ORGANIC MATTER AND TRACE METAL PRESERVATION IN PENNSYLVANIAN BLACK SHALES

By

SRUTHI SUBBANNA

Master of Science in Environmental Science

Oklahoma State University

Stillwater, Oklahoma

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ORGANIC MATTER AND TRACE METAL
PRESERVATION IN PENNSYLVANIAN
BLACK SHALES

Thesis Approved:

Dr. Dee Ann Sanders

Dr. Anna Cruse

Dr. Eliot Atekwana

Dr. A. Gordon Emslie

Dean of the Graduate College

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LIST OF DEFINITIONS

(Source – Miles, 1989)

Aerobic/Oxic – Having free air or oxygen. Specifically applied in geochemistry to water column and near surface sediment conditions with sufficient levels of dissolved oxygen to support aerobic bacteria, approximately equivalent to > 0.2 ml/l. Chemical and bacterial oxidation of organic and inorganic components can occur.

Aliphatic – The term originally meaning fatty, but currently defined as organic compounds which are non-aromatic and non-polar, such as alkanes, alkenes, and alkynes, i.e. organic compounds which are open chain and those cyclic compounds which resemble open chain compounds in their chemical reactions.

Alkanes – Carbon and hydrogen compounds which are saturated i.e. contain no carbon-carbon double bond or triple bonds.

Alkenes – Carbon and hydrogen compounds containing carbon-carbon double bonds.

Alkynes – Compounds with carbon-carbon triple bond.

Allochthonous organic matter – Organic matter which is deposited some distance laterally from where it was formed before incorporation into a sediment is said to be allochthonous e.g. terrestrial plant material deposited in marine sediments.

Amorphous kerogen – Kerogen which lacks distinct form or shape.

Anaerobic/Anoxic – Without free oxygen. The term is dominantly applied in organic geochemistry to water column, surface or near surface sedimentary environments, with insufficient oxygen to support aerobic bacteria.

Aromatic compounds – Originally meant ‘fragrant’ compounds, but now defined as benzene and those compounds which resemble benzene in their chemical behaviour. They are unsaturated and are represented as containing one or more rings with conjugated (alternating) carbon-carbon double and single bonds, in realit these are delocalized and form an orbital ring current.

Asphaltenes – The heavy molecular weight component of crude oils or sediment extracts which is soluble in carbon disulphide or insoluble in normal heptane. Chemically they are polyaromatic nuclei linked by aliphatic chains or rings and functional groups.

Autochthonous organic matter – The term autochthonous is usually used to denote organic matter originating in, or over, the water column above a depositional site, implying little or no horizontal transport.

Biological marker/Biomarker – Compounds or characteristics of compounds, found in petroleum or rock extracts which indicate an unambiguous link with a natural product with a natural product are known as biomarkers.

Bitumen – A well-used but ill defined geochemical term which has several meanings. It can be that fraction of organic matter in sedimentary rocks which is soluble in organic solvents. It may be the precursor to oil, or be the substance which occurs naturally in veins, pools, or dispersed in reservoir or source rocks. It is also used synonymously with organic matter which may be thermally extracted from rocks, and used informally to mean tar, pitch, and asphalt.

Carbon cycle – The turnover of organic carbon in plants, animals and rocks as a continuous cycle of respiration, photosynthesis, growth, decay, and preservation in sediments is called the carbon cycle.

Carbon preference Index (CPI) – The ratio of the abundance of odd carbon number normal alkanes to even number normal alkanes measure from gas chromatography of the saturate fraction of an oil or extract is known as Carbon Preference Index.

Catagenesis – The principal hydrocarbon generation zone. Elimination of hydrocarbon side chains and alicyclics takes place, and kerogen eventually reaches a maturity equivalent to anthracite, with no further hydrocarbon generation.

Chromatography – A technique for separating mixtures of chemical compounds based on their physical and chemical properties.

Column Chromatography – The type of chromatography commonly used to separate the bulk chemical components of crude oils and extracts. The fractions are separated by virtue of their polarity, and the polarity of the solvents is increased during the separation of the different fractions.

Diagenesis – Diagenesis in petroleum geochemistry refers to that stage of alteration where changes are dominantly due to biological, physical, and low –temperature chemical alteration, not severe thermal alteration processes.

Diterprenoids – Common C_{20} constituents of higher plants comprising four isoprene units.

Dysaerobic/dysoxic – loosely used to describe water conditions which are between aerobic and anaerobic. Specifically used to describe water with a content of between 0.1 to 0.2 ml/l of dissolved oxygen.

Eluent – The mobile liquid phase used to separate chemical fractions of oil during liquid chromatography is called eluent.

Euphotic zone – the upper part of a water column which is penetrated by sunlight, enabling photosynthesis to proceed.

Eutrophic – Nutrient rich. Usually applied to water in lakes.

Flame Ionization Detector (FID) – The FID system is the normal hydrocarbon detection system used in gas chromatography. It operates on the basis that organic compounds produce ions when they burn in a hydrogen flame and cause a measurable current.

First-order reaction – A reaction in which the rate of reaction is proportional to the concentration of the reactants.

Fulvic acids – Those organic acids found in soils and shallow sediments which can be extracted using sodium hydroxide and sodium pyrophosphate. Fulvic acids are the acid soluble portion of the extract.

Gas Chromatography (GC) – The separation of mixtures of compounds by partition between a mobile gas phase and stationary liquid phase is called gas chromatography.

Hetero compounds – Organic compounds which contain elements other than carbon and hydrogen.

Humic – A general term for organic matter which is derived from vascular land plants.

Humic acids – High molecular weight organic acids whichc an be extracted from soils and near surface sediments by sodium hydroxide and sodium pyrophosphate.

Humin – High molecular weight organic matter in soils and sediments which is insoluble in sodium hydroxide and sodium pyrophosphate.

Isoprenoids – Compounds such as hydrocarbons, alcohols, and esters built from multiples of the isoprene unit.

Kerogen – Insoluble organic matter which is preserved in sedimentary rocks.

Metagenesis – A high level of maturation spanning the gap between inorganic and organic metamorphism, where methane is the only hydrocarbon product.

NSO – An abbreviation for nitrogen, sulphur, oxygen compounds of crude oils. It is the fraction which elutes with polar solvents.

Organic facies – A distinctive assemblage of kerogen components which can be virtually identified or has characteristic chemical composition.

Resins – The fraction of crude oil or sediment extracts which elutes with methanol during liquid chromatography. It contains high molecular weight NSO compounds.
Soxhlet extraction – A method for removing the soluble organic matter from rocks using hot solvent refluxing.

Terprenoids – The group term which describes alkanes, alkenes, alcohols etc. derived from two isoprene units. Loosely used to describe all related classes of natural products and biological markers, irrespective of number of carbon atoms.

Total organic Carbon (TOC) – A measure of the organic cabon in a rock, expressed as weight percent, used as a fundamental parameter in classifying source rocks in conjugation with kerogen type and maturation.

Source - Miles Jennifer A, 1989, Illustrated Glossary of Petroleum Geochemistry, Oxford Science Publications.

CHAPTER I

INTRODUCTION

Black shales are fine-grained, organic-rich, laminated sediments produced by anoxic conditions in a geological surface. Black shales are of great importance as a principal source of petroleum (Demaison and Moore, 1980 and Gelinas et al., 2001). Anoxic conditions occurs due to a combination of excess demand of oxygen as compared to its supply coupled with barriers to resupply, resulting in an environment which has depleted oxygen (Demaison and Moore, 1980). Alternatively, Calvert and Pederson (1990) have suggested that high productivity is the main cause for the development of organic rich shales with anoxia being a by-product of increased carbon loads. Regardless of the ultimate mechanism for the formation of black shales, the organic carbon-rich black shales form an integral part of the trace metal geochemical cycles as they have large quantities of both the redox sensitive and the sulfide forming trace metals (Brumsack, 2005).

It has long been recognized that black shales are rich in organic matter and that they contain high concentrations of trace elements like iron, molybdenum, uranium, vanadium, nickel, chromium and cobalt (e.g. Vine and Tourtelot, 1970; Leventhal, 1980). Recently, correlations between the organic matter and concentration of trace metals in the black shales have been observed by many workers (Cruse and Lyons, 2004; Leventhal 1980; Wilde et al., 2004; Sageman and Lyons, 2005). However, a clear understanding of the reaction mechanism leading to this correlation is lacking. The relationship between organic matter, trace metals and redox conditions would aid in the development of quantitative models of paleoenvironmental conditions that existed when the rocks were formed. Quantitative paleoredox models will better constraint our understanding of the global climatic changes.

A study of trace metal content of black shales are thus of relevance for two reasons:

a. The scientific understanding of the detailed composition with respect to the association between organic matter and trace metal which could be used as a paleoenvironmental proxy.
b. Black shales are an important source of petroleum, so that an increased understanding of association between trace metal and organic matter could be of economic importance.

1.1 OBJECTIVES/HYPOTHESIS OF THE THESIS

Over the years most of the studies involving black shale compositions have examined the whole rock trace metal concentrations rather than considering concentrations in individual components. Hence it remains unclear as to how the individual composition of organic matter and trace metal composition. Recently, Abanda and Hannigan (2005) used sequential extraction method to determine the relative abundance of trace metals in sulfide, carbonate, silicate and organic fractions. The results demonstrate that 20% of the total trace metal present in the rock was fixed the organic fraction (Abanda et Hannigan, 2005).

Considerable study has been done to study the relation of trace metals and organic matter in black shales. Leventhal (1980) in his work showed how concentration of uranium is related to the (non alkane)/alkane ratio of organic matter. The two samples analyzed (from Overton county, Tennessee and Rowan county, Kentucky) showed a linear relation between the (non alkane)/alkane ratio and uranium content with an increase in (non alkane)/alkane ratios showing corresponding increase in uranium content (Leventhal, 1980). Wilde et al. (2004) conducted a study on molybdenum as proxy for black shales. The results of this study indicated that while molybdenum is highly correlated to the TOC content, the slope of the lines varied for different shales (Wilde et al., 2004).

In brief this thesis aims to study the qualitative and quantitative estimation of the organic matter and trace metal present in Pennsylvanian cyclothemic black shales. While models for the deposition of these units invokes the development of deep water and resulting anoxia, previous work (Cruse and Lyons, 2004) has shown that bulk trace metal abundances in these units vary across the basin between two sites. Specifically, differences in iron and organic carbon concentrations appear to support a hypothesis that organic carbon composition is a first-order control on trace metal concentrations preserved in black shales. The two regions vary greatly with respect to the type of organic matter deposited, the detrital input and influence of hydrothermal vents.

The following are the hypotheses for the study

a. There will be considerable variation in the organic matter content of black shales from north (IA) to south (OK) i.e. from the terrestrially dominated in Iowa to the marine dominated in Oklahoma.
b. Differences in organic matter will result in differences in the types of bonds that can be formed between metals and organic matter, which will be manifest as differences in the amounts of trace metals fixed primarily in the extractable organic matter pool.
c. Concentrations of redox sensitive metals in the bitumen will vary. While it is expected that metals like Fe and Zn will be present as sulfides other metals like Mo, U, V and Ni will be found in the bitumen fraction.

1.2 LITERATURE REVIEW

1.2.1 ANOXIA

Biologically mediated redox reactions form the basis of the inorganic processes that control the distribution of oxidizing agents such as NO_3^{2-}, SO_4^{2-} and trace metals across the depositional and digenetic gradients in sedimentary basins (Tribovillard et al., 2006). Aerobic organisms utilize dissolved oxygen present in the interstitial waters in oxic conditions for various metabolic activities when degrading organic matter. With the reduction in concentration of dissolved oxygen, the organic matter is further degraded by organisms which have the capacity to use secondary oxidant sources like iron and manganese oxides or sulfates. Then, when these oxidants get exhausted, organic matter is broken down via an oxidative- reductive disproportionation of carbon that is when the rate of organic matter degradation is more than the rate of oxygen renewal, anoxia results.

Anoxia can occur either because of insufficient circulation of oxygen, which prevents renewal of oxygen in selected zones, or by excessive utilization of oxygen during organic matter degradation. This is true for both sediment pore waters and sedimentary basins (seas and coastal oceans). However in sediments the development of anoxia is also dependent on factors such as intensity of bioturbation, and the composition and texture of the sediment (Tribovillard et al., 2006; Morford et al., 1999). These physical factors control the replenishment of oxygen in pore waters below the sediment water interface.

A combination of these processes results in the formation of separate layers of waters where an oxic (well oxygenated) layer is separated from the underlying anoxic and/or euxinic (anoxic-sulfidic) water by the chemocline. Recent work in the Black Sea, the largest modern anoxic basin, has highlighted how sediment beneath the anoxic waters are enriched in both organic matter and trace metals (Lyons et al. 1992, 2003; Yarinick et al., 2000; Werne et al., 2002).

The presence or absence of oxygen likely also controls the nature, type and quantity of the organic matter present. For example, Hedges et al. (1995) found that when coastal sediments were subject to long term exposure to oxic conditions, a decrease in the organic concentration was observed which was comparable to values of deep ocean deposits instead of coastal sediments (Hedges et al., 1995).

1.2.1.2 RESPONSE OF TRACE METALS TO ANOXIA

Formation and composition of black shales depends on various factors like environmental conditions, presence of other metals and organics etc. each of which in its own way can help in unveiling partially the origin, the processes of formation or the composition of the black shale. Organic matter present in the black could be of allochthonous origin or of autochthonous origin. When the organic matter present in the sample has been deposited from a distance by lateral movement it is termed allochthonous in nature, while organic matter originating and depositing in the same place is termed autochthounous in nature (Tissot and Welte, 1978).

Froelich (1978) undertook a study on the changes in the concentrations of Fe^{2+}, Mn^{2+}, PO_4^{3-}, NO_3^{2-}, O_2, and total carbon dioxide (TCO_2) during oxidation of organic matter in closed systems. Figure 1 shows the changes observed in concentration of Mn2+ with depth in core 5GCl from pelagic sediments of the eastern equatorial Atlantic. In the figure, it can be observed that, there is an increase in Mn concentration followed by a decrease.

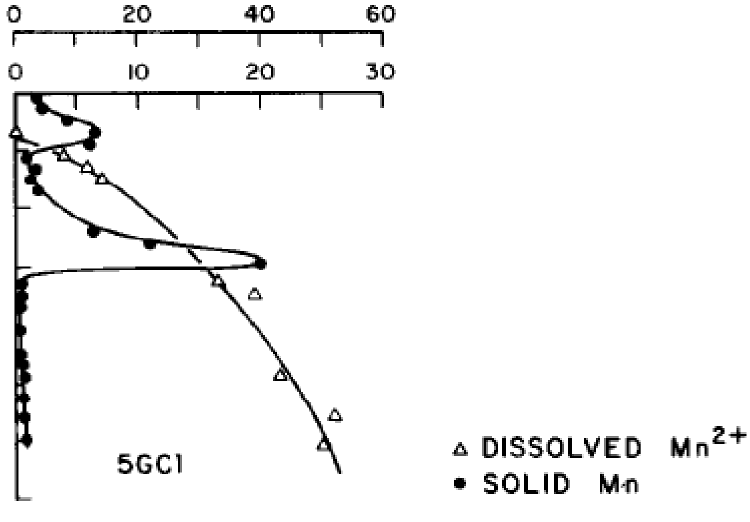


Figure 1 – Changes in Mn concentrations with depth (Source – Froelich et al., 1978)

Mn concentration is reduced in sediments deposited under a euxinic water column. Mn that is transported as oxyhydroxide is remobilized because of reductive dissolution (Morford and Emerson, 1999). Under anoxic conditions Fe forms pyrite, which results in its enhancement in organic-rich sediments (Lyons et al. 1997, 2003). Metals like Mo, U, V, Ni, Zn, and Pb that are redox sensitive in nature, either precipitate with sulfide minerals or pyrite or interact with organic matter. The result of these processes is an enrichment in sediments deposited under anoxic water column conditions (Coveney et al., 1991, Morford and Emerson, 1999) .

Cruse and Lyons (2000, 2004) used an integrated sedimentological-geochemical model to further constrain the deposition of the black shale facies in Pennsylvanian cyclothems. Focussing on the Hushpuckney shale (Missourian), they used Fe-C-S systemiatics and sedimentalogical characteristics to establish that the water column redox conditions varied between euxinic in Oklahoma and anoxic/euxinic in Iowa. Thus their results tend to support a model of black shale development in response to increased preservation of organic matter under anoxic conditions. (Cruse and Lyons 2000, 2004). Subsequent work on the trace metal concentrations in the (anoxic) black shale and over and underlying gray shales suggested that water-column redox conditions are not the only factors affecting the trace metal concentration of black shales (Cruse and Lyons, 2004).

Other factors such as variations in the organic matter source and the presence of additional inputs of metals to the basin (such as hydrothermal vents) also appear to affect the magnitude of trace metals enrichments in these shales (Cruse andt Lyons, 2004). This thesis aims to test the hypothesis of that organic matter is a primary control on trace metal fixation in black shales by characterizing the extractable organic matter present in these rocks, and relating those changes to trace metal concentrations. Further constraining the organic matter-trace metal relationship in black shales represents an important step forward in quantifying cycles associated with the formation of the black shales.

1.2.2 FORMATION OF BLACK SHALES

A set of multiple controls influence the accumulation of organic matter in black shales. Some researcher's state that there is enhanced preservation of the marine organic matter occurs under reduced conditions, others have said high marine surficial productivity enhances the preservation (Demaison and Moore, 1980, Calvert and Pederson, 1990). Models showing a combination of the above two have also emphasized the preservation of marine organic matter above productivity (Rimmer, 2004).

Although several models have addressed control of marine organic matter for the preservation of Devonian-Missippian black shales, it has been also established by geochemical and petrographic analysis that one of the factors contributing to the formation of these black shales is also the presence of terrestrial organic matter (Rimmer et al., 2004). Studies have also indicated that the internal layer in smectite and mixed layer clays could also play an important role in the presence, preservation and accumulation of organic matter in black shales (Kristin et al., 2004).

Kerogen is formed by the diagenesis of organic matter. Figure 2 illustrates how sedimentation and diagenesis results in the formation of kerogen and geochemical fuels. As can be seen from the figure in the first stage biopolymers are degraded to amino acids and sugars. Part of these are used up by microbes either as a source of energy or as a cell constituent while the rest undergoes polymerization and condensation at or near water sediment interface to form fulvic acids, humic acids and humin. Increased condensation and insolubilization results in the formation of kerogen.

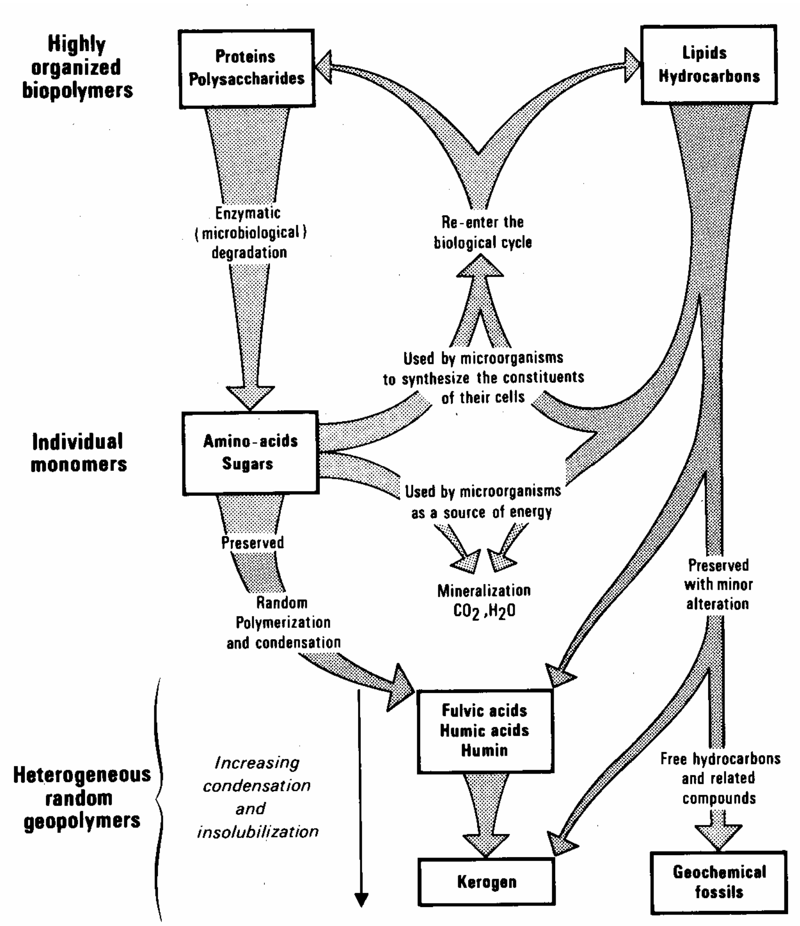


Figure 2 – Diagenetic sequence of organic matter (Source – Tissot and Welte, 1978)

1.2.3 ORGANIC MATTER IN BLACK SHALES

The purpose of studying organic matter in black shales is to try to determine the origin of the organic matter based on the presence and distribution of individual organic compounds. Biochemicals that are produced by living organisms constitute biomarkers mainly because they remain relatively stable when diagenesis occurs. One of the examples is of chlorophyll phytol side chain. Under anoxic conditions it forms a 20C phytane while in dysoxic condition it forms a 19C pristane (Potter et al., 2005, Wignall, 1994). Studies on higher plants have indicated that these usually have a dominance of the odd numbered n alkanes with more of nC_{29} and nC_{31} present in them. *n*-alkanes in biological material have a dominance of odd carbon atoms to even carbon atoms (Welte et al., 1968).

Carbon Preference Index is defined by Bray and Evans (1961) as "the mean of two ratios which are determined by the sum of odd carbon numbered n paraffins by the sum of even carbon numbered *n*-paraffins over given concentration ranges" (Bray and Evans, 1961). Three grains i.e. oats, barley and maize were studied by Cooper and Bray (1963) and CPI of the same were calculated to 9.2, 7.2 and 5.1 respectively (Cooper and Bray, 1963) further confirming that higher plants have a greater CPI value.

Studies were conducted on recent marine and ancient marine sediments and crude oil and the CPI values observed were 2.4 to 5.5 for recent sediment and a much lower value of approximately 1 for crude oil. Although some samples of ancient sediment showed values of 1.5 to 2.5, they were mostly in the range of 0.9 to 1.5. The ancient sediment included outcrops and core shale and limestone sediments form the Cretacious, Jurassic, Pennsylvanian, and Missipian ages (Cooper and Bray, 1963).

Higher plant waxes exhibit a strong dominance of odd to even numbered carbon atoms usually grater than nC_{23} with maximum at nC_{27}, nC_{29}, nC_{31} and with high CPI. (Simoneit 1974, 1977; Welte et al.,1968). While organic matter of terrigenous origins have organic carbon dominance form nC_{23} onwards, organic matter originating from marine sources has n alkanes with a dominance at less than nC_{23} with a maximum usually at nC_{17}. The phenomenon which was observed in samples of Jurassic age claystones. A hump was also observed at nC_{23} which was interpreted as originating form the algal biodegradation of different organic constituents. (Stuermer and Simoneit, 1978, Simoneit 1977). 7 and 8-methyl heptadecane which are major components of lipids of blue-green algae (Philip et al, 1976, Hans and Calvin, 1970, Han et al, 1968) have been identified by Philip et al (1976) in the sediment samples form Virgin islands which are major components of lipids of blue green algae (Philip et al, 1076, Hans and Calvin, 1970, Han et al, 1968) making a reference that the origin of these components is from blue green algae.

Unlike higher plants algae usually contain low molecular weight alkanes and alkenes with dominance of either nC_{15} and/or nC_{17}. nC_{15} dominance indicates organic matter in a sample is probably from brown marine algae while C_{17} dominance indicates organic matter origin as a red algae (Oro et al., 1967, Han et al., 1968, Simoneit, 1978, Youngblood et al., 1978). Alkanes which are structurally similar to alkanes of higher plants discussed above are also present in phytopathogenic fungi (Weete, 1971).

Study conducted on diterprenoid compounds of deep sea sediments revealed that while for a characteristic marine and terrigenous distribution the range in n alkanes observed were nC_{12} to nC_{20} (maximum at nC16) and nC_{20} to nC_{30} (maximum at nC_{24} or nC_{28}) respectively with an even to odd dominance of carbon atoms (Simoneit, 1976). One can observe dominance of even numbered carbon atoms to odd numbered carbon atoms because of the reduction of fatty acids by microbes under suitable environmental conditions (Welte and Ebhardt, 1968)

Work done on petroleum by Philippi showed whether the origin of organic matter was terrestrial or marine based on the $nC_{21}+nC_{22}/nC_{28}+nC_{29}$ ratios. The study concluded that organic matter in oil from terrestrial origin had a low ratio from 0.6 to 1.2 while those of marine origin had a much greater ratio of 1.5 to 5.0 (Philippi, 1974).

1.2.3 TRACE METALS IN BLACK SHALES

Trace metals in sea water are present in either a dissolved form or adsorbed to suspended particles. Biotic or abiotic processes can cause removal and transfer of the soluble trace metals from the water column to sediments. Biotic processes are mainly those which involve uptake of the trace metals by microorganisms as a nutrient source while abiotic processes include mineral precipitation reactions in response to changes in redox conditions and are more efficient under reducing conditions (Tribovillard et al., 2006).

One of the earliest studies on trace metals in black shales was conducted by Goldschmidt in 1954. In his study, he suggested that enrichment of certain types of trace metals like molybdenum (Mo), vanadium (V), copper (Cu), zinc (Zn), or uranium (U) is found in organic-rich shales (Goldschmidt, 1954). Subsequently, Vine and Tourtelot (1970) undertook a study where they synthesized available data on a range of trace metal concentrations in ancient North American black shales. One main conclusion was that the elements which are enriched in black shales are not dependent on factors like the age, environment and type of organisms in the black shale deposit (Vine and Tourtelot, 1970). The depositional environment of black shales range from off-shore deep water environments as described by Heckel (1977, 1991) to near shore shallow water environment as described by Coveney et al (1991). It has been established that a wide range of trace metals are present in black shales by works of Covenoy and Glascock (1989), Coveney et al (1987), Vine and Tourtelot (1970), however the mechanism by which the trace metals are fixed in black shales are not clear. Coveney and Glascock (1989) created models showing metal mineralization occurring either by precipitation of sulfide minerals from the anoxic waters or by interaction of organic matter with sea water.

Further, Brumsack (2006) studied the trace metal enrichment in two different geographic environments - sediments deposited under coastal upwelling (like in Gulf of California, off Peru or off Namibian coast) and in euxinic basins such as the Black sea. In upwelling zones, Co concentration are comparable to that present in sapropels. Variable Mn concentrations were observed which could be because of the environmental conditions being anoxic in nature. There is also a probable chance of hydrothermal input as high concentrations of Ag, Cu, and Zn were found which would require other additional metal sources (Brumsack, 2006).

Trace metals are involved in the bio-geochemical cycles of the oceans. One of the important factors influencing transfer of trace metal from the biogeochemical cycle to the sediment is the exposure time to molecular oxygen. Another important factor facilitating trace metal fixation is presence of hydrogen sulfide in the water column or at the interface of sediment and sea water. (Brumsack, 2006)

Black shales have usually enriched quantities of trace metals, especially some metals which have a strong affinity for organic matter like U, Co, Ni, etc. Since they are present in abundance, the convention to interpret trace metal results is in the form of ratios like V/Cr (Potter et al., 2005). Rimmer (2003) also used geochemical ratios like Ni/Co, V/Cr, and V/(V+Ni) to determine the paleo environmental conditions of Devonian – Mississippian black shales of three different ages - Sunbury, Cleveland and Huron. The

Ni/Co and V/Cr ratios suggests anoxic conditions during Sunbury accumulation, anoxic to dysoxic conditions during Cleveland accumulation and dysoxic to oxic during Huron accumulations (Rimmer, 2003).

While a lot of individual work has been done on the presence of trace metals and organic matter in black shales, a combined study of both has not be done effectively a lot in this area. A study conducted by Mossman et al. (2005) presented data on organic matter in black shales in the Paleoproterozoic Franceville Series, Gabon. The carbonaceous marine formation (FB) in the region is rich in organic carbon and gave a good overview of a high organic matter low trace metal concentration in black shales. The organic matter in this area was present more in the form of kerogen and other types of solid bitumen. While kerogen and solid bitumen both are autochthonous in nature, solid bitumen was at one time a viscous liquid while kerogen does not migrate once it has been deposited. Also, the affinity of organic matter to trace metals is not consistent both of which were the reason for their study (Mossman et al., 2005).

