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THE CHARACTER OF ORGANIC MATTER AND THE PARTITIONING OF TRACE AND RARE EARTH ELEMENTS IN BLACK SHALES; BLONDEAU FORMATION, CHIBOUGAMAU, QUEBEC.

MAI 1987

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ABSTRACT

This study attempts to quantify the role of organic matter in Precambrian black shale sediment-hosted metal deposits. Samples were taken from stratigraphic drill core of the Blondeau Formation from Lac Barlow near Chibougamau and from Bignell Township, 6km west of the Grenville Front.

The study is divided into two parts; A) characterization of the organic matter, and B) determination of the partitioning of trace and rare earth elements (REE) between organic matter and sulfides.

Initial characterization of the organic matter by reflected light microscopy revealed the presence of two supermature varieties; 1) in-situ organic matter and 2) remobilized organic matter. Gas phase chromatography-mass spectrometry revealed the presence of soluble kerogen, a third species of organic matter. This indicates that under certain conditions, volatile forms of organic matter coexist with highly evolved organic matter. Scarce data exists concerning Precambrian life; soluble kerogen, a chemical fossil, preserves a tangible record of biologic substances present in the depositional environment with an age estimated to be 2.8 Ga.

The second part of the study pertains to the chemical nature of shale with respect to two of its components; the sulfide and organic fractions. The following results were found: 1) the sulfide content is twice that of the organic carbon present, 2) organic matter contains significant trace metals; (for example, gold, zinc, and chromium), 3) organic matter seems to preferentially incorporate heavy rare earth elements while sulfides seem to favour light rare earth elements, and 4) sulfides and/or organic matter, where sufficiently abundant, can control the REE distribution seen in black shales.

In addition, a preliminary examination of samples taken from Bignell Township reveals decreased total REE content that grows more pronounced for the lighter REE, compared to the samples taken from Barlow Township, 55 km further west.

These findings lead us to conclude that organic matter plays a significant role in both the formation of sediment-hosted precious metal deposits and in the geochemical profile of black shales.

RESUME

Cette étude a pour but de quantifier le rôle joué par la matière organique localisée dans des shales noirs Archéens hôtes de dépôts métallifères. Les échantillons étudiés proviennent de forages stratigraphiques effectués dans le secteur du lac Barlow, région de Chibougamau.

L'étude se divise en deux parties; A) caractérisation de la matière organique, et B) détermination de la répartition des éléments traces et des terres rares contenus dans la matière organique et dans les sulfures. L'abondance des éléments dans les deux fractions est ensuite comparée.

L'étude en lumière réfléchie des caractéristiques de la matière organique révèle la présence de deux variétés très évoluées; 1) matière organique in-situ et 2) matière organique remobilisée. La chromatographie en phases gazeuses couplée à un spectromètre de masse révèle une troisième variété de matière organique, un kérogène soluble. Ces résultats suggèrent que, sous certaines conditions, des formes volatiles de matière organique coexistent avec de la matière organique très évoluée. Il existe peu de données concernant la vie à l'Archéen. Ainsi, le kérogène soluble, un fossile chimique, constitue un reflet tangible de substances biologiques présentes, il y a 2,8 Ga., dans l'environnement de déposition.

La deuxième partie de l'étude vise à déterminer la nature chimique des shales en fonction de deux de ces composants; les sulfures et la fraction organique. Les résultats suivants ont été obtenus: 1) la proportion de sulfure est deux fois plus grandes que celle de la matière organique, 2) la matière organique contient des proportions significatives de métaux en traces (ex. Au, Zn et Cr), 3) la matière organique semble avoir tendance à incorporer les terres rares lourdes alors que les sulfures semblent plutôt favoriser les terres rares légères, et, 4) lorsque les sulfures et/ou la matière organique sont suffisamment abondants, ils contrôlent la distribution des terres rares contenues dans les shales noirs.

De plus, une étude préliminaire des échantillons provenant du canton de Bignell localisé 6km à l'ouest du front de Grenville, révèle que le contenu en terres rares diminue, en particulier les terres rares légères, comparativement aux résultats obtenus à partir des échantillons provenant du canton de Barlow, localisé 55km plus à l'ouest.

Ainsi, nous croyons que la matière organique influence nettement la géochimie des shales noirs et qu'elle joue un rôle significatif dans la formation des gisements de métaux précieux localisés dans des sédiments.

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CHAPTER I

INTRODUCTION

1.0 OBJECTIVES

Most trace or rare earth element (REE) studies of black shales are based upon the results of whole rock analyses. This study analyzes the components of black shales separately. It is a novel approach that may lead to a greater understanding of the metallogenic processes governing the mobility and fixation of the metallic elements.

The Blondeau Formation of the Chibougamau area, Québec consists of volcanic and sedimentary rocks that were deposited in a shallow, anoxic basin (Archer, 1983). The object of this study are the numerous beds of black shale that are intercalated within the sedimentary layers. They contain abundant sulfides and a graphitic substance of unknown nature.

The main goals of the study are 1) to determine the nature of the graphitic material present in the shale and 2) to study the partitioning of metallic, trace, and rare earth elements between the different components of the black shales. A comparison of drill core from the Blondeau Formation, located 6 and 55 km from the Grenville Front, give an estimate of the effect of increasing metamorphism on the observed distribution of the elements.

Conclusions drawn from studies of this type can aid in the synthesis of fluid transport models for the emplacement of shale-hosted metal deposits. The results of this study may provide a tool for exploration in the Chibougamau area and in areas having a similar geological context.

1.1 THE LOCATION AND GEOLOGY OF THE STUDY AREA

1.1.1 Location

The study area is located within the Matagami - Chibougamau volcano-sedimentary "Greenstone" belt (Figure 1), part of the Superior structural province of the Canadian Shield. The project is based on samples from stratigraphic sections through the Blondeau Formation. The stratigraphic drill core comes from 1) 22 km west of Chibougamau (the Lake Barlow section) and 2) Bignell Township, 6 km from the Grenville front (the Bignell section) (Figure 2). The Lake Barlow section consists of 14 diamond drill holes that were drilled in Lake Barlow along the boundary line separating Barlow and Cuvier townships. The distance between the two sections is approximately 65 km.

The Lake Barlow stratigraphic drilling was undertaken by the Ministère de l'Energie et des Ressources du Québec in 1979. The drill core is stored at the resident geologist's office in the town of Chibougamau. The Bignell stratigraphic section is stored at the Camchib

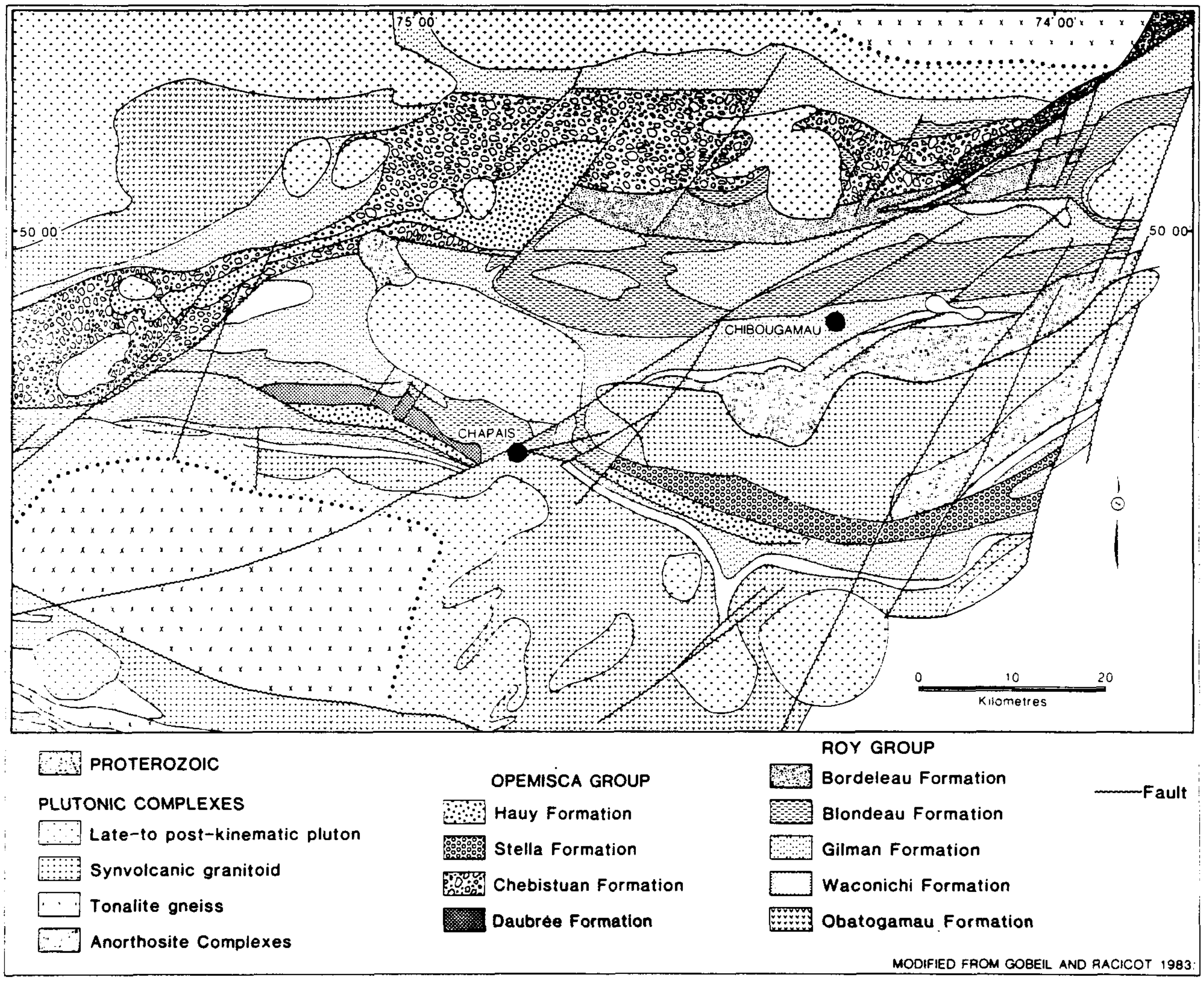


Figure 1: The Matagami-Chibougamau greenstone belt; Chapais-Chibougamau area (after Gobeil and Racicot, 1983).

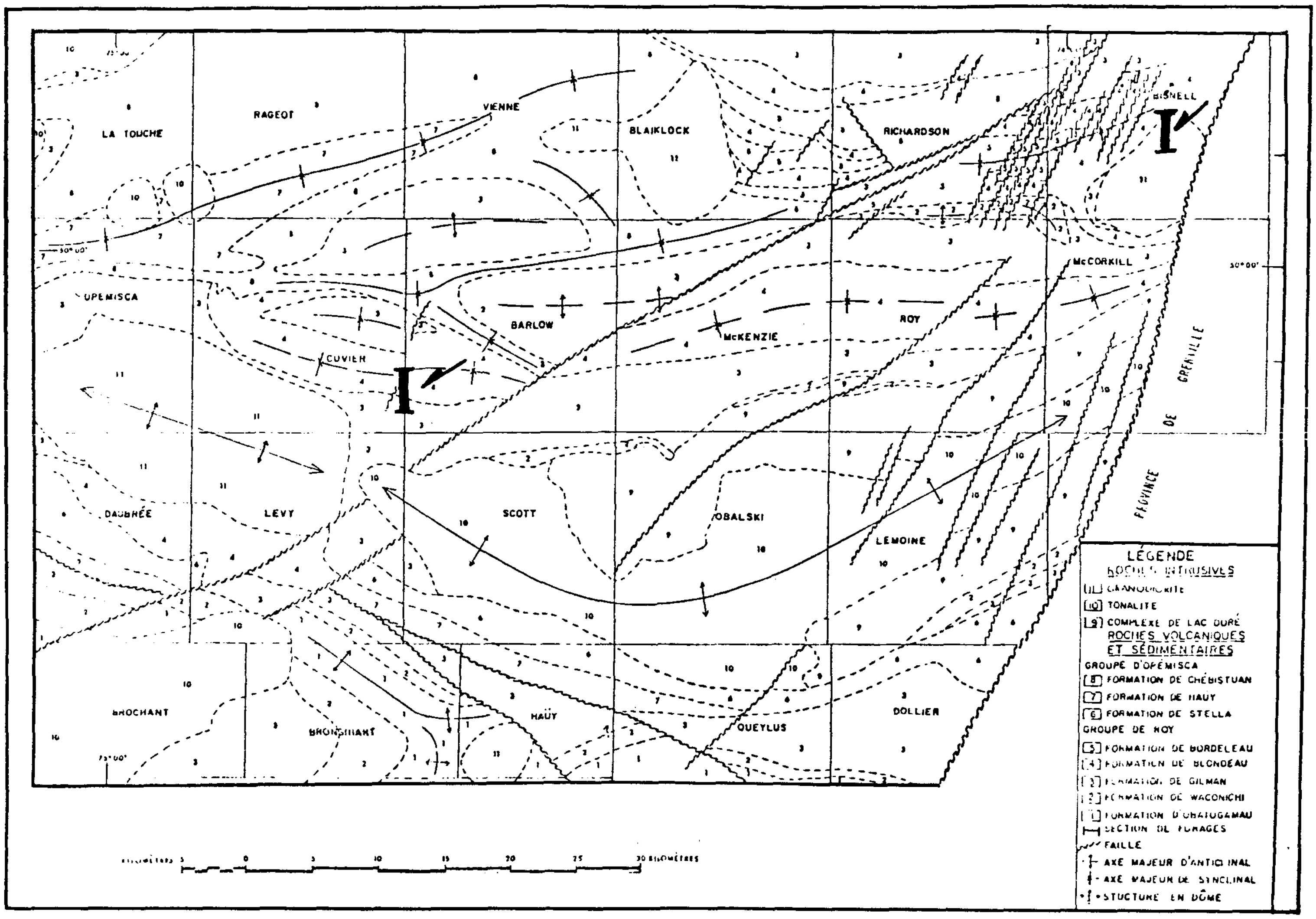


Figure 2: The geology of the Chibougamau region including the locations of the Lake Barlow and Bignell stratigraphic sections (after Allard et al.,1979).

Inc. Chibougamau office.

1.1.2 Stratigraphy

The stratigraphic sections expose strata from the Gilman and Blondeau formations of the Roy Group. They are intruded by discordant dikes and sills of the Cummings Complex (Figures 3,4). The Roy Group is divided into two cycles of volcanic activity; the first comprises the Waconichi and Obatogamau Formations and the second, the Blondeau and Gilman Formations (Allard et al., 1979).

The Gilman Formation is a 3650 m thick sequence of pillow basalts, comagmatic sills, and occasional lenticular accumulations of hyaloclastics and pyroclastics (Cimon, 1979).

The Blondeau Formation is described as a 1000 m thick sequence of volcano-sedimentary rocks composed of rhyolitic flows, felsic tuffs and agglomerates, siliceous and graphitic tuffs, shales, and graywackes. Minor mafic flows and volcaniclastics are also found (Allard, 1976; Archer, 1983). Worth noting are numerous small sediment-hosted deposits rich in sulfides. Detailed petrographic analyses of the Blondeau Formation drill cores by Archer (1983) reveal that near surface pyroclastics and shore facies sediments related to emergeant vulcanism are intercalated with the black shales; the shales were deposited in a shallow basin ($\leq$ 200 m in depth).

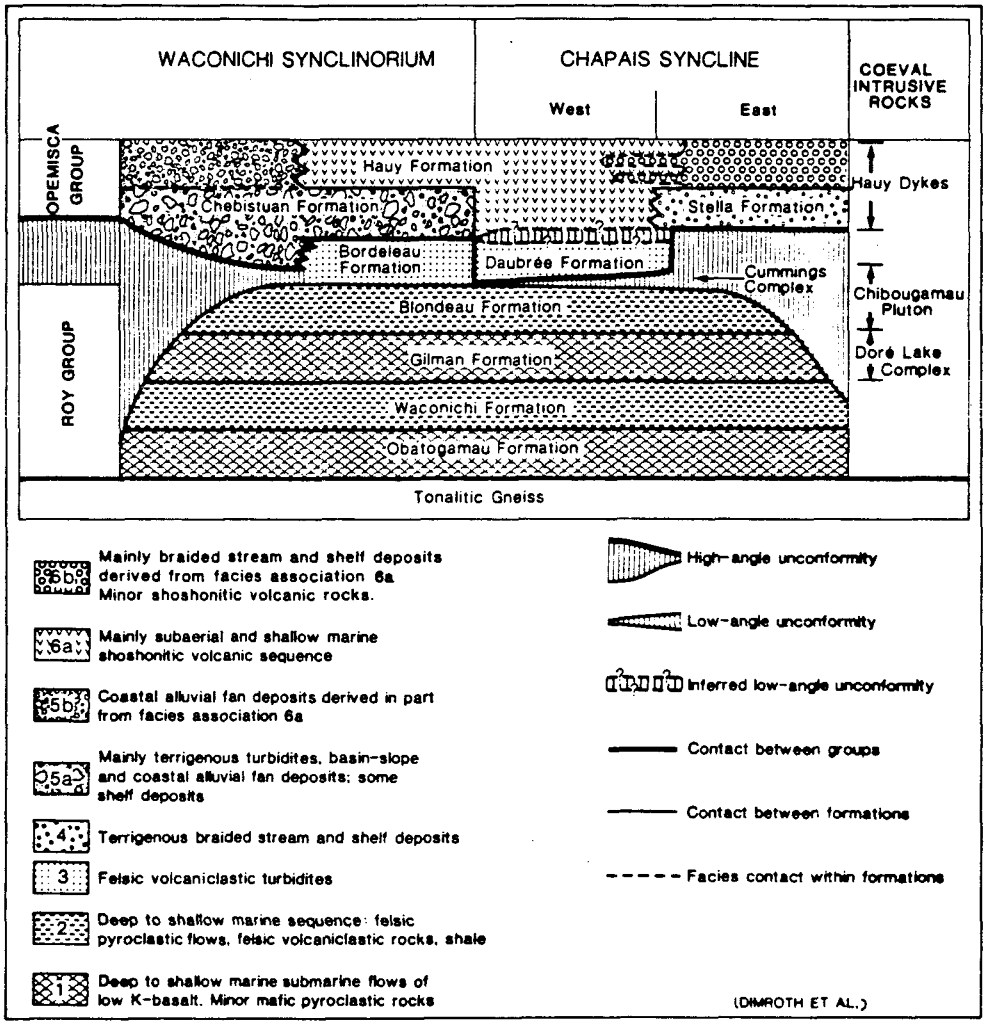


Figure 3: Stratigraphy of the Chibougamau area (Dimroth et al, 1985)

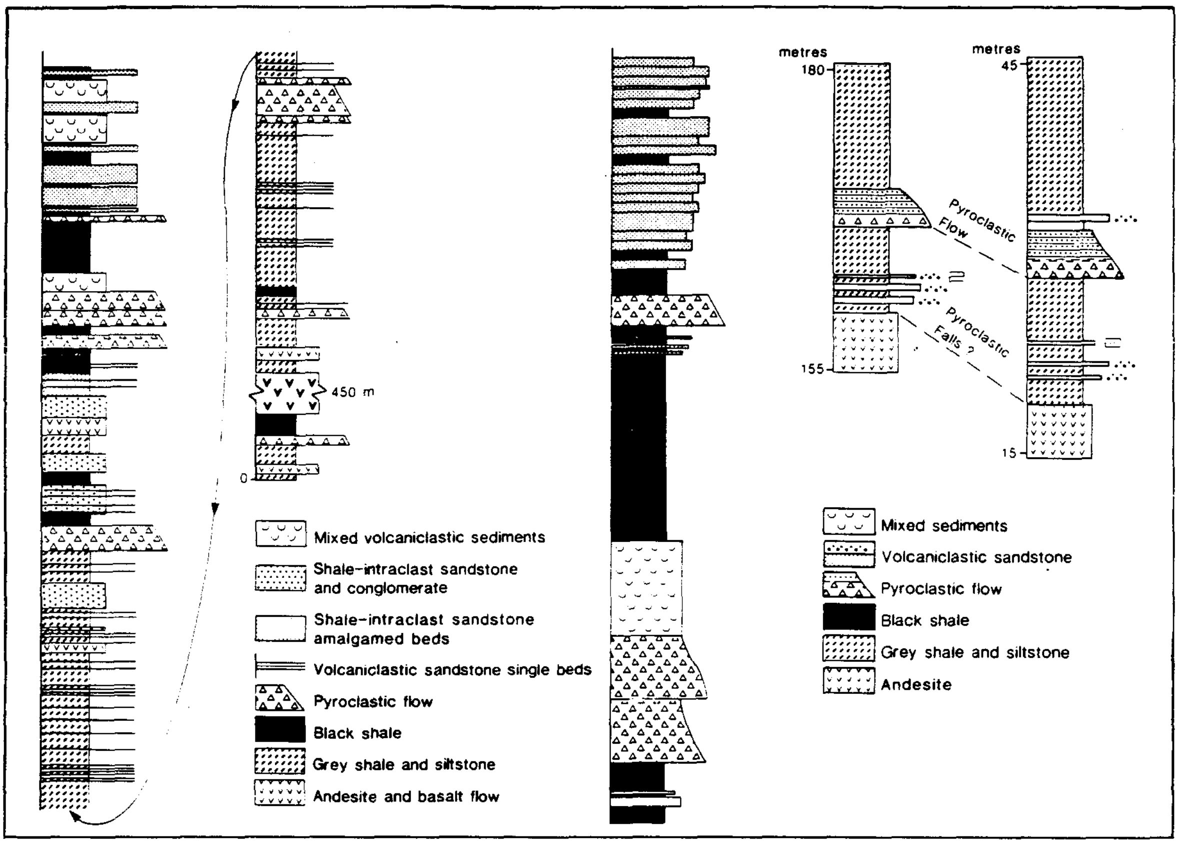


Figure 4: The stratigraphic drill section Ba-79 (Archer, 1983)

Additionally, the shales were deposited in an anoxic environment where organic matter and sulfides were preserved.

The Cummimgs Complex consists of Roberge, the Ventures, and the Bourbeau sills. They consistently occur in the same stratigraphic order; an ultramafic sill, the Roberge Sill, is found at the base, while the least mafic sill, the Bourbeau Sill, occurs at the top (Duquette, 1970).

1.1.3 Structure

The stratigraphic section was drilled on the southern flank of the Chibougamau Syncline, a major east-west fold generated during the Kenoran Orogeny. The syncline is an isoclinal fold with an axial plane dipping steeply southward. It is part of the Chibougamau Synclinorium which traverses the Chibougamau-Chapais region. This Kenoran fold system is superimposed upon a north-south series of folds that may have been formed during the emplacement of the Chibougamau Pluton (2.5-2.7 G.A)(Krogh and Davis, 1971). The interference of the two fold systems has produced "saddle and dome" structures throughout the area (Allard et al.,1979; Archer,1983). A well developed schistosity roughly paralleling the bedding plane is observed in the drill core.

Numerous faults are observed on a regional scale. Some of these faults contain mineralization of economic significance. One such example is the north-east to north-south trending system related to the Taché lake deposits and the east-west system to the Gwillim and Cooke mines. Faults in the study area are minor or have not been recognized.

Minor folds and faults play an integral role in our model of ore deposits associated with organic matter.

1.2 PREVIOUS STUDIES

The best syntheses of the geology of the Chibougamau area are contained in the Geological Association of Canada excursion booklet B-1 (Allard et al., 1979) and the CIM special volume 34 (Guha and Chown, 1984).

Directly pertinent to this study is the recent work on the Barlow Lake stratigraphic section. Two unpublished Masters' theses were completed by Archer and Dembele in 1983 and 1987 respectively. These theses and the accompanying papers (Archer, 1984; Carignan et al., 1984) provide the geological and geochemical background of the samples on which the present thesis is founded. Carignan et al. (1984) established a chemo-stratigraphic profile and determined the whole rock major and trace element abundances for each of the lithologies. Archer (1983) conducted a sedimentologic and petrographic study that reconstructs the depositional environment.

No previous studies exist regarding the organic matter or REE abundances in black shales of the Chibougamau region. In contrast, there is neither a shortage of trace element analyses of shales, nor studies of the character of organic matter in shales. Vine and Tourtelets' summary paper (1970) documents several studies concerning the behavior of trace elements in black shale-hosted mineral deposits. Haskin et al., (1964) have evaluated the REE content of diverse sediments normalized to their standard, the "North American shale Composite". Relevant to the present study is Wildeman and Haskins' "Rare Earths in Precambrian Sediments" (1972). Ilchik (Ilchik, et al., 1986) document the maturation and character of organic matter related to the Alligator Ridge gold deposits.

Recently researchers have begun investigating the role of organic matter in metal deposition. Kucha (1983) detected Au, Pt, Pd, and Ag along with other elements in the black shales of the Zechstein Basin, Germany. He also identified soluble kerogen in these shales. McQueen and Powell (1983) has demonstrated that a spatial and/or temporal relationship exists between Pb-Zn deposits and organic matter in carbonates at Pine Point. Furthermore Beveridge et al. (1983) demonstrates that living bacteria can incorporate metals directly into the cell cavity.

An extensive bibliography search for REE and trace element studies indicates that very little work has been done on REE and trace element partitioning in black shales. Some results are available for the REE present in suspended organic matter and sediments near the ocean floor (Murphy and Dymond, 1984). Two studies report preliminary estimates of trace element content and partitioning in the organic components of black shales (Keith and Degens, 1959; Krauskopf, 1955). Prior to the present study, it appears that no single paper has dealt with the partitioning of REE and trace elements between the organic and sulfide fractions in relation to trace and REE content of the whole rock.

1.3 METHODOLOGY

The objectives of this study are 1) to determine the nature of the graphitic material present and 2) to study the partitioning of trace and REE between a) the whole rock, b) the organic matter fraction , c) the sulfide fraction, and d) the clay mineral fraction in black shales of the Blondeau Formation.

These goals were realized using well known techniques with a few adaptations. Figure 5 shows a flow sheet of the steps required to obtain the results. The first part of the study was to determine the quantity and nature of the organic matter present in the black shales. This was done through examination of polished and polished thin sections, whole rock powders, and soluble kerogen extracts.

The organic matter was first identified through the use of reflected light microscopy. Identification was corroborated by percent absolute reflected light and microhardness tests. Complete combustion of whole rock powder within a gas analyzer allowed the determination of the percent total organic carbon present in the rock. The whole rock powder was then subjected to controlled pyrolysis which determined if soluble or volatile organic matter was present.

Extraction of the soluble organic matter was obtained by chloroform recirculation. The chloroform-organic matter solutions were then analyzed by gas phase chromatography-mass spectrometry.

Trace element and REE partitioning studies performed separately on the whole rock, sulfide, and organic matter fractions. The current separation techniques for clay minerals, which consist of pulverization and centrifuging in water, were not effective in this study.

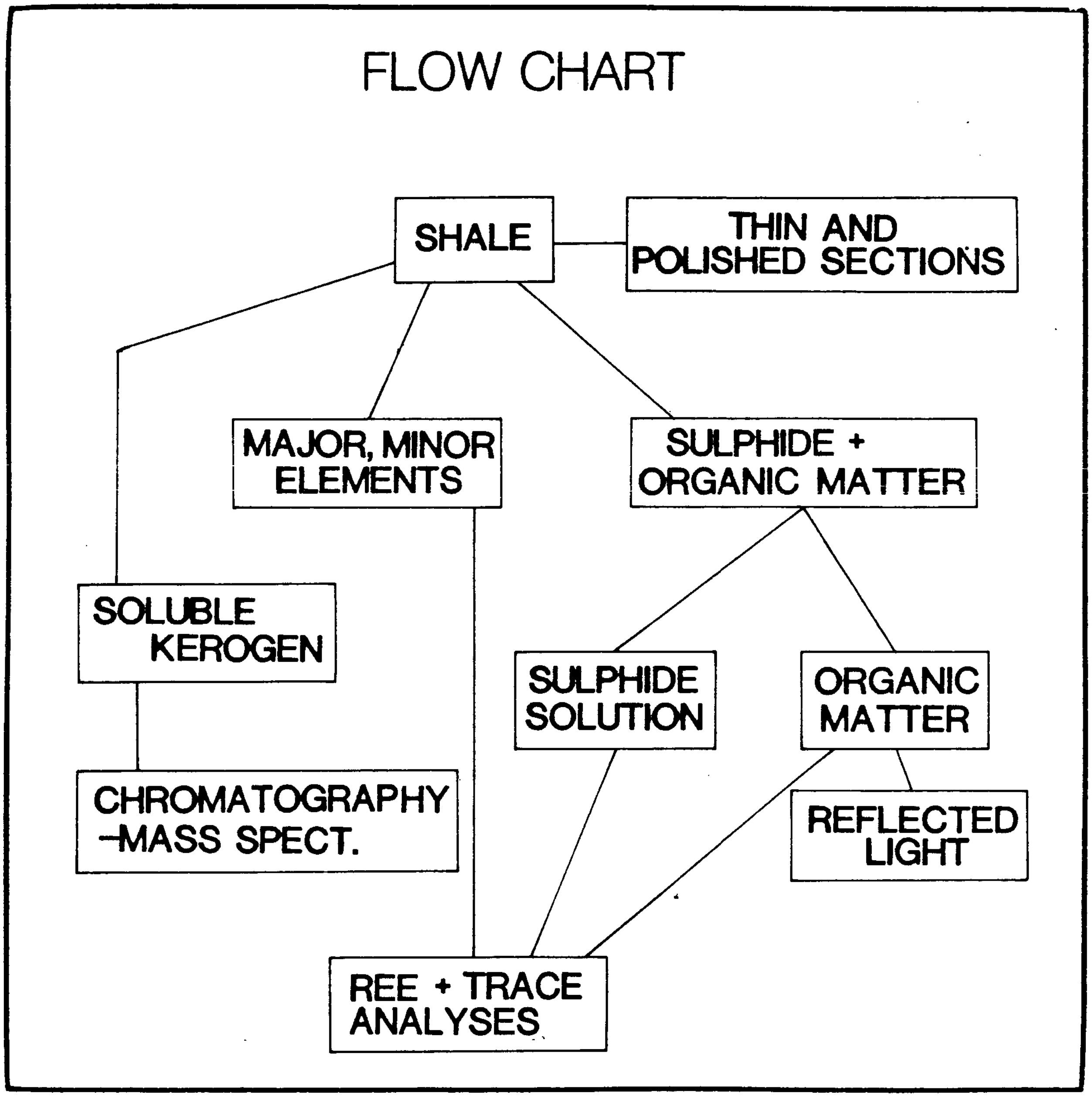


Figure 5: Flow sheet of the study

Sample Preparation

The organic matter and sulfide fractions were separated from the shale by dissolving the silicate fraction with hydrofluoric acid. The sulfide-organic matter residue was then treated with aqua regia to make a quantitative separation of the soluble sulfides and insoluble organic matter.

Once the three fractions were separated they, in addition to blanks, were analyzed as follows:

1) **whole rock**
   - Clay mineralogy: x-ray diffraction.
   - Major and minor oxides: atomic absorption and x-ray fluorescence.
   - Trace element analyses: atomic absorption.
   - Rare earth element, corroborative trace element, and precious metal contents: instrumental neutron activation analysis (I.N.A.A.)

2) **sulfides**
   - Trace elements: atomic absorption.
   - Rare earth element, corroborative trace element and precious metal contents: I.N.A.A.

3) **organic matter**
   - Quantitative identification by reflected light microscopy
   - Carbon isotopes $^{13}C/^{12}C$: pyrolysis mass spectrometry.
   - Rare earth element, all trace element, and precious metal contents: I.N.A.A.

1.4 Acknowledgements

I would like to express my sincere gratitude to the professors and personnel of le Module de Sciences de la Terre at l'université du Québec à Chicoutimi, notably Dr. Jayanta Guha, my thesis director, the conceptual father of this research project, Dr. A. Fowler, my co-director for his critical guidance (presently at University of Ottawa) and Mr. Richard Lechasseur, the technician in charge of chemical analyses for the department.

This study was made possible through the financial support of I.N.R.S. Géoressources along with the technical and moral support of the Professors, and staff members, whose endless patience was greatly appreciated, during my stay at I.N.R.S. Géoressources. I was employed as an "étudiant stagière" for the better part of two years. I wish to thank Dr. Yvon Héroux, my co-director, for his guidance and his expertise in the classification of the diverse insoluble organic substances in this study and to Real Gosselin for help in using the pyrolysis equipment. Dr. A. Chagnon produced the X-ray spectra and identified the clay mineralogy for this study.

I wish to thank Mr. R. Massé of I.N.R.S. Santé at Montréal who performed the first mass-spectrometry gas-phase chromatography analysis of the soluble organic matter fractions, and especially Dr. F.X. Garneau of the Biochemistry department at Université du Québec à Chicoutimi for his identification of the composition of the soluble organic substances. (Mr. Garneau continues to work upon the problems related to the hydrocarbons identified in this study).

Dr G. Kennedy of the department of Nuclear Physics at Ecole Polytechnique de Montréal, guided my passage through the domain of Rare Earth Element geochemistry. His aid at the theoretical and technical level was most deeply appreciated and instumental to the completion of the REE analysis.

I wish to thank both the resident géologist, Andre Gobeil, of the Chibougamau office of Québec's Ministère de l'Energie et des Ressources for providing access to the drill core of the Barlow Township stratigraphic section, and the Camchib Exploration Company for access to the Bignell Township core samples of the Blondeau Formation.

CHAPTER II

PETROLOGY

2.0 PETROGRAPHY

Petrographic studies of the black shales of the Blondeau Formation are greatly hindered by the opacity of the thin sections (Figure 6). An examination using transmitted light microscopy shows that the shales are very fine grained and contain abundant opaque material finely dispersed throughout the thin sections (Figure 6). The grain size of the shales ranges from .01 to .005 mm in diameter. In terms of granulometry, these "shales" are mudstones; the quartz and plagioclase feldspar fractions are commonly greater than 1/256 mm (0.004 mm), the grain-size limit established for clays.

The mineralogical composition of the shales is fairly constant except for variation in the abundance of the quartz and plagioclase fraction. Angular to subrounded quartz and plagioclase make up 35 to 40 % and 5 % of the shales respectively. Fine laminae, very rich in quartz and plagioclase silt, are occasionally interspersed in the shale samples. Altered pumice and microlitic shards approximately 0.01 mm in size may occur within these zones. The rest of the shale is composed of 50 to 60 % clay sized minerals of indeterminate character. They are mixed with very fine, black organic matter and sulfides. Chemical analyses show that the organic matter averages 1.7 % and the iron sulfides 3.6 % of the total composition of the shale. The organic matter and sulfide content of the shales is surprisingly low considering the opacity of the samples in thin section.

It is important to know the abundance of detrital minerals rich in trace elements and REE that occur in the shale (Blatt et al.,1980). Zircon and apatite contain up to 4100 ppm Ce and 2700 ppm Yb respectively (Grommet et al.,1984). Monazite grains have high concentrations of REE and of U and Th (Deer et. al., 1966). Significant concentrations of these detrital minerals can explain erratic geochemical trends. Two of the samples did contain minute quantities of zircon in thin section while monazite and apatite were not observed. Subsequent chemical analysis provided a further check; samples were tested for Zr (for zircon), Th and U (for monazite), and P (for apatite). No significant quantities of these elements were found.

