete beds. Spessartine garnet (≤ 0.5 mm) and ilmenite (≤ 0.5 mm long) occur as larger grains within the groundmass. Some garnets contain tabular ilmenite inclusions. Folds are visible in thin section and hand sample.

Mineral Sample # Point	pyrrhotite CR-95-009 56	pyrrhotite CR-95-009 57	chalcopyrite CR-95-009 60
Cu	-	-	36.34
Fe	58.94	59.12	30.51
S	38.90	38.58	34.14
Total	97.84	97.7	101



Min Samp # Pnt	garnet 009 5	garnet 009 6	garnet 009 8	garnet 009 9	garnet 009 16	ilmen 009 11	ilmen 009 12	ilmen 009 13	ilmen 009 14	ilmen 009 15
SiO_2	36.35	36.27	36.89	37.06	36.76	4.09	1.18	0.21	0.25	0.34
TiO_2	0.26	0.23	0.07	0.18	0.09	50.55	51.72	51.78	53.50	52.56
Al_2O_3	20.47	20.43	20.87	20.76	20.42	0.18	-	-	-	-
FeO	12.49	10.44	18.52	17.98	10.90	27.49	29.95	27.97	30.40	29.87
MnO	28.21	29.57	22.29	21.70	29.21	18.05	17.72	19.03	16.85	17.52
MgO	0.18	0.29	0.47	0.40	0.24	-	-	-	-	-
CaO	2.80	3.05	2.55	2.40	2.78	-	-	0.16	-	0.05
Na_2O	-	-	0.18	-	0.12	0.12	0.17	0.12	0.10	0.25
Total	100.8	100.3	101.8	100.5	100.5	100.5	100.8	99.26	101.1	100.6

CR-95-010 Beaverbank Highway site
Lithology: pelitic slate

Mineralogy:		
	fine-grained groundmass	85%
	pyrrhotite (poikiloblastic)	10%
	pyrite (rims and inclusions)	5%
	chalcopyrite (inclusions)	minor

Slaty cleavage, fine-grained, dark-grey. Pyrrhotite grains (≤ 3 mm) are rounded and contain inclusions of chalcopyrite and silicate minerals. Pyrrhotite is rimmed and replaced by pyrite along fractures. Quartz veins (< 1mm thick) appear to be rimmed by haematite in places. Discrete beds and folds are visible in thin section. Sulphides are concentrated along cleavage which is perpendicular to bedding.

Mineral Sample # Point	cpy 010 15	cpy 010 34	pyrite 010 17	pyrite 010 18	pyrite 010 20	pyrite 010 22	pyrite 010 32	pyrite 010 33	pyrite 010 39
Cu	36.47	34.86	-	-	-	-	-	-	-
Fe	30.90	30.54	46.38	43.98	47.00	46.86	46.50	46.28	46.40
As	-	-	0.25	0.27	0.34	0.25	0.35	0.12	0.39
S	34.46	34.92	52.80	49.03	52.98	52.49	53.41	53.76	53.79
Ti	-	-	-	3.86	-	-	-	-	-
Total	101.8	100.32	99.43	97.14	100.3	99.61	100.26	100.16	100.58

Mineral Sample # Point	py 010 36	po 010 21	po 010 24	po 010 30	po 010 31	po 010 37	po 010 38	po 010 39
Cu	-	-	-	-	-	-	-	-
Fe	46.78	60.59	60.33	59.87	59.94	59.87	59.89	59.86
As	0.23	-	-	-	-	-	-	-
S	53.63	39.57	39.31	39.58	39.76	39.52	40.06	40.08
Ti	-	-	-	-	-	-	-	-
Total	100.65	100.15	99.65	99.45	99.7	99.38	99.95	99.93

CR-95-011	Eastville	
Lithology:	calcareous quartzite	
Mineralogy:	pyrrhotite	35%
	garnet	30%
	fine-grained groundmass	25%
	calcite	10%
	pyrite (inclusions)	minor
	chalcopyrite (inclusions)	minor

