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A SYNGENETIC MODEL FOR THE ORIGIN OF THE
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# A SYNGENETIC MODEL FOR THE ORIGIN OF THE COPPER MINERALIZATION IN THE PRECAMBRIAN NONESUCH SHALE, WHITE PINE, MICHIGAN

By

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# ABSTRACT

# A SYNGENETIC MODEL FOR THE ORIGIN OF THE COPPER MINERALIZATION IN THE PRECAMBRIAN NONESUCH SHALE, WHITE PINE, MICHIGAN

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Copper mineralization in this shale is mainly restricted to organic-rich, reduced beds in the lower sixty feet of the unit. A syngenetic model is proposed for the origin of this mineralization where by Cu would be introduced into these deltaic sediments by clay-organic-Cu complexes. The clay (smectite) and Cu ions would be derived from weathering of Cu-rich volcanic uplands.

The Cu contents of three clays present in this shale (cholorite-illite intergrowths, chlorite cement, and detrital chlorite) are used to test the model. The intergrowths are alteration products of the original smectite. With this model, they derive Cu from Cu-smectite complexes and from sediment pore-water after alteration, whereas the cement only absorbs Cu from pore-water. The intergrowths are found to contain .121% Cu; detrital chlorite has .099% Cu, and chlorite cement has .087% Cu, which tends to support the syngenetic model.

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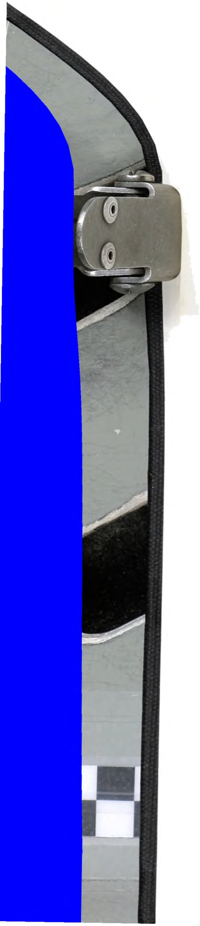

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# INTRODUCTION

The Precambrian Nonesuch Shale is a six hundred foot thick mineralized unit overlying the Copper Harbor Conglomerate, in the northwest Upper Penninsula of Michigan (Fig. 1). This formation is divided into three members, the lowest of which is the Parting Shale, followed by the Upper Sandstone, and finally, the Upper Shale.

Copper mineralization is dominantly restricted to the organic-rich, dark grey, reduced beds in the lower Parting Shale and the lower Upper Shale members (Fig. 2; Alyanak, 1974). The copper occurs principally as disseminated chalcocite, with disseminated native copper occurring mainly in the Parting Shale. Occasionally native copper appears along bedding planes and in fractures in the lower Parting Shale and upper most regions of the Copper Harbor formation. A definite correlation exists between the location of reduced lithologies and the occurrence of copper (Ensign et al., 1968). Red (oxidized) lithologies contain only trace mineralization relative to the ore content found in reduced areas.

The origin of this mineralization is controversial and has been attributed to both syngenetic and

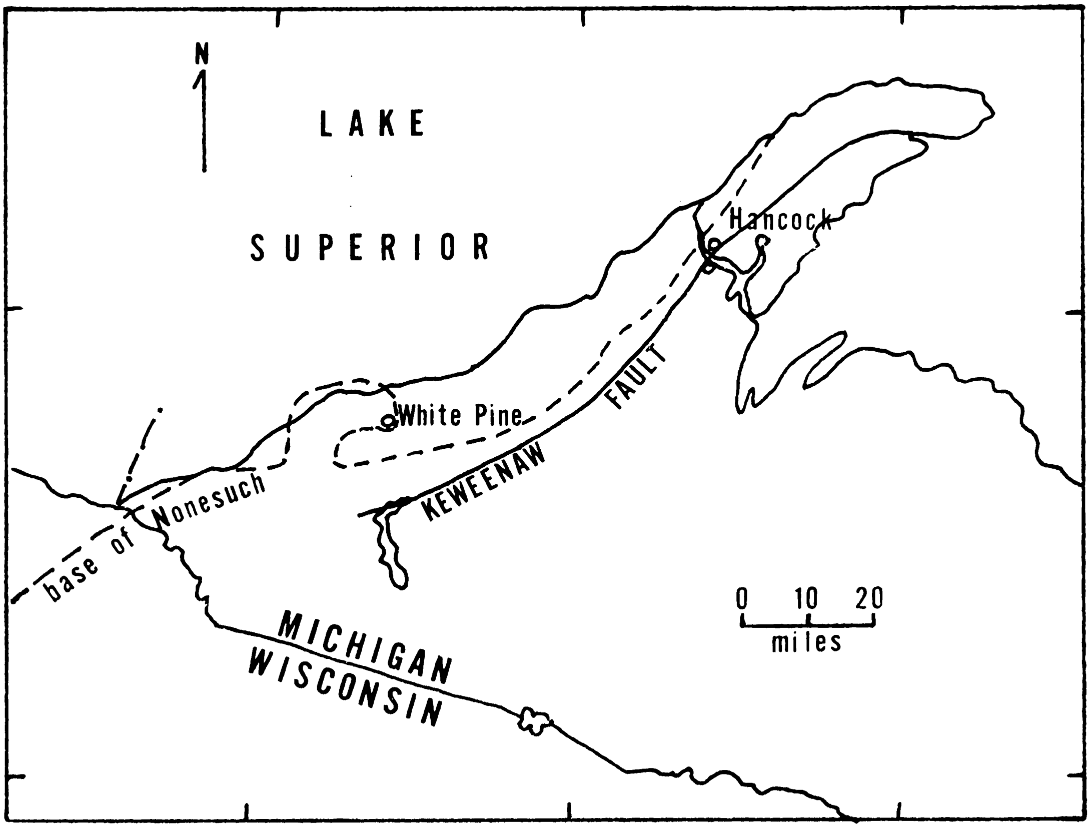

Figure 1.--Geographical location of the Nonesuch Shale.