It was observed that the lowermost samples of the black shales have less of organic carbon and more of potassium (K), barium (Ba), chromium (Cr), and silver (Ag). The most probable reason for this could be that during early diagenesis there was alteration of the sediments by oxidizing fluids. Another reason could be hydrothermal variation at these locations. While studying the geochemistry of the bitumen in the location, it was observed that metals were hosted either in carbon or by aluminous phases. Metals hosted in carbon are mostly the organometallic complexes while the origin of those hosted in aluminous phases is unknown. This gave a new direction to their study with respect to a nuclear fission reactor, Bangombe, buried at approximately 12m depth, radioactive waste from which could be the cause of metals hosted in aluminous phase (Mossman et al., 2005). Thus trace metal – organic matter in black shales could also highlight problems, if any, concerning improper storage and disposal of nuclear wastes.

Study on correlation between total organic carbon and trace metal has been done by Algeo (2006), wherein he mentions that in low total organic carbon (TOC) samples i.e. those having less than 10% by weight, there is pronounced TOC- Trace Metal (TM) covariation. He further mentions that in high TOC (i.e. those with greater than 10% by weight) the TMs exhibit either of the two patterns

a. are weakly covariant and strongly enriched with TOC, e.g. Mo, U, V, Zn, and Pb
b. are strongly covariant and weakly enriched with TOC, e.g. Cu, Ni, Cr, and Co

He also went further to explain the TOC-TM relationship as follows

a. In dysoxic conditions, because TM resides domninantly in the detrital phases, the TM concentrations are relatively low and invariant
b. In nonsulfidic anoxic condition, it was observed that there was strong covariation with TOC and modest TM enrichment, due to saturation with respect to TMs in the organic fraction.
c. In euxinic condition, weak covariation of TM with TOC and strong TM enrichment was observed due to the formation of TM-bearing sulfides or oxyhydroxides. The formation of such minerals is not TOC dependent.

Thus based on the pattern of TOC-TM covariation, one can estimate the proportion of TM in the detrital, organic, and sulfidic fractions of the samples (Algeo et al., 2006).

Mn exhibits very different chemical behavior compared to other TM. For example with increasing benthic anoxia, Mn becomes more depleted, depletion does not commence in anoxia, instead it commences under dysoxic conditions, and "Depletion is time integrative" (Algeo et al., 2006)

1.2.4 PENNSYLVANIAN CYCLOTHEMS

The Pennsylvanian of midcontinent North America is characterized by cyclic deposits of shales and limestones known as cyclothems (Heckel 1977, 1979, 1986). Studies conducted by Heckel (1984) highlights on the formation of black shales by "marine transgression-regression depositional cycles". Heckel (1984) divided the Midcontinent cyclothem into four stages formation of limestone by slow transgression, formation of black shales by a deep inundation, formation of limestone by slow regression, and formation of terrestrial non carbonate strata covering the limestone by withdrawal.

The waxing and waning of the Gondwanan glaciations resulted in the eustatic rise and fall of sea level which caused transgression and regression of epeiric seas in the Midcontinent. These transgressions and regressions resulted in deposition of cyclic layers of shale and limestone (Figure 3). Changes in the rate of the transgression – regression cycles could result in variations to the basic cyclothem model, for instance certain characteristics of a basic cylothem could be missing when the rate of transgression and regression is greater (Heckel, 1977, 1986).

According to Algeo (2004), the core shales of the Pennsylvanian Kansas-type cyclothems are more enriched with redox-sensitive trace metals as compared to gray shales and other organic-rich black shale deposits. The concentrations of these redox-sensitive are often used as indicators of paleo-redox conditions. Pennsylvanian cyclothemic shales represent an ideal environment to use trace metal in this way because:

a. Core shales consist of two layers, an upper layer of bioturbated gray shale and a lower layer of laminated black shale and these represent a wide range of redox conditions (which include mildly dysoxic, strongly anoxic, euxonic).
b. Since according to Heckel (1986), core shales represent depositional systems that occur in a duration of approximately 10,000 years, the chances of variation in any other chemical factor other than the benthic oxygen level is not expected.

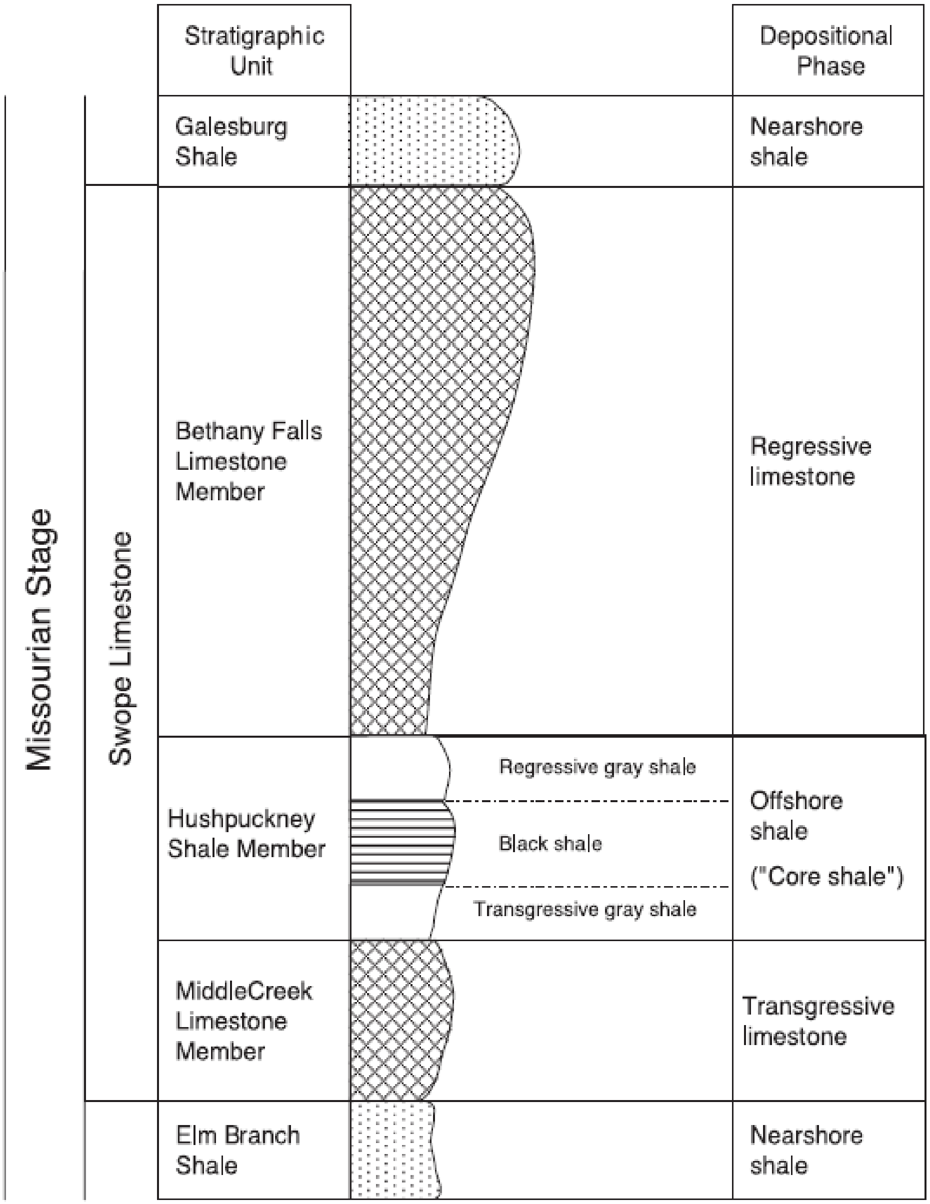


Figure 3 – Kansas type Pennsylvanian cyclothem of mid-continent North America – Stratigraphic section (Source – Cruse and Lyons, 2004)

CHAPTER II

METHODOLOGY

2.1 SAMPLING POINTS

Layers of well stratified shale and limestone can be observed in a typical Kansas type Pennsylvanian system of mid-continent North America which is typically called as cyclothem and is depicted in Figure 3 (Heckel, 1977, 1986, Cruse and Lyons, 2004). The focus of this study are the black shales and are represented in figure 3.

The black shale samples were taken from two locations i.e. Oklahoma (core C-TW-1) and Iowa (core IRC), the geographic location of which is shown in figure 4. The C-TW-1 core shale samples were taken at 8824.20, 8827.50, 8828.70, 8829.95, 8831.50, 8833.40, 8834.80, 8841.68, 8846.93, 8852.03, 8913.98, 8919.95, 8931.25, 8938.00, 8944.15, 8945.70, 8947.40, 8951.55, 8952.85, and 8954.10 cm depth. The IRC core shale samples were taken at 36602.31, 36605.21, 31611.66, 31615.66, 31619.86, 31623.34, 31626.36, 31629.89, 31634.41, 31638.96, 31646.43, 31649.08, and 31652.83 cm depth.

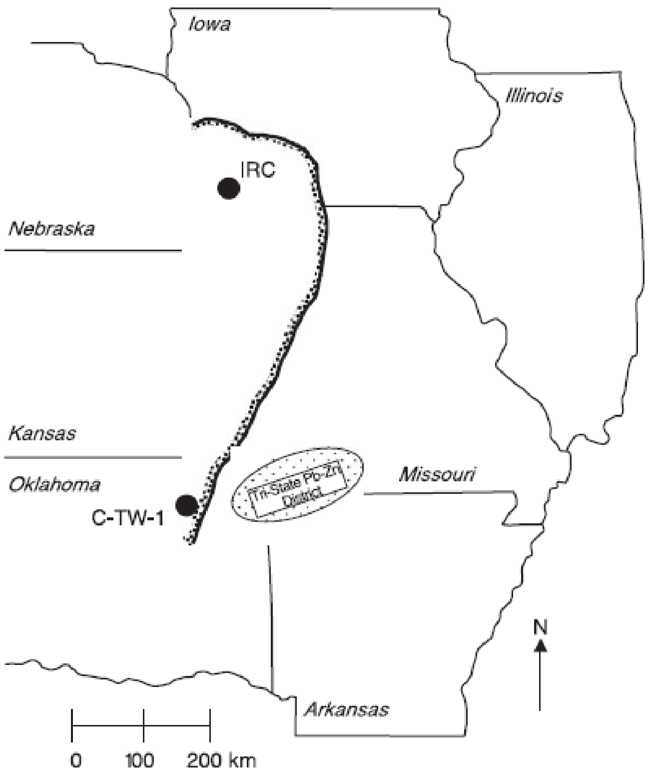


Figure 4 – Geographic location showing from where the samples where taken (Source – Cruse et Lyons, 2004)

2.2 ANALYSIS OF ORGANIC MATTER

Analysis of organics present in the black shales involved the following steps.

a. Extraction using soxhlet apparatus
b. Separation of saturated hydrocarbons, aromatic hydrocarbons, and resins by column chromatography
c. Further qualitative and quantitative analysis by gas chromatography

Each stage has been discussed in detail below. The procedure followed were standard procedures as described by Zubrick, 1984 in the organic chem lab survival manual, sixth edition.

2.1.1 SOXHLET EXTRACTION

All glassware and thimbles used for soxhlet extraction were baked at 420°C for 24 hours.

2.1.1.1PROCEDURE

1. A few boiling chips were added to a round bottom flask. Benzene or Chloroform was added as the extraction solvent, and the flask was placed on the heating mantle.
2. A known quantity (1g-4g depending on amount of sample available) of the powdered rock sample was added to the thimble and was then placed into the soxhlet by using forceps. The soxhlet apparatus was connected to the round-bottom flask condenser.
3. Water circulation in the condensers was started.
4. The heating elements were turned on to start the solvents boiling. The time when it was turned on and when it started to boil was noted.
5. The solvent refluxed continuously for 48-72 hours until that the solvent in the soxhlet siphon tube was transparent, indicating completion extraction of bitumen from the rock.
6. After the soxhlet apparatus was turned off, it was allowed to cool. The thimble was lifted with forceps to allow the solvent inside the thimble to drain into the soxhlet.
7. The solvent in the siphon tube was transferred to the flask which was then filtered through a teflon (0.45 micron 47mmOD) laminated filter. The flask and the siphon tube were rinsed thoroughly with fresh solvent.

8. The solvent was then transferred to a tared vial and dried under the hood. The amount of bitumen extracted was calculated. This extracted bitumen was then run in column chromatography to separate into saturate hydrocarbons, aromatic hydrocarbons, and resins.

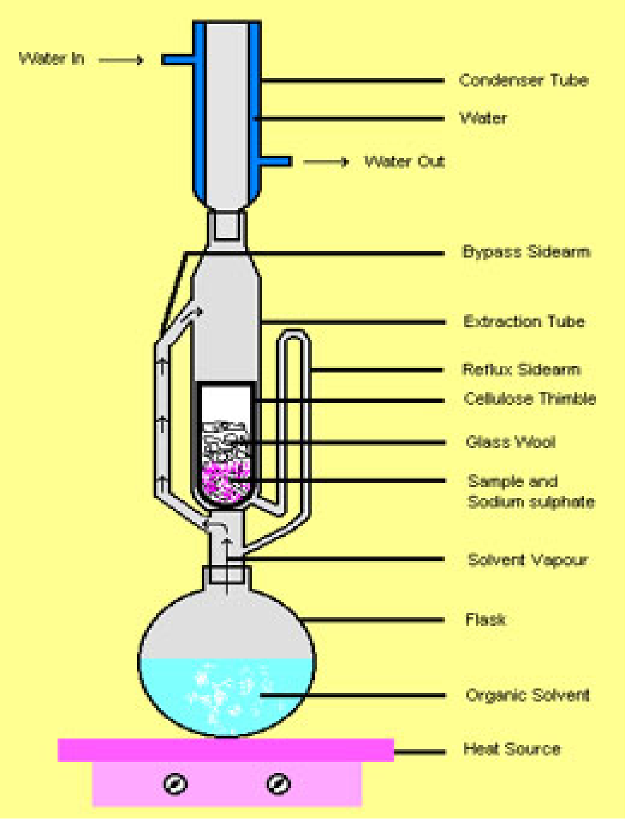


Figure 5 – Schematic representation showing the components of Soxhlet extraction (Source – Bergoin Francois and Bening Michael, n.d., retrieved from http://web2.slc.qc.ca/jmc/www/Chemweb/oldchemweb/extractionmethods.htm on October 20, 2006)

2.1.2 COLUMN CHROMATOGRAPHY

Column chromatography was performed to separate the extracted bitumen into saturate hydrocarbons, aromatic hydrocarbons, and resins. Columns were prepared using silica (Grade 923 and 62) and alumina. Glass wool was baked at 420°C for 24 hours.

2.1.2.1 PREPARATION OF COLUMNS

1. Silica gel and alumina were baked at 420°C for 24 hours. It was then cooled in the dessicator.
2. Silica and alumina were partially deactivated by adding 5% (1:20 w/w) and 1% (1:100 w/w) water respectively. The material were mixed thoroughly and allowed to stand for 24 hours before the actual preparation of the column.
3. The cotton plug was removed from a disposable (5ml) sterile serological pipette. A small ball of baked glass wool was pushed to the tip of the pipette using a glass rod. A small piece of GF/A filter paper was cut and pushed to the tip of the pipette.
4. Silica gel grade 923 and 62, and alumina were mixed with iso-octane in a small flask. Care was taken that none of them got dried out and that they did not have any air bubbles.
5. The disposable serological pipettes were mounted on burette stand and silica (923) gel slurry was added to the pipette until just above the 2ml mark on the column. For even distribution and removal of air bubbles the column was gently tapped using the glass rod.

6. Silica gel grade (62) was then added until just above the 0 mark.
7. Approximately 2 to 3 cm of alumina slurry was added to the column. The column was then stored in a graduated cylinder, completely immersed in iso-octane.

2.1.2.2 COLUMN CHROMATOGRAPHY

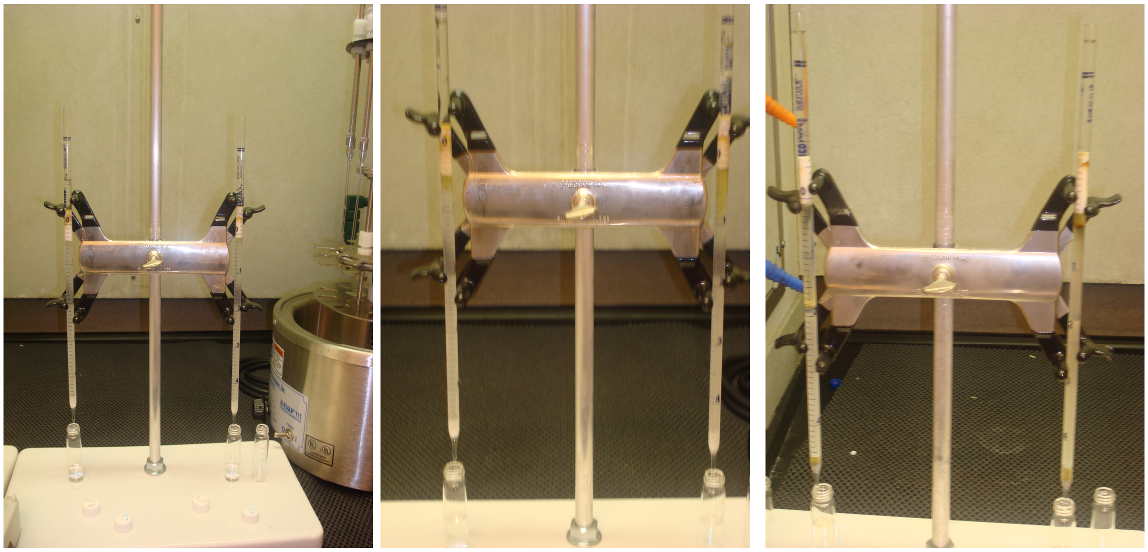
To run the bitumen samples in the prepared columns, the asphaltene fraction of the bitumen was first separated from the maltene fraction.The extracted bitumen was first dissolved in chloroform. It was then evaporated in a nitrogen evaporator until approximately 1 ml chloroform was left in the vial. Iso-octane was added to the vial and again evaporated. The procedure was repeated 3 times so as to ensure all of the chloroform was removed and replaced with iso-octane. The fraction that remained in the vial was filtered using a 0.45 micron Teflon filter. The filtrate, i.e. the maltene fraction, was subject to column chromatography. The asphaltene fraction that remained in the filter was dissolved using chloroform and added to a separate tared vial. The amount of asphaltene fraction present was calculated.

The maltene fraction that was obtained was evaporated in the nitrogen evaporator until it reached a volume of approximately 1 ml and was run in the Si-Al column using different solvent for separation of the different fractions, as follows:

1. The packed column was placed on the burette stand and the solvent was allowed to drip into a waste container. Care was taken that the column never became dry.

2. The deasphaltened sample was added to the column and as the sample moved down, iso-octane was added as an eluent. Approximately 3ml was collected in the waste beaker, after which the saturated hydrocarbon eluted with iso-octane was collected in a tared and baked 2-dram vial.
3. After approximately 3.5ml of the saturate fraction was collected, the sample was eluted with the aromatic hydrocarbon solvent benzene. Additional saturate faction was collected until it was observed that the aromatic front, which has a distinct yellow color, had moved down to the 4ml mark on the pipette.
4. A new tared and baked 2-dram vial was taken to collect the aromatic fraction. After approximately 3.5ml of the aromatic fraction was collected, the remaining material was eluted with the polar solvent benzene/methanol (60:40 v/v). Collection of the aromatic fraction was continues until the polar fraction had moved down, which was dark brown.
5. The resin fraction was collected in a new tared and baked 2-dram vial. This fraction was collected until the eluate became colorless.

Samples were dried and the saturate, aromatic and the resin fractions obtained by column chromatography were calculated. Before the saturate fractions obtained by column chromatography were run on a gas chromatograph (Perkin Elmer Claras 500), the volume was reduced to approximately 3ml by nitrogen evaporator. The C14 – C32 saturate () were analyzed at the beginning of a run, as well as after every 10 samples, to ensure instrument performance.



Stage 1 – Saturates

Stage 2 – Aromatics

Stage 3 - Resins

Figure 6 – Photograph showing separation of organic matter by column chromatographic method to saturate hydrocarbons (Stage 1), aromatic hydrocarbons (Stage 2), and resin fraction (Stage 3).

2.1.3 GAS CHROMATOGRAPHY FLAME IONIZATION DETECTOR (GCFID)

The parameters used in the instrument during analysis are as follows. The column length was 60m, and column flow – 2.5mL/min. the method that was used for injection was splitless. Approximately 2.0 µL of sample was injected. An air flow of 350 mL/min, and a H_2 flow of 35 mL/min into FID was maintained. The results obtained are discussed in subsequent sections of the thesis.

2.2 ANALYSIS OF TRACE METALS

Quantitative analysis of trace metals was performed using the following steps

a. Acid digestion of trace metals using microwave digester
b. Quantitative analysis by inductive coupled plasma optical emission spectroscopy.

It was not possible to quantify metals in the bitumen due to small sample size. Therefore, the extracted rock was analyzed for trace metals. The amount of each metal present in the unextracted shale samples were previously reported by Cruse and Lyons (2004). The difference in concentration between extracted and unextracted samples is the equal to the concentration in the extracted bitumen.

2.2.1 MICROWAVE DIGESTION

The black shale samples were dissolved using microwave acid digestion. The procedure and program followed for the microwave digestion was similar to that of Ianni et al (2003) modified using procedures from Lipinski et al (2003) and Horckmans et al (2005).

1. Approximately 0.5g sample was added to ae teflon vial inside the microwave digester with 10 ml aquaregia (3:1 HNO3:HCl).
2. Apparatus was placed in the microwave digester unit and heated as follows 250 W – 5 min, 320 W – 5 min, 380 W – 10 min, Fan (for cooling) – 10 min. the samples were allowed to cool inside the microwave.
3. The digested samples were transferred to a glass beaker. The Teflon vessel was rinsed thoroughly with 2% nitric acid.
4. The samples were heated in a heating mantle to evaporate the acid. 2% nitric acid was added to the dried sample and evaporated.
5. The above procedure was repeated 3 times so that all of the concentrated acid gets evaporated and just 2% nitric acid remains.
6. The sample was filtered and brought to 10 ml using 2% nitric acid.
7. After completion of one set of microwave digestion, the microwave digester vessels were cleaned thoroughly with wet cloth and dried, followed by a cleaning run. The cleaning run included the following program 1000W – 20min, Fan (for cooling) – 10min. 4ml nitric acid was added during this run.

2.2.2 INDUCTIVE COUPLED PLASMA – OPTICAL EMISSION SPECTROSCOPY (ICP-OES)

The acid digested samples were analyzed for different metals in ICP-OES. The metals analyzed included uranium (U), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), strontium (Sr), rubidium (Rb), sodium (Na), magnesium (Mg), potassium (K), galium (Ga), cesium (Cs), calcium (Ca), aluminium (Al), zinc (Zn), manganese (Mn), and vanadium (V).

2.2.2.1 PROCEDURE

1. The acid-digested samples as per the steps mentioned above were further diluted (approximately 1:25) before analysis using 1% nitric acid for uranium and 2% nitric acid for all other metals and analyzed in the ICP-OES.
2. Standards were prepared in 1% nitric acid for uranium and 2% nitric acid for all other metals.
3. Concentrations measured were in the diluted samples were converted to the concentrations in the original samples using the following formula

$$\text{Concentration in ppm} = \frac{I_0 \times W_1 \times W_3}{W_2 \times W_4 \times 1000}$$

where

I_0 – Concentration obtained from ICP-OES

W_1 – 10 ml. First dilution

W_2 – Amount of initial sample taken in g.

W_3 – Total weight after second dilution

W_4 – Weight of sample in second dilution

1000 – Conversion factor to ppm.

CHAPTER III

RESULTS

3.1 RESULTS OBTAINED BY ANALYSIS OF ORGANIC MATTER

Organic fractions separated by column chromatography were dried and the sample weights were recorded. This gave the amount of saturate hydrocarbons, aromatic hydrocarbons and the NSO's (resins and asphaltenes) present in the samples. Tables 1 and 2 lists the organic fractionations in bitumen extracted in both benzene and chloroform, respectively, in the Oklahoma black shale samples while Tables 3 and 4 lists the organic fractionation of bitumen extracted using benzene and chloroform, respectively, in the Iowa samples. The bitumen in the Oklahoma and Iowa samples were first extracted using benzene. However the amount of bitumen extracted by benzene in the Iowa samples was very less and hence the bitumen in the samples were again extracted by using chloroform as the solvent instead of benzene. Difference between the amount of bitumen extracted by use of two solvents can be seen in tables 3 and 4. it can be observed that while bitumen extracted by use of benezene in the IRC black shale core range from 1.2 to 3.2 mg/g, the amount of bitumen extracted by use of chloroform was much greater in the range 2.28 – 8.79 mg/g. Bitumen from only two samples of the C-TW-1 core was extracted by use of chloroform as solvent. This was done to check if use of chloroform as solvent would enhance the amount of bitumen produced. No such difference was observed in the amount of bitumen extracted by use of two different solvents.

Figure 7 shows a plot of bitumen versus depth in C-TW-1 and IRC core shale samples. The figure clearly shows that at lower depths the amount of bitumen extracted is more as compared to as we go deeper. Around the middle there is a big difference in the amount of bitumen extracted (8852.03cm to 8913.92 where bitumen drops from approximately 10mg/g to approximately 4.5mg/g). As we go deeper, we can observe an increase in bitumen extracted (from approximately 3.15mg/g to 4.44 mg/g). Figure 8 shows a plot of depth versus TOC (values from Cruse and Lyons, 2004) and bitumen, to show the relation between the two.

The amount of saturate hydrocarbon and aromatic hydrocarbon present in the C-TW-1 core (S:0.9 – 2.5 mg/g; A:0.4-1.5mg/g) is more than the amount that was present in the IRC core shale samples (S:0.12 – 0.49mg/g; A: 0.06-1.04mg/g using benzene as solvent; S:0.15 – 0.57mg/g; A: 0.30-0.86mg/g using chloroform as solvent). Conversely, NSO (resins and asphaltene) fraction was found to be a more in the IRC core shale samples extracted using chloroform as solvent (R:0.64 – 3.48mg/g;P:0.62 – 3.88mg/g) as compared to the C-TW-1 (R:0.7 – 2.5mg/g; P:0.1-1.4mg/g) core shale samples. Resin and asphaltene fraction extracted using benzene as solvent in the IRC core (R:0.24 – 1.04mg/g;P:0.01-1.03mg/g) shale samples were less than that of C-TW-1 shale samples.

Black shale samples from Oklahoma and Iowa were analyzed on the GC-FID for qualitative and quantitative determination of individual saturated hydrocarbons. The maximum and minimum peaks were determined from the chromatograms. Other ratios like pristine/Phytane (Pr/Ph), Pristane//nC_{17} (Pr/nC_{17}), Phytane/nC_{18} (Ph/nC_{18}), and CPI

(Carbon preference Index) were also calculated which is shown in the table below. Tables 5 and 6 lists the values for the bitumen extracted in benzene and chloroform respectively in the Oklahoma black shale samples while Tables 7 and 8 lists the organic fractionation of bitumen extracted using benzene and chloroform in the Iowa samples. The maximum peak obtained for all Oklahoma samples except one was nC_{19}. For Iowa while most samples showed a maximum at nC_{19}, some did show variation with a maximum at nC_{18} or nC_{32}. There was no trend observed with respect to the minimum. A detailed discussion on the results obtained can be seen in the discussion section.