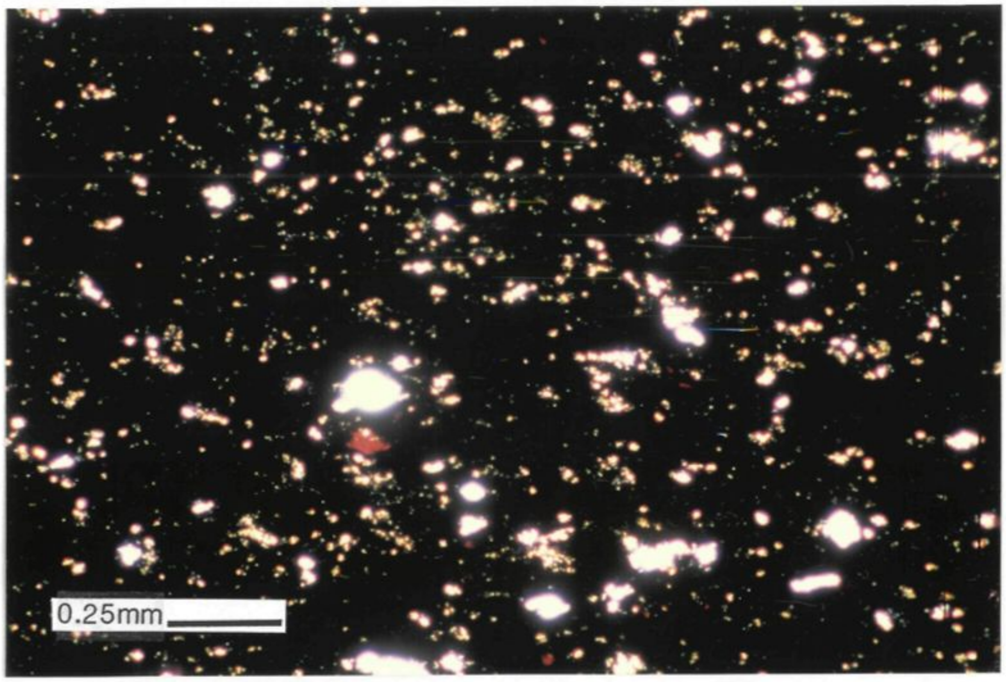


Figure 6: Photomicrograph of black shale. Note opacity.

2.1 METAMORPHISM

X - ray diffraction of the clay mineral fraction ($\leq$ .004 mm or 4 microns) was used to identify the clay mineralogy and to establish the metamorphic grade of the shales of the Lake Barlow and Bignell Township sections.

In the Lake Barlow stratigraphic section the x-ray diffraction pattern has small chlorite peaks and large, well-defined, interstratified tri-octahedral illite and smectite peaks in the clay - sized fraction (Figure 7). Quartz and plagioclase are also well defined in the spectrum; clay mineral separation techniques do not give a clay fraction pure enough for discrete trace element studies.

It is difficult to establish the upper limit of metamorphism by X-Ray Diffraction. The presence of smectite, illite, and chlorite is ambiguous; the minerals in question could be either detrital or hydrothermal in origin (Weaver and Pollard, 1973).

One possibility is that retrograde smectite-illites formed during hydrothermal alteration and partially overprint the chlorite-albite-epidote greenschist assemblage. Local intrusive activity is one possible source of the hydrothermal alteration. Another possibility is that the chlorite may be detrital in origin. In which case, the smectite-illite mineralogy suggests that very low greenschist facies metamorphism was the maximum grade attained.

The chlorite present in thin section does not appear to be detrital; they are well formed sheets and plates that are found within the schistosity of the rock.

Since the shales of the Lake Barlow section have been metamorphosed to greenschist facies they must have undergone subsequent hydrothermal alteration during which the smectite-illite minerals formed. Two of the possible sources of hydrothermal alteration in the area are local faults and intrusives. An intrusive body was identified in the Barlow Lake area, the Cummings Complex (Duquette, 1970). However, the sills of the Cummings Complex are pre-metamorphic. They could not be responsible for this hydrothermal event. The only remaining possibility is the hydrothermal alteration associated with the east-west fault system in the area.

In contrast, the shales in the Bignell Township, 6 km from the Grenville front, have undergone upper greenschist facies metamorphism. The Bignell shale sample's XRD spectra (Figure 7) show a complete absence of the smectite - illite peaks, and large well-defined chlorite peaks. Also Muscovite is present in thin sections and is parallel to the schistosity defined by fine opaque parallel laminae.

Conclusions

1) In the Lake Barlow stratigraphic section the x-ray diffraction pattern, of the clay mineral separates, shows small chlorite peaks and large, well-defined, interstratified tri-octahedral illite and smectite peaks.

2) Smectite-illites, probably of hydrothermal origin, partially overprint the chlorite-albite-epidote greenschist assemblage.

3) The chlorite present in thin section does not appear to be detrital; they are well formed sheets and plates that are found within the schistosity of the rock.

4) The black shales have been metamorphosed to greenschist facies, and have undergone subsequent hydrothermal alteration during which the smectite-illite phyllosilicates formed.

5) The shales in the Bignell Township have undergone upper greenschist facies metamorphism. The Bignell shale sample's XRD spectra show a complete absence of the smectite - illite peaks, and large well-defined chlorite and muscovite peaks.

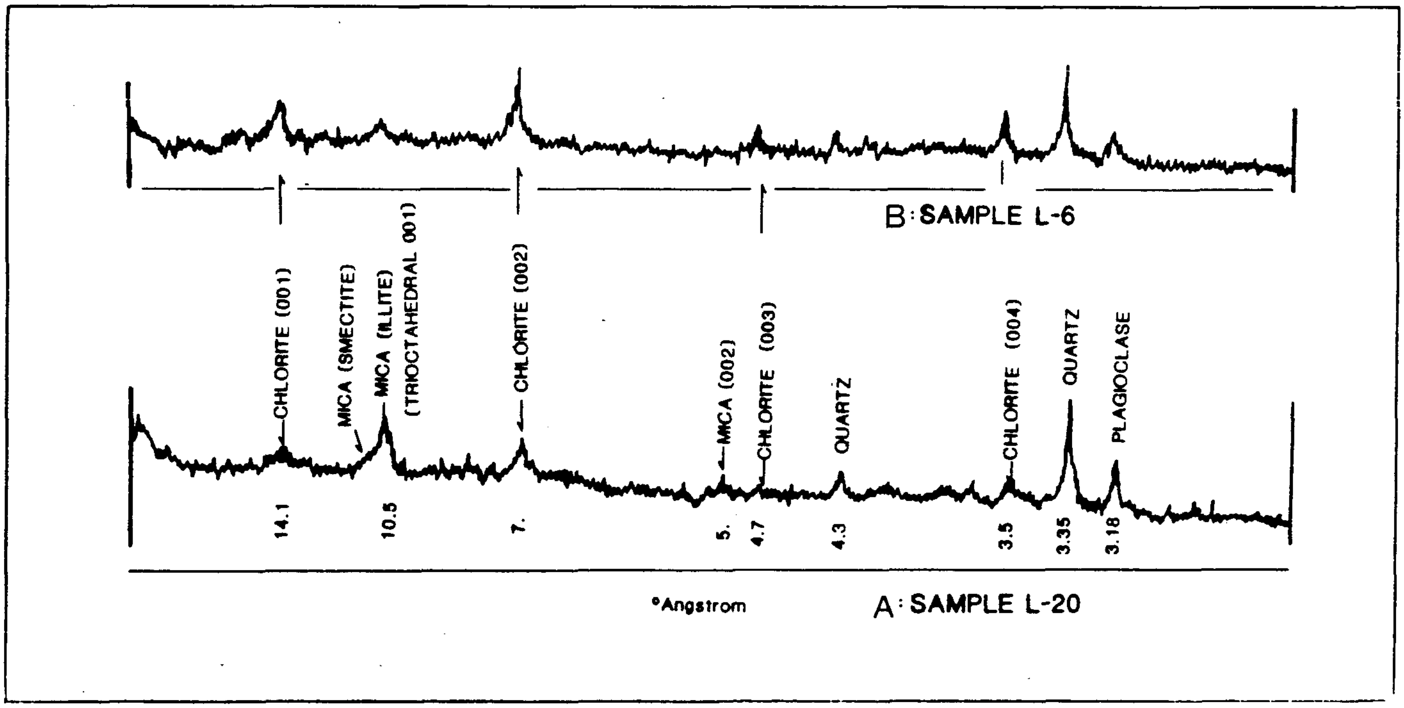


Figure 7; Clay mineral X-ray diffraction patterns: A, Barlow; B, Blondeau.

CHAPTER III

THE CHARACTER OF ORGANIC MATTER

3.0 OPTICAL PROPERTIES

A significant amount of opaque material is visible in the thin sections of the black shales. Two substances were distinguished by reflected light microscopy; 1)iron sulfides and 2) a substance that appears homogenous, amorphous, and gray-brown in color in plane polarized light. The substance has a low value of absolute reflected light equal to 5 % and has a strong orange-yellow anisotropy in polarized light .

Until now the second substance has been identified as graphite. Certain varieties of graphite have a minimum value of 5% absolute reflected light and graphite generally has an orange-yellow anisotropy and a grayish brown coloration (Uytenbogaardt, 1971). The above observations substantiate the conclusion that the substance is graphite. However, graphite always has a sheet-like morphology and is inelastic with a Vickers hardness value of 5 to 15 (Uytenbogaardt, 1971). The substance in question was observed to be amorphous and totally elastic. It did not retain a Knoop pyramid impression long enough to measure, even at increased pressures and times. Graphite can be indented with a 100 gm pressure within 60 seconds. The unknown material was tested at 200 gm with 180 seconds impression time with no impression.

The substance that best corresponds to the physical properties observed is organic matter. Researchers in the field of insoluble organic matter all rely on the properties of color, anisotropy, % absolute reflected light, and morphology for the microscopic identification of organic matter (Héroux, pers.comm). No references to the elastic property were found. This property should be added to the list of physical properties used to identify organic matter. It has the advantage of being a quantitive measure not open to interpretation to the same degree that color or morphology are.

3.1 Classification

The organic matter is found as; 1) remobilized in veins and 2) dispersed througout the shale.

The remobilized organic matter is always associated with quartz and occurs in millimetric veinlets that both cross-cut and parallel the planar openings in the schistosity or fissility of the shale (Figure 8). Subsequent to the accumulation and induration of the organic matter in the veinlets brittle, concoidal fractures developed and some transport occurred. Isolated fragments of the organic matter can now be matched to nearby masses as in a "jig-saw puzzle".

Organic matter is also found distributed as fine foliated plates in the schistosity of the shale. It is disseminated in a pervasive manner throughout the shale and does not appear to have undergone significant transport (Figure 9).

No biological structures, such as cell walls or plant tissues, were observed. The organic matter is classified as super-mature pyrobitumen based on its lack of internal structures and % absolute reflected light value (Durand and Monin, 1980; Y.Héroux 1983 pers.comm). It is highly evolved organic matter of undetermined origin.

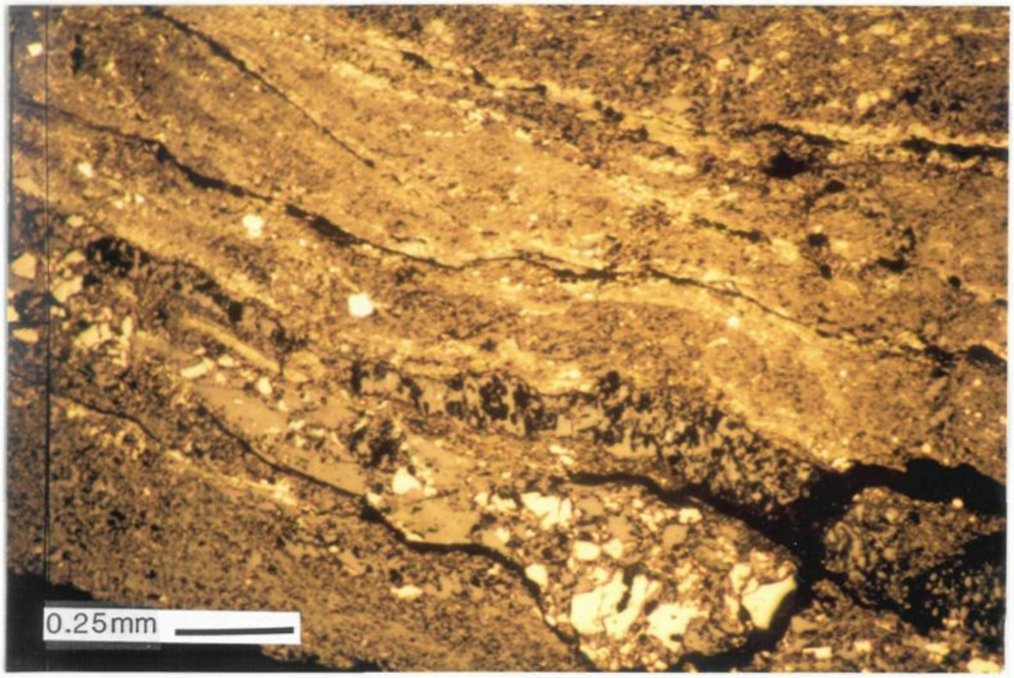


Figure 8: Photomicrograph of remobilized organic matter

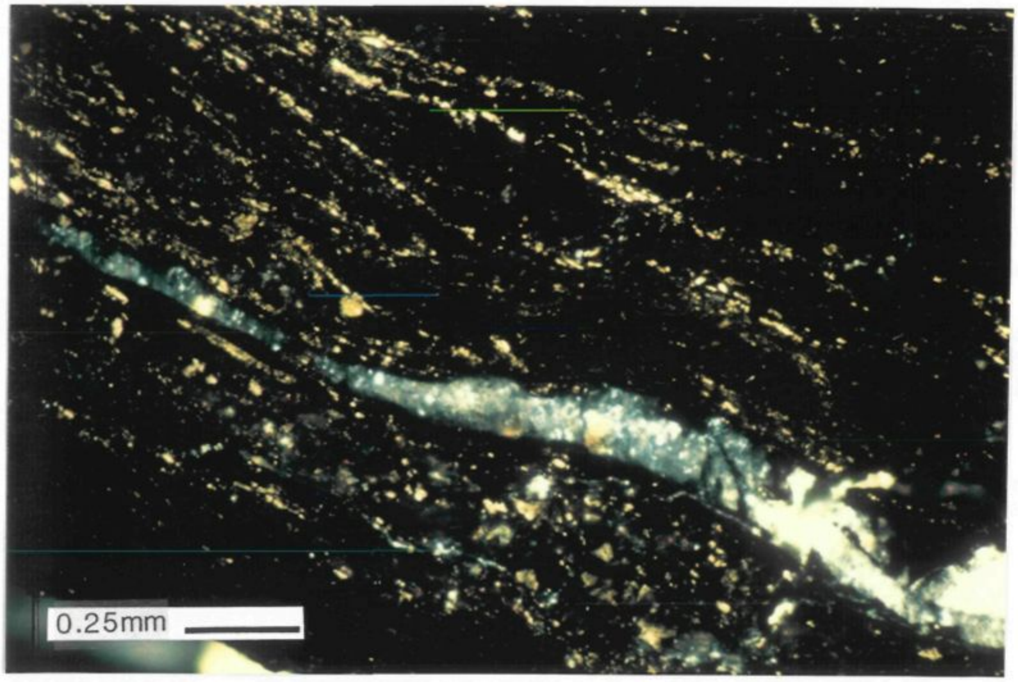


Figure 9: Photomicrograph of in situ organic matter

300°C are proportional to the volatile or soluble organic matter present while those generated from 300 to 550°C show the presence of less volatile to insoluble organic matter. This test gave the first indication that the shales of the Blondeau formation contained soluble organic matter. A very small peak was observed at the lower end of the temperature scale (Figure 10). Further investigation was nessecary to determine the exact composition of the soluble organic matter.

3.2.2. GC-MS Analysis of Soluble Organic Matter.

GC-MS (gas phase chromatography-mass spectrometry) detects the individual volatilized organic molecules of different size and mass that form the complex organic compounds. Analysis was performed on a greasy residue derived from the evaporation of the filtrate of a chloroform and shale solution. The powdered shale had been placed in glass-sealed flasks and agitated for 48 hours with an ultrapurified "omnisolve" chloroform. It was then filtered. Initially the solution was made in a "SOXLET" chloroform recirculator, but contaminants appeared from three sources; the filters, the apparatus' condensation column, and the laboratory grade chloroform. This solution was discarded.

3.2 ORGANIC GEOCHEMISTRY

3.2.1. Soluble Organic Matter

Organic matter analysis entails a test for the presence of soluble organic matter. This type of organic matter may be dissolved in chloroform and is called kerogen (Durand and Monin,1980). The test is usually reserved for samples that are not thermally evolved as volatile products are believed to be no longer present in rocks containing the super-mature varieties of organic matter (Héroux, pers.comm.). However it is not clear at what point the soluble organic matter disappears as diagenesis progresses. Time, temperature, and diffusion rate of the volatile products are important parameters governing the degradation of organic matter. Factors such as permeability play a major role in the dissipation of the volatile components of organic matter. Shales generally have a relatively low permeability and it is possible that the volatile products were trapped within them.

Samples of whole rock powder were run in an apparatus called "Rock-Eval". It operates using pyrolysis of the samples by a temperature controlled oven that increases the temperature in small increments until all carbon compounds are converted to CO_2. The CO_2 is measured and plotted on an intensity graph; peaks generated at 250 to

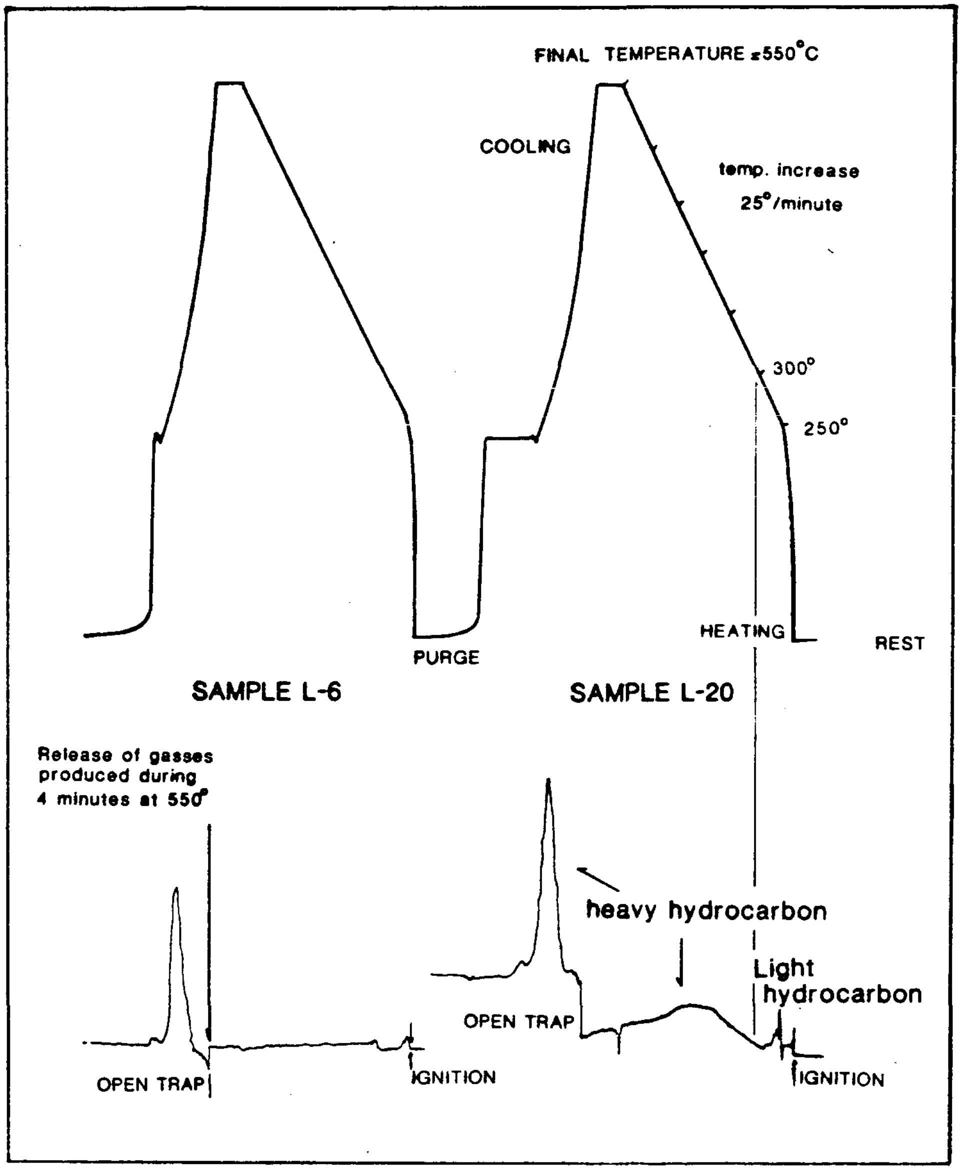


Figure 10: spectrum from Rock-Eval

GC-MS detected the following organic compounds in the soluble organic matter (Figure 11);

1) 2.6-DI-TERTIARY-BUTYL-4-ETHYL-PHENOL	(45.1%)
2) 2.6-DI-TERTIARY-BUTYL-BENZOQUINONE	(24.2%)
3) METHYL ESTER OF C_{16} FATTY ACID	(5.8%)
4) METHYL ESTER OF C_{18} FATTY ACID	(7.2%)
5) DI-ETHYL PHTHALATE	(0.9%)
6) DI-BUTYL PHTHALATE	(2.7%)
7) C_{14} ALCANE	(0.25%)
8) C_{15} ALCANE	(0.98%)
9) C_{16} ALCANE	(0.93%)
10) C_{17} ALCANE	(0.74%)
11) C_{18} ALCANE	(0.14%)
12) 2 unidentified compounds	(10.4%) (12.8%)

3.2.3. Interpretation of GC-MS Results

To find soluble organic matter associated with super-mature pyrobitumen is very surprising. Despite the precautions taken the list of compounds present in the soluble extract are largely contaminants. Compounds numbered 1 through 6 in the previous section are contaminants. 2.6 di-tertiary-butyl-4-ethyl-phenol (or butylated hydroxyethylbenzene), 2.6 di-tertiary-butyl-benzoquinone (possibly an oxidation product of 2.6 di-tertiary-butyl-4-ethyl-phenol), is also an antioxidant found in plastics.

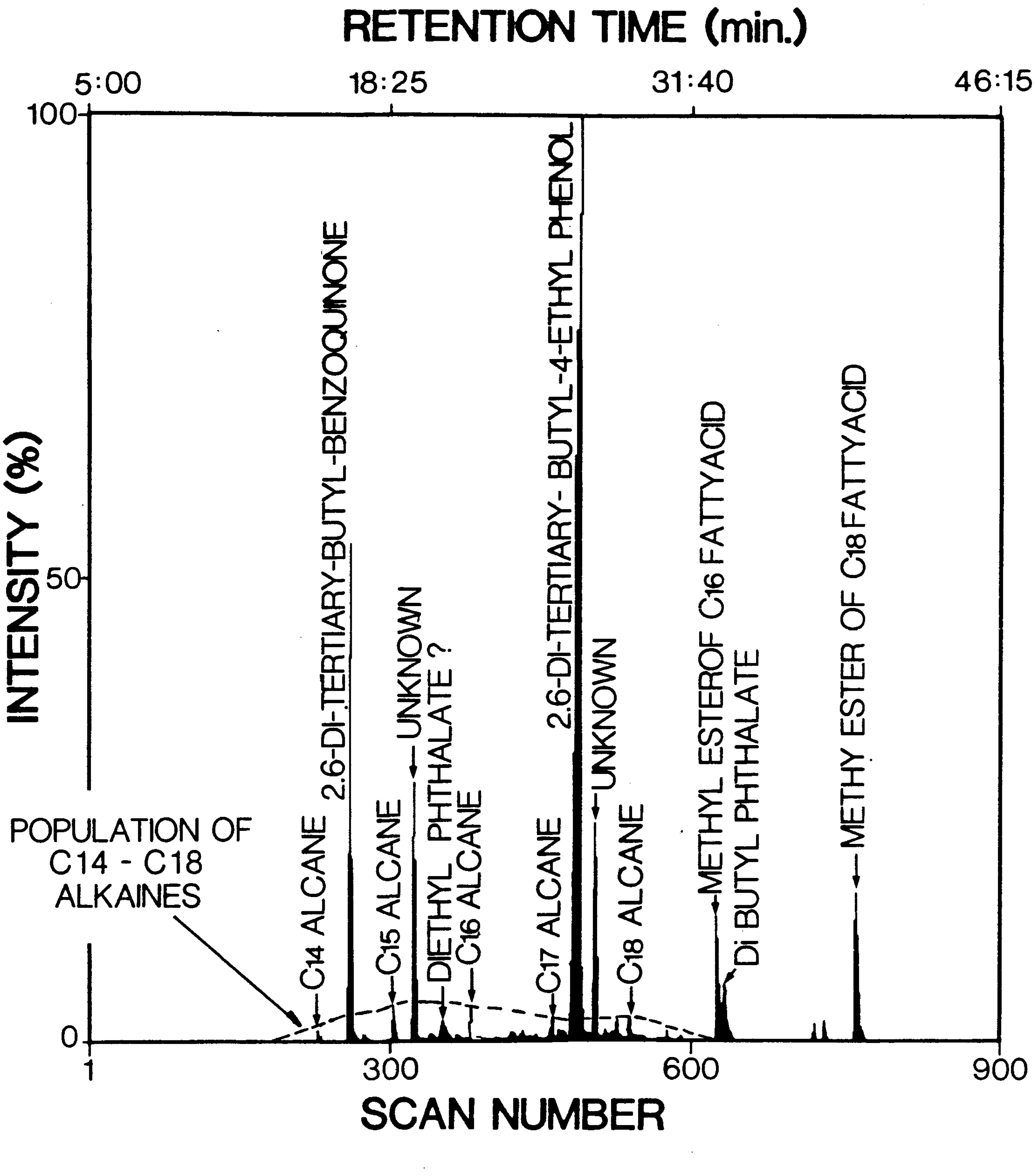


Figure 11: Chromatogram of GC-MS; intensity / retention time.

The phthalates are also suspect; phthalates are used in the plastics industry as polymerizing agents of polyethylene molecules (F. Garneau, unpublished results. pers.comm.; B. Seymour, pers. comm.).

Research in the field of extractable organic matter (EOM) is largely based on such hydrocarbons as the acyclic normal chained alkanes detected in these samples. These alkanes are possibly dissolved from the largely insoluble pyrobitumen (Y. Héroux; pers.comm.) or present as disseminated volatiles within the shales. These products (material taken into solution by chloroform) are, by definition, soluble organic matter (Durand and Monin; 1980). The only acceptable method of recuperating contaminant-free EOM is by progressively finer grinding of the samples with repeated chloroform washing (Holland and Schidlowsky, 1982; McKirdy and Hahn, 1982). This was the method employed in this study and yet detectable amounts of contaminants of indeterminate origin are visible in the chromatogram. The contaminants decrease during progressive grinding and washing, to a point where the contaminants, give discrete peaks and no longer mask the detection of the less abundant hydrocarbon population. The peak intensities for the contaminants are very large compared to the minute peaks observed for the alkane group. This in itself is not conclusive; The alkanes may or may not be related to the source of the contaminants (F. Garneau; pers. comm. unpublished results; B. Seymour, pers. comm.).

A detailed review of the steps used in the preparation of the soluble extract has subsequently revealed that all of the contaminants present are characteristic of the Nalgene plastic bottles in which the core samples were stored prior to agate grinding and glass bottle extraction. The materials in the first washings are not the same as those detected in the final washings in reruns of the analyses (thin layer chromatography on silica gel plates). Detailed analyses (Gas-chromatography mass-spectrometry) have yet to be performed on these different washings.

Unfortunately, it has been subsequently determined that alkanes may possibly be produced during the processing of the polyethylene sample containers. (F. Garneau; pers. comm. from the Nalgene Corporation in Rochester, New York).

An additional test for EOM was performed directly on the pulverized shale, that was never stored in polyethylene, using vacuum pyrolysis-mass spectrometry (Figure 12). The higher temperature combustion aided in the release of the more resistant acyclic isoprenoid alkanes C_{19} (pristane) and C_{20} (phytane)(Figure 12). They differ slightly in molecular structure when compared with the acyclic normal chain alkanes that were detected with the previous technique (McKirdy and Hahn, 1982) (Figure 13). None of the nalgene contaminants were observed.

The exact nature of the alkanes present in the Nalgene polyethylene containers will be determined in the course of ongoing studies. Analyses of the polyethylene's alkane character will conclusively prove or disprove the presence of alkanes due to contamination.

Notwithstanding these problems, the alkanes C_{14} through C_{18} show a relatively smooth complete bell curve; an indication of a natural extract. Naturally occurring hydrocarbons tend to be found in regular groups adhering to bell curve distribution in contrast to the spiked incomplete nature of profiles of reintroduced hydrocarbons resulting from industrial processes and such (B. Seymour, pers. comm., McKirdy and Hahn, 1982).

The alkane population (C_{14}-C_{20}) detected in these samples, resembles those found in the Brazilian Quadrilatero Ferrifero black shales (2.0 - 2.8 Ga)(Figure 14). The alkane profile of this study, composed of dominantly of normal alkanes (C_{15} dominant), best fits an origin related to algae, bacteria, and cyanobacteria in McKirdy and Hahns' classification (1982) (Figure 15). The observed pyrobitumen is an amorphous "bitumenite"; this also indicates an algal and/or a bacterial origin (McKirdy and Hahn, 1982).

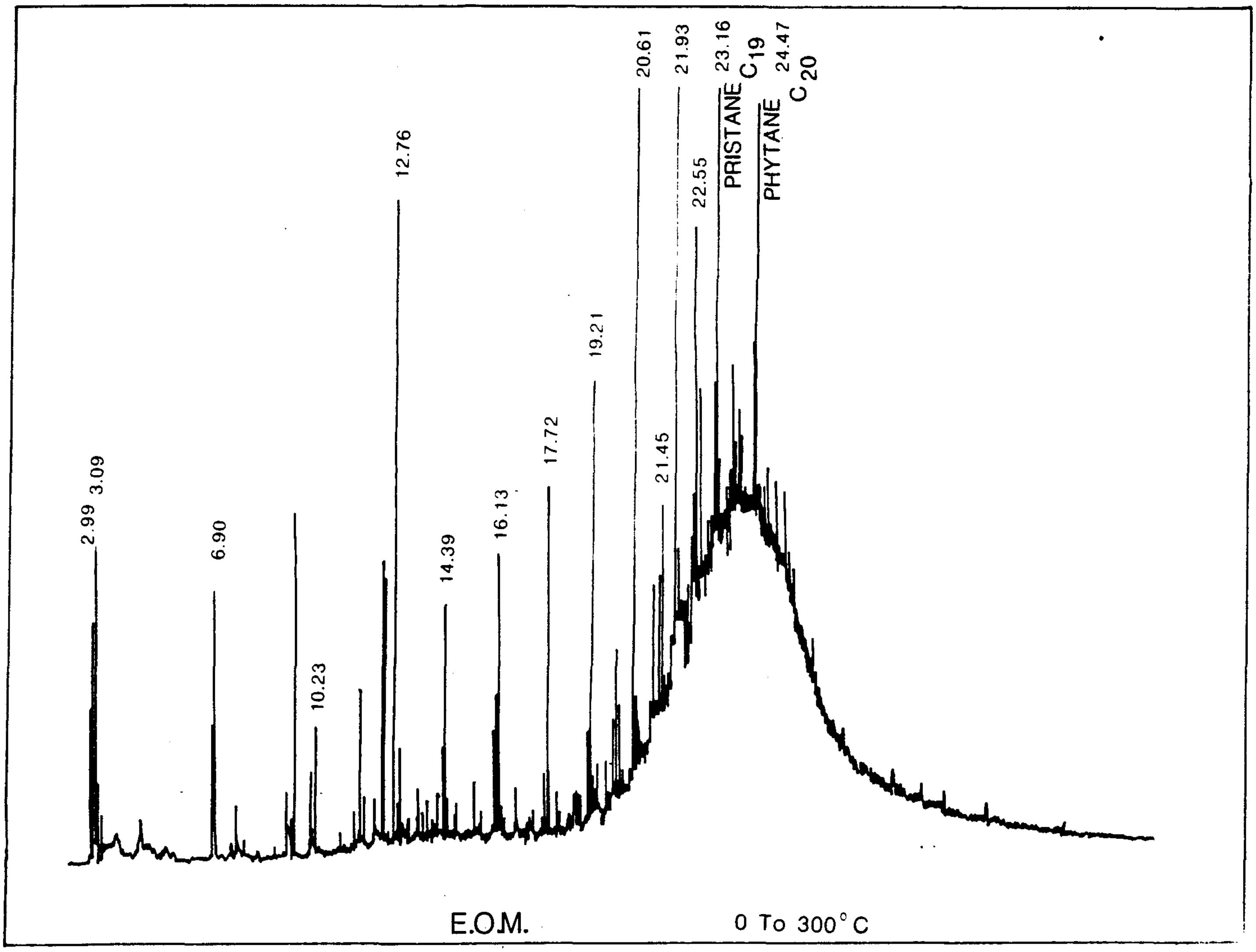
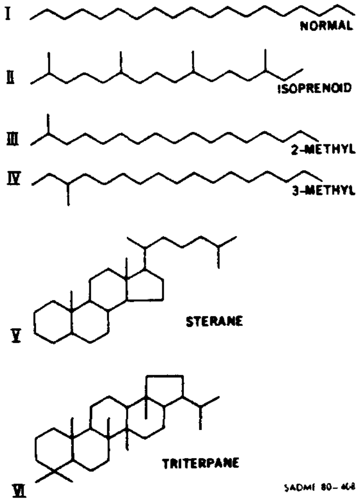


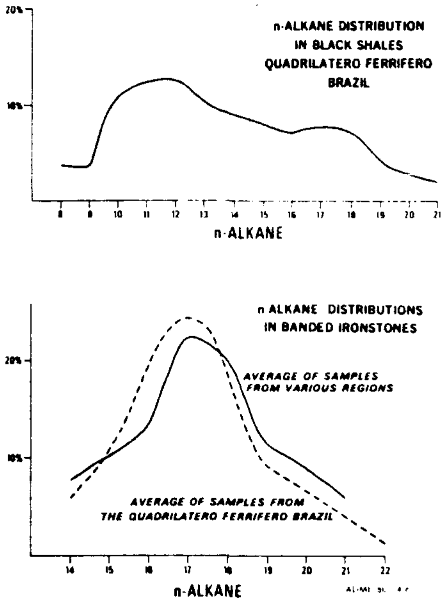
Figure 12: C_{19} and C_{20}. Intensity (Y) versus retention time (X).



- Carbon skeletons of various types of hydrocarbon chemical fossils found in ancient sediments.

Figure 13: molecular structure of alkanes (Mc Kirdy and Hahn, 1982): C_{14} to C_{18} are normal alkanes, C_{19} (pristane) and C_{20} (phytane) are isoprenoid.