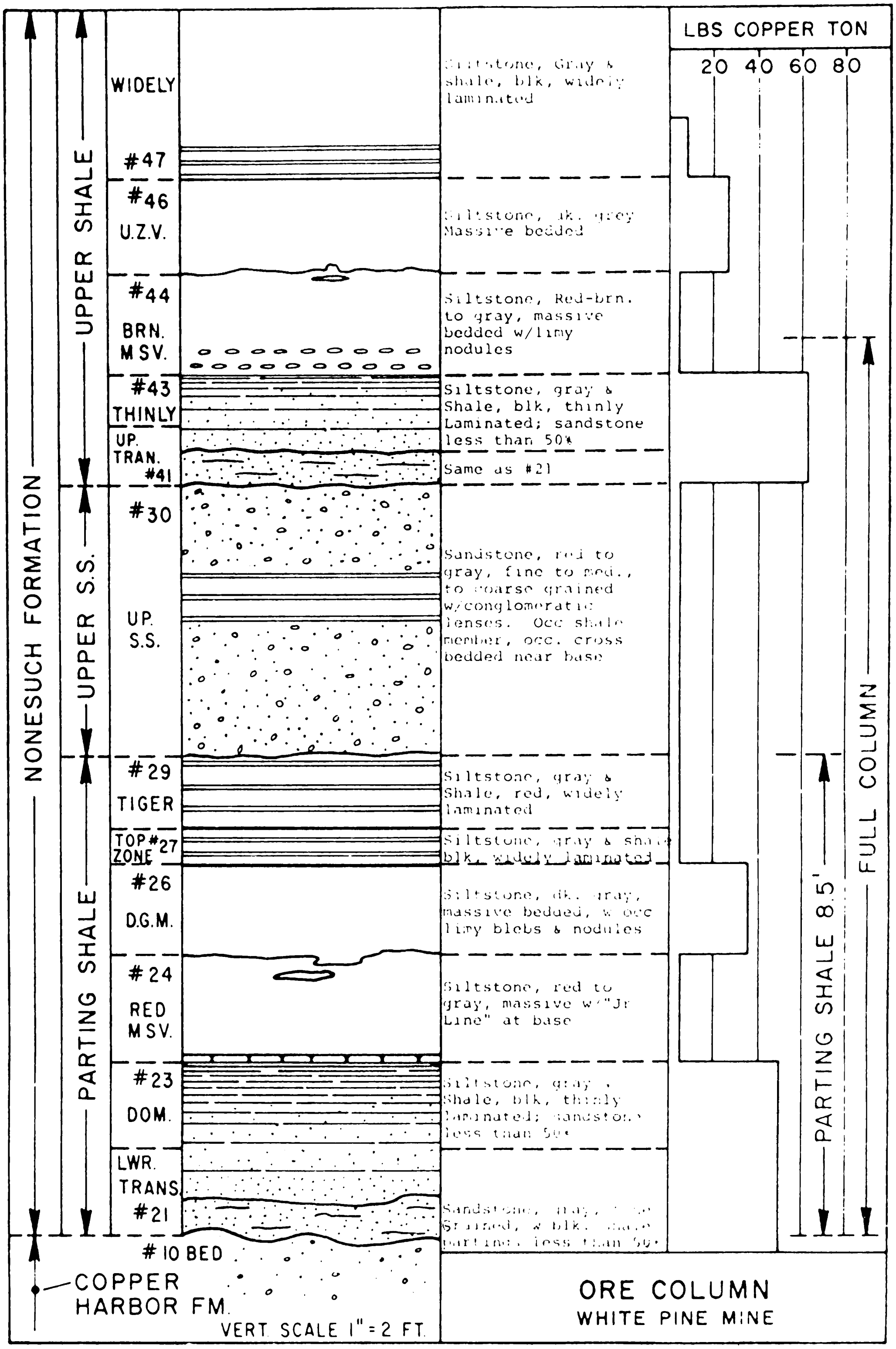

Figure 2.--Ore column of the lower Nonesuch Shale at White Pine (after Alyanak and Vogel, 1974).

epigenetic processes. The syngenetic proponents (Jost; Alyanak & Vogel; Vogel, McBride, & Ehrlich) cite the following major characteristics of the ore body as supporting their model: its vast lateral distribution, restriction of the ore to specific stratigraphic units, homogeneity of metal content in ore along stratigraphic horizons, predominance of sulfide mineralization, and the close association of smectite alteration products (chlorite & illite) with these Cu-sulfides.

Epigenetic proponents (White & Wright; Brown & Trammell; Ensign et al.; and others) stress different characteristics of the ore body that lend credence to their model: the apparent replacement of Fe-sulfides by Cu-sulfides, mineralization in the upper regions of the Copper Harbor Conglomerate, lowering of the height of Cu-mineralization over a region underlain by a thick reduced bed, distribution of the more soluble (Cd, Pb, & Zn) sulfides in the upper fringe of this mineralized zone, and the cross-cutting nature (with respect to bedding) of this upper fringe surface.

# DEVELOPMENT OF THE EPIGENETIC MODEL

Discussion of the origin of Cu mineralization in the Nonesuch Shale began with the discovery of native copper deposits, located within this unit, along the White Pine fault. Workers supported an epigenetic-hydrothermal origin for this native copper, due, in part, to its halo-like deposition around the fault zone (Butler & Burbank, 1929; White & Wright, 1954; Amstutz, 1958; and Brady, 1960). Later, when the Cu-sulfide mineralization was discovered in the siltstones and shales of the Nonesuch unit, workers also assumed a hydrothermal origin for this ore (Sales, 1959; Joralemon, 1959, 1963; and Ohle, 1963). However, there is a definite difference in the ore distribution between the fault zone deposits and the sulfides in the major portion of the Nonesuch Shale. The Cu-mineralization is patchy and very irregular in distribution, where the falt zone cuts sandstone beds within this unit (Lower and Upper Sandstone formations, beds No. 10 & 30). In contrast, ore horizons away from the fault zone are fairly stratiform, within reduced horizons, and individual lithologies are mineralized over large distances.

