

THESIS

ORGANIC GEOCHEMISTRY OF MESOPROTEROZOIC NONESUCH FORMATION AT
WHITE PINE, MICHIGAN, USA

Submitted by

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ABSTRACT

ORGANIC GEOCHEMISTRY OF MESOPROTEROZOIC NONWSUCH FORMATION AT WHITE PINE, MICHIGAN, USA

The quality and quantity of the preserved organic matter (OM) in the Mesoproterozoic Nonesuch Formation at White Pine are evaluated in this project. Specifically, I have considered whether the rocks had source rock potential and whether there is a relationship between the OM and copper mineralization. The copper mineralization and hydrocarbons migration pathways are hypothesized to be related. There are three possibilities for the relationship. The copper ore fluid may have migrated with the hydrocarbons. The copper may also have precipitated where the hydrocarbons had accumulated, or the copper precipitated where there were accumulations of OM.

Three cores (42C, 37F, and 30G) from in or near the White Pine mine were described and analyzed. The sampled core intervals are mostly from the Lower Nonesuch Formation with some from higher intervals. The overall lithology is gray laminated siltstone, with some sandy siltstone and lesser shale and sandstone. The core samples have various colors, with brown to dark brown samples hosting organic matter. The most abundant minerals are quartz, feldspar

(plagioclase, orthoclase), mica, and some rock fragments; calcite and chlorite are mostly found as cement.

Various analyses were done to investigate the organic matter. For estimating the maturity, kerogen type, and potential source rock quality, samples were subjected by the Rock Eval pyrolysis. Also other techniques were used for evaluating maturation, including ultraviolet microscopy and vitrinite reflectance microscopy; it was determined that the majority of samples have little to no vitrinite-like material.

The organic matter as analyzed by the UV microscope is observed to be of three types, kerogen, bitumen, and oil inclusions. The oil inclusions are mostly found in the sandy siltstone samples. The organic matter is mostly not fluorescent possibly because it is overmature or immature; it contains less than about 10% pyrolyzable hydrocarbons. The organic matter may have been produced from remains of organisms like algae and fungus deposited within a lacustrine and/or transitional marine environment. The generative potential of the organic matter is in the poor to fair range. The range of TOC (total organic carbon) content is between 0.01 and 0.86 wt %. The highest value is detected above the mineralization zone in the Upper Nonesuch Formation.

The kerogens of the Nonesuch Formation are types III and IV, types that usually are gas prone, or have no hydrocarbon potential. The samples may have been oxidized by copper bearing fluids which altered the organic matter and reduced its potential to produce hydrocarbons. Overall, the organic matter of the lower Nonesuch Formation at White Pine has no potential to produce hydrocarbons.

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I must thank my husband; I would not have made it this far without his support. I thank him for the countless help on working on my thesis, work with me on preparing samples for some analysis, and driving me to Kentucky to do some lab work.

Finally, I would like to thank all my family and my friends who helped me through two years of graduate school; I would not be in this far without their support, they always have been there for me and keeping me on the right track.

DEDICATION

This thesis is dedicated to the soul of my parents, who taught me and always supported me. For

all my family and my friends who provide me the unlimited love and support.

To my beloved husband, Ahmad who is always ready to engage with the struggle to support

me, who has been a great source of motivation and inspiration.

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1. Introduction:

1.1 The aim of this study:

In this project I am investigating unusually well preserved Precambrian organic matter (OM). In particular I consider whether the host rocks had source rock potential and whether there is a relationship between the OM and the copper mineralization present in part of the strata studied. The OM is within the mudstone and sandy siltstone of the Mesoproterozoic Nonesuch Formation in the Mid-Continent Rift in northern Michigan. At White Pine, Michigan, the Nonesuch Formation has been studied as the host of native copper and copper sulfide ore. There has been some work on hydrocarbons within the White Pine Copper deposits, including a study of water washing of oil (Mauk and Burruss, 2002). Other earlier studies (e.g. Kelly and Nishioka, 1985, Ho and Mauk, 1996) have shown that the formation may have included good hydrocarbon source rocks. One previous study focused on the textural characteristics that may have controlled paleopermeability at the time of copper mineralization (King, 2009). That study suggested that it is important to understand the paleopermeability in order to follow the fluid movements, including hydrocarbon migration, within the Nonesuch Formation. One goal of this study is to evaluate these Precambrian rocks as

former source material for oil and gas generation, and to estimate the generated quantity. In addition, I will explore the origin of the preserved OM, and explore the hypothesis that copper mineralization and hydrocarbons migration pathways were related. It was determined that there is no potential for economic generation of oil from the Nonesuch Formation. But, the importance of this project is twofold: (1) it may improve understanding of the relationship between organic matter maturation and copper mineralization, a relationship suggested by Lewan et al. (2008) in a study of the Kupferschiefer deposits and (2) it may contribute to improve records of Precambrian OM that may assist in global correlations of early Paleozoic and Precambrian successions.

1.2 Hypothesis:

Copper mineralization is hypothesized to show a relationship to organic matter maturation. The study area rocks host organic matter. The Nonesuch Formation has copper deposits precipitated by ore fluids; however, did the copper ore fluids also affect the maturation of organic matter or migration of hydrocarbons? If so, was oil or any other hydrocarbons produced in the Nonesuch Formation, and was oil present at the time of copper mineralization? These possibilities and the existence or lack of some characteristics of organic matter could

allow better understanding of copper mineralization in the Nonesuch Formation and the environment for copper to precipitate from the metalliferous fluids.

1.3 Abbreviations used in Text:

TOC: Total organic carbon, OM: Organic Matter, HI: Hydrogen Index, OI: Oxygen index, S1: Quantity of free volatile Hydrocarbons, S2: the amount of generated hydrocarbons by cracking of nonvolatile organic matter, S3: Carbon Dioxide formed from organic matter, T_{max} : the temperature of the maximum released hydrocarbons, PI: Production Index, Ro: Vitrinite Reflectance, UV: Ultraviolet.

2. Background:

2.1 General Occurrence of carbon in sedimentary rocks:

Carbon is recycled through the biosphere by biological activities like photosynthesis. The recycling processes mainly depend on plants and animals. Plants called phytoplankton use carbon dioxide to form the necessary molecular bound carbon to build their cells. Animals or “zooplankton”, eat the plants and give off the carbon as CO_2 which is then recycled by plants. In addition, oxidized dead organisms release carbon to CO_2 and to organic molecules, (figure 1).

Some of the released carbon molecules have been buried and since life’s beginning have produced hydrocarbon accumulations. Carbon in sediments exists in two types: oxidized and reduced. The oxidized carbon is usually found as carbonates, while the reduced is found as organic matter created by biological activities. The total organic carbon (TOC) is the full amount of organic compounds that contain carbon within sediments or water; it constitutes the reduced or the total oxidizable carbon.

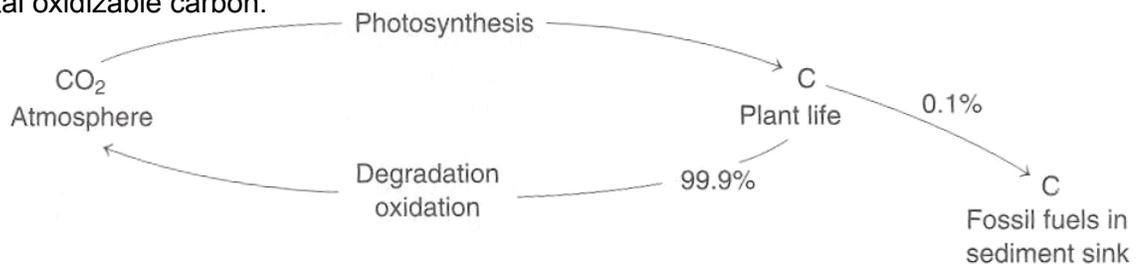


Fig (1) Carbon cycle through the biosphere by photosynthesis and oxidation, Hunt (1995)

Zooplankton and phytoplankton comprise about 90% of ocean life (Hunt 1995). The sedimentary environments, whether marine or lacustrine, have different amounts of oxygen. If it has more than 1 ml/l of dissolved oxygen it is an oxic environment, 1 to 0.1 ml/l of dissolved oxygen it is suboxic, and less than 0.1 ml/l it is anoxic environment (Hunt, 1995). The oxygen percent depends on many parameters, for example the activities of organisms, water table, and depth of sediments. Some organisms, like calcareous fossils (animal), have to live in an oxic environment to survive; others can live with less oxygen or no oxygen such as dysaerobic organisms and sulfate reducing bacteria, respectively. Hunt, 1995 explained the reason why there is no systematic relationship between the activities of organisms and TOC in sediments. He suggested that the preservation of organic carbon is more essential than the production. Organic carbon can be produced and accumulate in different environments; however, the preservation factor is different. The factor would be about 0.01% in highly oxidized environment like the central Pacific, while 10% in a reducing environment such as the Black Sea.

Within oxic environments, the deceased organisms fall down through the water and can be partially consumed by marine animals and some microorganisms. There are also some particles, like fecal pellets, which can reach the sea bottom without being consumed. In addition, some soft bodied organisms like worms, can burrow up to several centimeters within the marine

sediments, which may increase the oxygen diffusion at the sea bottom. In this oxidized environment, the TOC of the deep marine sediments hardly ever reaches 1% and it is usually between 0.05 and 0.5% (Hunt 1995, p114), Fig (2).

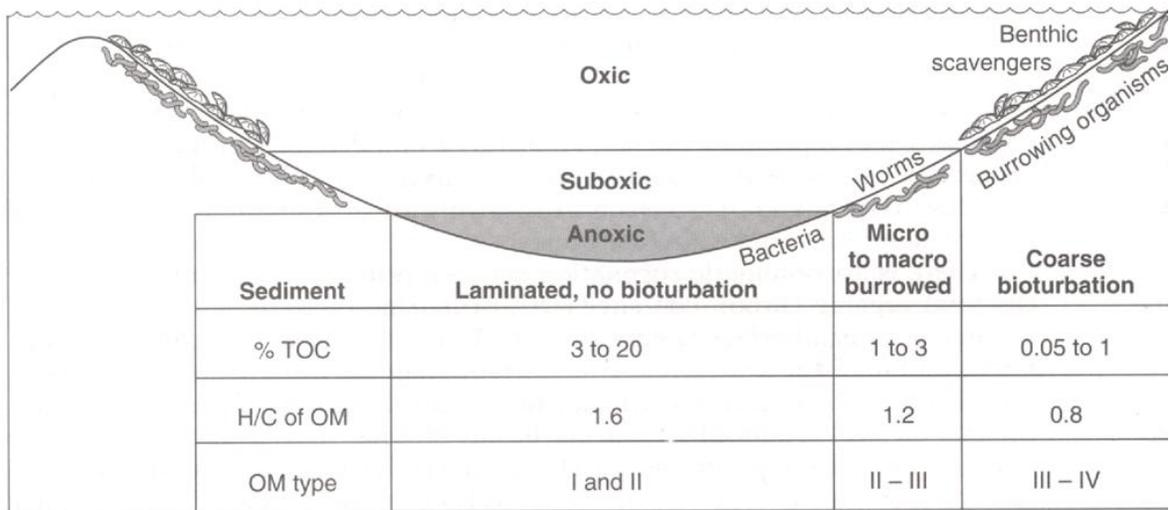


Figure (2) illustrates the marine and lacustrine sedimentary environments and indicates the H/C ratio, TOC in %, and the type of organic matter in the environments. Hunt 1995.

2.2 Sc

Hydrocarbon source rocks as seen in figure (3) are defined as organic-rich rocks that are able to produce enough hydrocarbons by a natural process to form a marketable accumulation of oil and/or natural gas (Hunt 1995). The source rocks can be active, producing hydrocarbons within their present setting, or can be inactive because of uplift with erosion and cooling or not being buried deeply enough. The source rocks that host the organic material are usually fine

grained, calcareous, dolomitic, or siliceous shale, or argillaceous limestones. These organic-rich fine-grained source rocks are one aim of oil and gas exploration, so the oil exploration companies use highly sophisticated techniques to characterize the source rock properties like, maturity, organic matter quality and quantity. When organisms die, their remains are deposited in the mud on the bottom of the ocean or lake where they used to live. With exposure to increased temperature of burial deep under young sediments, the remains of the organisms are modified into materials such as bitumen, kerogen, or petroleum. The temperature to cause modification is generally ranges between 60 and 200°C in the subsurface; the oil window is about 60–160 °C, and the gas window ca. 150–200 °C.



Fig (3) shows a specimen of hydrocarbon source rock (shale), Carboniferous, Spitsbergen, <http://oilandgasgeology.com/>

2.3 Kerogen:

Kerogen is defined as organic matter in sediments that is insoluble in normal petroleum solvents (figure 4). Kerogen is a term applied to organic material that is included within source rock where the organics are converted to oils. Chemically, it has long chains of biopolymers that include carbon, hydrogen and oxygen with small amounts of nitrogen and sulfur. The kerogen is divided into different types based on the ratio between the carbon, hydrogen, and oxygen. These types are: type I, II, III, and IV. Types I and II are related to sapropel which is organic matter created under anoxic conditions within marine sediments and these types mostly generate oil. They both have high atomic hydrogen-to-carbon (H/C) ratios of about 1.5 in type I and about (1.2 – 1.5) in type II. In addition, they both have low atomic oxygen-to-carbon (O/C) ratio (<0.1). Type III is related to humic kerogen and sapropelic kerogen. The humic kerogen is created by lignin of higher land plants, and this type could generate gas and some waxy oil. Type IV typically consists of black opaque material; it comprises inertinite and some vitrinite. Type IV is considered to have no hydrocarbon generation potential, and sometimes is a true kerogen that was created from higher plants and organic matter and that has been oxidized many times (Killops, and Killops, 2005, p.139). Type III and IV have low H/C, less than 1.0 in

type III and 0.5 in type IV. They both have high O/C of up to 0.3 in type III and 0.2 – 0.3 in type IV. They are more oxidized and hydrogen-poor compared to the other kerogen types.

In general in sedimentary environments, Kerogen has four sources lacustrine, marine, terrestrial, and recycled (e.g. Tissot and Welte 1978; Selley 1985). Lacustrine and marine kerogens have generated the most oil, while terrestrial organic matter has produced coal.

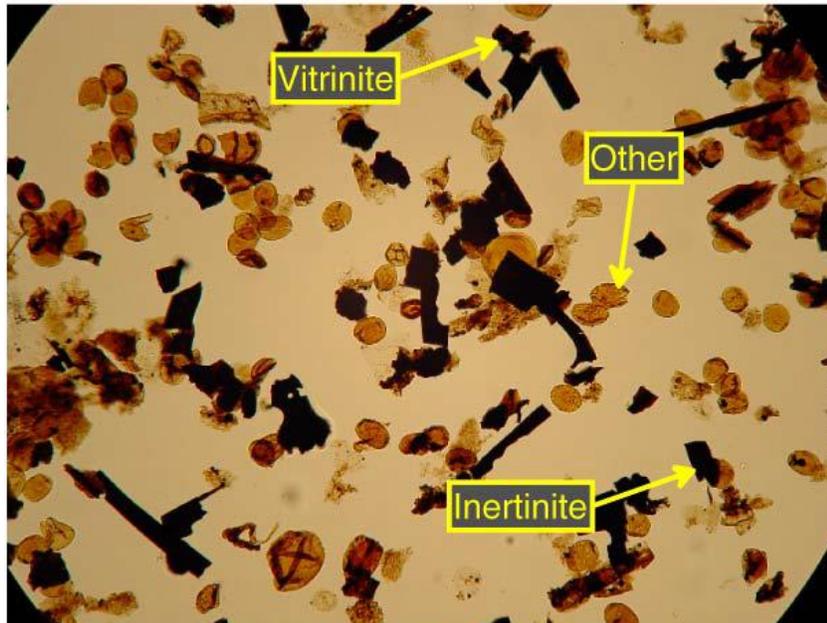


Figure (4)
kerogen, the
400x
2008)

shows the dispersed
approximate scale is
(Kuncheva et al.

2.4

Bitumen:

Bitumen is a product that is chemically created from a mixture of complex natural hydrocarbons and oxidized products (figure 5). In addition, it is what is left of the crude oils when the elimination of volatile components occurs. The majority of natural bitumens contain sulfur and some heavy metals such as nickel, vanadium, lead, chromium, mercury and

also arsenic, selenium, and other toxic elements. Bitumens can provide good preservation of plant and animal molecular fossils.



Figure (5) illustrate an extracted bitumen sample,

<http://eaps.mit.edu/geobiology/biomarkers/extraction.html>

2.5 Oil:

Crude oils can be found within sediments in different geologic environments, (figure 6). They can occur as accumulations within reservoirs, trapped hydrocarbons within minerals, or isolated trapped oils. Generally, the organic matter that has deposited in the sediments converts to kerogen which is insoluble material. The sediments become lithified organic-rich strata that have the potential to generate hydrocarbons when buried and heated. Usually, oil is the liquid product on maturation of type I and III kerogens.

The hydrocarbon fluids in oil inclusions are usually trapped during mineral recrystallization, cementation, or overgrowth formation. Oil inclusions and oil in pore space can be identified by using an ultraviolet light microscope because the organics of crude oil release fluorescence as a reaction to the blue light of an ultraviolet microscope. The fluorescence is a reflection of the chemical composition of the oils, which contains aromatic and saturated hydrocarbons.



Figure (6) shows

Crude oil samples,

<http://projects.exeter.ac.uk/amshaw0/projects/optical-profiling-of-petrochemical-product>

3. Petroleum potential of Precambrian rocks

The Precambrian Era preceded the Cambrian, which began about 545 million years ago. It is the geologic age that has the earliest living organisms, like microscopic bacteria. As seen

in figure (7), the Precambrian is divided into two major periods after the Hadean, which is the time of few preserved rocks except the meteorites.

During the early Precambrian, the continents were smaller in size than in any other later period and had igneous rocks as surfaces with no evidence of life. Some high features, for example mountain ranges and plateaus, were formed. The oceans during the Precambrian were not confined to basins, but covered most of the continents with shallow seas. The sediments were transported by the oceans waves and currents, and deposited on the sea bottom. Below the sea floor, sediments were compacted and cemented into sedimentary rocks. In addition, some new minerals crystallized, for instance quartz, clay minerals, and calcium carbonate, from dissolved constituents of sea water derived from erosion of igneous rock.

Here is a brief explanation of Precambrian periods:

Archaean: when the earliest life in rocks were recorded by carbon isotopes. Sulfate reduction was also detected by isotopic evidence. Stromatolites are one macroscopic fossil recording life in that period. Mostly, the organisms were unicellular organisms and bacteria.

Proterozoic: it is divided into three periods as defined in the geological time scale (Walker and Geissman, 2009):

Paleoproterozoic: the Paleoproterozoic age ranges between 2500 to 1600 Ma. It was from this age that the oldest body fossil cell “Eukaryotic fossil” has been found in rocks 1.8-1.9 Gyr old, (Brocks and Summons, 2003).

Mesoproterozoic: It is the Nonesuch Formation age, and it was the time when some radiation of Eukaryotes was recorded. The age of this period is 1600 to 1000 Ma.

Neoproterozoic: it was 1000 to 542 Ma ago. This was the time of radiation of multi cellular life. At the end of this period, some animal evidence was preserved along with trace fossils.

3.1 The Inventory of petroleum in Precambrian rocks:

There are petroleum shows within Proterozoic sediments in several places around the globe, including the United States, Oman, Canada, Australia, Russia, China, Morocco, and Venezuela. Several studies, e.g. Becker and Patton (1968), hypothesize that the hydrocarbons were created in younger rocks and then migrated to the Precambrian rocks. However, other studies, e.g. Dutkiewicz et al. (2006), documented oil shows originating in Proterozoic rocks. In addition, there are some other studies like the ones that have been done on the Nonesuch Formation of Michigan, Oman oil, and condensate oil of eastern Siberia, that have shown that the oil was created in Proterozoic rocks.

3.2 Roper Group:

Dutkiewicz et al. (2006) have discussed the Mesoproterozoic Roper Group oil inclusions.

The Roper Group is one of the oldest unmetamorphosed sedimentary basins around the globe; it is located in northern Australia (figure 8). It contains oil inclusions and hydrocarbon shows, oil stained gas seeps, and solid bitumen. This group is separated from the McArthur Basin sediments that occur beneath it by a regional unconformity. The area of this study is a shallow marine clastic succession with quartz arenite and shale. It has minor intervals of carbonate and laminated shelf mudstone. The sequence stratigraphy recorded five major cycles; each one coarsens upward. The Roper Group sequence is also intruded by a dolerite sill.

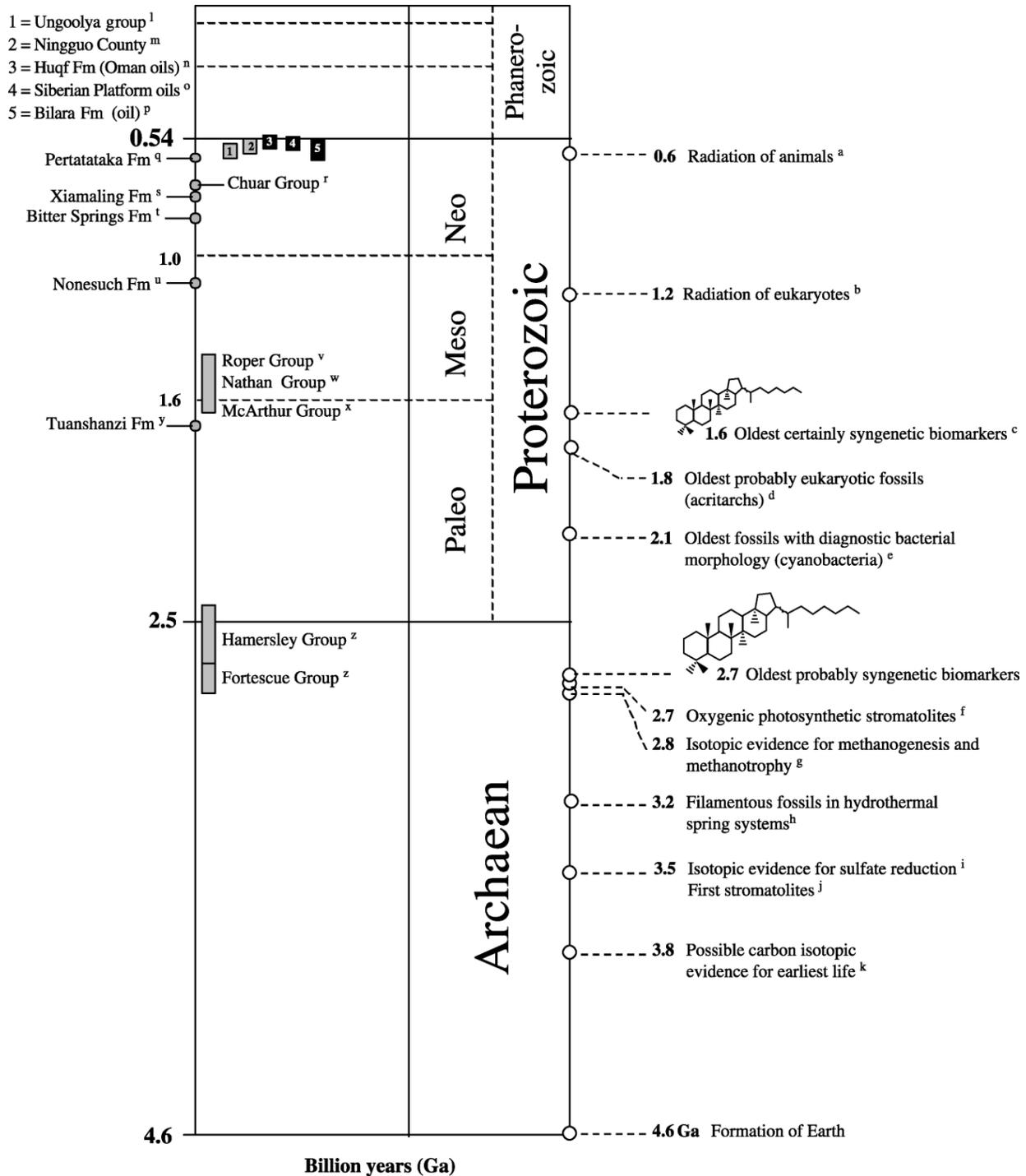


Figure (7) demonstrates the geological timescale with significant biological events, and observations of well-preserved Precambrian biomarkers, Brocks and Summons (2003)

The main potential petroleum source is recognized as the organic rich marine Velkerri Formation which is glauconitic shale. The total organic matter is about 1-3 % with a maximum of 8 %. The kerogen is type I and II with varying maturity. Because of low porosity, this formation is still holding its generated hydrocarbons. In some wells, the Velkerri Formation is underlain by the Bessie Creek Sandstone and is overlain by the younger McMinn Formation. The last formation contains fine to coarse grained sandstone interbedded by shales that have total organic carbon values of 1-3 % (Dutkiewicz et al. 2006). The authors used several techniques, including optical microscopy fitted with UV and transmitted light, scanning electron microscopy, backscattered electron dispersive spectroscopy (BES), and X-ray mapping to evaluate the oil inclusions and the solid bitumen within the Roper Group. This study concludes that the petrography of the oil inclusions and the solid bitumen implies that the oil migration occurred after the major compaction phase and diagenesis. This event is marked by quartz overgrowths, cementation, and precipitation. There are some preserved fluid inclusions and solid bitumen that show that the rock once had a hydrocarbon charge. Some sandstone and dolerite samples show that oil inclusions are the indicator for extensive oil migration that was followed by emplacement of the dolerite sill. The most abundant oil inclusions are within the Bessie Creek Sandstone. They were trapped at temperatures about 60° C within transgranular

fractures. The oil inclusions within the dolerite sill are a mixture of highly mature condensate and low maturity oil. The Velkerri Formation and the deeper Barney Creek Formation are the most likely source rocks for the hydrocarbons. Other studies on the petroleum potential of Precambrian rocks include the study of the group of South Oman oils. This oil has been generated from the Precambrian Huqf Formation and Paleozoic sediments. A Precambrian Sinian age formation in Russia is also reported to have oil production. These examples illustrate that hydrocarbon accumulations are found in unaltered and somewhat metamorphosed Precambrian rocks around the world. However, the Precambrian kerogens have low hydrogen content, and the quantity of oil generated may not be large with the exception of rare organic rich sediments (Hunt, 1995).

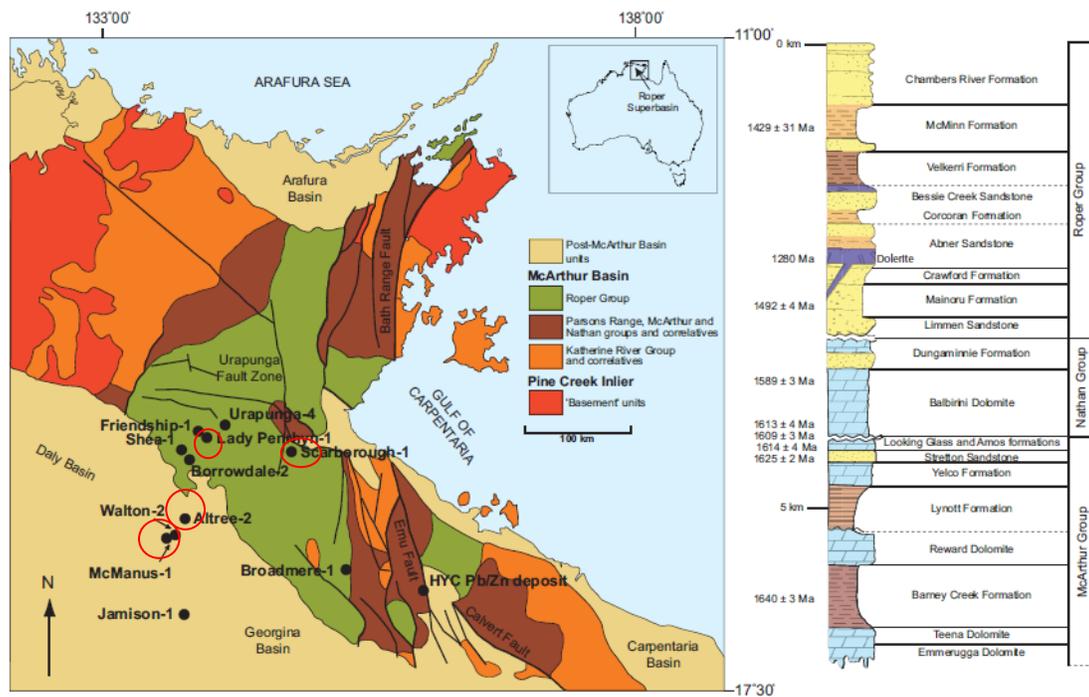


Figure (8) illustrates the McArthur geological map and stratigraphic column of the Roper Group. The red circles represent the locations of oil exploration wells, Dutkiewicz et al. (2006)

4. Geology Setting:

4.1 Geology of the Midcontinent Rift in Michigan:

Michigan has a complex geologic history, (figs 9, 10). In strata of many ages, it has abundant fossil plants and organisms, including layers of Precambrian graphitic "coal". In addition, Michigan has different ore deposits and valuable minerals, for example, iron ore in Precambrian sediments, and Precambrian volcanic rocks were the source of copper mined since the 1840's. Therefore, Michigan is one of the important mining areas in the United States. There are some rocks reported to be as old as 3.5 billion years. Michigan is in the central lowlands of the United States and belongs to the craton, which is an area of bedrock that is exceptionally stable. During the late Precambrian, the Mid- Continent Rift system was formed. Michigan has some volcanic rocks which filled the Midcontinent Rift during the Meso to Neoproterozoic. This rift is about 2000 km long and it extends from the Lake Superior region southwest to Kansas and southeast into central Michigan.