3.2 RESULTS OBTAINED BY ANALYSIS OF TRACE METALS

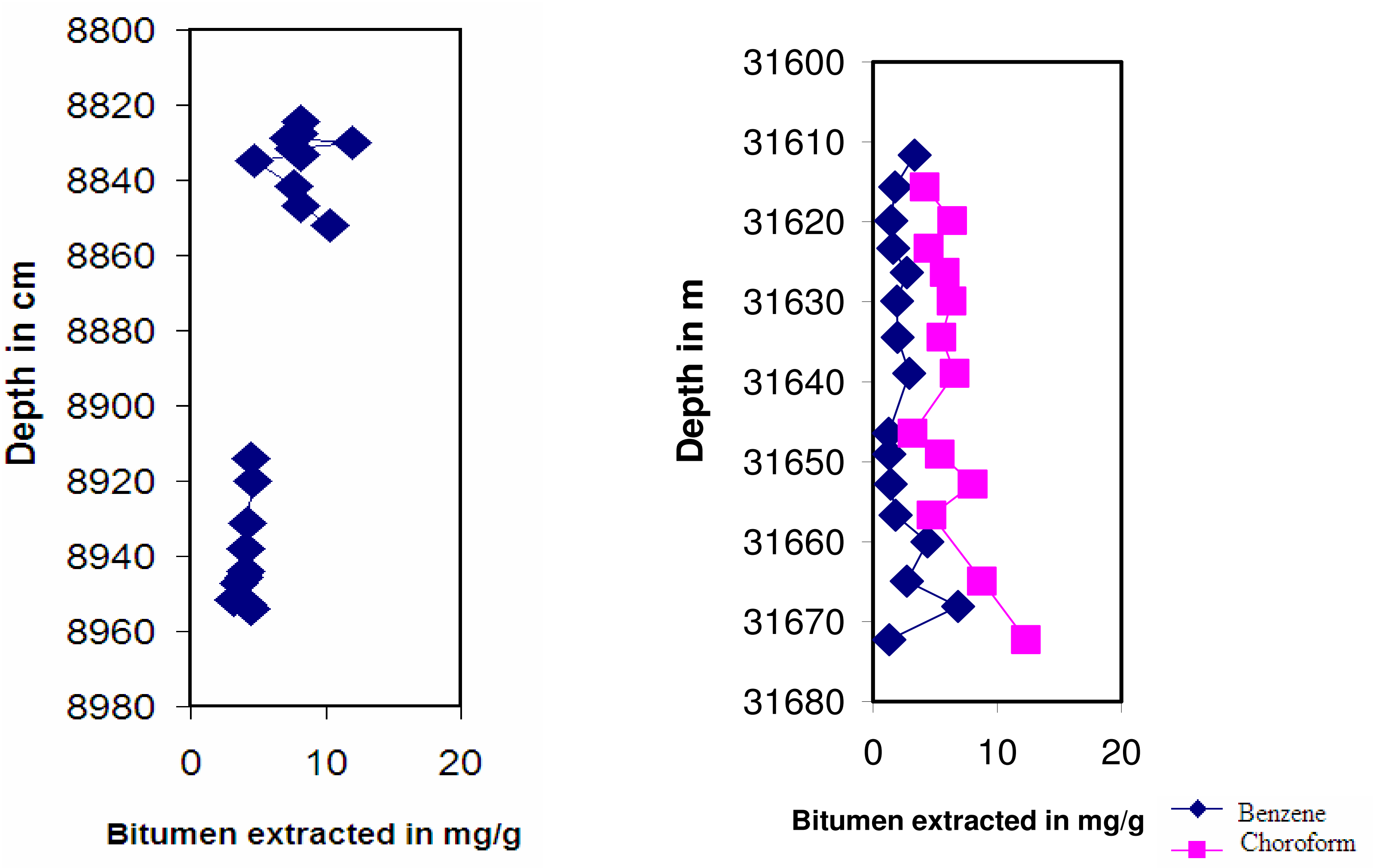
Results obtained for trace metals analyzed in the ICP-OES are as shown below. Tables 9 and 10 show the quantitative and qualitative estimation of the extract of Oklahoma black shale samples after bitumen has been extracted using benzene and chloroform respectively. Tables 11 and 12 show the quantitative and qualitative estimation of the extract of Iowa black shale samples after bitumen has been extracted using benzene and chloroform respectively. Metals like Fe, Na, K, Ca, and Al were found in high concentrations in both the Oklahoma and the Iowa shale samples. However to get a better insight we need to calculate the ratio of metals like Fe to that of Al which is done in the discussion section of the thesis. On comparison the results obtained with the results of Cruse and Lyons in bulk sample, there was a definite reduction observed in concentration of some metals like vanadium, magnesium, lead, nickel, and zinc. Uranium did not show much reduction while iron surprisingly showed an increase.

CHAPTER IV

DISCUSSION

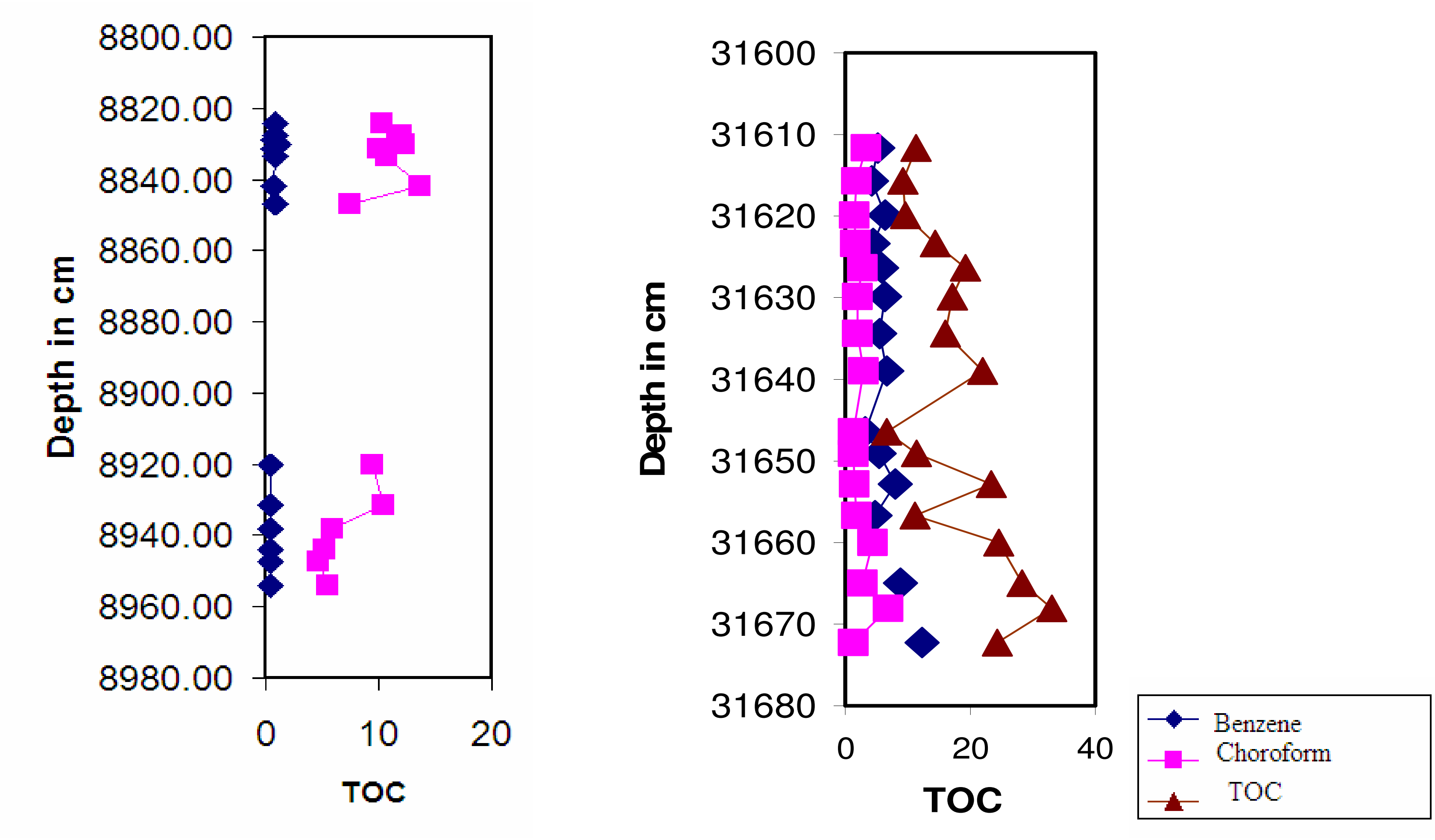
4.1 BITUMEN COMPOSITION

The organic analysis of the core shale samples from Oklahoma (C-TW-1) and Iowa (IRC) showed considerable difference. First, extractable organic matter from C-TW-1 was less polar as compared to the IRC shale samples (Figure 7A and 7B). Figure 7A shows the amount of bitumen extracted using benzene in C-TW-1 shale samples while figure 7B shows the amount of bitumen extracted using benzene and chloroform in the IRC shale samples. Chlorform is polar in nature, and higher amount of bitumen extracted by use of chloroform as solvent implies that the organic matter present in the shales samples of Iowa are highly polar in nature as like dissolves like. Bitumen from two of the C-TW-1 samples were extracted by use of chloroform as solvent and the amount extracted was approximately the same as that extracted by use of benzene as solvent. Hence all C-TW-1 samples were not extracted using chloroform as solvent. Figures 8A and 8B show plots of depth versus bitumen and TOC (values taken from Cruse and Lyons, 2004) in C-TW-1 and IRC core shale samples respectively. This was done to study any correlation in the amount of bitumen extracted to the TOC content in the rock. As can be seen in figure 8, there is direct correlation between the TOC content and bitumen extracted. This could be further confirmed by graph plotted of TOC versus bitumen (Figure 9A and 9B) where one can observe a direct correlation between the two. Similarly, graph was plotted for IRC shale samples.



(A) (B)

Figure 7 – Graph showing amount bitumen extracted from black shale samples at different depths in A) C-TW-1 using benzene as solvent and B) IRC using benzene and chloroform as solvent.



(A) (B)

Figure 8 – Graph showing relation of bitumen extracted with TOC from previous work by Cruse and Lyons (2004) in A) C-TW-1 and B) IRC core black shale samples.

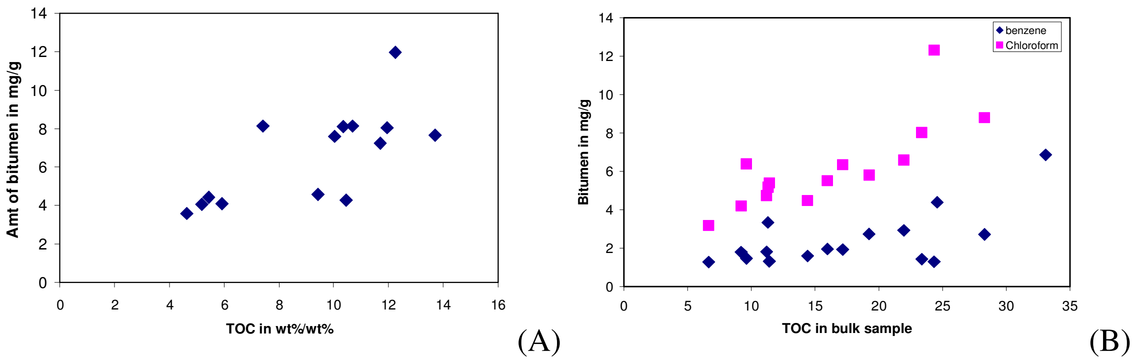
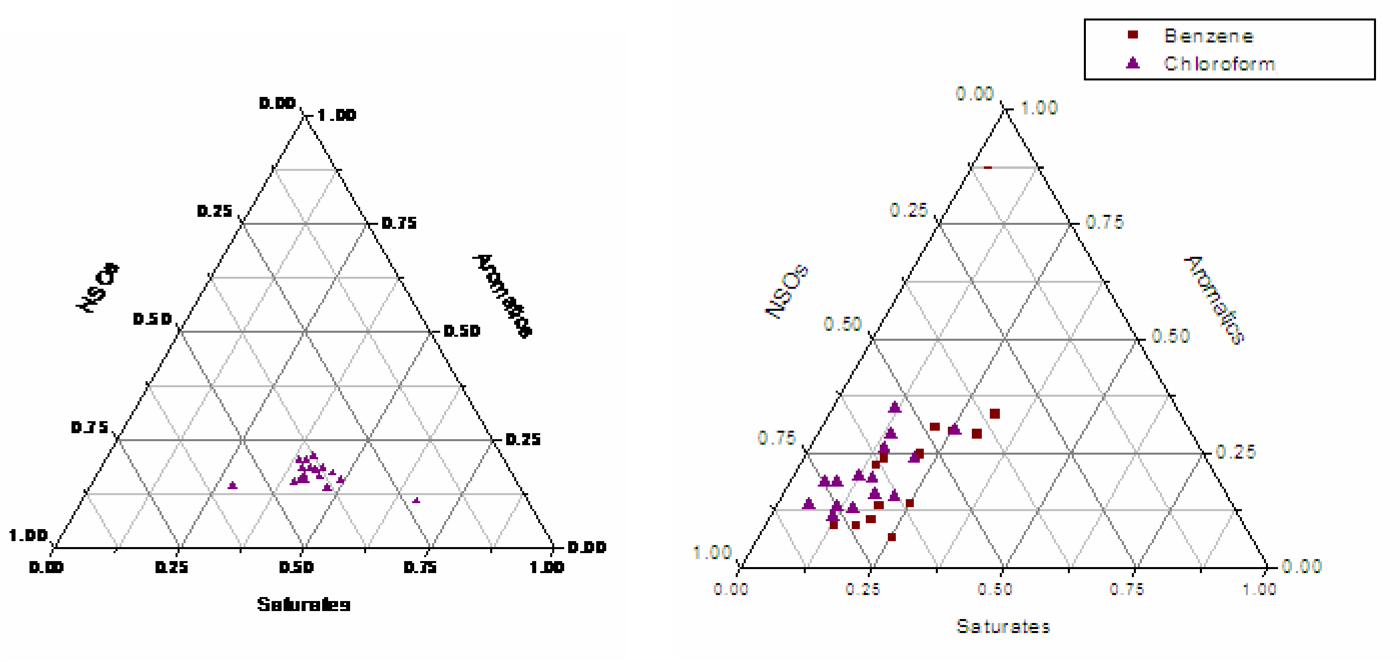


Figure 9 - Graph showing relation of bitumen extracted and Total organic Carbon (TOC) in bulk sample (values obtained from Cruse and Lyons, 2004) in A) C-TW-1 and B) IRC core shale samples.

Figures 10A and 10B show the ternary diagrams of bitumen composition extracted from the C-TW-1 and IRC samples. Resins and asphaltenes are combined to give NSO's (Nitrogen, Sulfur, Oxygen compounds), and the amounts of saturates, aromatics, and NSO's are then normalized to 100% (Table5, Table 6, Table 7, and Table 8).



(A)

(B)

Figure 10 – Ternary Diagram of fractionation of A) bitumen extracted using benzene as solvent in C-TW-1 core shale samples and B) bitumen extracted using benzene and chloroform as solvent in IRC core shale samples

As can be seen in figure 10, the saturate fraction constitutes half of the total bitumen extracted from the C-TW-1 samples while the remaining 50% is shared by the aromatics and the NSO's. The aromatic fraction was approximately the same for all the samples.

In comparison, the IRC samples consisted of less saturate fraction and a considerably larger NSO fraction. A comparison of samples extracted using benzene and chloroform shows that amount of saturate extracted using benzene is greater than that using chloroform. This is probably because of the non polar nature of the organic matter present in IRC core shale samples. The IRC core shale samples are observed to be extremely rich in NSO. Although having higher concentration of NSO indicates the maturity of the sample (Tissot and Welte, 1978; Killops and Killops, 2002), we know from study by Hatch and Newell (1999) discussion that IRC core shale samples are immature in nature relating to oil generation (Tissot and Welte, 1978; Killops and Killops, 2002; Hatch and Newell, 1999). Organic matter of terrestrial origin are rich in NSOs (Wayne, 1970) and hence, it is probable that IRC shale samples have more terrestrial organic matter in them which is giving rise to the high NSO concentration. Cruse and Lyons (2004) showed that all IRC core shale samples had more metals present in them as compared to the C-TW-1 shale samples (Cruse and Lyons, 2004). This is with the exception of Iron which was observed to have higher concentrations in the C-TW-1 samples. One of the probable reasons explained in the paper was that the organic matter that is present in the C-TW-1 core shale samples are not very efficient in fixing metals, as opposed to the organic matter present in the IRC core shale samples. NSOs are excellent scavengers of trace metals (Cruse and Lyons, 2000) and high concentration of NSO observed in the IRC core shale samples is a step forward in explaining the above theory.

4.2 ORGANIC MATTER SOURCE

The chromatograms of the saturate hydrocarbon fraction of the two shale samples analyzed in GCFID were very different in their basic nature (Figure 11 and Figure 12). The C-TW-1 core shale sample chromatograms showed more types of biomarkers as compared to the IRC core shale samples. The two C-TW-1 samples that were extracted using benzene and chloroform were compared. Qualitatively, one of samples showed great resemblance in the chromatograms produced regardless of solvent, although quantitatively they were different. However, the second sample (294.017B) showed a lot of difference both inqualitative and quantitative terms. All samples need to be extracted using chloroform as solvent to better understand this discrepancy. The hump that was observed in some of the samples in the C-TW-1 core shale samples showed an increase till 8852.03 cm depth (Figure 11) followed by a drop and was almost consistent throughout for the rest of the samples. For IRC core, the chromatograms of saturate hydrocarbon, extracted by different solvents was similar. The hump that was observed in the C-TW-1 samples was not significant in the IRC samples. Some variation was observed which could be attributed to the use of different solvents. Benzene is an aromatic ring with alternate single and double bonds between carbon atoms (Formula – C_6H_6). There is no net dipole in the benzene molecule as the charge gets balanced. However Chloroform (Formula $CHCl_3$) is polar in nature as the charge does not get balanced. Since “like dissolves like”, more bitumen extracted in the IRC core shale samples is due to the polar nature of the organic matter in the samples.

These results were compared with those extracted from coal (Welte and Tissot, 1978). It was observed, with the intention to compare it with the above chromatograms so as to help in determining whether IRC could be of terrestrial origin based on the biomarker sequence in the chromatograms. However it was observed that depending on the stage of coal formation, the biomarker distribution varies (Welte and Tissot, 1978) and hence cannot be used as a conclusive factor in determining the origin of organic matter in the shale.

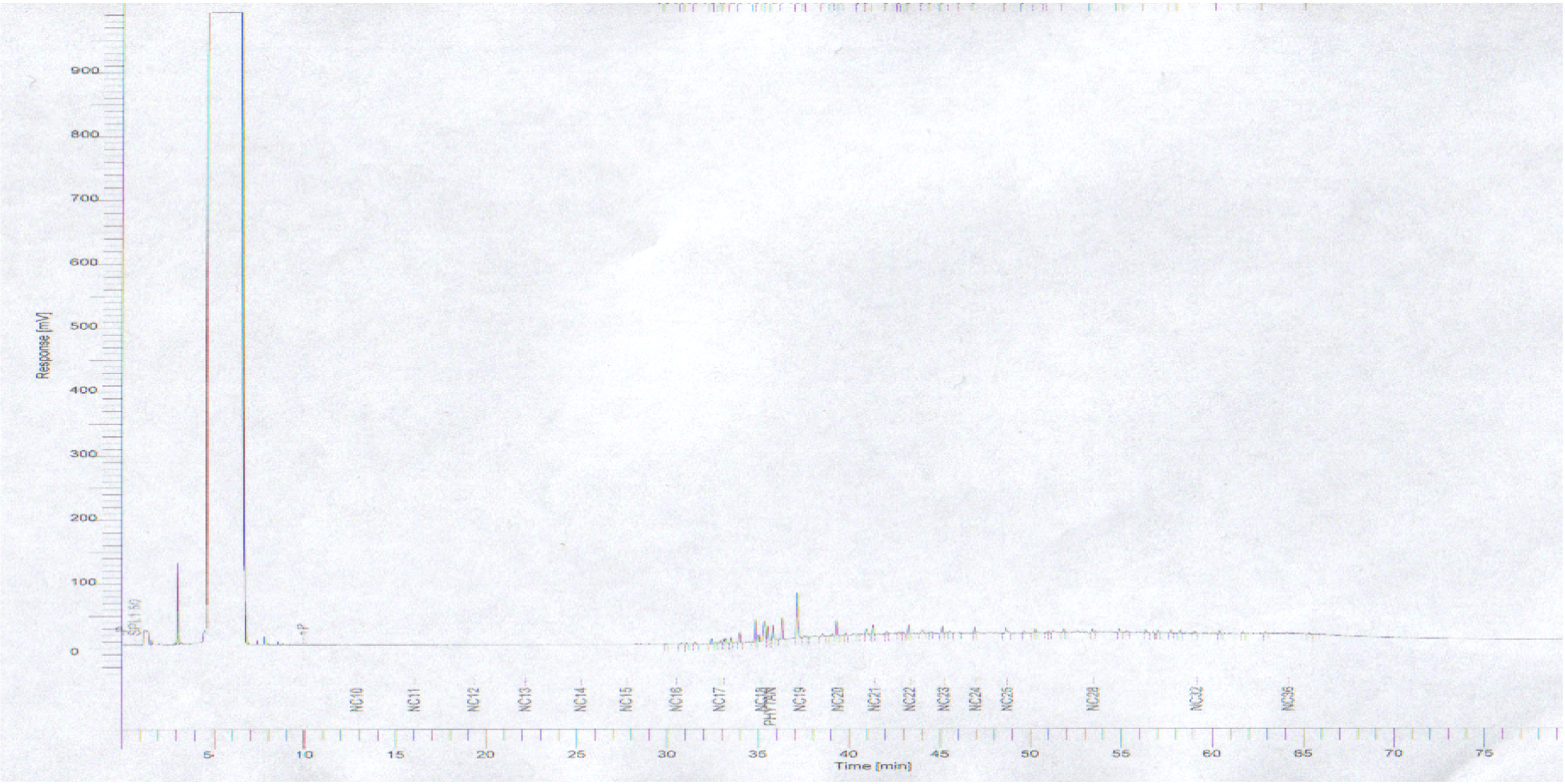
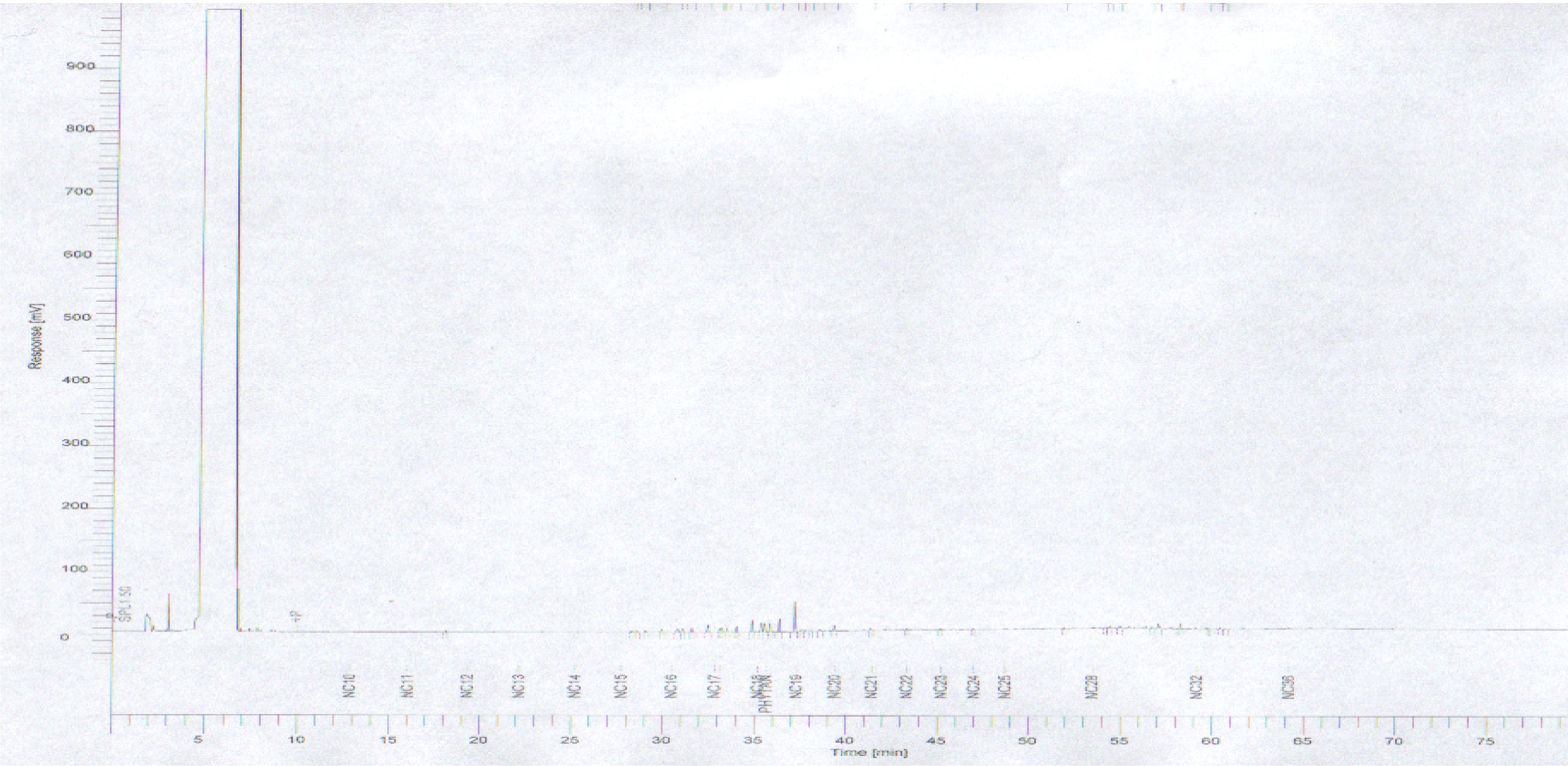


Figure 11 - Chromatogram obtained after sample C-TW-1 (294.0 14B) was extracted in benzene and was run in gas Chromatography Flame Ionization Detector (GC-FID).



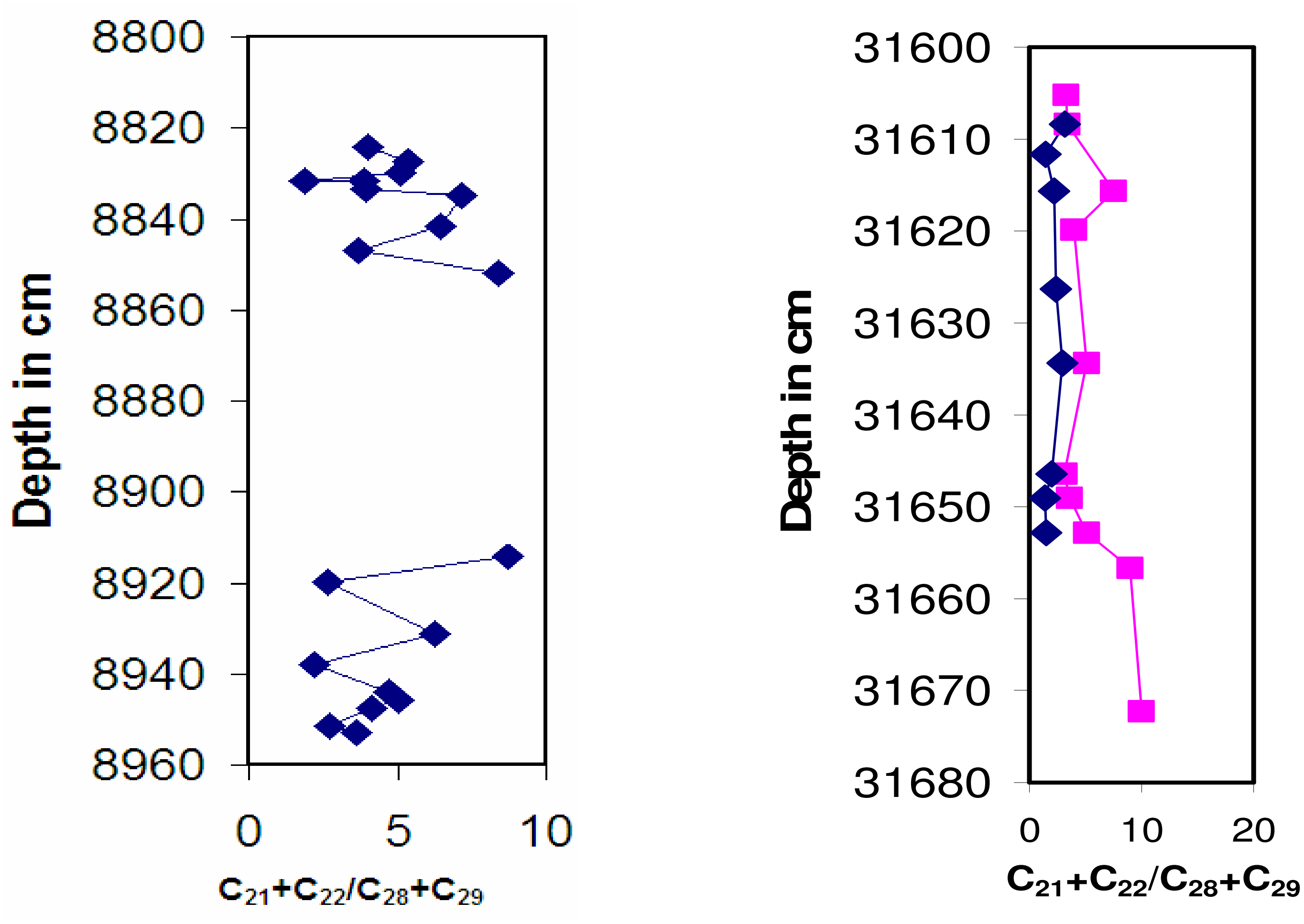
(B)

Figure 12 – Chromatogram obtained after sample IRC(1036.78B) was extracted in benzene and was run in gas Chromatography Flame Ionization Detector (GC-FID).