The Composition of Kerogen and Hydrocarbons



Distributions of n-alkanes in banded iron formations and black shales, Quadrilatero Ferrifero, Brazil. Average profile for banded iron formations based on samples from Brazil, Africa, India, N. America, and Russia.

Figure 14: Alkanes in ferrifero shales (Mc Kirdy and Hahn, 1982).

Hydrocarbons with potential as Precambrian biological markers.

Hydrocarbon type	Characteristic feature	Possible source(s)
normal alkanes	▶ C_{12}-C_{21} with odd carbon-number preference C_{15} or C_{17} dominant	algae, bacteria, cyanobacteria
	C_{22}-C_{35} with odd carbon-number preference	chlorophytes of Botryococcus type, certain cyanobacteria
	C_{20}-C_{32} with even carbon-number preference	anaerobic bacteria
	C_{22} prominent	dinoflagellates, zooplankton (via diagenetic reduction of $C_{22:6}$ fatty acid)
branched alkanes	7- and 8-methylheptadecane	cyanobacteria
	C_{16}-C_{30} iso and anteiso alkanes	bacteria
	C_{13}-C_{20} regular isoprenoids	photosynthetic algae, certain bacteria
	C_{21}-C_{40} regular and irregular isoprenoids (incl. squalane)	archaebacteria
cyclic alkanes	C_{27}-C_{35} pentacyclic triterpanes of hopane series	prokaryotes
	steranes	algae, cyanobacteria
	4-methylsteranes	dinoflagellates, methanotrophic bacteria
	n-alkylcyclohexanes	algae (via diagenetic intramolecular cyclization of n-fatty acids), thermoacidophilic bacteria
aromatic	methyl-branched alkylbenzenes	archaebacteria
	mono- and polyaromatic steranes and triterpanes	algae, bacteria

Figure 15: Origin of soluble organic matter (McKirdy and Hahn, 1982).

3.3. CARBON ISOTOPE STUDIES

$^{13}C/^{12}C$ was determined for selected samples in the two sections studied, to see if samples of different thermal maturation could be distinguished by carbon istopes. The pyrobitumen of this study has evolved to a point where, optically, it very closely resembles graphite (% absolute reflected light = 5%). The % ARL of pyrobitumen would continue to give a value of 5 % with increasing maturation, even if completely converted to graphite. The organic matter samples taken from Bignell Township give the same % ARL as those from Barlow Township.

The organic matter in the two sections does not show a significant difference in % ARL. Although, the organic matter samples have optical properties very similar to graphite, they are chemically very different from graphite (due to the presence of hydrocarbons). However, the samples differ from each other by a very small degree isotopically.

Carbon isotopes were analysed in four samples taken from the two geographically separate study areas. $^{13}C/^{12}C$ ratios were established in these pyrobitumen samples in order to test for a chemical difference between the samples. Compared to the standard "PeeDee Formation belemnite", $^{13}C/^{12}C$ gives the following results:

Bignell Township section: at 6 km from the Grenville front;

$^{13}C_{PDB}$ = -51 and -51 per mil

Lake Barlow section: at 55 km from the Grenville front;

$^{13}C_{PDB}$ = -49 and -50 per mil

Galimov (1980) showed that the removal of volatiles with increasing thermal maturation of organic matter is responsible for the progressive depletion of the light carbon isotope; ^{12}C. Methane is the most common degradation product produced by the maturation of bitumen or kerogen. The production of methane utilizes the "heavy" isotopes, ^{13}C more readily than the "light" isotopes. Thermally evolved organic matter will therefore be progressively "lighter" in isotopic composition as maturation increases.

Galimov (1980) reports values of -23 to -30 per mil for precambrian kerogen younger than 2 Ga and -28 to -38 per mil for kerogen older than 2 Ga. There is only a small difference exhibited between the two groups of samples; -1 per mil (2% of the recorded values). Carbon isotopes are of limited use for evaluating the chemical differences in the two groups of super-mature pyrobitumen found in this study.

3.4 Conclusions

We found the following results:

- The graphitic material in the black shales of the Blondeau Formation is amorphous organic matter.

- The organic matter is present in 3 different forms; insoluble remobilized bitumenite, insoluble in situ bitumenite, and soluble organic matter: the alkanes 14 through 20.

- The optical and chemical nature of the organic matter indicates possibly a bacterial and/or an algal source.

- Carbon isotope studies show the pyrobitumen to have a very light isotopic composition, with samples from the Bignell Township being the lightest;

Bignell section: at 6 km from the Grenville front;
$^{13}C_{PDB}$ = -51 and -51 per mil.
Barlow section: at 55 km from the Grenville front;
$^{13}C_{PDB}$ = -49 and -50 per mil.

CHAPTER IV

MAJOR AND MINOR ELEMENTS IN BLACK SHALES

4.0 MAJOR ELEMENT ANALYSES

Major element analyses were performed only on the whole rock. The results were compared to previous shale analyses (Table 1) performed on the Barlow Lake stratigraphic section (Carignan, et al., 1984).

The results are presented on a volatile-free oxidized iron basis (Fe_2O_3 is total iron). Carbon and sulphur were determined in two separate aliquants of shale prior to combustion. The oxide contents of this study closely resemble the results of Carignan et al. (1984). However, minute differences between the two studies are apparent, as in the SiO_2 analyses (Figure 16 and 17). As noted in the petrology section, the shales contain abundant silt sized plagioclase and quartz grains. The abundance of the quartz and plagioclase fraction varies greatly in thin section from one sample to the next. Also, zones of silicification were noted in the shales at certain locations. Carignan et al. (1984) report an average of 63.83 percent SiO_2. An average of 69.98 and 71.49 percent SiO_2 were measured in the respective Bignell and Barlow stratigraphic sections in the present study.

Other differences worth mentioning were for CaO, P_2O_5, and Fe_2O_3. Carignan et al. report 2.96 percent CaO, 0.24 percent P_2O_5, and 5.31 percent Fe_2O_3. In this study 8.14 and 4.87 percent CaO, 0.034 and 0.066 percent P_2O_5, and 0.61 and 1.09 percent Fe_2O_3 were obtained for the Bignell and Barlow stratigraphic sections, respectively. These differences are most likely due to the inhomogeneous sulfide distribution and fine calcite veining in the sampled sections.

It was not possible to use the same samples as Carignan et al. (1984). Notwithstanding, this study reports values very similar to those of Carignan et al. The small analytical differences observed were to be expected, even under the best of conditions

Table 2 compares the results of the whole rock average analyses of the standard "North American Shale Composite (N.A.S.)(Gromet, et. al., 1984) with the samples of this study. The major difference noted between the two sets of results is the percent SiO_2 and Na_2O. The Lake Barlow stratigraphic section is slightly richer in SiO_2 and Na_2O. Locally the shales of the present study are silicified

Oxide	Samples L1-L6	L9-L22	Carignan et al.(1984)
SiO_2	69.98	71.49	63.83
Al_2O_3	12.42	12.96	14.69
Fe_2O_3	8.14	4.87	5.31
Na_2O	2.62	3.92	3.10
K_2O	2.64	2.71	2.20
CaO	0.61	1.09	2.96
MgO	3.35	2.34	2.00
P_2O_5	0.034	0.066	0.24
MnO	0.039	0.039	0.09
TiO_2	0.29	0.40	0.07
Total*	100.1	99.9	
CO_2	4.14a	7.81a	3.25
S	2.61a	1.71a	1.10
		Total	98.84

*Total weight percent oxides after combustion. CO_2 analyses (a) (total organic carbon only, in this study) and S(b) determined prior to combustion.

Table 1 Comparison of major oxide analyses.

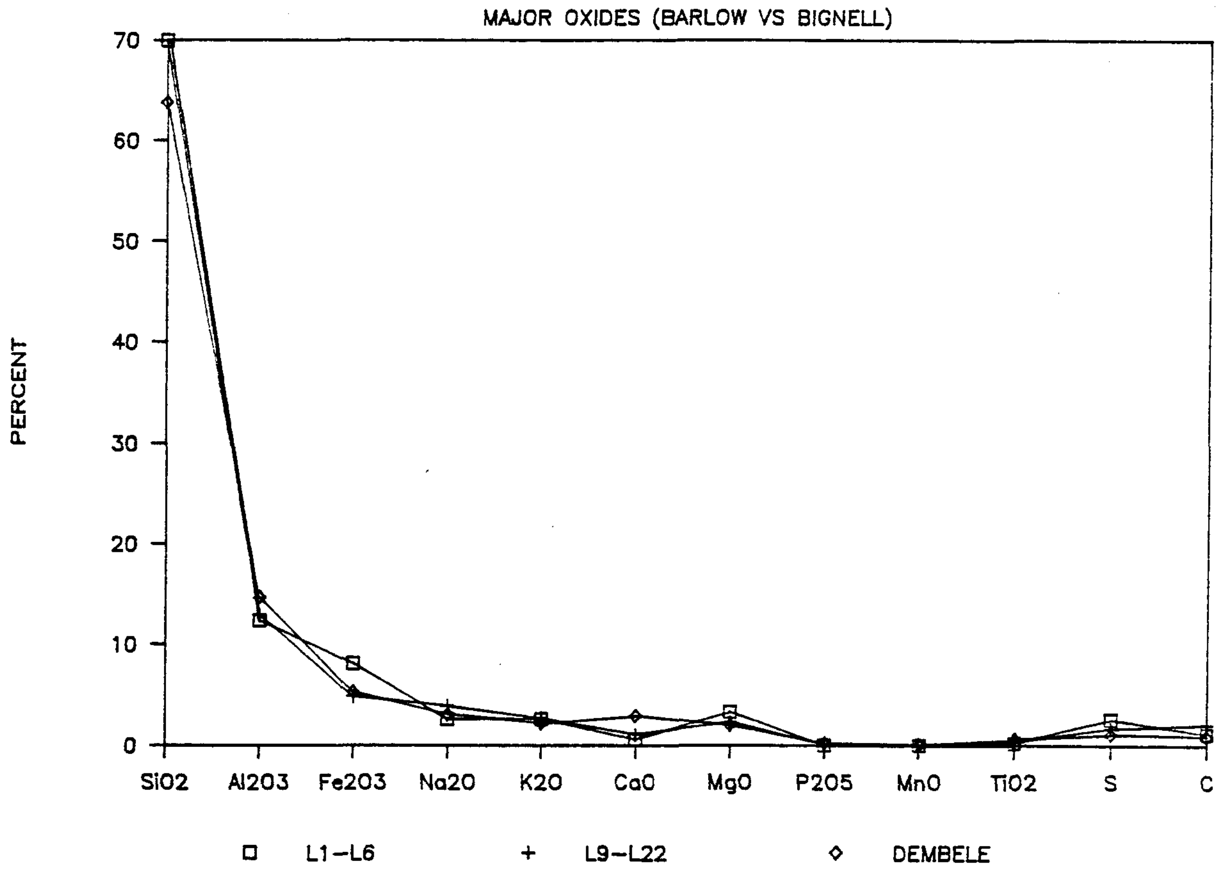


Figure 16; Major oxides present in shales

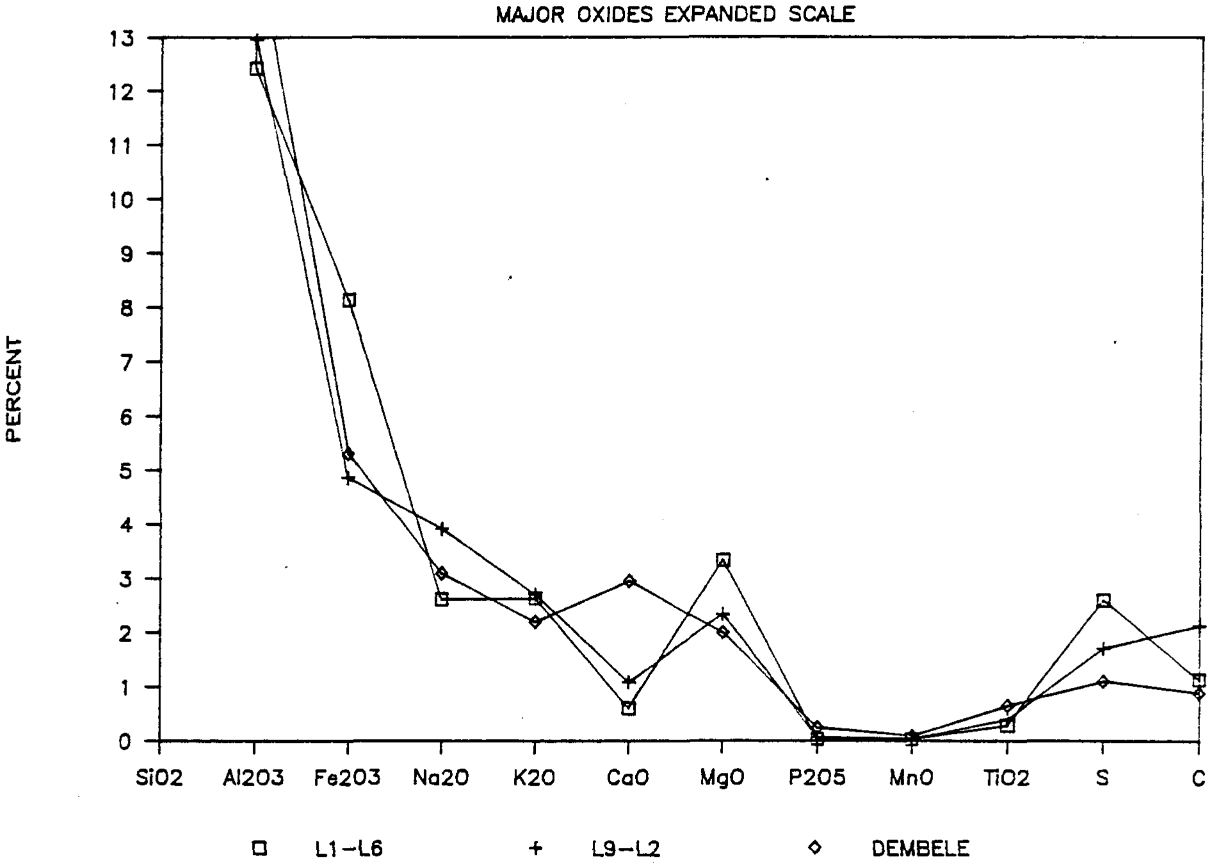


Figure 17; similar to Figure 16, with expanded scale.

Oxide	Samples L1-L6	L9-L22	North American Shale
SiO_2	69.98	71.49	64.80
Al_2O_3	12.42	12.96	16.90
Fe_2O_3	8.14	4.87	6.28
Na_2O	2.62	3.92	4.36
K_2O	2.64	2.71	2.93
CaO	0.61	1.09	5.02
MgO	3.35	2.34	1.57
P_2O_5	0.034	0.066	0.50
MnO	0.039	0.039	0.10
TiO_2	0.29	0.40	1.06
Total*	100.1	99.9	100.0
CO_2	4.14a	7.81a	
SO_3	6.5a	4.3a	

* (Total weight percent oxides after combustion.)

a (CO_2 (total organic carbon only) and SO_3 determined prior to combustion.

Table 2 Comparison of Major oxides: North American shale composite and shales of this study and in thin section plagioclase (albite) is visible. These mineralogical variations are probably responsible for the small analytical difference measured for the shales of this study compared to the N.A.S. The shales of the Bignell and Lake Barlow stratigraphic sections have greater SiO_2 and lower Al_2O_3 values in comparison to the NAS. Many factors could be responsible for this difference; the type of weathering of the source rock, differing maturity or sedimentation rates giving NAS more phyllosilicates and less detrital quartz than the shales of this study, and differing source rocks (Sawyer, 1986). Possibly the Blondeau Formation had a more acidic source than the composite source of the NAS. Petrographically, the shales contain abundant feldspar and quartz; the coarser layers are clearly quartzo-feldspathic.

4.1 ORGANIC CARBON VERSUS SULPHUR

In this section the variation of S (as SO_3) extrapolated to sulfides, versus organic carbon, has been investigated. This is a preliminary attempt to quantify the relationship of organic matter to the fixation, precipitation, or concentration of sulfides.

While there were no quantitative analyses of percent carbon determined for the organic matter in this study all carbon present in the shales is directly proportional to the organic matter present. The organic matter studied in this study is highly evolved and contains over 90 percent carbon.

All of the organic carbon and respective sulphur analyses were plotted on an binary graph (Figure 18a). Statistically, the population of samples appears to have no correlation. When fitted to a curve by the least squares method the samples have a correlation coefficient of 0.311. The samples were tested at a confidence level of 100 percent (all samples used) (Figure 18 a). Statistically there is no trend or relation to the points on the graph.

However, with visual inspection of the plotted data points, a trend easily detected within the sample population. There are 4 samples which clearly do not behave as the main group; at present there is no explanation for the anomalous behaviour of these samples.

When all the samples are plotted on a histogram, (Figure 18b) the samples which are anomalous are easily distinguished. The most frequent values are found in the limit of 1 to 2 for the ratio of S/C. The mode (the most frequent value) is 1.5, the median (the average of frequency) is 2.7 for the ratio of the ratio of S/C. Four values of the ratio of S/C are beyond 1 unit of standard deviation from the median; one value of 0, one value from

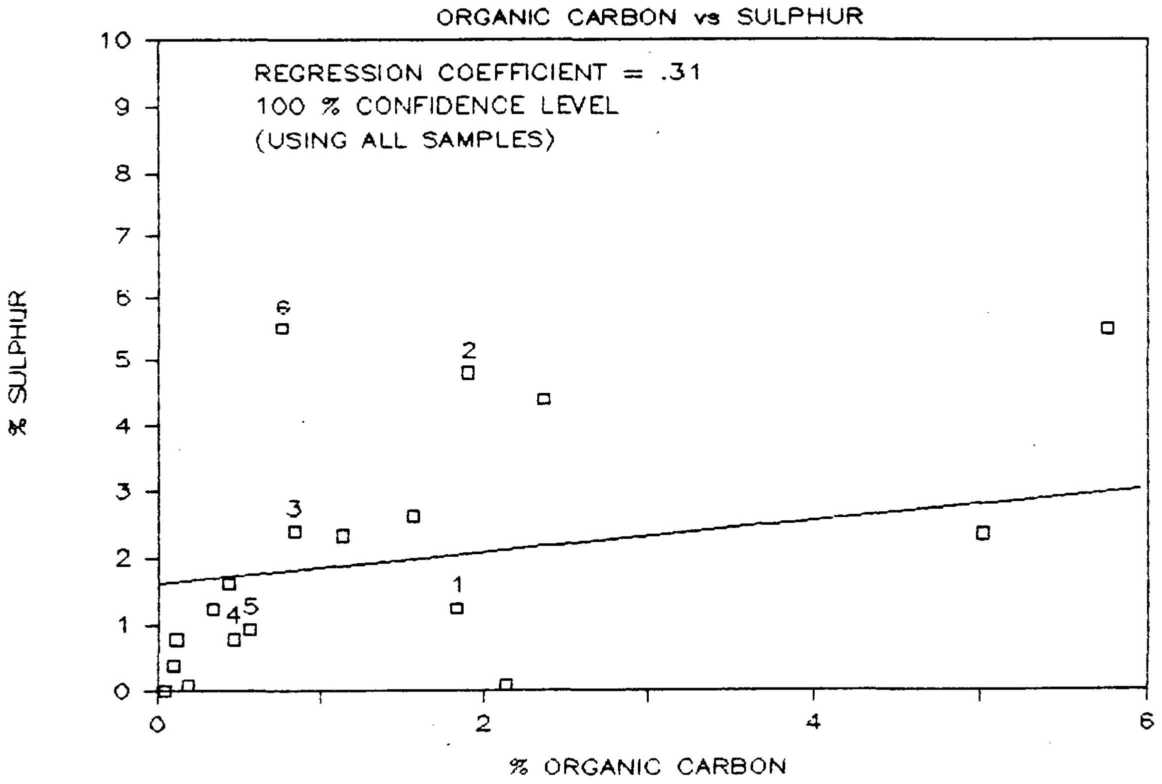


Figure 18a; Binary graph of organic carbon and respective sulphur analyses.

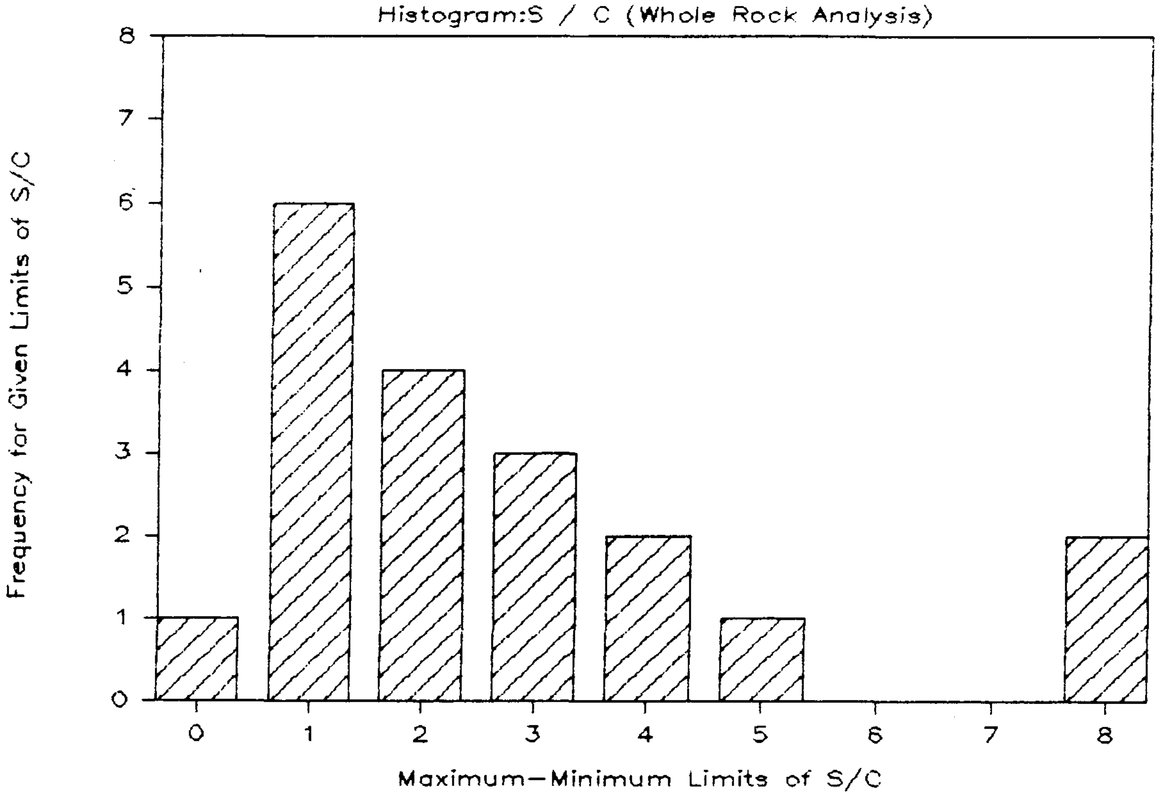


Figure 18b; The ratios of S/C plotted on a histogram the limit of 4 to 5, and two values from the limit of 7 to 8.

While there is admittedly no statistical nor scientific justification for dropping unexplained data points, the remaining data gives a better impression of the relation of organic carbon to sulfur. 85% percent of the analyses were retained. This falls between the 96% limit (2 units of standard deviation) and the 68% limit (1 unit of standard deviation) from the average value in a gaussian distribution (Cheeney, 1983).

Using 85 percent of the samples the calculated coefficient of correlation is 0.70. Values over 0.5 imply a nonrandom relationship for the variables, in this case organic carbon and sulphur. The ongoing work may establish the reason for the anomalous behavior in certain samples.

Where S = Y and C = X, the function that describes their behavior at a 68% confidence level (1 degree of freedom) is :

Y = .663 X + 1.09; with a regression coefficient of 0.70.

From the above equation the ratio of S/C is approximately 1.18 or close to 1 part organic carbon for every 1 part sulphur in the shales of the Lake Barlow and Bignell Township sections. However, considering that there is

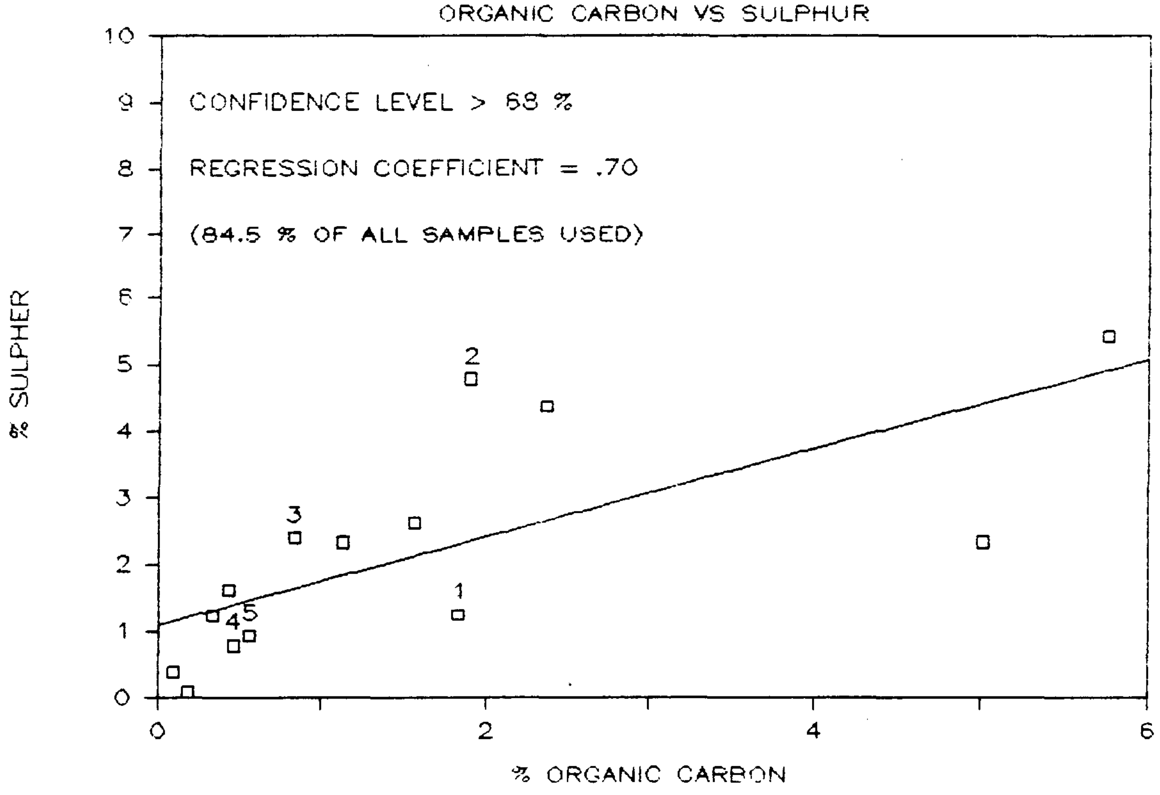


Figure 19; S versus C; samples analyses replotted on a binary graph no correlation when all the data is plotted (coefficient of correlation = 0.311), this relationship could just as easily be coincidental.

4.2 Sulphur Versus Sulfides

Sulphur was compared to Fe_2O_3 in order to see if sulphur was proportional to the sulfides present in the shales. This was required in order to show that organic carbon's influence over sulphur, could be extrapolated to control over the sulfides. Pyrite was the only sulfide of significance in the two stratigraphic sections.

The plot of S/Fe_2O_3 values on a binary graph shows a somewhat diffuse, linear field of points (Figure 20). The coefficient of correlation for the calculated line is 0.47, very close to 0.5. A trend is apparent.

Using exactly the same treatment as for the ratio of S/C, a histogram of frequency for the ratio of S/Fe_2O_3 was determined (Figure 21) and a new regression calculated (Figure 22). Two values were dropped (both contain abundant chlorite (up to 23% Fe_2O_3 by weight; Deer et al., 1966) with no visible sulfides; high Fe_2O_3, low S). The coefficient of correlation for 90 % of the analyses was 0.78 (at 1 degree of freedom; 68% confidence limit).

Where S = Y and Fe_2O_3 = X, the equation of the line is :

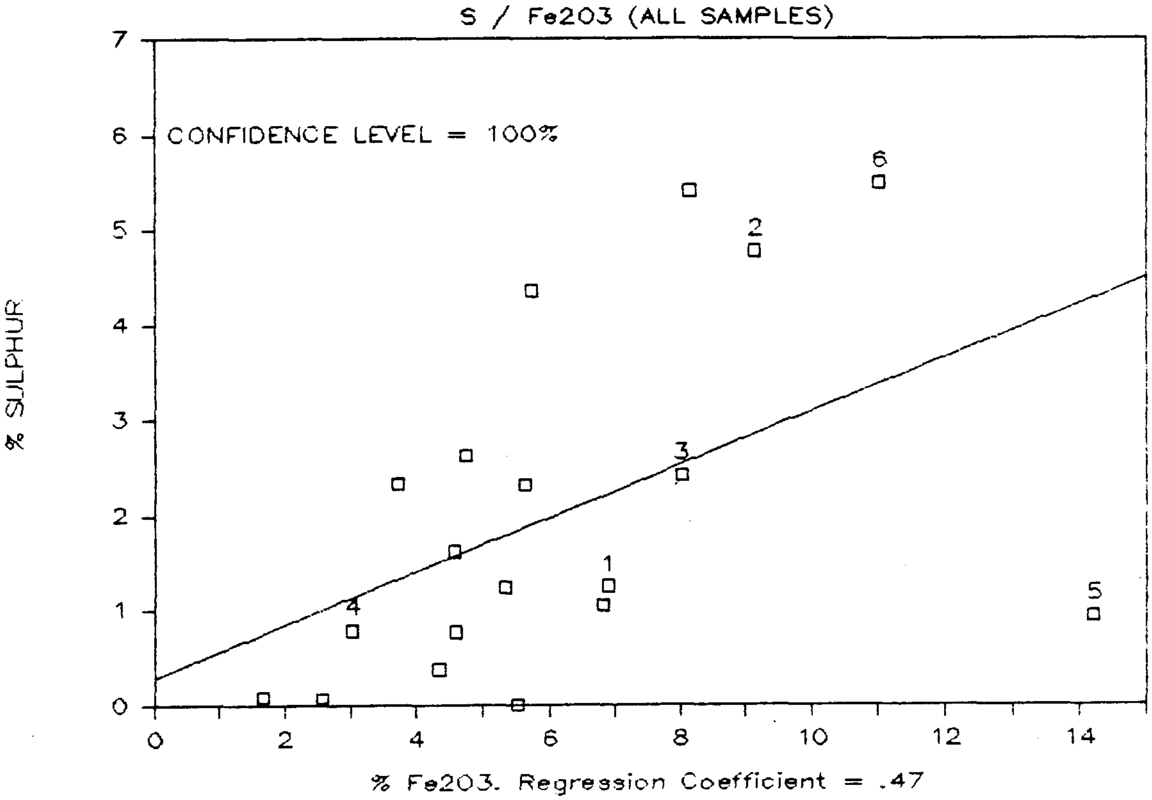


Figure 20; The regression for the ratio of S/Fe_2O_3 values: binary graph of all samples.

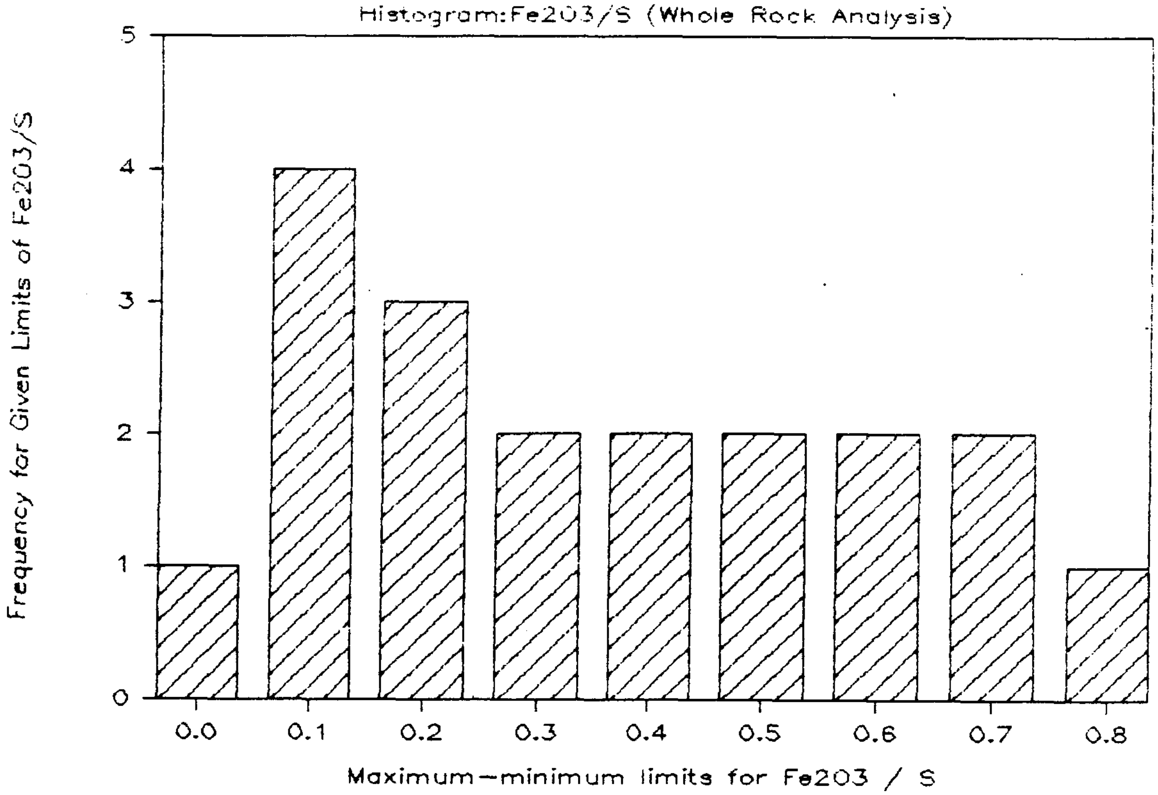


Figure 21; histogram of frequency for the ratio of S/Fe_2O_3

$Y = .576 X + -1.07$.

The slope equals 0.576, the Y intercept equals -1.07, with a coefficient of correlation of **0.78.**

The ratio of S/Fe_2O_3 is approximately 0.58. The ratio of S/Fe would be 0.83 (Fe_2O_3 equals 1.14 times Fe), or .83 parts S for 1 part Fe_2O_3 in the shales from the two sections. By stoichiometry, there is 1.18 parts S for 1 part Fe in pyrite. The excess Fe is probably in other mineral phases such as chlorite and other phyllosilicates. Also there may be pyrrhotite present which stoichiometrically contains .71 to .41 parts sulphur for one part Fe, which would be relatively more enriched in Fe than Pyrite.

4.3 Conclusions

We find the following results;

- There is a correlation between organic carbon and sulphur. The equation that best describes their behaviour is;

Sulphur = 0.663 Carbon + 1.09; with a correlation coefficient of 0.70, within 2 units of standard deviation or the 68% confidence level.