Van Schmus (1992) describes the pre-rift basement and the Midcontinent Rift in general. He divides the pre-Midcontinent Rift geology into six major provinces. First, the Superior Province which is the southern part of the Canadian Shield formed the oldest Precambrian

basement. This mostly consists of greenstone belts, granitic plutonic rocks and granitic gneisses that formed in tectonic belts during the Late Archean about 2.7 Ga. There is a major crustal boundary that is the Great Lakes Tectonic Zone. It is located south of Lake Superior. To the south of the Great Lakes Tectonic Zone, there are gneissic and migmatitic rocks that were metamorphosed during the Archean. During the Early Proterozoic phase, the Niagara Fault system caused a major break along the southern margin of the Archean craton that is located in Wisconsin and the Upper Peninsula of Michigan. In addition, the fault system continues southwest into northwest Iowa and southeastern Minnesota (Van Schmus, 1992). The other five provinces are: 1) the Penokean Orogen, which is one of the main Early Proterozoic magmatic belts and is located in the southern of the Superior Province in northern Wisconsin. 2) The central Plains Orogen, which in the north part contains orthogneisses considered to be the oldest rocks in this orogen and having a composition of amphibolite, diorite, tonalite and granodiorite, to granite. 3) Anorogenic plutons formed around 1.5 to 1.3 Ga that mark melting of Early Proterozoic crust. And mostly were formed from melt of older Proterozoic crust. 4) Granite-Rhyolite Provinces which are provinces of 1.37 Ga granitic and felsic volcanic rocks occurring in the subsurface of southwestern of Missouri, southern part of Kansas, most of Oklahoma, and northern part of Texas. 5) Grenville Province which forms the eastern boundary

of the pre-rift region, a collisional orogen which is formed about 1100 Ma. It contains crustal rock groups that formed during the Archean age and during the earlier Proterozoic (Van Schmus, 1992) and was the site of major orogenic activity about 1100 Ma.

4.2 Keweenawan stratigraphy:

Based on Van Schmus (1992), the stratigraphy of the Keweenawan was divided into three or four main suites which are: Syn-rift deposits composed of volcanic rocks, mafic intrusive bodies, and negligible inter-flow clastic sedimentary rocks; post-volcanic and late- to post-rift clastic rocks, including some minor interlayered volcanic rocks; within the Lake Superior region, the sedimentary rock units, include the Copper Harbor Conglomerate, Nonesuch Formation, and the Freda Sandstone of the Oronto Group. Post-rift rocks include some clastic sedimentary units that were deposited within wide crustal depressions superimposed on the rift system. In general, these rocks fill subsurface basins in different states such as Iowa, Nebraska, and Kansas, (Van Schmus, 1992). The syn-rift volcanic and post-volcanic sediments form the Bergland and Oronto Groups within the Keweenawan Supergroup (King 2009). The Oronto Group consists of three formations which are: the Copper Harbor Formation, Nonesuch Formation, and Freda Formation, (Figure 10). The Copper Harbor Conglomerate is between

100 and 1800 meters thick. It overlies the Porcupine Volcanics in Wisconsin and in northern Michigan is on the top of the Portage Lake Volcanics. The Copper Harbor Formation deposition represents the transition between the volcanic-fill and the clastic-sedimentary rocks of the rift. The Copper Harbor Formation is a thickening basinward sequence, with conglomerate and sandstone deposits that may vary in thickness (Elmore, 1984), with basaltic lava flows called the Lakeshore Traps (King, 2009). The Freda Formation, which overlies the Nonesuch Shale Formation, is a sequence of red-brown sandstone, siltstone, and mudstone which is about 3700m thick (http://www.minsocam.org/msa/collectors_corner/vft/mi2b.htm). It contains coarsening-upward and fining-upward sequences (King, 2009).



Figure (9) a map of Michigan State shows the area of study, Dorr and Eschman (2001).

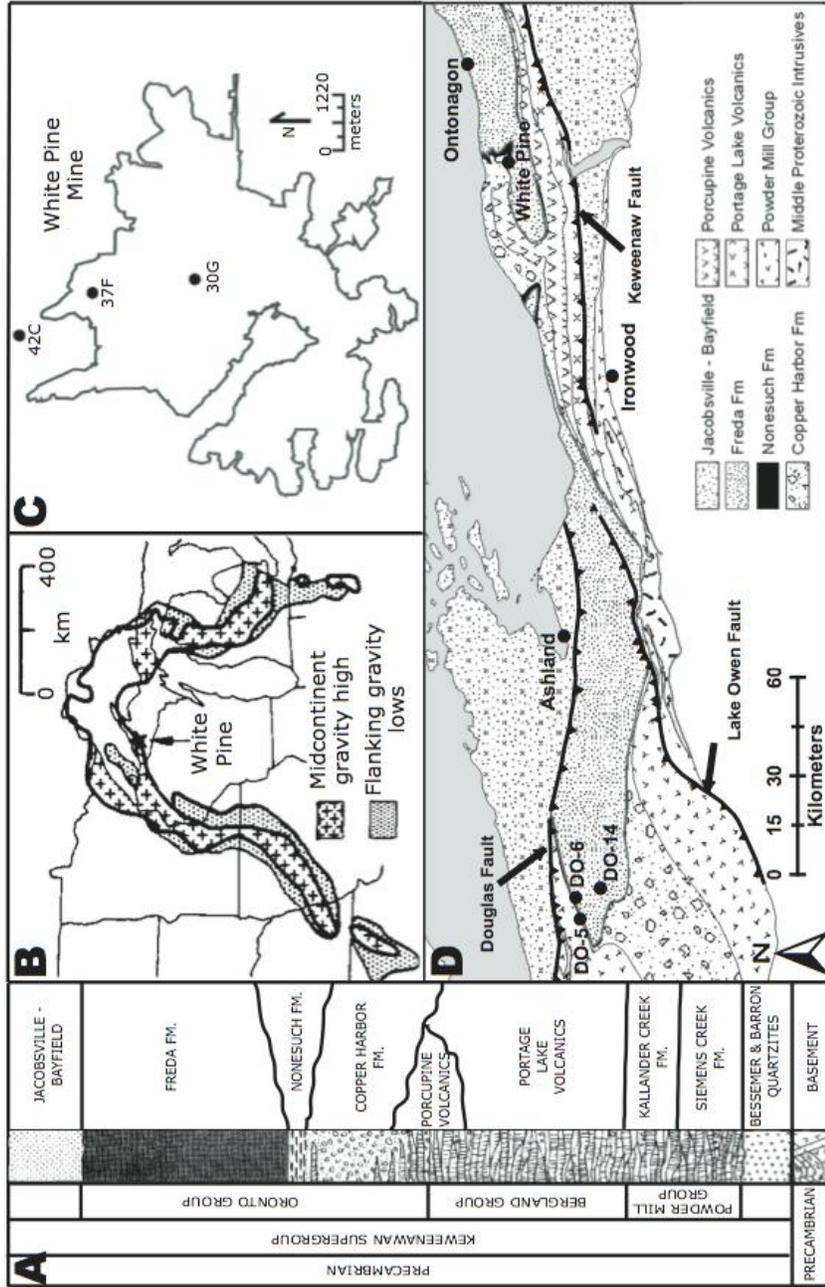


Figure (10) demonstrates a Stratigraphic column, extent of the Midcontinent rift system, geology of the area around White Pine Mine, the position of the cores studied from the white Pine Mine, Study area with general geology. (King, 2009).

4.3 Nonesuch Formation:

The Nonesuch Formation is one unit of sedimentary rocks that filled the Midcontinent rift. It was deposited in the Keweenawan trough in northern Michigan (Upper Peninsula) and northern Wisconsin, and hosts copper deposits. Its outcrop extends for about 225 km by 11 km from north of Calumet, Michigan to the southwest near Mellen, Wisconsin. It was deposited in the middle of the Proterozoic, in Mesoproterozoic time. The Nonesuch Formation is a transgressive-regressive sequence. The Nonesuch Formation is up to 600 feet thick and mostly contains green to gray siltstone, shale, and some sandstone (fluvial). In general, most of Nonesuch Formation is laminated and the color of the siltstone varies between dark to light gray. The light colored laminae are calcareous. The darker colors are mostly caused by the presence of organic matter. There are some common sedimentary structures observed within the Nonesuch Formation, including rip-up clasts, ripple marks that vary between symmetrical and asymmetrical, syneresis and desiccation cracks, graded bedding, dikes with clastic sediments, cross-bedding, and gypsum (King, 2009). Underneath this formation there are about 2300-5500 feet of red sandstones and conglomerates of the late Keweenawan Copper Harbor Formation. Because of the limited fossil content within the Proterozoic Nonesuch Formation, it is difficult to determine the sedimentary environment. The environment is debated. It could be a

lacustrine environment because of the red-bed alluvial deposits that cover and underlie the Nonesuch Formation (Imbus et al. 1990); or, it could be marine (a shallow, marginal sea). Elmore et al. (1989), and Elmore et al. (1984), suggested that the red-brown fine grained sandstone, mudstone, and siltstone may be an indicator of the sedimentary environment. Some research suggested that it was formed in a transition from a lacustrine to a fluvial environment. In addition, they suggested that the Nonesuch Formation is a part of a transgressive-regressive sequence.

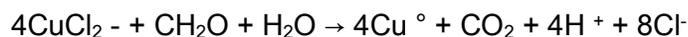
5. Organic Matter and White Pine Copper Deposit:

Many mineral deposits in sedimentary rocks are within strata that have organic matter, which suggests that the organics were involved in precipitation of the ore minerals. The organic rich layers of the Nonesuch shale leak oil into the White Pine copper mine. There is also oil that has been trapped within calcite crystals occurring within the copper iron sulfide bearing veins in the Nonesuch shale at White Pine Mine (Kelly and Nishioka 1985).

The stratigraphy and the copper mineralized zones of the lower Nonesuch Formation are demonstrated in Figure (11). The minerals and the organic matter are generally observed in the cupriferous zone in the sequences. An ore deposit requires concentration of metals above average crustal levels. The process to accomplish this enrichment may involve migration of heated water through deposits. Minerals of the country rocks are leached by the hot water, and moved to the deposition location, where organic matter can play a role in the formation of ore deposits. The migrating fluids may precipitate the ore minerals through chemical processes which include the oxidation of organic matter (Ho and Mauk 1996, Ho et al. 1990). Butter and Burbank (1929) studied the copper mineralization and hydrocarbons within the White Pine deposits. They argued that the copper distribution is the same as the distribution of organic

matter, with both occurring in the shale and the shaley sandstone in beds and along faults. They suggested that the organic matter has more widespread horizontal distribution than the copper within the beds. They did not know the source of hydrocarbons, but they suggested that there were two sources for the hydrocarbons within White Pine. First, it seemed that the hydrocarbons were derived from the bituminous shale or a similar series of rocks that occurred below. Alternatively, hydrocarbons were carried in by the same hot waters that carried the copper. However, the shales did not appear to be leached. They considered that there was a relationship between the copper and the carbonaceous substance. They thought that the hydrocarbons may have accumulated before the time of copper deposition, and that the hydrocarbons were active when the copper precipitated in all productive regions in the mines.

Mauk and Hieshima (1992) have discussed in detail how the organic matter oxidation can occur with reduction of an oxidized species, by reactions such as that shown in the following equation:



1 molecule of CH_2O is oxidized to CO_2 because of reduction of 4 atoms of Cu^+ to Cu° .

Otherwise, the organic matter may be oxidized by sulfate reduction, and sulfide might then react with metal species.

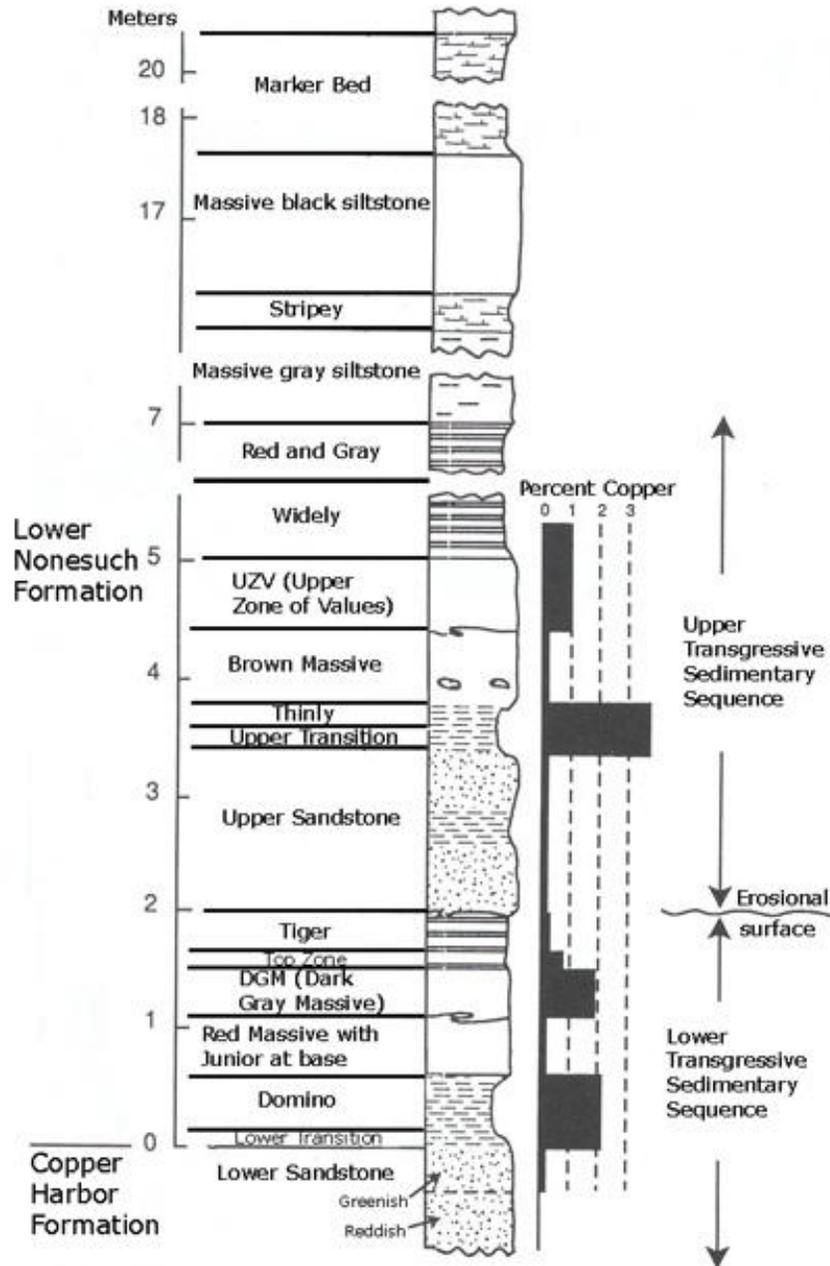
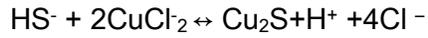
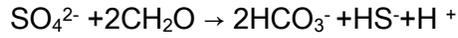
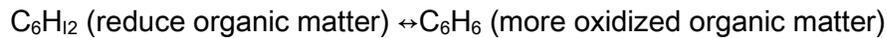


Figure (11) shows the Stratigraphy and location of copper mineralization in the lower Nonesuch Fm. Modified from Brown (1993), and King (2009)

The last reaction forms chalcocite, or If ferric iron is available it forms pyrite, which is usually formed during early diagenetic processes by reaction of hydrogen sulfide with ferric iron.

This reaction can occur at temperatures below 90°C by the action of bacteria.

Cupriferous brines can convert pyrite to chalcocite, forming 2 moles of chalcocite for each mole of precursor pyrite:



This reaction involves the reduction of sulfur from S⁻ to S²⁻; it needs an oxidation reaction that may involve organic carbon. These reactions may have been effective at White Pine if the organic matter played a direct role in precipitation of ore minerals, like native copper. In addition, when sulfide reacts with cuprous ions to form chalcocite, the organic matter cooperates in a direct role. Otherwise, it plays both an indirect and a direct role, first when it forms pyrite which is afterwards replaced to form Cu-sulfides. In general, organic matter composition and occurrence can be controlled by ore mineralization. The mineralization of Kupferschiefer deposits of Poland, which are very similar to White Pine, Michigan, is understood to be formed by thermochemical sulfide production by reaction of sulfate with organic matter (Mauk and Hieshima, 1992).

In my study area, the main mineralization of the White Pine copper deposit in Michigan occurs in the lowermost 5 m of the Nonesuch Formation. This part, as seen in the stratigraphic column (figure 11), is divided into twelve beds. The mineralization is commonly observed as native copper, chalcocite, bornite, chalcopyrite, and pyrite. Native copper is generally associated with chalcocite (King, 2009). The occurrence of pyrite characterizes the upper limit of the cupriferous zone. The mineralization at the White Pine copper deposit happened during early to mid-diagenesis which is around 10 Ma after deposition of the Nonesuch Formation (Brown, 1971). The event has been explained through a hydrologic model for mineralization. Basinal oxidized fluids flow across the Lake Superior basin through the Copper Harbor Formation. Then, the fluids moved through the reducing facies of the overlying Nonesuch Formation at White Pine. Some studies imply the northern limit of the Lake Superior syncline may be the fluid source that drives fluid migration at White Pine (Brown, 2006). There might be a secondary mineralization event at White Pine which was created by compression from the rift failure approximately 30-50 Ma after the major mineralization event (Mauk et al. 1992). In this case, the mineralized fluids are assumed to be the same fluids that caused deposition of the great amounts of native copper in the Keweenaw native copper deposit in basalts to the northeast (Mauk et al., 1992). In this event, the mineralization is found principally along faults in

and adjacent to the copper bearing strata. This late event might have been caused by fluids migrating upward along reactivated faults. The mineralization in this event is seen as sheet copper, bedding-parallel chalcocite veins, stockwork veins, and disseminated native copper (Mauk et al.1992). In the copper bearing lower member of the Nonesuch shale, there is a relationship between copper and the organic matter of the shales. The percentage of copper is correlated with the percentage of the organic carbon content. This leads to the interpretation that the precipitation of the copper ore deposits was both caused by the organic matter of the Nonesuch shale and that organic content controlled its distribution. The organic matter likely predated the copper and may have been formed when the shale of Nonesuch was deposited. Barghoorn, Meinschein, and Schopf (1965) have found evidence for this in a study that is based on the presence of porphyrins (organic molecules) and some plants tissue and fragments. They were involved in the biologic process by the time of shale deposition or may be earlier. Based on Barghoorn, Meinschein, and Schopf (1965), Dorr and Eschman (2001) reported that porphyrins are affected quickly by hydrothermal high temperature and may be chemically broken down. Russell (1960) also suggested that in the presence of oxygen and heat, porphyrin molecules, which are found in many petroleums, break apart rapidly at temperatures above 250 °C. The copper, however, was deposited at lower temperatures and did not form at the same

time was the organic molecules. Ridge (1968) suggested that the native copper migrated from the lava and was deposited into the Nonesuch beds after they had been buried.

6. Methodology:

Sixty samples were taken from three cores. These were analyzed by different methods at Colorado State University and different labs in the USA and Canada. They all were mainly analyzed in order to study the relation between the organic matter content and its maturity, and copper mineralization.

6.1 Study area and Site description:

Three drill cores that intersect the Nonesuch Fm were logged and sampled, (figure 10). The three cores, 30G, 37F, and 42C, from the White Pine Mine are complete from just above the mineralized zone in the Marker Bed down to the upper Copper Harbor Fm, (figure 11) and include skeleton core in the upper Nonesuch Formation. These cores are from within and next to the White Pine Mine at White Pine, Michigan, and to the southwest of the native copper deposits on the Keweenaw Peninsula. Some sampled strata at White Pine contain abundant copper mineralization. Some samples were also taken from higher intervals than the lower Nonesuch Formation, including above the mineralized zone in an interval with the finest grained lithology. The Nonesuch Formation in this area is mostly shale, siltstone, and sandstone. The

samples were also logged from zones above the mineralization zone, including Stripey and Massive black siltstone (King, 2009).

6.2 Laboratory procedures:

- Sample Collection:

The sixty samples are from collected cores drilled through the Nonesuch Formation. Twenty of them were prepared later for additional analyses. Overall, two cores out of the three contain abundant copper mineralization and organic matter. Thin sections were prepared for petrographic and geochemical work from the study cores, which are 37F, 42C, and 30G. Overall, the finest grained samples were from incomplete skeleton core intervals well above the ore zone, see figure (11).

- Core descriptions

Core description was done of the lithology and stratigraphy of sedimentary rocks, mineralogy, grain size, and the presence of organic matter, laminations, bedding, and any other sedimentary structures, and color. Moreover, it provides a complete visual description of the studied strata overall. Particular attention was paid to the nature and abundance of copper mineralization and the content of organic matter.

6.3 Inorganic Geochemistry:

- Thin section (petrography):
 - Transmitted light and Reflected light:

The 45 samples were prepared for petrographic analysis. They were cut to 30-microns thick, and polished. Two main methods, transmitted and reflected-light microscopy, were used to describe the thin sections in Colorado State University laboratories, (fig 34). These petrographical studies were done to see the mineralogical composition of the thin section samples, the organic matter distribution within the rock, lithology, grain size, laminations, and bedding, with special attention paid to copper mineralization. Essentially, I was trying to determine the amount of organic matter and its relation with the copper mineralization. For all petrographic analyses, observations were made by looking at thin sections in two dimensions.

6.4 Organic Geochemistry:

- UV light:

Ultraviolet (UV) microscopy is a method that causes petroleum fluids and some solid organics to produce light, or fluoresce. The fluorescence release of organic molecules is due to electronic transitions involving carbon-carbon double bonds. The chromophore is the part of a

molecule can be energized by incident light. The UV light is aimed at the sample and the released light is transmitted through the microscope into the eyepiece camera. It is connected to different combinations of optical components like, filters, lenses, beam splitters, fiber optics (fig 35).

In general, the use of this method depends on the relationship between fluorescence and the chemical composition of the petroleum or organics within the samples. The main part that causes fluorescing components in organics is the aromatic hydrocarbons. UV microscopy was used to differentiate the hydrocarbon type, whether kerogen, bitumen, or oil inclusions, based on texture and petrography for each one. Usually, among these types, the most strongly fluorescing are kerogen and oil inclusions.

- Vitrinite reflectance:

Vitrinite reflectance is a common method that is used to study organic matter and determine its maturity in sedimentary rocks. Vitrinite is a type of maceral found in coal and some kerogen. It forms from lignin, cellulose, and tannins of vascular plants, like bark. It can be derived from humic or other organic matter (Almashramah, 2011).

There are two techniques used to prepare samples to be measured for vitrinite reflectance (Hunt, 1995). The first one involves removing mineral matter by acids like hydrofluoric and hydrochloric. The remains are placed in epoxy and polished. The second technique is used on whole-rock samples, or thin sections, rather than the kerogen concentrate. To measure the degree of reflectivity we use a microscope. The maximum vitrinite reflectance value, which is 15 %, is for graphite. The reflectivity basically rises with temperature and time. The reading of vitrinite reflectance varies and depends on the maximum temperature of the rock. Relatively, it changes with the maturity when the molecule of vitrinite changes with temperature. Hunt (1995) found that when the reflectance rises it is due to the degree of linking of aromatic rings within the vitrinite. The reflectivity values of organic matter that can produce hydrocarbons are ranged between 0.5 and 2.0 according to Killops and Killops (2005). The values that are in the range of 0.5-0.6 indicate immature organic matter (Killops and Killops 2005) and temperatures lower than 50 °C (Almashramah 2011). Values ranging up to 1.3% indicate the oil window, and values of 2.0 % suggest wet gas and above 2.0 % indicate dry gas (Killops and Killops 2005). Values around 3.0 show that the organic matter is overmature (Almashramah 2011).

In my study the vitrinite-like reflectance has been evaluated at the University of Kentucky, Center for Applied Energy Research. In this study, I am stating the results of vitrinite reflectance

as vitrinite-like due to the absence of remains of terrestrial plants in the rock. The reflectance values were obtained to determine the thermal maturity of organic matter. However, the study was done on Precambrian samples with hardly any amount of vitrinite. The term vitrinite-like in this study is used to illustrate the organic matter maturity. Vitrinite-like measurements are normally used on older rocks than Devonian and Carboniferous, like Silurian and pre-Silurian. The calibration of this method mainly depends on the spore color index in samples that include vitrinite-like particles (Belaid, Krooss, and Littke, 2009).

The data may either be reported simply as Ro%. Almost all of the reflectance data is represented as maximum reflectance. To prepare the sample for this study, first we cut small pieces from the core. Then, put in about 2 oz of resin and 2.7 cc of hardener to make the rock sample in a mold. Later in the last step we polish the sample to make it easier to be seen under the microscope by using a 50X objective lens (fig 36-37). Hunt, (1995) states that two principal standards are used in these methods macerals of vitrinite: telocollinite, desmocollinite. The reflectance of desmocollinite is lower than the reflectance of telocollinite. Therefore, Buiskool Toxopeus (1983) argued that there is a difference between them of about 0.1–0.3% Ro at the same rank.

- Rock Eval:

Rock-Eval is a pyrolysis tool that is designed to measure hydrocarbon potential and generative history from whole-rock samples. It was developed by the French Petroleum Institute. This method provides several measurable parameters like S_1 , S_2 , S_3 , T_{max} , TOC, HI, OI, and PI. The main point in using this method is to calculate the quantity of the organic matter content that is detected by a flame ionization detector (FID) during pyrolysis, and predict the quantity of hydrocarbon that would be produced during rock maturation. Rock–Eval pyrolysis is also one of the most widely used methods for studying the organic matter quality by using the relationship between S_2 and TOC.

The main idea of this method is based on the selective detection of types of hydrocarbon compounds and how much carbon dioxide is generated from organic matter in the rock during programmed heating. Several parameters are obtained by this technique. The first peak of hydrocarbons (S_1) represents the quantity of free hydrocarbons (HC—bitumen) (Peters and Simoneit, 1982) that is thermally extracted from the rock (mg HC/g sample). The second peak (S_2) comprises the amount of hydrocarbons generated through thermal cracking of nonvolatile organic matter (kerogen) (mgHC/g sample). Carbon dioxide formed from the organic matter during pyrolysis of kerogen is analyzed as a third peak (S_3) (mg CO_2 /g) using a thermal

conductivity detector (TCD). Carbonate lithologies can cause a problem since some inorganic S₃ can be produced. Other parameters can be calculated like, T_{max}, HI (hydrogen index (HI = [100 x S₂]/TOC)), OI (oxygen index (OI = [100 x S₃]/TOC)), and the kerogen type.

- Kerogen type:

For analyzing the Kerogen type by using Rock Eval data, we can study the relation between the atomic HI mg HC/g TOC, and OI mg HC/g TOC. The Van Krevelen diagram figure (12) (Glennie 2009) demonstrates that the Kerogen types and these types as described by the Pennsylvania Department of Conservation and Natural Resources.

http://www.dcnr.state.pa.us/topogeo/oilandgas/sourcerock_quality.aspx

Kerogen type analysis is mainly based on the atomic H/C and O/C, as shown in a source rock study by Van Krevelen diagram, (Figure 12) (Peters and Cassa, 1994). They suggested that the results of high hydrogen content shown in the HI and H/C in kerogen may be considered as oil generative potential. In addition, the kerogen can be affected by the maturation and the production and release of high hydrogen content products. It may be depleted in H related to C at high maturity. As a result of the catagenesis, the kerogen may turn into pure carbon which is graphite (Peters and Cassa, 1994).