This discrepancy led White and Wright (1954) to speculate on other possible mechanisms for the mineralization. One early method they considered, and failed to develop, was the syngenetic precipitation of the copper sulfides. The explanation they preferred involved the upward migration of a mineralizing solution from the Copper Harbor Conglomerate. White & Wright (1966) and Brown & Trammell (1966) restated this theory to propose that ascending connate waters passed through the Nonesuch Shale, after the entire unit had been deposited, and produced a sequence of mineralization. In this model, minerals of low Cu content, originally present in the sediment, were replaced by minerals with a higher percentage of Cu, as the mineralizing solution passed upward through the sediment.

Ensign et al. (1968) stipulated that the mineralizing solution passed through the sediment before compaction and dewatering occurred because compaction was visible around knots of chalcocite. They characterized the top of the cupriferous zone as being almost parallel to bedding where it occurred in "favorable" (grey-black, reduced) horizons and steep where it crossed "unfavorable" (red, oxidized) beds. The authors also documented a deep depression in the top of the Cu-mineralization fringe over a relatively thick, highly mineralized, reduced bed (No. 23), in a lower part of the Nonesuch unit. They

suggested that these two features could best be explained by the epigenetic model, with an ascending mineralizing solution.

Brown (1971) and White (1971) reiterated this theory, that mineralization occurred by replacement of low Cu minerals along an upward advancing mineralizing front, but they specified that syngenetic pyrite was the dominant mineral being replaced. White (1960, 1971) and Brown (1971, 1974) also noted the very restricted occurrence of Cd-Pb-Zn sulfides, which were found at the top of the cupriferous zone and in pyritic sections of bed No. 61. Brown (1974) suggested that the presence of these more soluble sulfides in the upper fringes of the cupriferous zone indicated their being transported in the outer regions of the mineralizing solution.

# DEVELOPMENT OF THE SYNGENETIC MODEL

Most workers suggest that the source rocks for the Nonesuch deltaic sediments were Middle Keweenawan basalts and andesites plus metasediments and granites that outcropped to the south of the White Pine area and provided sediment to the northward building Nonesuch delta. The dominant weathering product of these volcanics (assuming a fairly temperate climate because of the abundant organics present in this unit, Meinschein et al., 1964) would be smectite, plus lesser proportions of vermiculite, illite, and kaolinite (Grim, 1968). After deposition in deltaic muds, smectite and vermiculite alter to chlorite-illite intergrowths (Hower et al., 1976; and Grim, 1968). To simplify the following discussion only smectite will be considered; however, vermiculite could easily substitute for smectite in all processes that will be mentioned.

Jost (1968) discussed this clay alteration process and concluded, based on texture, that most of the authigenic chlorite he found in the Nonesuch Shale was originally smectite. Considering the works of Heydemann (1959) and Mackenzie (1963), which showed that a smectite (montmorillonite) would selectively absorb Cu from

solution and form a strong bond with the ion, Jost suggested that smectite in the Nonesuch system would adsorb Cu from the weathering solution and retain the metal until deposition in the delta. He stated that Cu would have been present in the weathering solution because the source rocks for the Nonesuch sediment included the Cu-rich Portage Lake Lave Series. He also proposed that clays which were deposited in dark, reduced sediments would have had their adsorbed Cu reduced to form chalcocite or native copper, and that the close association of chlorites with Cu-sulfides, present in Nonesuch samples on a microscopic level, supported this mechanism, and thus, the syngenetic model.

Alyanak and Vogel (1974) compared the framboidal nuclei of chalcocite grains, from the mineralized zone of the lower Nonesuch Shale, with framboidal pyrite found immediately above this zone. They showed that the framboidal chalcocite was morphologically different from the framboidal pyrite. Also, the pyrite texture, which was dominantly euhedral in the nonmineralized zone, was not reflected by the chalcocite grains. These observations did not support a replacement of pyrite for the origin of this chalcocite.

Vogel, McBride, & Ehrlich (1976) studied the copper content of the clay fraction (chlorite-illite intergrowths) from Cu-rich black shales in the lower

Nonesuch unit. They concluded, based on electron spin resonance and chemical analysis of the clay size material, that Cu and Fe ions had entered octahedral sites in the clays. The authors stated that the presence of Fe III indicated that the original unaltered clay (a smectite) was formed in an oxidizing weathering environment. They also pointed out that Cu could enter octahedral clay sites during the breakdown of clay-organic-Cu complexes, after deposition in the deltaic sediments. The authors proposed that the Cu was adsorbed from the weathering solution by clay-organic complexes, rather than by just the clay particles themselves. This assumption was based on work by Mortland (1965) which demonstrated the ease with which clay-organic complexes from in natural systems. Also, works by Ermenko (1966) and Hodgson et al. (1966) showed that most Cu in natural water systems is complexed by organic acids. These three studies, combined with the well documented, abundant organics in this Precambrian unit (Meinschein et al., 1964; Barghoorn et al., 1965; and Jost, 1968) support the conclusion that clay-organic-Cu complexes were present in the Nonesuch sedimentary system.