Fine-grained, grey, cleavage (not well developed). Pyrrhotite occurs as elongate poikiloblastic grains (≤ 6 mm), appearing along bedding planes. It occurs as a "groundmass" on one side of the slide. It is difficult to tell if this is an exceptionally large poikiloblastic grain or if it is a high concentration of smaller disseminated grains. Pyrrhotite contains inclusions of garnet, pyrite and chalcopyrite. Garnets (≤ 0.5 mm) are euhedral and subhedral and some grains contain sulphide inclusions. Calcite occurs in carbonate-rich layers.

Mineral Sample # Point	pyrrhotite CR-95-011 18	pyrrhotite CR-95-011 19	pyrrhotite CR-95-011 21	pyrrhotite CR-95-011 22	pyrrhotite CR-95-011 23	pyrrhotite CR-95-011 24	pyrite CR-95-011 20
Fe	60.29	60.10	60.06	60.03	60.39	59.77	54.48
S	40.03	39.92	39.92	39.92	40.20	39.69	35.53
Si	-	-	-	-	-	-	1.85
Al	-	-	-	-	-	-	1.88
Mg	-	-	-	-	-	-	0.47
Total	100.32	100.02	99.97	99.95	100.59	99.46	94.21

CR-95-012	Eastville	
Lithology:	calcareous quartzite	
Mineralogy:	fine-grained groundmass	35%
	garnet	35%
	pyrrhotite	15%
	calcite	15%
	pyrite	minor
	chalcopyrite	minor

Fine-grained, grey, cleavage (not well developed). Pyrrhotite grains are both rounded and elongated and contain inclusions of pyrite and chalcopyrite. Elongate grains (≤ 5 mm) are concentrated along bedding planes. Rounded grains (≤ 1 mm) are more disseminated. Garnet (≤ 0.2 mm) is euhedral and subhedral. Calcite occurs in veins (< 1 mm thick) and in carbonate-rich layers.

Mineral Sample # Point	pyrrhotite CR-95-012 25	pyrrhotite CR-95-012 26	pyrrhotite CR-95-012 27	pyrrhotite CR-95-012 28	pyrrhotite CR-95-012 29
Fe	59.71	59.76	60.50	60.01	60.01
S	39.95	39.98	39.92	39.84	39.69
Total	99.67	99.74	100.42	99.84	99.70

CR-95-013	Eastville	
Lithology:	quartzite (psammitic)	
Mineralogy:	fine-grained groundmass	95%
	ilmenite	5%
	garnet	minor
	calcite	minor

Fine-grained, grey, cleavage (not well developed). Tabular ilmenite grains (< 1 mm) and subhedral garnets (< 1 mm) are disseminated throughout the slide. Thin calcite veins (< 0.1 mm thick) are visible in thin section. No sulphides appear in this thin section.

CR-95-014	Eastville	
Lithology:	pelitic slate	
Mineralogy:	fine-grained groundmass	65%
	pyrrhotite	15%
	calcite	15%
	pyrite	minor
	chalcopyrite	minor
	ilmenite?/rutile?	minor

Fine-grained, dark grey, cleavage (not well developed). Pyrrhotite (≤ 7 mm) is elongated and contains inclusions of pyrite, chalcopyrite, titanium oxides and silicate minerals. Garnet (≤ 0.8 mm) is subhedral and anhedral and some grains contain inclusions of pyrrhotite. Calcite veins (≤ 5 mm thick) occur and calcite also rims garnet and pyrrhotite minerals. Pyrrhotite and garnet minerals are concentrated along bedding planes.