4.3 SATURATE BIOMARKERS

4.3.1 ALKANE DISTRIBUTIONS

Organic matter derived from marine sources typically contains smaller *n*-alkanes than nC_{24} and has a peak at $nC_{17.}$ In contrast terrestrial higher plants have an alkane distribution dominated by nC_{27}, nC_{29} or nC_{31}. (Stuermer and Simoneit, 1978; Simoneit 1974, 1977; Welte 1968). Terrestrial higher plants also contain more odd numbered carbon atoms to even numbered carbon atoms. In C-TW-1 samples all samples but one () have a maximum at nC_{19}. There is no specific pattern that the maximum and minimum value for IRC samples, however, in general till 31638.96cm depth the maximum value is at nC_{19} (Figure 13; Table 7). However as depth increased one can observe the maximum shifting to nC_{23} and $nC_{32.}$ indicating a shift from dominant marine to dominant terrestrial origin. Philippi (1974) studied the composition of petroleum with respect to its organic matter and on the source of the organic matter. They separated the *n*-alkanes by distillation process. He showed that organic matter of terrestrial origin has an (nC_{21}+nC_{22}/nC_{28}+nC_{29}) ratio of 0.6 – 1.2 while that of marine origin has a higher ratio from 1.5 – 5.0. Both the C-TW-1 and the IRC shale samples show a ratio of greater than 1.5(Figures 13), although the values are generally higher for the C-TW-1 samples as compared to the IRC. Figures 13A and 13B show variation of the ratio with respect to depth in C-TW-1 and IRC core shale samples respectively. A sequential increase and decrease can be observed in the ratio values with respect to depth. In IRC core shale samples, the ratio is observed to be a lot more with samples extracted using chloroform as compared to with benzene (Figure 13).



(A) (**B**)

Figure 13 – Graph showing biomarker ratio $nC_{21}+nC_{22}/nC_{28}+nC_{29}$ at different depth in A) C-TW-1 and B) IRC core shale sample

4.3.2 PRYSTANE/PHYTANE

Phytol, present in chlorophyll, is the precursor for formation of pristane and phytane. In the presence of oxygen phytol forms phytenic acid which loses carbon dioxide to form pristene. This reacts with hydrogen forming pristane. Phytane on the other hand is formed under reduced conditions. In absence of oxygen phytol forms dihydrophytol which loses a water molecule to form phytane (Welte and Tissot, 1978). Thus, pristane is formed under oxygen rich condition while phytane is formed in oxygen-deficient conditions and hence the ratio is an organic proxy for paleoenvironemtnal conditions.

A ratio of less than 1 indicates anoxic condition while a ratio greater than 1 indicates oxic conditions. A ratio approximately equal to 1 does not imply anything specifically as the origin could be either oxic or anoxic. (Peters et al., 2005)

While many of the IRC samples showed absence of prystane, only one C-TW-1 sample showed no prystane. The samples from C-TW-1 have ratios 0.5 – 1.3 shows a clear indication of anoxic paleoenvironemntal conditions initially followed by oxic and again followed by anoxic conditions (Figure 14; Table 5). However in IRC, no such trend is observed and many samples have no pristane (Table 7). However, based on how pristane is formed we can conclude that anoxic conditions probably existed which is the reason behind pristane probably never being formed in the IRC shale samples.

Figure 14 shows the trend of the ratio with respect to depth. There is an increase in the ratio followed by a decrease in the C-TW-1 core shale samples. In IRC samples too the ratio decreased with depth showing increase in anoxic conditions with depth.

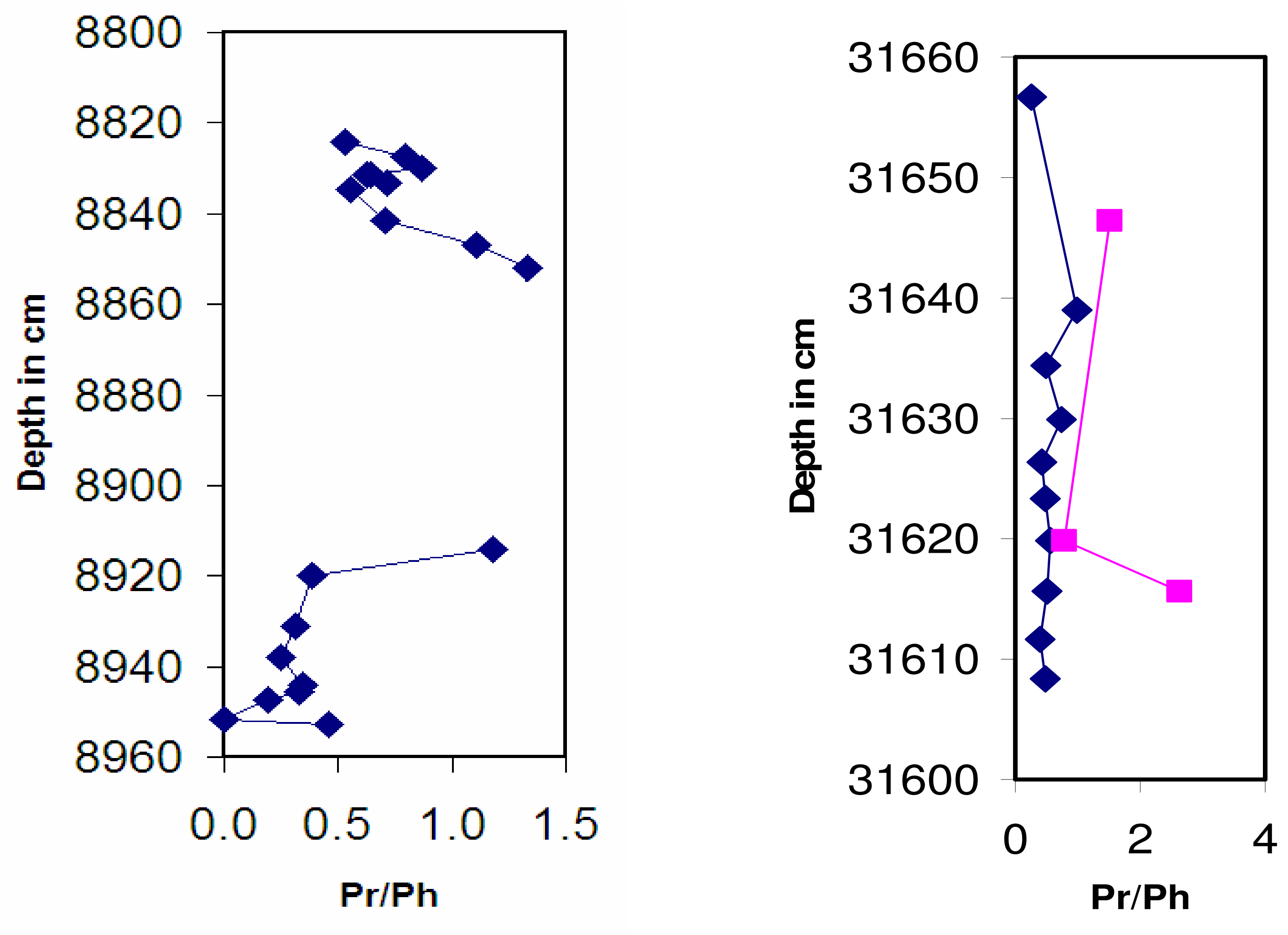
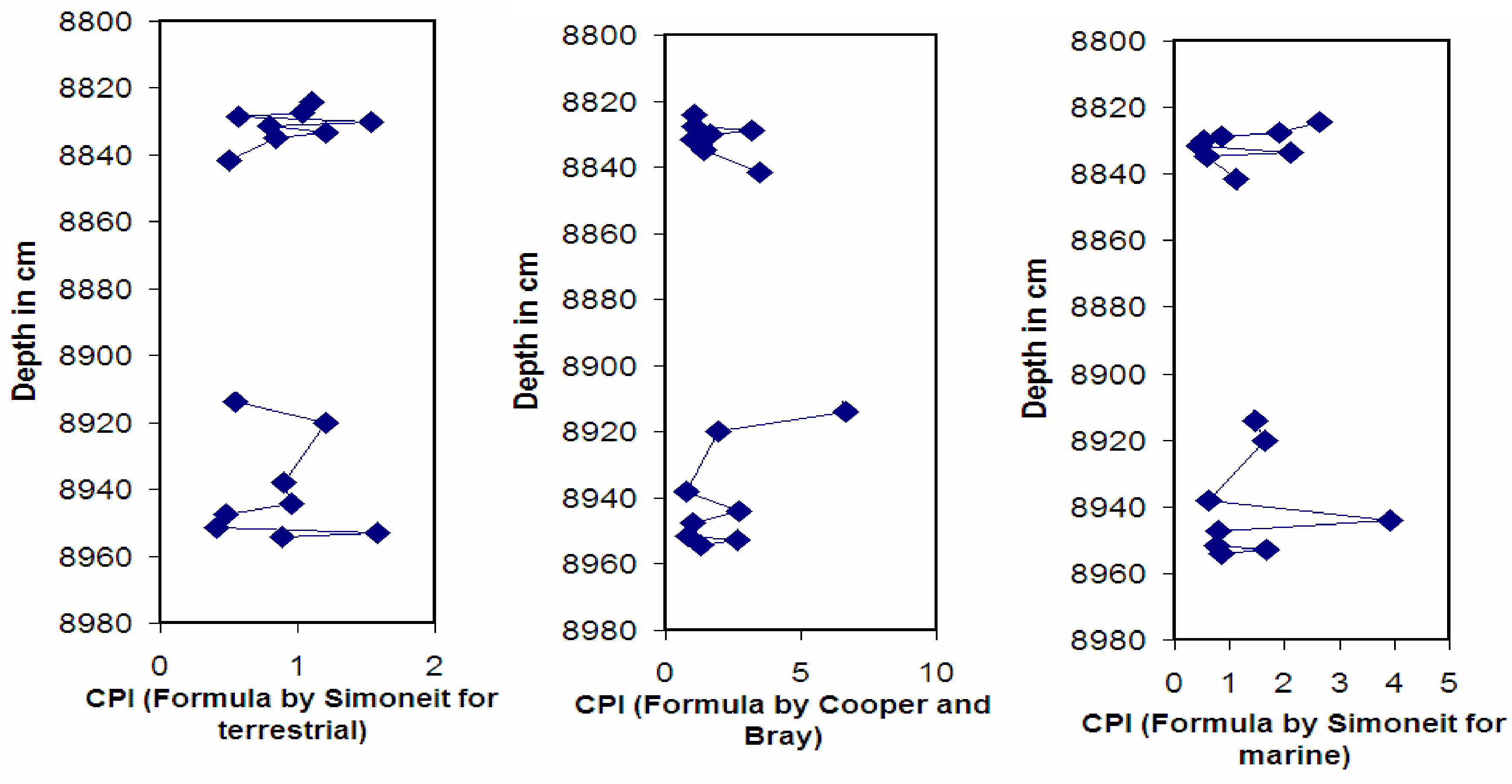


Figure 14 – Graph showing biomarker ratio Pr/Ph at different depth in A) C-TW-1 and B) IRC core shale sample

Other ratios like Pristane/nC_{17} and Phytane/nC_{18} were also calculated (Table 6). An increase in the ratio is indicative of maturity in the samples (Peters et al., 2005a, 2005b). An increase in the ratio was observed in both the core samples with depth till around the middle, following which the ratio started to decrease. This indicates presence of more mature organic matter along the center region of the complete shale sequence which was common in both locations i.e. C-TW-1 and IRC.

4.3.3 CARBON PREERENCE INDEX

Carbon preference index in the ratio of odd to even numbered carbon atoms present in a sample. A predominance of odd carbon atoms over even carbon atoms is observed in terrestrial organic matter. Analysis of organic matter present in higher plants by Cooper and Bray showed that they have a high CPI ratio of grater than 5 (Cooper and Bray, 1963). Carbon Preference Index (CPI) was calculated by two the formula described by Cooper and Bray (1963). This is the most common method of detrmining CPI and has been used in many studies (e.g. Simoneit, 1978). The CPI value for C-TW-1 shale samples was mostly in the range of 0.4 to 1.1 and it was almost the same for the two samples that were extracted in chloroform. The same was not true for IRC shale samples wherein the difference in values between samples extracted by benzene and chloroform is evident as can be seen in Table 6. Simoneit (1981) developed specific formulae for organic matter that was expected of marine or terrestrial origin. CPI was calculated using these formulae for samples analyzed by USGS to check on its relevancy with the study. Figure 15 shows CPI calculated from data analyzed by USGS in the C-TW-1 core shale samples.



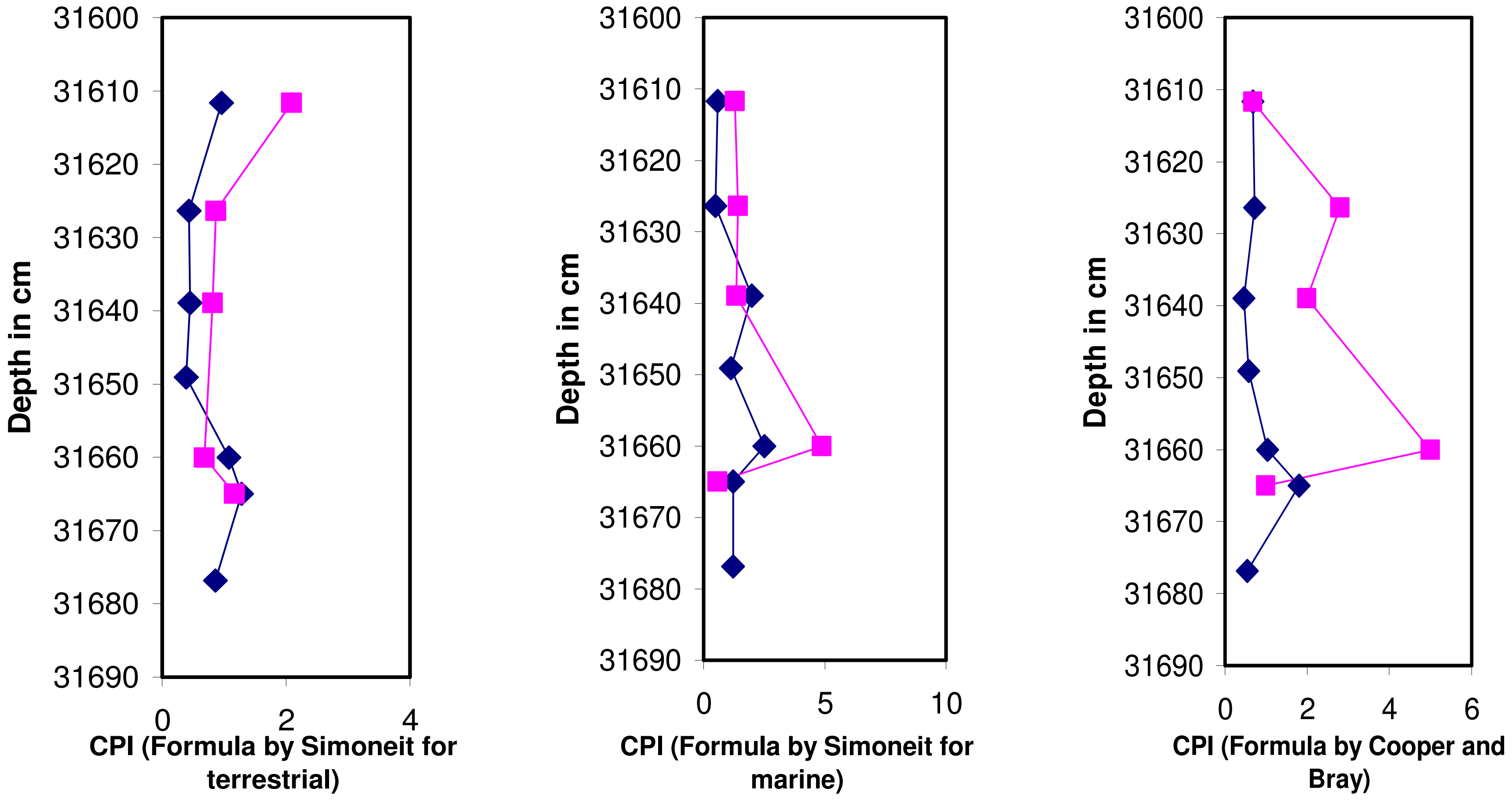
(A) (B) (C)

Figure 15 – Graph showing biomarker ratio CPI at different depth for C-TW-1 core shale samples analyzed by USGS by using different formula A and C) By Simoneit (1978) for terrestrial and marine organic matter respectively and B) By Cooper and Bray(1963)

As can be observed in figure 15, CPI values for organic matter of marine origin is more than that of terrestrial origin. CPI formula by Cooper and Bray showed high values. Similarly figure 16 shows CPI values calculated by the three methods in IRC core shale samples.

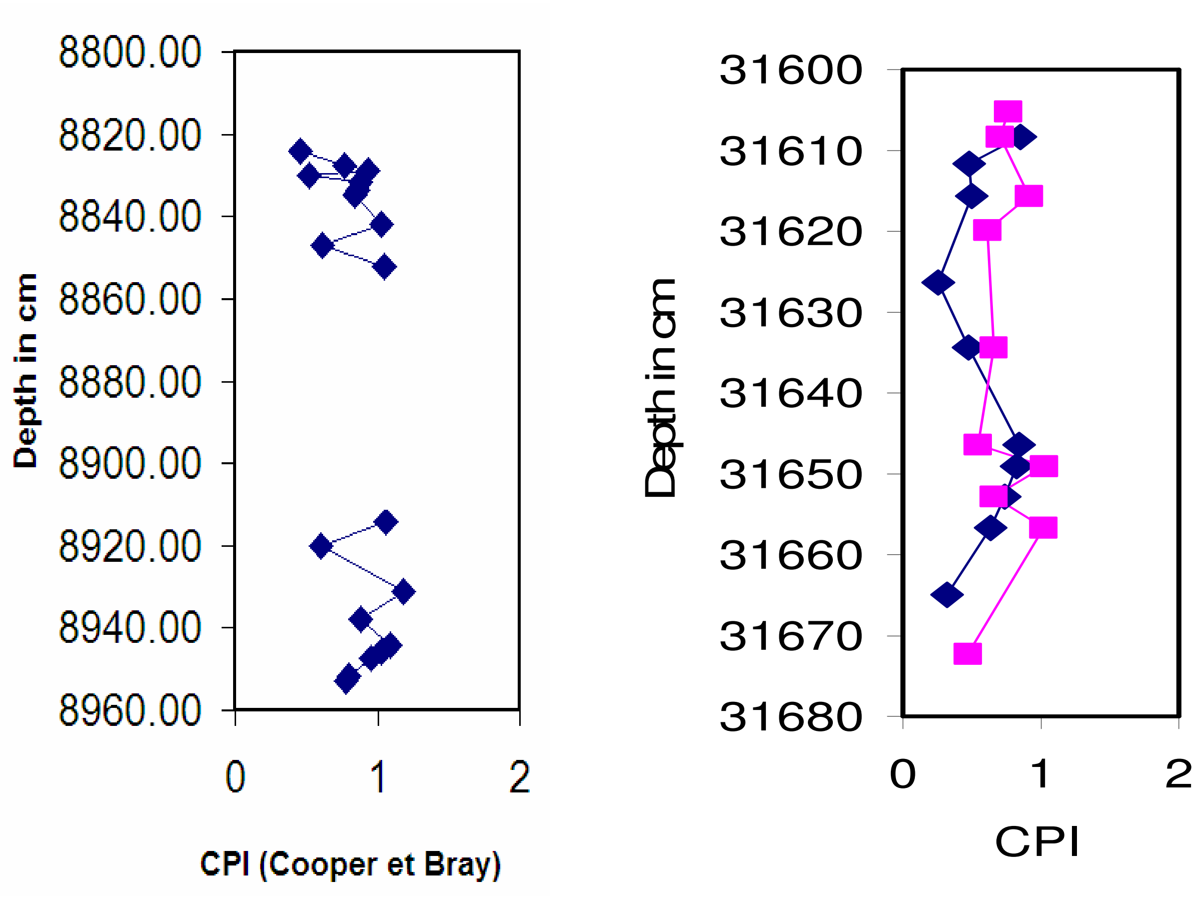
As can be observed here, with the exception of one sample, the values for CPI by marine and terrestrial origin formula is around the same, while CPI by Cooper and Bray is less as compared to the C-TW-1 core shale samples. For the samples we analyzed, CPI was calculated only by Cooper and Bray method. Figures 17 shows the variation with depth in the C-TW-1 and IRC core shale samples.

The CPI value for C-TW-1 shale samples was mostly in the range of 0.4 to 1.1 and it was almost the same for the two samples that were extracted in chloroform. The same was not true for IRC shale samples wherein the difference in values between samples extracted by benzene and chloroform is evident as can be seen in Table 6. A high CPI of value greater than 1 is indicative of organic matter being of terrigenous origin (Cooper and Bray, 1963). Since, the CPI values are in both the shale samples are more or less the same, the organic matter of botht he sources could be marine in nature.
Shale samples from both the regions showed a relatively high CPI value, with shales from C-TW-1 showing a slightly higher value than shales from IRC



(A) (B) (C)

Figure 16 – Graph showing biomarker ratio CPI at different depth for IRC core shale samples analyzed by USGS by using different formula A and C) By Simoneit (1978) for terrestrial and marine organic matter respectively and B) By Cooper and Bray(1963)



(A) (B)

Figure 17 – Graph showing biomarker ratio CPI at different depth for A) C-TW-1 and B) IRC core shale samples by using ther formula by Cooper and Bray(1963).

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4.4 COMPARISON OF TRACE METAL CONCENTRATION IN EXTRACTED AND UNEXTRACTED SAMPLES

The metal composition in the extracted sample was compared with the metal composition in the unextracted sample. It can be observed that in most metals there has been a substantial decrease in the concentration of metals. It is highly recommended that bulk sample analysis be done for the trace metal concentration using the same procedure and instrument for better analysis of the results (Figure 18 and Figure 19).

In IRC core shale, trace metal analysis was done in samples extracted by benzene and chloroform. Here too one can observe a decrease in the ratios as compared to the bulk samples analyzed by Cruse and Lyons (2004). Use of different extraction procedures did not have considerable effect on the amount of trace metals present. Pb was absent in most IRC core shale samples and hence comparison graph for Pb was not plotted for IRC core shale samples.

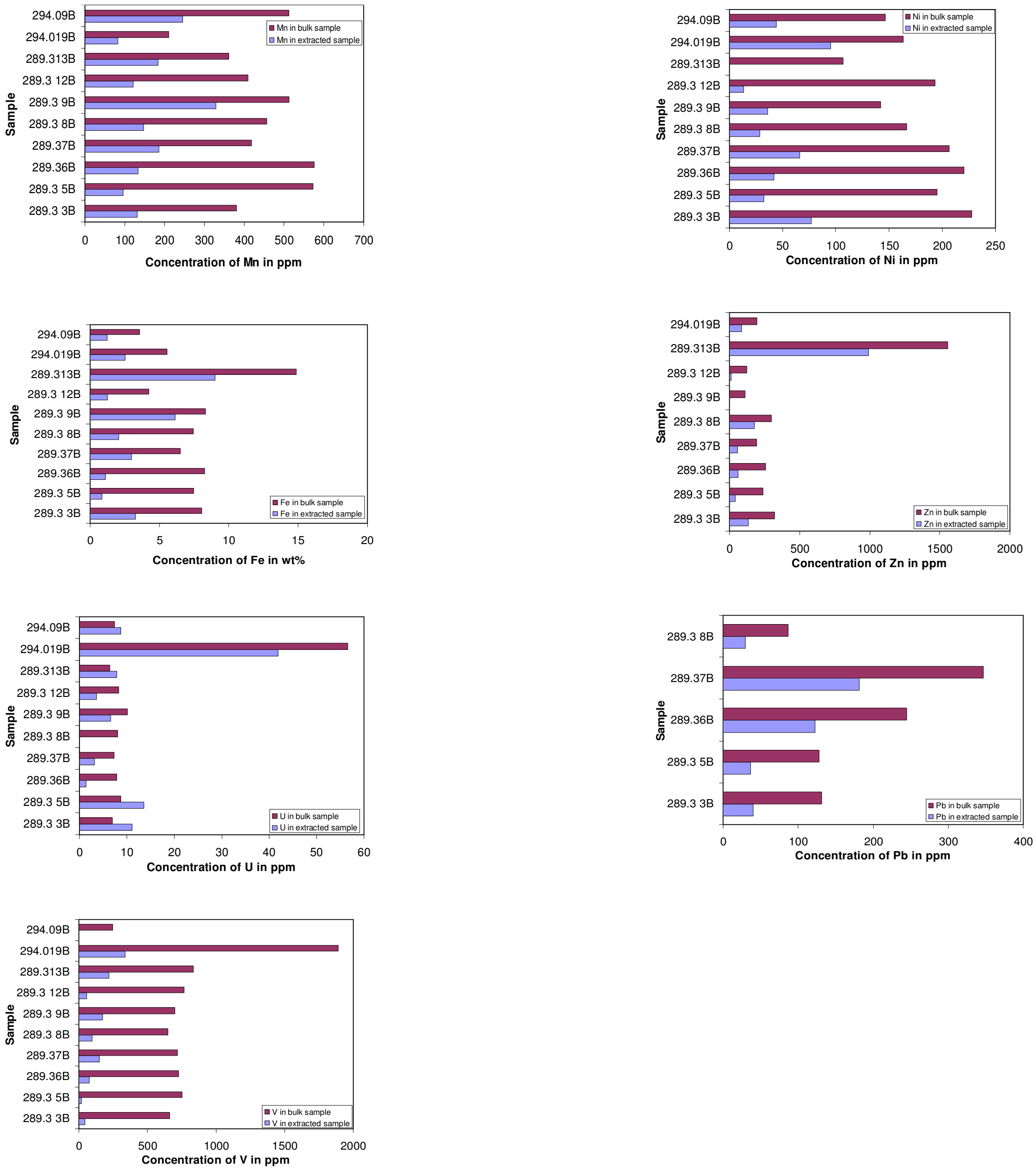


Figure 18 – Graph showing comparison of metal concentration in the extract after bitumen was extracted off the bulk sample (present work) and bulk sample (calues from Cruse and Lyons, 2004) in C-TW-1 core shale samples.