## DISCUSSION OF THE SYNGENETIC MODEL

### Burial Diagenesis in the Nonesuch Shale

Weaver (1967) noted that older (pre-Mesozoic) shales tend to be enriched in illite and chlorite. Consistent with this observation, the siltstones and shales of the Nonesuch unit contain abundant chlorite-illite intergrowths. In other areas, these have been shown to be alteration products of smectites (Hower et al., 1976). This process, as documented in modern sediments from drill cores of Gulf Coast deltaic clays, involves the following reaction:

$$\text{Smectite} + \text{K-spar} + \text{mica} = \text{chlorite} + \text{illite} + \text{quartz}$$

Wiese (1973) determined that the Parting Shale (lowermost zone in the Nonesuch Shale unit) contained at least 5% K-spar and 10-15% muscovite (plus other minerals). Therefore, all the necessary phases and components are present in the sediment to produce the observed chlorite-illite association.

The fact that only moderate temperatures controlled the alteration of the Nonesuch clays is documented by the presence of porphyrins in the organic

fraction of this sediment (Barghoorn, 1965), and also, by the presence of djurleite and pink bornite (Brown, 1971). According to Abelson (1959), porphyrins cannot withstand temperatures greater than 200°C for 1000 years, and the temperature tolerance decreases with increasing age of the sediment. In the case of the two, temperature sensitive, Cu-sulfide minerals, Brown states that djurleite breaks down to chalcocite and digenite at temperatures above 93°C, while pink bornite exsolves chalcocite at temperatures above 75°C. Since there is no chalcocite exsolved from pink bornite in the Nonesuch samples, Brown suggests that the temperature during and after the formation of this mineral may have been as low as 75°C.

The reaction rate of smectite, altering to chlorite and illite, described by Hower et al. (1976) is temperature dependent. In the Gulf Coast sediments, some smectite is not completely reacted in the 100-175°C temperature interval, and the authors specify that total conversion of the smectite to illite and chlorite requires temperatures greater than 175°C or longer reaction times. This reaction time factor explains the complete alteration of the smectite in the Nonesuch Shale.

## Mechanism for Adsorption of Cu by Clay Particles

When considering the bonding of Cu to a smectite (montmorillonite), Steger (1973) demonstrated that Cu could be adsorbed on three structurally different sites on the clay and complexed organics. One adsorption site is the lattice hydroxyls exposed on edges or crystal defects. Openings through silicate nets also allow Cu ions to penetrate to interior lattice hydroxyl positions, however, Steger found that the Cu ions had to be completely dehydrated to enter these interior positions. The final adsorption sites exist on organics complexed to the clays; they are phenol and carboxylic acid groups. Steger's results show that the organic sites on the complexed clays have the highest affinity for Cu. He specuates that this is due to the formation of chelate bonds with the Cu ions, instead of the formation of complexes. Chelation has been previously demonstrated to be the dominant method of adsorption in Cu-organic systems (Schnitzer & Khan, 1972).

McBride & Mortland (1974), in a later study, also documented the migration of Cu ions into hexagonal holes and empty octahedral sites within a smectite (montmorillonite). They found, as did Steger, that only dehydrated Cu ions could penetrate the clay structure. Thus, it is highly unlikely that smectite could absorb Cu into an interior position directly from sediment pore water. An intermediate step, such as adsorption to complexed organics, would be necessary to dehydrate the ion. After this dehydration, Cu could enter the clay structure. Vogel, McBride, & Ehrlich (1976) studied the Cu content of the clay fraction (<2μ) in a Cu-rich black shale from the lower Nonesuch unit, and found that the .96% Cu in the clay could not be removed by standard leaching techniques (NaTPB-NaCl). Their value of .96% Cu was found to be excessive and probably resulted from the presence of discrete fine-grain native copper or chalcocite in the clay film.

## Mechanism for the Formation of Cu-Sulfides

If these clay-organic complexes were deposited in reduced deltaic sediments, the organics would have been metabolized by bacteria. This process creates $H_2S$, a strong reducing agent, as a by-product. Cu released from organic-clay complexes by this bacterial metabolism would be easily reduced to form the Cu-sulfide, chalcocite, which could explain the close association of chalcocite with chlorite-illite intergrowths that Jost (1968) found in the Nonesuch samples.

Clay-organic-Cu complexes deposited in oxidized sediments would have had their organics oxidized and removed from the system. Copper released from these

complexes would diffuse through the sediment pore-water and infiltrate reduced lithologies where the Cu would react with $H_2S$ to form chalcocite (or if the potential for reduction is high, it could become native copper). This migration of Cu ions in the pore-water could account for the solution features that the epigenetic proponents cite as supporting their mineralization model (these features are listed in the Introduction).

## Test for the Syngenetic Model

A test of the model is to determine whether the Cu content of the chlorite-illite intergrowths is significantly greater than the Cu content of the detrital chlorite or chlorite cement. As previously discussed, the most probable origin for the intergrowths is from alteration of smectite deposited in the delta sediments. With the syngenetic model, these clays could absorb Cu during the breakdown of their adsorbed organic-Cu complexes. This Cu would be redistributed in the clays as montmorillonite converted to chlorite and illite.

In natural water systems and soils, clays themselves have been shown to be only a minor trace element sink (Jenne, 1977). Instead, they act as mechanical substrates for the adsorption of organics and secondary minerals, which then complex the trace elements. Thus, only minor amounts of these elements, in this case Cu,

enter the clay structure. A major limiting factor in this process could be the fact that the Cu ions must be dehydrated before they can enter interior clay lattice positions. Since Cu ions complexed to organics are dehydrated, the main opportunity Cu has to enter the clay lattice is when the organic-Cu complexes adsorbed on exterior and interlamellar clay surfaces are disturbed. Therefore, Cu can enter the smectite structure after deposition of the clay-organic-Cu complexes in the Nonesuch deltaic sediments.