Mineral Sample # Point	pyrrhotite CR-95-014 12	pyrrhotite CR-95-014 13	pyrrhotite CR-95-014 14	pyrrhotite CR-95-014 15	pyrrhotite CR-95-014 17	pyrite CR-95-014 16
Fe	59.73	59.38	59.94	59.39	59.25	46.18
S	39.95	39.85	39.95	40.15	39.79	52.76
Total	99.67	99.23	99.89	99.55	99.04	98.94

CR-95-015	Eastville	
Lithology:	calcareous sandy-slate (semi-pelitic)	
Mineralogy:	fine-grained groundmass	30%
	calcite	30%
	garnet	30%
	ilmenite	10%
	pyrite	minor
	chalcopyrite	minor

Fine-grained, light-grey, cleavage (not well developed). Subhedral and anhedral garnets (< 0.2 mm) and ilmenite laths (< 0.2 mm) are disseminated throughout the slide. Minor sulphide grains (< 0.5 mm) are present. Calcite-rich layers are interbedded with silicate-rich layers. Folding is visible in thin section.

CR-95-016	Eastville	
Lithology:	sandy-slate (semi-pelitic)	
Mineralogy:	fine-grained groundmass	70%
	pyrrhotite	15%
	garnet	15%
	ilmenite	minor
	pyrite	minor
	chalcopyrite	minor
	arsenopyrite	minor

Fine-grained, grey, cleavage (not well developed). Pyrrhotite grains (≤ 2 mm) are elongated and contain inclusions of pyrite, chalcopyrite, arsenopyrite and silicate minerals. Garnet (< 0.5 mm) is anhedral and subhedral, disseminated throughout certain beds and in some areas it appears to be rimming many of the pyrrhotite grains. Ilmenite laths (< 0.5 mm) are disseminated and only occur in certain layers. Sulphides appear to be concentrated along bedding planes.

CR-95-017	Eastville	
Lithology:	pelitic slate	
Mineralogy:	fine-grained groundmass	35%
	garnet	30%
	pyrrhotite	15%
	pyrite	10%
	calcite	10%
	ilmenite	minor

Fine-grained, grey, cleavage (not well developed). Pyrrhotite grains (< 3 mm) are rounded and disseminated throughout certain beds. Pyrrhotite appears to contain inclusions of anhedral garnet. Pyrite occurs in veins (< 1 mm thick) and as elongate grains (≤ 5 mm). Subhedral and anhedral garnets (< 0.5 mm) are disseminated throughout the groundmass and form rims around the pyrrhotite grains. Two calcite veins cut the thin section (larger is 2 mm thick). Sulphides appear to be concentrated along bedding planes.

Appendix B

BC Research Initial Test Procedure

BC Research Initial Test Procedure

1. Initial Test

(a) Sample - The sample selected must be taken in such a manner that it is truly representative of the type of mineralization being examined. A composite made up of split drill core or of randomly selected grab samples should be satisfactory. The number of samples to be examined will depend on the variability of the mineralization and must be left to the discertion of the geologist taking the samples. The bulk sample is crushed to a size which can be conveniently handled, (ie -2 inch) and then thoroughly mixed and approximately a 2 lb portion split out, using the usual coning and quartering technique. This sample is then pulverized to pass a 100 mesh screen and used for assay, the titrarion test, and the confirmation test if necessary.

(b) Assay - The pulverized sample is assayed in duplicate for total sulphur. The use of a Leco furnace is recommended, although a chemical oxidation technique followed by barium sulphate precipitation is satisfactory. The total sulphur assay value is expressed as pounds of sulphuric acid per ton of sample, assuming a 1:1 conversion factor, which is the acid-producing potential of the sample.

(c) Titration Test - Duplicate 10 gram portions of the pulverized sample are suspended in 100 ml of distilled or de-ionized water and stirred for approximately fifteen minutes. The natural pH of the sample is then recorded and the sample titrated to pH 3.5 with 1.0 Normal sulphuric acid and left stirring. If an automatic titrator is used the test is continued until less than 0.1 ml of acid is added over a 4 hour period. If manual titration is used, the addition of acid is repeated every half-hour (approximately) until the pH change over a 4 hour period is 0.1 pH unit or less. The total volume of acid added is recorded and converted to lbs per ton of sample. This is the acid consuming ability of the sample, ie:

$$Acid\ consumingability\ (lbs/ton) = \frac{mL\ of\ 1.0N\ H_2SO_4 \times 0.049 \times 2000}{weight\ of\ sample\ (grams)}$$

$$For\ a\ 10\ gram\ sample = mL\ 1.0N\ H_2SO_4 \times 9.8$$

Note: to get acid consuming ability in units of kg/tonne, the mL of acid is multiplied by 4.5 (C.Cole personal communication).