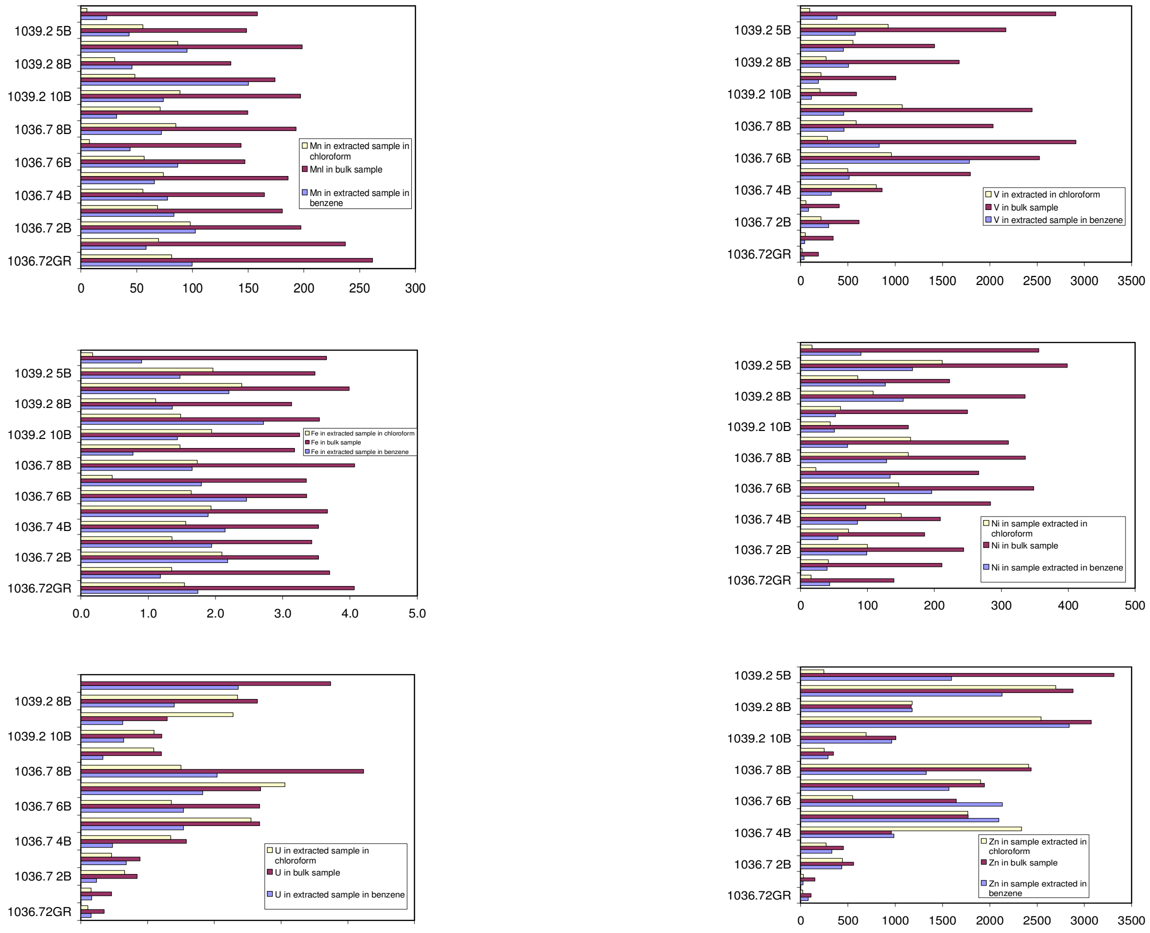
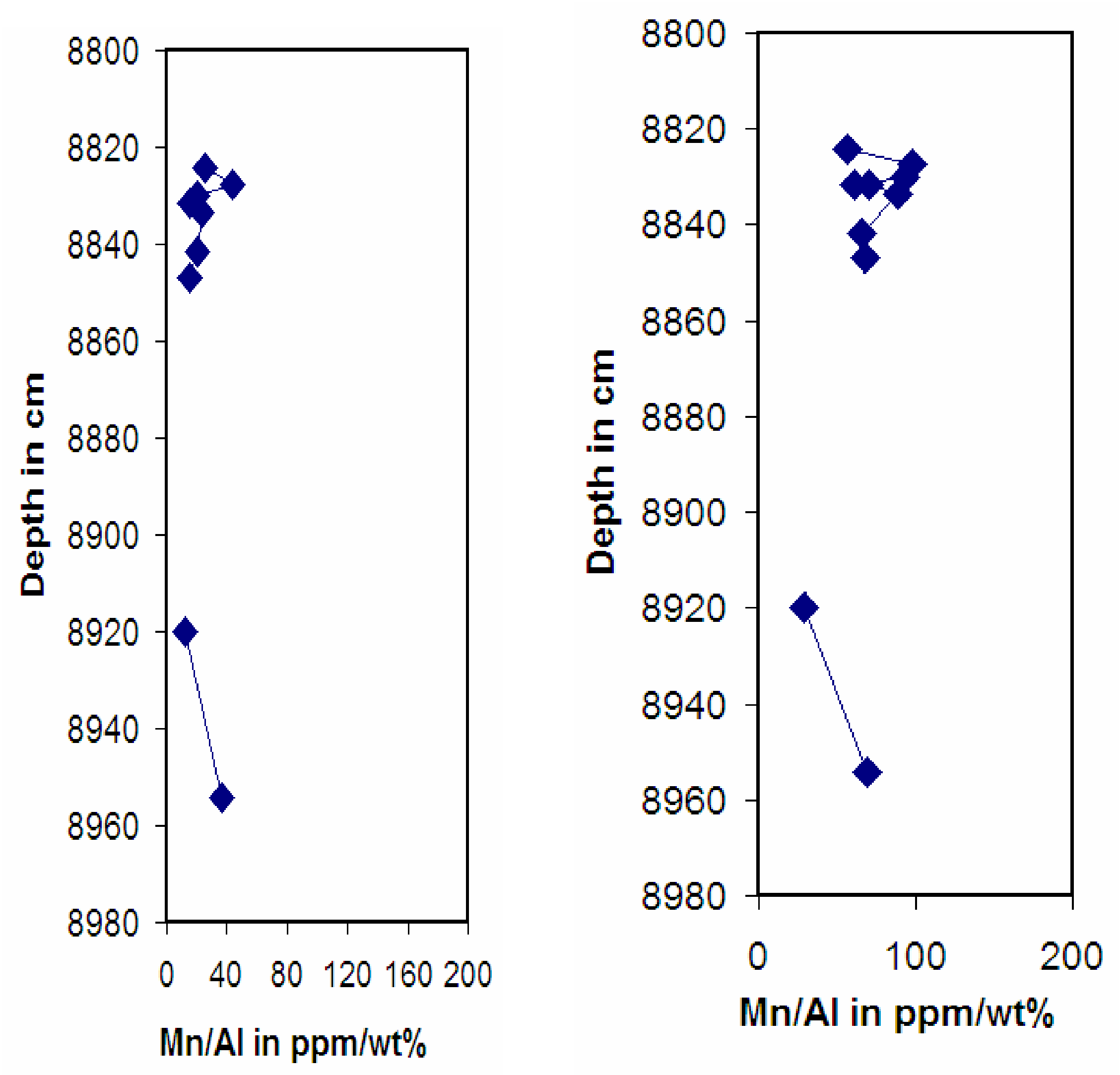


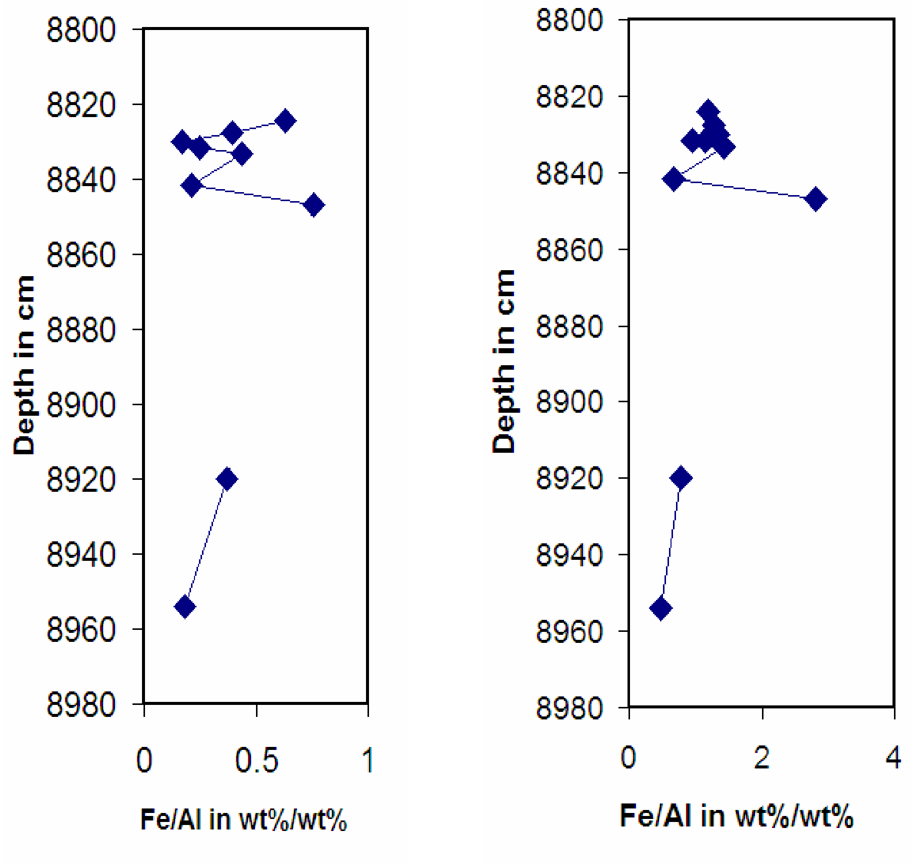
Figure 19 – Graph showing comparison of metal concentration in the extract after bitumen was extracted off the bulk sample (present work) and bulk sample (calues from Cruse and Lyons, 2004) in IRC core shale samples.

Comparison of the concentration of metals with respect to depth in the extracted sample and the bulk sample was done (Figures 20 - 25). The figures clearly shows that the Mn/Al, Fe/Al, and U/Al ratios in the extract are less as compared to the values obtained by Cruse and Lyons (2004) in the whole rock. This could imply that Mn, Fe, and U were probably extracted with the bitumen, or that concentration of Al was greater since we have compared the ratios. However from previous graphs of comparison of metal concentrations, we can observe a reduction in metal concentration, probably implying that a proportionate decrease in Al was also observed along with other metals. For the IRC samples while the U/Al ratio in the extracted rock was almost the same, the Mn/Al ratio and Fe/Al ratio was less as compared to ratios in bulk sample.



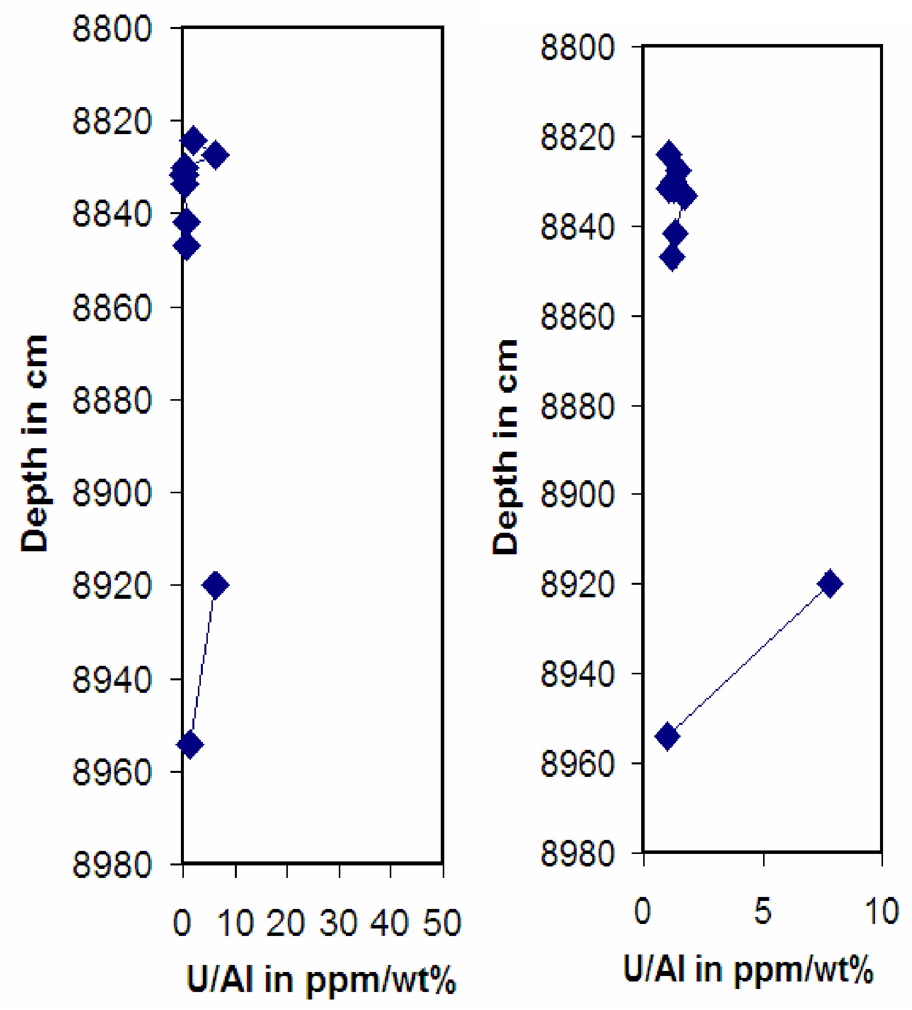
(A) **(B)**

Figure 20 – Graph showing comparison of Mn/Al ratio in the extract after bitumen was extracted off the bulk sample (present work) and bulk sample (values from Cruse and Lyons, 2004) in C-TW-1 core shale samples.



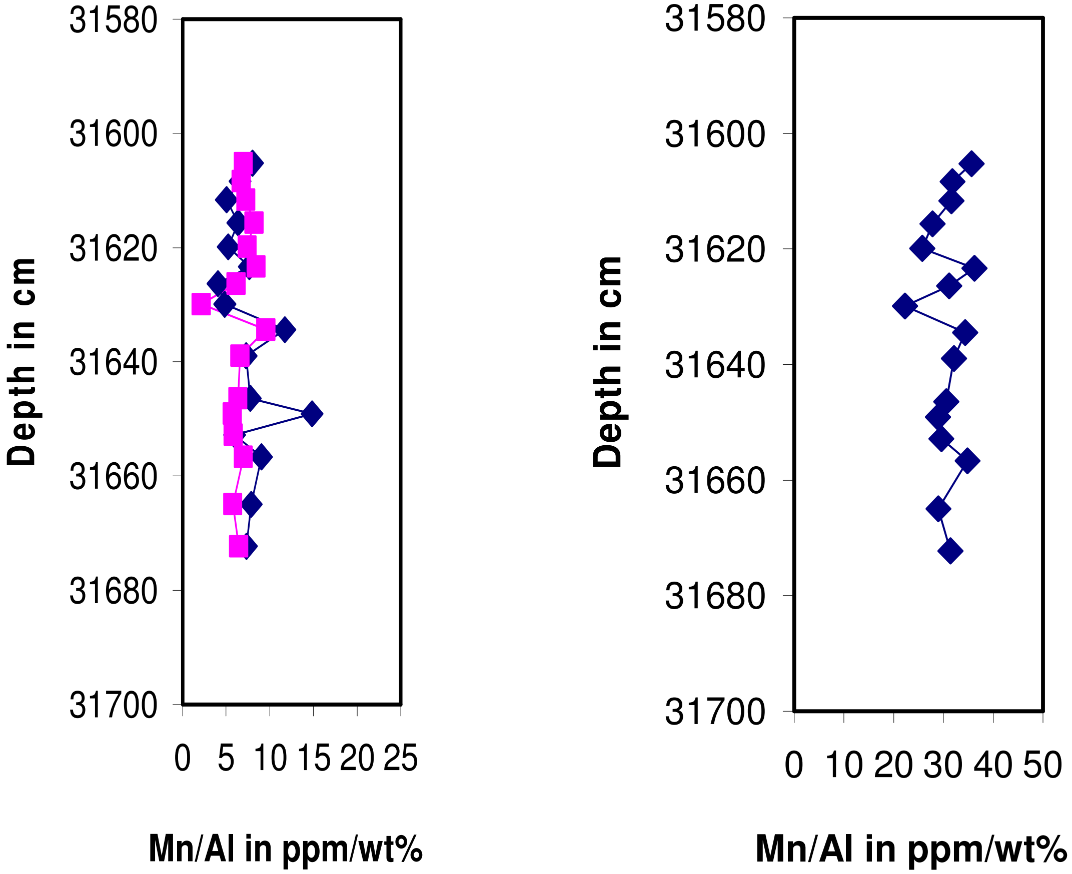
(A) (B)

Figure 21 – Graph showing comparison of Fe/Al ratio in the extract after bitumen was extracted off the bulk sample (present work) and bulk sample (calues from Cruse and Lyons, 2004) in C-TW-1 core shale samples.



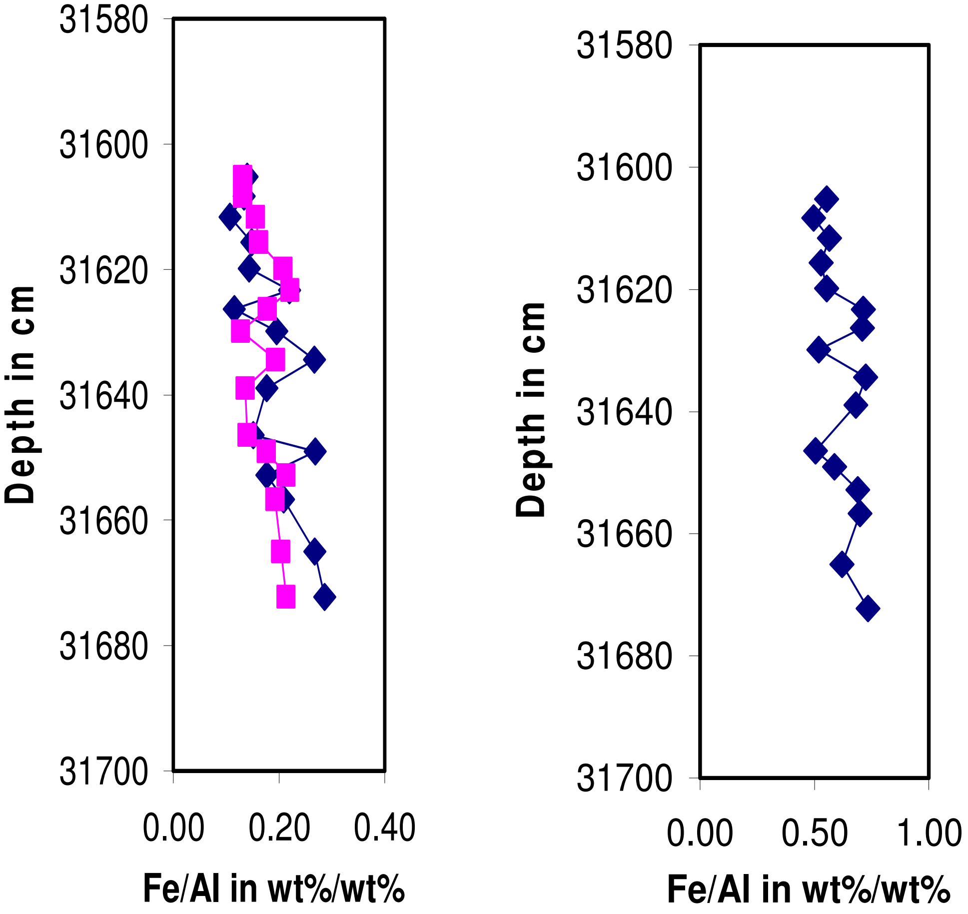
(A) **(B)**

Figure 22 – Graph showing comparison of U/Al ratio in the extract after bitumen was extracted off the bulk sample (present work) and bulk sample (calues from Cruse and Lyons, 2004) in C-TW-1 core shale samples.



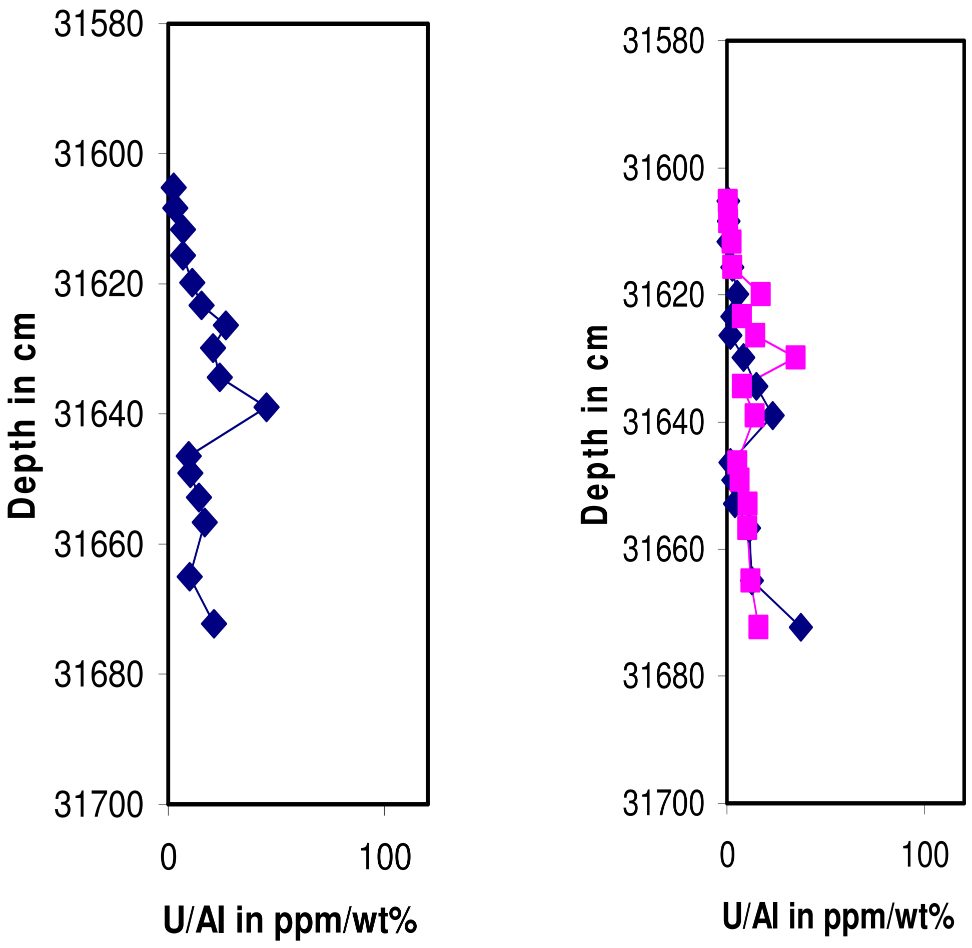
(A) (B)

Figure 23 – Graph showing comparison of Mn/Al ratio in the extract after bitumen was extracted off the bulk sample (present work) and bulk sample (calues from Cruse and Lyons, 2004) in IRC core shale samples.



(A) (B)

Figure 24 – Graph showing comparison of Fe/Al ratio in the extract after bitumen was extracted off the bulk sample (present work) and bulk sample (calues from Cruse and Lyons, 2004) in IRC core shale samples.



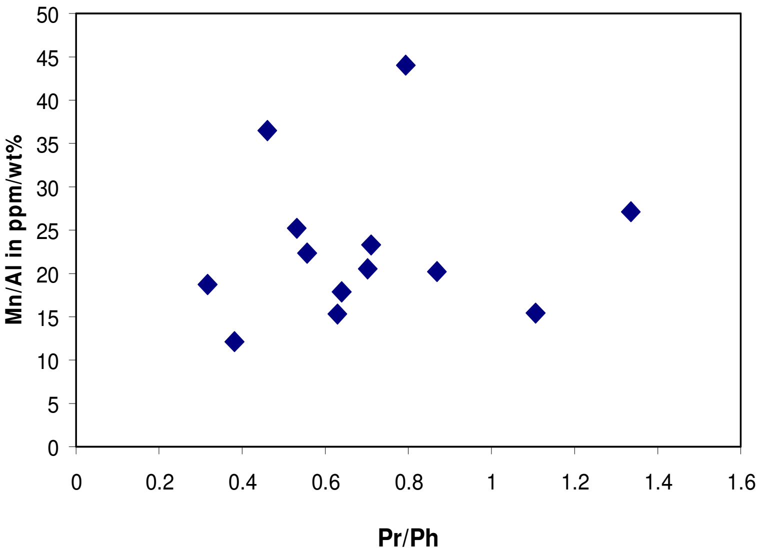
(A) (B)

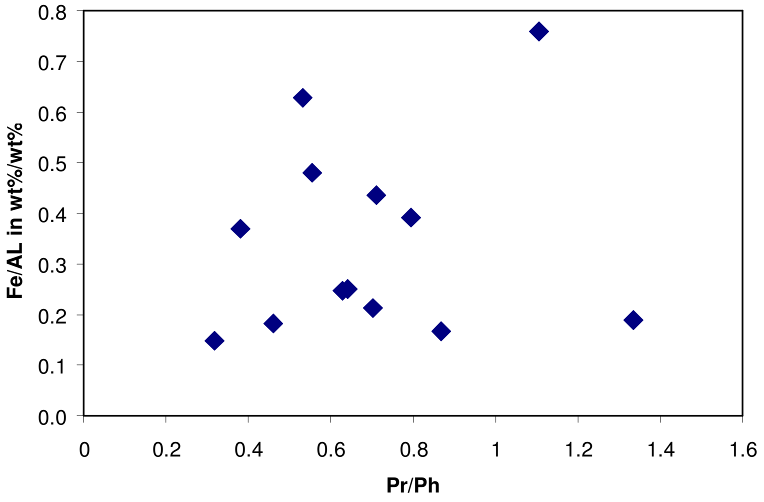
Figure 25 – Graph showing comparison of U/Al ratio in the extract after bitumen was extracted off the bulk sample (present work) and bulk sample (calues from Cruse and Lyons, 2004) in IRC core shale samples.

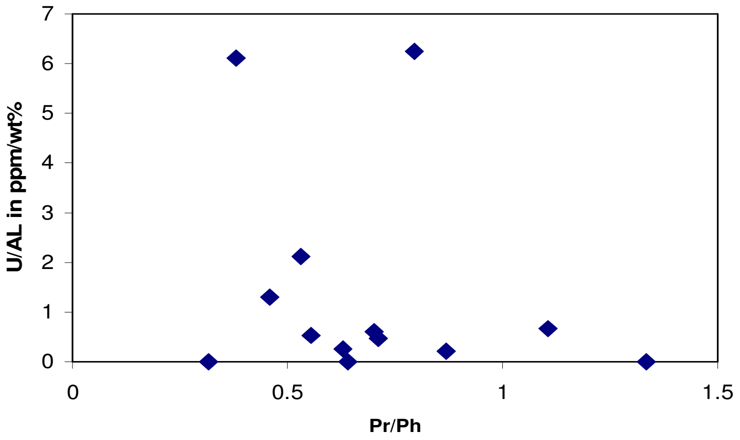
4.2.2 REDOX VARIATIONS

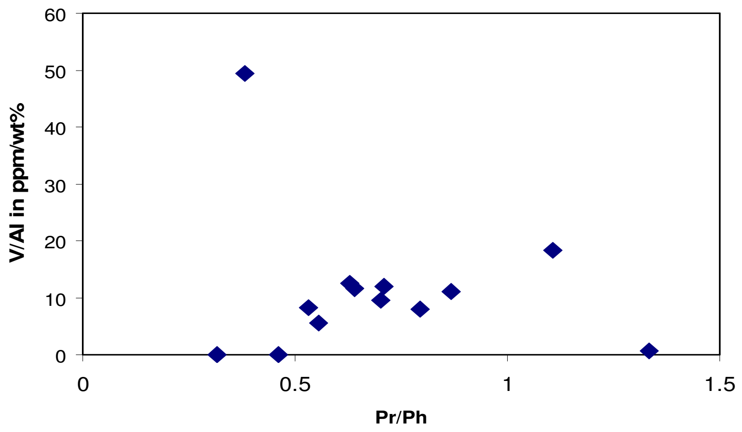
Variation of metal concentration with respect to Pr/Ph ratio was studied in the samples. A linear relationship was observed for vanadium and lead whereas the other did not show any concrete relation although an increase in the ratio with increased Pr/Ph ratio was observed. Figure 26 shows the relation of Pr/Ph with respect to the different metal concentrations.

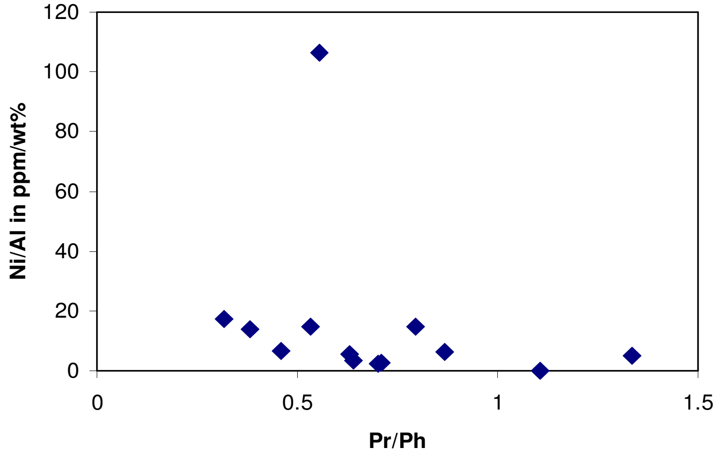
For IRC core shale samples a linear relation was observed for all metals except lead. Lead was absent in most of the samples and hence no relation could be established. The above is true only for samples extracted in benzene as samples extracted using chloroform as solvent did not show presence of a lot of *n*-alkanes and hence Pr/Ph ratios could not be calculated (Figure 27).