These complexes are attacked soon after deposition (Degens, 1967), and the organic residues (i.e., humic acid, fulvic acid, etc) produced by this microbial decomposition may become stabilized by recomplexing to clays. Humic acid is the dominant residue involved in the recomplexing. It is more abundant and much less soluble in water than fulvic acid. In addition, its heavier molecular weight causes humic acid to be more easily adsorbed on clay surfaces. This is inferred from work by Mortland (1968) which shows that, within a group of related organics, those with heavier molecular weights have a greater tendency to be adsorbed on clay surfaces. Similarly, Malcolm (1964) notes that fulvic acid is important in the soluble transport of trace metals, whereas, humic acid is important in trace element retention by stream sediments.

An acidic pH is necessary for these organic residues to recomplex to interlamellar and exterior surfaces on a smectite (Mortland, 1970). Reduced sediments in the Nonesuch delta would have maintained an acidic pH by the production of $H_2S$ from decomposed organics. This acidity prevents humic acid from complexing Cu because Bondarenko (1972) demonstrated that Cu-humic acid complexes were only stable in "neutral and weakly alkaline" solutions. Therefore, these conditions preclude the formation of new Cu-organic complexes on smectite in the sediment.

Later, smectite alters to chlorite and illite and redistributes its Cu content between these clays. During this alteration, the smectite may create an increased negative interlayer charge by substituting $Al^{+3}$ for $Si^{+4}$ in tetrahedral positions and $Mg^{+2}$ (and possibly Cu) for $Fe^{+3}$ in octahedral positions. The smectite's original lattice charge may arise from either its tetrahedral or octahedral layers, which will affect the nature of the ionic substitution necessary to increase the negative interlayer charge. This facilitates the uptake of $K^+$ necessary for the conversion to illite. Fe and any excess Mg ions that are expelled from octahedral sites in the smectite during its alteration from chlorite layers in the smectite-illite structure. Cu ions could substitute in the chlorite structure for both octahedral Fe or Mg and for Al in gibbsite interlayers in these new

chlorite layers. Therefore, Cu originally absorbed into the smectite structure would now be redistributed between octahedral positions and gibbsite sheets in the newly formed chlorite-illite intergrowths. However, the chlorite and illite could also absorb Cu ions directly from the pore-water during their formation. Thus, the chlorite - illite intergrowths take Cu into their structure in two stages: first, during the breakdown of Cu-organic-clay complexes when Cu enters the smectite structure, and second, during the formation of chlorite-illite intergrowths when Cu may be absorbed from the pore-water.

With the epigenetic model, clays would not come in contact with Cu until a mineralizing solution infiltrated the sediment from below, before compaction and dewatering. Smectite, in reduced areas, would possess the adsorbed humic substances, as previously discussed, and would be unable to complex Cu ions from the mineralizing solution because of the acidic pH that prevails in the reduced sediments. It has also been shown that smectite cannot incorporate Cu into its structure directly from solution because the ions are hydrated. However, when the smectite alters to chlorite and illite, the new clays could absorb Cu from the sediment pore-water.

Detrital chlorite in the mineralized shale would have difficulty incorporating Cu because its lattice was previously formed and is stable in the environment of deposition. However, it may already contain Cu introduced by its initial environment of formation and may possibly pickup additional Cu from the weathering solution or minor organics complexed before deposition.

Chlorite cement from mineralized sands, interbedded with ore-bearing shales, in the lower Nonesuch unit could incorporate Cu directly from the sediment pore-water. Its Cu content would be a function of both the Cu concentration in the adjacent pore-water and the amount of Cu that the chlorite structure can tolerate.

Therefore, if the Cu contents of the clays are very similar, it would support the epigenetic model. On the other hand, if the chlorite-illite intergrowths contain more Cu than the chlorite cement, it would support the syngenetic model because the Cu in the chlorite-illite intergrowths could be derived from the breakdown of Cu-organic complexes and/or from solution during the alteration of smectite. However, the Cu in the chlorite cement could only be derived from the pore-water. A test of the syngenetic model would be to determine the Cu content of the chlorite-illite intergrowths and the chlorite cement in the same sample. Unfortunately,

chlorite cement only occurs in sandstones, and chlorite-illite intergrowths appear in shales or siltstones within the Nonesuch unit. The samples were, therefore, selected from adjacent, interbedded lithologies.

# PROCEDURES FOR EVALUATIONG THE SYNGENETIC MODEL

Three areas of study have been defined to evaluate the viability of the syngenetic model as an origin for Cu-sulfide mineralization in the lower Nonesuch Shale. The first involves identification of three types of clay minerals in the modern shale: detrital chlorite, chlorite cement, and chlorite-illite intergrowths, (from the Domino and Junior Shale units and the Upper Sandstone) and calculation of the amount of Cu each clay contains. To determine if the variation in Cu content between the clays is genetic or due to change, the average percentage of Cu in each clay type is compared using "Student's" t Test. The electron microprobe is used in the determination both of the clay types and their Cu content.

The second area of this investigation involves determining whether the compositions of the clay matrices inhibit the detection of Cu. Two clays (detrital chlorite and chlorite cement) are used for the study, and microprobe data is collected for six elements (Cu, K, Al, Fe, Mg, & Si). The data is analyzed by a computer program--EMPADR--which reports the results as weight percents of

the oxides of the six elements mentioned. If the matrix of either of these clays inhibits detection of Cu on the microprobe, the computer program compensates for it. Comparison of the weight percent Cu data of detrital chlorite and chlorite cement from the first study with the corrected data calculated for these clays by the computer shows the exact dimensions of this matrix effect (if it does exist).

The third study is undertaken to observe whether any Cu ions may still be complexed to disseminated organics in the modern shale. An organic-rich sample from the Domino unit (Vogel sample #7-2-2) was selected for dissolution. The dissolved organic fraction is analyzed for Cu by Atomic Absorption Spectrophotometry.