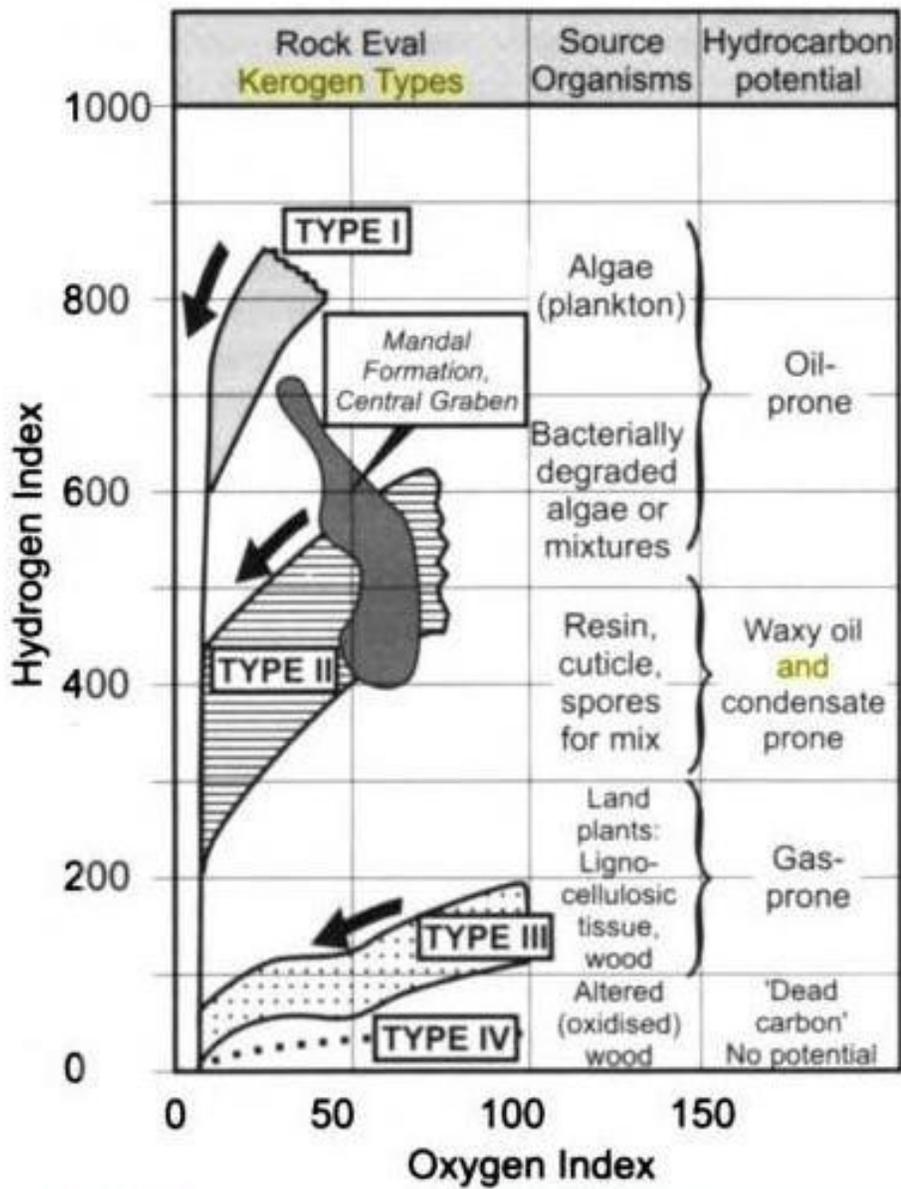


Figure (12) shows the kerogen types, its origin, and what type of hydrocarbons that can produce, (Glennie 2009).

- Type I kerogen:

Sapropelic

It contains alginite, amorphous organic matter, cyanobacteria, freshwater algae, and land plant resins. Its H/C ratio is > 1.25 , and O/C ratio < 0.15 . Basically, it forms from lacustrine algae and only in reducing lakes and other unusual marine environments

- Type II kerogen:

It derives from two sources:

- 1) Planktonic: marine, H/C ratio is < 1.25 ; O/C ratio is about 0.03 to 0.18. Its production is a mix of gas and oil.
- 2) Sulfur: Similar to the previous type, but with higher sulfur content.

- Type III kerogen

This type has low H/C. There are some organics that are low in hydrogen, like polyaromatics, and they are mostly derived from higher plants, so are not applicable in sources of organic matter in a Precambrian study case. Type III kerogen chemical compounds include vitrinite, telinite, collinite, huminite, and so-called humic or woody

kerogen. These generate natural gas or rarely associated condensate if the thermal maturation is sufficient.

➤ Type IV kerogen

This type of kerogen has a low H/C of about 0.5 and relatively high amount of O/C of about 0.2 – 0.3. In general, Type IV kerogen is oxidized and hydrogen-poor.

Kerogen type III can produce gas, while type IV seems not to produce hydrocarbons (table 1) (Peters and Cassa, 1994).

[ht http://en.wikipedia.org/wiki/Kerogen](http://en.wikipedia.org/wiki/Kerogen)

6.5 Maturity:

Organic matter maturation requires a temperature higher than 60°C. To determine the kerogen maturity we need to understand the T_{max} , and PI values. T_{max} is the temperature at which the maximum amounts of S₂ hydrocarbons are generated during Rock-Eval pyrolysis. The immature range of T_{max} is 400°C -430°C; T_{max} - 430°C -450°C represents the mature range, and $T_{max} > 450^{\circ}\text{C}$ signifies the supermature range. It depends on the kerogen type found in the source rock and the maturity. By plotting its value versus the Hydrogen Index (HI), we can

illustrate the different maturation paths of different kerogen types. The production index (PI) is the ratio of previously created hydrocarbon to the potential of hydrocarbon from further maturation of kerogen $[S1 / (S1 + S2)]$, as determined during Rock-Eval pyrolysis. Immature or extreme postmature organic matter results are indicated by low ratios. The high ratios show either the mature stage or contamination caused by migrated hydrocarbons or drilling additives.

Table (1) shows the quality of organic matter (Peters and Cassa, 1994).

Quality of Organic Matter				
Kerogen Type	Main Composition	Hydrogen Index (HI) (mg HC/g TOC)	S2/S3	Main Product Expelled at Peak Maturity
I	amorphous/alginate	>600	>15	oil
II	Exinite	300-600	10-15	oil
II/III	exinite/vitrinite	200-300	5-10	mixed oil and gas
III	Vitrinite	50-200	1-5	gas
IV	Inertinite	<50	<1	none
<i>* Approximate ranges based on thermally immature source rocks</i>				

7. Results:

7.1 Core logs:

Full description of core logs is in Appendix B. Figure (11) demonstrates the stratigraphic column including the Nonesuch Fm. It shows the Cu content within the mineralized zones.

All three cores, 30G, 37F, and 42C, are divided into units with slight lithologic differences. The hand specimens of this study are mostly brown to dark brown color due to the presence of the organic matter. Some of the described samples were taken from units in the upper part of the formation. Generally, their lithology is gray laminated siltstone and there are no detectable copper minerals within these units in all three cores. Cores 30G and 37F, which are within the White Pine deposit, have almost the same lithologies. They both contain stratigraphic units of the lower Nonesuch Formation, and have abundant copper mineralization zones within the lower beds. Core 42C, which is taken from north of the White Pine deposit, includes less copper mineralization. Core 42C has a chalcocite zone within the Upper Transition. In general, the mineralized zones in all cores are found within organic rich layers.

To give general information about these units within the entire core, I will start with the upper most part of the Lower Nonesuch Formation which is the Marker Bed:

- Marker Bed:

This is dark brown- gray laminated siltstone. It has calcite cement and small-medium sized calcite nodules up to 50 μm and that decrease in abundance with depth in core 42C. The cores 42C and 37F have some very thin organic layers which are less than 1 cm thick, with dark color caused by OM; OM is low in this bed in core 30 G. The Marker Bed becomes less laminated and more massive black siltstone downward, and hosts less calcite cement. The core of this unit has a lot of missing parts due to the friable sediments.

- Massive black siltstone:

This is black-gray laminated calcareous siltstone, and contains some bleached zones that have calcite cement. This unit has repeated stratigraphic sequences of seven rock types at the base. These are widely laminated gray siltstone, reddish shale, widely laminated gray siltstone, grayish black shale, massive gray siltstone. In addition, it has massive reddish brown siltstone with thinly laminated gray siltstone, and fine sandstone.

- Stripey:

This is a black-gray shaley siltstone that contains abundant white calcareous laminations with calcite veins. In addition, it has some organic rich layers, and may contain bitumen that is filling the pore space in core 37F at the base of this unit.

- Massive Gray Siltstone:

This unit is relatively thin in core 30G (14.7 ft) and thicker in both core 37F (about 18 ft) and core 42C (about 19 ft). It is black shaly siltstone in 30G, and greenish gray siltstone in 37F and 42C due to the clay minerals cementing it. In general, it is laminated and friable with a fair amount of OM, very few calcareous laminae, and has soft sediment deformation within core 42C.

- Red and Gray unit:

This is a light gray to black gray laminated siltstone with some white thin laminae of calcite. It has some calcite veins within core 30G, while no calcite veins were detected at 1190-1191 ft within 42C core. There are a few greenish gray shaly layers in core 42C with a fair amount of OM. There are copper minerals, a sulfide which is bluish gray probably chalcocite, and some shiny small mica-like grains.

Lower Units:

Below these units there are two sequences, the upper sequence is thicker than the lower sequence. Because the thickness of these units is less than the upper part, I am describing them together as lower units. The first sequence includes: Widely, Upper Zone of Values, Brown Massive, Thinly, Upper Transition, and Upper Sandstone. Some calcareous layers are within this sequence. The grain size becomes a little coarser at the bottom of this sequence. Upper Transition and the Upper Sandstone are generally greenish-red-gray sandstone. They may contain OM and sulfide in some levels. They have fine-medium conglomerate clasts at the base, and soft sediment deformation at the base that formed by secondary processes. The soft sediment deformation in this unit is present as slumps that are usually found in the sandy siltstone and mudstone. These typically form because of gravitational instability of the deposited sediments. This deformation forms before the sediment lithifies. It is described as a reaction to some tectonic events, steep slopes (Farrell 1984).

The lower sequence is Tiger, Top Zone, Dark Gray Massive, Red Massive, Domino, Lower Transition, and Lower Sandstone (upper Copper Harbor Formation). The upper six units are commonly reddish-bluish laminated gray siltstone; they have some organic laminae and

calcite, and contain native copper at the base. The Upper Copper Harbor Formation is medium to fine sandstone, which becomes coarser with depth. It is light-reddish gray, and may contain bitumen flakes at the top of the Copper Harbor in core 42C.

As we go down within cores 30G and 37F, copper mineralization is mostly first seen in the base of the Widely. The most abundant copper mineralization zones are in the Upper Zone of Values, Thinly, Upper Transition, Top Zone, Dark Gray Massive, Domino, and Lower Transition.

7.2 Petrography:

- Mineralogy:

The sampled lithologies are laminated siltstone, sandy siltstone, or sandstone with some shaley layers. The mineral content and the sedimentary structures have been studied by reflected light and transmitted light microscope. Overall, the most abundant minerals are quartz and feldspar (plagioclase, orthoclase) (Figs. 13A and B). Furthermore, the samples have some phyllosilicate minerals, including chlorite, and white mica, such as muscovite. In addition, more rock fragments are found in the sandstone samples such as the Copper Harbor Formation,

organic matter in most of the samples, copper minerals are in some of the samples, and calcite in almost all samples; see tables 2, 3, 4, 5, and 6.

Calcite (figure14) and chlorite (figure15) with varied colors like red and green (in the core samples) are found as cement in the rock samples. The calcite is mostly found within the fine sandstone and siltstone as veins as seen in figure (16) or as cement, while the chlorite is found in the mudrocks as clay minerals grains or as cement. The sandstone might be harder than the mudrocks in this area because there is more cement in the sandstone than the mudrocks, and it has more quartz grains. Some samples have no calcite like 42C-2, 42C-3, and 42C-4 from Stripey, Widely, and the Upper Zone of Values, respectively. In other cores, these zones may have calcite as cement such as in some samples. Chlorite is the cement for some samples such as 37F-13, 6, 42C-3, 4 within the Upper Nonesuch Formation, Upper Transition, Widely, and Upper Zone of Values zones, respectively. The variation of sample color is controlled by the mineral and organic content. For example, the reddish layers of clay in Tiger from 37F core are due to hematite in the rock matrix. The greenish gray color in the Massive Gray Siltstone zone in 42C core is due to chlorite content and reddish gray in the Upper Sandstone in 30G core is caused by the hematite and the organic matter. Throughout, the dark gray, black gray and light gray colors are because of the organic matter and pyrite content, for example the Red and Gray

zone in core 42C. The more calcite cement beds have the less copper mineral content they have, as seen in 42C-4, 5, and 37F-12, 9, and 3. I interpret this to be a result of the copper minerals having replaced the calcite by dissolution during the diagenesis process as seen in the figure of sample 37-9 in the figures appendix. Chalcocite is recognized in some zones like the Upper Zone of Value, and Copper Harbor Formation, and native copper is seen in 37F-9 in the Dark Gray Massive unit (figures 17). Furthermore, Mineralization was observed as sulfide (mostly chalcocite) and native copper.

7.3 The organic matter:

The organic matter observed with the UV microscope presents as three types, kerogen, bitumen, and oil inclusions. The organic matter is mostly not fluorescent. Most of the bitumens were seen as residue within the pore spaces of the samples, possibly because the bitumens were dissolved by fluids, during diagenesis, or during the thin section preparation by chemicals; therefore, it was not easy to distinguish the bitumen within some samples, for example 37F-11 and 42C-10.

Most of the organic matter was presented as kerogen and oil inclusions, for instance in 37 F-9, 12 and 42 C-8, 10, and 11. The oil inclusions are mostly found in the sandy siltstone

samples, because the sandy grains fracture during diagenesis and trap fluids from the surrounding pore space, as in 37-F 1, 7 and 42C-6.

Worden et al. (1998) explained how oil inclusions are found in sandstone; they suggested that the sandstone pore spaces are already filled with formation water before the oil moves toward the reservoir rocks. In this case, the oil may replace the water. The pore space may fill with oil; however, some of the original water still exists. This water is called saturation water (SW) and, its presence depends on the rock permeability, capillary pressure and wettability in the oil–water–rock system. The wettability of a two-phase fluid system could affect the fluid that is in contact with surfaces of the rock grains. When the water is coating the sand grains, the oil cannot get into contact with the grain surfaces and may not get trapped, and vice versa. When the system is water wet, oil is surrounded by water in the pores. In the oil-wet system, water content becomes limited and the limited pore space necessitates particularly high capillary entry pressures. In addition to that, fine grained sandstone with low porosity may impede the oil movement and the amount of oil movement may resemble that of water-wet sandstones (Worden et al. 1998). Or, the oil inclusions have been trapped grain fractures, which make it irreducible.

Table (2) illustrates the depth and the locations of the core

Sample	Core	Drill Depth (ft)	Drill Depth (m)	Stratigraphic Unit(s)	Height above base of Nonesuch (m)
37F-13	37F	940.0	286.5	Skeleton Core	40.5
37F-1	37F	1020.4	311.0	Massive Black Siltstone	16.0
37F-2	37F	1024.4	312.2	Stripey	14.8
37F-3	37F	1052.9	320.9	Widely	6.1
37F-4	37F	1056.4	322.0	Upper Zone of Values	5.0
37F-5	37F	1058.8	322.7	Brown Massive	4.3
37F-6	37F	1060.0	323.1	Upper Transition	3.9
37F-7	37F	1062.0	323.7	Upper Sandstone	3.3
37F-8	37F	1064.8	324.6	Tiger	2.4
37F-9	37F	1069.1	325.9	Dark Gray Massive	1.1
37F-10	37F	1071.9	326.7	Red Massive w/ Junior and Domino	0.3
37F-11	37F	1072.2	326.8	Lower Transition	0.2
37F-12	37F	1073.5	327.2	Copper Harbor	-0.2
42C-12	42C	1040.0	317.0	Skeleton Core	54.4
42C-1	42C	1168.5	356.2	Massive Black Siltstone	15.2
42C-2	42C	1169.9	356.6	Stripey	14.8
42C-3	42C	1197.4	365.0	Widely	6.4
42C-4	42C	1204.2	367.0	Upper Zone of Values	4.3
42C-5	42C	1205.7	367.5	Brown Massive	3.9
42C-6	42C	1206.9	367.9	Upper Transition	3.5
42C-7	42C	1210.0	368.8	Upper Sandstone	2.6
42C-8	42C	1216.3	370.7	Dark Gray Massive	0.6
42C-9	42C	1217.8	371.2	Red Massive w/ Junior	0.2
42C-10	42C	1217.9	371.2	Domino	0.2
42C-11	42C	1220.2	371.9	Copper Harbor	-0.5

Table(3) shows the mineralogy of 37F core, Pl for plagioclase, Or for orthoclase, B for biotite, M for muscovite, WM for white mica, RF for rock fragments, and O.M for organic matter. The organic matter scale based on (Beicip, 1991, K.E. Peters, 1986, and Basu and Raul, 1996). I did not include 30G because it is very similar to 37F in content.

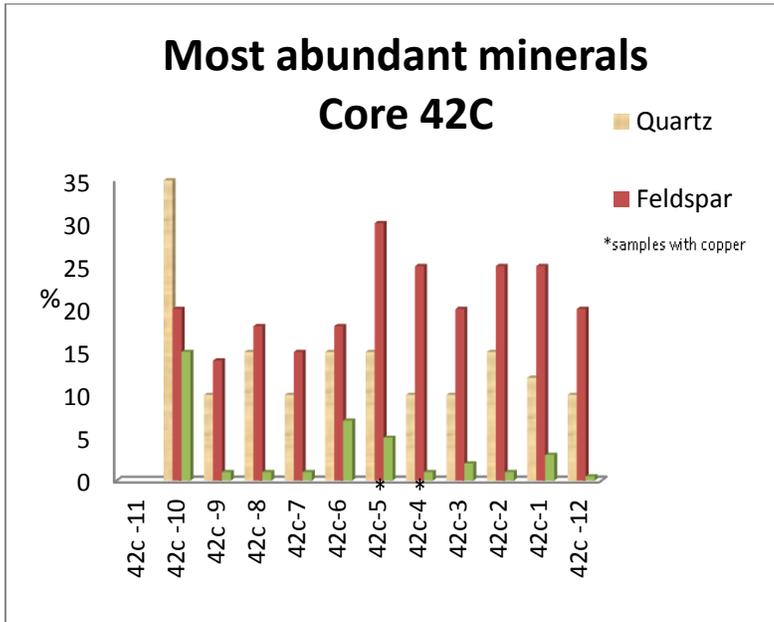
Sample number	Quartz %	Feldspar %		RF %	Mica %			Chlorite %	Calcite %	accessory minerals %	Others	O.M	Rock name
		or	pl		WM	B	M						
37F-12	20	25		15	0.5			3	0.2	Rutile, copper minerals	36	0.2-0.5	sandstone
37F-11	15	25		10	10			8	1	rutile	1.0	0.2-0.5	Sandy shale
37F-10	10	3		2.0	0.0			4	10	rutile	71	0.01-0.2	Laminated siltstone
37F-9	10	15		1.0	5.0			5.0	0.0	Rutile sulfides copper minerals	64	0.01-0.2	Massive siltstone
37F-8	7.0	15		1.0	25			15	0.0	Rutile copper minerals	37	0.01-0.2	Laminated siltstone
37F-7	10	12		3.0	25			5.0	2.0	Rutile, copper minerals	43	0.2-0.5	sandstone
37F-6	10	15		3.0	20			15	2.0	Rutile copper minerals	33	0.2-0.5	Sandstone with Shale
37F-5	10	15		0.0	5			2.0	5.0	rutile	63	0.01-0.2	siltstone
37F-4	7	20		0.5	15			2.0	0.0	Rutile copper minerals Pyrite	37.5	0.21-0.5	Massive siltstone
37F-3	15	18		1.0	15			15	0.0	Rutile, Copper Pyrite	36	0.21-0.5	Massively laminated siltstone
37F-1048.5	10	15		0.5	15			13	0.0	Rutile copper	46.5	0.2-0.5	Massive siltstone
37F-1029.4	10	5.0		2.0	5.0			1.0	20	rutile	57	0.2-0.5	Laminated siltstone
37F-1026	10	5.0		1.0	10			15	10	rutile	49	0.2-0.5	laminated siltstone
37F-2	10	5.0		1.0	10			1.0	10	rutile	63	0.2-0.5	Laminated siltstone
37F-1	10	25		2.0	15			8.0	3.0	rutile	37	0.2-0.5	Massive siltstone
37F-1020	15	20		3.0	10			10	3.0	rutile	39	0.01-0.2	Laminated siltstone
37F-1017.8	10	20		1.0	5.0			5.0	0.5	Rutile,	63.5	0.01-0.2	Massive siltstone
37F-1011	10	15		1.0	10			15	30	Rutile,	19	0.01-0.2	Laminated siltstone
37F-13	12	10		2.0	10			60	0	rutile	6.0	0.01-0.2	Widely laminated silt stone
37F-48	10	15		5.0	8.0			20	0.0	rutile	42	0.2-0.5	Thinly laminated siltstone

Table (4) shows the mineralogy of 42C core. See the abbreviation in table (3)

Sample number	Quartz %	Felds par %		RF %	Mica %			Chlorite %	Calcite %	accessory minerals%	Others	O.M	Rock name
		Or	pl		W	B	M						
42c - 12	10	15		0.0	10			30	0.0	rutile	35	0.01-0.2	Massive siltstone with Thinly laminated siltstone
42C-1120	5.0	10		0.5	15			30	0.0	Rutile pyrite?	39.5	0.2-0.5	Laminated siltstone
42C-1155	12	20		0.5	15			30	0.5	Rutile, sulfide	22	Less than 0.5	Laminated siltstone
42c-1	10	20		0.5	20			15	2.0	rutile	32.5	0.2-0.5	Thinly laminated siltstone
42C-1169	12	20		2.0	10			10	25	rutile	21	0.2-0.5	Laminated siltstone
42c-2	12	25		3.0	10			5.5	0.0	rutile	44.5	0.2-0.5	Thinly laminated siltstone
42c-3	15	25		1.0	10			25	0.0	rutile	24	0.01-0.2	laminated siltstone
42c-4	10	20		2.0	15			15	0.0	Rutile pyrite copper minerals	38	0.2-0.5	Massive siltstone
42c-5	10	25		1.0	8.0			8.0	1.0	Rutile pyrite copper minerals	47	0.01-0.2	Massive siltstone
42c-6	15	30		5.0	1.0			3.0	1.0	rutile	45	0.01-0.2	Sandy shale
42c-7	15	18		7.0	15			5.0	0.5	rutile	39.5	0.01-0.2	Sandstone with siltstone laminae
42c - 8	10	15		1.0	20			15	0.0	rutile	39	0.01-0.2	Massive siltstone
42C-1217	10	12		1.0	15			6.0	0.0	rutile	56	0.01-0.2	Siltstone with few shaly layers
42c - 9	15	18		1.0	5.0			5.0	0.0	rutile	56	0.01-0.2	Massive siltstone
42c - 10	10	14		1.0	25			6.5	0.0	rutile	43.5	0.01-0.2	Thinly laminated siltstone
42c - 11	35	20		15	0.0			1.0	0.0	rutile	29	0.01-0.2	sandstone

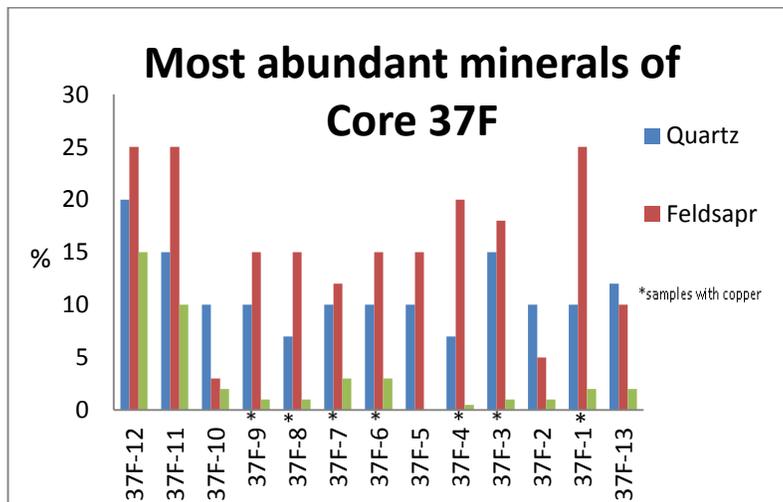
Table (5) shows the mineralogy of 30G core. See the abbreviation in table (3).

Sample number	Quartz %	Feldspar %		RF %	Mica %			Chlorite %	Calcite%	accessory minerals%	Others	O.M	Rock name
		or	pl		WM	B	M						
30G-300	25	5.0		0.5	3.0			2.0	0.0	rutile	60.5	0.2-0.5	Laminated sandy siltstone with shaly layers
30G-586	5.0	10		0.5	5.0			3.0	30	Rutile pyrite ?	64.5	Less than 0.01	Laminated siltstone
30G-587	3.0	5.0		3.0	15			20	3.0	Rutile sulfide	51	0.01-0.2	Laminated siltstone with shaly layers
30G-597.4	5.0	10		1.0	10			8.0	0.5	rutile	65.5	0.2-0.5	Laminated siltstone
30G-599	10	8.0		1.0	8.0			5.0	0.5	rutile	67.5	0.01-0.2	Thinly laminated sandy siltstone
30G-600	15	10		5.0	10			3.0	12	rutile	45	0.01-0.2	Laminated sandy siltstone with shaly layers
30G-631	3.0	15		0.5	10			5.0	0.0	rutile	66.5	0.01-0.2	Laminated sandy siltstone with shaly layers
30G-637	5.0	5.0		1.0	10			25	2.0	rutile	52	0.01-0.2	Thinly laminated siltstone with few dark layers



42C-12	Marker Bed
42C-1	Massive Black Siltstone
42C-2	Stripey
42C-3	Widely
42C-4	Upper Zone of Values
42C-5	Brown Massive
42C-6	Upper Transition
42C-7	Upper Sandstone
42C-8	Dark Gray Massive
42C-9	Red Massive w/ Junior
42C-10	Domino
42C-11	Copper Harbor

Figuer13-A



37F-13	Marker Bed
37F-1	Massive Black Siltstone
37F-2	Stripey
37F-3	Widely
37F-4	Upper Zone of Values
37F-5	Brown Massive
37F-6	Upper Transition
37F-7	Upper Sandstone
37F-8	Tiger
37F-9	Dark Gray Massive
37F-10	Red Massive w/ Junior and Domino
37F-11	Lower Transition
37F-12	Copper Harbor

Figure 13-B

Figures (13 A and B) demonstrates the most abundant minerals in cores 42C and 37F.

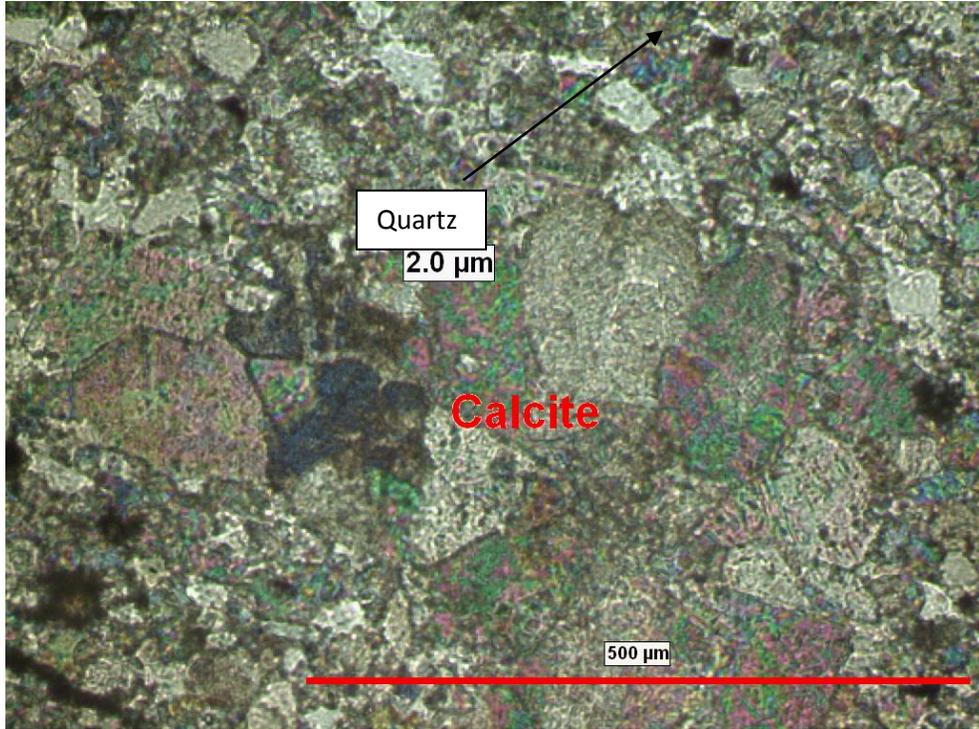


Figure (14) shows quartz grains and calcite as cement Stripey with high interference color under XPL from sample 37F-2.