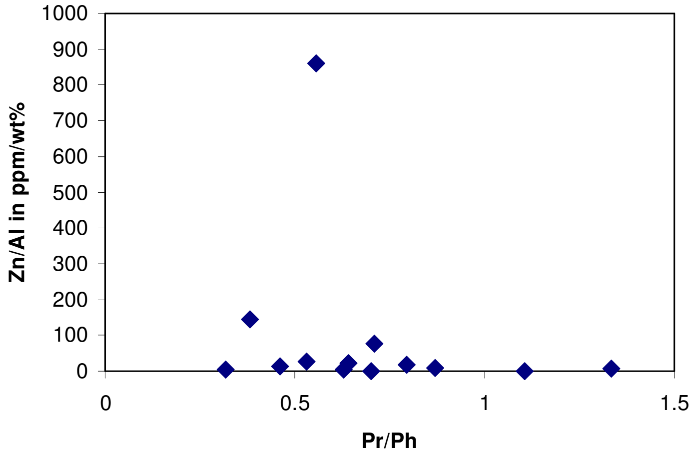

Mn/Al in ppm/wt%
50
45
40
35
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Pr/Ph


Fe/AL in wt%/wt%
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Pr/Ph


U/AL in ppm/wt%
7
6
5
4
3
2
1
0
0
0.5
1
1.5
Pr/Ph


V/Al in ppm/wt%
0
10
20
30
40
50
60
0
0.5
1
1.5
Pr/Ph


Ni/Al in ppm/wt%
0
20
40
60
80
100
120
0
0.5
1
1.5
Pr/Ph


Zn/Al in ppm/wt%
0
100
200
300
400
500
600
700
800
900
1000
0
0.5
1
1.5
Pr/Ph

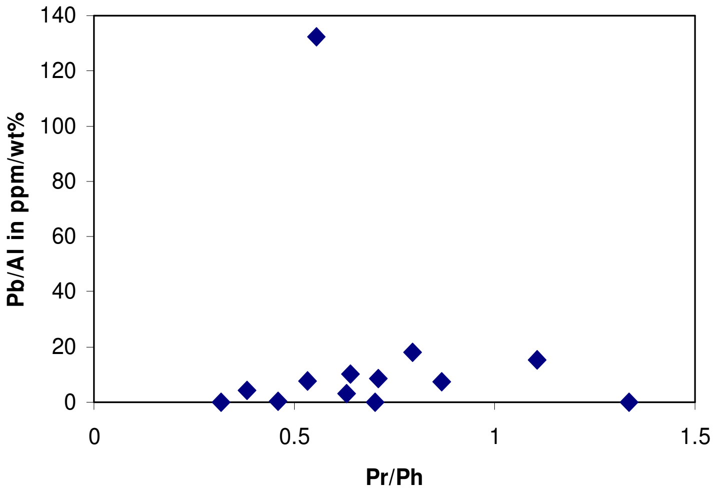
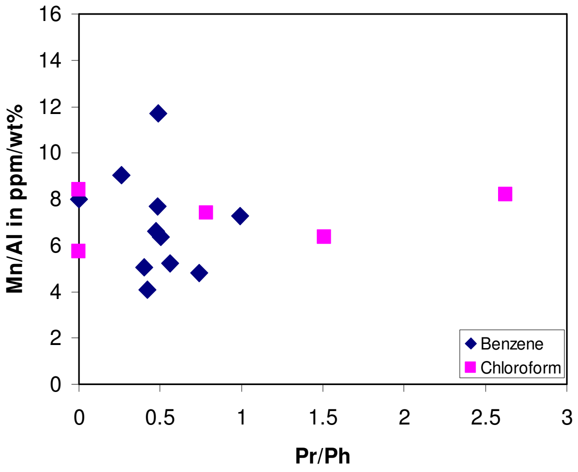
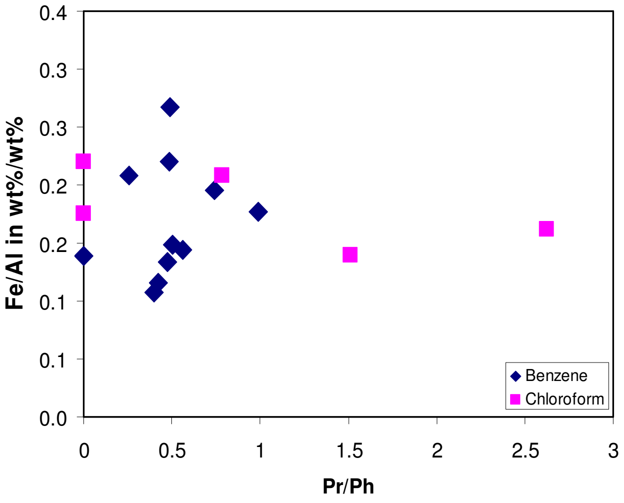
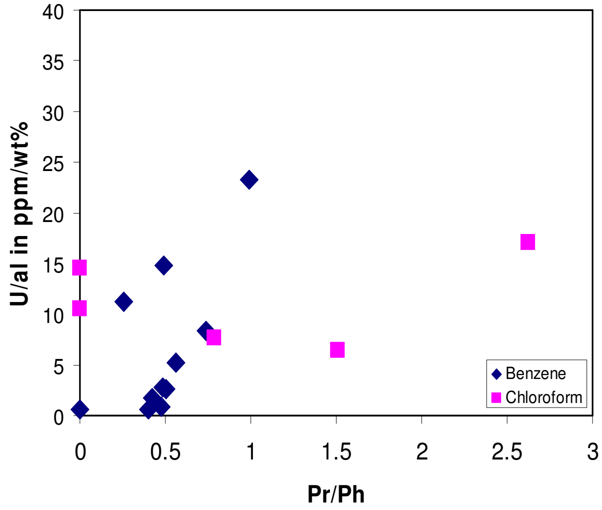
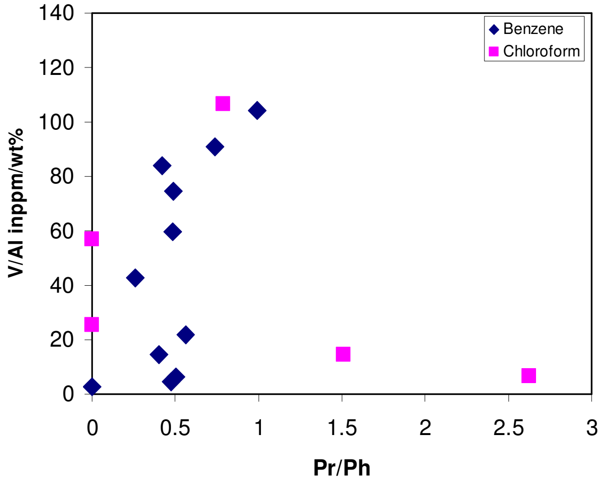


Figure 26 – Graph showing effect of biomarker ratio Pr/Ph on metal concentration in extract after bitumen was extracted off the bulk sample (present work) and in C-TW-1 core shale samples.




0.4
0.3
0.3
0.2
0.2
0.1
0.1
0.0
0
0.5
1
1.5
2
2.5
3
Fe/Al in wt%/wt%
Pr/Ph
◆ Benzene
■ Chloroform


40
35
30
25
20
15
10
5
0
0
0.5
1
1.5
2
2.5
3
U/al in ppm/wt%
Pr/Ph
◆ Benzene
■ Chloroform


140
120
100
80
60
40
20
0
0
0.5
1
1.5
2
2.5
3
V/Al inppm/wt%
Pr/Ph
◆ Benzene
■ Chloroform

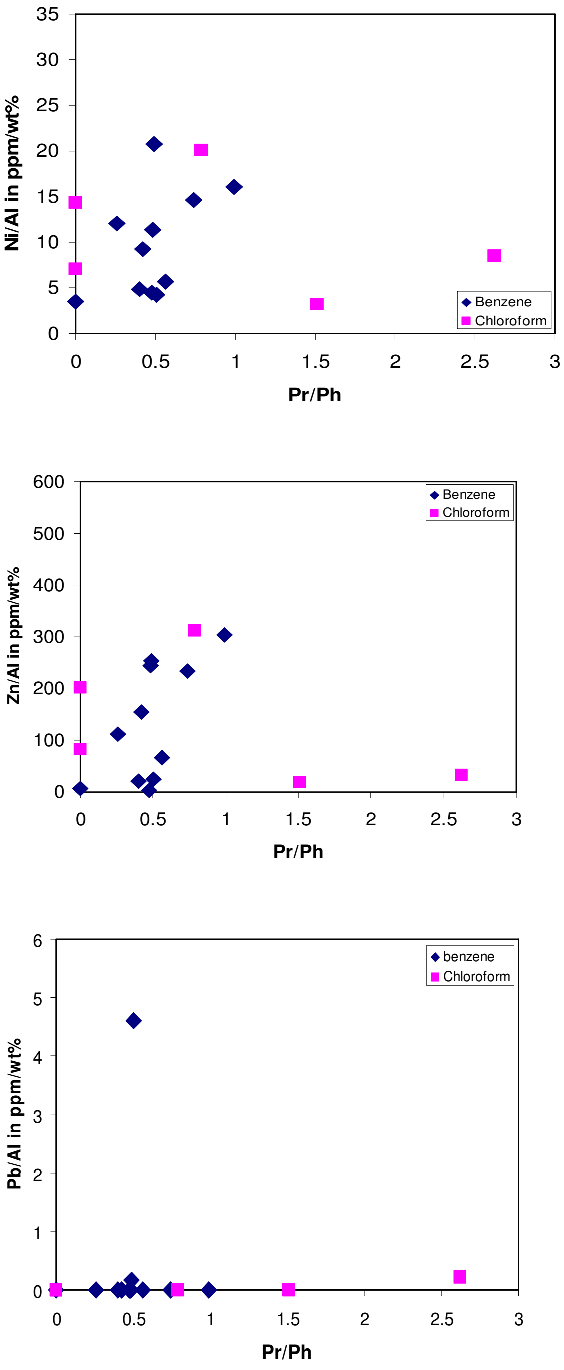
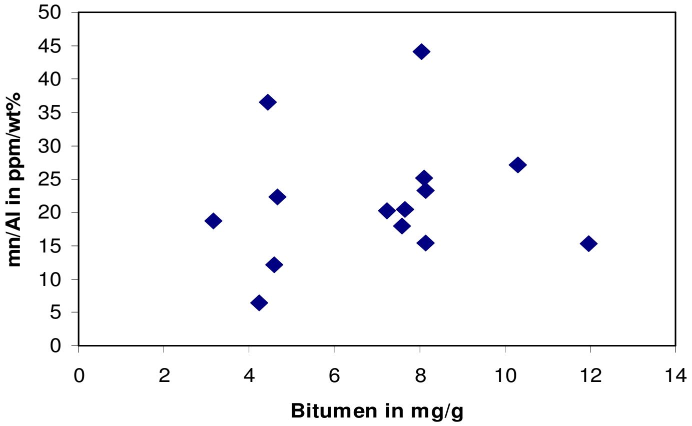


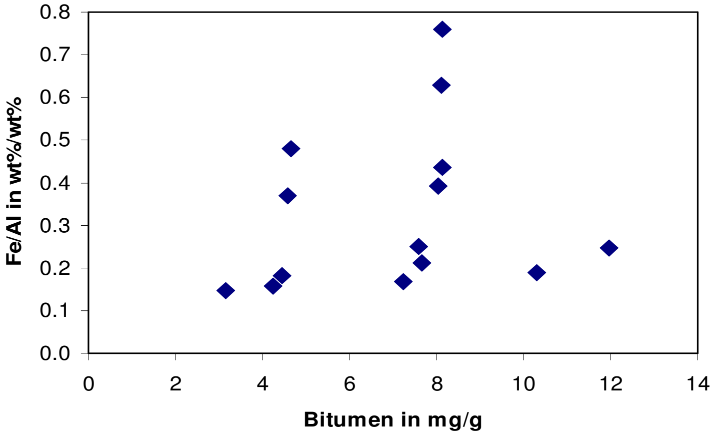
Figure 27 – Graph showing effect of biomarker ratio Pr/Ph on metal concentration in extract after bitumen was extracted off the bulk sample (present work) and in IRC core shale samples.

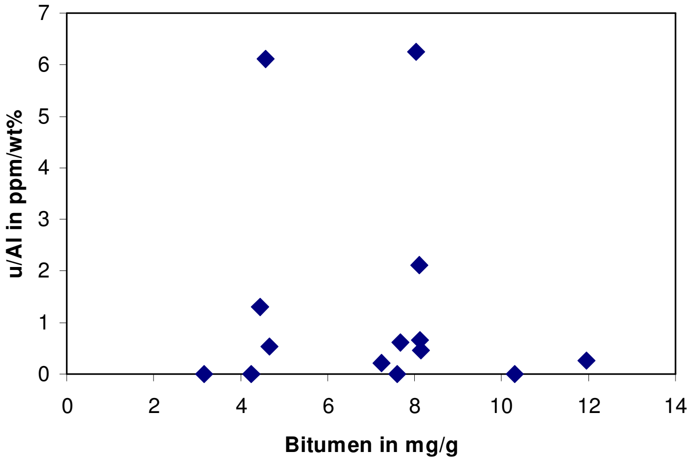
4.2.3 METALS AND ORGANIC MATTER

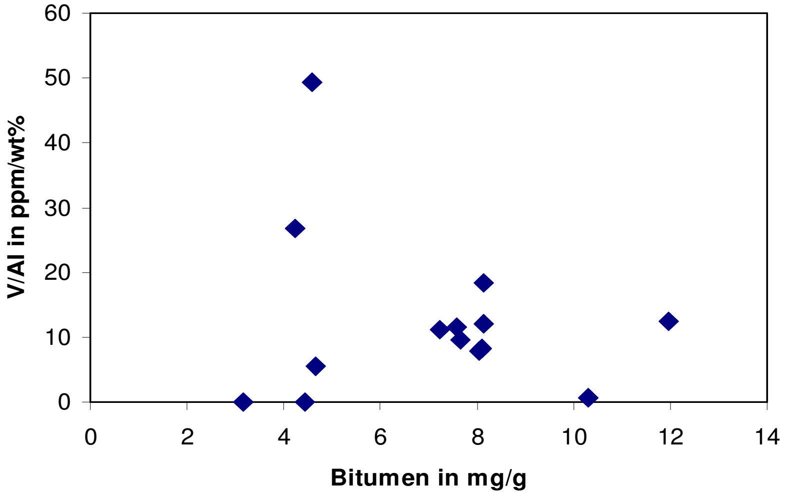
4.2.3.3 BITUMEN AND METALS

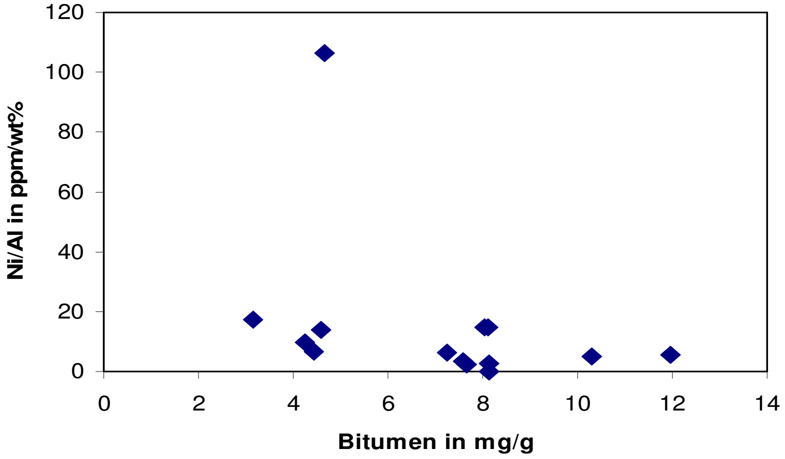
Similar studies were conducted for bitumen and compared with its relation with respect to metals present. The observation was similar as with TOC and metals i.e. there was a reduction in the metal concentration but the pattern that changes in bitumen concentration had with respect to metals was similar. Thus the metal concentration is definitely related to the organic matter present in the shale samples in both the cores. It is also observed in the IRC core shale samples, that while the bitumen extracted with benzene is not so much related to the concentration of metals, the bitumen extracted with chloroform is related (Figure 28 and Figure 29). This would mean that there is a definite correlation between metal concentration and the polar organic matter extracted using chloroform. This could be further confirmed by following similar step of investigation of bitumen extraction by use of chloroform as solvent for C-TW-1 samples.

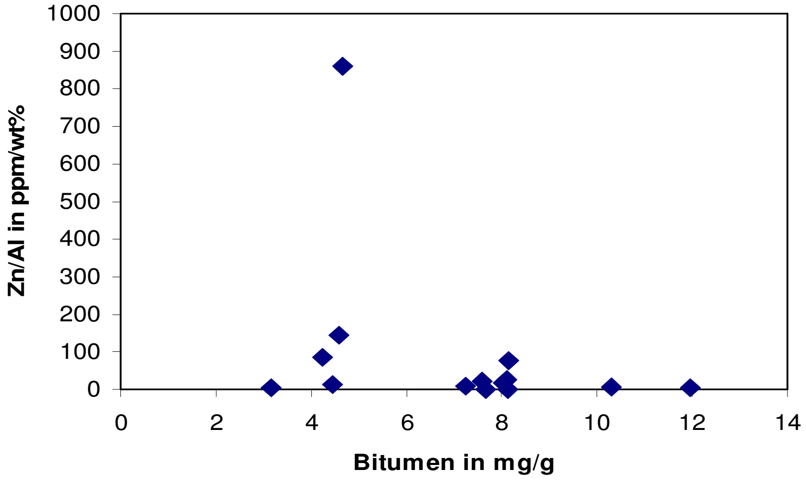

mn/Al in ppm/wt%
50
45
40
35
30
25
20
15
10
5
0
0
2
4
6
8
10
12
14
Bitumen in mg/g


Fe/Al in wt%/wt%
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
12
14
Bitumen in mg/g


u/Al in ppm/wt%
7
6
5
4
3
2
1
0
0
2
4
6
8
10
12
14
Bitumen in mg/g


60
50
40
30
20
10
0
V/Al in ppm/wt%
0
2
4
6
8
10
12
14
Bitumen in mg/g


120
100
80
60
40
20
0
Ni/Al in ppm/wt%
0
2
4
6
8
10
12
14
Bitumen in mg/g


1000
900
800
700
600
500
400
300
200
100
0
Zn/Al in ppm/wt%
0
2
4
6
8
10
12
14
Bitumen in mg/g

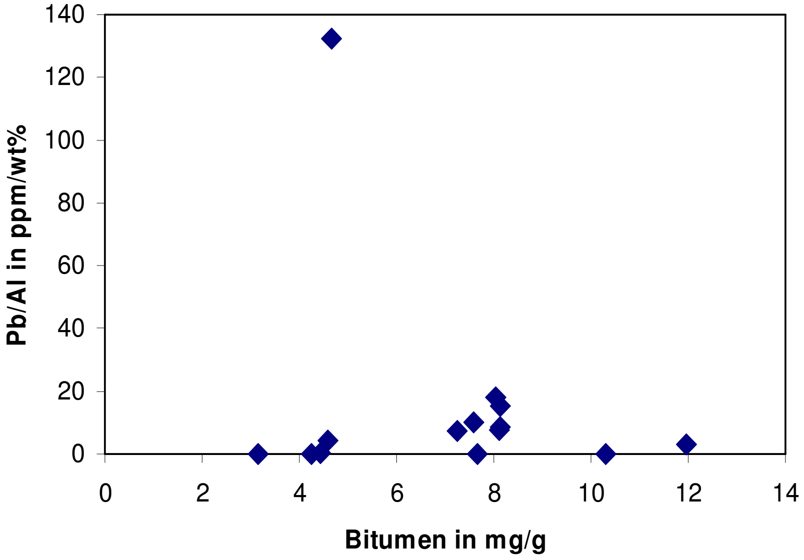
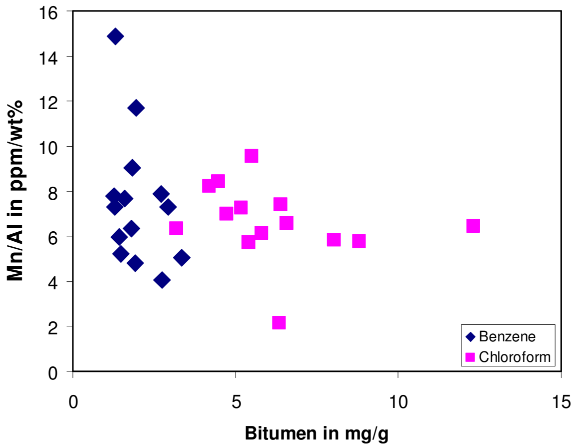
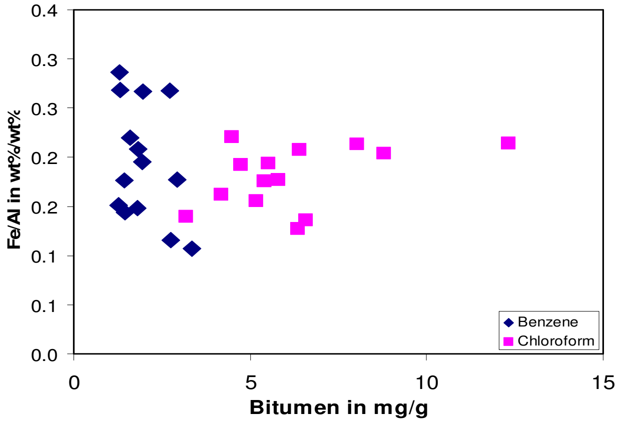
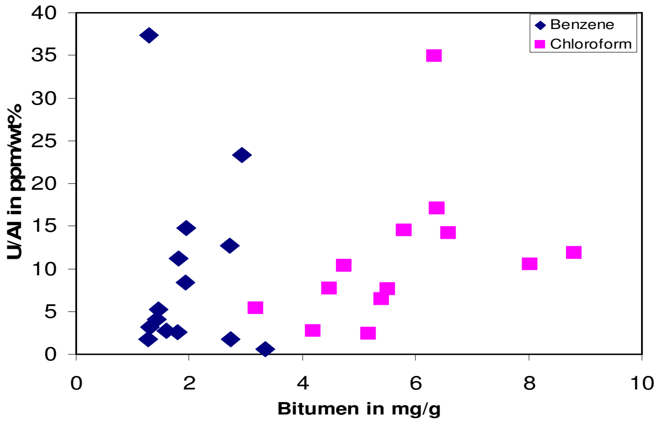
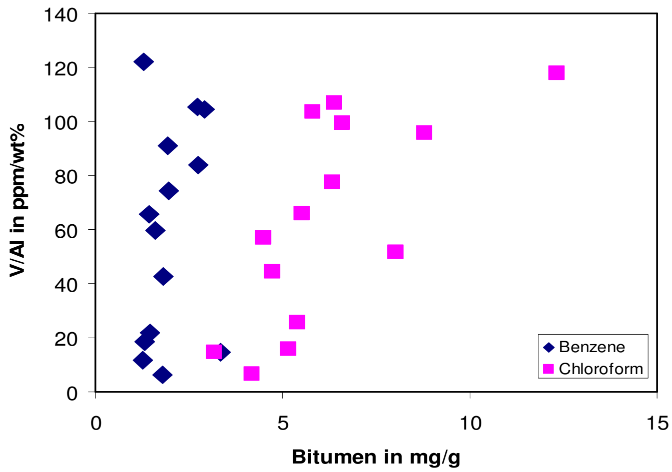


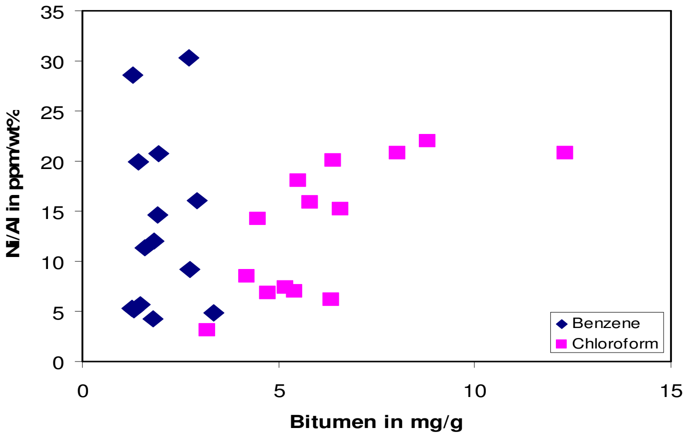
Figure 28 – Graph showing effect of bitumen extracted on metal concentration in extract after bitumen was extracted off the bulk sample (present work) and in C-TW-1 core shale samples.

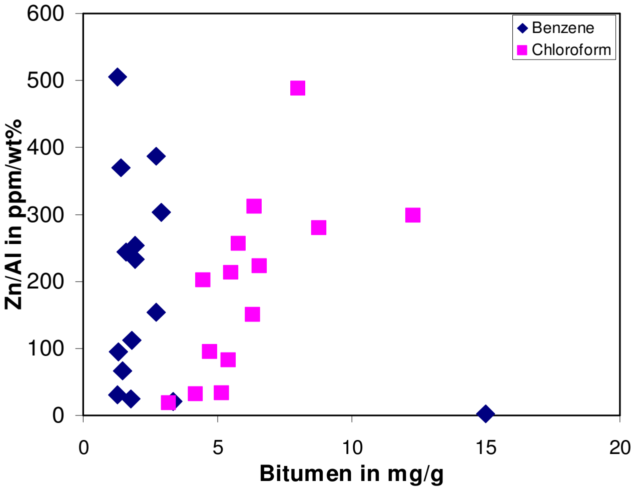

Mn/Al in ppm/wt%
16
14
12
10
8
6
4
2
0
0
5
10
15
Bitumen in mg/g
◆ Benzene
■ Chloroform


Fe/Al in wt%/wt%
0.4
0.3
0.3
0.2
0.2
0.1
0.1
0.0
0
5
10
15
Bitumen in mg/g
◆ Benzene
■ Chloroform


U/Al in ppm/wt%
40
35
30
25
20
15
10
5
0
0
2
4
6
8
10
Bitumen in mg/g
◆ Benzene
■ Chloroform


V/Al in ppm/wt%
0
20
40
60
80
100
120
140
0
5
10
15
Bitumen in mg/g
◆ Benzene
■ Chloroform


Ni/Al in ppm/wt%
0
5
10
15
20
25
30
35
0
5
10
15
Bitumen in mg/g
◆ Benzene
■ Chloroform


Zn/Al in ppm/wt%
0
100
200
300
400
500
600
0
5
10
15
20
Bitumen in mg/g
◆ Benzene
■ Chloroform

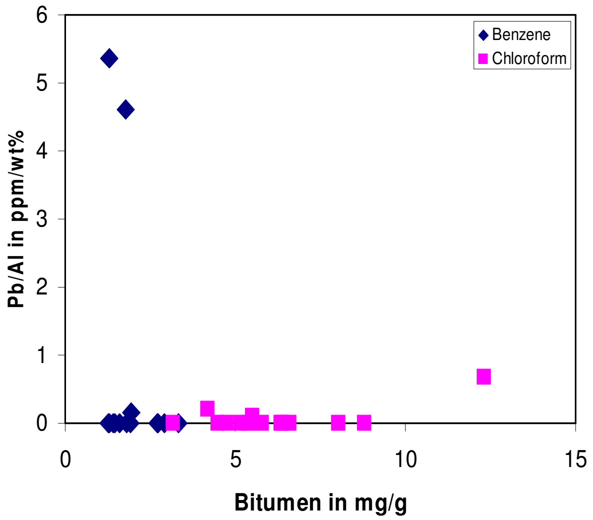
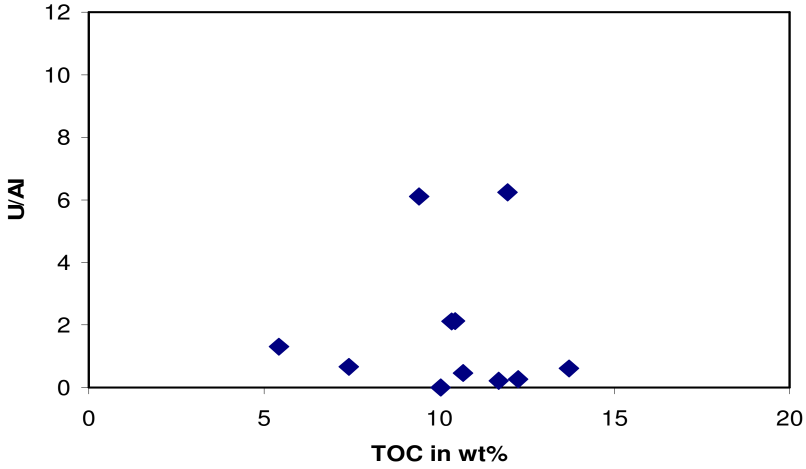
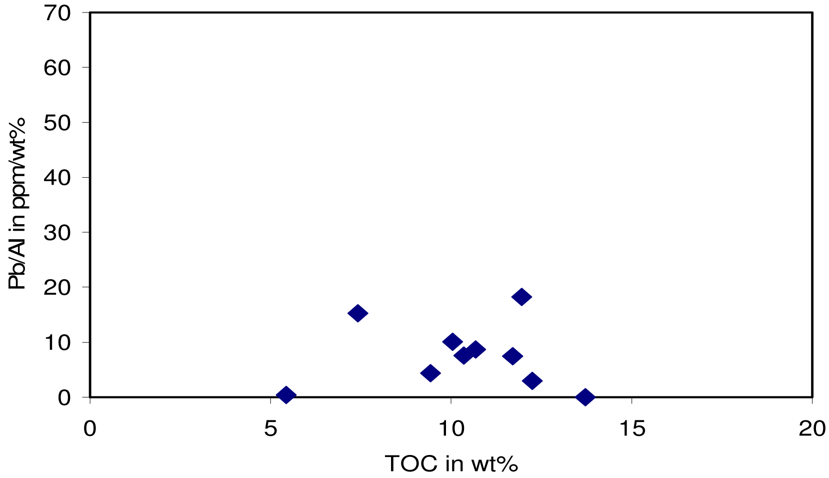


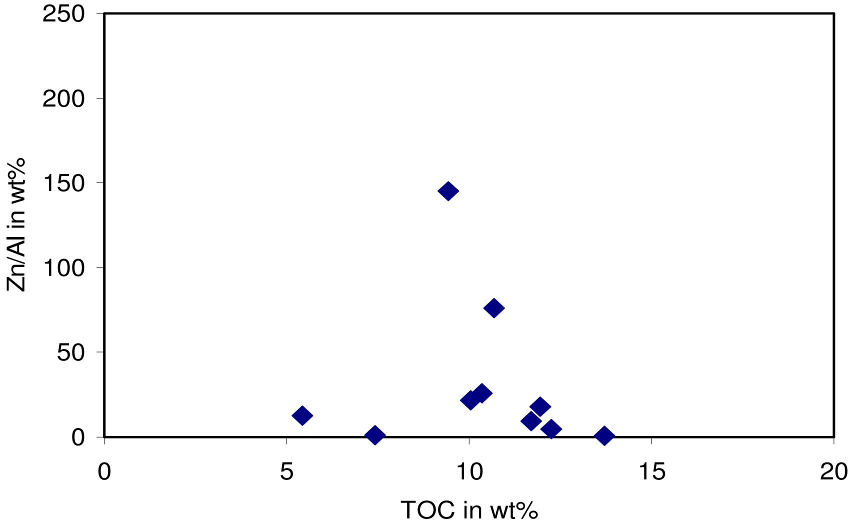
Figure 29 – Graph showing effect of bitumen extracted on metal concentration in extract after bitumen was extracted off the bulk sample (present work) and in IRC core shale samples.