## Determination of the Copper Content in the Clays

The electron microprobe was used for this analysis. Current across the filament was 25 kilovolts (the amount needed to excite Cu radiation from the sample). Beam current was adjusted to .4 microamps on a quartz grain to insure a count rate of 20,000 counts in 10 seconds. The three spectrometers were set to read Cu, K, and Mg, respectively. Diffraction peaks were maximized with the chart recorder. Background settings were calculated by adding .075A to the peak values. Samples were

polished following the procedure outlined by Woodbury and Vogel (1970).

A clay film standard of known Cu content (2.9%) was analyzed at the beginning and end of data collection. Three peak and three background readings were taken from different locations on the standard and averaged. The same method was followed for analysis of detrital chlorite, chlorite cement, and chlorite-illite intergrowths. Due to the fine grained nature of the sediment, it was easiest to locate and identify the clays using a sample current image on the oscilloscope. Polaroid pictures were taken of this sample current, and K, and Mg X-ray images (Plates 1-3).

Ten grains of each clay type were analyzed for Cu, K, and Mg, and the variance and standard deviation values calculated for the Cu data. "Student's" t Test (Langley, 1968) was then applied to this Cu data to determine if the difference between these values was due to chance or an inherent difference in Cu content between the clays (Table 1).

The following formula was employed for the t Test:

TABLE 1.--Microprobe and "t" Test data on the Cu content of the clays.

| Chlorite-illite Intergrowths | Detrital Chlorite | Chlorite cement |
|---|---|---|
| % Cu | % Cu | % Cu |
| .1270 | .1051 | .0489 |
| .1039 | .1112 | .0792 |
| .1130 | .0966 | .0927 |
| .1065 | .1031 | .1022 |
| .2415 | .1057 | .1021 |
| .1115 | .0960 | .1060 |
| .1024 | .1169 | .0917 |
| .1105 | .0931 | .0834 |
| .1032 | .0726 | .0542 |
| .0888 | .0937 | .1077 |
| Avg. .1208 | Avg. .0994 | Avg. .0868 |
| $S^2 = 1702.2 \cdot 10^{-6}$ | $S^2 = 134.05 \cdot 10^{-6}$ | $S^2 = 390.36 \cdot 10^{-6}$ |
| S = .0413 | S = .0116 | S = .0198 |
| t = used as parent population | t = 5.834 | t = 16.130 |

$$t = \frac{\sqrt{n}\ x|M-m|}{a}$$

n = # of measurements in each sample

M = mean of parent population

m = mean of sample group

S = standard deviation of the sample
(A 98% probability level was used)

### Clay Matrix Effects on Cu Detection

The electron microprobe was also used for this study. As before, current across the filament was 25 KV, and beam current was .4 microamps on quartz. Six elements were analyzed for: Cu, Si, Al, Fe, Mg, & K. The standards for these elements were: native copper, quartz, corundum, hematite, Mg oxide, and orthoclase. Diffraction peaks and background readings were determined as outlined. Only detrital chlorite and chlorite cement were compared to determine any matrix effects on Cu detection. Three grains of each clay were probed at five different locations for peak and background readings of the six elements. Standards were run at the beginning and end of data collection to check for current drift.

This probe data was then fed into a computer program--EMPADR--(Rucklidge and Gasparrini, 1969) designed to analytically reduce the probe's count data to weight percents of the elements and oxide percents.

It also compensates for any reduction in counts for an element due to the type of matrix being probed. These computed weight percents of Cu metal for detrital chlorite and chlorite cement were then compared to the data from Table 1 to determine the degree to which matrix inhibition influenced this probe data.

## Determination of the Cu Content of the Organics

A Perkin-Elmer Atomic Absorption Spectrophotometer was used in this organic dissolution study. Chloroform was selected for the organic solvent, as recommended by Corless (1968) and Burrell (1965c), since it would dissolve any organics in the sample without disturbing Cu from other sources. Methanol was mixed with the chloroform in a 3:2 ratio of methanol to chloroform to give a suitable flame for analysis (Angino & Billings, 1967). A 1:1 ratio (methanol/chloroform) was tried but did not burn as well as the 3:2 mixture.

The standard stock solution was prepared by dissolving 1 gram of Cu metal powder in 10 ml. of $HNO_3$ and then diluting the Cu solution to 1 liter by adding the 3:2 methanol/chloroform mixture. This forms a 500 ppm solution. The stock solution was then diluted, through intermediate steps, to form standard solutions of 6, 5, 3, 1, 0.75, 0.5, and 0.25 ppm. The upper limit of linearity is 5 ppm, and the lower detection limit of the

Cu tube is 0.25 ppm. A blank of the 3:2 methanol/chloroform mixture was also included with the standards.

The organic shale sample was selected from an organic-rich lens in the Domino unit. It was prepared by crushing on a ball mill until the particles were silt size. Six preparations were made from this sample using various amounts of rock powder and three different mixing techniques. The mixing techniques were modified because the methanol/chloroform solution is unstable. Chloroform dissolves organics, while methanol precipitates them, which, depending on the speed of the reaction, could affect the Cu analysis.

The first two samples contained 0.5 g. and 1.0 g. of powdered shale, and 100 ml of a previously mixed 3:2 methanol/chloroform solution was added to each. They were centrifuged within 15 minutes and the supernatant solution analyzed for Cu on the atomic absorption unit immediately afterward. The second pair of samples contained 2.0 g. and 5.0 g. of powdered shale. 40 ml of chloroform was added, and they sat overnight to ensure dissolution of the organics, before 60 ml of methanol was introduced. They were then centrifuged and analyzed, just as the first samples. The final pair of samples contained 1.0 g. and 3.0 g. of powdered shale. 40 ml of chloroform was added first followed 10 minutes later by

60 ml of methanol. The solution stood for one hour before centrifuging and analysis.