(d) Interpretation - If the acid consuming value (in lbs of acid per ton of sample) exceeds the acid-producing potential (lbs per ton) then the sample will not be a source of acid mine drainage and no additional work is necessary. If the acid consumption is less than the acid-producing potential, the possibility of acid mine water production exists and the confirmation test should be conducted.

Appendix C

US Environmental Protection Agency's Acid Base Accounting Test Procedure

* Note: Some of the terminology in this procedure is different than that used in Chapter 4. Changes were made in order to clarify the comparison of the results from both tests.

ie:
Neutralizing Potential (NP) = Acid Consuming Ablity (AC)
Net Neutralizing Potential (Net NP) = Net Acid Consumption (Net AC)

Standard Acid Base Accounting

Objectives

- to determine the balance between acid producing and acid consuming components of a mine waste

Principles of Test

Acid base accounting comprises two distinct measurements:

1. determination of the neutralization potential (NP) of a sample
2. calculation of the acid potential (AP) of the sample.

The difference between the two values, the net neutralization potential (Net NP), allows classification of the sample as potentially acid consuming or producing. As a first evaluation, a positive value for the Net NP indicates that the sample is a net consumer of acid. To facilitate comparison of values, NP, AP, and Net NP are all expressed in units of tonnes $CaCO_3$ equivalent per 1000 tonnes.

The neutralization potential is determined by treating a sample with excess standardized hydrochloric acid, heating to ensure complete reaction. A fizz test is employed to ensure that the amount of acid added is sufficient to react all of the acid consuming minerals present. The unconsumed acid is titrated with standardized base to pH 7 to allow calculation of the calcium carbonate equivalent of the acid consumed.

The acid potential is determined by analyzing for total sulphur and calculating AP by assuming (1) total conversion of sulphur to sulphate, and (2) 4 moles H^+ are produced per mole pyrite oxidized.

Equipment

1. Aluminum foil
2. 250 mL Erlenmeyer flask
3. Hot plate
4. Buret, 50 or 100 mL (0.1 mL graduation), one for each acid and one for each base
5. pH meter, equipped with a combination pH electrode

Reagents

1. Distilled (or deionized) water, preferably CO_2-free (store in container equipped with an ascarite tube)
2. Certified grade, 0.1 N hydrochloric acid, for standardization of bases
3. Approximately 0.1 N sodium hydroxide, standardized
4. Approximately 0.5 N sodium hydroxide, standardized
5. Approximately 0.1 N hydrochloric acid, standardized
6. Approximately 0.5 N hydrochloric acid, standardized
7. Approximately 25 percent hydrochloric acid, for fizz test

Procedure

1. Submit a sample of the test material for total sulphur analysis.

2. Determine paste pH as described in this manual.

3. Use certified 0.1 N hydrochloric acid to standardize the 0.1 N and 0.5 N sodium hydroxide solutions, and then use the sodium hydroxide solutions to standardize the 0.1 N and 0.5 N hydrochloric acid solutions.

4. Place approximately 0.5 g of sample (minus 60 mesh) on a piece of aluminum foil or in a small shallow dish. Add one or two drops of 25 percent HCl to the sample. The presence of carbonate will be indicated by a bubbling or an audible "fizz". Rate the "fizz" as indicated in Table 1.

5. Weigh 2.00 g of the sample (minus 60 mesh) into a 250 mL Erlenmeyer flask and add the volume and normality of HCl as indicated by the "fizz" rating in Table 1.