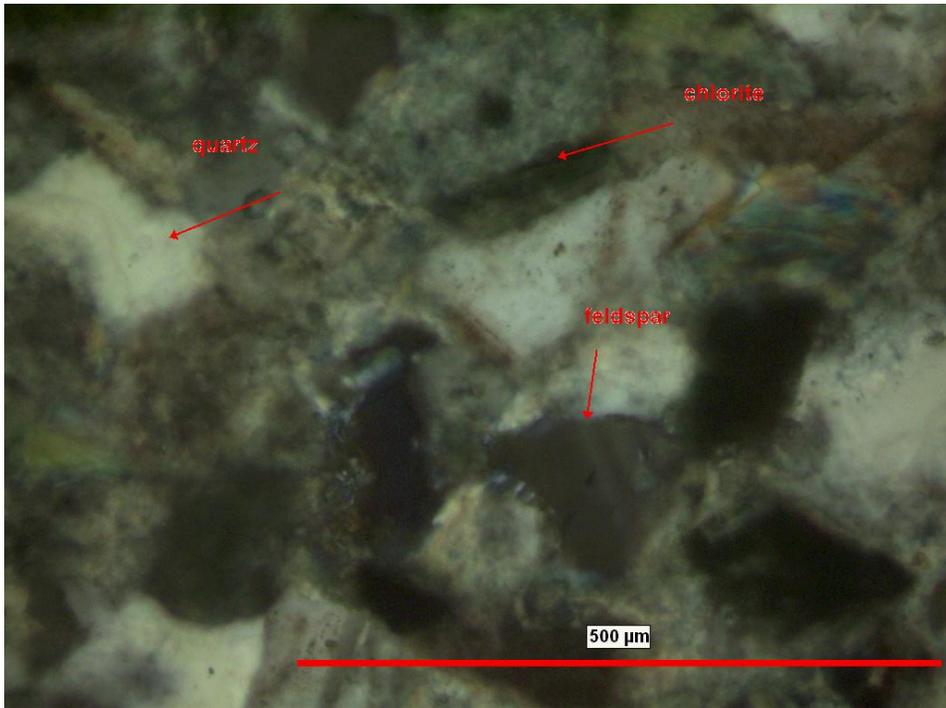


Figure (15) Illustrates sample 37f-12(Copper Harbor); it shows quartz and feldspar grains, with chlorite as cement.

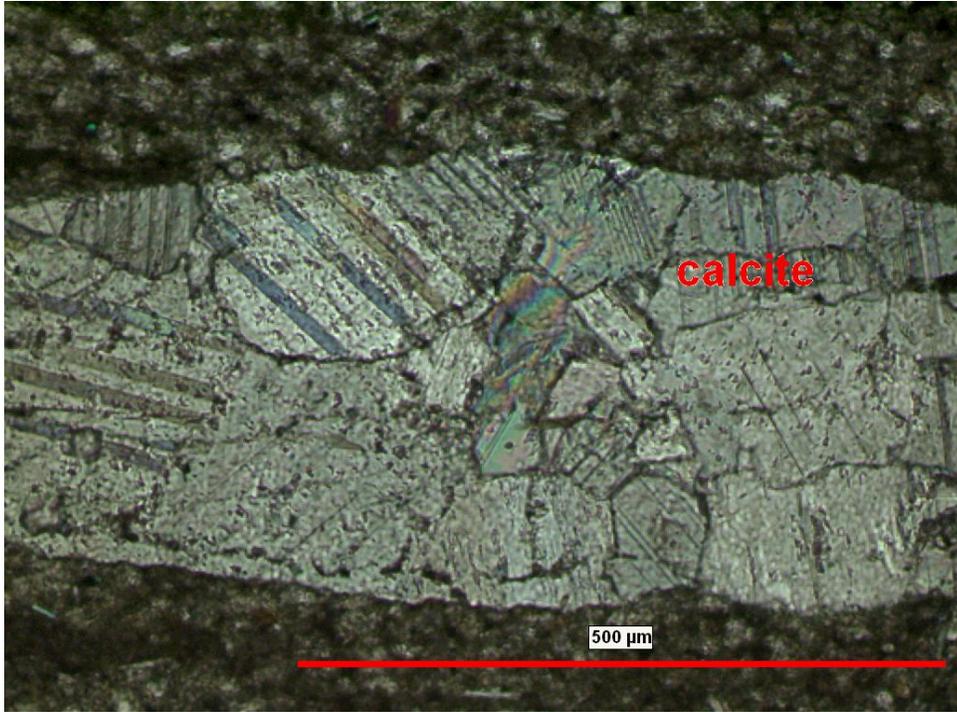


Figure (16) shows a calcite vein in sample 42c-1 parallel to the bedding (Massive Black Siltstone), with clay as matrix.

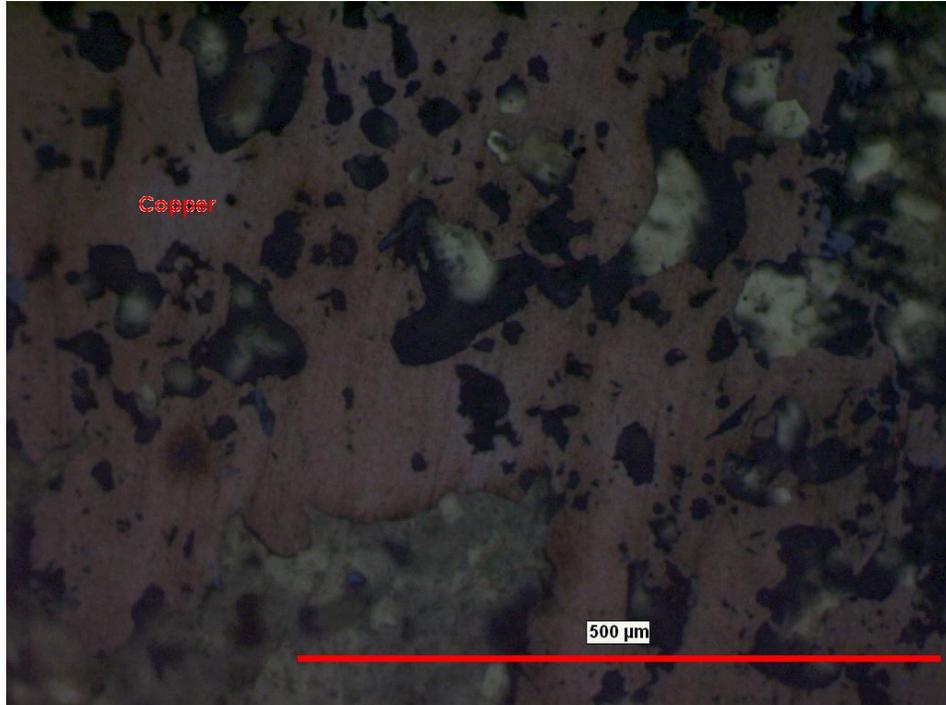


Figure (17), Sample 37-9 shows the copper mineralization replacing and overgrowing the grains in the Dark Gray Massive unit, including clay, and quartz grains.

Some samples have possible alginite (appendix A-sample 37-4) which is a component of some types of kerogen, alongside amorphous organic matter, it was observed in some units such as Massive Black Siltstone, Widely, and Brown Massive In this study high organic matter

Within the Lower Nonesuch Formation is found within copper mineralization intervals, as in 37F-9, 8, 7, and 42C-4, 5. The copper mineralization with the organics is mainly found as copper sulfide (chalcocite) or native copper. Organic matter quantity was assessed by using transmitted and reflected light microscopy on all three cores as well as using Rock Eval to measure TOC. The detectable TOC values ranged between 0.01% and 0.86%. Organic-rich laminae, which are less than 1 cm thick, are found within the thinly or massive laminated siltstone and shale, and sandstone with shaley layers. The samples that have detectable TOC and relatively high Cu mineralization are from the Upper Zone of Value (37F-4 and 42C-4), the Upper Transition (37F-6 and 42C-6), Lower Transition (37F-11), and from below the Lower Nonesuch Formation in the Copper Harbor Formation, (37F-12 and 42C-11). There are some other samples that have the highest measurable TOC, but are way above the mineralization zone, for example 37F-1 and 42C-1 from the massive black siltstone, and 37F-2 and 42C-2 from Stripey. However, there are some samples that have detectable copper with very low TOC, for example 42C-10 from Domino. In general, High OM was detected within the Lower

Nonesuch Formation within Cu mineralization (Upper Sandstone, Tiger, Dark Gray Massive, and Brown Massive).

7.4 The distribution of Cu and S with depth:

Based on King (2009) and the inorganic geochemical data in table (7), I have compared a relation of Cu and S content to the depth, figures (18 A and B, 19 A and B, 20 A and B). The lower Nonesuch Formation as seen in figure (11), is generally observed as the cupriferous zone in Michigan in the region of White Pine. The main interesting minerals are chalcocite, bornite, chalcopyrite, and pyrite. The native copper is usually found with chalcocite. Many of the samples in core 30G have Cu content less than 2000ppm and S less than 0.2%; core 42C and core 37F are almost within the same range. These samples with low Cu and S are mostly from the dark gray colored zones such as Stripey (37F-2, 42C-2), Widely (42C-3), and Dark Gray Massive, and from sandstone samples with some laminated siltstone such as 37F-7 from the Upper Sandstone zone. There is no direct relationship between Cu and S with depth (fig 21 A-B) within the Nonesuch Formation. The copper content is higher in the lower Nonesuch Formation, while the pyrite content is higher above the copper zone. Therefore, the mineralized zones were divided into three zones: Pyrite zone (40 ft above), Copper zone (the lowest 20 ft), and low sulfur zone (in between the last two zones).

In addition, there are measurable TOC values within the beds that have sulfur and are copper rich, see the next section and the highest values were measured above the copper zone (pyrite zone). The color of beds, which usually depends on the OM content, plays a role in this comparison. The dark gray siltstones and sandstones, or shale typically contained S, Cu, and TOC. High S with low Cu indicates pyrite. But the highest Cu values are in samples with low TOC, so cannot be regarded as reliable measurements.

Table (8) shows the results of the TOC and programmed pyrolysis data. S_1 and S_2 represent different types of hydrocarbon content in the rocks. S_1 ranges from 0.02 to 0.35 mg HC/g rock, while the S_2 range is 0.02 to 0.96 mg HC/g rock. They are in the poor to fair range of generative potential. TOC content ranges between 0.01 and 0.86 wt %. The highest value is for 42C-1120 and 42C-1155 from the Upper Nonesuch Formation which are above the copper mineralized zone (pyrite zone). The generative potential within the Nonesuch Formation sample is still in the poor-fair range. In addition, HI can be used with TOC, S_1 , and S_2/S_3 (table 9) to determine and describe the potential of the shale as source rock or the shaly rock in this area. The HI range is between 24 and 300 mg HC/gC_{org}, which can produce gas, gas and oil, or oil.

Table (7), represents the trace elements of cores 42C, 30G, and 37F, Cu and S content. They are listed in stratigraphic order. The dashed line stands for Cu-Fe transition, King, 2009.

Height above the base of the Nonesuch Fm. (m)	Analyte Unit Detection Limit	Cu	Hf	Mo	Ni	Pb	Rb	S	Sb	Sc	Sr
		ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm
		1	0.5	2	1	5	20	0.001	0.2	0.1	2
40.5	37F-13	548	5.1	<2	58	9	90	0.04	1.0	19.2	93
16.0	37F-1	83	5.5	<2	46	15	40	0.55	2.1	17.2	142
14.8	37F-2	71	3.8	11	41	288	<20	1.52	4.8	12.5	134
6.1	37F-3	44	6.3	<2	52	40	80	0.13	1.0	18.5	117
5.0	37F-4	>10000	5.9	<2	51	12	60	0.35	0.8	18.4	113
4.3	37F-5	320	5.2	<2	40	<5	100	0.01	0.9	15.5	101
3.9	37F-6	>10000	7.3	<2	51	8	60	2.22	0.8	19.0	128
3.3	37F-7	719	6.2	<2	68	10	70	0.02	0.6	18.1	131
2.4	37F-8	3640	5.8	<2	67	16	100	0.09	1.1	23.8	118
1.1	37F-9	>10000	5.6	<2	44	6	<20	0.43	0.8	16.9	105
0.3	37F-10	1290	5.1	<2	40	11	50	0.03	0.8	15.1	112
0.2	37F-11	>10000	9.8	<2	54	10	60	0.83	0.6	20.2	140
-0.2	37F-12	881	6.1	<2	27	7	30	0.02	0.3	9.5	148
54.4	42C-12	215	6.0	<2	52	8	100	0.09	1.0	20.8	93
15.2	42C-1	65	5.1	<2	41	13	<20	0.17	1.3	16.3	127
14.8	42C-2	289	5.1	<2	55	24	80	0.18	0.8	18.5	119
6.4	42C-3	55	6.4	<2	56	8	60	0.03	0.7	20.2	108
4.3	42C-4	196	6.2	9	48	437	90	0.39	1.8	15.7	108
3.9	42C-5	631	5.2	<2	44	7	40	0.02	0.7	15.4	102
3.5	42C-6	>10000	6.9	<2	43	14	40	0.52	0.7	16.0	172
2.6	42C-7	289	6.1	<2	52	8	70	0.01	0.7	16.2	131
0.6	42C-8	2060	5.5	<2	68	15	100	0.05	0.9	21.4	108
0.2	42C-9	2500	5.5	<2	51	8	80	0.06	0.8	16.1	103
-0.5	42C-10	9220	5.4	<2	33	8	40	0.22	0.4	7.1	146
	42C-11	215	6	<2	52	8	100	0.093	1	20.8	93

Depth(ft)	Analyte	Cu	Hf	Mo	Ni	Pb	Rb	S	Sb	Sc	Sr
	Unit	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm
	Detection Limit	1	0.5	2	1	5	20	0.001	0.2	0.1	2
54	30G-38	56	4.6	< 1	< 5	8	48	23	110	1.68	1.6
595.6	30G-37	61	4.5	< 1	< 5	4	37	26	50	1.2	2.6
597.7	30G-36	66	5.2	< 1	< 5	7	50	36	70	1.01	3
600.3	30G-35	61	4.3	< 1	< 5	6	47	122	80	1.61	3.7
605.6	30G-34	212	6.5	< 1	< 5	< 2	66	1.68	80	0.024	0.4
611.4	30G-33	99	5.5	< 1	< 5	< 2	54	1.2	70	0.011	0.4
618.8	30G-32	70	5.9	< 1	< 5	< 2	63	1.01	80	0.013	0.4
623.2	30G-31	79	6	< 1	< 5	< 2	61	1.61	80	0.036	0.4
628.1	30G-30	308	5.4	< 1	< 5	< 2	59	0.024	< 20	0.146	0.7
624.7	30G-29	23	5.2	< 1	< 5	< 2	62	0.011	< 20	0.017	0.6
633.7	30G-28	>10000	5.1	< 1	< 5	< 2	58	0.013	< 20	1.65	0.3
631.9	30G-26	7560	5.6	< 1	< 5	< 2	49	0.036	50	0.191	0.4
637.9	30G-27	2330	5.4	< 1	< 5	< 2	61	0.146	80	0.055	0.4
644	30G-25	>10000	5.9	< 1	< 5	< 2	51	0.017	60	0.69	0.3
645.9	30G-24	>10000	6.2	< 1	< 5	< 2	69	1.65	70	0.297	0.6
646.9	30G-22	>10000	7.6	< 1	< 5	< 2	63	0.191	70	0.903	0.4
647.3	30G-23	432	7.3	< 1	< 5	< 2	73	0.055	50	0.013	0.4
648.8	30G-20	2350	9	< 1	< 5	< 2	28	0.69	50	0.054	0.7
654	30G-21	41	5.1	< 1	< 5	< 2	20	0.297	30	0.001	0.4

Continuous to table (7)

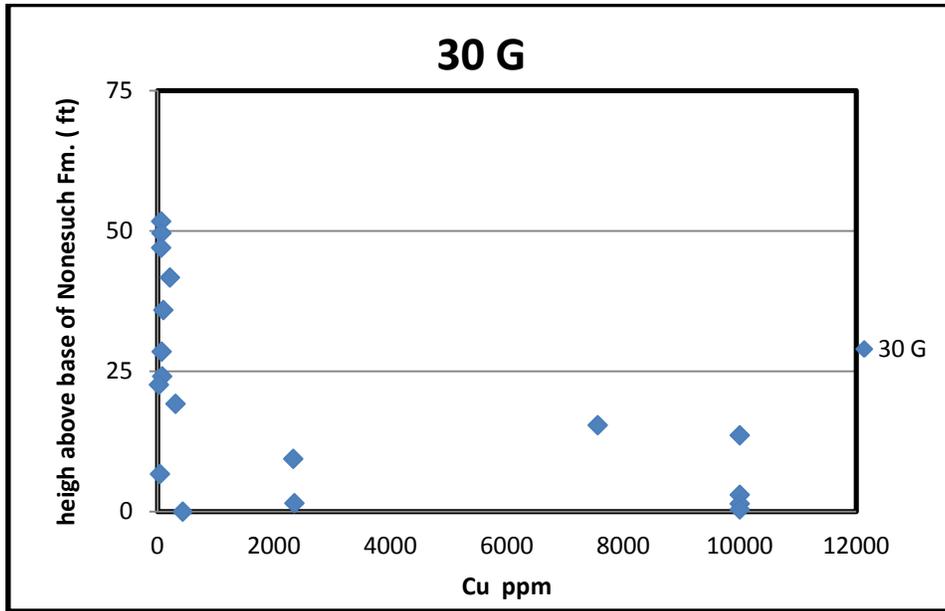


Figure 18-A

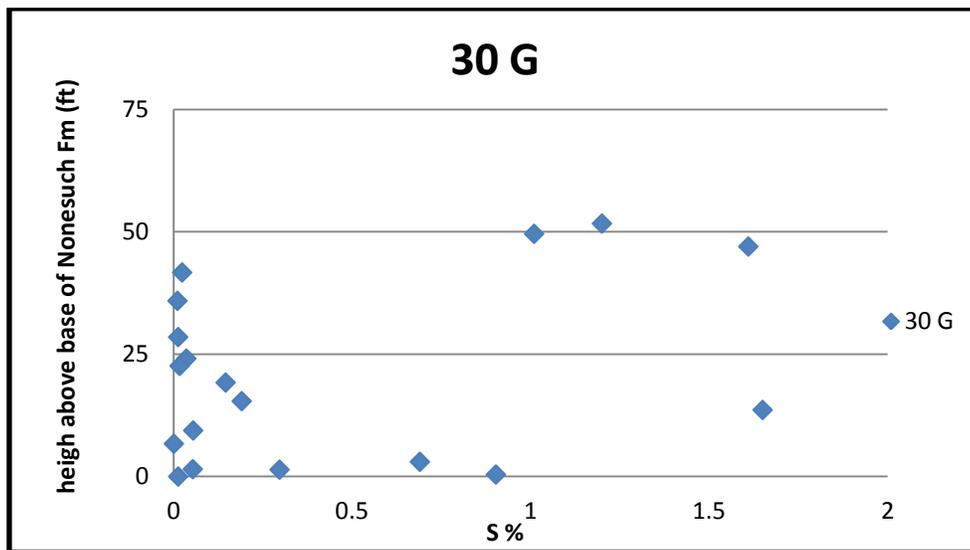


Figure 18-B Figures (18 A and B) give a graphical relation between Cu and S with depth in core 30G. 10000 ppm is the maximum limit of the analysis for Cu.

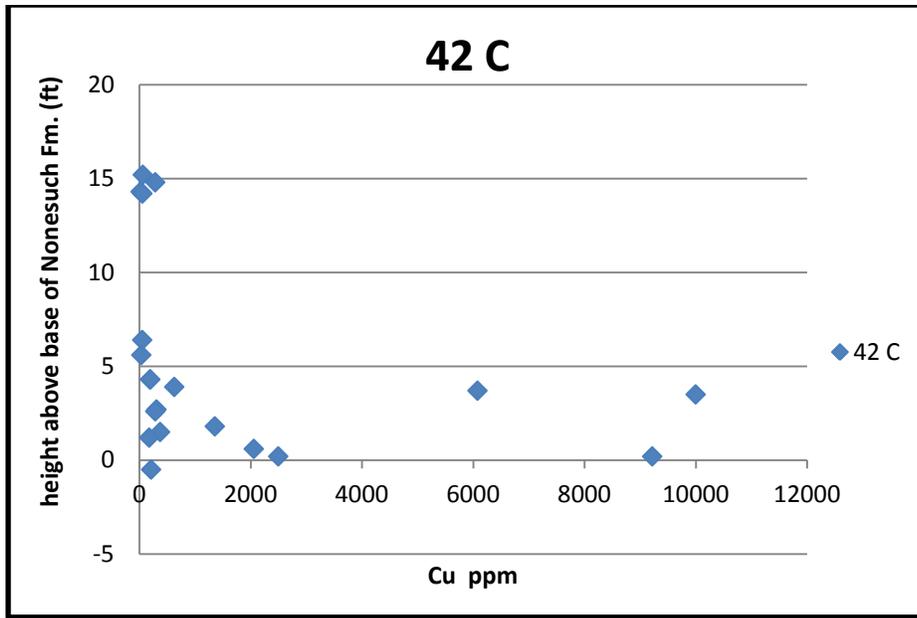


Figure 20-A

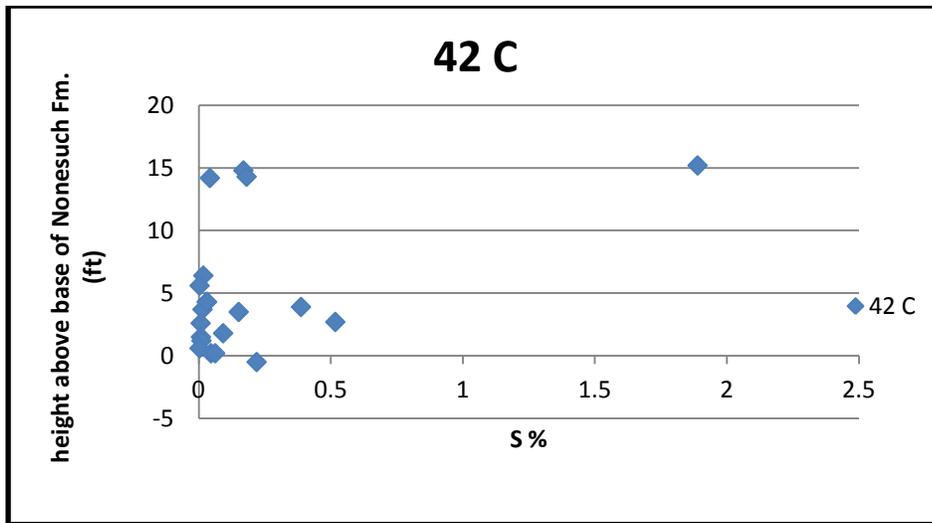


Figure 20-B

Figures (20 A and B) shows the relation of Cu and S to depth in core 42C. 10000 ppm is the maximum limit of the analysis for Cu.

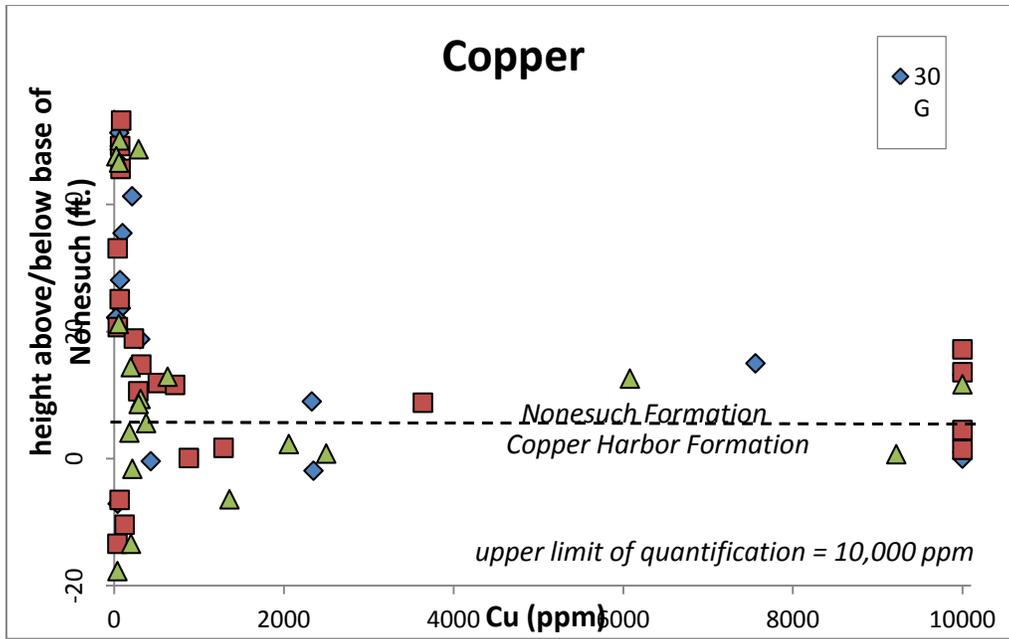


Figure 21-A, note: 10,000 values are not included

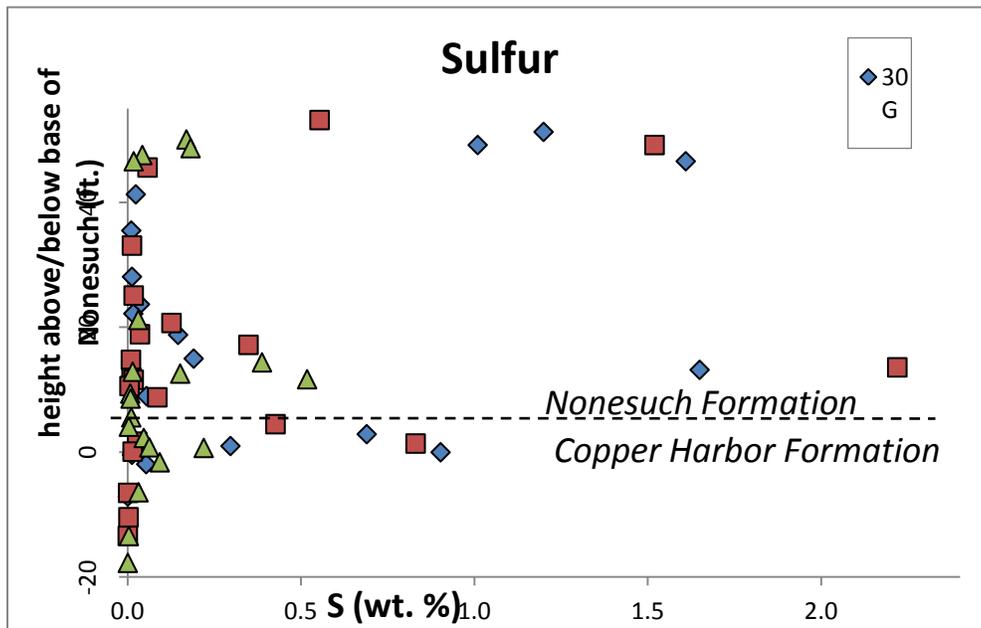


Figure 21-B

Figures 21-A and B show the increasing relationship of and Cu, S values with depth, the used data are according to King, 2009.

Table (8) shows the Total Organic Carbon Programmed Pyrolysis

Data, done by Weatherford Laboratories.