When analyzing each pair of samples, the atomic absorption unit was zeroed using the 3:2 methanol/ chloroform blank. The Cu wave length was maximized at 326.4A, and the slit setting was 4(.7) nm. All of the standards were run once, then one sample was analyzed followed by two standards. The two standards would have been those that bracketed the sample's absorbance units. However, since no sample showed any absorbance for Cu, the standards were randomly selected to check for variation in the readings from the first standard values.

# RESULTS AND DISCUSSION

## Copper in the Clays

When analyzing the data from Table 1, it is apparent that the three different clay types possess different average Cu contents. Chlorite cement contains the least with an average Cu content of .087%. Detrital chlorite contains an intermediate average Cu value of .099%. The chlorite-illite intergrowths possess the highest average Cu content at .121% (see Fig. 3). By comparing the detrital chlorite and chlorite cement values to that of chlorite-illite, through use of "Student's" T Test, detrital chlorite is shown to have a "t" value of 5.83 for 10 samples, while the "t" value for chlorite cement is even larger, t = 16.13.

One makes the basic assumption with the t Test that there is no significant difference between sample values (i.e., percent Cu in each clay type). The larger "t" becomes, the less likely it is that this hypothesis is true. For a sample size of ten, there is a 98% probability that the difference between any sample and the parent population with a "t" value of greater than 4.3 is not due to chance. Both of the calculated "t" values for these clays exceed 4.3, which indicates that the

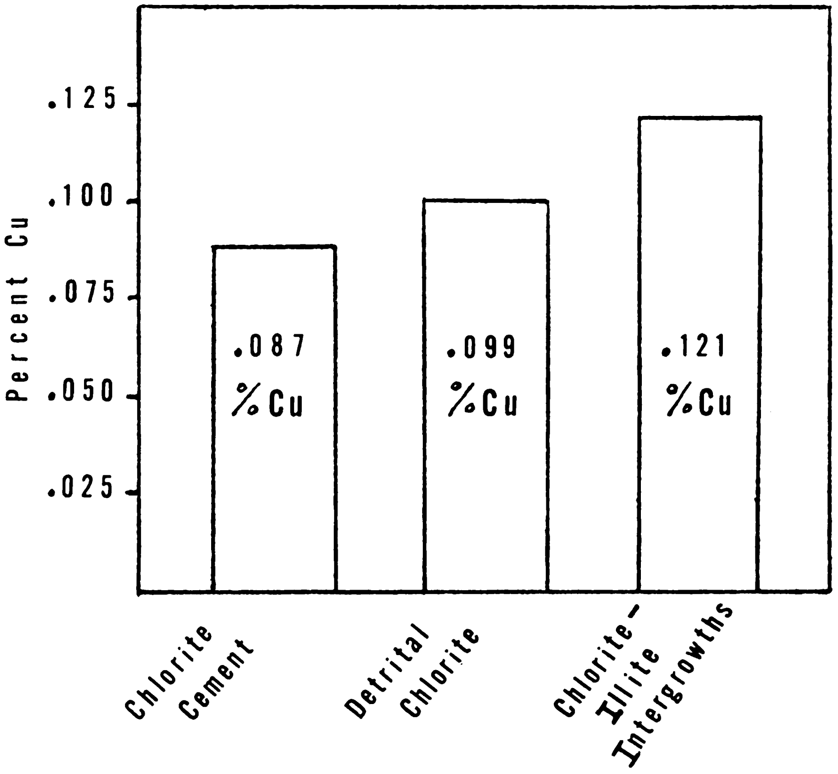

Figure 3.--Percent Cu in the clays.

difference in Cu content between the clays is not due to chance variation, but represents a genetic difference inherent in the clays.

## Matric Effects on Cu Detection

The concentration of Cu in the two clays determined by the EMPADR computer program shows very little variation between these values and those taken directly from the microprobe analyses mentioned in the first section. The Cu values calculated by the computer program, using six elements, are more accurate than the straight probe data but the process was too time consuming for the purposes of this study, and the initial probe data proved, in comparison, that it did not significantly deviate from these computed values.

Chlorite cement has a computed average weight percent for Cu metal of .050%. The initial probe data gives a Cu content for the chlorite cement of .087%. The computed average weight percent of Cu in the detrital chlorite is .096%, whereas the initial probe data has a Cu content of .099%. The .037% difference in Cu content between computed and initial chlorite cement data is due to the effect of Fe. The higher the amount of Fe in the clay, the greater the amount of Fe radiation absorbed by Cu ions when the sample is irradiated by an electron beam. This enhances the production of Cu radiation by

the sample. The detrital chlorite has a lower percent Fe and, thus, a much smaller difference between Cu values. The chlorite-illite intergrowths also possess only a small amount of Fe and, therefore, would be expected to show only a minor difference in Cu content between the computed and initial probe data.

This data comparison shows that, in the present research, the composition of the clay matrix does not significantly impair an accurate determination of the percent Cu present in the clays.

## Cu Content in the Organics

The organic dissolution study shows that disseminated organic material, from an ore-bearing section of the Nonesuch Shale, does not possess complexed Cu ions. This test was performed mainly to determine the validity of the initial estimate of .96% Cu made by Vogel, McBride, & Ehrlich (1976) for the clay fraction of the lower Nonesuch Shale. This value is approximately eight times greater than the largest percentage of Cu found in any clay in the present study. It was believed possible that the remaining Cu missing from the clays could have been complexed to organics in the sample studied, and thus, included in the clay fraction analysis. This assumption was disproven when no Cu was found in any of the powdered shale samples.

# CONCLUSIONS

Evidence presented in this study concerning the amount of Cu present in three clays from the Nonesuch Shale tends to support the syngenetic model. The higher percentage of Cu in the chlorite-illite intergrowths, over the detrital chlorite and chlorite cement, lends credence to the proposition that the original smectite possessed adsorbed organic-Cu complexes which brokedown after deposition allowing some of this complexed Cu to enter octahedral positions in the clay structure. The chlorite cement contained the lowest percent Cu because it formed after mineralization. The intermediate amounts of Cu found in detrital chlorite are most likely a combination of Cu acquired during the chlorite's initial formation and minor amounts of Cu absorbed during weathering or deposition.