Table 1. Volume and Normality of HCl for Use in NP Determination on Basis of Fizz Rating (2g Sample)

	HCl	
Fizz Rating	(mL)	(Normality)
None	20	0.1
Slight	40	0.1
Moderate	40	0.5
Strong	80	0.5

6. Heat the pulp nearly to boiling, swirling the flask frequently until reaction is complete, indicated when no further gas evolution is visible and particles settle evenly over the bottom of the flask.

7. Add distilled water to make a total volume of 125 mL and boil contents of flask for 1 minute. Cool to slightly above room temperature. Cover tightly and cool to room temperature.

8. Titrate the contents of the flask using 0.1 N or 0.5 N NaOH (corresponding to the normality of HCl used in step 5) to pH 7.0. Titrate with NaOH until a constant reading of 7.0 remains for at least 30 seconds.

9. If less than 3 mL of NaOH is required to obtain a pH of 7.0 in step 8, it is likely that insufficient acid was added in step 5 to neutralize all the acid consuming minerals in the sample. Repeat the test using the next higher volume or strength of HCl as indicated in Table 1.

Calculations

1. The neutralization potential, NP, of the sample is given by:

$$NP = \frac{50\,a\,[x - (b/a)\,y]}{c}$$

where: NP = neutralization potential in tonnes $CaCO_3$ equivalent per 1000 tonnes of material

a = normality of HCl

b = normality of NaOH

c = sample weight in grams

x = volume of HCl added in mL

y = volume of NaOH added to pH 7.0 in mL

2. The acid potential, AP, of the sample in tonnes $CaCO_3$ equivalent per 1000 tonnes, is given by:

$$AP = \text{Percent sulphur} \times 31.25$$

3. The net neutralization potential, Net NP, in tonnes $CaCO_3$ equivalent per 1000 tonnes of material is given by:

$$\text{Net NP} = NP - AP$$

Interpretation of Results

As shown in the calculations, the Net NP of a sample is given as the difference between the NP and AP values. According to the standard method, a sample is defined as a potential source of ARD (potentially toxic) if it has a net potential deficiency of 5.0 tonnes of calcium carbonate equivalent per 1000 tonnes of material, ie. Net NP values of -5 or greater (more negative). Regardless of the acid base account, materials which have a pH of less than 4.0 in a pulverized rock slurry in distilled water are defined as being acid-toxic.

Reporting of Results

The results of the test should be tabulated to provide the following information:

Sample description, paste pH, total sulphur analysis (% S), NP (tonnes $CaCO_3$ equivalent per 1000 tonnes), AP (tonnes $CaCO_3$ equivalent per 1000 tonnes), Net NP (tonnes $CaCO_3$ equivalent per 1000 tonnes)

Advantages of Test

- Widely used and accepted method.
- Rapid and easy to perform.
- Low cost; can be used to screen a large number of samples for further selective and more detailed evaluation.
- Determines the maximum amount of neutralization potential and acid potential available in a sample.

Disadvantages of Test

- Rates and extent of acid producing and neutralizing reactions are not determined.
- In using total sulphur analysis for calculation of AP, acid generating and non-generating sulphur species are not differentiated; AP might be overestimated.
- Calculation of AP is based on one stoichiometry of reaction. In practice, the actual stoichiometry might vary significantly.
- Method does not indicate the pH to which the sample can neutralize during extended contact with acidic water.
- Method does not distinguish between reactive, readily available acid consuming minerals and less reactive species which might be important in the long term.
- The boiling procedure might give overestimation of neutralization potential.
- For some samples, reproducibility of the NP determination is poor. In such cases, NP is often found to be affected by the quantity of acid added in the digestion stage.

References

Sobek, A.A., Schuller, W.A., Freeman, J.R. and Smith, R.M., 1978. Field and Laboratory Methods Applicable to Overburdens and Minesoils, EPA 600/2-78-054, 203pp.