Client ID	Sample Type	Sample Prep	Leco * TOC	RE			Tmax ** (°C)	Ro, % **	HI	OI	S2/S3	S1/TOC	PI	Notes		Lab ID
				S1	S2	S3								Checks	Pyrogram	
30G-631.6	Powder Rock	NOPR	0.21	0.05	0.05	0.34	477	**	24	163	0.1	24	0.50	TOC	f	3402097943
42C-1204.2	Powder Rock	NOPR	0.10	0.10	0.13	0.28	363	**	129	277	0.5	96	0.43	TOC	f	3402097945
37F-1026	Powder Rock	NOPR	0.02	0.02	0.02	0.19	495	**	111	-1	0.1	110	0.50	TOC RE	f	3402097947
30G-300	Powder Rock	NOPR	0.37	0.11	0.15	0.26	438	**	41	71	0.6	30	0.42	TOC	f	3402097949
30G-586	Powder Rock	NOPR	0.73	0.28	0.73	0.52	436		100	71	1.4	38	0.28	TOC RE	n.lhs2sh,hs2sh	3402097951
42C-1155	Powder Rock	NOPR	0.86	0.29	0.72	0.24	436		84	28	3.0	34	0.29	TOC RE	n.lhs2sh	3402097953
30G-597.4	Powder Rock	NOPR	0.23	0.08	0.28	0.22	473	**	120	94	1.3	35	0.22	TOC	f	3402097955
42C-1217	Powder Rock	NOPR	0.01	0.04	0.03	0.35	443	**	300	-1	0.1	403	0.57	TOC RE	f	3402097957
30G-599	Powder Rock	NOPR	0.29	0.10	0.31	0.25	425	**	105	85	1.2	35	0.25	TOC	f	3402097959
42C-1168	Powder Rock	NOPR	0.23	0.12	0.36	0.19	556	**	154	81	1.9	52	0.25	TOC	hs2p.lhs2sh	3402097961
42C-1197.4	Powder Rock	NOPR	0.01	0.04	0.11	0.11	524	**	846	-1	1.0	307	0.27	TOC	f	3402097963
42C-1120	Powder Rock	NOPR	0.87	0.35	0.96	0.19	424	**	110	22	5.1	40	0.27	TOC	n.lhs2sh	3402097965
37F-1048.5	Powder Rock	NOPR	0.02	0.02	0.03	0.18	441	**	187	-1	0.2	121	0.39	TOC RE	f	3402097967

Values with a -1 are invalid values because pyrogram is flat and the values are close to zero for S1 and S2

Notes:	Pyrogram:
* - not measured or invalid value for Tmax	f - flat S2 peak
** - Total Organic Carbon, wt. %	n - normal
S1 - volatile hydrocarbon (HC) content, mg HC/g rock	hs2sh - low temperature S2 shoulder
S2 - remaining EC generative potential, mg EC/g rock	hs2sh - high temperature S2 shoulder
S3 - carbon dioxide content, mg CO2/g rock	hs2p - low temperature S2 peak
	hs2p - high temperature S2 peak
	PI - Production Index = S1 / (S1+S2)
	NOPR - Normal Preparation
	LECO - TOC on Leco instrument
	RE - Programmed pyrolysis or TOC on Rock Eval instrument
	SRA - Programmed pyrolysis by SRA Instrument
	EXT - Extracted Rock

Table (9) shows the S_2/S_3 values, the mineralized samples, and from which units.

Sample	S ₂ /S ₃	Mineralization	Lithology	Unit
30G-300	0.57692	-	Laminated sandy siltstone	Above the Marker Bed
30G-586	1.40385	-	Laminated siltstone	Marker Bed
30G-597.4	1.27273	pyrite	Laminated siltstone	Massive Black Siltstone
30G-599	1.24	pyrite	Laminated sandy siltstone	Massive Black Siltstone
30G-631.6	0.14706	Cu	Laminated siltstone	Upper Zone of Values
37F-1026	0.10526	-	Laminated siltstone	Widely
42C-1120	5.05263	pyrite	Laminated siltstone	Above Marker Bed
42C-1155	3	-	Laminated siltstone	Marker Bed
42C-1168	1.89474	pyrite	siltstone	Massive Black Siltstone
42C-1197.4	1	-	siltstone	Widely
42C-1204.2	0.46429	Cu	Laminated siltstone	Upper Zone of Values
42C-1217	0.08571	Cu	Siltstone with shaly lyres	Red Massive

7.6 Kerogen type and quality:

According to the Rock Eval pyrolysis results in table (8) and the Van Krevelen diagram (Fig 22), the kerogen types are III and IV. Type III is usually gas prone, while type IV has no potential, figure (12). The figures (23) and table (8), show that the amounts of pyrolyzable hydrocarbons in the Nonesuch Formation are less than about 10% of the TOC. However, there is a positive relationship between S_1 , S_2 , and TOC which points to the contribution of S_2 from TOC.

To evaluate the quality, we need to determine whether the organic matter is capable of producing hydrocarbons or not. The quality of all samples of Nonesuch Formation kerogen was determined by the Rock–Eval pyrolysis see figures (24). Most of samples are in the gas-prone

to inert zone of III and IV kerogen types. Therefore, the OM is not capable of producing good quality hydrocarbons.

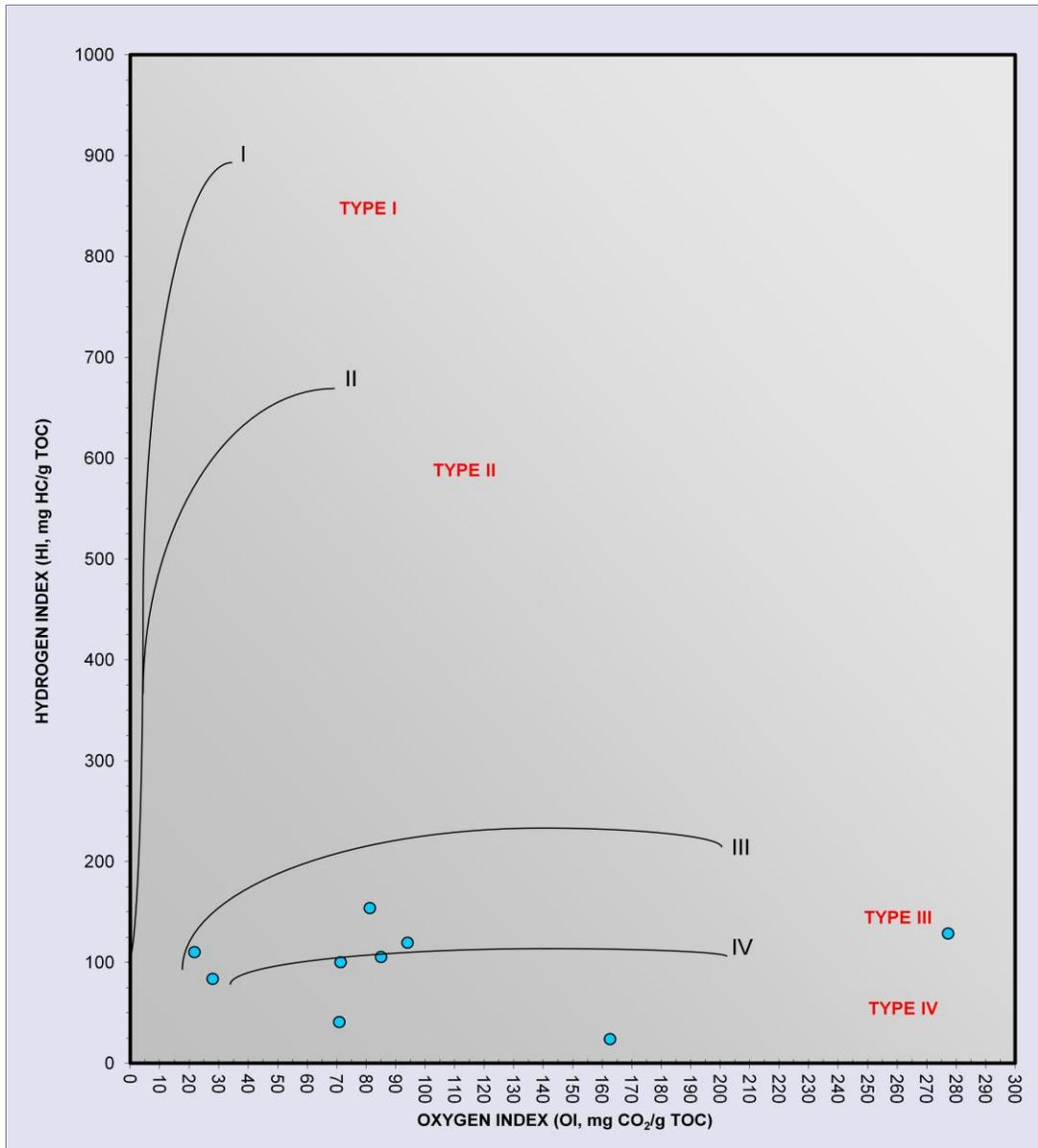


Figure (22) The Van Krevelen diagram showing the composition of samples analyzed in this study, Weatherford 2011.

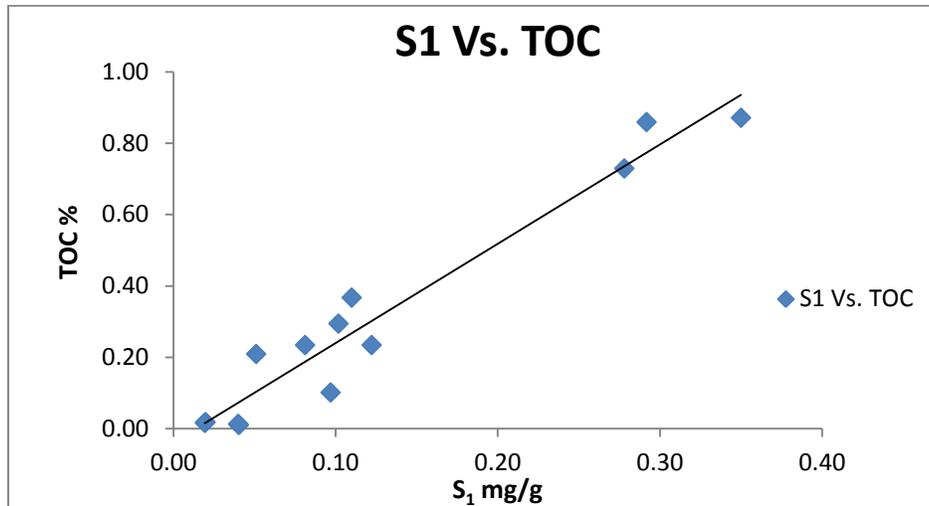


Figure 23-A

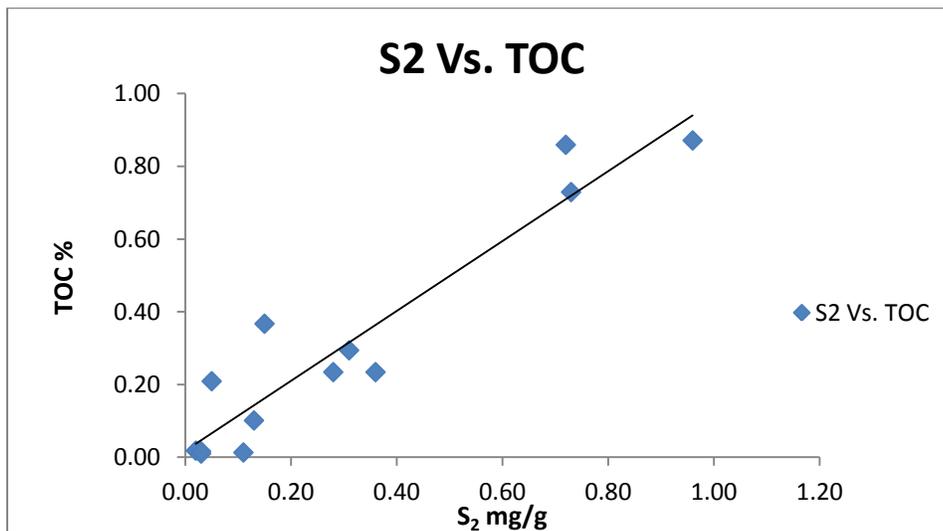


Figure 23-B

Figures 23 A and B show that the amounts of pyrolyzable hydrocarbons of Nonesuch Formation in terms of S₁, S₂, and TOC, the data are from table (8).

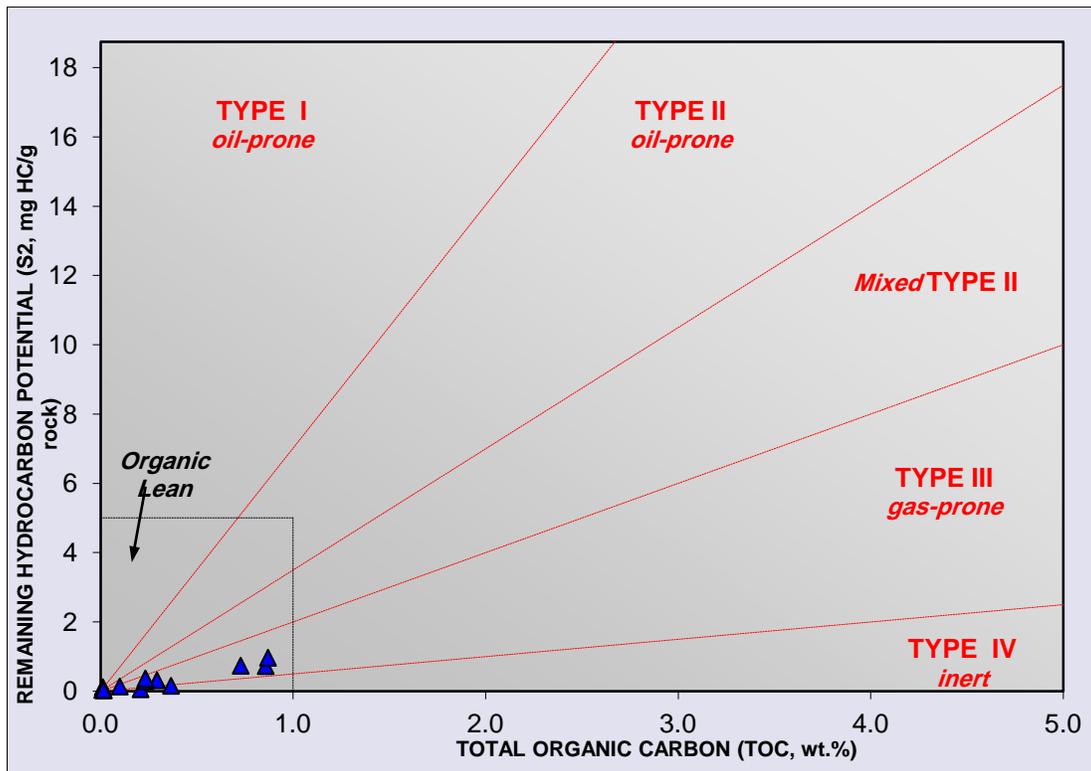


Figure (24) demonstrates a plot of TOC and S₂ to evaluate the kerogen quality.

7.7 Thermal Maturation of Organic Matter:

The S₂ values (table 8 and fig 25) below 0.2 are inaccurate and cannot be used to determine the maturation (Peters 1986). In addition, the S₂ values are mostly derived from a flat peak in table (8). Samples 30G-631.6, 42C-1204.2, 37F-1026, 30G-300, 30G-597.4, 42C-1217, 30G-599, 42C-1168, 42C-1197.4, and 37F-1048.5 should be excluded from further consideration due to the small amount of S₂. The plot between T_{max} and HI (26) shows that samples 30G-599 and 42C-1120 with 105 and 110 mg HC/g TOC, respectively, have T_{max} 424

and 425°C and are immature; samples 30G-597.4, 30G-631.6, and 37F-1026 are mature-postmature and might produce condensate gas or be in the dry gas window. Meanwhile, the other samples are mature and could generate oil. These results are not certain, especially the ones at the oil window range. The relation between Tmax and PI (figure 27) shows almost the same results as the Tmax and HI graph (fig 26). The samples at 470 °C and higher are in the high conversion stage in maturity. In addition, the samples with T_{max} between 430 and 460°C are in the intensive generation and expulsion phase or oil window level of maturity, while the samples at less than 430°C Tmax may be stained or contaminated. The hydrocarbons are likely to be contaminated or immature source rocks (Peters 1986).

One property of sedimentary rocks can be preserved organic material. The sedimentary organic matter may be buried and preserved up to higher temperatures, in a reducing environment. Figure (28) shows how the maturity changes with depth, and some samples are within the mineralization zones such as sample 42C-1204.2. It was taken from the Upper Zone of Values, contains copper and sample 42C-1120, which was taken from above the Marker Bed unit has pyrite. In addition, three samples are pointed out by a circle (figure 28) to represent that they have enough S_2 to give valid measurements of T_{max} . The PI or $[S1 / (S1 + S2)]$ ratio also indicates the level of maturity; the values which are less than 0.01 shows the immature stage; in

addition, they have very low T_{max} . The mature stages PI values are 0.10 to 0.15 and 0.25 to 0.40. Greater than 0.4 PI indicates the late mature stage.

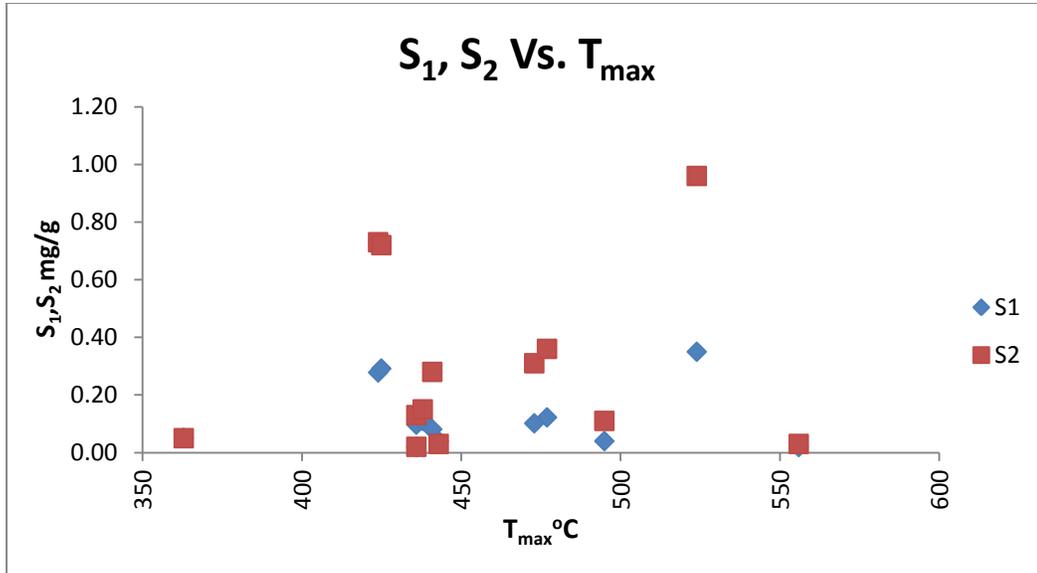


Figure (25) shows relation between S₁, S₂, and T_{max}

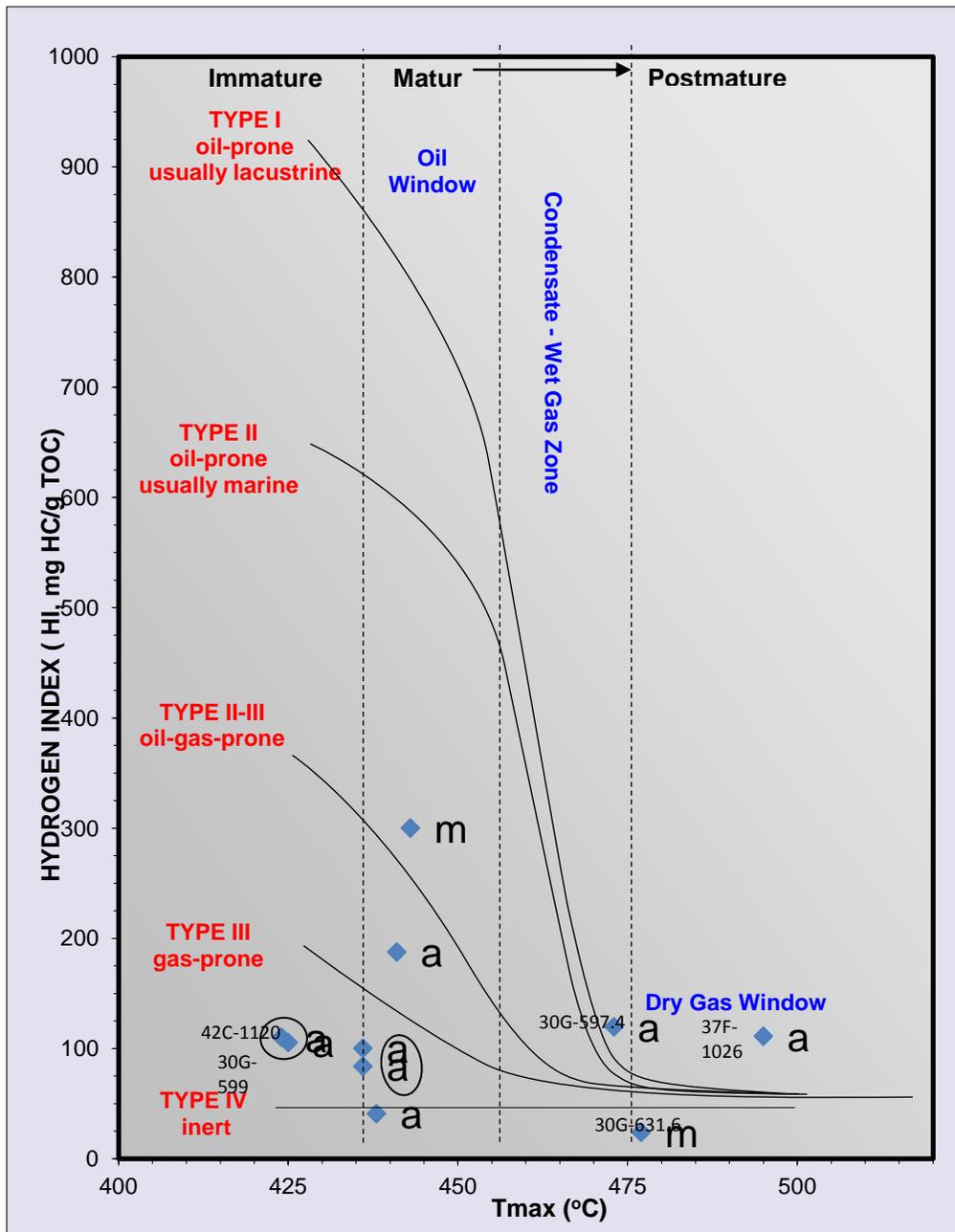


Figure (26) shows a plot between T_{max} and HI to determine the maturation level, a: above the mineralization zone, m: mineralization zone. The circled samples are to represent that they have enough S₂ to give valid measurements of T_{max}. The others have low S₂, so they might exclude from further considerations.

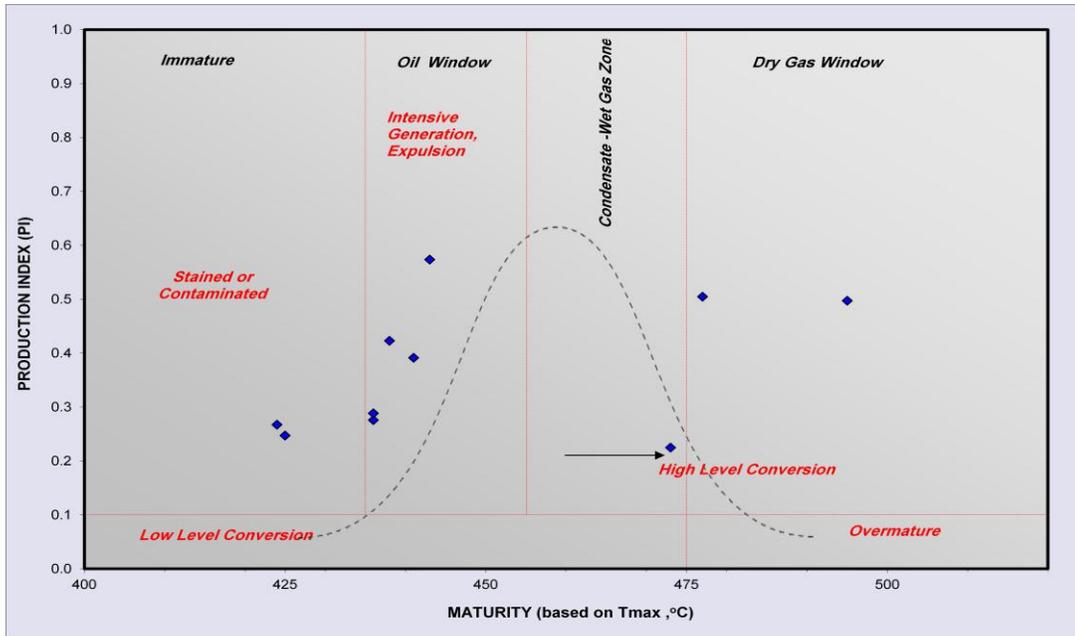


Figure (27) illustrates a plot between T_{max} (maturity) and PI to show the kerogen conversion and maturity.

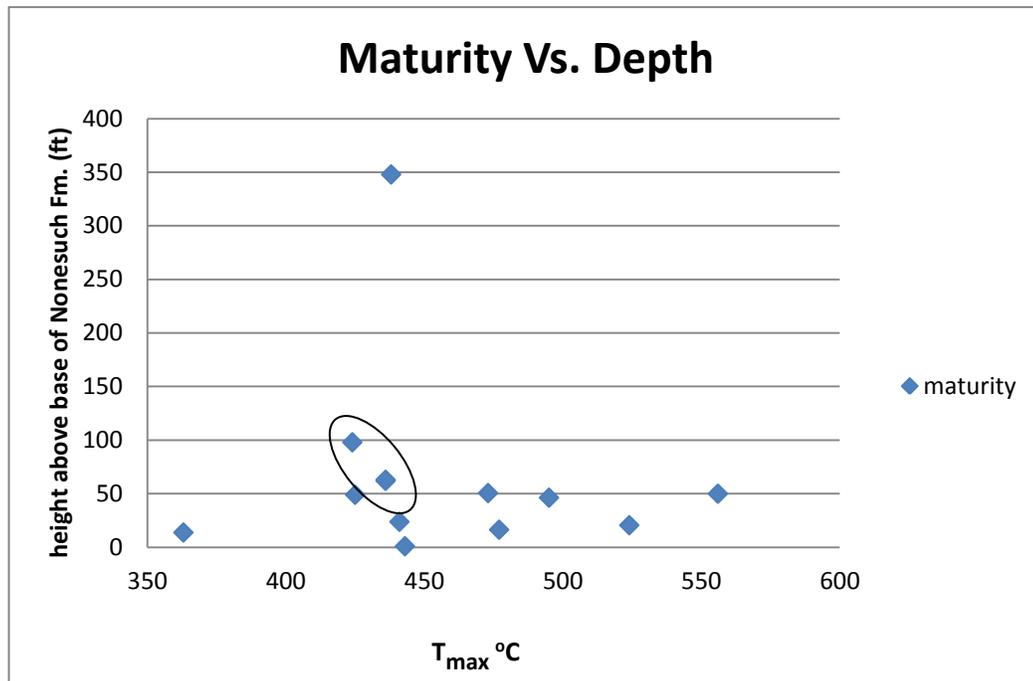


Figure (28) represents a plot of changes of maturity with depth; the depth is height above the base of the Nonesuch Formation, the table shows the samples with mineralization. Three samples pointed out by a circle to represent that they have enough S₂ to give valid measurements of T_{max}. The other samples have low S₂, so they might exclude from further considerations.

7.8 Reflectance of Vitrinite-like of kerogen:

Because of the absence of vitrinite during the Proterozoic, I used the vitrinite-like reflectance as a thermal maturity index for the Mesoproterozoic Nonesuch Formation deposited at White Pine.

Buchardt and Lewan (1990) and Belaid et al. (2010) have explained the technique of using vitrinite-like material. The vitrinite-like term has been used to describe macerals of intermediate reflectance when there is no clear evidence of its origin. The vitrinite-like reflectance may possibly be used as a maturity parameter. Buchard and Lewan found that heating can control the reflectance of vitrinite-like particles and the effect is similar to that of vitrinite in younger shales. There are different sources for the vitrinite-like organic matter; it could be created from polysaccharides of graptolites and chitinozoans, algae, or fungi, (Buchardt and Lewan 1990).