4.2.3.1 TOC AND METALS

Metal concentrations in extracted samples were compared with bulk TOC reported in Cruse and Lyons (2004). Figures 30 and 31 show the relation between the two in C-TW-1 and IRC core shale samples. When compared with Cruse and Lyons, it can be observed that the pattern is the same although the concentration is reduced in the samples. This confirms that some metals is extracted with the bitumen and hence a reduction can be observed. This is true for both the C-TW-1 and the IRC core shale samples.


12
10
8
6
4
2
0
U/Al
0
5
10
15
20
TOC in wt%


70
60
50
40
30
20
10
0
Pb/Al in ppm/wt%
0
5
10
15
20
TOC in wt%


250
200
150
100
50
0
Zn/Al in wt%
0
5
10
15
20
TOC in wt%

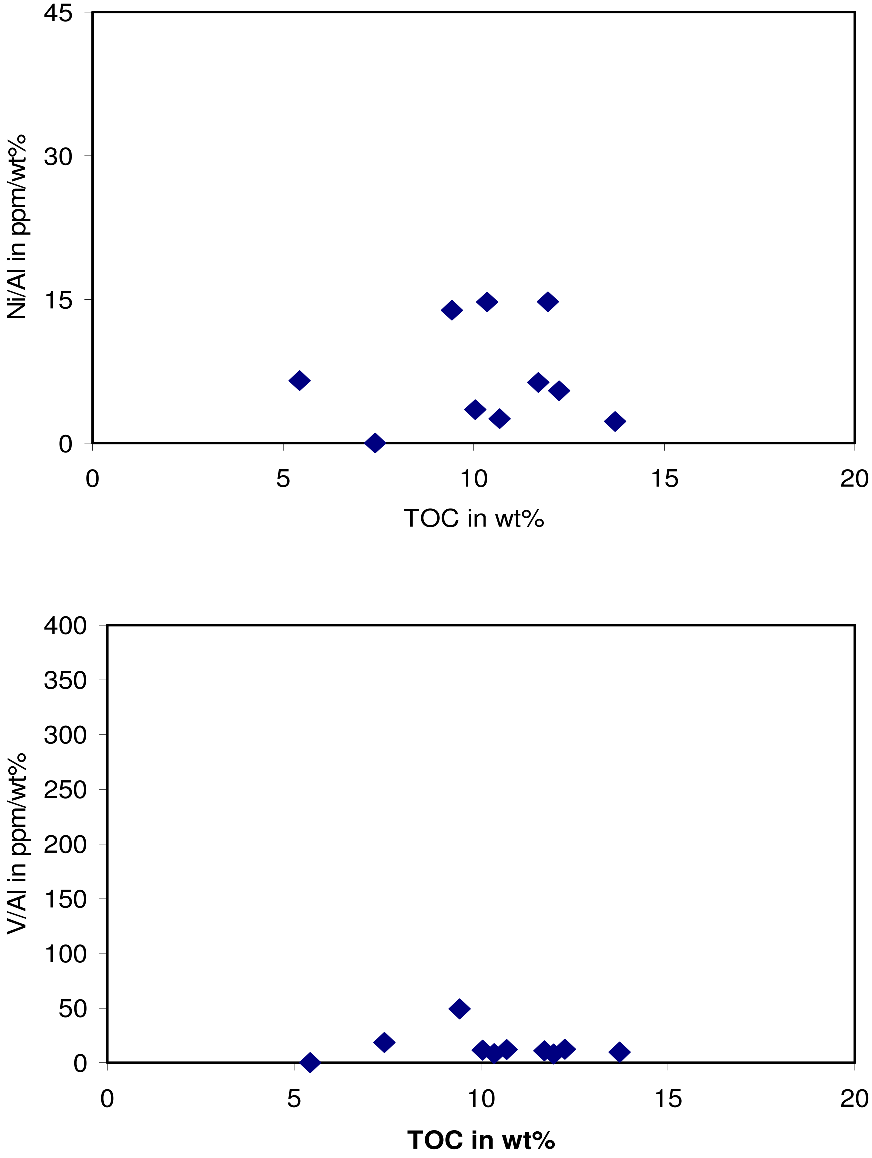
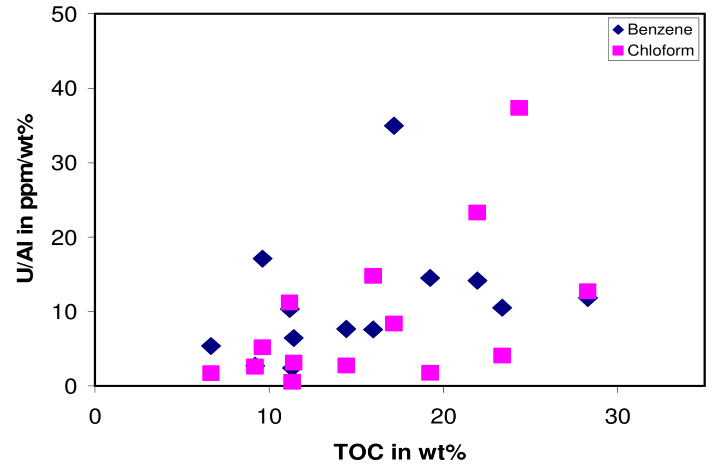
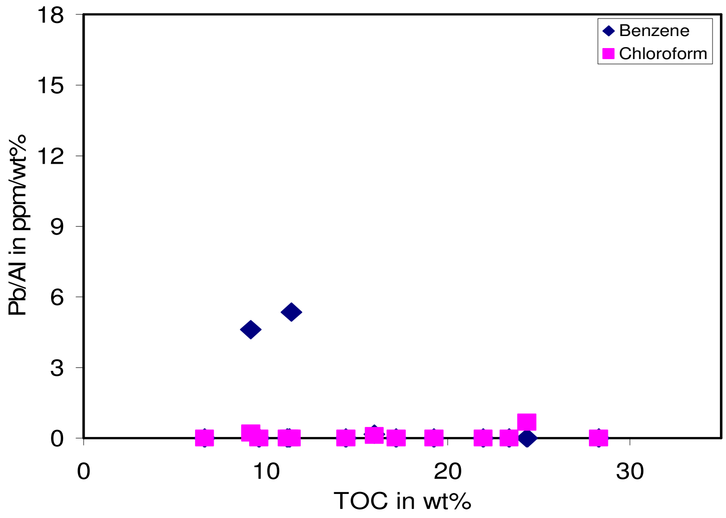
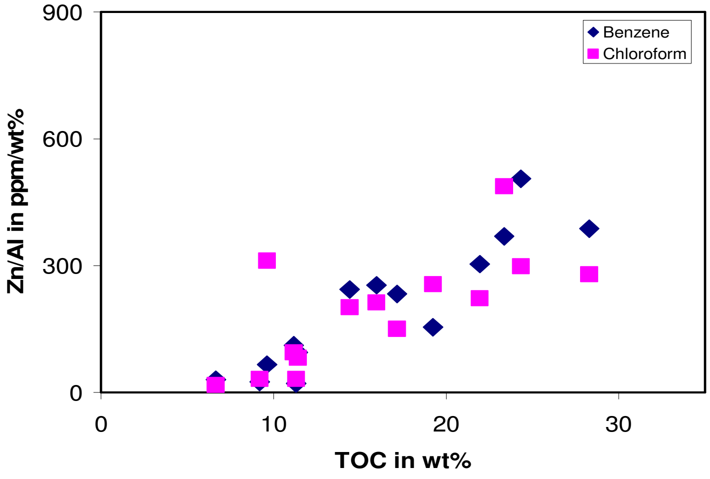
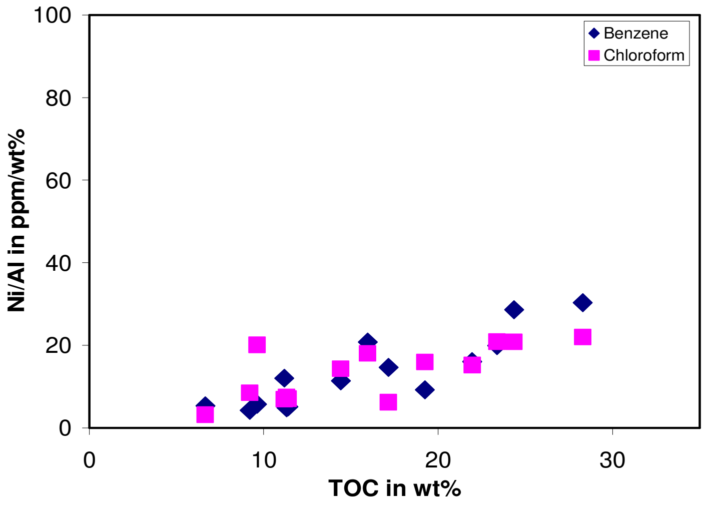


Figure 30 – Graph showing effect of total organic cabon (TOC) in bulk samples (work by Cruse and Lyons, 2004) on metal concentration in extract after bitumen was extracted off the bulk sample (present work) and in C-TW-1 core shale samples.


50
40
30
20
10
0
0
10
20
30
U/Al in ppm/wt%
TOC in wt%
◆ Benzene
■ Chloform


18
15
12
9
6
3
0
0
10
20
30
Pb/Al in ppm/wt%
TOC in wt%
◆ Benzene
■ Chloroform


900
600
300
0
0
10
20
30
Zn/Al in ppm/wt%
TOC in wt%
◆ Benzene
■ Chloroform



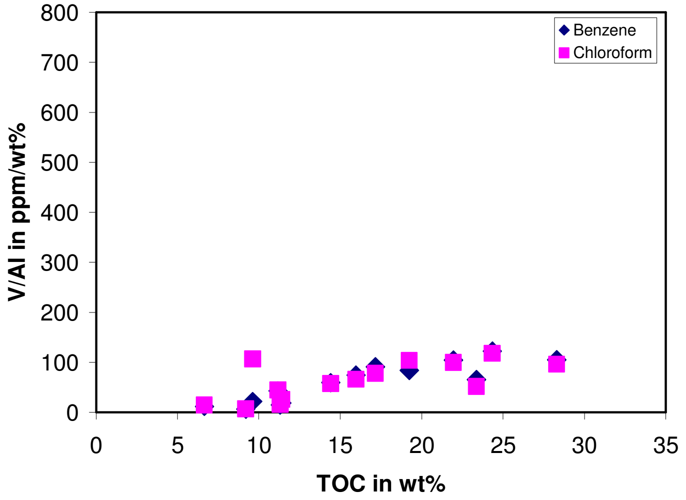
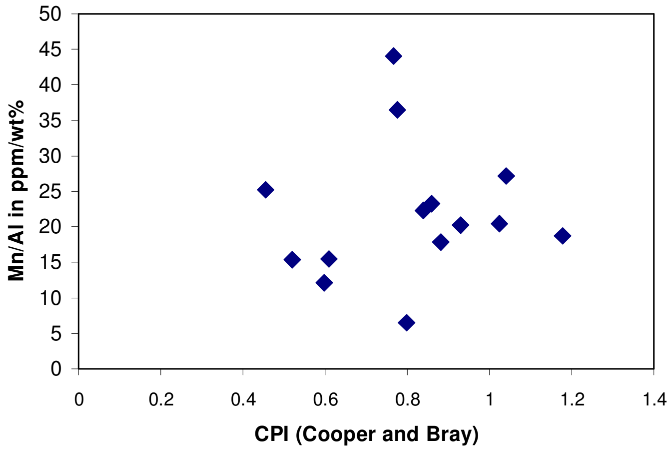


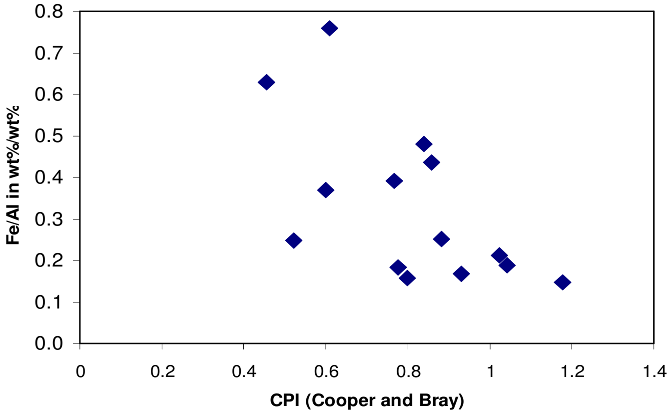
Figure 31 – Graph showing effect of total organic cabon (TOC) in bulk samples (work by Cruse and Lyons, 2004) on metal concentration in extract after bitumen was extracted off the bulk sample (present work) and in IRC core shale samples.

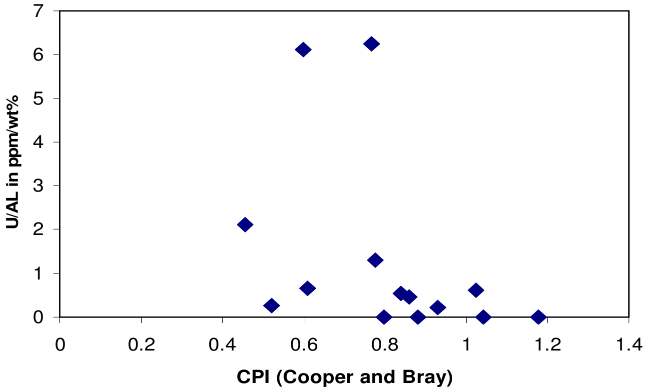
4.3.3.1CPI AND METALS

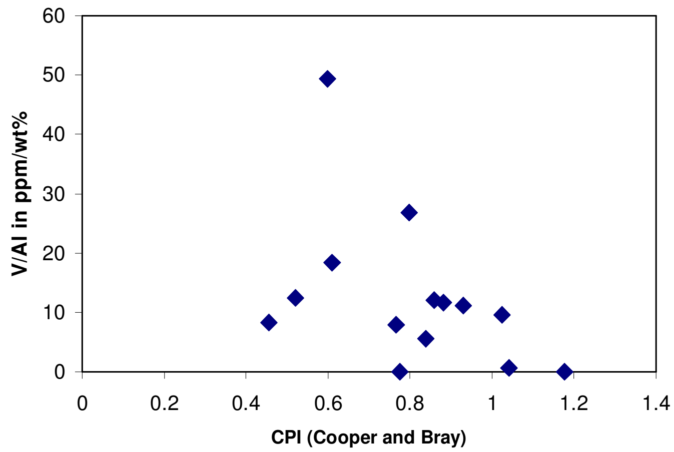
Similarly, the metal concentrations were studied with respect to the CPI calculated by the method Cooper and Bray (1968) had suggested. The relation seen between CPI and metal concentration is similar to the relation between the metal and total organic carbon in Cruse and Lyons, 2004. For most samples in C-TW-1 shale, for a CPI of 0.4 – 1.1 which was the normal value range for the samples, the Mn/Al ratio of 10-30, Fe/Al of 1-4, U/Al of less than, V/Al of 5-15, and Ni/Al and Pb/Al of less than 20 was observed. Zn was absent in most samples (Figure 32 and Figure 33).

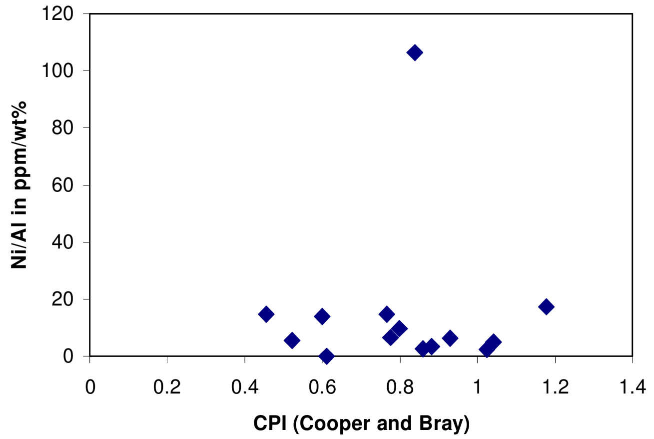
For IRC ,core shale samples, the Mn/Al ratio was mostly in the range 5-8, Fe/Al in the range 1.25-2, and U/Al was less than 10.V/Al, Ni/Al and Zn/Al did not show any such predominant ratio while Pb was absent in most samples. If we compare the two cores, we observe that metal concentrations is correlated to CPI in IRC core shales while no definite correlation is observed for the C-TW-1 core shale samples. However it is observed that an increase in CPI resulted in increase in a decrease in the metal ratios. Since metal concentration were analyzed in the extract and not the bitumen, it could be that an increase in metal concentration in bitumen would be observed with respect to CPI calculated.

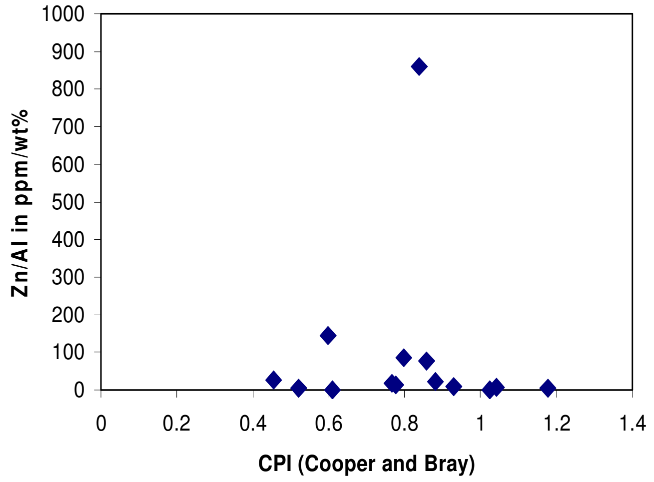

Mn/Al in ppm/wt%
50
45
40
35
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
CPI (Cooper and Bray)


Fe/Al in wt%/wt%
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
CPI (Cooper and Bray)


U/AL in ppm/wt%
7
6
5
4
3
2
1
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
CPI (Cooper and Bray)


V/Al in ppm/wt%
60
50
40
30
20
10
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
CPI (Cooper and Bray)


Ni/Al in ppm/wt%
120
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
CPI (Cooper and Bray)


Zn/Al in ppm/wt%
1000
900
800
700
600
500
400
300
200
100
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
CPI (Cooper and Bray)

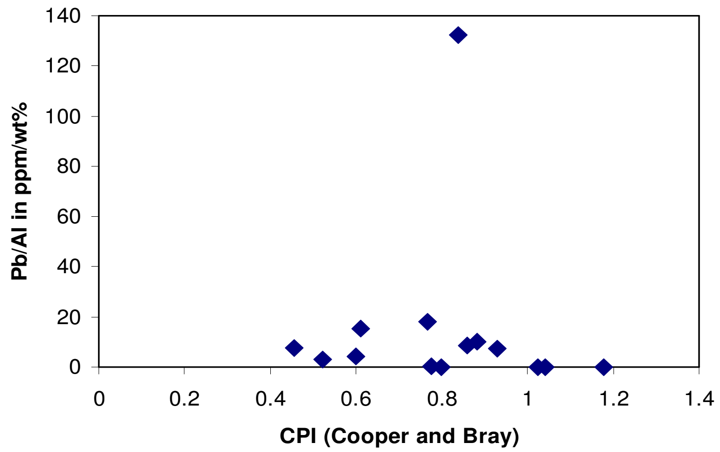
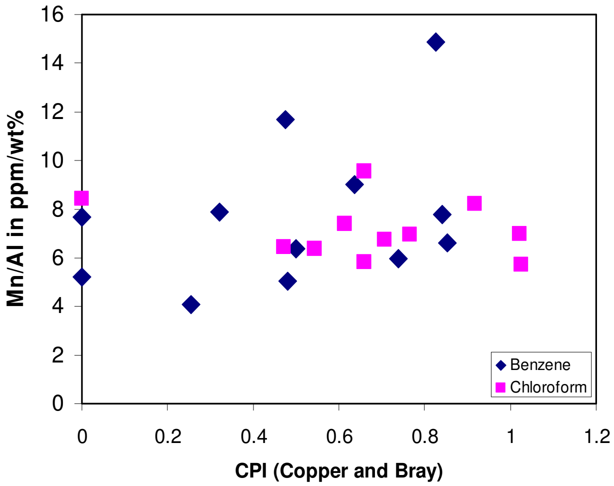
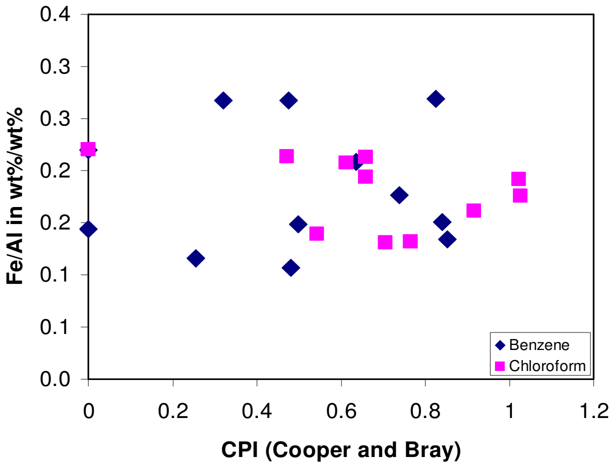
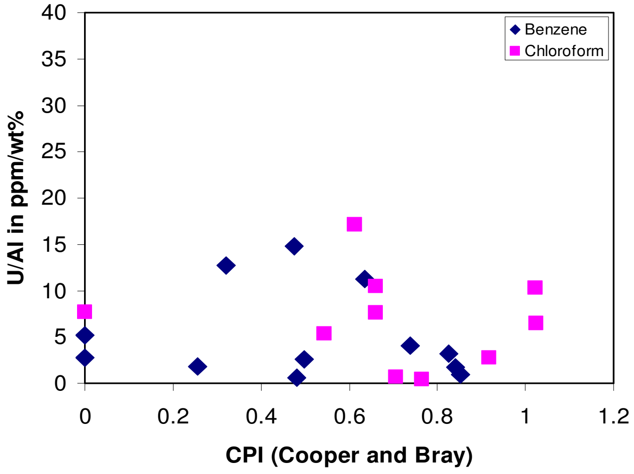
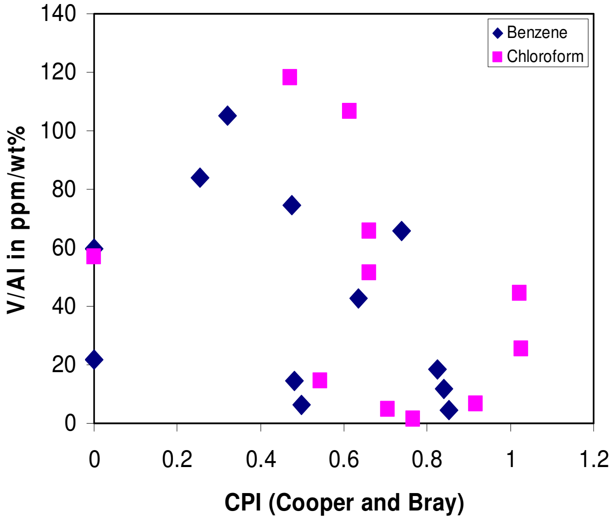


Figure 32 – Graph showing effect of biomarker ratio Carbon Preference Index (CPI) on metal concentration in extract after bitumen was extracted off the bulk sample (present work) and in C-TW-1 core shale samples.




Fe/Al in wt%/wt%
0.4
0.3
0.3
0.2
0.2
0.1
0.1
0.0
0
0.2
0.4
0.6
0.8
1
1.2
CPI (Cooper and Bray)
Benzene
Chloroform


U/Al in ppm/wt%
40
35
30
25
20
15
10
5
0
0
0.2
0.4
0.6
0.8
1
1.2
CPI (Cooper and Bray)
Benzene
Chloroform


V/Al in ppm/wt%
140
120
100
80
60
40
20
0
0
0.2
0.4
0.6
0.8
1
1.2
CPI (Cooper and Bray)
Benzene
Chloroform

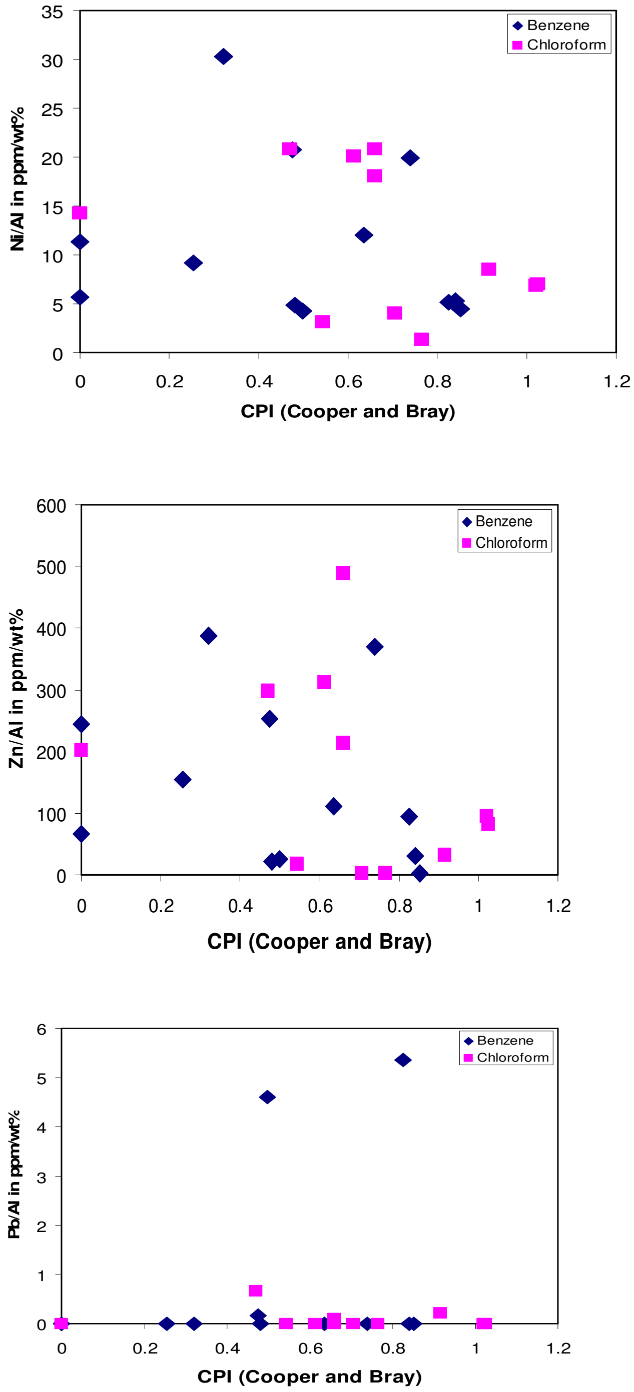


Figure 33 – Graph showing effect of biomarker ratio Carbon Preference Index (CPI) on metal concentration in extract after bitumen was extracted off the bulk sample (present work) and in IRC core shale samples.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The C-TW-1 and IRC black shale samples were analyzed for their organic and trace metal content. While fractionation of organic matter indicated a terrestrial origin for the organic matter in the IRC samples and marine origin for the C-TW-1 samples, study of biomarkers was indicative of presence of marine organic matter in both the samples, although a definite difference was observed in the nature of organic matter both qualitatively and quantitatively. However, a more detailed study needs to be done to further confirm the results. The maximum and minimum values for the organic matter, the CPI values calculated, all indicate that C-TW-1 samples are of marine origin while IRC samples are of terrestrial origin. Further Pr/Ph ratios indicated the paleoenvironemntal conditions when the rock was formed in terms of whether it was oxic or anoxic. It was observed that at lower depths the environment was anoxic in nature. With increasing depth the environment became oxic at around the middle range subsequently becoming anoxic again in both the C-TW-1 and IRC samples. Variation was also observed in the type of organic matter present. While some of the samples of IRC had maximum values of nC_{19} like the C-TW-1 samples which had its maximum at nC_{19} throughout, at increased depth maximum values were for nC_{23} and nC_{32}.