From the above equation the ratio of S/C is approximately 1.18 or close to 1 part organic carbon for

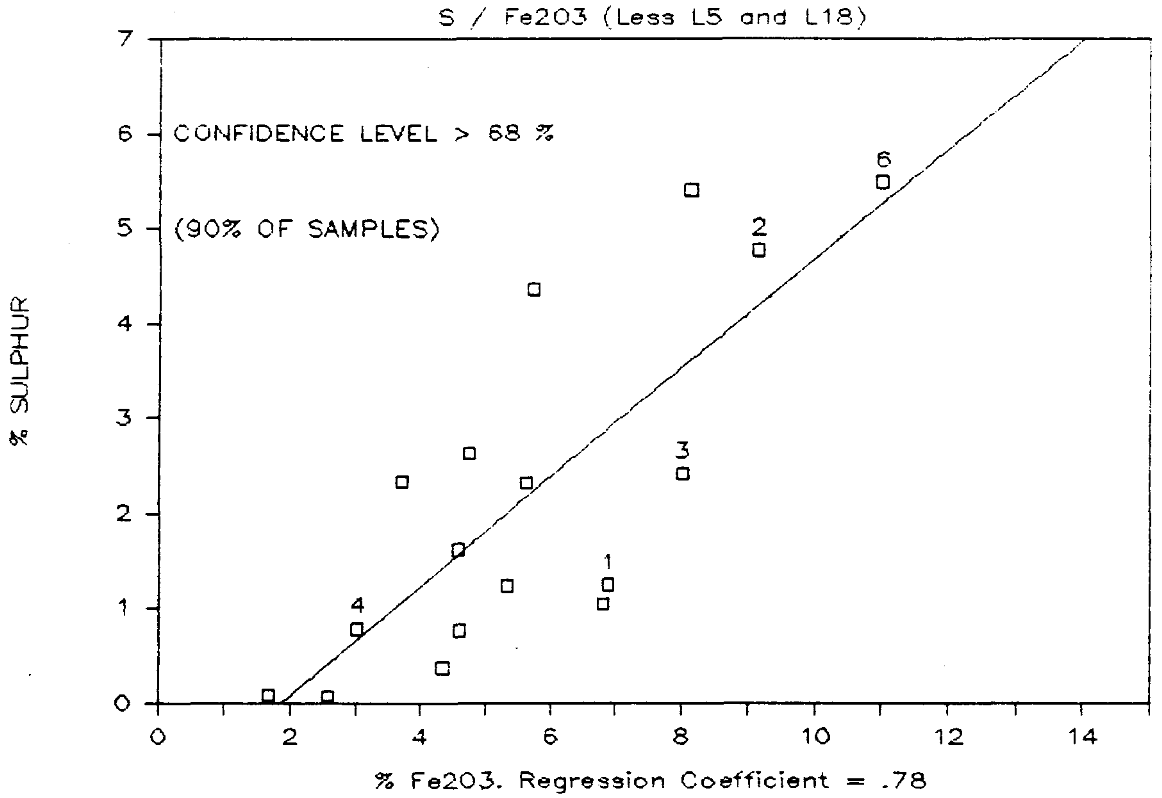


Figure 22; The least squares regression for the ratio of S/Fe_2O_3 less two samples.

1 part sulphur in the shales of the Lake Barlow and Bignell Township sections.

- Sulfur can be correlated with total iron;

Sulphur = 0.576 Fe_2O_3 - 1.07, with a correlation coefficient equal to 0.78, within 2 units of standard deviation or the 68% confidence level.

The ratio of S/Fe_2O_3 is approximately 0.58. The ratio of S/Fe would be 0.83 (Fe_2O_3 equals 1.14 times Fe), or .83 S for 1 Fe_2O_3 in the shales from the two sections.

CHAPTER V

TRACE ELEMENTS IN BLACK SHALES

Trace element analyses were performed on the whole rock as well as on the sulfide and organic matter fractions. The objectives in this part of the study are; 1) to quantify the contents of trace elements in the sulfide and organic matter fractions, and 2) to determine the effect that these components have on the concentration of trace elements in the shale.

There is no shortage of trace element analyses of shales; Vine and Tourtelets' summary paper (1970) documents several studies of behavior of trace elements in black shale hosted mineral deposits and notes brief references to graphite and organic matter or oil. More direct relation of metals and OM in black shales can be found in Kucha's (1983) study of Soluble OM extracted in chloroform. He discovered 2 to 50 ppm Au and a few ppm of Pt to be present in the soluble OM the black shales of the Zechstein Basin in Poland.

5.0 TRACE ELEMENTS IN ORGANIC MATTER

All the samples were oxidized in a high-temperature furnace to convert insoluble organic compounds to CO_2, H_2, and N_2. The resulting ash was dissolved in acid and then analysed by atomic absorbtion. The minute sample mass of organic matter yielded metal concentrations too low to be detected by the apparatus. The analyses had to be performed with an alternate technique.

Instrumental neutron activation analyses (INAA) was the technique selected to complete the analyses. INAA was chosen from the available methods for the relative ease of sample preparation and high sensitivity for metals even with reduced sample weights.

In the present study the content of Au, Zn, Co, and Cr was determined for each of the organic matter samples (Figure 23). Au, Zn, Cr, and Co average 0.25, 354.3, 169.8, and 9.6 ppm respectively. All of the values are high with respect to the average trace metal content of the whole rock. Au is nearly 50 times richer in the organic matter fraction than in the whole rock; consistently about 0.25 percent Au. Zn and Cr are respectively about 3 and 1.8 times richer than Zn and Cr in the whole rock. Conversely, Co is actually about 2 times richer in the whole rock than in the organic matter fraction (Table 3).

The organic matter fraction demonstrates an enrichment in gold relative to the other elements. When Au detected in the organic matter fraction is compared to the percent organic carbon analysed in the whole rock (Figure 24) there is no apparent relation. This is also true for Au in the whole rock compared to the percent organic carbon in the whole rock (Figure 25). The points are spread randomly across the graph fields. Although generally enriched in Au, organic matter does not appear to determine the abundance of Au in the whole rock. When the contents of Au from the whole rock and the organic matter fraction are compared, we see a weak correlation for samples L13-L20 (Figure 26).

The manner in which gold is present in the organic matter is not understood. There is no indication that Au is "complexed" to organic matter by this type of analysis despite its presence in significant quantities (0.25%). Kucha's (Kucha, 1983) results do not support the presence of "gold complexes" in organic matter. Quantitative analysis cannot define the manner in which Au is present in organic matter.

The other trace metals were compared to Au in order to see if they were related in some way. Zn, Cr, and Co compared to Au give values that plot randomly (Figures 27, 28, and 29).

TRACE ELEMENT CONTENT: (ppm)

	WHOLE ROCK (WR)	ORGANIC MATTER (WR)	OM/WR
Au	0.0056	0.2460	43.9
Zn	122.7	435.5	3.6
Cr	101.4	178.2	1.8
Co	17.0	9.3	0.6

Table 3 Trace element content: whole rock versus organic matter fraction

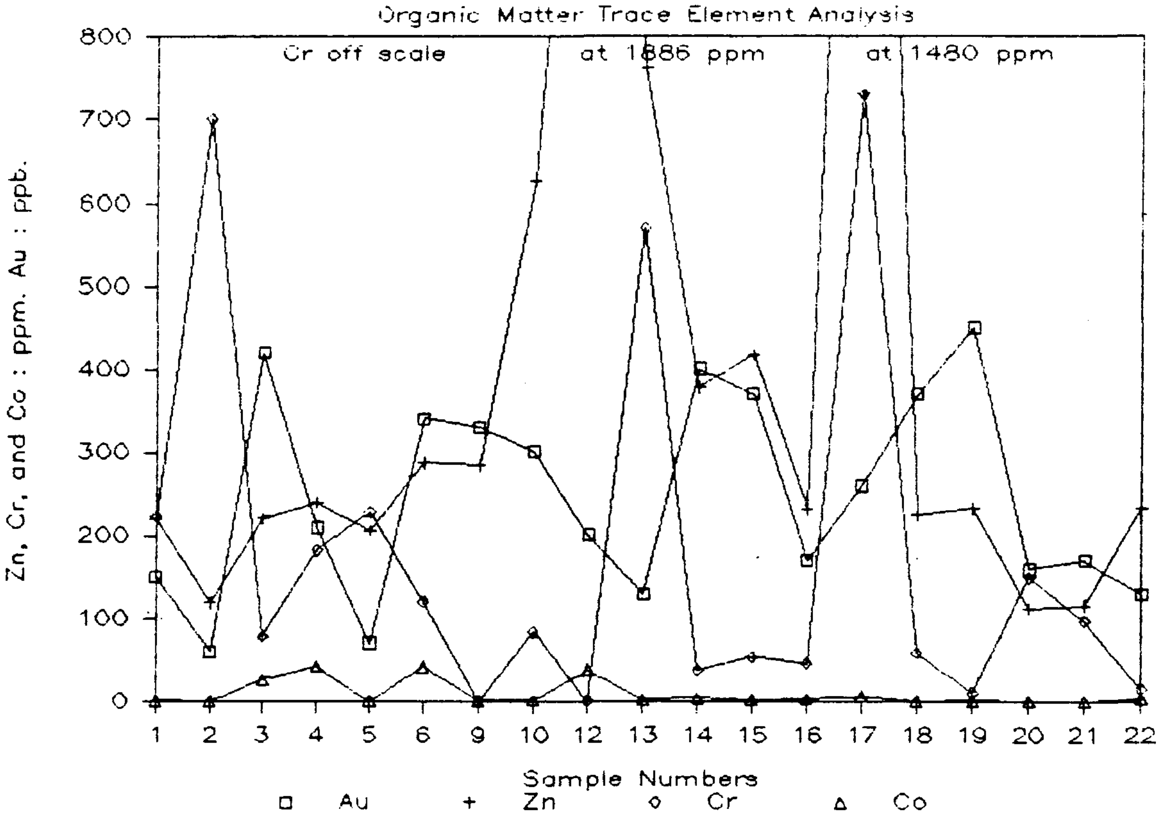


Figure 23; Au, Zn, Co, and Cr in organic matter

Organic carbon determined for the whole rock was compared to the sum of the whole rock trace elements. No apparent relation could be detected between the content of trace elements and organic carbon or organic matter.

5.0.1 Conclusions

- Organic matter is enriched in trace elements relative to the whole rock most notably for gold.
- There does not appear to be strong control over the trace element content in the whole rock exerted by the organic matter.

5.1 TRACE ELEMENTS IN SULPHIDES

The content of Au, Zn, Cr, and Co was determined for the sulfide fraction. The samples were prepared by dissolving the sulfides present in the sulfide - organic matter residue that remains after removal of the silicate fraction by hydrofluoric acid. The sulfides are dissolved in heated "aqua regia" prepared from a solution of 1 part nitric and 3 parts hydrochloric acid. The solution was suitable for atomic absorption and was sufficiently concentrated in metallic ions to allow detection.

Microscopic examination indicates that the principal sulfide present is FeS_2. The results of the analyses of

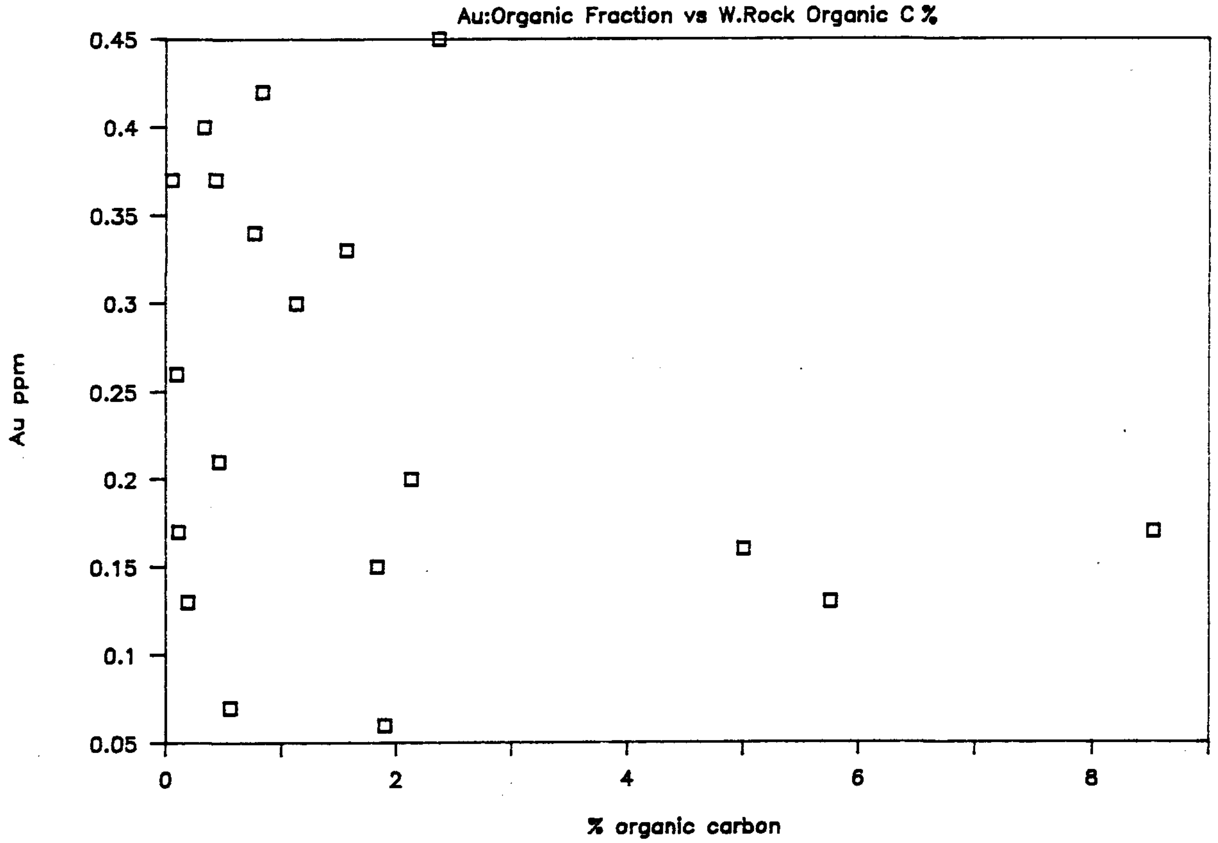


Figure 24; Au organic matter vs organic carbon whole rock

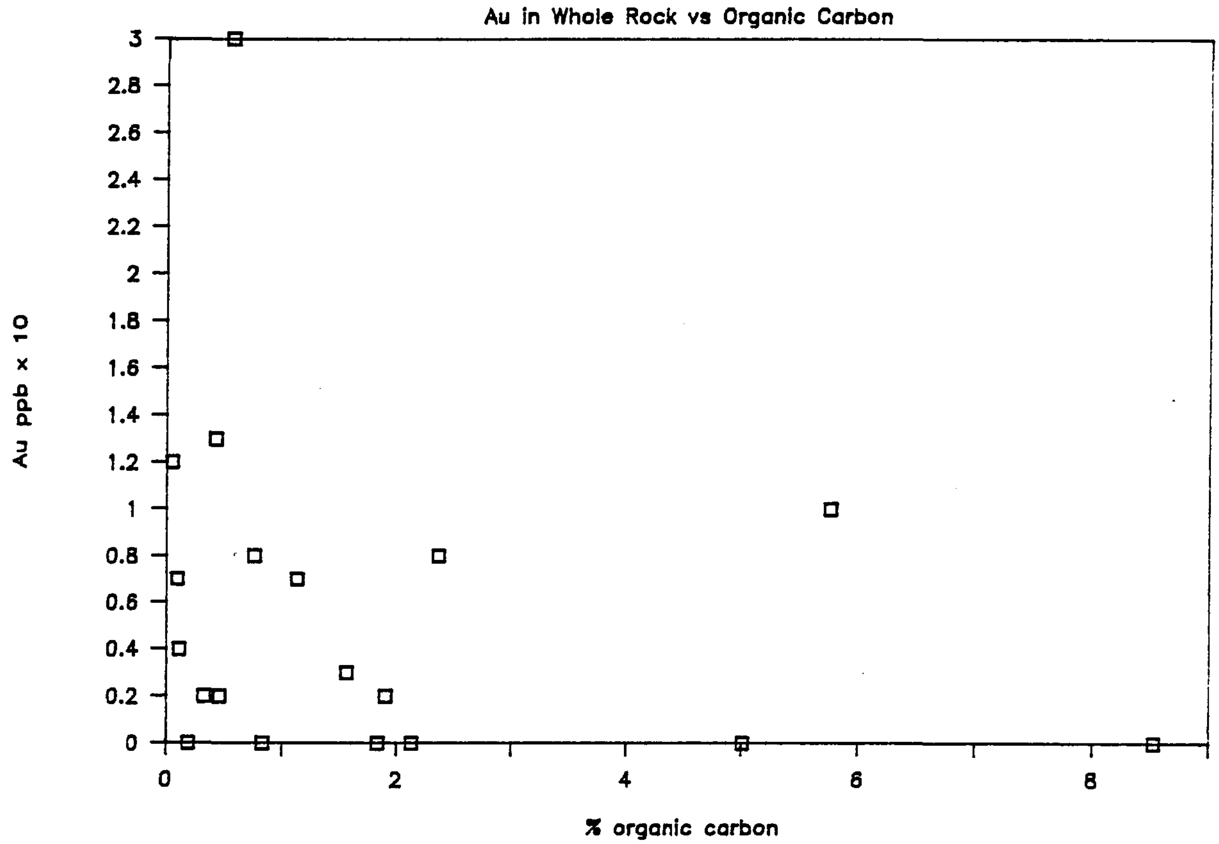


Figure 25; Au whole rock vs Organic carbon whole rock

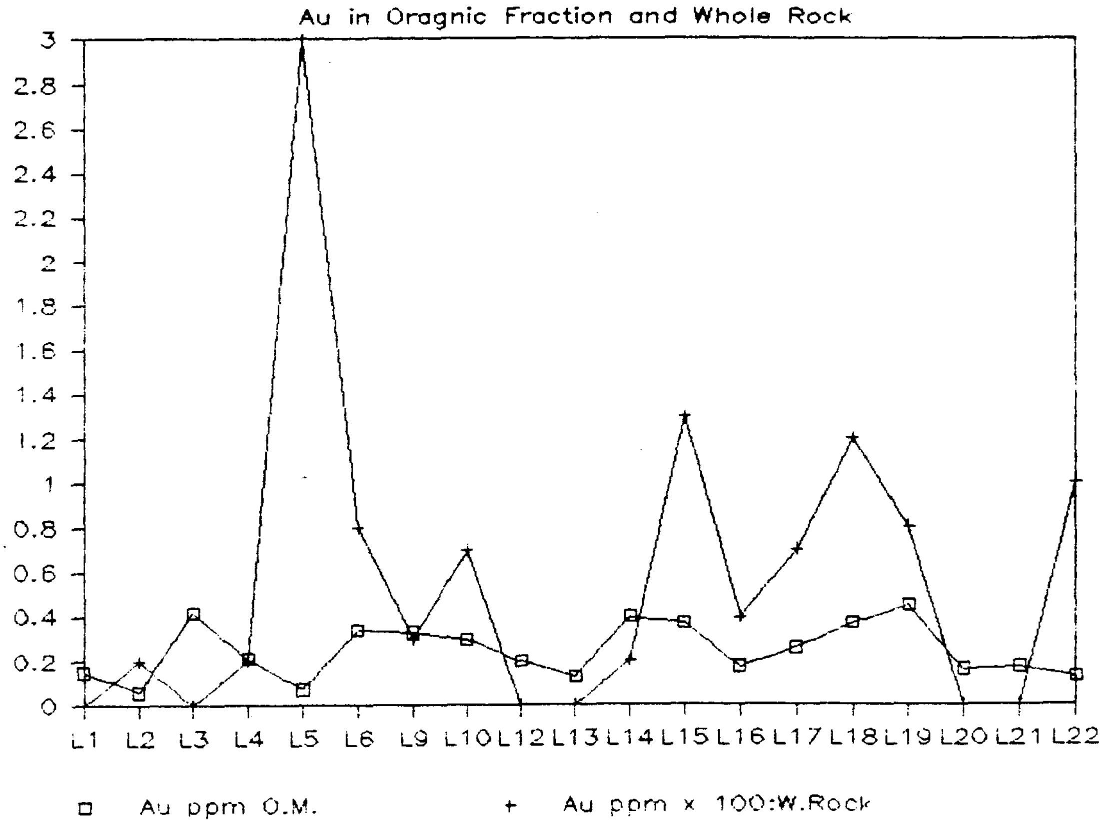


Figure 26; Au whole rock compared to Au organic matter

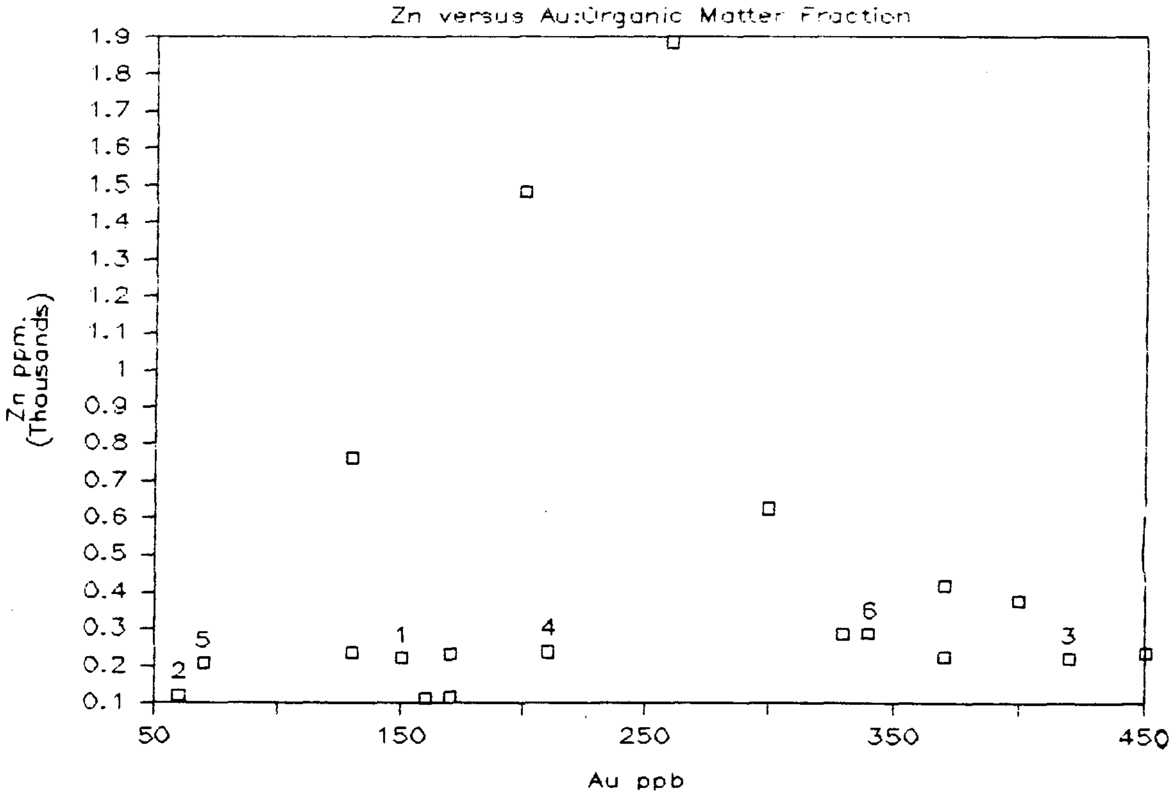


Figure 27; Test for control over Au in organic matter by Zn present.

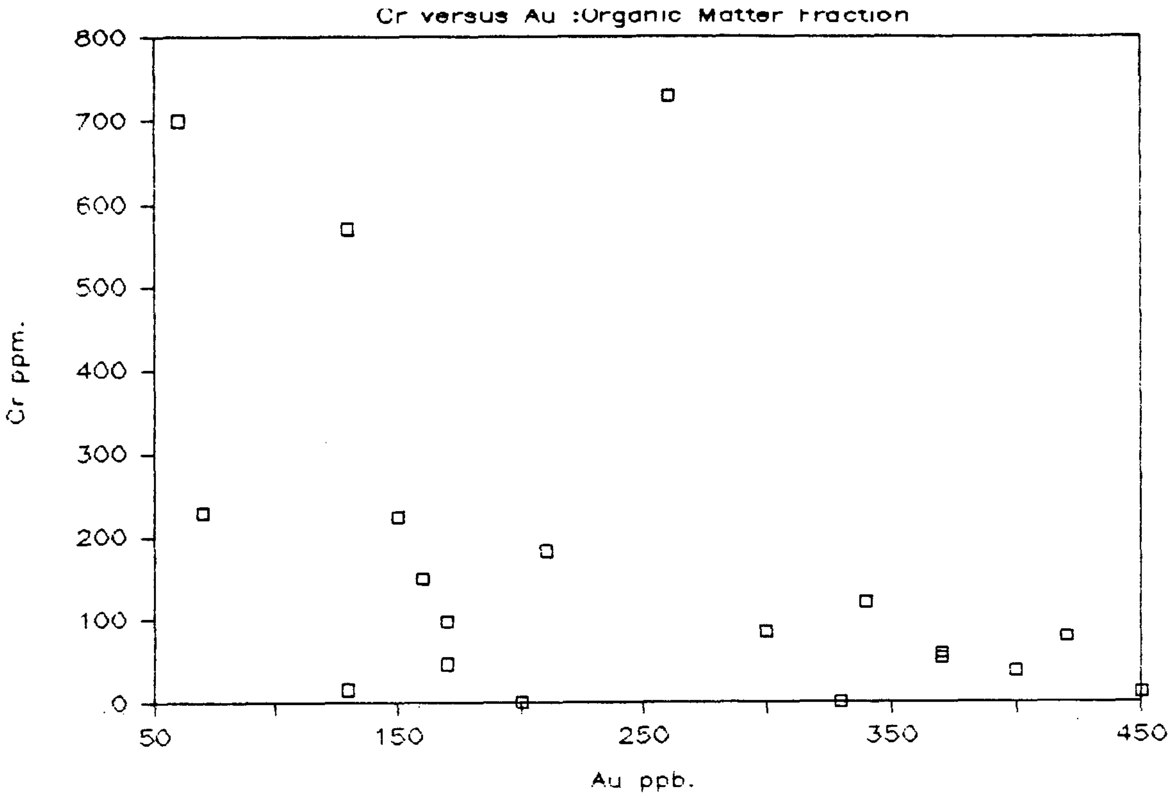


Figure 28; Test for control over Au in organic matter by Cr present.

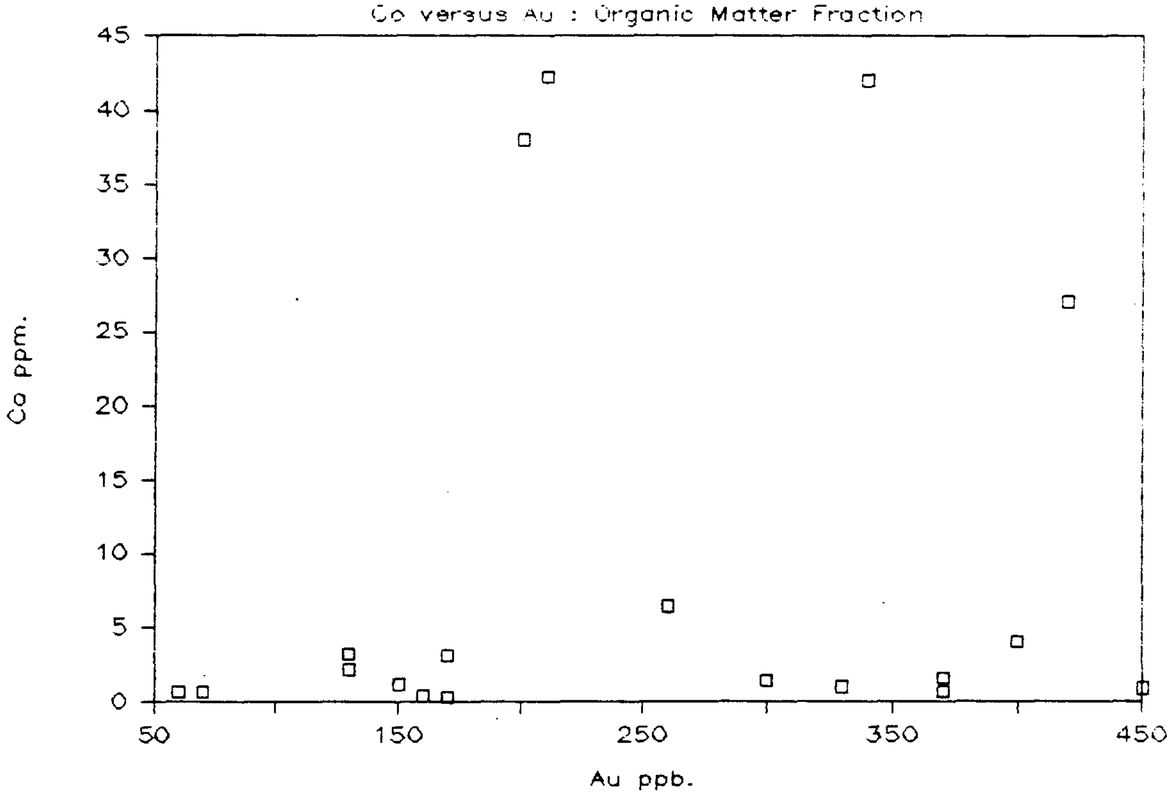


Figure 29; Test for control over Au in organic matter by Co present.

total Fe compared to S in section **4.1.3**, "Sulphur Versus Sulfides" indicate that the pyrite may also be associated with pyrrhotite. The only other sulfide species, chalcopyrite, was found only in a single instance. It can be presumed that the trace elements present in the aqua régia solution come from substitution within the molecular structure of the sulfides or are from submicroscopic imperfections of other unidentified sulfide species. Ni, Cr, and Co can substitute for Fe in pyrite, (Deer, et. al.,1966) but Zn would very likely be from sphalerite .

The content of Au, Zn, Co, and Cr was determined for each of the sulfide samples (Figure 30). Au, Zn, Cr, and Co average 0.747, 698, 811, and 359 ppm respectively (Table 4). As was the case with the organic matter fraction all of the values are high with respect to the average trace metal content of the whole rock. Au is nearly 133 times richer in the sulfide fraction than in the whole rock. Zn and Cr are respectively about 5 and 8 times richer than the content of the whole rock. In contrast to the low average value of Co in organic matter, sulfide is about 20 times richer than in the whole rock.

The same comparisons were performed for the sulfide fraction as for the organic matter fraction in the previous section. Au in the sulfide fraction is compared to sulphur analysed in the whole rock (Figure 31) there is no apparent relation. This is also true for Au in the whole rock compared to sulphur (Figure 32). The points are spread randomly across the graph fields in much the same fashion as seen in the comparable organic matter graphs. The same conclusion is true for sulfides: although rich in Au, sulfides do not appear to determine the abundance of Au in the whole rock. However, there is a weak correlation for some samples; some high sulfide Au values correspond to high whole rock shale Au values (Figure 33).

The other trace metals were compared to Au in order to see if they were related in some way. Zn, Cr, and Co compared to Au give values that plot randomly (Figures 34,35, and 36).

Sulphur from the whole rock analysis was compared to the sum of the trace elements present in the whole rock. No apparent relation could be detected between the content of trace elements and sulphur or (by extrapolation) sulfides.

5.1.1 Conclusions

- Sulfides are enriched in trace elements relative to the whole rock most notably for gold. The gold content is very erratic compared to the constant values for gold in the organic matter fraction.

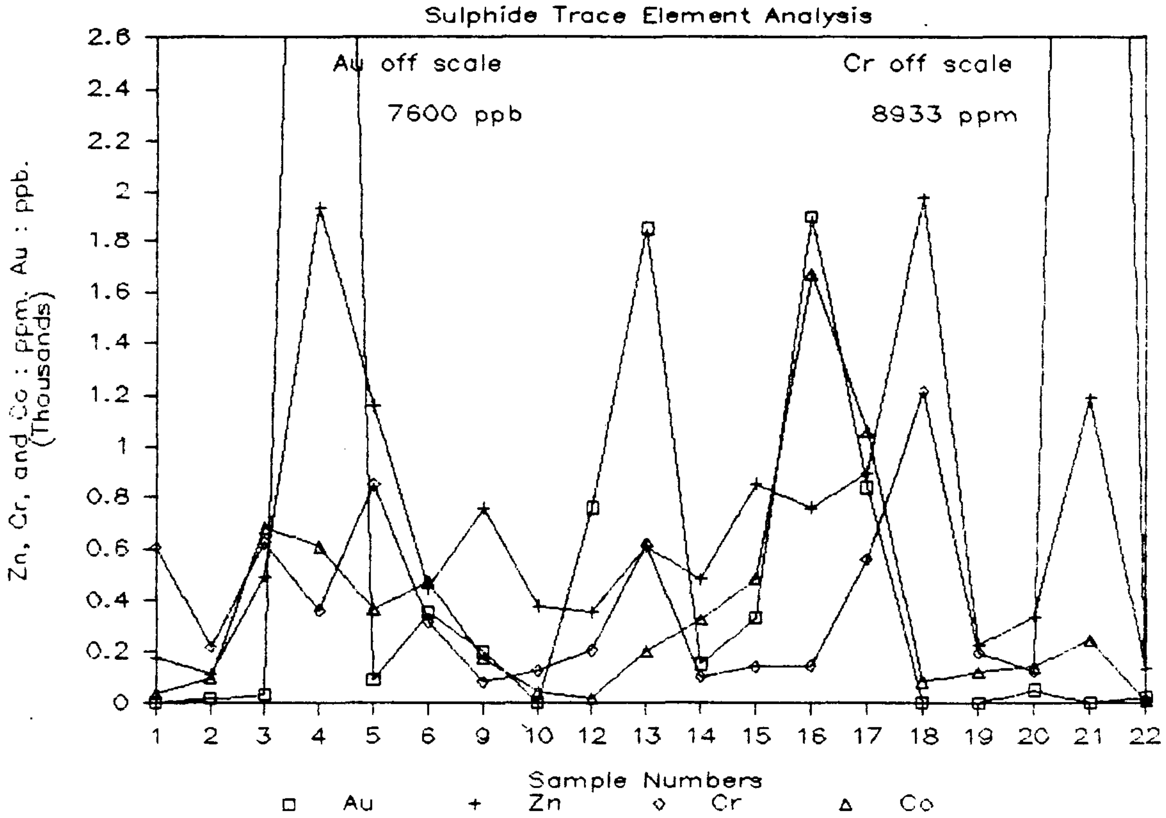


Figure 30; All trace elements in sulfides.