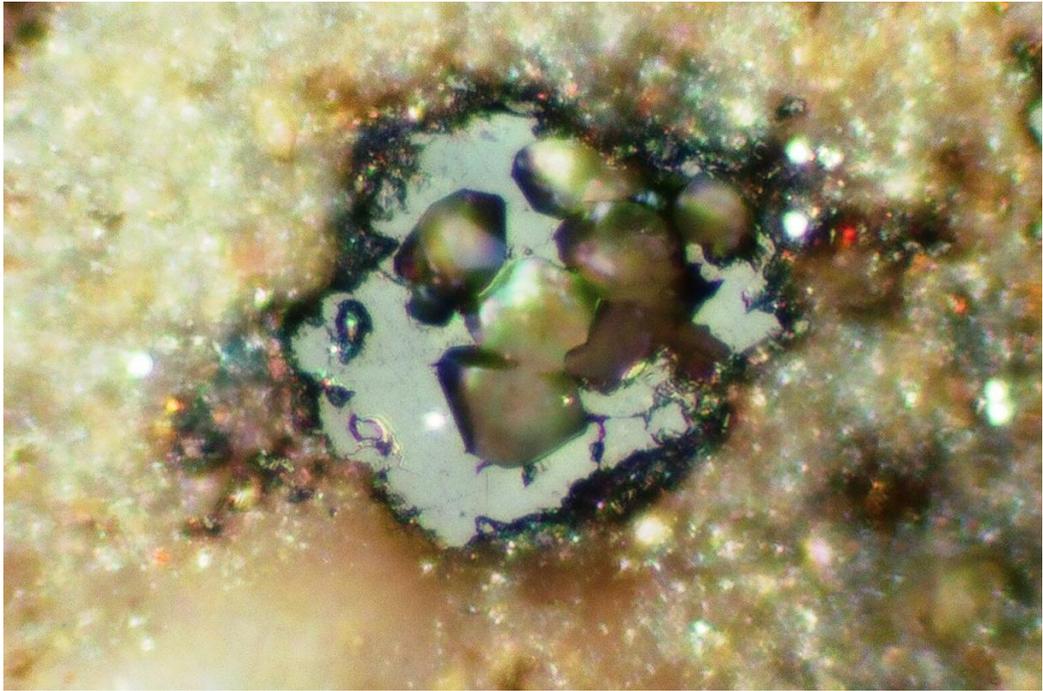
The reflectance of vitrinite-like particles was measured on some Nonesuch Formation samples; most of the samples have no vitrinite-like reflectance. About ten measurements have been done on each sample. The reflectance average of sample 30G-300 was about 0.35% which is immature, and for 30G 598 the reflectance is 0.95% which is early mature according to Killops and Killops (2005) (table-10). The only relatively high value was in sample 30G-633 which is about 10.4 % which indicates postmature organic matter. The OM or probable fungus in this sample take a porous and spherical shape, and is associated with quartz grains that formed during secondary processes (figs-29 A, B and C, 30, and 31).

No Rock Eval data were obtained for 30G-633, 30G-300, and 30G-598. The samples with high reflectance, but data for nearby sample, 30G-631.5 show low TOC, HI, S1, S2, and relatively high OI. That means the kerogen type of these samples in this range including 30 G-633, is type IV. They are oxidized and have no potential to produce hydrocarbons. Moreover, the fluorescence observations by UV light on the samples is pretty low.

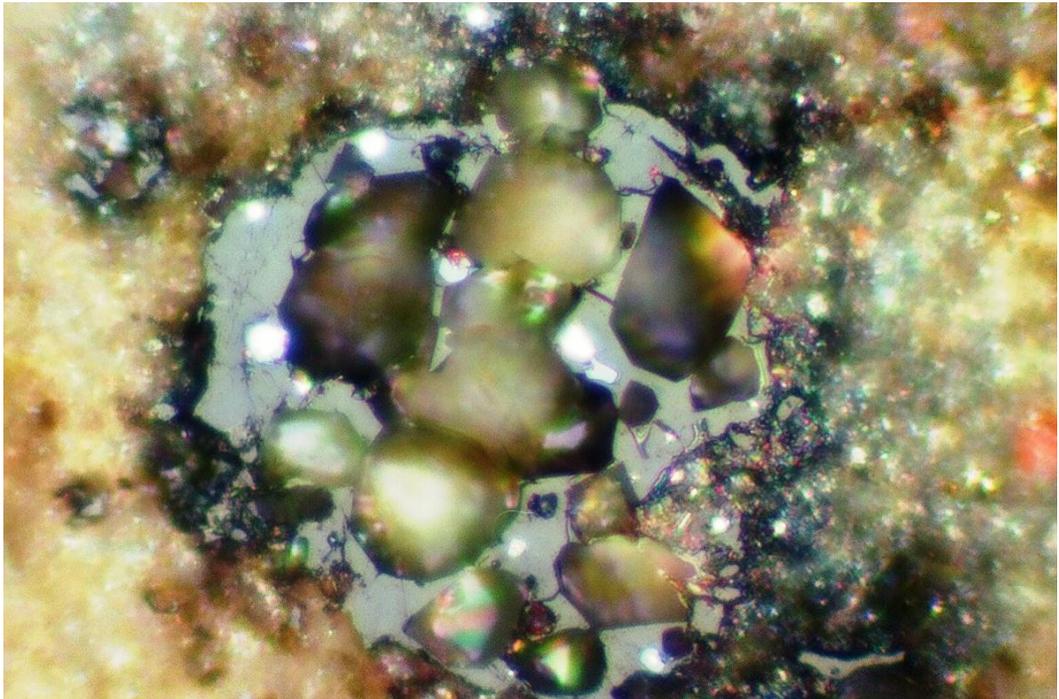
Considering the age of the rocks, the appearance of maceral matter in sample 42C-1168 would be described as solid bitumens. Mostly, the vitrinite like reflectance is little or no reflectance. According to Killops and Killops (2005), above the Marker Bed 0.35%, indicates the OM is immature. Massive Black Siltstone (0.95%) is mature, solid bitumens. While the Upper Zone of Values (10.4%) is postmature, and type IV kerogen.

Table (10) shows the reflectance of vitrinite scale with the main fluids evolved (Killops and Killops, 2005).

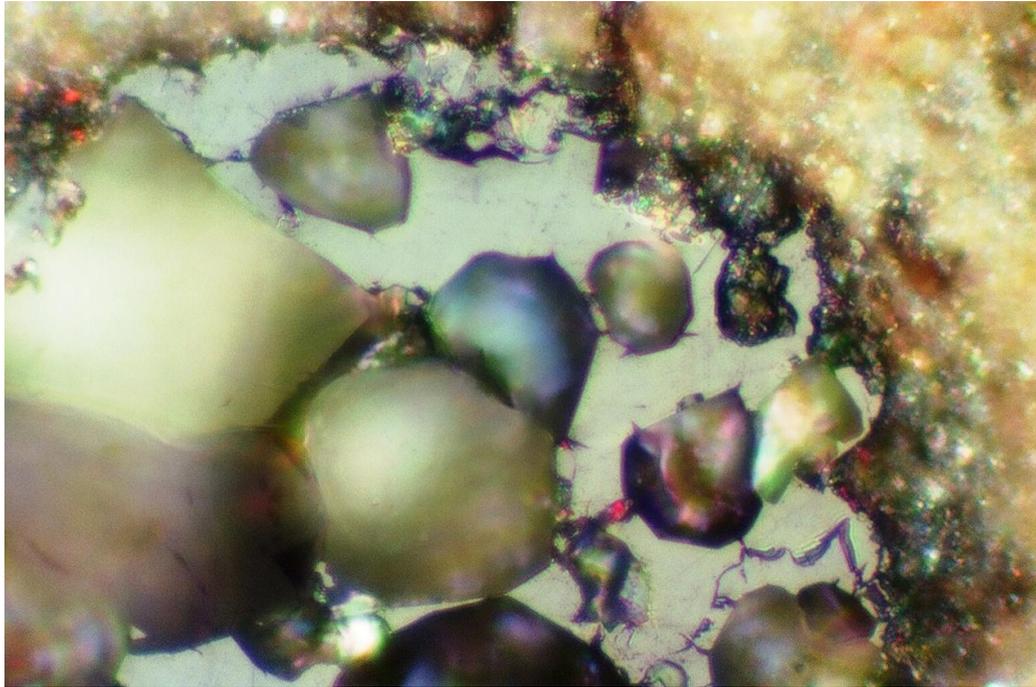
stage	zone		main fluids evolved	approx vitrinite reflectance (R_0)
diagenesis	immature		carbon dioxide & water	0.5–0.6%
catagenesis	oil		liquid hydrocarbons	
	wet gas		gaseous hydrocarbons	1.3%
metagenesis	dry gas		methane	2.0%



29-A



29-B



29-C

Figures (29 A, B and C) show the vitrinite-like reflectance of probable fungus in sample 30G-633 with average of vitrinite-like reflectance of about 10.3890%, photo scale is 25 μ m.



Figure (30) demonstrates the vitrinite-like reflectance of maceral as solid bitumens in sample 42C-1168.

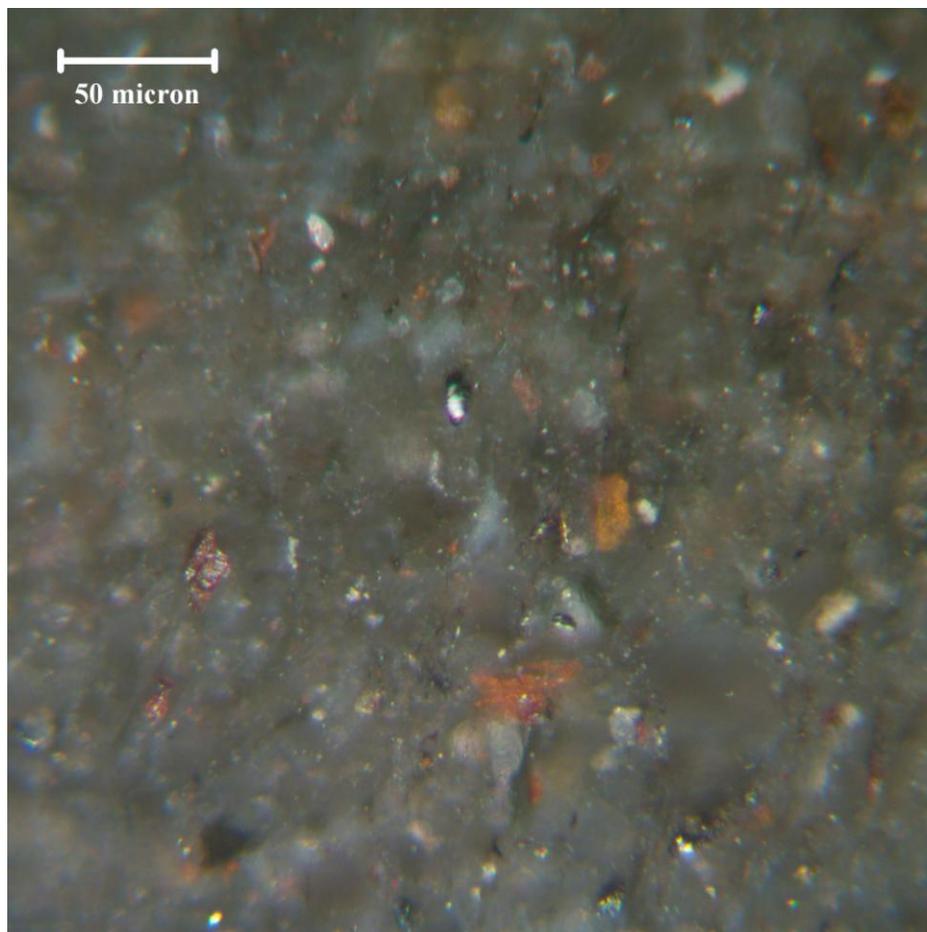


Figure (31) demonstrates the vitrinite-like reflectance of maceral as solid bitumens in sample 37F-1046.

8. Discussion:

This study was done by using samples from the Nonesuch Formation at White Pine, MI. The samples studied give a look at the mineralized lower part of Nonesuch Formation, specifically, the copper mineralization and organic matter, and a comparison with samples higher in the Nonesuch Formation. The mineralization of this part of the Formation may have been controlled by fluids that carried both copper and hydrocarbons through the Nonesuch Formation. The study shows that there is a relationship between the Cu deposits, S content, and OM.

8.1 The Organic Geochemistry and Depositional Environments:

This study and the study of Elmore et al. (1989) show the sediments of the Nonesuch Formation in Michigan are fine grained and probably lacustrine with possible transitional marine facies; the siltstone, and fine sandstone organic matter were likely deposited and preserved under anoxic conditions (figure-32). The organic matter possibly originated from algae and fungal remains that would have been living during the Mesoproterozoic. After burial, the organic matter formed kerogen, bitumens, alignite, and oil inclusions. From geochemical data such as Rock Eval pyrolysis and the absence of vitrinite, the kerogens that were created from these

organisms are shown to have transformed during diagenetic processes to types III and IV; the maturity ranges from immature to postmature. This result would be an indicator of the type of organisms during the Mesoproterozoic at White Pine.

8.2 The relationship between TOC and Cu, S:

In northern Michigan, the Cu-rich ore zone in the lower Nonesuch Formation is within the lowest 5 m. By studying cores 37F, 30G and 42C, it can be seen that the mineralized zone stretches from Stripey to the base of the Nonesuch Formation. Within Stripey and Widely in cores 42C, 37F, and 30G, the Cu was detected as chalcocite and based on King (2009) and my observations, pyrite was also seen at the top of these zones and above. The dark colored beds such as Stripey (37F-2, 42C-2), and Widely (42C-3) have detectable S of 1.52%, 0.18%, and 0.03%, respectively (table 8 and 4) and are also Cu rich zones, and organic matter was seen by transmitted and reflected light microscopy. In the beds higher in the section, including the Marker Bed and above the organic matter was detectable. For example in samples 30G-300 (above the Marker Bed) and 30G-586 (the Marker Bed), TOC is 0.37% and 0.73%, respectively. However, these zones are not part of the mineralized zone.

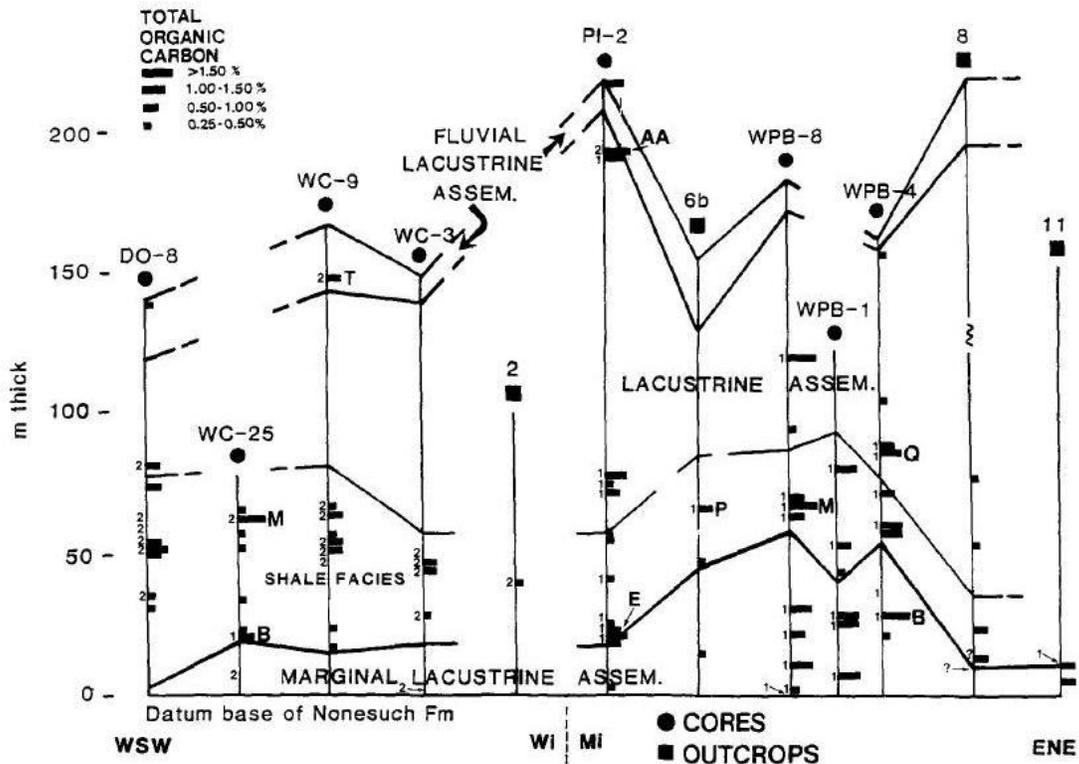


Figure (32) illustrates the relationship between depositional environment interpretations and TOC of Nonesuch

Formation at White Pine, WP: White Pine, Elmore et.al (1989).

There is no a direct relationship between the Cu, S, and OM content. Although, according to my observations, there is higher pyrite 40 ft above the base of the Nonesuch Formation, higher copper content in the lowest 20 ft of the Nonesuch Formation and low sulfur content in between these two zones (Fig. 33). I think that the main process causing migration of the hydrocarbons; and precipitation of the copper deposits could be the same which is a hydrothermal fluid. These hydrothermal fluids may have been oxidizing, but became reduced

and precipitated sulfides (pyrite) in some zones such as 30G-586, 42C-5, and 37F-4. The precipitation of copper minerals may have been caused by the same fluids. I believe this richness of S, Cu and TOC within the different intervals was caused by the mineral precipitating fluids. King, (2009) suggested that the copper was precipitated as chalcocite by sulfide that was produced by the sulfate reducing bacteria.

8.3 Total Organic Matter (TOC):

Data on the calculated quantity and quality of OM from the black to gray siltstone or sandstones beds with interbedded black shale layers or greenish siltstone, are used to evaluate whether the organics could have produced an economic accumulation of hydrocarbons or not.

In addition, these data show the relationship of organic matter to the Cu minerals.

The source of the organic matter was not macroscopic fossils or plants because there is no evidence for higher plants during the Precambrian, but probably was from algae and/or fungi as I have observed. The Precambrian Era includes all of geologic time prior to 545 million years ago, and so the organic matter may have been buried for a long time and cooked to become overmature. The organics that have low or no fluorescence under a UV light source so are interpreted as poor in hydrogen, as the fluorescence of organics is due to the enrichment in hydrogen content. The samples with the highest TOC values, 0.87, 0.86, and 0.73 are taken

from 42C-1120, 42C-1155, and 30G-586, respectively. These samples are taken from sections that are higher than the copper mineralization zone, but they have pyrite sulfides. They each have rather low HI values ranging between 50 and 200 (mg HC/g TOC).

According to Peters and Cassa (1994) these values of TOC are in the fair range, 0.5-1 (wt. %), for generation of hydrocarbons. In general, the TOC values are in the poor-fair range, and are unlikely to produce hydrocarbons. The low values of TOC (below 1 wt %) are interpreted to be due to secondary oxidation of organic carbon; the amount of OM in Kupferschiefer has been decreased by up to more than 20 times by the secondary oxidation at copper deposits (Pieczonka et al. 2008). The only detected kerogen types are III and IV, they both were cracked from very simple Precambrian organisms like algae and/or fungal remains in an oxidizing environment like lakes, or terrestrial environments, or oxidized by the hydrothermal fluids.

The thermal maturity is indicated generally by T_{max} and R_o . The highest T_{max} value is detected in sample 42C-1168 is 556 °C and is higher than 470 °C which represents postmature organic matter (Peters and Cassa, 1994). In addition, there are other low values in some samples which indicate immature organic matter, for example in samples 42C-1204.2, and 30G-

599 and the T_{max} is 363 and 424 respectively. There are no good R_o results in this study due to the absence of wood or coal fragments; therefore, I used vitrinite-like macerals. The average of vitrinite-like reflectance is 0.35%, 0.95%, and 10.3890% which are detected in samples 30G-300, 30G 598, 30G-633, respectively.

There are three samples that may have a relationship between organic maturity, which was determined by the relationship between T_{max} and HI, and copper mineralization. Samples 42C-1204.2, 42C-1155, and 42C 1120 have 0.1, 0.86, and 0.87 TOC, respectively. The last two samples have the highest TOC and high HI values; however, they have lower PI compared to the other samples. The organics in 42C-1120 ft and 42C-1155 may have been preserved under the same environment as the copper mineralization. However, I think that there is an obvious effect on the OM and OM maturity caused by the hydrothermal fluids (figure 33). In general, (figure 32) shows that the highest TOC, S_1 , S_2 , and T_{max} are detected within the pyrite zone; which represents the effect of the fluids on the OM within the Lower Nonesuch Formation. Moreover, S_3 value (CO_2) in the lower Nonesuch Formation (Cu zone) is higher than in the low S zone. That may indicate the OM was altered or oxidized by the hydrothermal fluids in the Lower Nonesuch Formation.

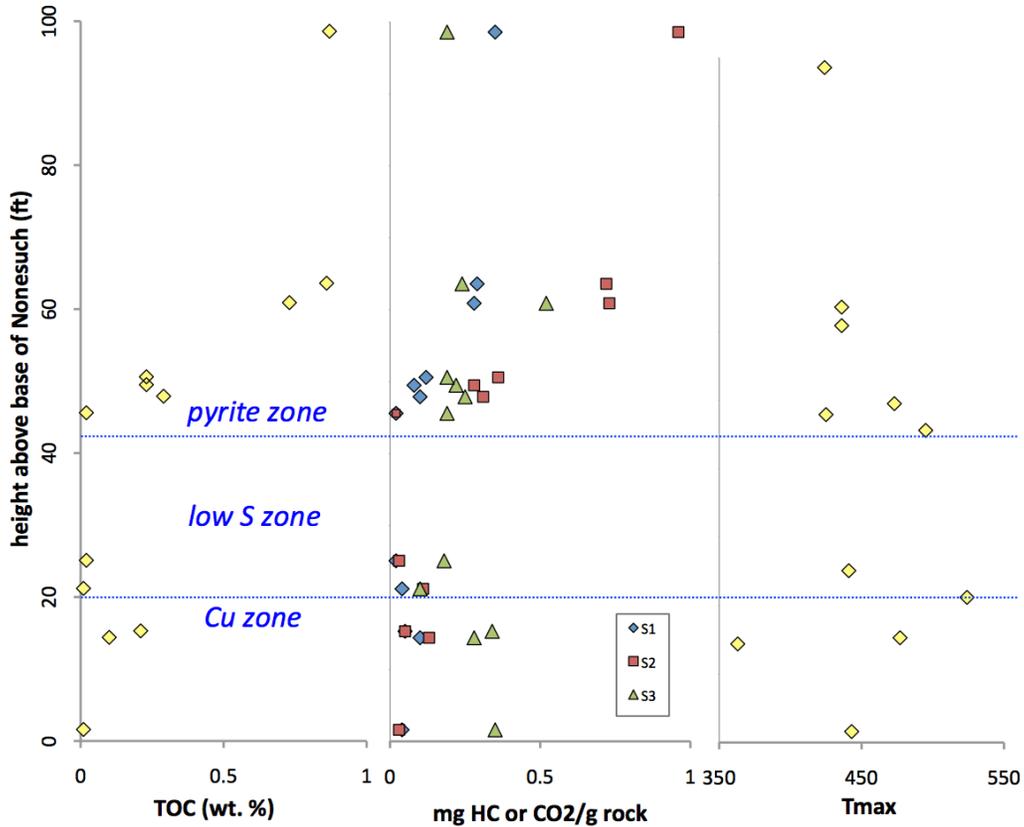


Figure (33) shows the relationship between TOC, S₁, S₂, and T_{max} with height above the copper mineralized zone.

Based on the microscopic studies and Rock Eval analysis, the TOC of the lower Nonesuch Formation at White Pine is not an economic accumulation and not able to produce hydrocarbons. The amount of organic material is relatively low, and the organic matter contains less than 10% pyrolyzable hydrocarbons (type III–IV) (Figure-14), which makes the formation a poor potential source. It is also not a petroleum source rock because all samples have low S₂ HC/g values.

According to the similarity between the Nonesuch Formation and the Kupferschiefer (Pieczonka et al. 2008), in lithology, mineralization, and the nature of the organic matter (oxidized OM), the TOC value, which is rather low, could be affected by secondary oxidation of some samples. These processes may be a result of the presence of copper bearing fluids and be recorded by the red colored strata of the oxidizing conditions like the Copper Harbor Formation (Pieczonka et.al, 2008).

Sari et al. (2005) suggested that organic matter deposited in lacustrine environments in general is a mixture of detrital materials such as spores, pollen, cuticles, and wood, but that obviously does not apply to the Proterozoic. Lacustrine TOC contents vary from less than 1% to over 60%, with the most common ranges between of 1 and 10%. In this study, the amount of organic material is much lower and the slope of the generation line is lower than those typical of lacustrine sediments (fig-22).

In general, the thermal maturity indicators are highly variable: the highest T_{max} (556 °C) in Massive Black Siltstone (pyrite zone), is postmature OM. Meanwhile, the lowest T_{max} (363 °C) were detected in the Upper Zone of Values (Cu zone) and (424 °C) in the Massive Black Siltstone (pyrite zone, they both in the immature OM range. In addition, the highest vitrinite-like reflectance (10.4%) measured in the Upper Zone of Values (Cu zone), and the lowest vitrinite-

like reflectance (0.35%) measured above Marker Bed (pyrite zone) and 0.95% in Massive Black Siltstone (pyrite zone). Therefore, the Copper mineralized zone (Upper Zone of Values) shows postmature reflectance and both mature and immature T_{max} . In addition, sample 42C-1217, which is one of the mature samples, from within the copper mineralized zone. The sample 30G-631.6 was detected within the mineralized zone is postmature. And there are some lower maturity values above the copper mineralization in samples with high TOC content, for example 42C-1120 ft and 42C-1155 (pyrite zone).

9. Conclusions:

Detailed optical and geochemical analyses were done on siltstone and fine grained sandstone samples that contain organic matter and copper minerals. Sixty samples were taken from the Nonesuch Formation, White Pine (MI). The samples of this study were principally analyzed to evaluate the organic matter content and maturity, and its relation to the copper mineralized zones. The techniques that have been used are: transmitted and reflected light microscopy, UV light microscopy, hand-sample core description, vitrinite reflectance, and Rock Eval analysis.

Quartz and feldspar (plagioclase, orthoclase) are the most common framework minerals. There are other minerals such as chlorite, white mica (muscovite), and rock fragments that are mostly found in the fine sandstone samples of the Nonesuch Formation and in the Copper Harbor Formation which underlies the Nonesuch Formation. Organic matter is seen in most of the samples, and copper minerals in some of the samples. Calcite and chlorite are found as cement. The dark gray colored siltstones such as in the Red and Gray zone have relatively high amounts of organic matter and have detectable pyrite content. The copper minerals have precipitated by hydrothermal fluid during the diagenesis processes. The copper was found

mostly as chalcocite in some zones like the Upper Zone of Value, and Copper Harbor Formation, and as native copper in 37F-9, figures (19). In general, the native copper is found with chalcocite.

Cu has a positive relationship with depth within the Nonesuch Formation; it generally rises in content with increasing depth. Sulfur has more complex relationship to depth with high values in both the Cu-mineralized zone and in the pyrite rich zone somewhat higher in the section. There is also detectable TOC within the beds that have sulfur and copper, as well as in some unmineralized samples. The existence of organic matter created reducing conditions that were suitable for copper precipitation. The richness of S, Cu, and TOC content within some zones may be caused by mineral precipitation by the hydrothermal fluids, which supports my hypothesis, and sulfate reducing bacteria could have been involved in this process during the diagenesis. The Cu mineralization in the Nonesuch Formation is epigenetic and was deposited by the hydrothermal fluids. Evidence to argue that the copper minerals were deposited after the sediments were buried is that some of the copper minerals were replacing and overgrowing the grains of sample 37F-9 (fig 17).

The Rock–Eval pyrolysis was used to evaluate the properties of organic material within the Mesoproterozoic samples. S₁ and S₂ both signify the nature of the hydrocarbon content of the lower Nonesuch Formation. The range of S₁ is 0.02-0.35 mg HC/g rock, and the S₂ range is 0.02-0.96 mg Hc/g rock. They represent the poor to fair range of generative potential. The HI varies between 24 and 300 mg HC/gC_{org}, which is in the gas, gas and oil, or oil range. The kerogen types of organic matter in the Lower Nonesuch Formation units were compared by using the S₂ vs. TOC (figure-23 A, B) diagram. The diagram shows that the TOC range is 0.01-0.86 wt %; the highest values were detected in 42C-1120 and 42C-1155 both above the mineralized zone in the Nonesuch Formation (pyrite zone); these values consistent with poor to fair generative potential. The Van Krevelen diagram and Rock Eval data indicated that the common kerogen types are III and IV, Type III can be gas prone, while type IV has no potential. Kerogen types III and IV normally suggest Phanerozoic plants, here suggest OM has been altered or data are questionable. Kerogen types III and IV and low fluorescence of OM suggest alteration of original algal and fungal organic matter. The lower Nonesuch Formation organic matter was formed in the Mesoproterozoic Era within lacustrine and transitional deposition environments in facies such as siltstone, and fine sandstone. The organic matter was preserved

under reducing and anoxic conditions. It was generated from organisms like algae and fungal remains

(Figures 29A, B, and C) show the reflectance of the vitrinite-like organic matter was low to undetectable. Most of samples have no detectable vitrinite-like reflectance. However, sample 30G-300 (above the Marker Bed unit) showed reflectance of about 0.35, and sample 30G-633 (Upper Zone of Values) is about 10.4 %. The samples may be oxidized by copper bearing fluids, which caused the organic matter have no potential to produce hydrocarbons. The Rock Eval data show that there is no systematic relationship to Cu or S, but show high variability.