Trace metals analysis was also analyzed on the C-TW-1 and IRC samples. A decrease in the U/Al and Mn/Al ratio was observed for the C-TW-1 samples and only a decrease in the Mn/Al ratio was observed in the IRC samples. This could imply the loss of these metals during the extraction of bitumen.

5.2 RECOMMENDATIONS

1. Use of non polar, slightly polar, and highly polar solvents for extraction of bitumen in the different samples would give better characterization of the different organic matter present in the samples as one solvent by itself would not suffice to give the whole picture of the organic matter present in the sample. A good idea would be use of iso-octane, benzene, benzene-methanol (60:40), and chloroform as solvents.
2. Qualitative analysis of aromatics would highlight better the paleoenvironmental conditions during the formation of rock. The above was not done due to sample limitation.
3. Qualitative and quantitative estimation of trace metals present in the bitumen should be done to confirm the conclusions derived with respect to it in the thesis.
4. Qualitative and quantitative estimation of trace metals in the NSO fraction would confirm as to whether metals are present in the NSO fraction.

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APPENDIX

TABLE 1 – Bitumen yield using benzene in C-TW-1 black shale samples.

Sample	**Depth** (m)	**Bitumen** (mg/g)	**Asphaltene** (mg/g)	**Saturates** (mg/g)	**Aromatics** (mg/g)	**Resins** (mg/g)	**Total**	**Percentage recovery** (%)
289.3 3B	8824.20	8.11	0.61	2.13	0.79	1.24	4.76	58.78
289.3 5B	8827.50	8.04	1.02	2.75	1.23	1.59	6.58	81.92
289.3 6B	8828.70	7.24	0.64	2.39	0.70	1.31	5.04	69.61
289.3 7B	8829.95	11.96	1.40	3.82	1.47	2.44	9.14	76.41
289.3 8B	8831.50	7.59	0.83	2.35	1.22	1.33	5.74	75.59
289.3 9B	8833.40	8.14	1.18	2.44	0.93	1.53	6.09	74.78
289.3 10B	8834.80	4.66	0.35	1.58	0.59	0.85	3.38	72.47
289.3 12B	8841.68	7.67	0.81	2.44	1.04	1.40	5.69	74.26
289.3 13B	8846.93	8.13	0.18	2.66	0.44	0.70	3.99	49.04
289.3 14B	8852.03	10.30	0.68	2.74	0.88	1.27	5.57	54.06
294.0 20B	8913.98	4.50	0.51	1.26	0.67	0.82	3.25	72.22
294.0 19B	8919.95	4.58	0.76	0.87	0.45	1.01	3.10	67.68
294.0 17B	8931.25	4.27	0.46	1.30	0.51	0.90	3.17	74.19
294.0 16B	8938.00	4.09	0.28	1.06	0.44	0.78	2.56	62.50
294.0 15B	8944.15	4.08	0.28	1.13	0.46	0.87	2.74	67.20
294.0 14B	8945.70	3.99	0.28	1.11	0.41	0.82	2.62	65.64
294.0 13B	8947.40	3.60	0.24	1.03	0.48	0.83	2.58	71.68
294.0 11B	8951.55	3.16	0.14	0.99	0.91	0.74	2.78	88.00
294.0 10B	8952.85	4.24	0.20	1.31	0.56	0.91	2.97	70.09
294.0 9B	8954.10	4.44	0.35	1.24	0.63	0.87	3.09	69.55

TABLE 2 – Bitumen yield using chloroform in C-TW-1 black shale samples.

Sample	**Depth** (m)	**Bitumen** (mg/g)	**Asphaltene** (mg/g)	**Saturates** (mg/g)	**Aromatics** (mg/g)	**Resins** (mg/g)	**Total**	**Percentage recovery** (%)
289.3 12B	8841.68	7.07	1.17	1.64	1.00	1.58	5.40	76.34
294.0 17B	8931.25	2.50	0.39	0.33	0.28	0.69	1.70	68.06

TABLE 3 - Bitumen yield using benzene in IRC black shale samples.

Sample	**Depth**	**Bitumen**	**Asphaltene**	**Saturates**	**Aromatics**	**Resins**	**Total**	**Percentage recovery**
	(m)	**(mg/g)**	**(mg/g)**	**(mg/g)**	**(mg/g)**	**(mg/g)**		**(%)**
1036.7 2 GR	36602.31	1.47	0.11	0.32	0.31	0.32	1.07	72.26
1036.7 1 GR	36605.21	3.26	1.03	0.47	0.26	0.11	1.87	57.50
1036.7 2B	31611.66	3.34	0.53	0.44	0.23	1.04	2.25	67.44
1036.7 3B	31615.66	1.79	0.22	0.24	0.36	0.71	1.52	85.00
1036.7 4B	31619.86	1.46	0.10	0.13	0.07	0.43	0.73	50.00
1036.7 5B	31623.34	1.59	0.00	0.09	1.05	0.24	1.39	86.88
1036.7 6B	31626.36	2.74	0.46	0.49	0.34	1.23	2.52	92.13
1036.7 7B	31629.89	1.93	0.19	0.47	0.50	0.33	1.49	77.21
1036.7 8B	31634.41	1.95	0.33	0.28	0.31	0.35	1.28	65.32
1036.7 9B	31638.96	2.92	0.02	0.29	0.07	0.76	1.15	39.23
1039.2 10B	31646.43	1.27	0.04	0.27	0.38	0.55	1.23	96.67
1039.2 9B	31649.08	1.31	0.02	0.24	0.29	0.42	0.97	74.00
1039.2 8B	31652.83	1.42	0.14	0.19	0.35	0.66	1.35	94.55
1039.2 7B	31656.68	1.82	0.14	0.14	0.21	0.47	0.96	52.75
1039.2 5B	31664.98	2.72	0.02	0.21	0.15	1.22	1.60	58.92

TABLE 4 – Bitumen yield using chloroform in IRC black shale samples.

Sample	**Depth** **(m)**	**Bitumen** **(mg/g)**	**Asphaltene** **(mg/g)**	**Saturates** **(mg/g)**	**Aromatics** **(mg/g)**	**Resins** **(mg/g)**	**Total**	**Percentage recovery** **(%)**
1036.7 2 GR	36602.31	2.29	0.74	0.37	0.43	0.65	2.19	95.74
1036.7 1 GR	36605.21	6.19	2.47	0.57	0.66	1.51	5.21	84.09
1036.7 2B	31611.66	5.17	0.62	0.35	0.31	1.73	3.02	58.33
1036.7 3B	31615.66	4.19	0.99	0.43	0.81	1.85	4.09	97.76
1036.7 4B	31619.86	6.38	1.57	0.54	0.61	3.49	6.20	97.19
1036.7 5B	31623.34	4.48	1.00	0.15	0.42	1.69	3.25	72.65
1036.7 6B	31626.36	5.80	2.34	0.42	0.53	1.80	5.08	87.68
1036.7 7B	31629.89	6.34	0.00	0.00	0.00	0.00	0.00	0.00
1036.7 8B	31634.41	5.51	1.30	0.41	0.87	1.70	4.29	77.79
1036.7 9B	31638.96	6.59	1.98	0.45	0.42	1.73	4.57	69.39
1039.2 10B	31646.43	3.18	0.88	0.31	0.49	1.35	3.03	95.33
1039.2 9B	31649.08	5.40	1.41	0.53	0.39	1.58	3.92	72.55
1039.2 8B	31652.83	8.02	2.91	0.31	0.64	2.51	6.36	79.33
1039.2 7B	31656.68	4.73	1.87	0.41	0.61	1.73	4.63	97.73
1039.2 5B	31664.98	8.80	3.88	0.38	0.35	2.42	7.02	79.80

TABLE 5 – Ratios of saturate hydrocarbons, aromatic hydrocarbons, and NSO compounds in bitumen (benzene extraction) in C-TW-1 black shale samples

Sample	**Pr/Ph**	**Pr/nC_{17}**	**Ph/nC_{18}**	**CPI**	$\frac{C_{21}+C_{22}}{C_{28}+C_{29}}$	**Maximum**	**Minimum**
289.3 3B	0.53	0.63	0.60	0.46	4.02	nC_{19}	nC_{23}
289.3 5B	0.79	1.30	15.48	0.77	5.36	nC_{19}	nC_{15}
289.3 6B	0.87	1.02	13.67	0.93	5.13	Ph	nC_{15}
289.3 7B	0.63	5.02	7.55	0.52	1.85	nC_{19}	nC_{17}
289.3 8B	0.64	1.99	20.10	0.88	3.85	nC_{19}	nC_{18}
289.3 9B	0.71	1.33	15.39	0.86	3.95	nC_{19}	nC_{18}
289.3 10B	0.56	1.19	0.46	0.84	7.17	nC_{19}	nC_{28}
289.3 12B	0.70	0.50	0.74	1.02	6.48	nC_{19}	nC_{32}
289.3 13B	1.11	2.47	20.81	0.61	3.68	nC_{19}	nC_{24}
289.3 14B	1.33	0.51	7.43	1.04	8.41	nC_{19}	nC_{32}
294.0 20B	1.18	0.85	7.07	1.05	8.70	nC_{19}	nC_{32}
294.0 19B	0.38	1.00	0.65	0.60	2.64	nC_{19}	nC_{16}
294.0 17B	0.32	0.82	0.33	1.18	6.26	nC_{19}	nC_{16}
294.0 16B	0.25	0.77	0.51	0.88	2.22	nC_{19}	nC_{16}
294.0 15B	0.34	2.04	0.51	1.09	4.71	nC_{19}	nC_{16}
294.0 14B	0.33	1.30	0.43	1.02	5.06	nC_{19}	nC_{32}
294.0 13B	0.19	0.82	5.55	0.96	4.13	nC_{19}	nC_{16}
294.0 11B	0.00	….	6.66	0.80	2.74	nC_{19}	nC_{32}
294.0 10B	0.46	3.10	4.20	0.78	3.64	nC_{19}	nC_{32}

TABLE 6 – Ratios of saturate hydrocarbons, aromatic hydrocarbons, and NSO compounds in bitumen (chloroform extraction) in C-TW-1 black shale samples

Sample	**Pr/Ph**	**Pr/nC_{17}**	**Ph/nC_{18}**	**CPI**	$\frac{C_{21}+C_{22}}{C_{28}+C_{29}}$	**Maximum**	**Minimum**
289.3 12B	0.46	0.23	0.37	0.95	7.58	nC_{19}	nC_{15}
294.0 17B	…	…	…	1.16	0.83	nC_{20}	nC_{23}

TABLE 7 – Ratios of saturate hydrocarbons, aromatic hydrocarbons, and NSO compounds in bitumen (benzene extraction) in IRC black shale samples

Sample	**Pr/Ph**	**Pr/nC_{17}**	**Ph/nC_{18}**	**CPI**	$\frac{C_{21}+C_{22}}{C_{28}+C_{29}}$	**Maximum**	**Minimum**
1036.7 2 GR	0	…	0.70	…	…	nC_{19}	Ph
1036.7 1 GR	0.47	0.49	0.30	0.85	3.18	nC_{19}	Pr
1036.7 2B	0.40	0.71	0.57	0.48	1.43	nC_{19}	nC_{24}
1036.7 3B	0.50	4.28	6.58	0.49	2.22	nC_{19}	nC_{32}
1036.7 4B	0.56	0.79	0.60	0	…	nC_{19}	nC_{16}
1036.7 5B	0.48	1.15	0.73	0	…	nC_{19}	nC_{17}
1036.7 6B	0.42	0.79	0.64	0.25	2.38	nC_{19}	nC_{28}
1036.7 7B	0.74	0.56	0.75	…	…	nC_{19}	nC_{32}
1036.7 8B	0.48	0.60	0.72	0.47	2.94	nC_{19}	nC_{24}
1036.7 9B	0.99	0.46	0.73	…	…	nC_{19}	nC_{32}
1039.2 10B	…	….	…	0.84	1.98	nC_{23}	nC_{20}
1039.2 9B	…	0	…	0.82	1.37	nC_{32}	nC_{17}
1039.2 8B	…	…	…	0.73	1.48	nC_{18}	nC_{17}
1039.2 7B	0.25	1.01	0.67	0.63	…	nC_{19}	nC_{32}
1039.2 5B	…	…	…	0.32	0	nC_{32}	nC_{25}
1039.2 3B	Not analyzed						

TABLE 8 – Ratios of saturate hydrocarbons, aromatic hydrocarbons, and NSO compounds in bitumen (chloroform extraction) in IRC black shale samples

Sample	**Pr/Ph**	**Pr/nC_{17}**	**Ph/nC_{18}**	**CPI**	**$C_{21}+C_{22}/C_{28}+C_{29}$**	**Maximum**	**Minimum**
1036.7 2 GR	…	…	…	0.7654	3.2861	nC_{18}	nC_{28}
1036.7 1 GR	…	0	0	0.7061	3.3646	nC_{18}	nC_{28}
1036.7 2B	Not analyzed						
1036.7 3B	2.6238	0.16	0.0416	0.9167	7.5523	nC_{18}	Ph
1036.7 4B	0.7862	0.2791	0.2653	0.6131	3.9828	nC_{19}	nC_{28}
1036.7 5B	0	…	2.7576	0	…	nC_{19}	nC_{18}
1036.7 6B	Not analyzed						
1036.7 7B	…	…	…	…	…	nC_{19}	nC_{32}
1036.7 8B	…	…	…	0.6597	5.0945	nC_{19}	nC_{32}
1036.7 9B	Not analyzed						
1039.2 10B	1.51	0.3778	0.1052	0.5439	3.1335	nC_{18}	nC_{24}
1039.2 9B	0	0	0.8357	1.0254	3.6109	nC_{18}	nC_{25}
1039.2 8B	…	…	0	0.6597	5.0945	nC_{18}	nC_{32}
1039.2 7B	…	0	0	1.0219	..	nC_{19}	nC_{32}
1039.2 5B	Not analyzed						
1039.2 3B	..	…	0	0.4707	..	nC_{19}	nC_{18}

Note - … indicates denominator was zero hence value is undefined
0 indicated numerator is 0 hence ratio is zero.

TABLE 9A – Trace metals present in shale following bitumen extraction (benzene) in C-TW-1 black shales

Sample	Depth m	U ppm	Cd ppm	Cr ppm	Cu ppm	Fe ppm	Ni Ppm	Pb ppm	Sr Ppm
289.3 3B	8824.20	11	0	33	5.8	3287	77	39	647
289.3 5B	8827.50	13	0	18	7.6	862	32	39	162
289.36B	8829.95	1.4	0	73	4.0	1105	41	49	68
289.37B	8831.50	3.2	0	158	2.2	3002	66	36	258
289.3 8B	8831.50	0	0	114	115	2065	28	83	176
289.3 9B	8833.40	6.5	0	209	1930	6150	35	122	523
289.310B	8834.80	5.8	0	64	14930	5276	1171	1455	331
289.3 12B	8841.68	3.6	0	49	4	1261	13	0	81
289.313B	8846.93	7.8	0	157	0	9022	0	181.25	818
289.314B	8852.03	0	0	39	58	3204	83	0	427
294.019B	8919.95	41	19	117	29	2526	95	30	258
294.011B	8951.55	0	0	0	0	1059	124	0	87
294.010B	8952.85	0	16	90	35	1766	110	0	185
294.09B	8954.10	8.7	0	12	10	1230	43	2.6	256

TABLE 9B – Trace metals present in shale following bitumen extraction (benzene) in C-TW-1 black shales

Sample	**Depth m**	**Rb ppm**	**Na ppm**	**Mg ppm**	**K ppm**	**Ga ppm**	**Cs Ppm**	**Ca Ppm**
289.3 3B	8824.20	453	1127	2608	2468	159	18	2258
289.3 5B	8827.50	314	556	1794	1101	105	6.4	3171
289.36B	8829.95	608	926	2878	3308	204	14	3256
289.37B	8831.50	785	1412	4382	5734	268	33	4919
289.3 8B	8831.50	611	1075	3519	3816	207	39	5476
289.3 9B	8833.40	1576	1975	6237	6734	538	63	12217
289.310B	8834.80	1914	1919	5443	4883	648	50	9225
289.3 12B	8841.68	686	1019	2977	2941	229	18	4106
289.313B	8846.93	1136	1633	3180	5606	402	27	2654
289.314B	8852.03	886	2027	7060	7808	305	65	20223
294.019B	8919.95	418	1150	3099	2948	144	24	5747
294.011B	8951.55	591	1135	3064	3391	197	24	7368
294.010B	8952.85	512	2076	7124	4106	177	18	25775
294.09B	8954.10	326	1341	4650	2950	109	28	17498

TABLE 9C – Trace metals present in shale following bitumen extraction (benzene) in C-TW-1 black shales

Sample	**Depth m**	**Al ppm**	**Zn ppm**	**Mn ppm**	**V ppm**
289.3 3B	8824.20	5227	134	131	43
289.3 5B	8827.50	2178	38	95	17
289.36B	8829.95	6606	62	133	73
289.37B	8831.50	12124	56	185	151
289.3 8B	8831.50	8238	178	147	95
289.3 9B	8833.40	14136	1072	328	170
289.310B	8834.80	11003	9464	245	61
289.3 12B	8841.68	5936	3	121	57
289.313B	8846.93	11889	12	183	218
289.314B	8852.03	16993	103	461	10
294.019B	8919.95	6848	993	82	338
294.011B	8951.55	7195	32	134	0
294.010B	8952.85	11274	965	73	301
294.09B	8954.10	6729	84	245	0

TABLE 10A – Trace metals present in shale following bitumen extraction (chloroform) in C-TW-1 black shales

Sample	**Depth m**	**U ppm**	**Cd ppm**	**Cr ppm**	**Cu ppm**	**Fe ppm**	**Ni ppm**	**Pb ppm**	**Sr ppm**
289.3 12 B	8841.68	19	0	14	0	1284	23	0	98
294.0 17B	8931.25	22	0	150	7.1	3453	54	28	385

TABLE 10B – Trace metals present in shale following bitumen extraction (chloroform) in C-TW-1 black shales

Sample	**Depth m**	**Rb ppm**	**Na ppm**	**Mg ppm**	**K ppm**	**Ga ppm**	**Cs ppm**	**Ca ppm**
289.3 12 B	8841.68	649	1169	3038	2324	216	15	4638
294.0 17B	8931.25	932	1904	5422	4695	320	41	25617

TABLE 10C – Trace metals present in shale following bitumen extraction (chloroform) in C-TW-1 black shales

Sample	**Depth m**	**Al ppm**	**Zn ppm**	**Mn ppm**	**V ppm**
289.3 12 B	8841.68	4118	43	129	29
294.0 17B	8931.25	10743	514	205	194

TABLE 11A – Trace metals present in shale following bitumen extraction (benzene) in IRC black shales

Sample	**Depth m**	**U ppm**	**Cd ppm**	**Cr ppm**	**Cu ppm**	**Fe ppm**	**Ni ppm**	**Pb ppm**	**Sr ppm**
1036.7 2GR	31605.21	7.6	0	68	6.7	1737	43	0	195
1036.7 1GR	31608.36	8.1	0	73	0	1184	40	0	117
1036.7 2B	31611.66	12	0	219	24	2182	99	0	240
1036.7 3B	31615.66	34	0	80	0	1943	56	60	150
1036.7 4B	31619.86	78	0	71	4.3	2141	85	0	209
1036.7 5B	31623.34	24	19	32	9.0	1889	98	0	91
1036.7 6B	31626.36	38	97	278	41	2459	196	0	157
1036.7 7B	31629.89	77	40	100	31	1788	134	0	81
1036.7 8B	31634.41	91	23	50	28	1651	128	1.0	260
1036.7 9B	31638.96	102	32	73	1.3	775	70	0	177
1039.2 10B	31646.43	17	0	66	3.5	1435	50	0	187
1039.2 9B	31649.08	32	0	191	1574	2716	52	54	418
1039.2 8B	31652.83	31	75	128	55	1359	153	0	104
1039.2 7B	31656.68	118	15	80	39	2199	127	0	314
1039.2 5B	31664.98	70	58	202	42	1473	167	0	170
1039.2 3B	31672.28	118	25	49	16	903	90	0	94

TABLE 11B Trace metals present in shale following bitumen extraction (benzene) in IRC black shales

Sample	Depth m	Rb ppm	Na ppm	Mg ppm	K ppm	Ga ppm	Cs Ppm	Ca Ppm
1036.7 2GR	31605.21	375	1661	7601	4604	129	24	14560
1036.7 1GR	31608.36	501	1215	5528	3171	169	15	9554
1036.7 2B	31611.66	616	1883	9670	7474	220	47	26046
1036.7 3B	31615.66	971	2917	8190	4501	334	18	29604
1036.7 4B	31619.86	876	2989	9191	5206	305	18	38146
1036.7 5B	31623.34	833	1944	8429	3051	286	39	26922
1036.7 6B	31626.36	739	2131	10998	8409	266	52	32164
1036.7 7B	31629.89	883	2883	5574	3667	302	35	8680
1036.7 8B	31634.41	391	1448	5855	1982	137	30	16074
1036.7 9B	31638.96	439	954	3826	1535	151	8	15259
1039.2 10B	31646.43	461	2077	6865	3454	160	49	33647
1039.2 9B	31649.08	480	1196	4094	4635	164	37	12516
1039.2 8B	31652.83	568	1877	5557	2717	196	40	21180
1039.2 7B	31656.68	496	2022	9003	3422	173	21	32194
1039.2 5B	31664.98	411	1137	5513	1972	144	12	17214
1039.2 3B	31672.28	452	757	3653	971	154	6	10645

TABLE 11C – Trace metals present in shale following bitumen extraction (benzene) in IRC black shales

Sample	**Depth m**	**Al ppm**	**Zn ppm**	**Mn ppm**	**V ppm**
1036.72GR	31605.21	12482	80	100	35
1036.71GR	31608.36	8853	26	58	41
1036.7 2B	31611.66	20362	435	103	296
1036.7 3B	31615.66	13109	329	83	82
1036.7 4B	31619.86	14878	987	78	323
1036.7 5B	31623.34	8592	2096	66	512
1036.7 6B	31626.36	21285	3290	87	1784
1036.7 7B	31629.89	9149	2134	44	832
1036.7 8B	31634.41	6179	1567	72	460
1036.7 9B	31638.96	4373	1327	32	456
1039.2 10B	31646.43	9496	290	74	112
1039.2 9B	31649.08	10111	963	150	188
1039.2 8B	31652.83	7692	2842	46	505
1039.2 7B	31656.68	10548	1178	95	451
1039.2 5B	31664.98	5503	2132	43	579
1039.2 3B	31672.28	3155	1594	23	385

TABLE 12A – Trace metals present in shale following bitumen extraction (chloroform) in IRC black shales

Sample	**Depth** **m**	**U** **ppm**	**Cd** **ppm**	**Cr** **ppm**	**Cu** **ppm**	**Fe** **ppm**	**Ni** **ppm**	**Pb** **ppm**	**Sr** **ppm**
1036.7 2GR	31605.21	5.3	0	54	0	1540	16	0	162
1036.7 1GR	31608.36	7.5	0	92	0	1352	42	0	137
1036.7 2B	31611.66	33	0	157	23	2097	100	0	305
1036.7 3B	31615.66	23	0	59	14	1356	71	1.8	163
1036.7 4B	31619.86	128	78	119	34	1557	151	0	312
1036.7 5B	31623.34	67	30	30	17	1932	125	0	208
1036.7 6B	31626.36	134	77	146	30	1639	147	0	361
1036.7 7B	31629.89	127	1.4	14	0	464	23	0	35
1036.7 8B	31634.41	68	33	49	20	1730	161	0.9	114
1036.7 9B	31638.96	153	82	184	31	1472	164	0	195
1039.2 10B	31646.43	75	0	105	0	1945	44	0	270
1039.2 9B	31649.08	55	0	73	4.3	1485	60	0	168
1039.2 8B	31652.83	55	52	75	28	1109	108	0	86
1039.2 7B	31656.68	129	0	105	14	2390	86	0	285
1039.2 5B	31664.98	114	78	352	57	1963	212	0	235
1039.2 3B	31672.28	117	6.1	20	4.2	175	17	0.5	19

TABLE 12B – Trace metals present in shale following bitumen extraction (chloroform) in IRC black shales .

Sample	Depth m	Rb ppm	Na ppm	Mg ppm	K ppm	Ga ppm	Cs Ppm	Ca Ppm
1036.7 2GR	31605.21	510	1450	6739	4323	173	23	12317
1036.7 1GR	31608.36	521	1376	6346	3831	175	18	10824
1036.7 2B	31611.66	633	2002	8942	4678	221	21	27360
1036.7 3B	31615.66	423	2229	5740	2799	148	12	21467
1036.7 4B	31619.86	428	1553	6761	2689	151	13	24014
1036.7 5B	31623.34	731	1923	8750	2651	251	16	29039
1036.7 6B	31626.36	488	1557	7306	3385	172	15	24249
1036.7 7B	31629.89	454	913	1956	1304	151	4	2685
1036.7 8B	31634.41	574	1775	7738	2846	196	19	20028
1036.7 9B	31638.96	451	1834	7595	3799	160	10	27657
1039.2 10B	31646.43	799	2267	9285	5284	273	26	41787
1039.2 9B	31649.08	675	1782	5428	2980	230	13	21042
1039.2 8B	31652.83	760	1412	4647	1786	257	6	11043
1039.2 7B	31656.68	896	2176	9755	4383	309	23	33022
1039.2 5B	31664.98	536	1558	7962	3686	187	20	22877
1039.2 3B	31672.28	37	119	664	303	13	2	1962

TABLE 12C – Trace metals present in shale following bitumen extraction (chloroform) in IRC black shales

Sample	**Depth m**	**Al ppm**	**Zn ppm**	**Mn ppm**	**V ppm**
1036.72GR	31605.21	11688	23	81	16
1036.71GR	31608.36	10315	29	70	49
1036.7 2B	31611.66	13493	441	98	213
1036.7 3B	31615.66	8384	269	69	56
1036.7 4B	31619.86	7491	2335	56	800
1036.7 5B	31623.34	8771	1769	74	500
1036.7 6B	31626.36	9235	2368	57	958
1036.7 7B	31629.89	3644	549	7.8	283
1036.7 8B	31634.41	8923	1903	85	588
1036.7 9B	31638.96	10803	2410	71	1074
1039.2 10B	31646.43	13961	251	89	203
1039.2 9B	31649.08	8453	693	48	216
1039.2 8B	31652.83	5206	2542	30	268
1039.2 7B	31656.68	12450	1180	87	555
1039.2 5B	31664.98	9634	2697	56	924
1039.2 3B	31672.28	817	244	5.3	96

VITA

Type Full Name Here – Sruthi Subbanna

Candidate for the Degree of

Master of Science

Thesis: ORGANIC MATTER AND TRACE EMTAL PRESERVATION IN PENNSYLVANIAN BLACK SHALES

Major Field: Environmental Science

Biographical:

Personal Data:
Born in Mumbai, India

Education:
Master of Science in Environmental Science (GPA – 3.75) Dec 2007
Oklahoma State University, Stillwater, OK
Post Graduate Diploma in Environmental Pollution Control Technology May 2003
Mumbai University, Mumbai, India
Bachelor of Science in Microbiology Mar 2001
Mumbai University, Mumbai, India

Experience:
Biosystems Department - OSU Jan 2007 – May 2007
Title: Teaching Assistant
Biosystems Department - OSU Feb 2006 - Dec 2006
Title: Research Assistant (Silt fence project)
Batliboi Environmental Engineering Ltd., Mumbai, India Feb 2004 - Jul 2005
Title: Technical Officer

Professional Memberships:
Society of Environmental ScientistsVITA

Name: Sruthi Subbanna Date of Degree: December, 2007

Institution: Oklahoma State University Location: Stillwater, Oklahoma

Title of Study: ORGANIC MATTER AND TRACE METAL PRESERVATION IN PENNSYLVANIAN BLACK SHALES

Pages in Study: 115 Candidate for the Degree of Master of Science

Major Field: Environmental Science

Scope and Method of Study:

The study involved organic matter and trace emtal analysis in black shale samples from Oklahoma and Iowa.

Findings and Conclusions:

Pennsylvanian black shale samples from two cores (Oklahoma, C-TW-1 and Iowa, IRC) were analyzed for their organic and trace metal content. The objective was to determine organic matter preservation and trace metal concentration. Organic matter in shales had a first-order effect on trace metal concentration. Organic geochemical proxies' results indicated a terrestrial origin for samples from Iowa, and a marine origin for Oklahoma samples. C-TW-1 core shale samples consisted of almost 50% saturate hydrocarbon fraction in the bitumen and IRC core shale samples were greatly rich in resins and asphaltene fraction. Trace metal in extracted obtained after removal of the bitumen fraction showed lower metal concentration compared to bulk samples, indicating the presence of metals the organic fraction. This study suggests that differences in the shale samples resulted from different origin and redox conditions during preservation.

Keywords:
Pennsylvanian, black shale, organic matter, trace metal, biomarker, paleoenvironment.

ADVISER'S APPROVAL: Dr. Dee Ann Sanders