TRACE ELEMENT CONTENT: (ppm)

	WHOLE ROCK (WR)	**SULPHIDES**	**S/WR**
Au	0.0056	0.747	133.4
Zn	122.7	698.2	5.7
Cr	101.4	811.4	8.0
Co	17.0	359.2	359.2

Table 4 Trace element content: whole rock versus sulfide matter fraction

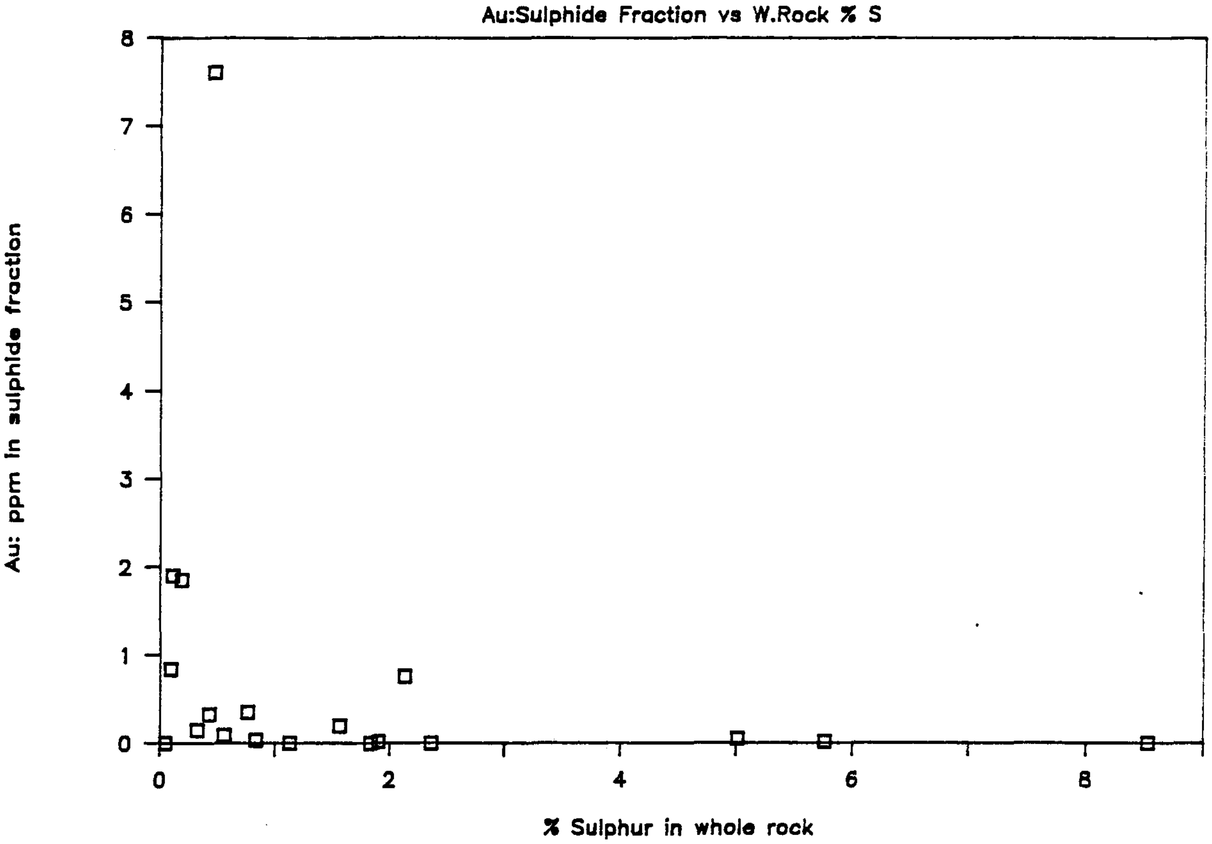


Figure 31; Au in sulfides vs sulphur whole rock

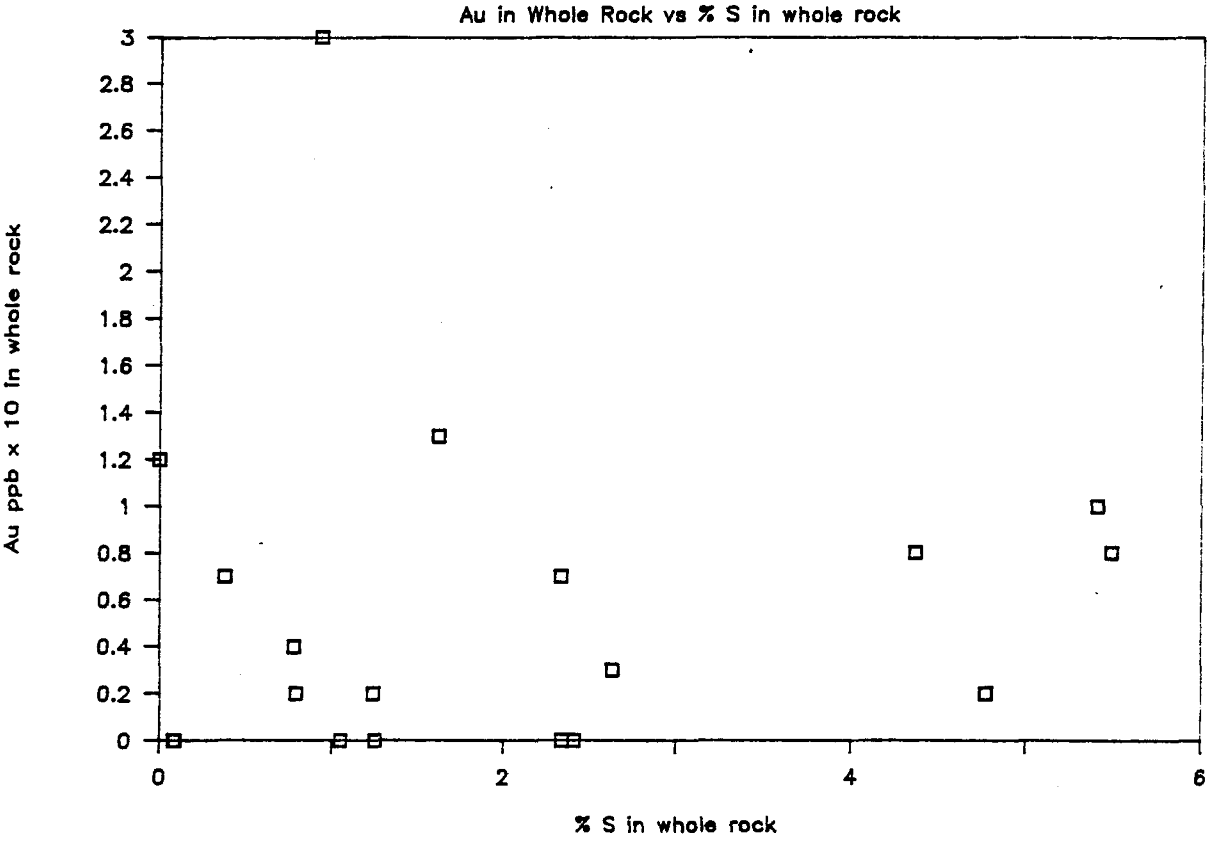


Figure 32; Au whole rock vs sulphur whole rock

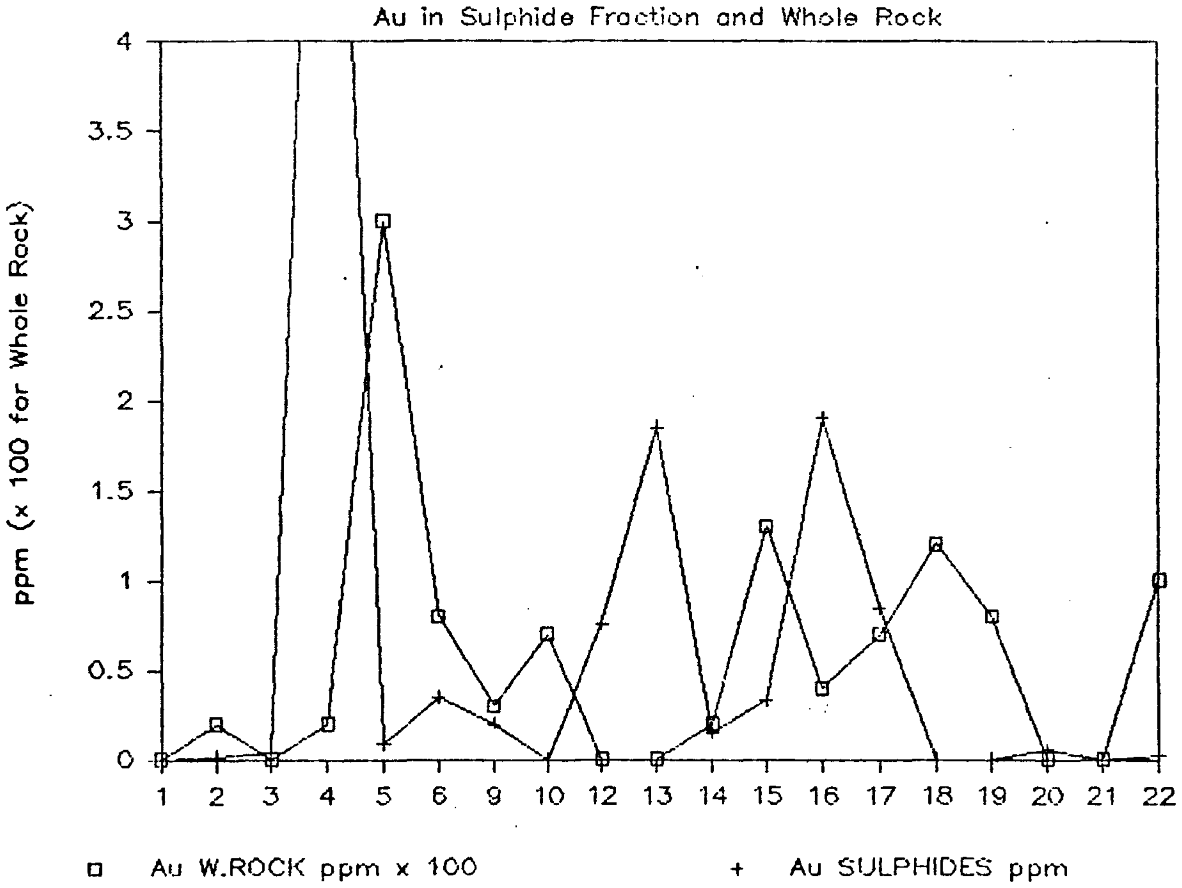


Figure 33; Au in whole rock compared to Au in sulfides

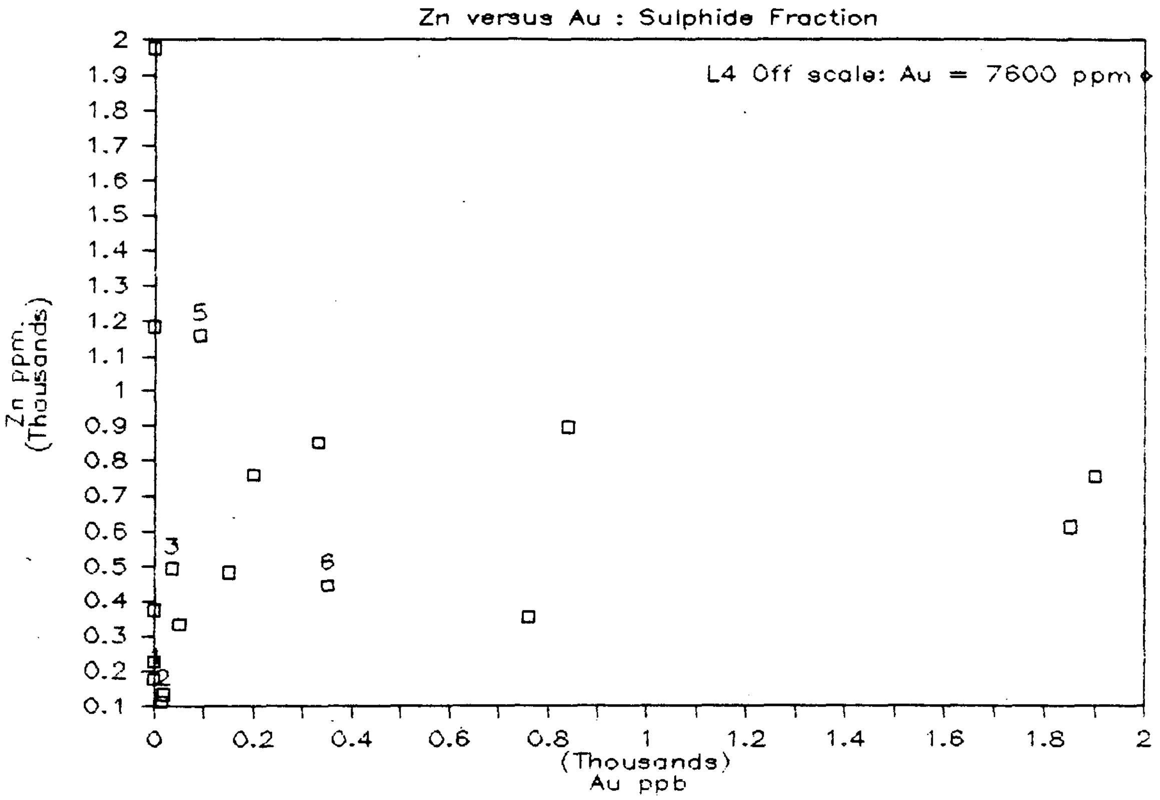


Figure 34; Test for control over Au in sulfides by Zn

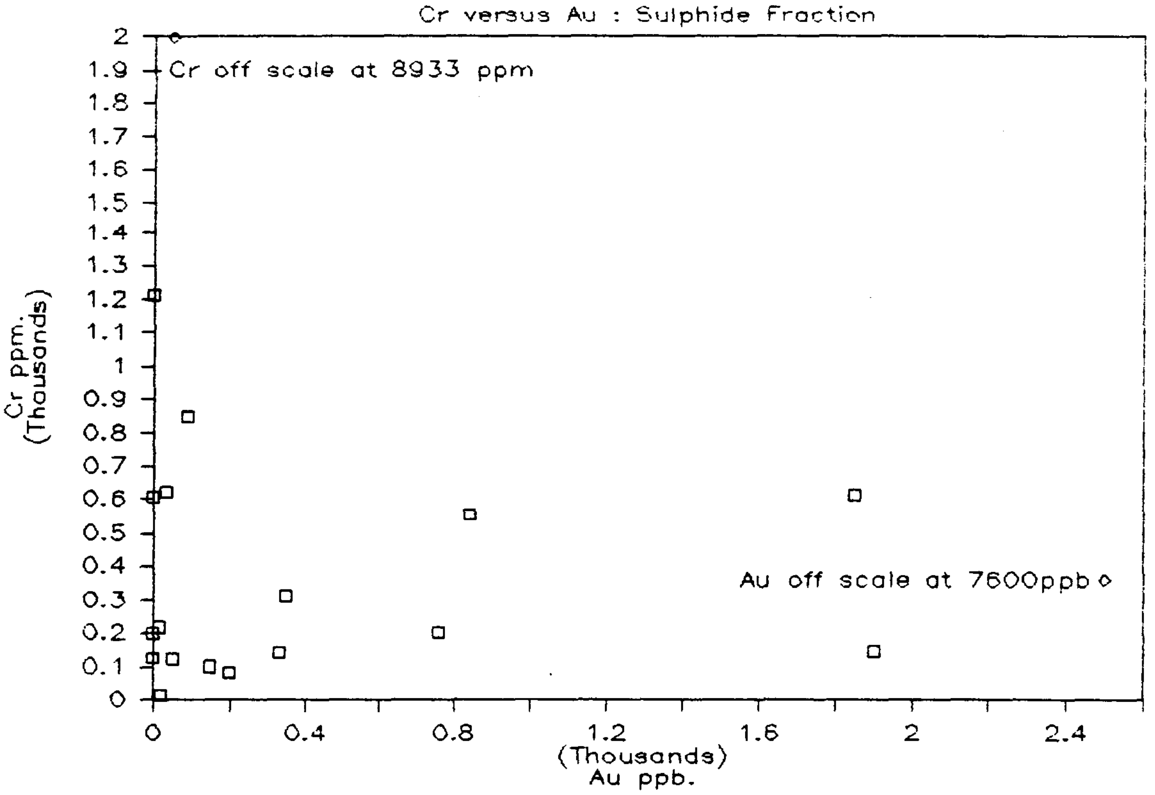


Figure 35; Test for control over Au in sulfides by Cr

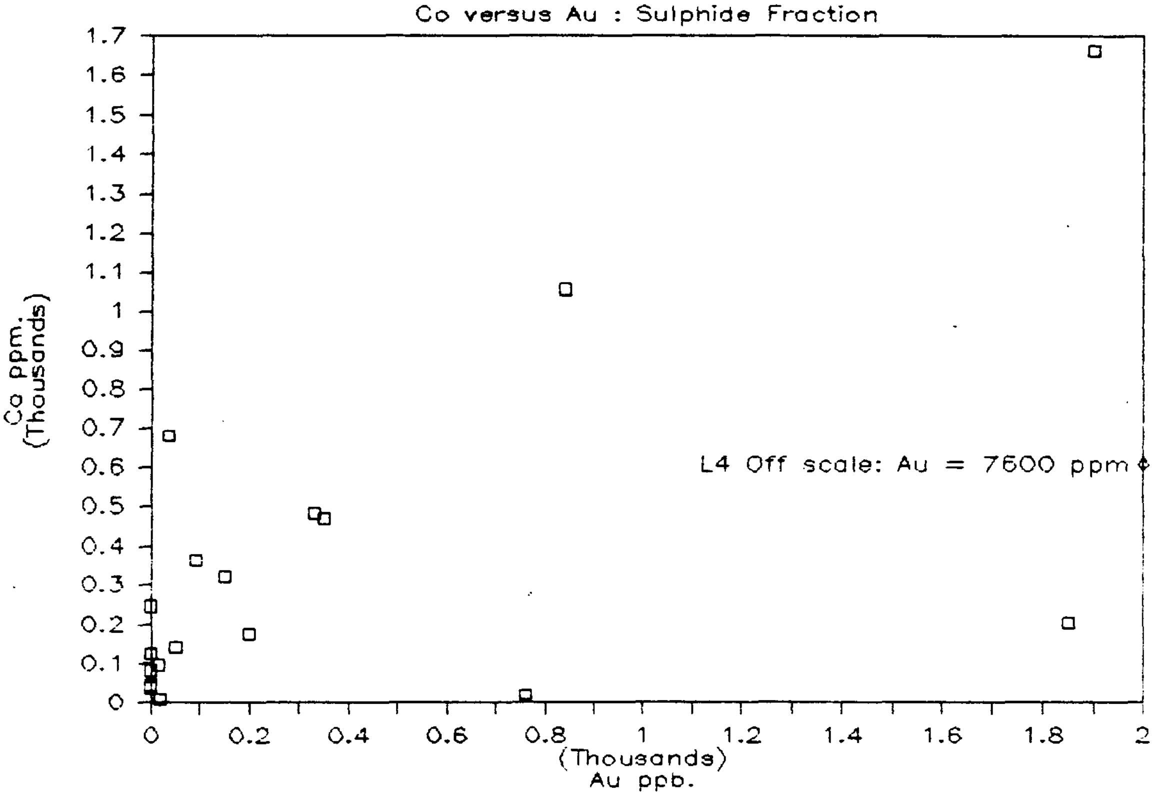


Figure 36; Test for control over Au in sulfides by Co

- There does not appear to be strong control over the trace element content in the whole rock exerted by the sulfides.

5.2 TRACE ELEMENTS IN WHOLE ROCK

The average values for Au, Zn, Cr, and Co are significantly lower than either the sulfide or organic matter fractions (Table 5). There is a only a slight difference between the samples from the Bignell and Lake Barlow sections: the samples from Bignell Township tend to have more numerous elevated values (Figure 37, 37a). This study has not produced any data that indicates what processes are responsible for this difference.

As shown in this chapter V (5.0.1. and 5.1.1), the trace element content in the whole rock is not controlled, to any significant degree, by the sulfide and organic matter fractions. Au in the whole rock compared to percent sulphur and carbon shows very weak correlation in one sample though generally none (Figure 37b). The same is true for Zn, Cr, and Co measured in the whole rock compared to Au (Figures 38, 39, and 40).

Sulphur and organic carbon (respectively, 4.9 and 6.65 percent of the composition of the shales) are not responsible for the total trace element content of the

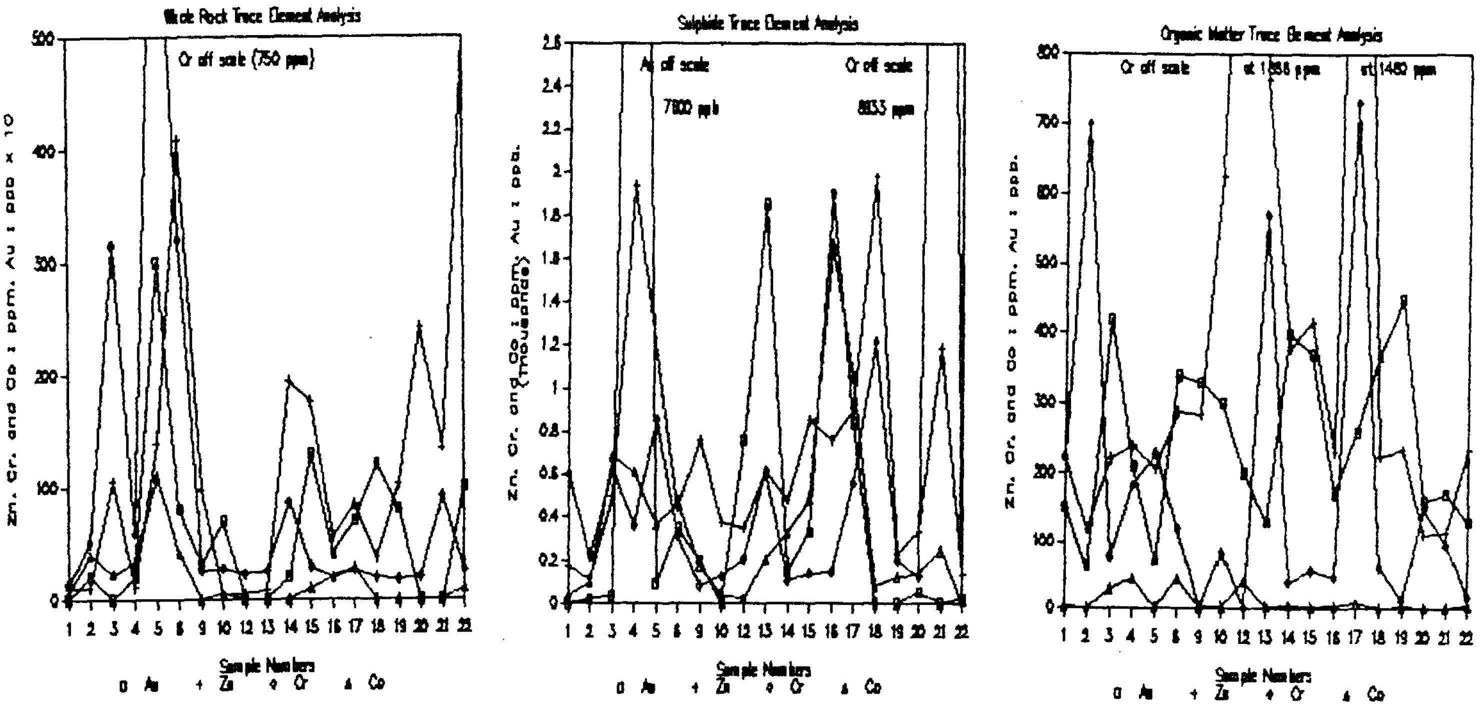


Figure 37: Comparison of trace elements in whole rock, sulfide, and organic matter analyses (Bignell section: samples 1-6; Barlow section: samples 9-22).

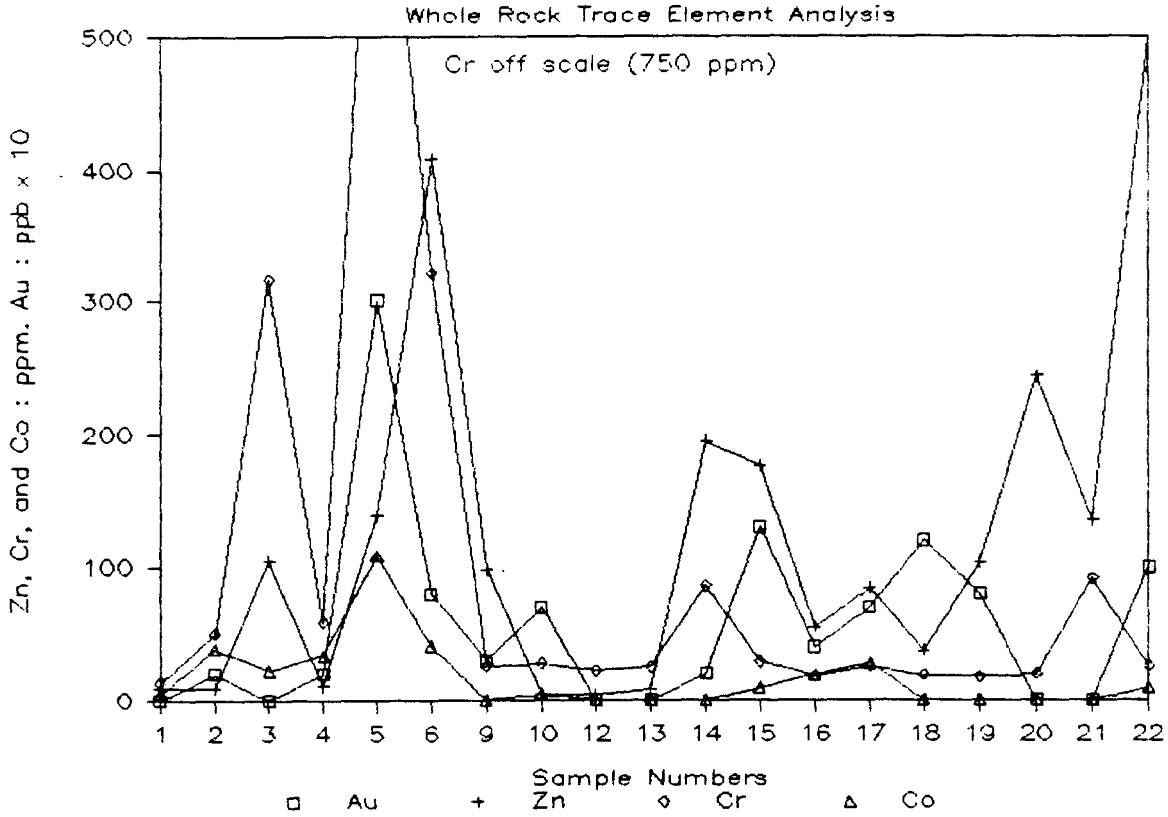


Figure 37a: Trace element analyses of whole rock.

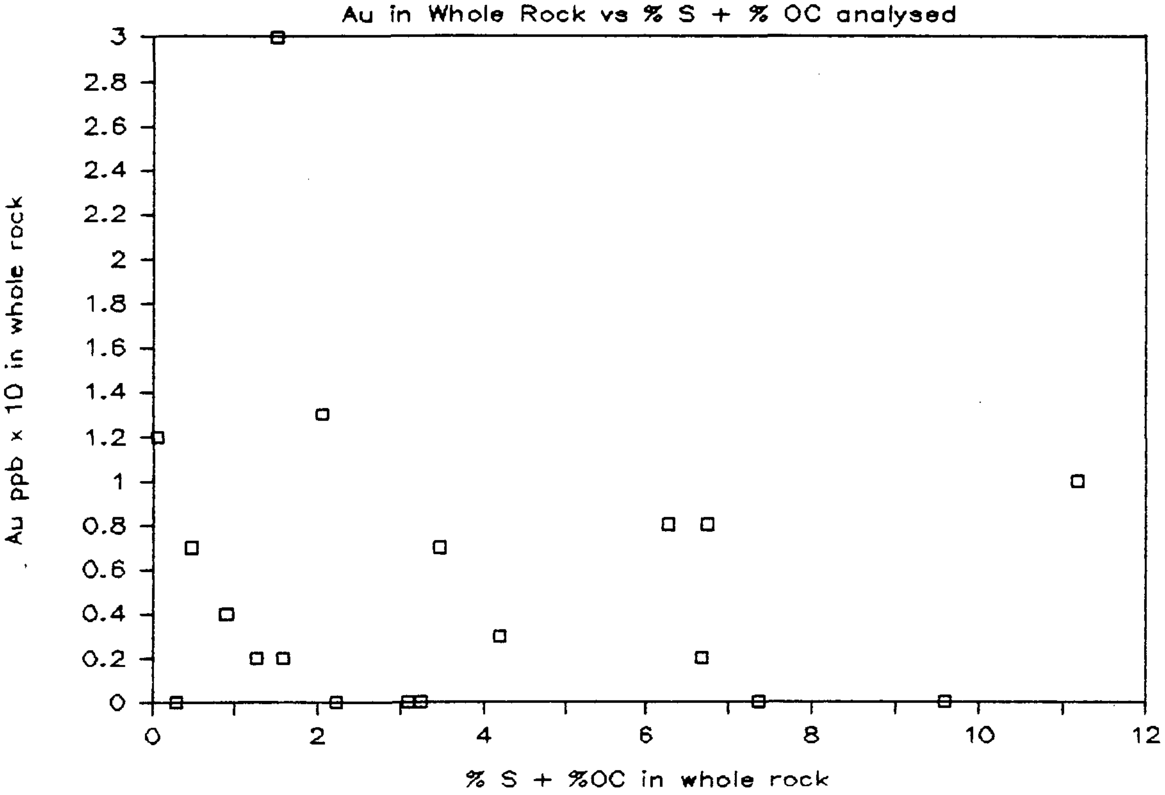


Figure 37b: Au in the whole rock compared to percent sulphur and carbon.

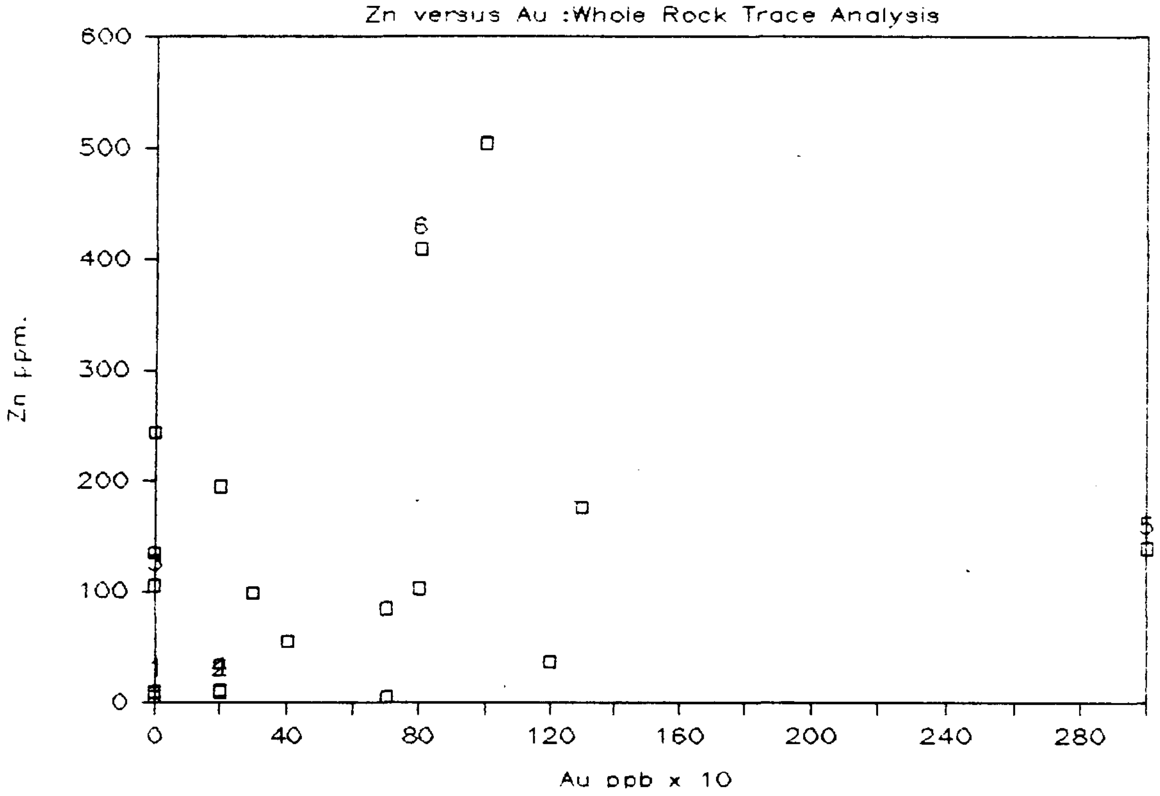


Figure 38: Au versus Zn in whole rock.