In this study the quality of kerogen types III and IV could be in the gas-prone to inert. The maturation level of these kerogens are in the range of immature to postmature, with the organic matter containing about less than about 10% pyrolyzable hydrocarbons. This range in maturation values may reflect inaccurate measurements made on very small amount of organic matter. Therefore, low TOC (< 1%) with low S₂ values of the lower Nonesuch Formation at White Pine is relatively incapable of producing good hydrocarbons and the quality of the Formation as a source rock is low. High variability in maturity indicators, T_{max} and R_o, suggests alteration has affected these parameters. Because the oxidizing hydrothermal fluids

ascended from the base, OM near the base may have been particularly prone to oxidation or destruction.

The mineralized zones are divided into three zones. The lowest 20 ft. is the Cu ore zone, pyrite-rich zone occurs above lower 40 ft, and S is low between Cu ore zone and pyrite zone (20 to 40 ft). In addition, the highest TOC values above Cu mineralization in pyrite-rich samples (OM in Cu mineralized zone may have been destroyed by hydrothermal fluids).

Overall low OM content increases likelihood of measurement errors in Rock Eval data. In addition, the relationship between TOC and Cu, low-S, and pyrite zones suggests hydrocarbons were not derived from younger rocks.

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- <http://www.oilandgasgeology.com/>

➤ <http://en.wikipedia.org/wiki/Kerogen>

Appendix A

Figures Appendix



Figure (34) shows transmitted and reflected-
light microscope

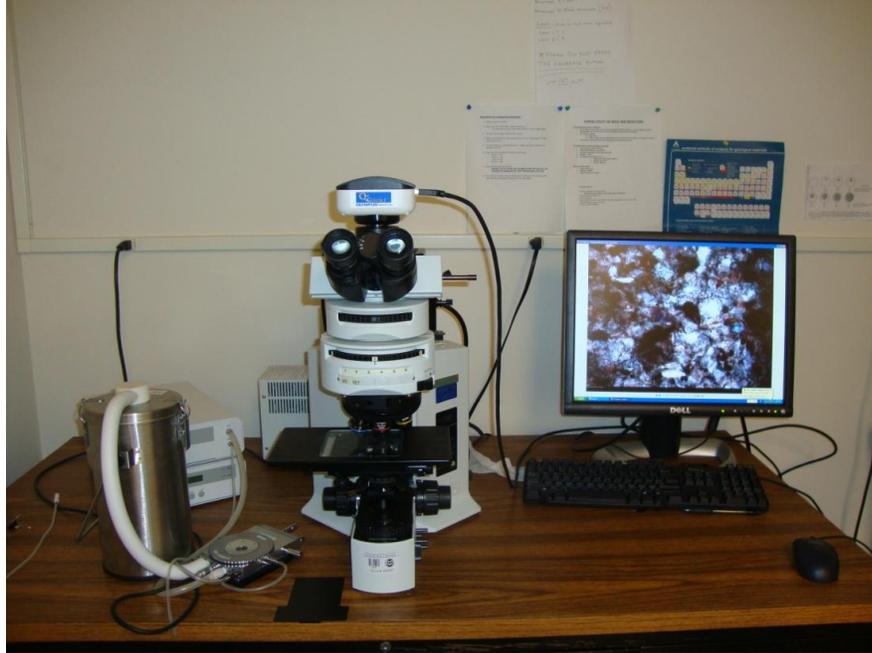


Figure (35) shows ultra violet
microscope



Figure (36) illustrates preparing the samples for Vitrinite reflectance.



Figure (37) shows vitrinite reflectance.

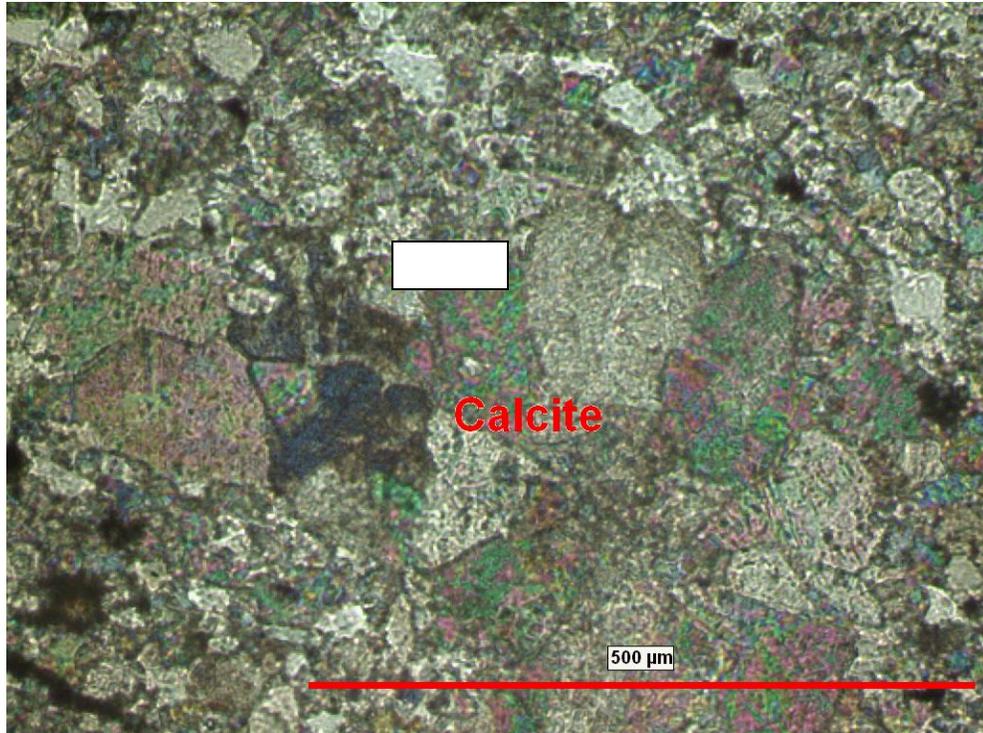


Figure (38) shows Sample 37-2 shows the calcite as cement with high interference color under XPL.

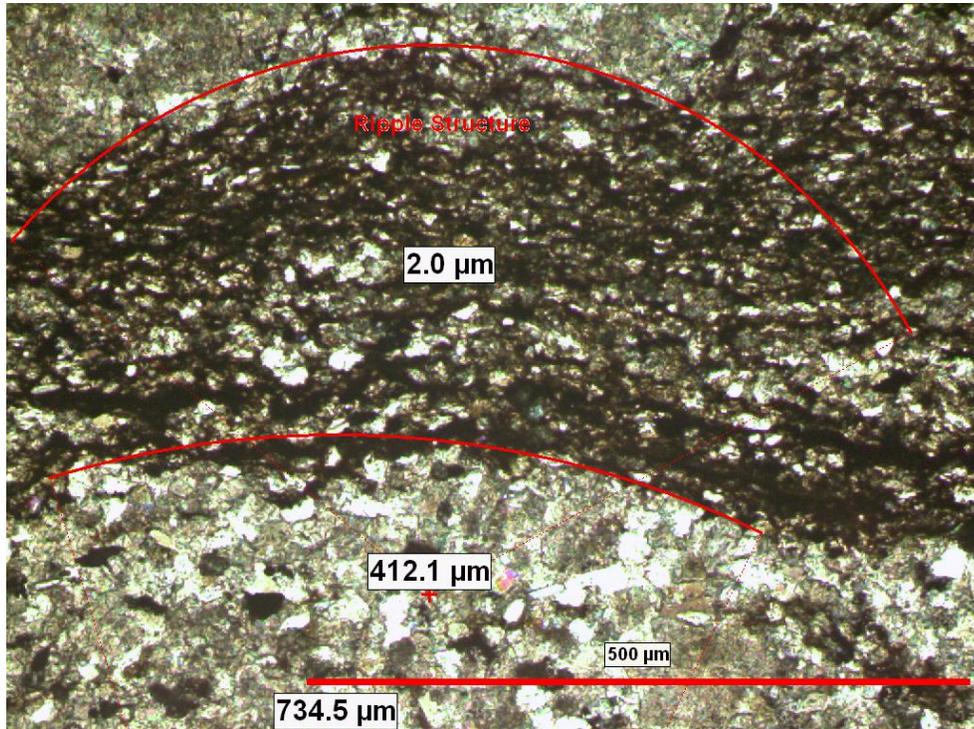


Figure (39) demonstrates sample 37-2 shows the sedimentary structure (ripple structure).

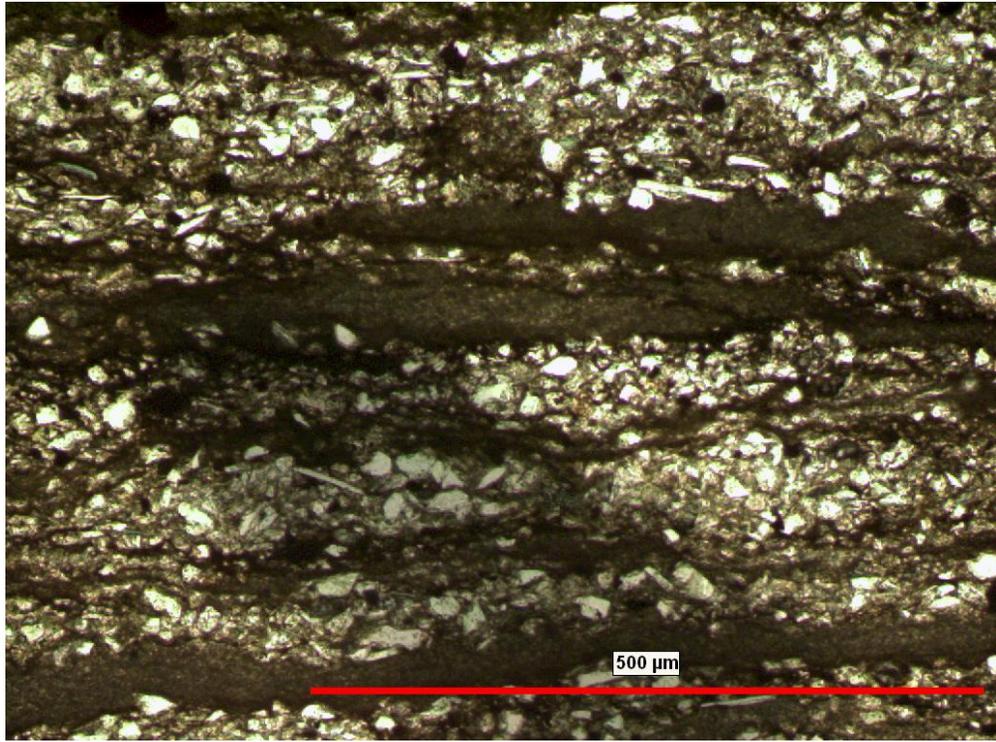


Figure (40) shows sample 37-4 demonstrates the lamination with the dark color of organic material.

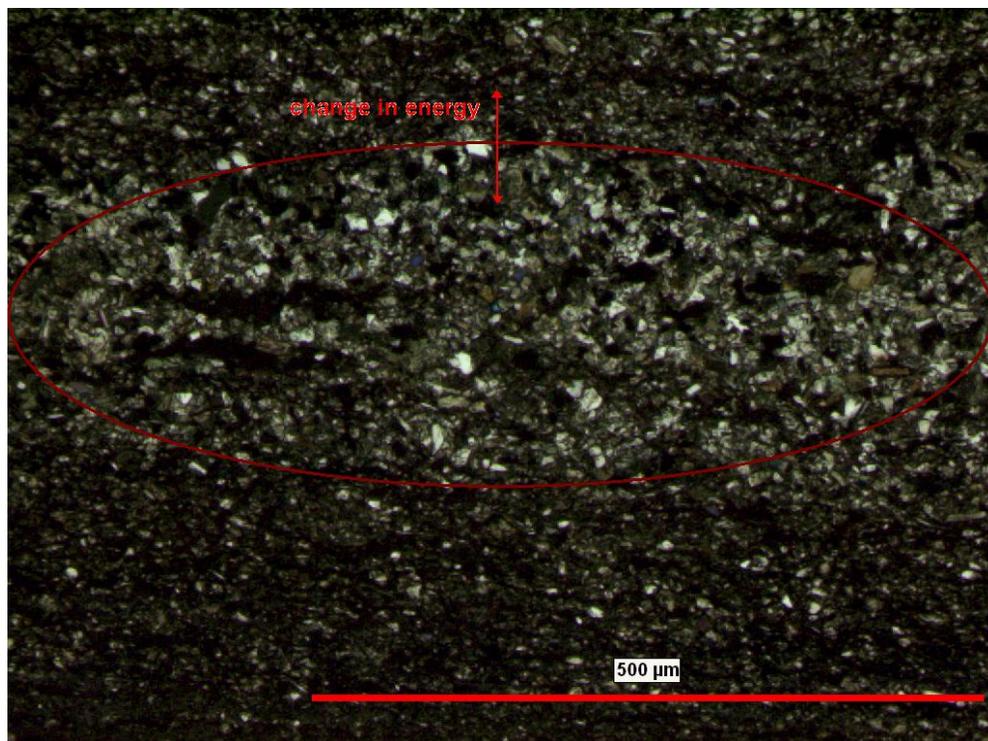


Figure (41) shows sample 37-4 shows the changes in lithology because there were changes in energy of the depositional environment.

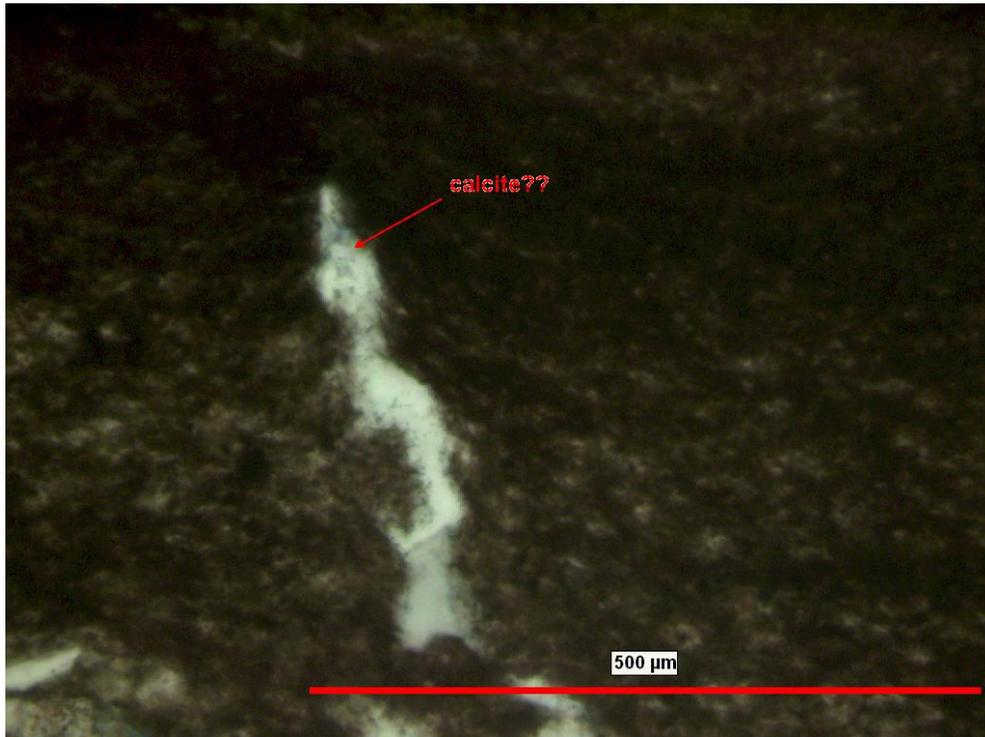


Figure (42) illustrates sample 37-1 illustrates the calcite vein as a secondary process.

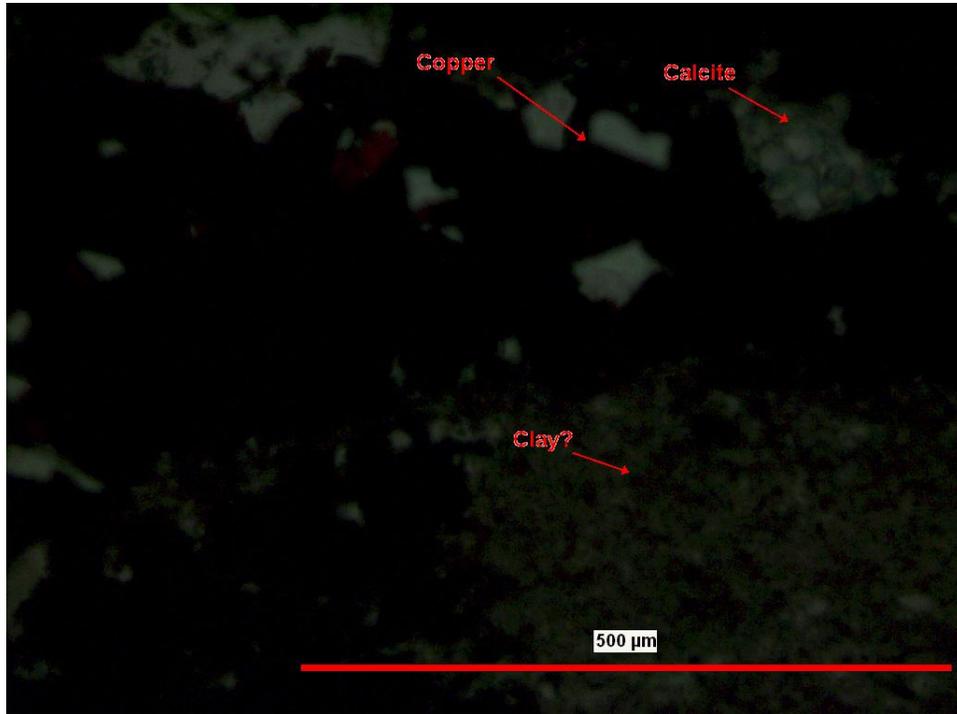


Figure (43) shows sample 37-8 shows copper, calcite, and clay minerals.

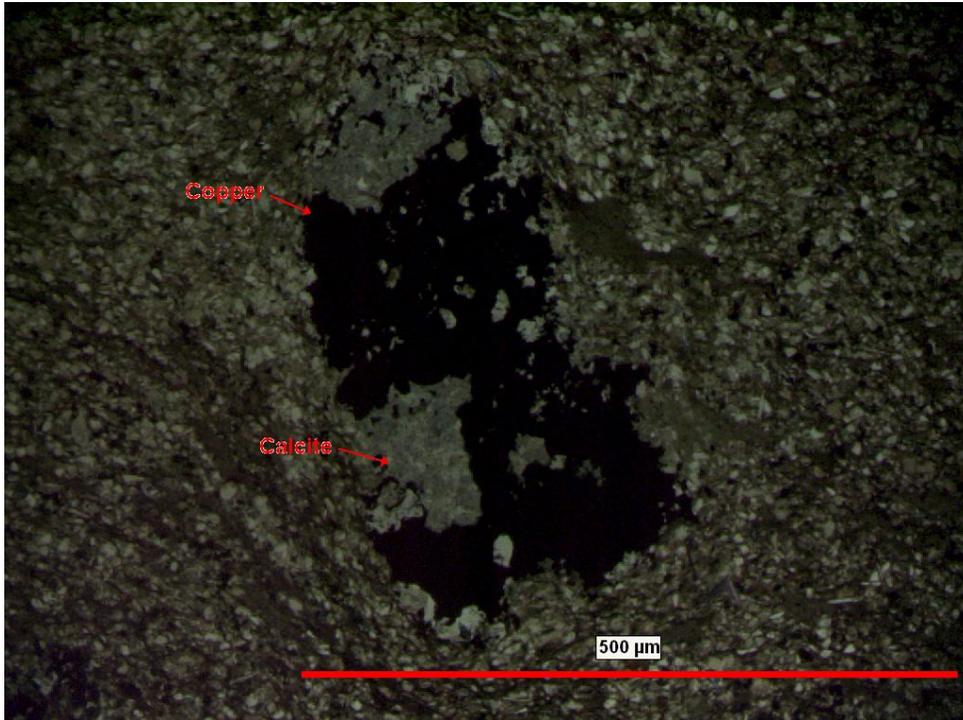


Figure (44) shows sample 37-9 illustrates how the copper replace the calcite depositions.

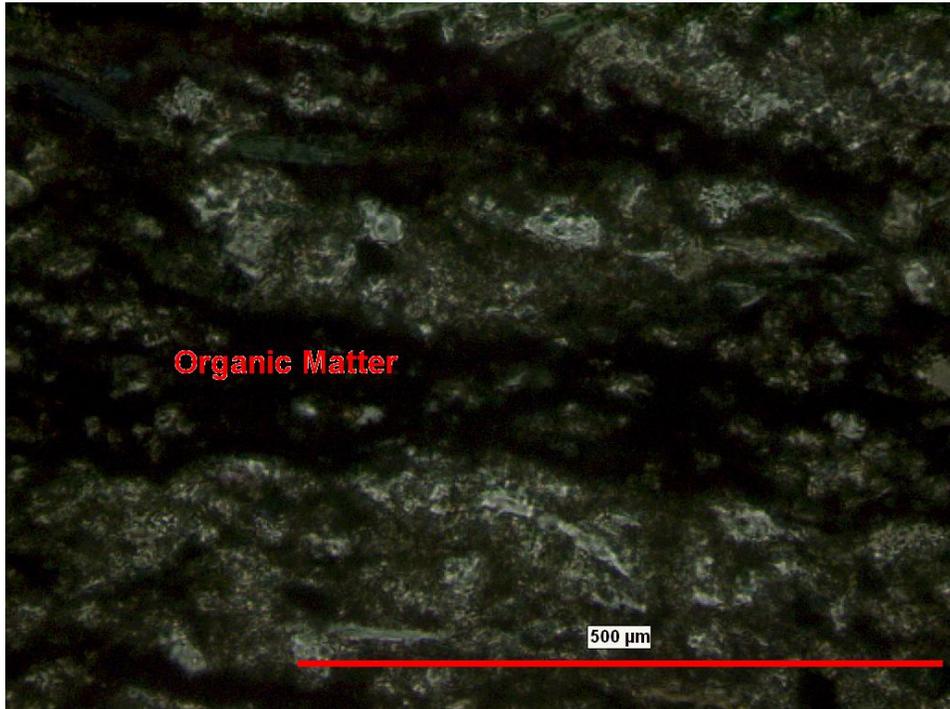


Figure (45) demonstrates sample 42c-2; the dark color shows the content of the organic material within the siltstone.

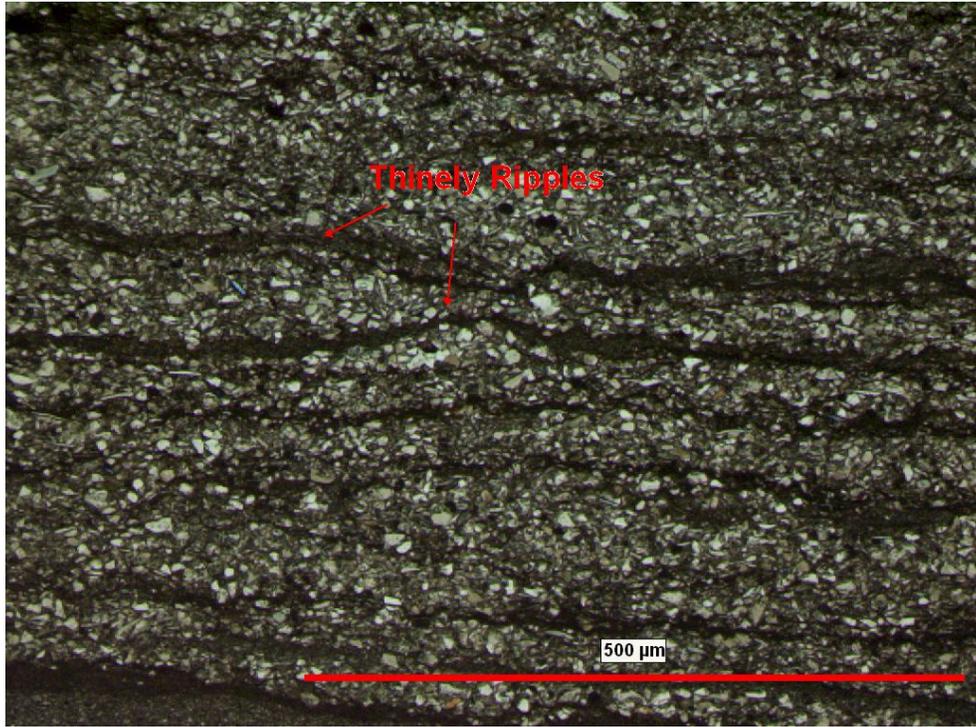


Figure (46) shows sample 42c-4 shows the ripple structure within the siltstone.

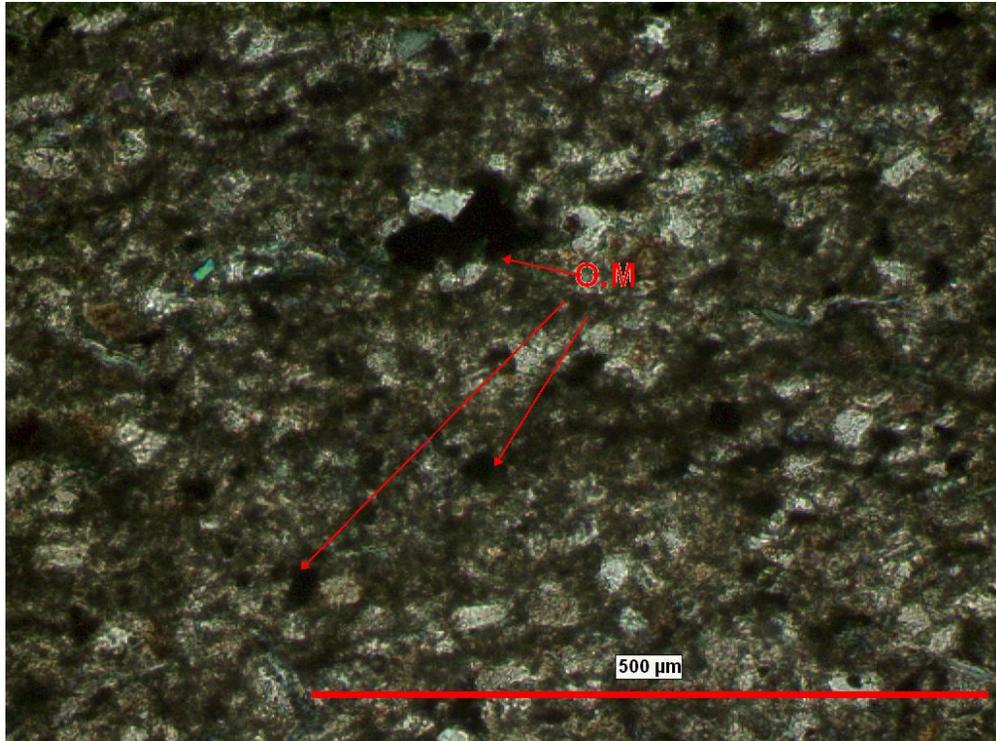


Figure (47) shows sample 42c-5 shows the distribution of the organic matter within the siltstone.

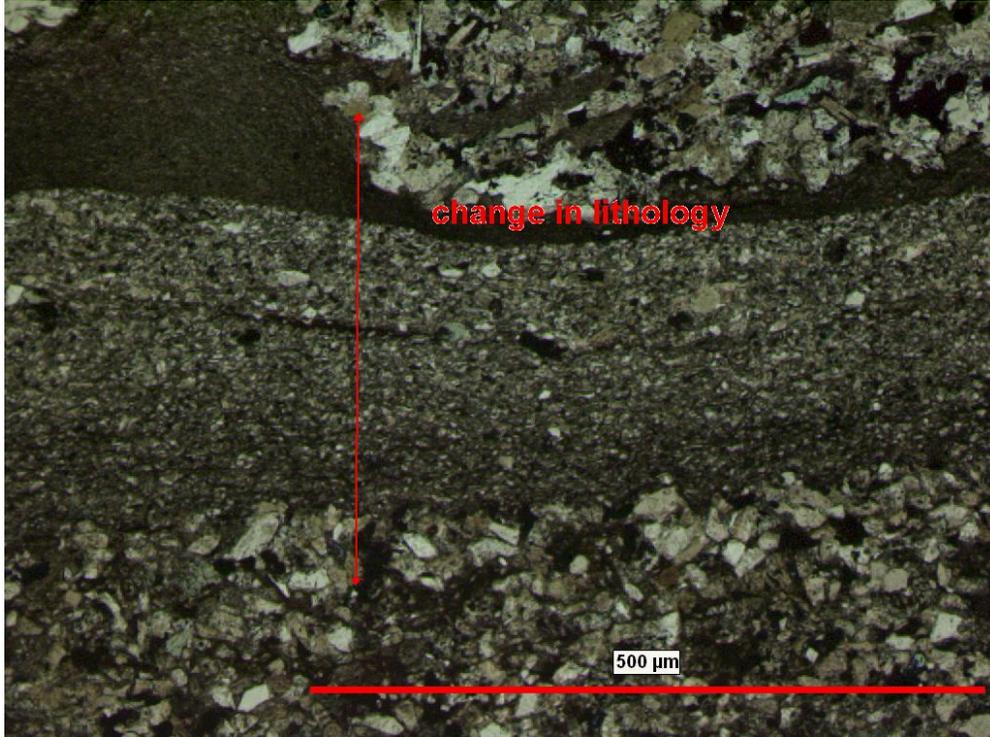


Figure (48) illustrates sample 42-5 demonstrates how the change in deposition energy can affect the lithology.