An aternate interpretation of the data is that the difference in Cu composition of the chlorite-illite intergrowths and the chlorite cement is due entirely to a difference in the Cu content of the connate waters at the time of formation of both clays. This interpretation cannot be completely ruled out because the chlorite-illite intergrowths occur in organic-rich beds in which the

pore-water would have a lower pH and Eh than the interbedded sandstone in which the chlorite cement occurs. However, both the organic-rich beds and the sandstone in which the chlorite cement appears are intimitely associated. The chlorite cement sample is from the Upper Sandstone 2 feet below the Upper Transition shale horizon. The sandstone unit is only 8 feet thick in the sample region and is surrounded by shale thicknesses totaling 60 feet. It would be difficult to maintain a difference in pore-water chemistry between these beds.

By analyzing the microprobe data from chlorite cement and detrital chlorite, reduced by the EMPADR computer program, it has been determined that these different clay compositions did not inhibit the detection of Cu by the probe. Therefore, the Cu contents calculated for the three clay types, using the initial probe data appear accurate. The calculated clay compositions for the chlorite cement and detrital chlorite show that the detrital chlorite contains approximately 1.5% $K_2O$ in its structure. This suggests the presence of minor illite interlayers in the chlorite. The detrital chlorite also possesses twice as much Cu as the chlorite cement. Cu may have substituted, in the detrital chlorite, for octahedral ions in the chlorite or illite layers or for Al in the chlorite's gibbsite interlayers.

Atomic absorption work has shown that no Cu remains complexed to organics in the lower mineralized section of the shale. The lack of this association implies either that the reducing environment was strong enough to precipitate all the Cu as Cu-sulfides or native copper, or that the Cu-organic complexes broke down with time. The later is the more probable explanation. Hoering (1971) determined that fulvic plus humic acids constitute up to 60% of the total organic matter in recent and ancient sediments, of both continental and marine origin, and these organic residues have a maximum residence time in the sediment of only "several thousand years" (Ellis et al., 1972). The Nonesuch Shale is over 600 million years old.

In this study and similar previous ones, clays have not proven to be capable of incorporating large amounts of trace metals in their structures. However, they do act as transport mechanisms for these ions and can also concentrate the ions in certain depositional areas. It was for this second reason that they were studied in relation to the Nonesuch Shale system. The present research does not mean to imply that clay-organic-Cu complexes were the sole source of Cu for this unit. The possibility that an additional source of Cu was available from a connate solution cannot be ruled out.

The results of this work do not, by themselves, prove the syngenetic model. However, if Cu entered the basin as a smectite-organic complex, it would be expected that the chlorite-illite intergrowths resulting from the alteration of this clay would have higher Cu contents than the chlorite cement.

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# REFERENCES

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# APPENDIX

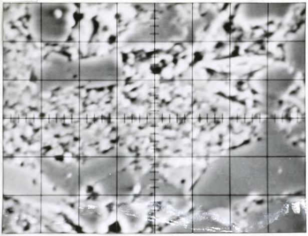

Plate 1a
Chlorite-illite intergrowth matrix surrounding quartz grains.

($1\text{cm}=15\mu$)

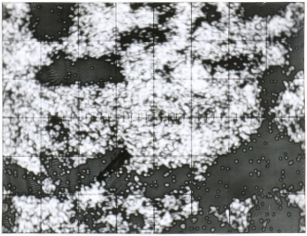

Plate 1b
Mg content of the chlorite-illite intergrowths in Plate 1a.

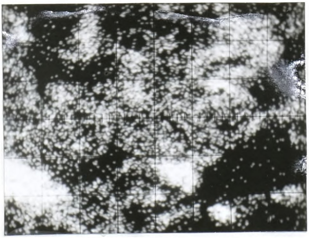

Plate 1c
K content of the chlorite-illite intergrowths in Plate 1a.

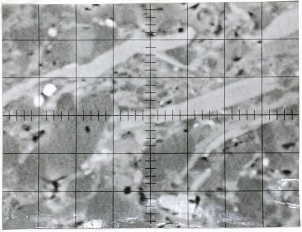

Plate 2a
Detrital chlorite flakes (1cm = 15μ)

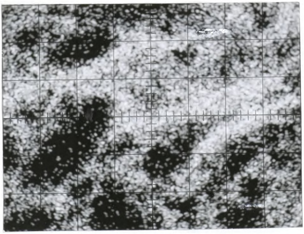

Plate 2b
Mg content of the detrital chlorite flakes in Plate 2a

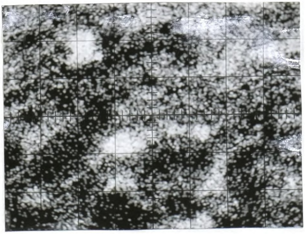

Plate 2c
K content of the detrital chlorite flakes in Plate 2a

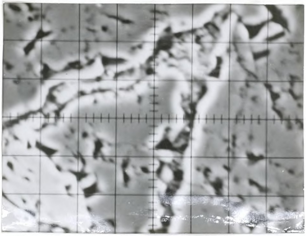

Plate 3a
Chlorite cement filling pore space between quartz grains
(1cm = 15μ)

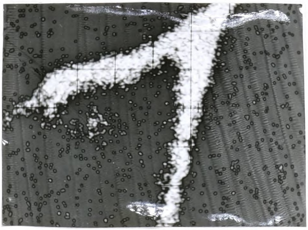

Plate 3b
Mg content of the chlorite cement in Plate 3a.

Plate 3c
K content of the chlorite cement in Plate 3a.