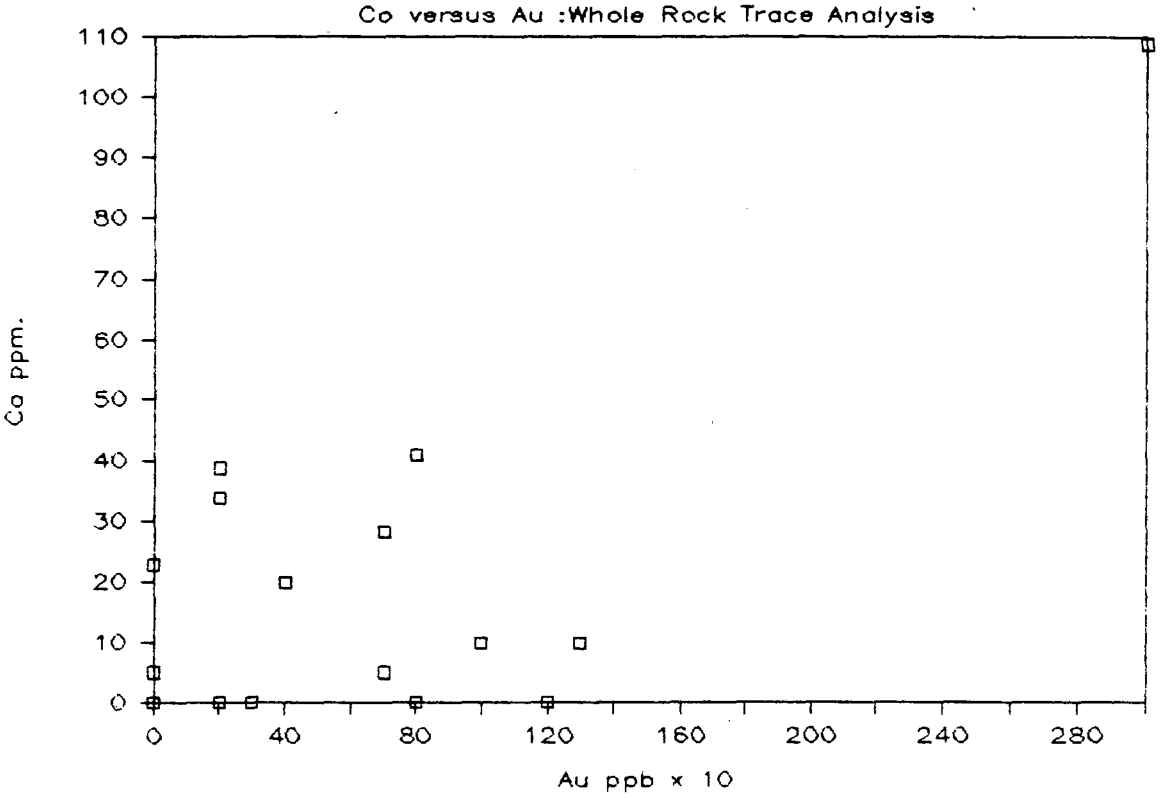


Figure 39; Au versus Co in whole rock

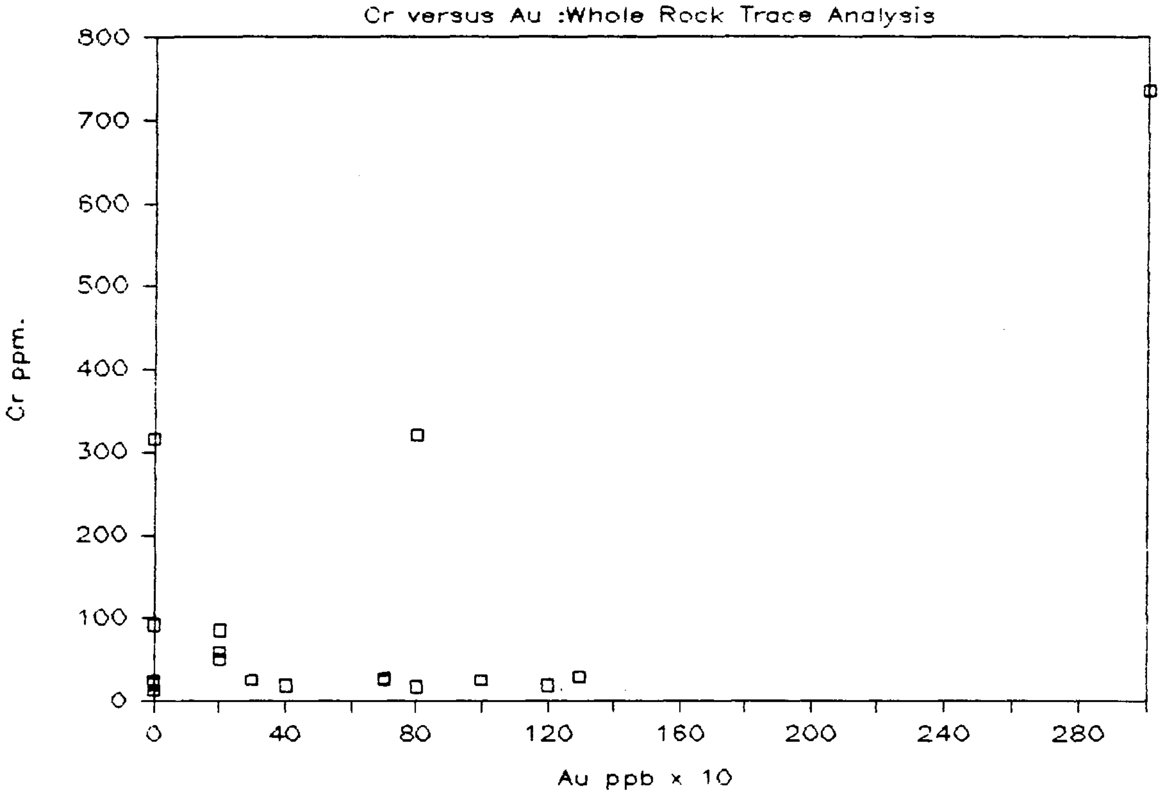


Figure 40; Au versus Cr in whole rock

TRACE ELEMENT CONTENT

(in ppm)

	WHOLE ROCK (WR)	**SULPHIDES (S)**	**S/WR**
Au	0.0056	0.747	133.4
Zn	122.7	698.2	5.7
Cr	101.4	811.4	8.0
Co	17.0	359.2	359.2

	WHOLE ROCK (WR)	**ORGANIC MATTER (OM)**	**OM/WR**
Au	0.0056	0.2460	43.9
Zn	122.7	435.5	3.6
Cr	101.4	178.2	1.8
Co	17.0	9.3	0.55

Table 5: Abundance of trace elements: Average analysis of whole rock versus average sulfide and organic matter analyses.

shales. This leaves unanswered the question of where the trace elements reside in the shales. This question can be answered in an indirect manner using the available results.

While the sulphur and organic carbon fractions account for a significant proportion of the shales (approximately 10%), they are still minor compared to either quartz and feldspar (65 - 75 % of the shales) or phyllosilicate fraction (35 - 25 % of the shale).

Chemical analyses show that shales of the Blondeau Formation contain 70 and 71.5% SiO_2 and approximately 12.5 and 13% Al_2O_3 in the respective Barlow and Bignell sections. Had these shales been dominantly clay bearing, the whole rock analyses of SiO_2 and Al_2O_3 should be much closer to the reported analyses for muscovite (48% SiO_2 and 27% Al_2O_3; Deer, et. al., 1966) and chlorite (26% SiO_2 and 20% Al_2O_3; Deer, et. al., 1966), which are the principal clay minerals in these sections.

Quartz does not contain significant trace elements and approaches 100% SiO_2 in chemical analyses. The most common trace metals are Fe and Ti, which are respectively less than 0 and 1 ppm of Quartz (Deer, et al.,1966). The plagioclase present, (less than 10% of the shale) can contain a negligible degree more Fe than quartz but contains no appreciable amounts of trace metals such as Au, Zn, Cr, and Co (Deer, et al.,1966).

Phyllosilicates and pore space are, by elimination, the source of most of the trace elements detected in the whole rock analyses. The analyses employed in this study do not provide quantitative results with respect to the clay mineral trace element content.

Apart from the phyllosilicates in the shale, the remaining sources of any significance for trace elements are the sulfide and organic matter fractions. The sulfides are relatively richer in trace elements than the organic matter fraction.

The trace element abundances for shale samples of the Bignell section are not significantly different form those of the Barlow lake section.

The most significant source of trace elements in black shales are apparently the phyllosilicate minerals and inter-grain pore space. The organic matter and sulfide fractions are the only other significant sources of trace elements in the black shales of the Blondeau Formation.

The samples from this study have much the same trace elements abundance as "anomalously enriched" shales reported by Vine and Tourtelet (1970) and Carignan et al.(1984) (Table 6). However, gold was not detected in the shale

SHALE TRACE ELEMENT CONTENT (ppm)

	(1)	(2)	(3)
	This study	Vine and Tourtelet: (1970)	Carignan et al.: (1984)
Au	0.0056	NA	NA
Zn	122.7	300	625.8
Cr	101.4	100	NA
Co	17.0	10	31.5
Cu	102.4	70	105.2
Pb	16.2	20	30.7
Ni	101.8	50	104.8

1) Averages of 19 black shales

2) Median value of the frequency histograms of 20 sets of black shale analyses

3) average of mixed fine sediment analyses including black shales

Table 6: Trace elements in whole rock analyses of black shales.

deposits mentioned by Vine and Tourtelet (1970). The shales of this study are very good source rocks for metals or metal rich solutions. It is possible that the black shales of the Blondeau formation contain gold mineralization; the mineralization may be related to thermally evolved organic matter previously thought to be graphite.

5.3 Conclusions from trace element studies

- the concentration of both the organic matter and sulfide fractions, in a given sample, range from tens to hundreds of times more than the corresponding clay mineral trace element content.

- Organic matter is enriched in trace elements relative to the whole rock; most notably in gold.

- Organic matter shows a consistent 0.25 ppm Au. While the Au values are elevated in the organic fraction, Au and percent organic carbon in the whole rock are not strongly related.

- Sulfides are enriched in trace elements relative to the whole rock; also notably for gold.

- In the whole rock, the average values for Au, Zn, Cr, and Co are significantly lower than found in either the sulfide or organic matter fractions. The samples from

Bignell Township tend to have more numerous elevated values.

- Sulphur and organic carbon are not solely responsible for the total trace element content of the shales. Phyllosilicates are the source of most of the trace elements detected in the whole rock analyses.

- The shales of this study are very good source rocks for metals or metal rich solutions.

- The Blondeau and Bignell black shale horizons may contain gold mineralization associated with organic matter.

CHAPTER VI

6.0 RARE EARTH ELEMENTS IN BLACK SHALES

In this portion of the study the rare earth element (REE) contents were determined in black shale, analyzed as a whole rock and subsequently the organic matter and sulfide fractions. The results would highlight any differences in the relative abundance or any partitioning of REE exhibited by the components of shale. The partitioning (if any) should provide clues to the metallogenic processes associated with the geological evolution of black shales in relation to shale hosted mineral deposits.

The REE content of irradiated samples of powdered samples was determined by Instrumental Neutron Activation Analyses (INAA). Lanthanum (La), Cerium (Ce), Neodymium (Nd), Samarium (Sm), Europium (Eu), Terbium (Tb), Holmium (Ho), Ytterbium (Yb), and Lutetium (Lu) were analyzed. La to Sm are light REE and occur on the left side of the graphs, Eu to Ho are medium weight REE, and Yb to Lu (the right side of the graphs) are the heavy REE.

REE studies of igneous rocks are traditionally based upon the normalization of the samples with the published REE contents of standards such as the Leedy

Chondrite analyses (Haskin and Haskin, 1966) or more recent REE analysis compilations such as the solar system abundance determined from the reexamination of numerous C1 type chondrites (Anders and Ebihara, 1982).

More relevant to this study would be a sedimentary standard. The most widely used, and felt to best typify REE in shales and sediments in general (Gromet et al, 1984), is the "North American Shale Composite (NAS)" (Haskin et al., 1968). The NAS was made from 40 well known shale samples from across North America.

The differences in the geological evolution of a shale and C1 chondrites are reflected in the REE content: shales are about 100 times richer in La to 30 times richer in Lu than the C1 chondrite analyses (Gromet et al., 1984). Logically, the shales in this study were compared to the sedimentary standard, NAS (Haskin et al., 1966).

There are numerous studies of REE content in shales and black shales available, from a variety of geological contexts. However, the study of REE in the organic matter in black shales does not appear in any publication prior to the present study (one reference was found for REE in suspended sediments rich in OM filtered from seawater; Murphy and Dymond, 1984); no single study treats the partitioning of REE between the organic, sulfide, and clay mineral components of the shales.

REE studies of shales are becoming more common; Haskin et al., (1964) have evaluated the REE content of diverse sediments in comparison with their standard, the "North American shale Composite". Specific mention of ancient shales similar to those of the present study are found in Wildeman and Haskins' "Rare Earths in Precambrian Sediments" (1972); the concentrations of REE and the REE profiles are nearly identical to those of the present study.

6.1 REE IN ORGANIC MATTER

Samples consist of organic matter (OM) derived from the separation of sulfide-organic matter residue by acid leaching and subsequent filtration. The results were obtained by instrumental neutron activation analyses on a homogenous mixture of insoluble OM residue and pure cellulose (see complete procedure in "Sample Preparation").

Tables 7 and 8 are, respectively, the REE analyses of the OM samples and the REE analyses normalized to NAS. We see that relative to the whole rock analyses, the OM samples are more concentrated in heavy REE but have light REE values that are similar. Scatter of single REE analyses of OM samples are greater than the scatter that was seen in the whole rock REE analyses; STD is very large in the light REE to medium weight REE analyses; in decreasing order, Eu, Nd, and Sm, (STD = 150, 133, and 119 % of the respective average REE). The STD for heavy REE Yb, Lu, and Ho are, respectively, 93, 87, and 50 % of the mean.

Again, the normalized REE were plotted on binary diagrams (Figures 41, 42, 43, 44, and 45). The normalized REE analyses for organic matter fraction plot on either side of the central line in the graph and have a positive slope indicating enrichement in heavy REE (climbing up to the right) for most of the analyses (the U.S.G.S. standard GSP-1 has a negative slope; Figures 41 and 45). Most samples show a small positive Eu anomaly that is exaggerated by a small negative inflection at Tb. (Several samples have incomplete REE analyses that may be due largely to the minute sample weights and counting geometry of the sample mixtures.) Though generally the REE profiles are more erratic it is possible to differentiate the two groups of samples. Samples L1 to L6 (Bignell samples) plot lower on the graphs for light REE relative to the profiles for L9 to L22 (Barlow samples); we shall see that the plots of the average REE profiles for the Bignell section, the Barlow section, and the average REE profiles for the entire sample population give 3 distinct REE profiles (Figure 46).

ORGANIC MATTER RARE EARTH ELEMENTS

Sample #	La (ppm)	Ce (ppm)	Nd (ppm)	Sa (ppm)	Eu (ppm)	Tb (ppm)	Ho (ppm)	Yb (ppm)	Lu (ppm)	SUM OF REE (ppm)
GSP-1S	197.00	435.00	209.00	29.03	2.00	0.94	1.11	1.35	0.33	875.8
L1	45.00	28.40	20.30	8.94	1.33	0.74	2.12	9.72	1.73	118.3
L2	9.64	13.00	6.70	1.23	0.30	0.03	0.60	3.48	0.63	35.6
L3	7.67	6.30	6.20	1.47	1.00	0.24	0.95	4.47	0.60	28.9
L4	24.50	38.40	19.70	5.50	1.50	0.53	1.33	4.90	0.76	97.1
L5	6.60	8.19	6.07	1.40	0.80	0.28	1.53	4.61	1.18	30.7
L6	26.60	35.40	15.50	4.33	0.90	0.73	0.76	2.68	0.88	87.7
L9	19.60	7.20	0.00	0.04	0.10	0.00	0.88	0.00	0.00	27.8
L10	29.80	37.40	17.80	4.70	1.60	0.59	0.90	3.20	1.10	97.1
L12	2.76	3.67	0.40	0.36	0.20	0.02	1.90	0.46	0.10	9.9
L13	4.80	10.60	0.40	0.95	0.27	0.03	1.30	2.87	0.40	21.6
L14	40.70	73.00	28.00	8.70	2.70	7.30	1.50	7.91	1.30	171.1
L15	45.30	50.50	21.20	4.96	2.00	0.70	1.13	8.48	1.40	135.7
L16	55.50	112.50	67.30	13.30	6.20	1.18	1.40	9.51	1.70	268.6
L17	102.60	191.60	100.40	18.90	8.00	1.90	3.20	16.30	2.50	445.4
L18	14.60	12.80	0.40	0.13	0.30	0.01	0.90	0.35	0.03	29.5
L19	15.20	14.10	0.00	0.12	0.26	0.00	0.50	0.00	0.00	30.2
L20	2.81	2.70	1.60	0.00	0.20	0.04	3.00	1.80	0.00	12.2
L21	10.50	14.20	6.10	1.30	0.65	0.00	1.80	1.60	0.30	36.5
L22	37.20	43.00	11.50	2.50	0.66	0.29	0.92	2.40	0.40	99.1
GSP-1	183.00	411.00	197.10	26.60	2.79	1.04	1.20	2.10	0.23	825.1
AVG.	26.39	37.00	17.35	4.15	1.53	0.77	1.40	4.46	0.79	

Table 7; The REE content in the organic matter samples.

O.M. REE NORMALIZATION; Wildeman and Haskin "North American Shale"

Sample #	La	Ce	Nd	Sa	Eu	Tb	Ho	Yb	Lu
GSP-1S	6.16	6.21	6.74	5.09	1.61	1.11	1.07	0.44	0.69
L1	1.41	0.41	0.65	1.57	1.07	0.87	2.04	3.14	3.60
L2	0.30	0.19	0.22	0.22	0.24	0.04	0.58	1.12	1.31
L3	0.24	0.09	0.20	0.26	0.81	0.28	0.91	1.44	1.25
L4	0.77	0.55	0.64	0.96	1.21	0.62	1.28	1.53	1.58
L5	0.21	0.12	0.20	0.25	0.65	0.33	1.47	1.49	2.46
L6	0.83	0.51	0.50	0.76	0.65	0.86	0.73	0.86	1.83
L9	0.61	0.10	0.00	0.01	0.08	0.00	0.85	0.00	0.00
L10	0.93	0.53	0.57	0.82	1.29	0.69	0.87	1.03	2.29
L12	0.09	0.05	0.01	0.06	0.16	0.02	1.83	0.15	0.21
L13	0.15	0.15	0.01	0.17	0.22	0.03	1.25	0.93	0.83
L14	1.27	1.04	0.90	1.53	2.18	8.59	1.44	2.55	2.71
L15	1.42	0.72	0.68	0.87	1.61	0.82	1.09	2.74	2.92
L16	1.73	1.61	2.17	2.33	5.00	1.39	1.35	3.07	3.54
L17	3.21	2.74	3.24	3.32	6.45	2.24	3.08	5.26	5.21
L18	0.46	0.18	0.01	0.02	0.24	0.01	0.87	0.11	0.06
L19	0.48	0.20	0.00	0.02	0.21	0.00	0.48	0.00	0.00
L20	0.09	0.04	0.05	0.00	0.16	0.05	2.68	0.58	0.00
L21	0.33	0.20	0.20	0.23	0.52	0.00	1.73	0.52	0.63
L22	1.16	0.61	0.37	0.44	0.69	0.34	0.88	0.77	0.83
GSP-1	5.72	5.87	6.36	4.67	2.25	1.22	1.15	0.68	0.48
AVG.	0.82	0.53	0.56	0.73	1.23	0.90	1.35	1.44	1.65

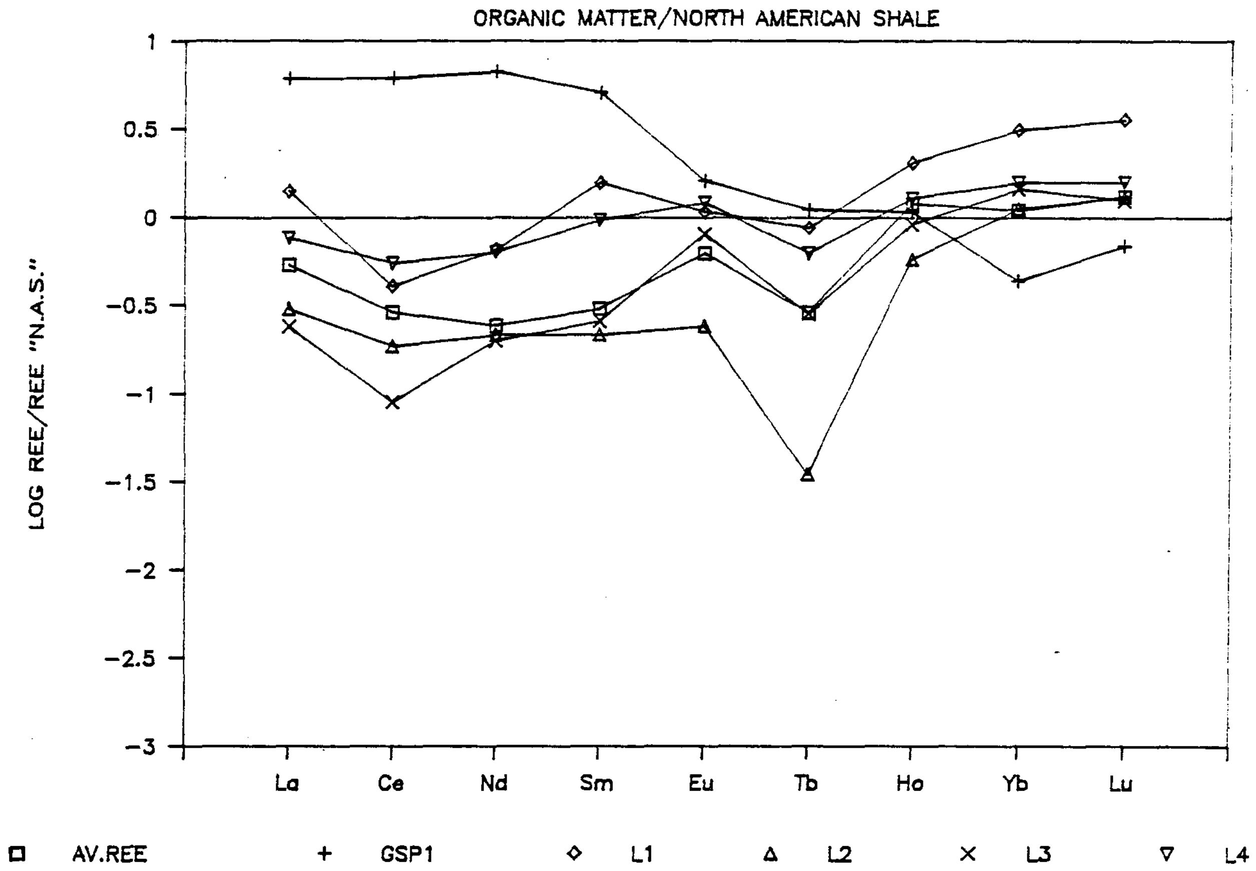
Table 8; REE normalized to NAS for Organic Matter

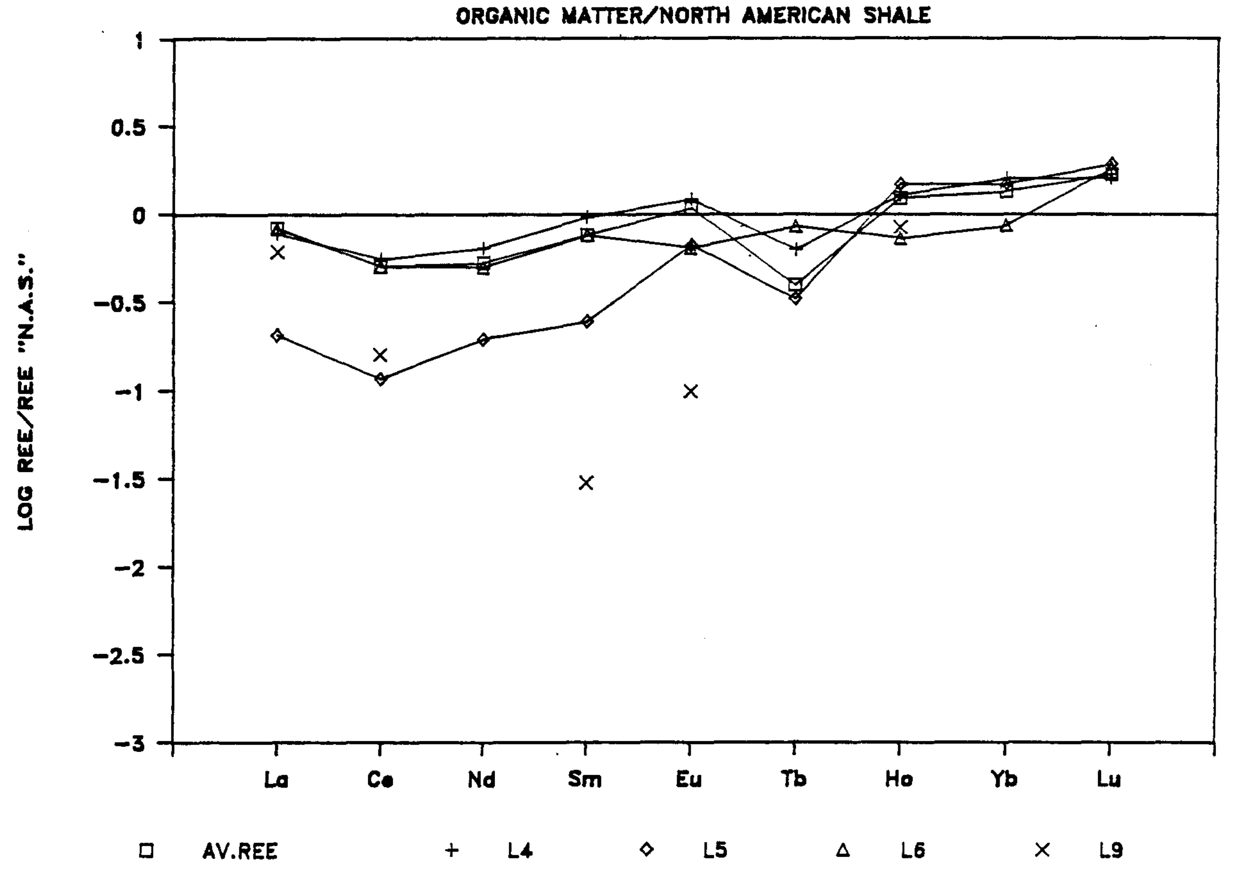
6.2 REE IN SULFIDES

Samples consist of sulfides derived by drying the acid filtered through sulfide-organic matter residue during the chemical separation of these two species. No mixing with cellulose was required for INAA. The residues are, logically, homogenous powders equal in composition to the sulfides that were present in the shale samples (the complete procedure is described in "Sample Preparation").

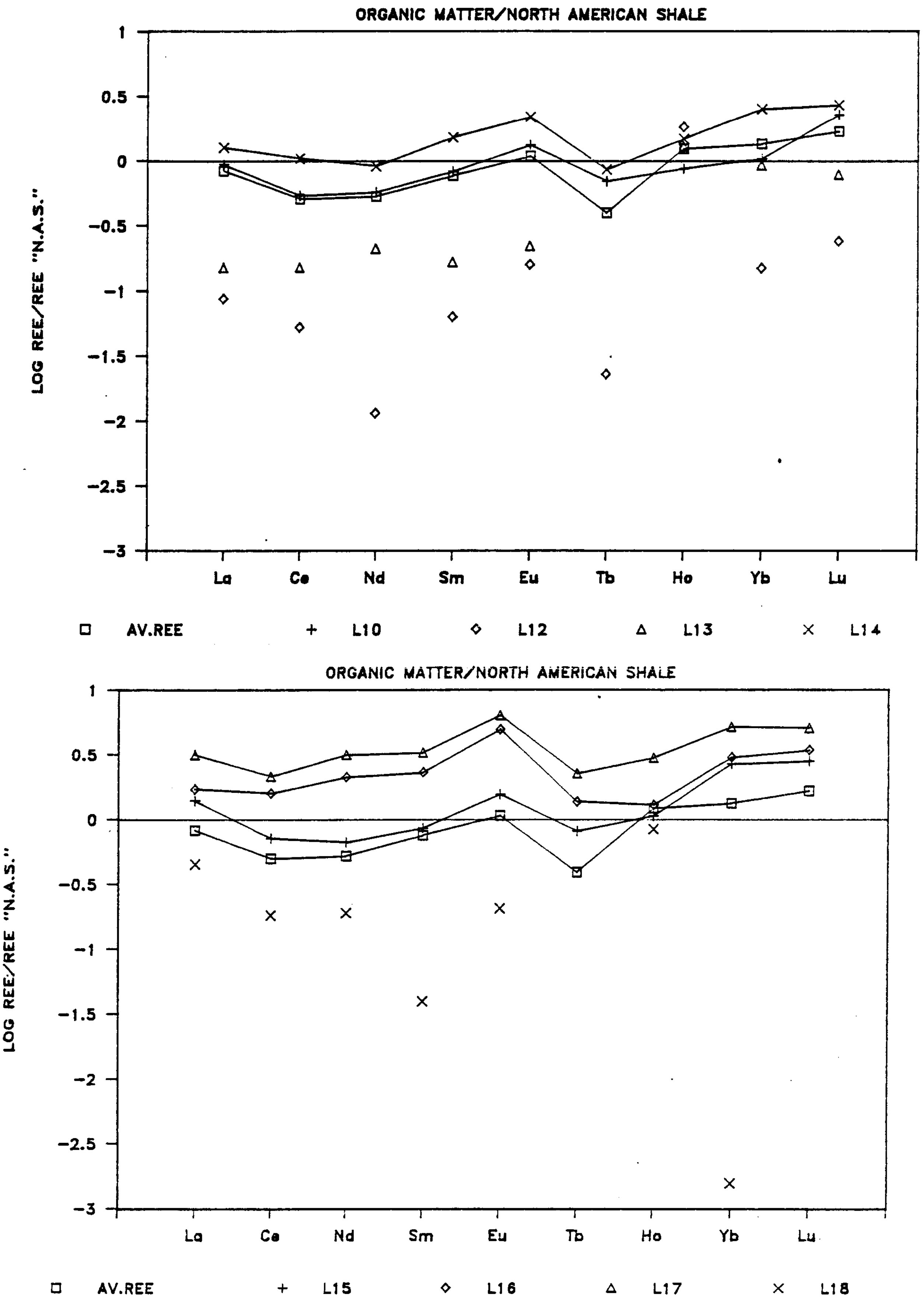
Tables 9 and 10 are the REE analyses of the sulfide residues respectively, in ppm and normalized to NAS. Many of the sulfide REE values reported in ppm are over 100 times higher than the REE found in the comparable whole rock analyses. Generally, compared to either the OM or whole rock analyses, there are much greater REE concentrations present in the sulfides. The avegage normalised REE values are all around 10 times NAS, although relatively there is a general tendency to higher light REE to medium weight REE values than heavy REE. This is different than what we have seen in either whole rock or OM REE analyses.

As was the case with OM, the scatter of individual analyses from the average value of a given REE is generally fairly marked. However, all sulfide samples have complete REE analyses. The standard deviation is lowest for Eu (STD = 105% of the average) and highest for La (Std = 183% Of the





Figures 41 and 42: REE profiles for samples L1 to L9 (and Average)



Figures 43 and 44: REE profiles for samples L10 to L18 (and Average)

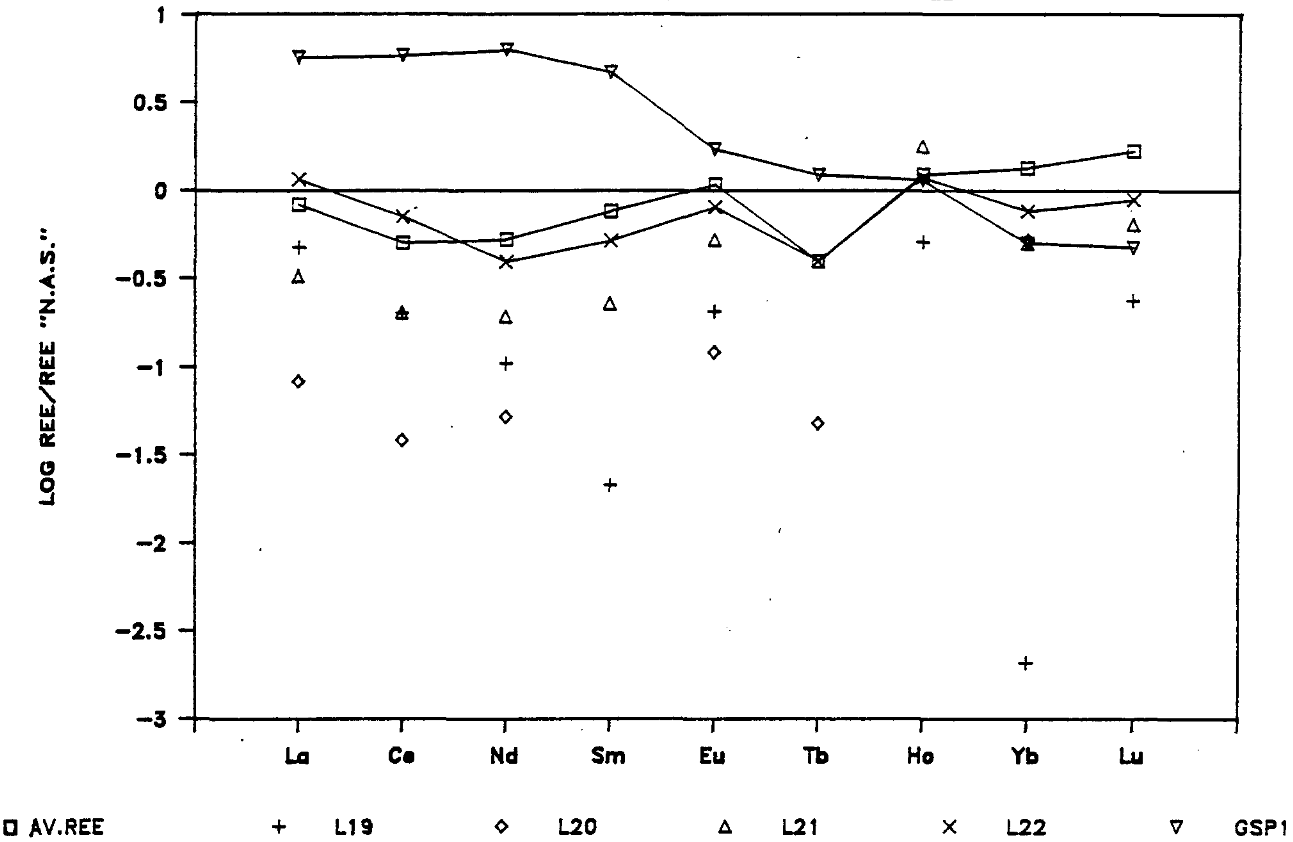


Figure 45: REE profiles for samples L19 to L22 (and Average)

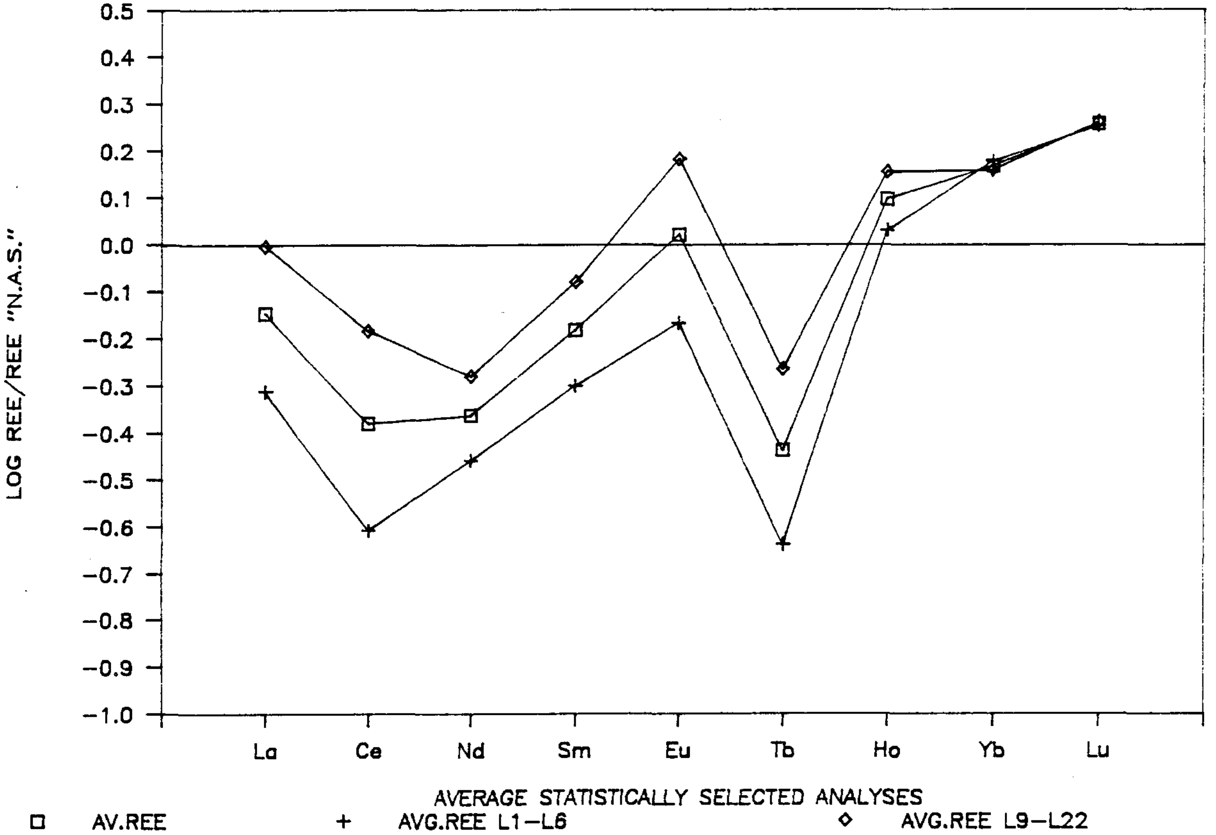


Figure 46. Profiles for average REE in shales samples in: (1) All samples; (2) Samples from Bignell section; (3) Samples from Barlow section.

average). Again, heavy REE analyses are generally less erratic than light REE analyses.