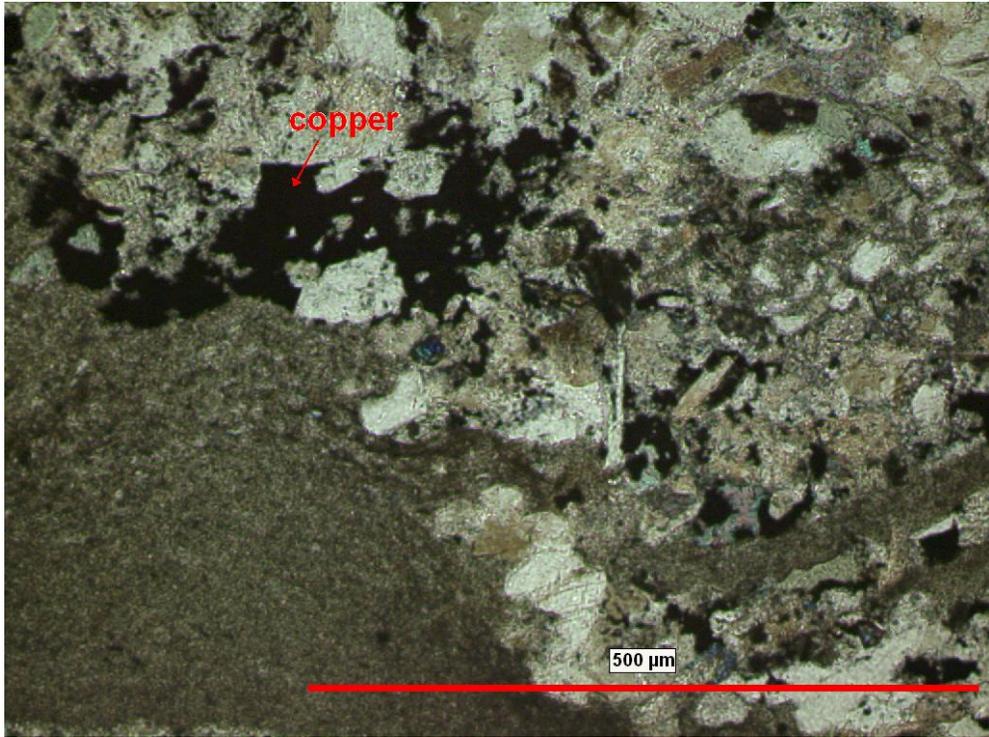


Figure (49) shows sample 42-5 demonstrates the copper mineralization within the siltstone.

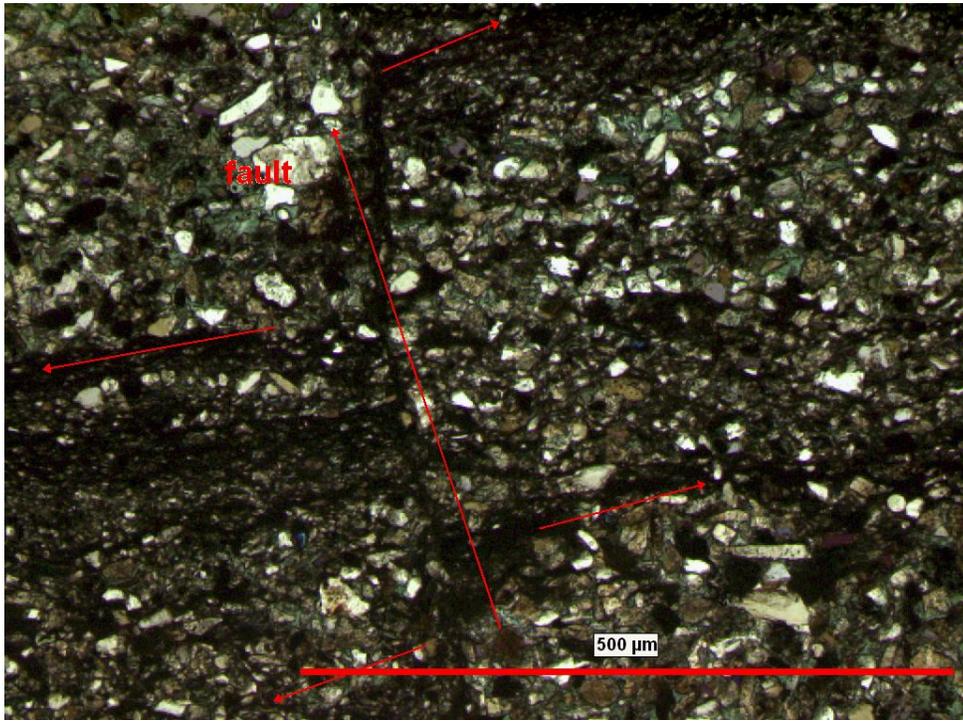


Figure (50) shows sample 42-7 shows the effect of faulting on the sediments.

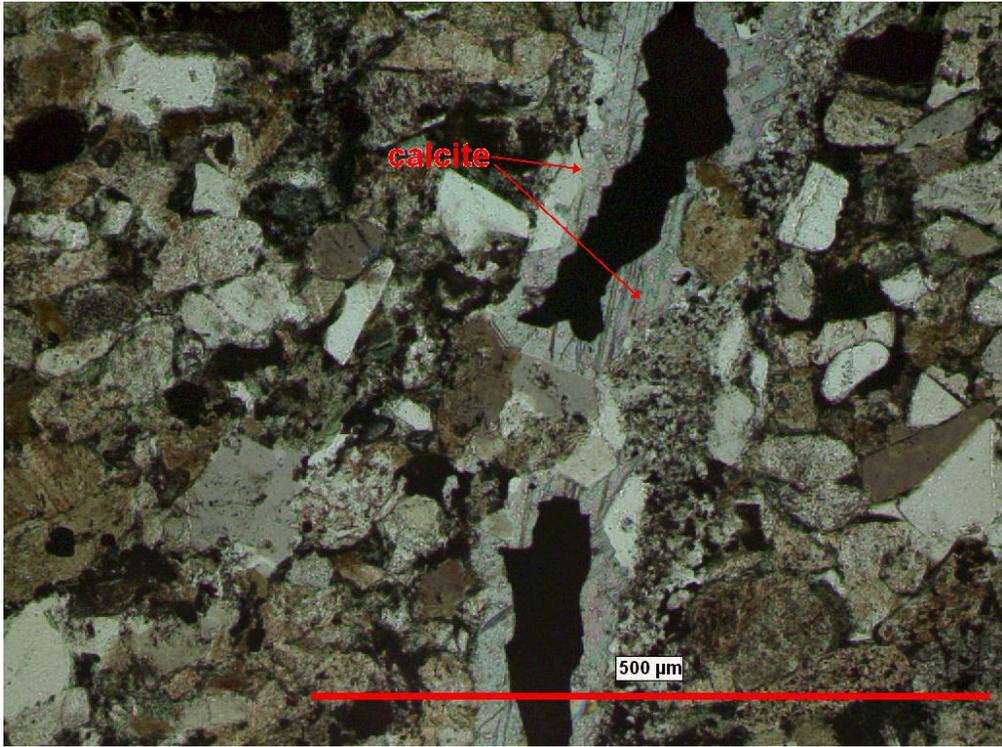


Figure (51) demonstrates sample 42c-11 shows the calcite as cement.

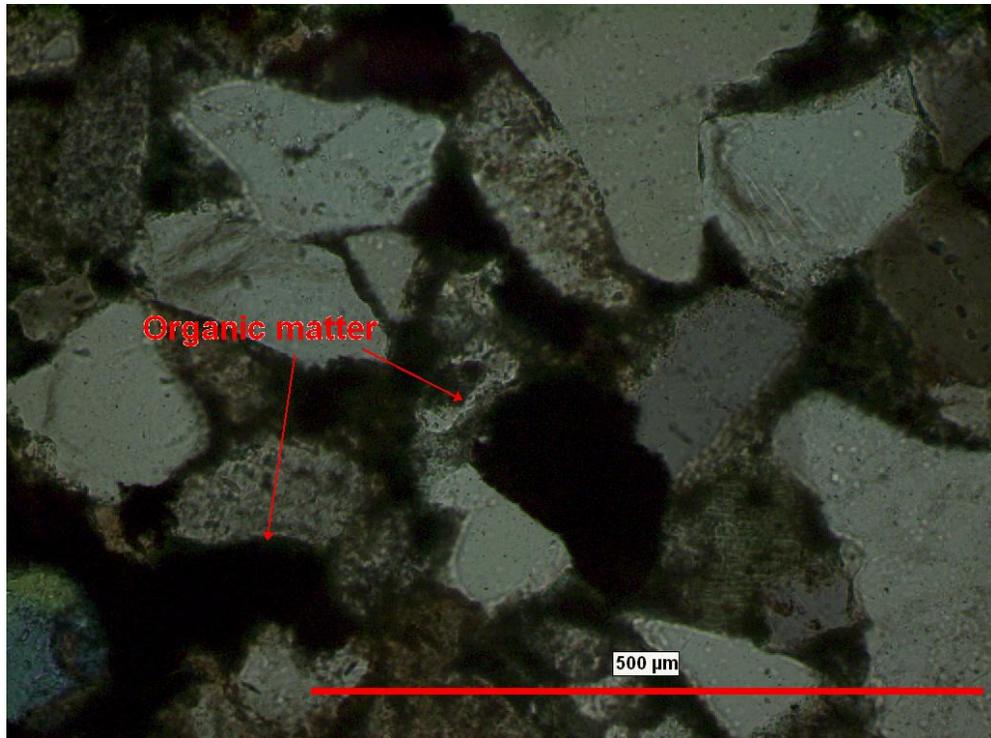


Figure (52) shows sample 42-11 shows the organic distribution within the sandstone.

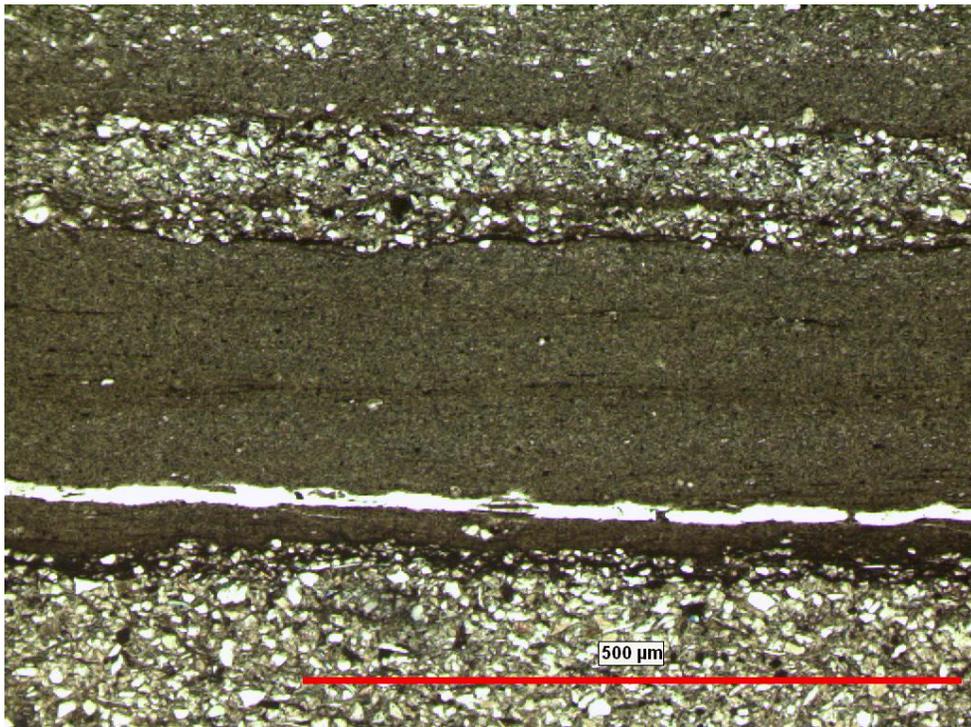


Figure (53) shows sample 42c-12 illustrates the massive siltstone with thinly laminated siltstone.

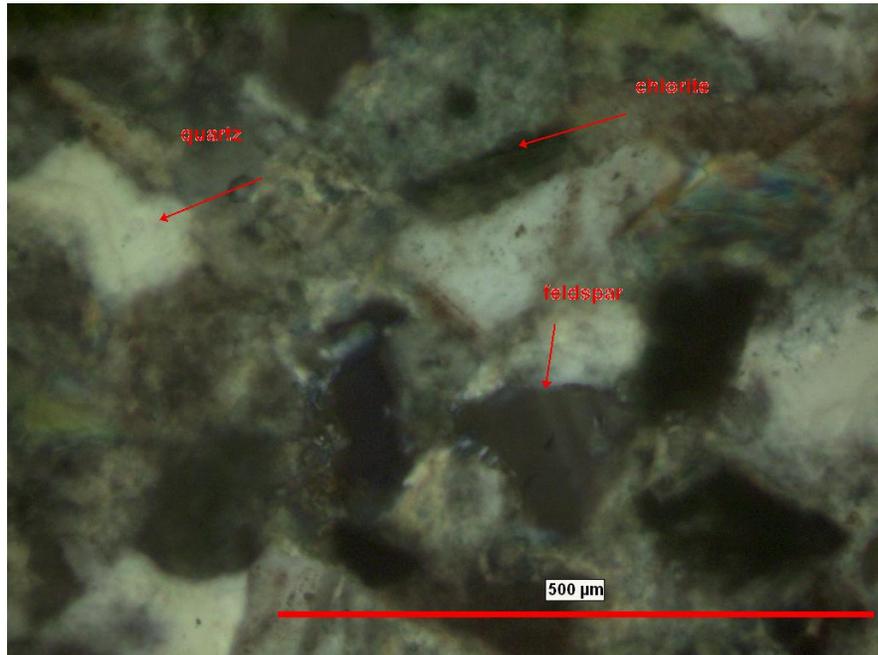


Figure (54) shows sample 37f-12 shows some major minerals that are quartz, feldspar, and chlorite as cement.

Appendix B

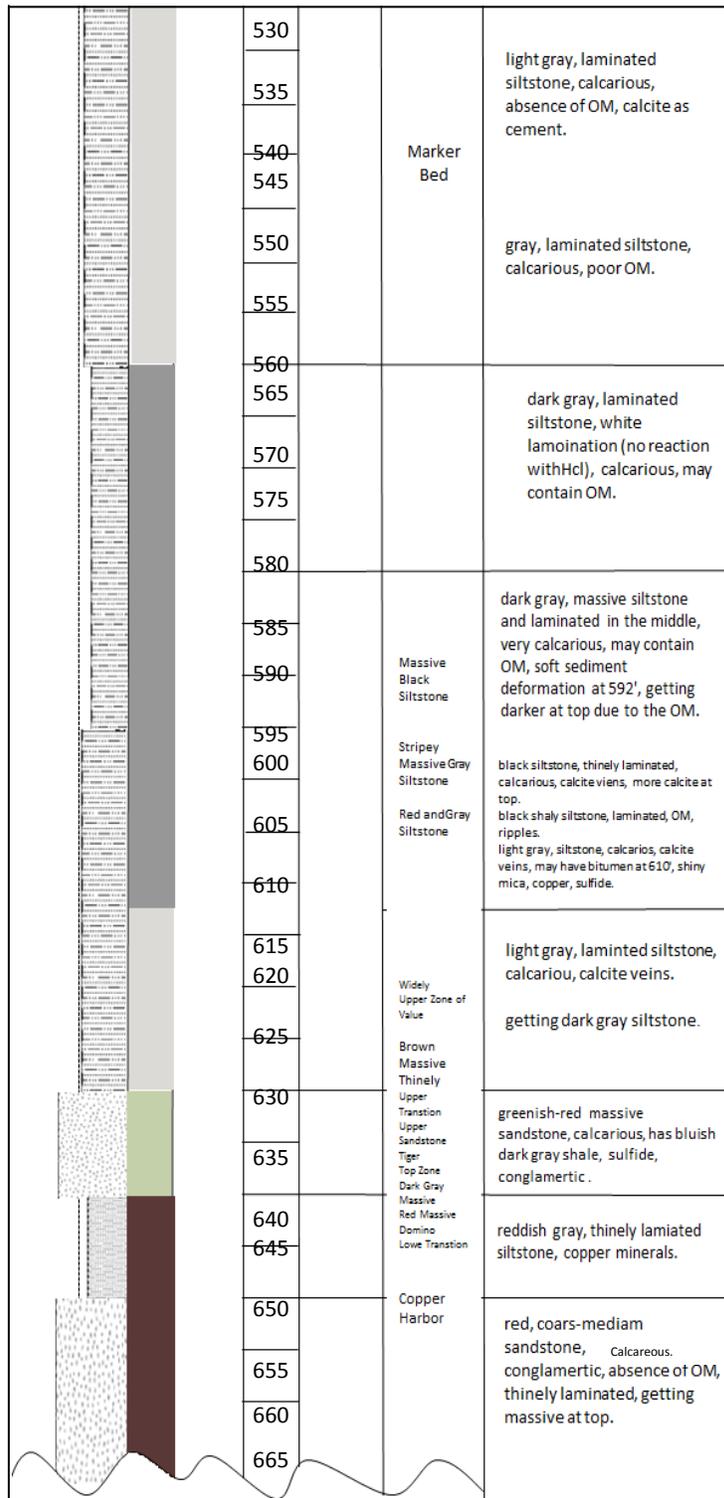
Grain Size		Color	Sample Depth	Depth f	Formation	Stratigraphic Bed	Comments
Sand	Silt/Clay						
				55			light gray, laminated siltstone, v. fine grains, absence of OM, silica,
				60			
				65			
				70			sandy siltstone
				75			reddish gray, thinly laminated siltstone, fine grains, calcareous.
				80			
				85			X
				90			same last description
				95			reddish-light gray, sandy siltstone, white lamination of silica (no reaction with Hcl).
				100			
				105			
				110			
				115			reddish gray, siltstone, white lamination of silica.
				120			light gray, laminated sandstone, v. fine grains, crossbedded, cemented by silica, well compacted.
				125			
				130			
				135			

	140			light gray with reddish lamination, laminated siltstone, silica, hematite.
	145			
	150			has a lot of missing parts.
	155			light gray with reddish color, sandy siltstone, white lamination, hard, cross bedded, calcarious.
	160			
	165			
	170			
	175			light greenish gray, hard, laminated, white lamination of calcite, glauconite, chlorite as cement, some missing parts.
	180			
	185			
	190			

	195			reddish gray, laminated siltstone, hard, calcarious, white lamination, calcite as cement. some missing parts.
	200			
	205			
	210			light gray, laminated sandy siltstone, calcarious, white lamination, calcite as cement, well compacted, cross bedded,
	215			
	220			
	230			
	235			
	240			
	245			
	250			reddish gray siltstone.
	255			light gray, laminated siltstone, calcarious, calcite as cement, poor OM.
260				
265			reddish light gray, laminated siltstone, hard, calcarious, ripples, calcite as cement.	
270				
275				
280			reddish dark gray, laminated siltstone, hard, calcarious, ripples, calcite as cement. has some missing parts.	
285				
290				
295				
300				

	305			<p>dark gray, laminated siltstone, calcarious, calcite as cement, may contain OM.</p>
	310			
	315			
	320			
	325			<p>reddish gray, massive siltstone, hard, calcarious, slumps, calcite as cement, laminated at top.</p> <p>has some missing parts.</p>
	330			
	335			
	340			
	345			<p>gray, thinly laminated sandstone, v. fine grains, calcarious, poor OM, calcite as cement.</p>
	350			
	355			
	360			

	365			reddish light gray, laminated sandy siltstone, cross bedded, calcareous, slumps, calcite as cement, has OM.
	370			
	375			
	380			
	385			
	390			
	395			
	400			
	405			
	410			
415				
420				
	425			reddish gray, laminated siltstone, cross bedded, hard, white lamination, calcareous, calcite as cement, absence of OM. has some missing parts.
	430			
	435			
	440			
	445			
	450			
	455			
	460			
	465			
	470			
	475			reddish light gray, laminated siltstone, calcareous, , calcite as cement, absence of OM. reddish-greenish gray, laminated sandy siltstone, calcareous, , calcite as cement, calcite veins, , slumps, absence of OM.
	480			
	485			
	490			
	495			
	500			
	505			
	510			
	515			
	520			
525				

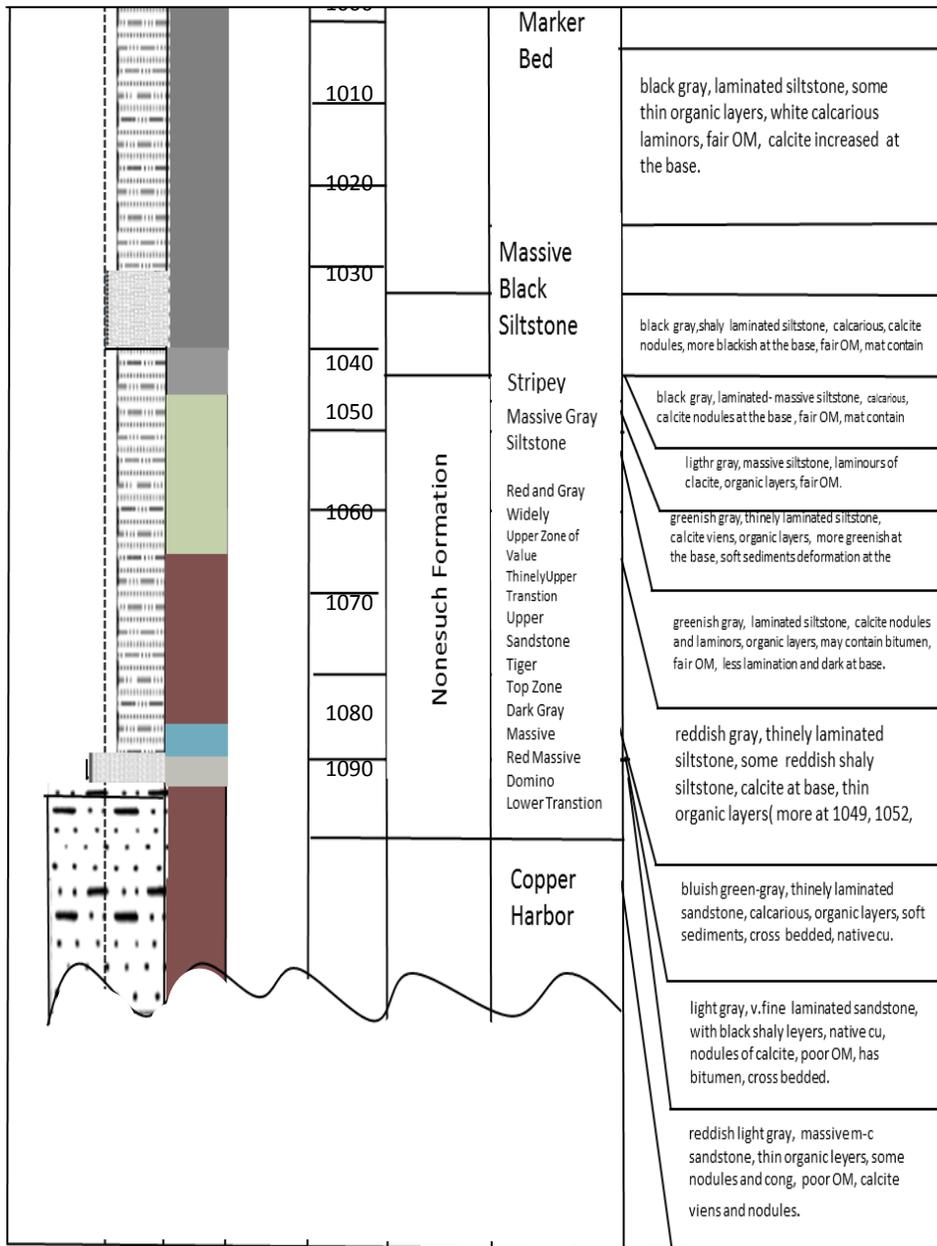


Corrections:

Thinly: thinly

calcareous: calcareous

Grain Size		Color	Sample Depth	Depth f	Formation	Stratigraphic Bed	Comments
Sand	Silt/Clay						
				770			light-dark gray, siltstone, thinly laminated, light-dark gray, siltstone, thinly laminated, calcite veins, calcareous, OM poor.
				780			
				790			
				800			light gray, massive siltstone, little calcite, cross bedding, OM v.poor, may contain Bitumens.
				810			gray, massive sandy siltstone, with reddish laminated layers at top and base, hematite reddish shaly siltstone, oxidation effect calcite veins, dissolution, OM poor.
				820			
				830			
				840			reddish gray, thinly laminated siltstone, hematitic siltstone, no calcite and OM.
				850			
				860			reddish gray, thinly laminated siltstone, hematitic siltstone, no calcite and OM.
				870			reddish gray, thinly laminated siltstone, hematitic siltstone, no calcite and OM.
				880			
				890			reddish gray, thinly laminated siltstone, hematitic siltstone, no calcite and OM.
				900			reddish gray, massive siltstone, laminar of calcite OM
				910			
				920			reddish gray, massive siltstone, laminar of calcite OM poor.
				930			light gray, fine massive sandstone, v. little calcite, v. poor OM, may contain Bitumen.
				940			greenish gray, thinly laminated siltstone, poor OM.
				950			
				960			
				970			gray, massive sandstone, little calcite, high porosity, v poor OM.
				980			black gray, laminated siltstone, some thin organic layers, white calcareous laminars, fair OM.
				990			



Corrections:

Thinly: thinly

calcarious: calcareous

Drill Hole: 42C		Location: White Pine Mine, MI		Unite: 531'-1230'			
Date: 02/13/2011		Logged: Aiyda Fourgani					
Lithologies:		Shale		Massive Siltstone		Widely Laminated Siltstone	
Thinly Laminated Siltstone		Sandstone with Shale Partings		Sandstone			
Grain Size	Color	Sample	Depth	Formation	Stratigraphic	Comments	
Sand	Silt/Clay	Depth	f		Bed		
			540			Reddish green, thinly laminated-massive siltstone, calcareous, OM at the base.	
			550			X	
			560			Reddish gray, thinly laminated sandy siltstone, calcareous, OM at the base.	
			570				
			580			Light gray, thinly laminated siltstone calcareous, cross bedded, OM at the base. c	
			590				
			600				
			610			X	
			620			Reddish light gray, laminated siltstone, calcareous, hematite, absence of OM.	
			630				
			640			X	
			650			Reddish gray, laminated sandy siltstone, calcareous, have organic layers.	
			660				
			670			Reddish gray, laminated sandy siltstone, calcareous, OM.	
			680				
			690			X	
			700			Like the last description. siltstone, calcareous, OM.	
			710			X	
			720			Like the last description	
			730			like the last description.	
			740			Dark gray, thinly laminated siltstone, calcareous. Dark reddish, siltstone.	
			750			X	

	750		dark gray, thinly laminated siltstone, calcareous, OM.
	760		dark gray, thinly laminated siltstone, calcareous, OM.
	770		gray, laminated siltstone, calcareous.
	780		reddish gray, siltstone
	790		like the last descriptor.
	800		Like the last description
	810		like the last description. greenish gray, thinly laminated siltstone, calcareous, poor OM.
	820		
	830		
	840		

	850			gray, thinly-massive laminated siltstone, calcareous, poor OM.
	860			
	870			
	880			
	890			
	900			Dark gray, thinly-massive laminated siltstone, calcareous, calcite veins, organic layers.
	910			
	920			
	930			
	940			light gray, thinly-massive laminated siltstone, calcareous, poor OM, may contain bitumen.
	950			
	960			
	970			Dark gray, thinly-massive- laminated siltstone, calcareous, OM.
	980			Gray-brownish gray laminated siltstone, calcareous, bitumen.
	990			
	1000			Greenish gray, thinly-massive - laminated siltstone, calcareous. More massive at the base.
	1010			
	1020			
	1030			
	1040			
	1050			
	1060			
	1070			
	1080			
	1090		Marker Bed	
1100				
1110		dark gray, thinly laminated siltstone, less calcareous, organic layers,		
1120				
1130				
1140			Same last description.	
1150				