Once more, the normalized REE analyses were plotted on binary diagrams (Figures 47, 48, 49, and 50). They all plot well above the zero line, of NAS parity. Samples L1 to L6, from Bignell Township (Figure 47), have a positive slope while Samples L9 to L22, from the Barlow Section (Figures 48, 49, and 50), have a flat slope with a positive "bulge" or anomaly from the light REE to medium weight REE. The sulfide fraction appears to demonstrate a slight tendency to enrichment in light REE to medium weight REE. As with the whole rock and OM profiles there is still a difference in the profiles of the Bignell and Barlow sections. REE profiles plotted from the calculated averages of the entire sample group, the Bignell and the Barlow sections clearly show this difference (Figure 51).

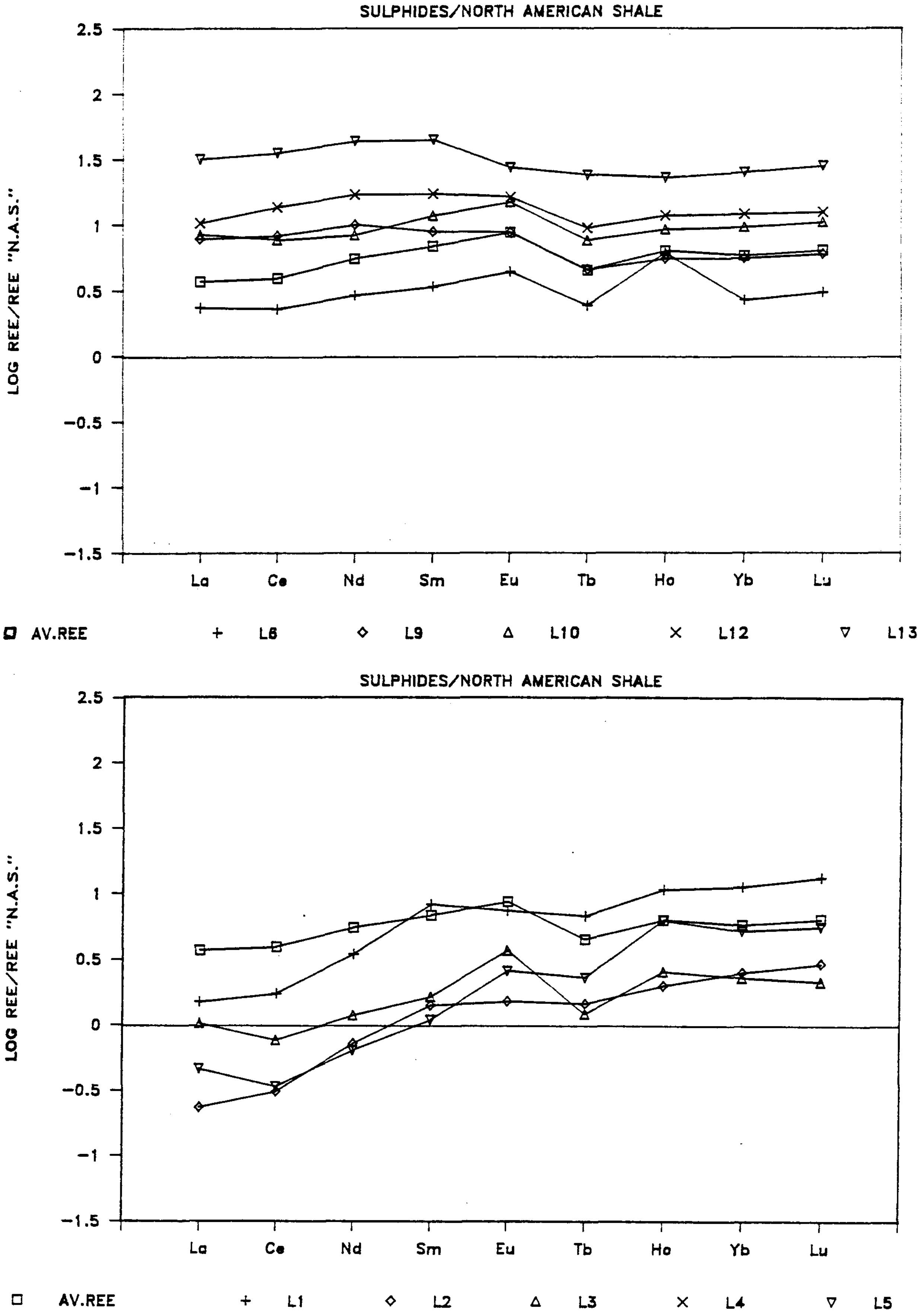
Sample #	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Tb (ppm)	Ho (ppm)	Yb (ppm)	Lu (ppm)	SUM OF REE (ppm)
L1	48.30	288.00	106.20	47.10	9.20	5.80	11.20	35.50	6.33	557.6
L2	7.60	21.80	22.60	7.70	1.90	1.24	1.92	7.90	1.40	74.1
L3	33.10	53.90	36.30	9.34	4.60	1.00	2.65	7.20	1.00	149.1
L4	165.00	391.00	212.30	49.20	13.60	4.00	8.47	11.90	2.33	857.8
L5	14.80	28.90	19.60	6.26	3.40	2.00	6.59	16.30	2.65	100.5
L6	74.90	160.80	89.20	19.46	5.46	2.10	6.36	8.43	1.50	368.2
L9	251.00	582.00	306.40	50.70	10.90	3.90	5.76	17.30	2.80	1230.8
L10	271.90	542.00	256.50	67.32	18.50	6.50	9.63	29.90	4.97	1207.2
L12	331.50	960.00	522.00	98.88	20.20	8.00	12.29	37.70	5.90	1996.5
L13	1020.00	2487.40	1420.75	255.98	33.90	20.40	23.80	78.60	14.80	5355.6
L14	343.00	770.70	395.00	79.16	22.30	6.70	8.80	23.80	3.79	1653.3
L15	330.00	698.00	378.70	98.48	26.70	11.20	17.80	47.00	6.90	1614.8
L16	46.20	172.40	136.40	33.80	16.70	2.90	5.60	13.70	2.40	430.1
L17	113.80	366.00	232.00	49.60	19.20	4.50	8.14	27.00	4.50	824.7
L18	2630.00	5683.70	3010.40	525.80	84.80	39.00	49.90	200.00	33.40	12257.0
L19	22.20	45.50	25.90	7.72	2.20	0.88	1.17	3.07	0.45	109.1
L20	228.90	479.00	244.10	44.60	19.80	2.81	4.33	12.10	1.59	1037.2
L21	82.50	198.00	105.60	23.60	6.20	1.75	2.54	7.40	1.20	428.8
L22	83.30	195.00	131.00	19.50	4.20	1.50	2.24	7.08	1.10	444.9
GSP-1	162.30	454.00	204.70	29.70	2.40	1.13	0.62	1.99	0.12	857.0
AVG.	320.95	743.37	402.68	78.64	17.04	6.64	9.96	31.15	5.21	

Table 9; The REE content in the sulfide samples.

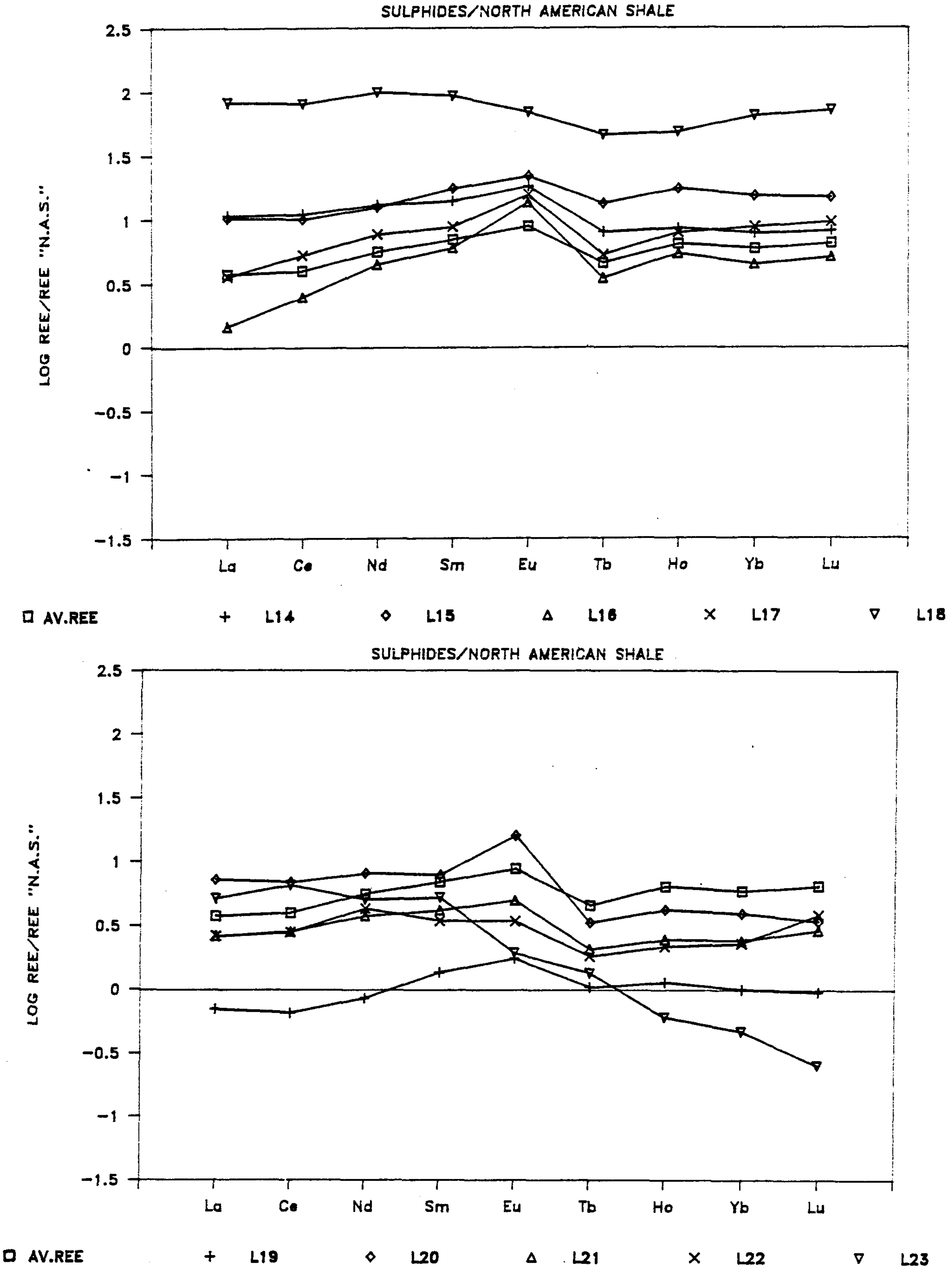
SULPHIDES REE NORMALIZATION; Wildeman and Haskin "North American Shale"

Sample #	La	Ce	Nd	Sm	Eu	Tb	Ho	Yb	Lu
L1	1.51	4.11	3.43	8.26	7.42	6.82	10.77	11.45	13.19
L2	0.24	0.31	0.73	1.35	1.53	1.46	1.85	2.55	2.92
L3	1.03	0.77	1.17	1.64	3.71	1.18	2.55	2.32	2.08
L4	5.16	5.59	6.85	8.63	10.97	4.71	8.14	3.84	4.85
L5	0.46	0.41	0.63	1.10	2.74	2.35	6.34	5.26	5.52
L6	2.34	2.30	2.88	3.41	4.40	2.47	6.12	2.72	3.13
L9	7.84	8.31	9.88	8.89	8.79	4.59	5.54	5.58	5.83
L10	8.50	7.74	8.27	11.81	14.92	7.65	9.26	9.55	10.35
L12	10.36	13.71	16.84	17.35	16.29	9.41	11.82	12.16	12.29
L13	31.88	35.53	45.83	44.91	27.34	24.00	22.88	25.35	30.83
L14	10.72	11.01	12.74	13.89	17.98	7.88	8.46	7.68	7.90
L15	10.31	9.97	12.22	17.28	21.53	13.18	17.12	15.16	14.38
L16	1.44	2.46	4.40	5.93	13.47	3.41	5.38	4.42	5.00
L17	3.56	5.23	7.48	8.70	15.48	5.29	7.83	8.71	9.38
L18	82.19	81.20	97.11	92.25	68.39	45.88	47.98	64.52	69.58
L19	0.69	0.65	0.84	1.35	1.77	1.04	1.13	0.99	0.94
L20	7.15	6.84	7.87	7.82	15.97	3.31	4.16	3.90	3.31
L21	2.58	2.83	3.41	4.14	5.00	2.06	2.44	2.39	2.50
L22	2.60	2.79	4.23	3.42	3.39	1.76	2.15	2.28	2.29
GSP-1	5.07	6.49	6.60	5.21	1.94	1.33	0.60	0.64	0.25
AVG.	10.03	10.62	12.99	13.80	13.74	7.81	9.57	10.05	10.86

Table 10; REE normalized to NAS for sulfides



Figures 47 and 48: REE profiles for samples L1 to L13 (and Average)



Figures 49 and 50: REE profiles for samples L15 to L22 (and Average)

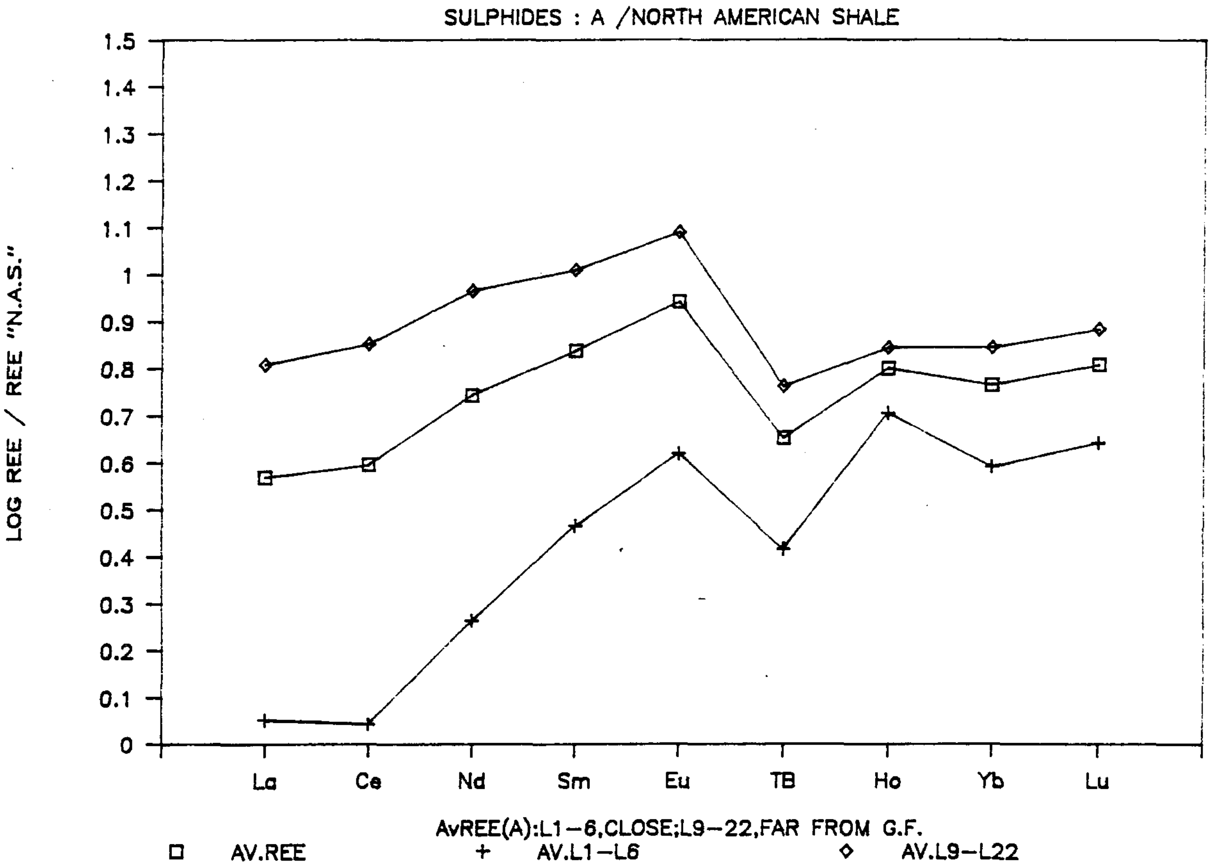


Figure 51: Profiles for average REE in sulfides in: (1) All samples; (2) Samples from Bignell section; (3) Samples from Barlow section.

6.3 REE: WHOLE ROCK ANALYSES

Table 11 depicts the REE analyzed in the shale samples. The REE values for each of the shale samples were then divided by the NAS REE values (NAS "normalized") and are shown in Table 12. The standard deviation (STD) calculated for each of the elements were usually close to 50% of the average value of a given element; the variation between individual REE analyses and the average or mean for a given REE seems to be quite small. The largest deviation is for Nd (mean = 19.7 ppm, STD = 10.97 or 54% of the average of Nd), followed by La, Tb, Ho, and Lu (each with an STD = to 50% of the mean). The least variation occurs in the Eu analyses (with a mean of 1.0 ppm and an STD of .3; 30% of the mean). Light REE to medium weight REE contents have negligibly less scatter than do heavy REE.

Normalized values greater than 1 are relatively few (0 on the y axis, represents a ratio of REE in samples to REE in NAS of 1.). Most values are less than one and the few greater than 1 are more common in the light REE (La to Sm). Note that samples L1, L13, L14, and L18 have almost all of the values greater than 1; heavy REE are progressively less abundant compared to NAS; Tb, Ho, and Lu are where most of the analyses less than 0.5 NAS occur. From the data it would appear that the shales are more abundant in light REE than

WHOLE ROCK RARE EARTH ELEMENTS

Sample #	La (ppm)	Ce (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Tb (ppm)	Ho (ppm)	Yb (ppm)	Lu (ppm)	SUM OF REE ppm)
L1	33.23	69.80	25.53	6.28	1.05	0.68	1.10	2.72	0.34	140.7
L2	17.66	37.10	15.21	3.77	0.77	0.38	0.76	1.58	0.19	77.4
L3	13.09	29.05	10.60	2.55	0.86	0.23	0.33	1.01	0.15	57.9
L4	11.83	26.60	10.38	2.89	0.79	0.25	0.30	0.92	0.14	54.1
L5	5.98	20.16	6.78	1.63	0.50	0.33	0.35	1.26	0.15	37.1
L6	13.45	30.20	11.83	2.65	0.76	0.24	0.27	0.60	0.14	60.1
L9	28.13	63.87	27.35	5.42	1.11	0.48	0.59	1.86	0.23	129.0
L10	14.86	31.50	15.72	4.73	1.44	0.47	0.67	1.76	0.27	71.4
L12	17.92	42.80	19.28	4.33	0.83	0.36	0.46	1.54	0.20	87.7
L13	33.80	79.80	39.20	6.18	0.96	0.65	0.86	2.42	0.31	164.2
L14	33.80	71.30	32.10	6.28	1.65	0.53	0.62	2.10	0.25	148.6
L15	24.90	51.80	19.40	4.89	1.08	0.50	0.61	1.84	0.23	105.3
L16	17.52	35.73	15.30	3.70	1.02	0.35	0.69	1.65	0.24	76.2
L17	14.20	33.32	14.40	3.72	0.93	0.35	0.52	1.78	0.20	69.4
L18	49.80	97.10	50.30	10.33	1.70	0.97	1.26	3.27	0.43	215.2
L19	16.60	34.30	13.00	2.63	0.61	0.22	0.20	0.69	0.12	68.4
L20	14.47	32.70	12.50	2.78	1.38	0.20	0.30	0.92	0.13	65.4
L21	16.71	36.40	13.70	3.26	0.81	0.36	0.42	1.19	0.15	73.0
L22	22.96	66.30	22.16	4.72	1.20	0.46	0.74	1.74	0.23	120.6
AVG.	21.00	45.75	19.59	4.33	1.01	0.42	0.57	1.62	0.22	

Table 11; REE in whole rock samples

WHOLE ROCK REE NORMALIZATION; Wildeman and Haskin "North American Shale"

Sample #	La	Ce	Nd	Sm	Eu	Tb	Ho	Yb	Lu
L1	1.04	1.00	0.82	1.10	0.85	0.80	1.06	0.88	0.71
L2	0.55	0.53	0.49	0.66	0.62	0.45	0.73	0.51	0.40
L3	0.41	0.42	0.34	0.45	0.69	0.27	0.32	0.33	0.31
L4	0.37	0.38	0.33	0.51	0.64	0.29	-0.29	0.30	0.29
L5	0.19	0.29	0.22	0.29	0.40	0.39	0.34	0.41	0.31
L6	0.42	0.43	0.38	0.46	0.61	0.28	0.26	0.19	0.29
L9	0.88	0.91	0.88	0.95	0.90	0.56	0.57	0.60	0.48
L10	0.46	0.45	0.51	0.83	1.16	0.55	0.64	0.57	0.56
L12	0.56	0.61	0.62	0.76	0.67	0.42	0.44	0.50	0.42
L13	1.06	1.14	1.26	1.08	0.77	0.76	0.83	0.78	0.65
L14	1.06	1.02	1.04	1.10	1.33	0.62	0.60	0.68	0.52
L15	0.78	0.74	0.63	0.86	0.87	0.59	0.59	0.59	0.48
L16	0.55	0.51	0.49	0.65	0.82	0.41	0.66	0.53	0.50
L17	0.44	0.48	0.46	0.65	0.75	0.41	0.50	0.57	0.42
L18	1.56	1.39	1.62	1.81	1.37	1.14	1.21	1.05	0.90
L19	0.52	0.49	0.42	0.46	0.49	0.26	0.19	0.22	0.25
L20	0.45	0.47	0.40	0.49	1.11	0.24	0.29	0.30	0.27
L21	0.52	0.52	0.44	0.57	0.65	0.42	0.40	0.38	0.31
L22	0.72	0.95	0.71	0.83	0.97	0.54	0.71	0.56	0.58
AVG.	0.66	0.65	0.63	0.76	0.82	0.49	0.55	0.52	0.45

Table 12; REE in whole rock samples normalized to NAS.

heavy REE and we could expect a profile that drops down to the right, or a negative slope.

The REE analyses and average REE (small "squares") normalized to NAS, are plotted in Figure 41. Also shown are the REE taken from the Bignell section close to the Grenville Front (Figure 52) and the Barlow section over 40km from the front (Figure 53, 54 and 55). As expected, the general trend is a slope which drops to the right indicating that, relative to NAS, the rock is enriched in light REE compared to heavy REE. The plots often show a positive Europium anomaly. Thin sections show that the shales contain fine detrital plagioclase feldspar; the probable source of the anomaly, as divalent Eu substitutes Calcium in the plagioclase molecule; Henderson, 1984).

Samples L1 to L6 (Bignell samples) plot lower on the graphs relative to the profiles for L9 to L22 (Barlow samples); we could predict that the average of the REE profiles of the Bignell section should plot lower than the average plots of both the Barlow section and that of the entire sample population (see the "discussion" at the end of this chapter).

The most significant finding here, is that there is a difference between samples from the section close and far from the Grenville Front. REE profiles plotted using the calculated averages for the entire sample population, the Bignell Section, and the Barlow Section best show this feature (Figure 56). It is still not clear whether this difference can be attributed to the source of the shales or the shales' proximity to the Grenville Front.

6.4 Conclusions

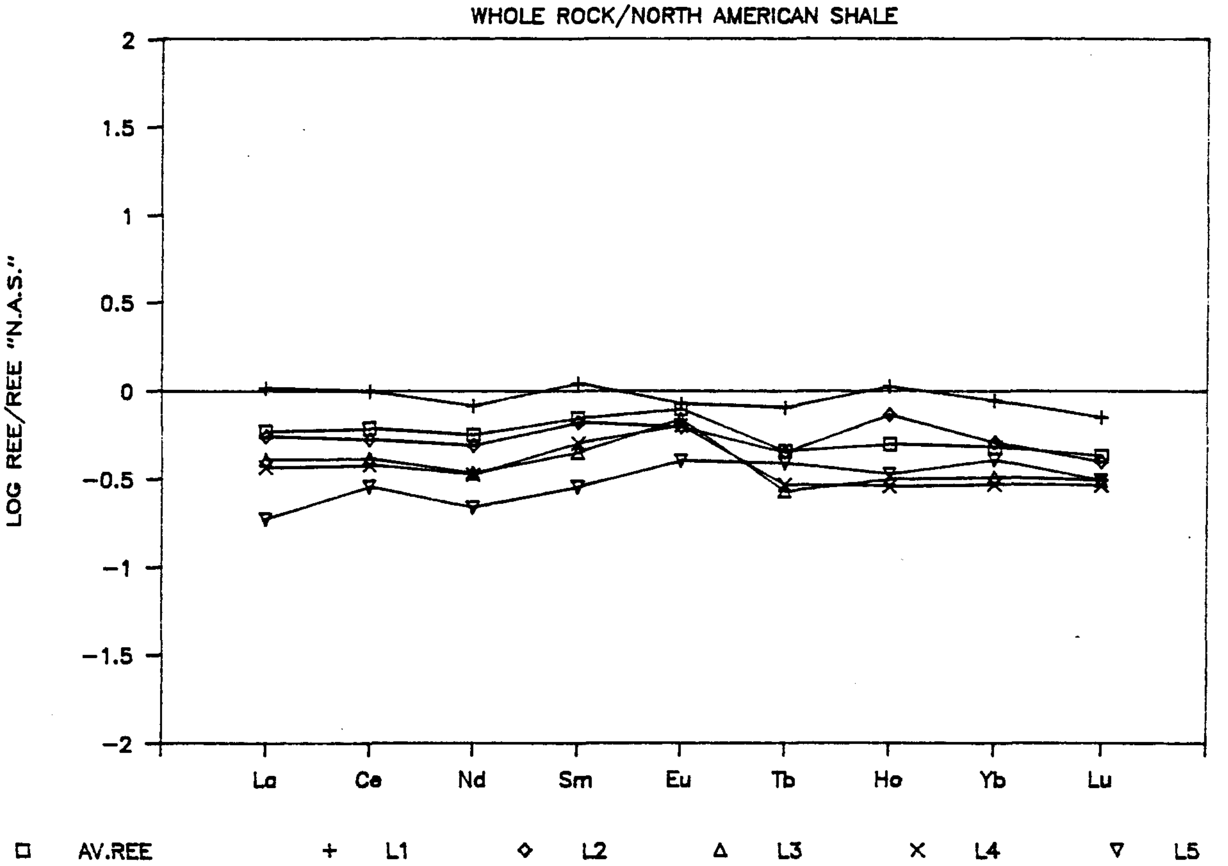
- The shales of this study have REE profiles similar to the standard "NAS"; the Barlow and Bignell shales have flat curves and REE concentrations similar to those of the NAS. There is a small positive Eu anomaly present that is due probably to the abundance of detrital plagioclase feldspar present in the rocks.

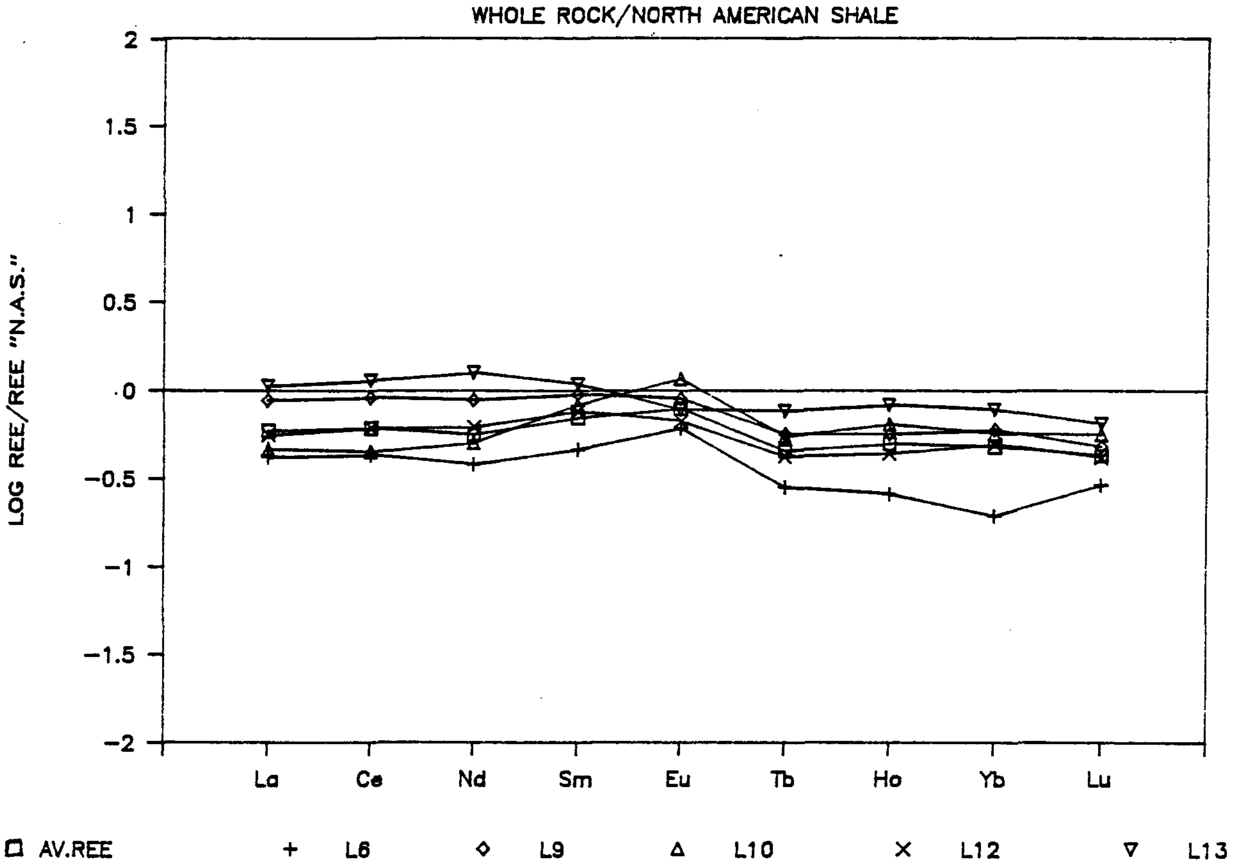
- Sulfides have possibly the strongest affinity towards REE in view of the strong overall enrichment in REE, relative to that of either OM or the whole rock.

- Organic matter appears to be more refractory with respect to the heavy REE compared to the light REE (note the "hook" upward at the right side of the graph (Figure 46).

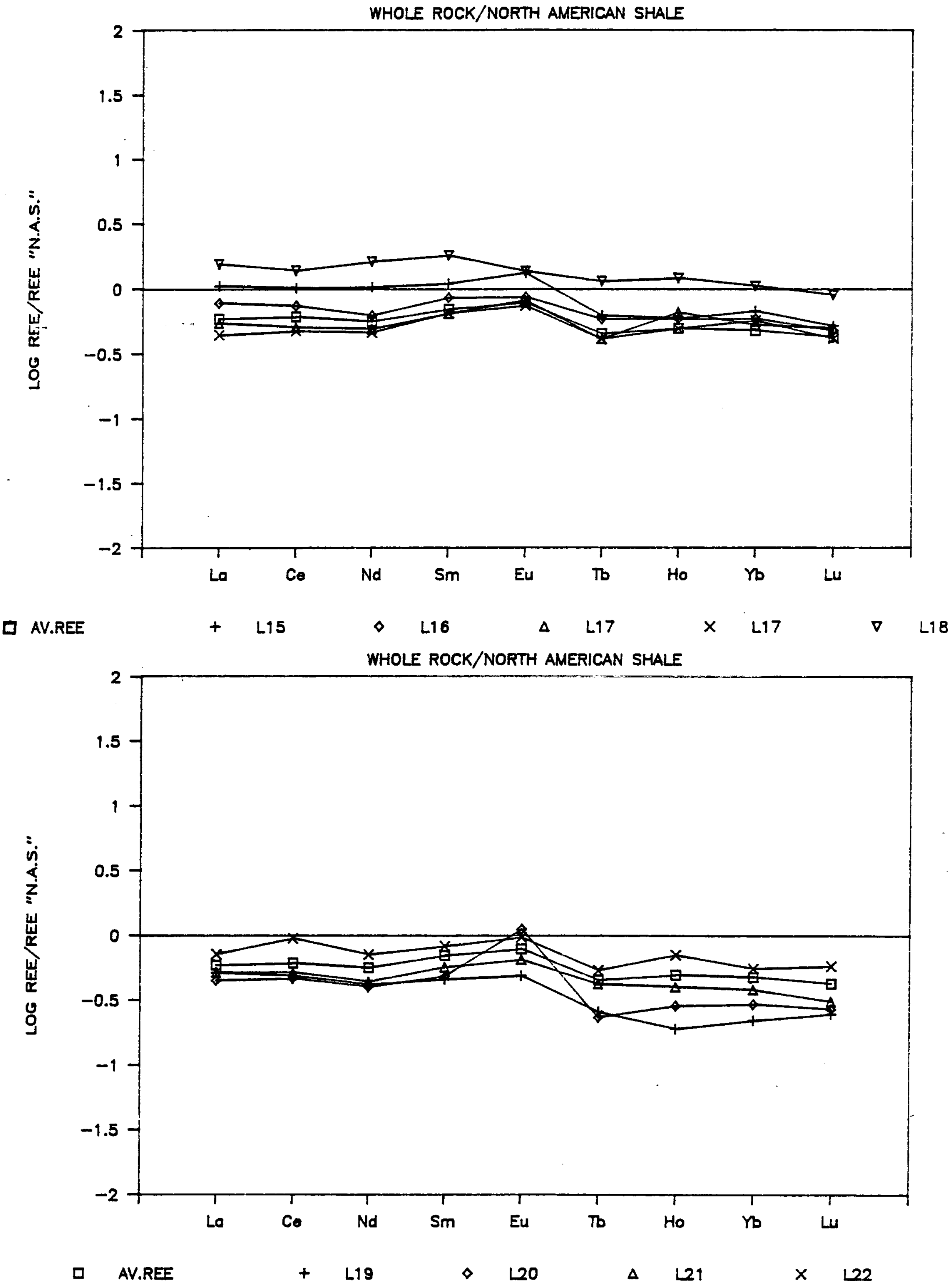
- The average sulfide fraction has REE profiles that exhibit a flatter slope with an enrichement in the light REE to medium weight REE in contrast to the organic matter fraction is enriched in heavy REE.

- Of the fractions present in the whole rock, only the sulfide fraction should be able to significantly control the





Figures 52 and 53: REE profiles for shale samples L1 to L13 (and Average)



Figures 54 and 55:REE profiles for shale samples L15 to L22 (and Average)

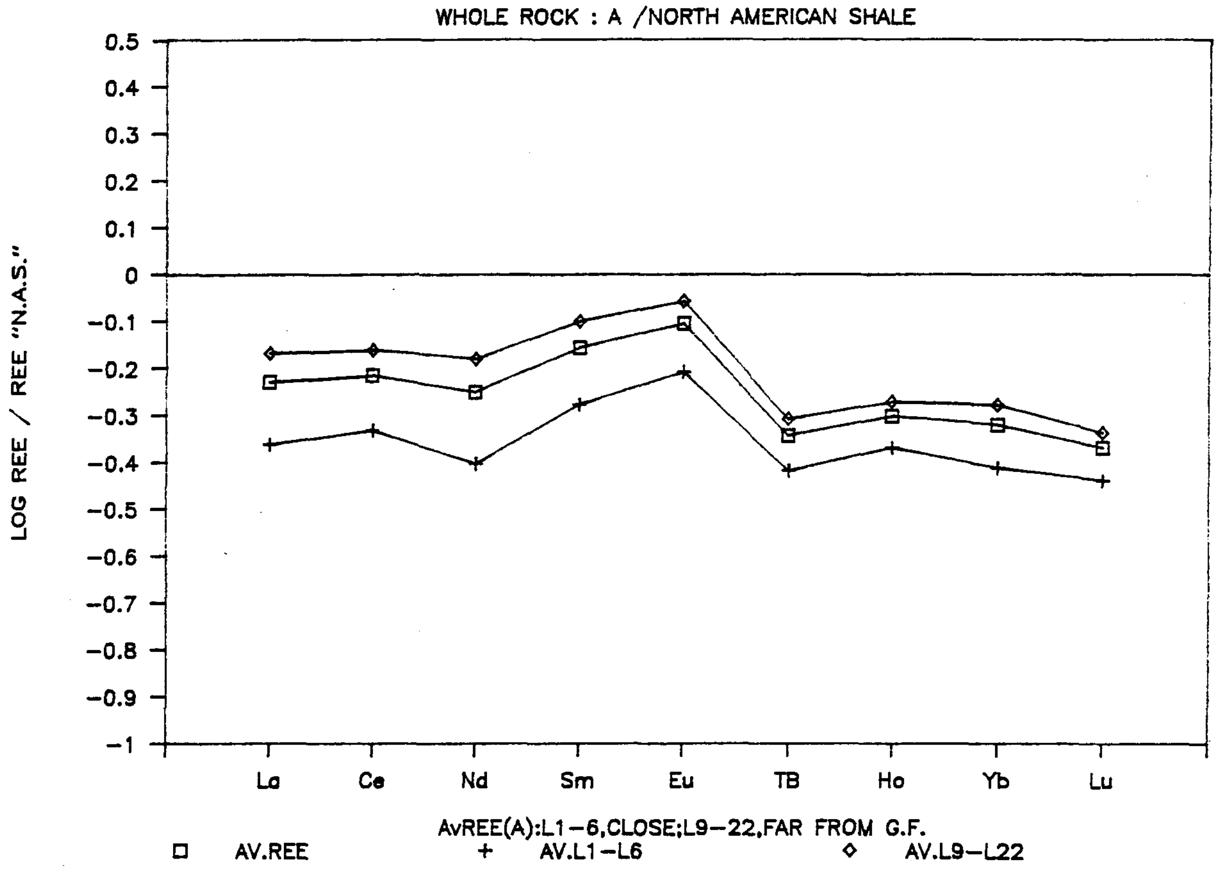


Figure 56: Profiles for average REE in shale samples in: (1) All samples; (2) Samples from Bignell section; (3) Samples from Barlow section.

type of profile seen in the analyses of the whole rock. Only the sulfides show strong enrichement in REE generally; OM has approximately the same order of magnitude of concentration as the REE found in the whole rock.

- None of the whole rock samples studied showed general profiles similar to the sulfide or OM fractions; compare Figures 52, 53, 54, and 55 (REE profiles of shale samples) with Figures 46 and 51 (average REE profiles for OM and for Sulfides).

- The average organic matter fraction, the average sulfide fraction, and the average shale sample, from Bignell Township, is depleted in REE relative to those taken from Barlow Township; the average REE profiles from the Barlow section lie above those from the Bignell section (naturally, the average for the entire sample populations of organic matter, sulfide, and shale would plot between the profiles from the Bignell and Barlow sections (Figures 46, 51, and 56).

- REE are possibly more mobile in black shales nearer to the "Grenville Front". The light REE show the greatest depletion or possible mobility of the REE analysed in the Bignell section. The data available does not substantiate nor does it provide the reasons for the apparent REE mobility.

CHAPTER VII

CONCLUSIONS AND DISCUSSION

7.1 The Character of Organic Matter

Conclusions

1) The graphitic material in the black shales of the Blondeau Formation is in fact organic matter.

2) The organic matter is present in 3 different forms; insoluble remobilized bitumenite, insoluble in situ bitumenite, and soluble organic matter (the hydrocarbons or alkanes 14 through 20).

3) The organic matter appears to be principally derived from algae and bacteria.

4) the black shales of the Blondeau Formation may have very limited vertical permeability; in the normal situation, volatile organic matter should not be present in the same rocks as those which have bitumenite that is thermally evolved to the supermature state (where % Absolute reflected light of bituminite approaches 5).

Discussion

These products should have been driven off by the onset of regional greenschist metamorphism, if not during diagenesis of the shales. Possibly, the physical nature of the shales may have provided a barrier which trapped hydrocarbons, or hydrocarbons were incorporated into the molecular structure of minerals present, during crystal growth, as fluid inclusions.

The physical nature of the sheet-like phyllosilicates is such that during deposition the sheets would be oriented parallel to the bedding. With a sufficiently dense overlapping of the horizontal sheets the sediments would have, at the outset, a permeability that would be reduced in the vertical sense. With increasing diagenesis and metamorphism and the recrystallization and growth of new minerals, perpendicular to the vertical load, the lateral permeability would increase relative to the vertical permeability; the shales should be most permeable parallel to the orientation of the phyllosilicates.

In thin section, the insoluble organic matter that occurs within the well-developed schistosity of the shales, shows evidence of lateral transport along the direction of the planes of the schistosity; isolated fragments of the organic matter can be matched to nearby masses.

Another possible explanation for the preservation of the alkanes, is that, with increasing metamorphism, pyrobitumen maturation released hydrocarbons that were captured during the formation and recrystallization of phyllosilicates and other mineral species. For example, minute quantities of hydrocarbons could have been locked between the plates formed during the growth of the crystalline structure of phyllosilicates.

7.2 Thermal Evolution of Black Shales; Organic Matter and Clay Mineralogy Studies

Conclusions

1) Insoluble and soluble organic compounds preserved in shales of the Blondeau Formation found in the Barlow Lake section may indicate a relatively low thermal evolution.

2) In the Lake Barlow stratigraphic section the x-ray diffraction pattern, of the clay mineral separates, shows small chlorite peaks and large, well-defined, interstratified tri-octahedral illite and smectite peaks.

Discussion

It is difficult to establish the upper limit of metamorphism; chlorite, smectite, and illite can be detrital or authigenic in origin, in addition to being the result of hydrothermal alteration or metamorphic processes (Weaver and Pollard, 1973)

One possibility is that retrograde smectite-illites formed during hydrothermal alteration and partially overprint the chlorite-albite-epidote greenschist assemblage. Local intrusive activity is one possible source of the hydrothermal alteration. Another possibility is that the chlorite may be detrital in origin. In which case, the smectite-illite mineralogy suggests that very low greenschist facies metamorphism was the maximum grade attained.

The chlorite present in thin section does not appear to be detrital; they are well formed sheets and plates that are found within the schistosity of the rock.

Since the shales of the Lake Barlow section have been metamorphosed to greenschist facies they must have undergone subsequent hydrothermal alteration during which the smectite-illite minerals formed. Two of the possible sources of hydrothermal alteration in the area are local faults and intrusives. An intrusive body was identified in the Barlow Lake area, the Cummings Complex (Duquette, 1972). However, the sills of the Cummings Complex are pre-metamorphic. They could not be responsible for this hydrothermal event. The only remaining possibility is the hydrothermal event associated with the east-west fault system in the area.

The shales in the Bignell Township, 6km from the Grenville front, have undergone upper greenschist facies metamorphism. The Bignell shale sample's XRD spectra (Figure 7) show a complete absence of the smectite - illite peaks, and large well-defined chlorite peaks. Also muscovite is present in thin sections and is parallel to the schistosity defined by fine opaque parallel laminae.

The shales of the Lake Barlow section show a hydrothermal event that postdates the formation of the chlorite and that is absent in the Bignell section.

7.3 Organic Matter And Sulfide Fixation

Conclusions

The following results were found;

1) There is a correlation between organic carbon and sulphur. The equation that best describes their behaviour is;

Sulphur = 0.663 Carbon + 1.09;

the correlation coefficient is 0.78 within 2 units of standard deviation or the 68% confidence level.

From the above equation the ratio of S/C is approximately 1.18 or close to 1 part organic carbon for 1 part sulphur in the shales of the Lake Barlow and Bignell Township sections.

2) Sulfur can be correlated with total iron;

Sulphur = 0.576 Fe_2O_3 - 1.07, with a correlation coefficient equal to 0.78, within 2 units of standard deviation or the 68% confidence level.

The ratio of S/Fe_2O_3 is approximately 0.58. The ratio of S/Fe would be 0.83 (Fe_2O_3 equals 1.14 times Fe), or .83 S for 1 Fe_2O_3 in the shales from the two sections.

Discussion

Recently researchers haves begun to investigate the role of organic matter in metal deposits. McQueen and Powell (1983) a demonstrates that a spatial or temporal relationship exists for Pb-Zn deposits and organic matter in carbonates at Pine Point. Beveridge et al.(1983) demonstrate that living bacteria can incorporate metals directly into the cell cavity.

In this study the statistical treatment of the data shows there is a positive correlation between organic carbon and sulphur, and that the sulphur content is proprortional to Fe or Fe_2O_3 (total iron). Carbon is therefore related to the principal sulfide which is pyrite.

However, it would seem that several factors could operate independently or in concert to form the mineralization associated with organic matter;

1) There is growing evidence that the sulfides formed by organisms that were directly responsible for sulfide fixation, through in-vivo physical or chemical processes such as cell-wall adsorption.

2) Sulfides could be formed indirectly by biologic activity through the release of metabolic by-products such as H_2S and SO_4, which produced a reducing environment that favored precipitation of sulfides.

3) Organic matter acting chemically as hydrocarbons associated with the transport of metals during remobolization (as soluble or insoluble organic matter, hydrocarbons, and or organic complexes of biologic origin).

Previous studies support all three of the above cases; 1) Beveridge demonstrates biological fixation of metals (Beveridge et al.,1983) with "Bacillus subtilis" that bond metals directly to cell walls in "ionic metal - synthetic sediment" suspensions. Seafloor mud from the Pacific Ocean yields bacteria with intra-cellular microcrystaline FeS_2 (Skripchenko and Lytkin, 1969).

2) An example of indirect biological sulfide fixation is that of precipitation of sulfides in peat bogs. Papunen (1966) shows that H_2S released during anaerobic bacterial metabolism creates conditions of eH and pH favourable to FeS_2 precipitation.

3) Evidence for the abiologic chemical role of organic matter in metal deposition is more subjective and scarce. Organic acids such as humic acid and precious metal thio complexes (Seward, 1973) are central to models in which organic matter plays a chemical role. Seward and others feel that organic compounds greatly increase solubility of metals and provide molecular capture sites in ore-forming solutions.

7.5. Trace Elements in Black Shales

7.5.1 Trace Elements in Organic Matter

Conclusions

1) Organic matter is enriched in trace elements relative to the whole rock most notably for gold.

2) There does not appear to be strong control over the trace element content in the whole rock exerted by the organic matter.

3) There is a constant response for Au (average = 0.25ppm) in the organic fraction. (see samples L1, 3, and

19; No Au detected in whole rock or sulfides allthough present in organic fraction)

7.5.2 Trace Elements in Sulfides

Conclusions

1) No apparent relation could be detected between the content of trace elements and sulphur or, by extrapolation, sulfides.

2) Sulfides are enriched in trace elements relative to the whole rock most notably for gold. However, there does not appear to be strong control over the trace element content in the whole rock exerted by the sulfide fraction.

7.5.3 Trace Elements In Whole Rock

Conclusions

1) The average values for Au, Zn, Cr, and Co are significantly lower than either the sulfide or organic matter fractions.

2) There is a only a slight difference between the samples from the Bignell and Lake Barlow sections: the samples from Bignell Township tend to have more numerous elevated values.

3) The trace element content in the whole rock is not controlled, to any signifigant degree, by the sulfide

and organic matter fractions.

4) Au in the whole rock compared to percent sulphur and carbon shows very weak correlation for rare samples though generally none. The same is true for Zn, Cr, and Co.

Discussion

The data for gold and trace elements in insoluble organic matter in this study can be compared to few other studies. Vine and Tourtelets' summary paper (1970) documents several studies of behavior of trace elements in black shale hosted mineral deposits and notes brief references to graphite and organic matter or oil; gold was not mentioned.

More direct relation of metals and OM in black shales can be found in Kucha's (1983) study of Soluble OM extracted in chloroform. Kucha (1983) reports Au, Pt, and Pd present in soluble organic matter extracted from shale hosted silver amalgam "pay zones" in the Polish Zechstein Basin precious metal deposits. He has measured 2-50 ppm Au, 8-50 ppm Pt, and 8-10 ppm Pd.

Kucha believes that some of the metals present in the shales are in the form of "organo-metallic" compounds, though is not able to elaborate on this point. There is no indication that Au is "complexed" to organic matter by this type of analysis despite its presence in signifigant quantities. Kucha's results do not prove or disprove the presence of "gold complexes" formed with organic matter. Quantitative analysis cannot define the manner in which Au is present in organic matter.

In the present study, it was determined that sulphur and organic carbon are not solely responsible for the total trace element content of the shales. By elimination the phyllosilicate phase is the source of most of the trace elements detected in the whole rock analyses. The precise process that binds the trace elements may be either physical (as in fluid inclusions), adsorptive, ionic, or covalent in nature. Vine and Tourtelet (1970) believe that the elements are adsorbed but this idea was not developed nor was any evidence mentioned that implicitly supported this trace element binding mechanism in shales. Cody (1971) has performed experiments that show how vandadium and boron are "sorbed to clays" but again the molecular processes are all inferred; the precise method of fixation is as yet undetermined. As is the case with the present study the previous studies are based on quantitative chemical analyses that cannot provide answers to the questions that surround the actual bonding processes of trace elements to clays.

Curiously, the trace elements are not necessarily chemically bonded, adsorbed, or even within the molecular structure of the phyllosilicates or the other components of the shales. Easily detectable levels of trace elements can be washed from shales with water (E.H. Sawyer, pers. comm.); simple physical capture, during sedimentation, of trace elements in solution in inter-grain spaces is possibly one of the most important mechanisms of trace element uptake in shales.

7.5.4 Gold and Sulfides in Black Shales

The statistical treatment of the organic carbon and sulfur data, in Chapter IV (section 4.1.1), shows there is a positive correlation between organic carbon and sulphur, and that the sulphur content is proprortional to Fe or Fe_2O_3, total iron (section 4.1.2). Carbon is therefore related to the principal sulfide which is pyrite. The sulfide fixation was very likely syngenetic. However trace elements such as gold, that are consistently concentrated in organic matter, appear to be fixed by chemical processes related to diagenesis or metamorphism.

The sulfides are fixed by organisms by in-vivo physical or chemical processes such as cell-wall adsorption, or were precipitated in a reducing environment, the result of biologal activity which released H_2S and SO_4.

In the case of certain trace metals, organic matter may be abiologically related to metal enrichment: If organic matter fixed metals during deposition, the metal content should be proportional to organic carbon present in the whole rock. In fact, the metal to organic carbon ratio, such as in the case of Au, is variable. The shales contain both in-situ and remobilized varieties of organic matter, and the undifferentiated organic matter fraction has a consistently high Au content.

Possibly the organic matter scavenges Au as it passes through the sediments in the remobilized state. A sample with abundant remobilized organic matter might be expected to have a high Au content. Unfortnately we cannot differentiate the two species of organic matter by bulk chemical analyses. Future ion probe studies could help to prove if in fact the remobilized organic matter is richer in Au than the in-situ variety.

Gold capture by organic matter is a chemical or abiological process associated with diagenesis or metamorphism of the shales. The transport of trace metals may be due to remobolization by soluble, or insoluble organic matter, hydrocarbons, and or organic complexes of biologic origin.

The shales of this study are very good source rocks for metals or metal rich solutions. The evidence shows that the Blondeau and Bignell black shale horizons may contain metal deposits. Gold mineralization could be associated with organic matter or "graphitic material", such as shale-hosted disseminated auriferous sulfide deposits.

Concentration of metals could be expected to occur in the same location as hydrocarbon deposits since metals seem to have a marked affinity for organic matter. Structural traps, faults, and porous reservoirs present in or adjacent to the shales may have appreciable gold contents that could have accumulated in a manner analogous to hydrcarbon deposits.

The Blondeau formation has yet to produce a signifigant shale hosted gold mineralization or massive sulfide deposit and in part this is blamed on the inability of electromagnetic techniques to differentiate sulfide deposits from supposedly worthless graphitic conductors (Archer, 1984). This study shows that these "graphitic" geophysical anomalies themselves are possible exploration targets.

7.6 Rare Earth Elements In Black Shales

Conclusions

1) The shales of this study have REE profiles similar to the standard "NAS"; the Barlow and Bignell shales have flat curves and REE concentrations similar those of the NAS. There is a small positive Eu anomaly present that is due probably to the abundance of detrital plagioclase feldspar present in the rocks.

2) The shale samples in Bignell Township, near to the "Grenville Front", are depleted in REE relative to the shale samples further away taken from Barlow Township; the average REE profiles of organic matter, sulfides, and shale samples from Barlow Township plots above those of the Bignell samples.

3) In each of the average profiles of the Bignell samples, the light incompatible REE (La, Ce, Nd, and Sm: in decreasing order) show the greatest depletion or possibly mobility.

4) The organic matter fraction is enriched in heavy REE relative to the sulfide fraction.

4) Sufides possibly have a strong affinity for REE, in general, in view of the overall REE enrichment

seen relative to either the OM or the whole rock REE contents.

5) Of the fractions present in the whole rock, only the sulfide fraction should be able to significantly control the type of profile seen in the analyses of the whole rock; the sulfides show strong enrichement in REE.

Discussion

An extensive bibliography search for REE and trace element studies indicates that very little work has been done on REE and trace element partitioning in black shales. Some results are available for the REE present in suspended organic matter and sediments near the ocean floor (Murphy and Dymond, 1984). Two studies report preliminary estimates of trace element content and partitioning in the organic components of black shales (Keith and Degens, 1959; Krauskopf, 1955). Prior to the present study, it appears that no single paper has dealt with the partitioning of REE and trace elements between the organic and sulfide fractions in relation to trace and REE content of the whole rock.

There are numerous studies of REE content in shales and black shales available, from a variety of geological contexts. However, no single study treats the partitioning of REE between the organic, sulfide, and clay mineral fractions of the shales, prior to the present study.

A single reference to organic matter-related REE was found which discussed the role of "biogenic debris" (undifferentiated organic matter, carbonate, and opal) in relation to REE partitioning in modern day seawater (Murphy and Dymond, 1984). Apparently biologic material accumulated in sediment traps at increasingly deep sampling sites accounts for up to 60 percent of the total REE measured. Below 1500 meters however, "alumino-silicate" (clay minerals) detrital particles contain more REE. The biogenic fraction dwindles to 20 percent at 3600 meters. Below this depth the clay minerals predominate in the sediment traps (from 75 to 86 percent of the trapped material). Absolute abundance of REE in the clay minerals appear to be about 1.5 to 2 times higher than in the biogenic debris; this can be estimated by comparing the REE measured for the trapped material at 500 meters (60 % biologic debris) and 3545 meters (86 % alumino-silicates).

While there are no quantitative REE analyses for the clay fraction in this study, the results for the organic and sulfide fractions provide information about REE behavior or partitioning in black shales. No previous studies have been made regarding the organic matter-sulfide REE partitioning within black shales, and as such there is no reference to compare the results of this study with.

The shales of this study have REE profiles similar to the standard "NAS". In addition, they have a similar major element make-up. The shales of the Blondeau Formation are fairly tyical, as such.

In pockets of concentrated sulfides or OM it might be possible to see a whole rock profile that is similar to either of the predicted profiles for the organic matter or sulphide average REE. However, no single sample studied exhibited the general profiles similar to the sulfide or OM fractions.

The two most important findings are:

1) In black shales, it would appear that organic matter has an affinity for heavy REE while the sulfide fraction have an affinity for the middle weight to light REE;

2) If the shales were originally similar in composition in the two areas, then REE are, possibly, more mobile in black shales in the samples nearer to the "Grenville Front", and the light REE the most mobile.

Two important questions remain unanswered in this study; Why is the OM enriched in heavy REE relative to the

the sulfide fraction?; What is responsible for the depletion of REE seen in the Bignell section?

The questions surrounding the differing sulfide and organic matter affinities, as well as the apparent mobilty of REE in the Bignell section noted in this study are difficult to answer. Very briefly, the smaller radii Heavy REE are somewhat more compatible than the larger radii Light REE in substitution for molecules in a crystalline lattice. If the shales were the same in composition initially, then mobility could be inferred. The dissolved REE in the depositional basin are dominantly in the associated with the phyllosilicate fraction. During compaction and increasing diagenesis of the shales REE would pass into the liquid phase to some degree; the Light incompatible REE will be the most depleted, relative to the Heavy REE. This could explain the observed differences between the Bignell and Barlow shales (A. Fowler, pers. comm.).

However, differences could also be explained by the provenance of the source of the sediments, the conditions present during deposition of the shales at the two sites in the basin (Sawyer, 1986). The problem becomes even more complex if a combination of these syndepositonal factors are combined with metamorphism and alteration.

Possibly these chemical compatiblity factors are important during diagenesis and migration of hydrocarbons and formation of sulfides as well. Then also, the initial conditions present in the depositional basin are just as important. Possibly, organic complexes formed during the maturation of bitumen or organic matter that are related to the uptake of REE in which the chemical compatibility factors favor the HREE in OM. What factors control the physical capture of REE during the uptake of metals (Beveridge et al., 1983) by living bacteria can incorporate metals directly into the cell cavity.

These questions, the study of the REE and trace element geochemistry of the phyllosilicates in Black Shales are the subject of continuing studies.

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ANNEX I

SAMPLE PREPARATION

1.1Initial treatment of all sampled material.

Core containing black shale was selected from the M.E.R.Q. stratigraphic drill sections taken from the the Blondeau Formation at Lac Barleau, west of Chibougamau. 21 samples were obtained by cutting the suitable cores lengthwise with a diamond saw. The samples were rinsed in a light detergent solution, dried,and placed in sample bags.

In the laboratory all samples were;

(1) washed in acetone and in hot detergent solutions,

(2) ground on all surfaces using moistened 200 mesh tungsten carbide grit on a rotating, glass-covered, polishing lap,

(3) washed with distilled water and detergent and rinsed with distilled water,

(4) dried and stored in wide mouth 250 ml Nalgene bottles.

Hand specimens about 3 cm in length were retained from each core sample. A thin polished section was cut from each of these hand specimens to view organic matter and sulphides in reflected light and to perform petrographic analyses in transmitted light. 20 mm polished sections suitable for ore microscopy were also prepared.

The remaining core sample in each plastic bottle was reduced to fragments 1 to 0.5 cc using a jaw crusher lined with porcelain plates to eliminate metal contamination. Between each shale sample the plates were cleaned with an abrasive jet of silica and rinsed with acetone soaked tissue paper. The shale chips were returned to their plastic containers and sealed.

1.2 Preparation of whole rock powders.

25 gram batches of chips were fed into a clean tungsten carbide shatter-box until 100 gm of powder were obtained for each sample. Before each new sample of shale was pulverized, the shatter-box was cleansed of any traces of foreign matter or previously crushed sample. The shatter-box was filled with 25 ml of silica sand and 50 ml of water and run for 4 minutes on the orbital shaker. At the end of this period the shatter-box was washed out with distilled water and air dried. Further manipulation of the shatter-box components were performed with tissue papers to protect the grinding surfaces from finger contact. All of the interior surfaces of the shatter-box were wiped-off with purified acetone and air dried. The shatter-box was precontaminated with 3 or 4 chips of shale ground for 3 minutes. After cleaning with compressed air, the sample was pulverized. The nalgene bottles holding the original sample chips were

quickly resealed and the resultant powders rapidly transferred to new containers in order to minimize air born laboratory contaminants.

The rock powders were divided as follows; 50 gm of powder for studies requiring unaltered rock powder and 50 gm for organic matter and sulphide analyses. Ample unground chips were reserved for future use.

1.3 Extraction and Separation of Organic Matter and Sulphides.

Extracting organic matter and sulphides from rock is described by Durand and Monin (1980) and involves little more than;

(1) pulverization of the rock and dissolving the silicate fraction in hydrofluoric acid,

(2) heavy liquid separation of the sulphide and organic fractions,

This technique was unsatisfactory in terms of producing separate sulphide and organic matter fractions.

HF attack yields a black residue comprised of organic matter and sulphides. However, the fine granulometry which results from shatter-box pulverization caused the residue to form a cohesive clot when added to bromoform. To circumvent this problem test samples of shale chips were pulverized in a suspension of water. The swirling action of the water removes particles below a certain grain size from further reduction in size. The resulting powder had a uniform granulometry that separated well in Bromoform. However, microscopic examination of the two fractions showed an incomplete separation.

The only way to provide a complete separation of with any certitude was to employ a chemical method. Aqua Regia dissolves the sulphide fraction from the sulphide-organic matter mixture. The acid was prepared using 1:3; nitric acid : hydrochloric acid.

Each of the samples were treated in the following manner;

(1) 50 gm of powdered sample were placed in 250 ml wide mouth plastic bottles resistant to HF and the stresses of centrifuging,

(2) reagent grade HF (70%) was added in 10 ml increments to the powdered samples. The bottles were filled to within 1 cm of bottle neck, (adding HF rapidly causes violent reaction and subsequent sample loss) (3) bottle caps were placed onto bottles, but not tightened (due to gas production)

(4) contents were stirred at 12 hour intervals during a 48 hour reaction period,

(5) after 48 hours the bottles were balanced in pairs, (by adding small quantities of distilled water to the lightest of each pair) sealed, and placed in a centrifuge,

(6) the liquid was decanted after centrifuging at 3500 r.p.m. for 20 minutes,

(7) steps (1) through (6) were repeated, (a total of 96 hours of HF attack)

(8) **washing;** after the final acid decantation, distilled water was added to the bottles to within 1 cm of the neck. The bottles were balanced in pairs, sealed, and agitated vigorously,

(9) the sample pairs were centrifuged as in step (6),then tested for HF with litmus paper, and decanted. Washing was repeated until water had a pH of 7.

(10)the bottles with organic matter-sulphide residue were placed in a fan-forced oven at 50°C. Each bottle was covered with a piece of filter paper to allow evaporation of water.

The resulting black powder was ready for chemical extraction of the sulphide fraction.

1.4 Chemical separation of sulphides and organic matter.

The following procedure ensures as complete a separation as possible. However, there may still be a problem: while theoretically all sulphides are in solution, it is possible that some sulphides are encapsulated by organic matter. This should not be a problem as the samples are sufficiently finely ground in the shatter-box.

The residues were treated in the following manner;

(1) the weight of the bottles with residue were recorded,

(2) the nalgene bottles containing the residues were placed in an empty thermostatically controlled tray for heating water,

(3) 20 ml of freshly mixed Aqua Regia were pipetted into each bottle. The caps were loosely wound onto the respective bottles.

(4) preheated water was added to the heating tray and simmered for 3 hours with the controls set at 90°C,

(5) using a syringe filter system (with individually weighed filter membranes) the acid solutions were extracted and transferred to 35 ml polyethylene bottles. Each used filter was placed in the corresponding 250 ml bottle to avoid discarding organic matter.)

(6) **Washing;** the 250 ml bottles were filled with distilled water to just below the neck. The bottles were balanced in pairs, sealed, and very gently agitated, (to keep the filters intact.)

(7) the 250 ml bottles were centrifuged at 10,000 r.p.m.

for 10 minutes and then decanted, (when pH.was not neutral additional washing was required)

(8) the samples were dried in a fan forced oven at 50°C.

(10)the weight of the bottles with organic matter and filters was recorded.

2 Sample preparation for trace and rare earth element analyses of sulphides and organic matter

2.1 Preparation for trace element analyses of sulphides

Atomic absorption requires that the analysed elements be in a solution. The Aqua-Regia sulphide solutions may be analysed without further treatment.

2.2 Preparation for trace element analyses of organic matter

Organic matter extracted during the earlier treatments was divided equally for atomic absorption and neutron activation analyses. There was not sufficient organic matter produced by the treatment of 50 gm of sample to perform trace element analysis by atomic absorption. Trace element studies had to be performed by neutron activation analysis. However, the procedure for dissolution prior to atomic absorption is the following;

(1) organic matter samples were weighed, transferred to

fire resistant crucibles, and reweighed.

(2) the crucibles were placed in an oven at 1700°C for 3 hours,(the samples were oxidized in this way to convert all carbon to CO_2,

(3) once cooled, the crucibles were reweighed. 10 ml of Aquà Regia were added and the crucibles were covered and simmered for 3 hours,

(4) Aqua Regia solutions were cooled and transferred to polyethylene bottles ready for atomic absorption.

2.3 Preparation of organic matter fraction for neutron activation analyses

There is not sufficient organic matter to fill the 2 dram containers for analyses. It is necessary to dilute the organic matter samples with pure cellulose powder. Homogenous mixtures of cellulose and organic matter were required for precise counting geometry.

(1) The weight of cellulose that could be compressed into the 2 dram containers was determined.

(2) 0.1 to 0.07 gm of organic matter was measured out from each sample and mixed with the known weight of cellulose with an agate mortar and pestle.

(3) The mixtures were placed in containers of a known weight.

(4) The containers were reweighed and lost cellulose and

organic matter were determined and subtracted from the original sample weight. (This was a negligible value for each sample.)

(5) The containers were welded shut and the samples were ready for neutron activation.

2.4 Preparation of sulphide fraction for neutron activation analyses

Manipulating highly toxic, irradiated liquids is hazardous and time consuming. In addition, corrosive Aqua regia could cause extensive damage to the nuclear reactor in the event of a sample leak. To eliminate these factors the samples were reduced to solids in the following way:

(1) the solutions were boiled dry and then 50 ml of HCl was added to each residue.

(2) two more dissolutions and evaporations in HCl were performed,

(3) the resulting evaporates were powdered in a mortar and pestle. The sample powders were transferred to polyethylene bottles for storage.

The resulting solids are a mix of metal chlorides. One test run was performed using the undiluted yellow residue. It was decided that it would be wise to use approximately the same mass as was measured for the organic matter analyses in order to duplicate the operating parameters as much as possible. The samples were diluted with cellulose in precisely the same manner as the organic matter. See the dilution procedures in section 2.3.

3 Sample treatment for whole rock analyses

3.1 Sample treatment for whole rock REE

Analyses of rare earth elements of powdered whole rock required no further treatment: the samples were weighed and sealed in preweighed neutron activation capsules.

3.2 Sample treatment for "Total Organic Carbon"

Total organic carbon refers to all carbon present in the rock after the dissolution of carbonates. Concentrated HCl is added to 1 gram of sample and heated gently for 30 minutes. The acid is filtered out and the sample dried. This procedure drives the carbon present in carbonates out of the samples. The samples were tested with a Perkin-Elmer gas analyser using a non-destructive electromagnetic furnace. Analyses require 1 milligram of recuperable sample. The samples were subsequently tested with a Leco Gas Analyser that consumed 1 gm of sample per analysis.

3.3 Sample treatment for "Rock-Eval" analyses.

This analytical technique requires the same sample preparation as that for the "Total Organic Carbon" analysis. Both analytical methods use the same technique; pyrolysis. However,"Rock-Eval" uses a lower temperature range and controlled temperature increase to detect the combustion products of volatiles or soluble kerogen.

3.4 Sample treatment for Mass Spectrographic Gas Chromatography

Where soluble kerogen was indicated by "Rock-Eval", an extract for chemical analysis was obtained in the following manner;

(1) 100 gm of untreated shale chips were soaked for 2 hours in 500 ml of glass-column-distilled chloroform in closed Erlenmyer flasks (This reagent is to be used at all times in this technique). The flasks were agitated every half hour,

(2) the spent chloroform was poured off. The chips were rinsed in new chloroform and dried,

(3) 1 to 0.5 cc shale chips were passed through porcelain jaw crushers set with a 3 mm gap, and then soaked for another 2 hours with agitation at half hour intervals,

(4) same operation as step (2)

(5) same operation as in step (3) but with jaw crushers set to 1 mm,

(6) 1mm chips are placed in tungsten carbide shatter box

(see cleaning procedures and pulverization in section 1.2: "Preparation of whole rock powders".

(7) shale powders are placed in flasks with 500 ml of chloroform, sealed,and agitated for 48 hours in a thermostatically controlled bath of heated water. The temperature was set at 50°C. The water has to be topped-up periodically to replace loss due to evaporation.

The chloroform solution can be removed by syringe filter and analysed. When dried the shale powders are recuperated.

3.5 Sample preparation for whole rock analyses of major, minor, and trace elements

Na, Mg, Al, Ti, Mn, Fe, Ca, Co, Cu, Zn, Pb, and Ni analyses were performed by Atomic Absorption. Solutions were prepared as follows;

(1) a minimum of 3 gm was accurately weighed into a high temperature crucible of known mass,

(2) the crucibles were fired at 1700°C. for 3 hours, and after cooling, reweighed, ("loss on ignition")

(3) 0.100 gm of fired sample was mixed with 1.00 gm of lithium metaborate and then fused into glassy pellets,

(4) the fused samples were dissolved in hot hydrochloric acid.

The filtered solutions were stored in polyethylene bottles till analysed.

K_2O, Al_2O3, SiO_2, and P_2O_5 had to be analysed by X-ray fluorescence. Al is analysed by X-ray fluorescence to provide a comparison with the values obtained by atomic absorption. Compressed powder pellets were prepared in the following manner;

(1) 1.000 gm of fired sample was mixed with 5.000 gm of lithium tetraborate, 1.000 gm of lanthanum oxide, and 0.0050 gm of NaBr,

(2) the mixtures were fused to pellets. Pellets were finely ground with 7.400 gm of boric acid in a shatter box,

(3) the resulting powder was compressed into pellets. These were encapsulated with boric acid during a final compression.